Synthetic and Structural Investigation of Molybdenum, Nickel and Zinc Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

ABSTRACT

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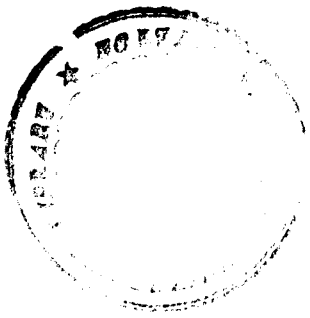

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ABSTRACT

CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

This chapter presents a brief account of importance of the metal ions selected in the present study i.e. molybdenum, nickel and zinc. It also presents a pertinent literature on the transition and non-transition metal complexes of acyl-, aroyl- and pyridoyl dihydrazines and their dihydrazones derived from their condensation with various aldehydes and ketones and related ligands. An attempt has been made to survey literature on all these ligands up-to-date.

CHAPTER – II

EXPERIMENTAL

In this chapter, the experimental details regarding the preparation of succinoyl dihydrazine and the ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone(H_4nsh) have been described. Procedure for elemental analyses, physico-chemical techniques and instruments used are also described in this chapter.

CHAPTER- III

Synthesis, Characterization and Structural Assessment of Monometallic Molybdenum(VI) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

This chapter deals with the synthesis, characterization and structural assessment of five monometallic molybdenum(VI) complexes derived from the tetrabasic octadentate ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh).

In the beginning, a brief account of literature survey with respect to coordination behavior of the ligands related to bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone such as acyl-, aroyl- and pyridoyl- dihydrazines and dihydrazones containing hydroxyl groups are discussed.

The following molybdenum complexes have been described in this chapter.

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ (3.2), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-pic})\cdot 2C_2H_5OH$ (3.3), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3\text{-pic})\cdot 2C_2H_5OH$ (3.4), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic})\cdot 2C_2H_5OH$ (3.5).

The complexes are either orange or orange-yellow in colour. All of the complexes are air stable solid powders and decompose without melting above 300 °C. They are all insoluble in common organic solvents such as ethanol, methanol, acetone, benzene, acetonitrile and ether. But all of them are soluble in highly coordinating solvents such as DMSO and DMF.

Molar conductance values for the complexes (3.1) to (3.5) lie in the range 2.16–2.81 $ohm^{-1}cm^2mol^{-1}$ which are consistent with their non-electrolytic nature in DMSO.

All of the complexes are diamagnetic, consistent with the +6 oxidation state of molybdenum in them. The ESR spectral studies also support the diamagnetic nature of the complexes.

The essential features of the ligand bands in the electronic spectra of the complexes suggests that the ligand is bonded to the metal centre in the same configuration as in the uncoordinated dihydrazone i.e. *anti-cis* configuration.

The electronic spectra of all of the complexes in addition to the intraligand bands exhibit a couple of bands in the region 408–435 nm. These bands are assigned to ligand-to-metal charge transfer transition. The electronic spectra of the complexes suggest that the two hydrazone parts of the ligand are present in different planes either in free state or in the coordinated state.

In the ^1H NMR spectra of the complexes (3.1) to (3.5) two proton signals observed in the region δ 11.61–12.73 ppm has been assigned to δ (OH) protons while the other two proton signals in the region δ 9.99–11.14 ppm downfield of TMS have been assigned to δ (NH) protons, respectively. The signals in the region δ 8.60–9.05 ppm has been assigned to azomethine (-CH=N) protons, whereas a multiplet in the region δ 7.19–8.23 ppm to naphthyl protons. Further, the two signals observed at δ 2.66 and δ 2.52 ppm, respectively are assigned to methylene protons.

The essential features of the ^1H NMR spectra of the complexes are similar to that of the uncoordinated dihydrazone and this suggests that the conformation of the dihydrazone remains unaltered on complexation. The only significant difference in the ^1H NMR spectra of the complexes (3.1) to (3.5) as compared to that of the free dihydrazone is that the δ(-CH=N) signals show an average down field shift by 0.66–0.44 ppm and this suggests the

involvement of azomethine group in coordination to the metal centre. The appearance of δ(OH) and δ(NH) proton signals in the form of doublets in all of the complexes suggests their non-involvement in coordination to the metal centre. This further suggests the existence of dihydrazone in the *anti-cis* configuration in these complexes. The solvent molecules present in the complexes are not bonded to the metal centre.

The complexes (3.2), (3.3), (3.4) and (3.5) have been characterized by ^{13}C NMR spectroscopy and are in good agreement with the findings of ^{1}H NMR spectroscopy.

The uncoordinated dihydrazone show a strong band at 1672 cm^{-1} and is assigned to ν(C=O) stretching vibration. The ν(C=O) band remains either unshifted in positon as in the complexes (3.1), (3.4) and (3.5) or shifts to lower frequency by 6 cm^{-1} as in the complexes (3.2) and (3.3). Such a feature associated with the ν(C=O) band in the IR spectra of the complexes (3.3) to (3.5) rules out the possibility of coordination of >C=O group to the metal centre because the >C=O group absorbs at almost in the same region in the complexes in which uncoordinated >C=O group have been reported to absorb in dihydrazone metal complexes. The ν(C=N) bands observed at 1633 and 1593 cm^{-1} in the free dihydrazone shift to lower frequency by 3–7 cm^{-1} in the metal complexes indicating coordination of N-atom of >C=N group to the metal centre.

In the free dihydrazone, a medium intensity band is observed at 1281 cm^{-1} has been assigned to ν(C-O) stretching vibration. This band remains almost unshifted in position in all of the complexes. Such a . feature associated with ν(C-O) band rules out the possibility of bonding through naphtholic oxygen atoms to the metal centre.

The appearance of strong to medium intensity bands in the region 950–895 cm^{-1} in the IR spectrum of the complexes (3.1) to (3.5) clearly indicates the presence of *cis*-MoO_2^{2+} group in these complexes. Further, the band of medium intensity in the region 778–792 cm^{-1} is assigned to the stretching vibration of the doubly bridged Mo_2O_2 moiety.

At the end of the chapter, the tentative structures for the complexes have been suggested.

CHAPTER – IV

Synthesis, Characterization and Structural Assessment of Homobimetallic Molybdenum(VI) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

The present chapter describes the synthesis, characterization and structural assessment of seven homobimetallic molybdenum(VI) complexes derived from bis(2-hydroxy-1-naphthaledyhe)succinoyldihydrazone.

After presenting in brief, the rationality for its relevance in relation to the first chapter, this chapter deals with the importance of multimetallic enzymes in various fields. Subsequently it describes the synthesis of the complexes followed by results and discussion.

The complexes described in this chapter were found to have the following composition:

$[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1), $[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ (4.2), $[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ (4.3), $[(MoO_2)_2(nsh)(3\text{-pic})_2]\cdot C_2H_5OH$ (4.4),

$[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5), $[(\mu_2\text{–}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$(4.6), $[(\mu_2\text{–}O)_2\ (MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$ (4.7).

The complexes are orange, light orange and light yellow in colour. All of the complexes are air stable solid powders and decompose above 300 °C without melting except the complex (4.6) which melt at 217 °C. All of the complexes are insoluble in water and common organic solvents such as ethanol, methanol, acetone, benzene, acetonitrile, chloroform and ether. But all of the complexes are soluble in DMSO and DMF.

All of the complexes are non-electrolyte in DMSO. All of the complexes are diamagnetic consistent with the presence of molybdenum in +6 oxidation state in these complexes with d^0 electronic configuration.

The electronic spectra of the complexes in addition to the ligand bands exhibit a new band in the region 429–436 nm and these bands are assigned to originate from ligand-to-metal charge transfer transition (LMCT).

The two proton signals observed in each of the region δ 11.61–12.73 ppm and δ 9.99–11.14 ppm downfield of TMS due to naphtholic -OH and secondary -NH protons, respectively in the ^{1}H NMR spectra of the free dihydrazone are absent in the ^{1}H NMR spectra of the

complexes (4.1) to (4.5) indicating collapse of amide structure of the ligand and its involvement in coordination in enol form through naphtholate oxygen atoms via deprotonation and carbonyl oxygen atoms via enolization cum deprotonation. On the other hand, the presence of δ (OH) and δ (NH) proton signals in the complexes (4.6) and (4.7) suggests that the dihydrazone is coordinated to the metal centre in the keto form. The upfield shift of δ (OH) and δ (NH) proton signals rules out the possibility of involvement of >NH and >C=O group in coordination. The most crucial feature of the ^{1}H NMR spectra of the complexes (4.1) to (4.5) is the merger of the doublets corresponding to δ (-CH=N) protons in the free ligand into a single resonance on complexation. This suggests that the dihydrazone, which exist in the *anti-cis* configuration in uncoordinated dihydrazone, isomerizes to attain *staggered* configuration in these complexes. On the other hand, in the complexes (4.6) and (4.7), δ(-CH=N) proton signals appear as doublets indicating that the dihydrazone coordinates to the metal centre in the *anti-cis* configuration in these complexes.

The co-ligand molecules such pyridine and substituted pyridines, 1, 10-phenanthroline and 2,2′-bipyridine are coordinated to the metal centre.

The complexes $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1), $[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ (4.3), and $[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5) have been characterized by ^{13}C NMR spectroscopy. The ^{13}C NMR spectral evidences support the conclusions drawn from ^{1}H NMR spectroscopy regarding coordination of dihydrazone to the metal centre. The ^{13}C NMR signals due to 3-picoline and 4-picoline molecules in the complexes (4.3) and (4.5) have also been assigned.

IR spectra of the complexes support the conclusions drawn from NMR spectroscopy regarding bonding of the ligand to the metal centre.

All of the dioxomolybdenum complexes show two strong to very strong bands in the region 884–956 cm^{-1}. This indicates the presence of *cis*-MoO_2^{2+} group in these complexes.

The tentative structures for the complexes have been proposed at the end.

CHAPTER V

Synthesis, Characterization and Structural Assessment of Zinc(II) Complexes Derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.

The introductory part of this chapter briefly dwells on the importance of zinc(II) and its complexes in various fields like biology and electrochemistry.

This chapter describes the following complexes

$[Zn(H_2nsh)(H_2O)]$ (5.1), $[Zn(H_2nsh)(py)]$ (5.2), $[Zn(H_2nsh)(2\text{-pic})]$ (5.3), $[Zn(H_2nsh)(3\text{-pic})]$ (5.4), $[Zn(H_2nsh)(4\text{-pic})]$ (5.5). $[Zn_2(nsh)(H_2O)_2]$ (5.6); $[Zn_2(nsh)(py)_2]$, (5.7) $[Zn_2(nsh)(2\text{-pic})_2]$ (5.8); $[Zn_2(nsh)(3\text{-pic})_2]$ (5.9), $[Zn_2(nsh)(4\text{-pic})_2]$ (5.10).

All of the complexes are yellow in colour and are air stable. The complexes (5.1), (5.3) and (5.4) decompose above 300 °C without melting while the complexes (5.2) and (5.5) melt with decomposition at 272 and 274°C, respectively. All of the complexes are insoluble in water and other common organic solvents such as ethanol, methanol, acetone, benzene and ether. However, all of them are soluble in DMSO and DMF.

The molar conductance values for the complexes lying in the range 2.3–3.1 $ohm^{-1}cm^2mol^{-1}$ in DMSO solution at 10^{-3} M dilution suggests that they are non-electrolyte in DMSO. All of the complexes are diamagnetic consistent with d^{10} electronic configuration of Zn^{2+} ion in these complexes.

Electronic spectra of the complexes in addition to the intraligand bands show additional strong absorption bands in the region 470–480 nm with molar extinction co-efficient (ε_{Max}) in the region 2247–2522 $dm^3cm^2mol^{-1}$ in the complexes (5.1) to (5.5) and 457–486 $dm^3cm^2mol^{-1}$ in the complexes (5.6) to (5.10) respectively. These bands are attributed to arise due to ligand-to-metal charge transfer transition and are responsible for the dark yellow colour of the complexes.

All of the complexes were characterized by ^1H NMR spectroscopy. The two proton doublets observed at δ 11.61 and δ 12.73 ppm downfield of TMS assigned to naphtholic -OH protons in the ^1H NMR spectrum of the free dihydrazone are downfield shifted on complexation and appear as singlets in the ^1H NMR spectra of the complexes (5.1) to (5.5). The appearance of δ (OH) signals in the ^1H NMR spectra of all of the complexes indicates

the presence of -OH group in the complexes. The downfield shift of these signals indicates coordination of naphtholic –OH group to the zinc centre.The δ (NH) signals which appear at δ 9.99 and δ 11.14 ppm in the ^{1}H NMR spectrum of the free dihydrazone disappears in all of the complexes suggesting collapse of amide structure of the dihydrazone and its coordination to the metal centre in the enol form. However, the ^{1}H NMR spectra of the complexes (5.6) to (5.10) do not show any signal due to δ (OH) and δ (NH). The absence of signals due to δ (OH) and δ (NH) in the ^{1}H NMR spectra of the complexes (5.6) to (5.10) indicates the coordination of dihydrazone to the metal centre in enol form through naphtholate oxygen atoms via deprotonation and carbonyl oxygen atoms via enolization.

The azomethine (>CH=N) proton signal which in the free dihydrazone appear at δ 8.60 and δ 9.05 ppm as doublets exhibit a downfield shift of the order of δ 0.29–0.69 ppm, respectively in the complexes (5.1) to (5.5). The downfield shift of the azomethine proton signal and its appearance in the form of doublets suggests coordination of azomethine nitrogen atom to the metal centre and the existence of dihydrazone in the *anti-cis* configuration in the complexes (5.1) to (5.5). However, the main feature of the ^{1}H NMR spectra of the complexes (5.6) to (5.10) is the collapse of the doublets corresponding to δ-CH=N signal in the free ligand into a single resonance. This ^{1}H NMR spectral feature of the complexes (5.6) to (5.10) suggests that the dihydrazone, which exists in the *anti-cis* configuration in the free state, attains *staggered* configuration in the complexes (5.6) to (5.10). Similar coordination mode of the related malonoyl dihydrazone to the metal centre has been reported by Gopinathan and co-workers and by Lal et al.

The naphthyl proton multiplet appears in the regions δ 7.06–8.23 ppm and δ 7.07–8.44 ppm respectively in the complexes (5.1) to (5.5) and (5.6) to (5.10). In addition to naphthyl proton signals in the region δ 7.06–8.23 ppm and δ 7.06–8.23 ppm in the ^{1}H NMR spectra of the complexes (5.2) to (5.5) and (5.7) to (5.10), some new signals are also observed in the region δ 7.77–7.79 ppm and these signals are attributed to arise due to *ortho* protons of pyridyl ring of pyridine, 2-picoline, 3-picoline and 4-picoline molecules.The complexes (5.3), (5.4), (5.5) and (5.8), (5.9) and (5.10) show a new signal at δ 2.07, δ 2.07 and δ 2.04 ppm assigned to methyl protons of 2-picoline, 3-picoline and 4-picoline molecules. These signals are upfield shifted as compared to their positions in the free molecules. Features associated with the pyridyl protons of pyridine, 2-picoline, 3-picoline and 4-picoline molecules and methyl protons indicates flow of electron density from ring nitrogen atom of these donor molecules.

A comparison of the IR spectra of the complexes with that of the free ligand (H_4nsh) suggests that the dihydrazone is coordinated to the metal centre in enol form in all of the complexes.

The ν(NH) band observed at 3244 cm^{-1} in the uncoordinated dihydrazone does not appear in the IR spectrum of all of the complexes. This suggests the destruction of amide structure of ligand in these complexes. The absence of bands due to secondary –NH group in the region 3240–3500 cm^{-1} in combination with the absence of amide I (>C=O) band in all of the complexes suggests collapse of amide structure of the dihydrazone as a result of enolization and its coordination through oxygen atom of >C=O group to the metal centre in the enol form. This is also corroborated by the absence of the very strong ligand band at 1672 cm^{-1} in the IR spectra of the complexes.

In the free dihydrazone, the ν(C=N) band appears as a couple of bands at 1633 and 1593 cm^{-1}. This band appears as a single band in the IR spectrum of the complexes (5.2) to (5.5) while as a couple of bands in the complex (5.1) and the complexes (5.6) to (5.10) in the region 1618–1602 cm^{-1} and thus shows either no shift as in the complexes (5.1) to (5.5) or shift to lower frequency by 1–2 cm^{-1} respectively. This indicates the coordination of azomethine nitrogen to the metal centre. The small shift in νC=N stretching frequency in the complexes is due to the difference of bonded species i.e. from >C=N..... H to >C=N→M . The amide III band at 1321 cm^{-1} in the free dihydrazone registers a shift to higher frequency by 7–20 cm^{-1} in all of the complexes showing the involvement of >C=O in coordination.

The band of weak intensity at 1540 cm^{-1} in the IR spectrum of the free dihydrazone is assigned to amide II + ν(C–O) (naphtholic). This band shifts to higher frequency in all of the complexes except the complex (5.1) in which it appear at 1508 cm^{-1} while it appears in the region 1542–1559 cm^{-1} in the complex (5.2) to (5.10). This band in the region 1508–1559 cm^{-1} in all of the complexes is assigned to ν(NCO^- vibration) of the newly formed NCO^- group as a result of enolization of the dihydrazone. This is further supported by the absence of -NH band in the IR spectrum of all of the complexes. The assignment of this band in the region 1508–1553 cm^{-1} remains quite tentative unless confirmed by isotopic substitution study.

A band of medium intensity observed at 1281 cm^{-1} due to ν(C–O) vibration in the free ligand, shifts to higher frequency by 2–7 cm^{-1} and appears in the region 1284–1288 cm^{-1} in

the IR spectra of all the complexes. The shift of ν(C–O) band to higher frequency indicates the coordination of naphtholic OH group to the metal centre in the complexes.

A new non-ligand band observed in the region 870–873 cm^{-1} in the IR spectra of the complexes (5.6) to (5.10) is assigned to the stretching vibration of the tetra-atomic species  resulted from involvement of naphtholate oxygen atom in bridge formation. The presence of this band indicates that the Zn(II) atoms are tethered together through naphthoxo bridging.

All of the complexes show a new weak intensity band in the region 1003–1010 cm^{-1}. This band is assigned to ring breathing mode of pyridine, 2-picoline, 3-picoline and 4-picoline molecules in the complexes (5.2) to (5.10). The presence of this band in these complexes further indicates the coordination of pyridine, 2-picoline, 3-picoline and 4-picoline molecules to the metal centre.

The structures for the complexes have been tentatively assigned.

CHAPTER VI

Synthesis, Characterization and Structural Assessment of Ni(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

The introduction part of the chapter describes in brief the rationality for selecting nickel in the present study. Subsequently, it describes the importance of nickel in various fields like industrial catalysis, biology and magnetism.

The following monometallic and homobimetallic Ni(II) complexes have been described in this chapter.

$[Ni(H_2nsh)(H_2O)_2]$ (6.1),$[Ni(H_2nsh)(py)_2]$ (6.2), $[Ni(H_2nsh)(2\text{-pic})_2]$ (6.3), $[Ni(H_2nsh)(3\text{-pic})_2]$ (6.4), $[Ni(H_2nsh)(4\text{-pic})_2]$ (6.5), $[Ni_2(nsh)(H_2O)_4]$ (6.6), $[Ni_2(nsh)(py)_4]$. (6.7), $[Ni_2(nsh)(2\text{-pic})_4]$ (6.8), $[Ni_2(nsh)(3\text{-pic})_4]$ (6.9), $[Ni_2(nsh)(4\text{-pic})_4]$ (6.10).

The complexes are brown, yellow, light brown and dark brown in colour. All of the complexes are air stable solid powders and decompose above 300 °C without melting. All of the complexes are insoluble in water and common organic solvents such as ethanol, methanol, acetone, benzene, acetonitrile, chloroform and ether, but all of them are soluble in DMSO and DMF.

The molar conductance values for the complexes (6.1) to (6.10) lie in the region 2.62–3.13 $ohm^{-1}cm^2mol^{-1}$ in 10^{-3} M DMSO solution indicating their non-electrolytic nature in this solvent.

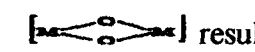
The magnetic moment values for the complexes (6.1) to (6.5) lie in the range 2.85–3.45 BM which is typical of an octahedral Ni(II) compound. However, in the homobimetallic Ni(II) complexes (6.6) to (6.10), the magnetic moment values lie in the range 1.14–1.73 BM i.e. 0.57–0.87 BM per Ni(II) ion. These values are considerably less than the values reported for spin free nickel(II) complexes indicating a strong metal-metal interaction in the structural unit.

The electronic spectra of the complexes recorded in DMF show red shift of ligand bands that gives good evidence of chelation of dihydrazone to the metal centre. In addition to the intraligand bands, all of the complexes exhibit a new band in the region 410–440 nm which has very high molar extinction co-efficient and is assigned to have its origin in the ligand-to-metal charge transfer transition, most probably, from naphtholate oxygen atoms to the metal centre, All of the complexes show two additional low energy bands in the region 500–900 nm which are characteristic of nickel(II) ion in octahedral coordination.

The band at 1672 cm^{-1} assigned to ν(C=O) stretching vibration in the free dihydrazone disappears in the IR spectra of all the complexes indicating that the ligand H_4nsh is coordinated to the metal centre in the enol form. The bands observed at 1633 and 593 cm^{-1} in the IR spectrum of the free dihydrazone are attributed to ν(C=N) stretching vibrations. These bands, on an average, shift to lower frequency by 2–3 cm^{-1} in all of the complexes indicating coordination of >C=N group to the metal centre.

The ν(C–O) band observed at 1281 cm^{-1} in the free dihydrazone shifts to higher frequency in all of the complexes and appears at ~ 1303 cm^{-1} as a medium intensity band. This indicates bonding through C-O oxygen atoms to the metal centres via deprotonation of the naphtholic –OH group

The complexes (6.2) to (6.5) and (6.7) to (6.10) show a new but very weak intensity band in the region 1076–1045 cm^{-1}. This band is assigned to ring breathing mode of pyridine and substituted pyridine molecules. The presence of this band in the IR spectra of the complexes indicates coordination of pyridine, 2-picoline, 3-picoline and 4-picoline molecules to the metal centre.

A new non-ligand band observed in the region 861–897 cm^{-1} in the IR spectra of the complexes (6.6) to (6.10) is assigned to the stretching vibration of the tetra-atomic species  resulted from involvement of naphtholate oxygen atom in bridge formation.

The complexes have been assigned to have distorted octahedral stereochemistry. The tentative structures for the complexes have been proposed.

CHAPTER VII

Synthesis, Characterization and Structural Assessment of Heterobimetallic Ni(II)-Zn(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

The introductory part of this chapter briefly describes the importance of bimetallic complexes in various fields like homogeneous catalysis, heterogeneous catalysis, multimetallic enzymes and synthesis of solid state phases of inductrial and technological importance.

The following heterobimetallic complexes derived frim bis(2-hydroxy-1-naphthaldehyde)succinoyl dihydrazone have been described.

$[NiZn(nsh)(H_2O)_3]$ (7.1), $[NiZn(nsh)(py)_3]$ (7.2), $[NiZn(nsh)(2\text{-}pic)_3]$ (7.3), $[NiZn(nsh)(3\text{-}pic)_3]$ (7.4), $[NiZn(nsh)(4\text{-}pic)_3]$ (7.5), $[ZnNi(nsh)(H_2O)_2]$ (7.6), $[ZnNi(nsh)(py)_2]$ (7.7), $[ZnNi(nsh)(2\text{-}pic)_2]$ (7.8), $[ZnNi(nsh)(3\text{-}pic)_2]$ (7.9), $[ZnNi(nsh)(4\text{-}pic)_2]$ (7.10).

The complexes are brown, orange, yellow and dark brown n colour. All of the complexes are insoluble in water and common organic solvents but are fairly soluble in DMF and DMSO.

All of the complexes are air stable solid powders and decompose without melting above 300°C. None of the complexes show weight loss below 160 °C ruling out the possibility of prexsence of water molecules in the lattice structure of the complexes. However, the complexes (7.1) and (7.6) showed weight loss in the temperature range 170–190 °C corresponding to three and two water molecules respectively. The complexes (7.2) to (7.5) and (7.7) to (7.10) showed weight loss at 220–240 °C corresponding to three and two molecules of pyridine/2-picoline/3-picoline/4-picoline. The expulsion of these neutral electron donor molecules at such a high temperature indicates the coordination of these molecules to the metal centre.

The molar conductance values for all of the complexes at 10^{-3} M dilution in DMSO solution fall in the region 2.81–3.21 $ohm^{-1}cm^2mol^{-1}$ which suggests that all of the complexes are non-electrolyte in DMSO.

The complexes (7.1) to (7.5) exhibit magnetic moments in the range 2.95–3.15 BM while the complexes (7.6) to (7.10) exhibit μeff values in the range 3.25- 3.42 BM. The μ_{eff} values for nickel(II) complexes have been reported to fall in the regions 3.00–3.30, 3.00–3.45 and 3.45–4.00 BM respectively having octahedral, 5-coordinate square-pyramidal and tetrahedral geometry, respectively. On the other hand the four coordinate square planar nickel(II) complexes have been shown to be diamagnetic. The experimental values of magnetic moment for the complexes rule out their tetrahedral or square planar structure. The magnetic moment values for the complexes (7.1) to (7.5) lie in the range 2.95–3.15 BM which indicates that these complexes have distorted octahedral stereochemistry. Literature reports suggest that majority of the five coordinate high spin Ni(II) complexes having square-pyramidal stereochemistry have magnetic moment values lying in the region 3.25–3 ?9 BM . The magnetic moment values for the complexes (7.6) to (7.10) fall in the range reported for high spin square-pyramidal complexes. Thus the complexes (7.6) to (7.10) can be said to have square-pyramidal geometry with considerable amount of distortion.

In addition to the ligand bands, the complexes show a weak additional band in the region 472–481 nm. This band is similar to the band observed in the precursor Zn(II) complex $[Zn(H_2nsh)(H_2O)]$ and is assigned to have similar origin in nature i.e. charge transfer transition. Accordingly this band is assigned to arise from ligand-to-metal charge transfer transition originating from naphtholate oxygen atom.

The heterobimetallic complexes (7.1) to (7.5) exhibit new bands in the region and 931–940 nm (ν_1) and 615–628 nm (ν_2). The position of these bands is typical of an octahedrally coordinated Ni(II) centre and rules out the square planar or tetrahedral structure. A comparison of the position of the bands in the regions 931–940 and 615–628 nm with the corresponding band in the spectra of $[Ni(H_2O)_6]^{2+}$ at 1175 and 740 nm and $[Ni(NH_3)_6]^{2+}$ at 935 and 570 nm suggests that ν_1 band bear similarity with that of the nitrogen donor ligands, while the second band ν_2 is intermediate between those observed for oxygen as well as nitrogen donor ligands but approaching towards nitrogen donor ligands. From this observation, it may safely be said that nickel atom is occupying N_2O_2 coordination chamber of the ligand. This suggests that the Zn(II) atom in the complexes (7.1) to (7.5) are displaced by Ni(II) atom. From this observation, it can be said that the Ni(II) occupies N_2O_2 coordination chamber while the zinc(II) occupies O_2O_2 coordination chamber. On the other

hand, the complexes (7.6) to (7.10) derived from nickel(II) precursor complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1), exhibit only one band in the region 965–967 nm and is similar in nature to that reported for high spin square pyramidal Ni(II) complexes. Hence these complexes are assigned to have five coordinate square-pyramidal stereochemistry and the band in the region 965–967 nm is assigned to the transition $^3B_1 \rightarrow {}^3E(F)$. A comparison of the position of this band in the region 965–987 nm with the corresponding band in the spectra of $[Ni(H_2O)_6]^{2+}$ at 1175 (ν_1) and $[Ni(NH_3)_6]^{2+}$ at 935 (ν_1) and those in the complexes (7.1) to (7.5) suggests that the ν_1 bands in these complexes is shifted away from the complexes derived from nitrogen donor ligands and towards complexes derived from oxygen donor ligands. It is imperative to mention that in the precursor nickel(II) complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1), the d-d bands appear at 845 and 564 nm. From this observation, it may safely be concluded that the nickel atom in the complexes (7.6) to (7.10) is most probably, coordinated to carbonyl oxygen atoms via enolization. This suggests that the Ni(II) atom which occupies N_2O_2 coordination chamber in precursor complexes is displaced by Zn(II) atoms in the hetrerobimetallic complexes. Thus it is suggested that in these complexes the nickel(II) occupies O_2O_2 coordination chamber while zinc(II) occupies N_2O_2 coordination chamber.

A comparison of the IR spectra of the heterobimetallic complexes with those of the uncoordinated dihydrazone (H_4nsh) suggests that the dihydrazone is coordinated to the metal centre in the enol form in all of the complexes.

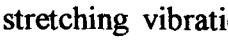
The IR spectra of the complexes do not show any strong band in the region 1630–1700 cm^{-1}. The feature of the IR spectra of the complexes in this region is similar to that of the precursor zinc complex $[Zn(H_2nsh)(H_2O)]$ (5.1) and Ni(II) complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1) . This suggests that the ligand is present in these complexes in the same form as that in the precursor zinc complex i.e. in the enol form.

The ν(C=N) band appears as a couple of bands in all of the complexes and are similar to that as observed in the precursor Zn and Ni complex. The ν(C=N) bands, on an average, show a negative shift of 3–4 cm^{-1} in metal complexes as compared to those in the free ligand and the precursor zinc and nickel complex. This shows that the azomethine nitrogen atoms are bonded to the metal centre. It is interesting to note that one of the ν(C=N) bands (1593 cm^{-1}) shifts to higher frequency by 8–11 cm^{-1} in all of the heterobimetallic complexes as compared to its position in the in the free dihydrazone whereas the other ν C=N band (1633 cm^{-1}) shifts to lower frequency by ~ 17 cm^{-1}. The shift of one of the ν(C=N) bands to higher frequency and the other band to lower frequency on complexation in these

complexes indicates inversion of azomethine group. Consequently, the axial >C=N group attains equatorial position while equatorial >C=N group attains axial position. The introduction of the positively charged metal ion in the ligand skeleton causes the reversal of azomethine group.

The fact that the ν(C=N) band appears as a couple of bands in the IR spectra of the Ni-Zn heterobimetallic complexes similar to that in the precursor Zn(II) and Ni(II) complex suggests that the two >C=N groups are not equivalent in all of the heterobimetallic complexes just as in case of the precursor Zn(II) and Ni(II) complex. Such an inequivalency of >C=N groups indicates the coordination of dihydrazone to the metal centre in *anti-cis* configuration. In this configuration the molecule is bent in such a manner that half portion of the dihydrazone remains out of plane of the molecule, while the other half remains in plane.

The complexes (7.2) to (7.5) and (7.7) to (7.10) show a new but very weak intensity band in the regions 1012–1014 cm^{-1} and 1051–1072 cm^{-1} respectively. These bands are assigned to ring breathing mode of pyridine and substituted pyridine molecules present in the complexes. The presence of this band in the IR spectra of the complexes (7.2) to (7.5) and (7.7) to (7.10) indicates their coordination to the metal centre.

A new non-ligand band observed in the region 773–780 cm^{-1} in the IR spectra of all of the complexes is assigned to the stretching vibration of the tetraatomic species  resulted from the involvement of naphtholate oxygen atoms in bridge formation.

The tentative structures for the complexes have been proposed at the end.

Synthetic and Structural Investigation of Molybdenum, Nickel and Zinc Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

BY

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MARCH, 2009

DEDICATED

TO

MY BELOVED PARENTS

DECLARATION

I, Mithun Chakrabarty, hereby declare that the subject matter of the thesis entitled "*Synthetic and Structural Investigation of Molybdenum, Nickel and Zinc Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone*" is the record of work done by me and the content of this thesis did not form the basis of the award of any previous degree to me or to anybody else to the best of my knowledge and that the thesis has not been submitted by me for any research degree in any other University/Institution.

This is being submitted to the North-Eastern Hill University for the degree of Doctor of Philosophy in Chemistry.

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This is to certify that the the thesis entitled "*Synthetic and Structural Investigation of Molybdenum, Nickel and Zinc Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone*" submitted by Mr. Mithun Chakrabarty for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the Ph.D. degree in Chemistry.

The work described in this thesis is original and has not been submitted for any other degree or diploma in this or any other university.

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CONTENTS

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(Mithun Chakrabarty)

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PREFACE

Studies on synthesis, characterization and structure of Mo(VI), Ni(II) and Zn(II) complexes derived from the polyfunctional ligand, bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone is the focal theme of the work described in the present thesis. The content of the thesis has been divided into seven chapters. Each chapter has been presented as a self contained one including relevant bibliography, while the chapters III to VII also contains section on a very brief Introduction justifying the specific objective of the work followed by a section on Experimental describing the synthesis of the complexes and Results and Discussion and finally the suggested structure of the complexes.

The first chapter (**Chapter I**) provides a brief account of importance of the metal ions selected in the present study i.e. molybdenum, nickel and zinc. It also provides a background pertaining to the work described in this thesis. The significance, interest and scope of some acyl-, aroyl- and pyridoyldihydrazines and their dihydrazones derived from their condensation with various aldehydes and ketones and related ligands have been described in this chapter.

The second chapter (**Chapter II**) provides the details of synthetic methods of preparation of ligands, details of instruments used and analytical methods used for the characterization of the complexes synthesized and described in this thesis.

The third chapter (**Chapter III**) of this thesis deals with the synthesis, characterization and structural assessment of the monometallic Mo(VI) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone incorporating pyridine, 2-picoline, 3-picoline and 4-picoline as coligands. The complexes reported in this chapter are of the type $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ (3.2), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-pic})\cdot 2C_2H_5OH$ (3.3), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3\text{-pic})\cdot 2C_2H_5OH$ (3.4), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic})\cdot 2C_2H_5OH$ (3.5).

The fourth chapter (**Chapter IV**) deals with the synthesis, characterization and structural assessment of homobimetallic Mo(VI) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone. The complexes described in this chapter are of the

type $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1), $[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ (4.2), $[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ (4.3), $[(MoO_2)_2(nsh)(3\text{-pic})_2]\cdot C_2H_5OH$ (4.4), $[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$ (4.6), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$ (4.7).

The fifth chapter (**Chapter V**) of the thesis presents an account of synthesis, characterization and structural assessment of Zn(II) complexes involving bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and the co-ligands pyridine, 2-picoline, 3-picoline and 4-picoline. The complexes described in this chapter are of the type $[Zn(H_2nsh)(H_2O)]$ (5.1), $[Zn(H_2nsh)(py)]$ (5.2), $[Zn(H_2nsh)(2\text{-pic})]$ (5.3), $[Zn(H_2nsh)(3\text{-pic})]$ (5.4), $[Zn(H_2nsh)(4\text{-pic})]$ (5.5). $[Zn_2(nsh)(H_2O)_2]$ (5.6); $[Zn_2(nsh)(py)_2]$, (5.7) $[Zn_2(nsh)(2\text{-pic})_2]$ (5.8); $[Zn_2(nsh)(3\text{-pic})_2]$ (5.9), $[Zn_2(nsh)(4\text{-pic})_2]$ (5.10).

The sixth chapter (**Chapter VI**) of the thesis describes the synthesis, characterization and structural assessment of monometallic and homobimetallic Ni(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and the co-ligands pyridine, 2-picoline, 3-picoline and 4-picoline. The complexes described in this chapter are of the type $[Ni(H_2nsh)(H_2O)_2]$ (6.1),$[Ni(H_2nsh)(py)_2]$ (6.2), $[Ni(H_2nsh)(2\text{-pic})_2]$ (6.3), $[Ni(H_2nsh)(3\text{-pic})_2]$ (6.4), $[Ni(H_2nsh)(4\text{-pic})_2]$ (6.5), $[Ni_2(nsh)(H_2O)_4]$ (6.6), $[Ni_2(nsh)(py)_4]$. (6.7), $[Ni_2(nsh)(2\text{-pic})_4]$ (6.8), $[Ni_2(nsh)(3\text{-pic})_4]$ (6.9), $[Ni_2(nsh)(4\text{-pic})_4]$ (6.10).

The final chapter of this thesis (**Chapter VII**) deals with the synthesis, characterization and structural assessment of heterobimetallic zinc(II) and nickel(II) derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and the co-ligands pyridine, 2-picoline, 3-picoline, 4-picoline. The electronic, IR and magnetic moment studies are consistent with the presence of Zn(II) and Ni(II) centres in all of the complexes. The complexes described in this chapter are of the type $[NiZn(nsh)(H_2O)_3]$ (7.1), $[NiZn(nsh)(py)_4]$ (7.2), $[NiZn(nsh)(2\text{-pic})_3]$ (7.3), $[NiZn(nsh)(3\text{-pic})_3]$ (7.4), $[NiZn(nsh)(4\text{-pic})_3]$ (7.5), $[ZnNi(nsh)(H_2O)_2]$ (7.6), $[ZnNi(nsh)(py)_2]$ (7.7), $[ZnNi(nsh)(2\text{-pic})_2]$ (7.8), $[ZnNi(nsh)(3\text{-pic})_2]$ (7.9), $[ZnNi(nsh)(4\text{-pic})_2]$ (7.10).

CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

Introduction

The present thesis embodies the results of investigations of reactions of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone, $MoO_2(acac)_2$, $Ni(OAc)_2 \cdot 4H_2O$ and $Zn(OAc)_2 \cdot 2H_2O$ and the characterization of the resulting complexes. The structural assessment of the complexes described in this thesis is based on the data obtained from elemental analyses, IR, ^1H NMR, ^{13}C NMR, conductivity measurements, magnetic susceptibility measurement and electronic spectral data. Accordingly, the present chapter gives a brief account of the importance of molybdenum, nickel and zinc in monometallic and heterometallic systems followed by description of bonding modes of dihydrazone ligand and literature survey on metal complexes of dihydrazones.

Molybdenum is the only element of the second transition series, being essential for life **[1, 2]**. The element molybdenum is present in two types of enzymes, one of these is nitrogenase **[3]** which is found in free living and symbiotic microorganisms and catalyses the reduction of dinitrogen to ammonia. The other category of molybdenum enzymes consists of hydroxylases or oxotransferases **[4]** which catalyses a variety of two electron oxidation-reduction reactions. As a constituent of enzymes, molybdenum also participates in redox reactions, viz. oxidation of aldehydes, xanthine and other purines **[5]**, and reduction of nitrate to molecular nitrogen **[6, 7]**. Molybdenum's biochemical role is based on its ability to facilitate electron exchanges and to form stable complexes with oxygen, nitrogen and sulfur containing ligands **[2]**.

Mixed metal-molybdenum oxides are used as efficient and selective catalysts for partial oxidation of light alkanes in petrochemistry **[8]**.

A cobalt, nickel or platinum promoted molybdenum catalyst is used in the hydrosulfurization and hydrodenitrogenation processes **[9, 10, 11]** whereby organo sulfur and nitrogen compounds in petroleum feed stocks are heterogeneously desulfurised and denitrogenated. Homogeneous molybdenum(VI) catalysts containing the *cis*-$[MoO_2]^{2+}$ unit are the basis of important industrial oxidation processes such as olefin epoxidation using alkyl hydroperoxides as the oxygen source **[12, 13, 14]**.The molybdenum compound $[NH_3Pr^i][Mo_7O_{24}] \cdot 3H_2O$ (PM-8) is proved to be significant in tumor growth suppression in bearing several human tumors and has shown anti-tumour activity against human gastric

cancer **[15]**. The polyoxomolybdenum anions have potential applications in catalysis, solid-state technology and medicine, including anti-tumor, anti-bacterial and anti-virus (HIV) activity **[17, 18]**.

In 1975, Zerner discovered that nickel is present in urease enzyme. The other enzymes of nickel are urease, E. Coli glyoxalase I (E. Coli Glx I), [NiFe]-hydrogenase, methyl-CoM reductase (MCR), Co-dehydrogenase (CODH) and acetyl CoA synthase (ACS) **[19]**.

Nickel occurs widely in bacterial hydrogenase which catalyzes the combination of hydrogen and oxygen, the reduction of sulfate ion, the production of methane and other reductive processes such as reduction of alkyl halides **[20]**. Nickel also occurs in urease obtained from jack beans **[21]**. Urease catalyses the hydrolysis of urea to ammonia and carbonic acid. Nickel complexes are also used as anti-oxidants **[22]** and are also used as catalysts for the oligomerization of ethylene **[23]**.

Nickel plays a prominent role in several areas of material chemistry. Some topical interplay between nickel coordination chemistry and material science exists in the use of Ni-containing alkoxides for the synthesis of ceramic materials by MOCUD and sol-gel processes, the preparation and nanoscopic dendrimers incorporating Ni, the construction of 3D hybrid inorganic-organic porous materials with Ni coordination units and the fabrication of supported Ni catalysts and Ni nano structures through nanotechnology. Paramagnetic high spin Ni^{II} has found particular attention in the field of molecular magnetism, culiminating in the recent discovery of the first single molecule magnets based on Ni^{II} centres **[19]**.

Zinc(II) is one of the most abundant divalent metal ion occurting in living organisms (2.30 g Zn for and average person) and is the second most abundant metal in the body and is a structural or catalytic component of more than 300 enzymes. It is an essential component of many protein seaffolds (e.g., carbonic anhydrase and zinc finger protein). Zn(II) plays critical roles in gene transcription and metalloenzymes function **[24]**.

Zinc(II) plays important role in several biological processes. Apart from enzymes with one zinc binding sites e.g., carbonic anhydrase and carboxypeptidase A, enzymes containing two or three zinc ions at the active sites are also of particular interest. Dinuclear Zn(II) cores are often seen in biological systems, such as phosphatases and aminopeptidases. In addition, some synthetic dinuclear zinc(II) complexes are found to have functions in RNA hydrolysis and dephosphorylation. In addition, the role of zinc in neuro-biology is a topic of substantial current interest **[25]**.

Zn(II) is used extensively as an anodic inhibitor for metallic corrosion protection **[26]**. Zinc has been shown to be a useful metal centre in hybrid organic-inorganic framework solids, particularly with di- and tri- carboxylic acids and diphosphonates, framing a wide range of coordination polymers, many stable to the removal of included solvent **[27]**.

The molecular complexes derived from transition and inner-trasition metals having the same or different metal ions are of interest in areas like homogeneous catalysis **[28]** and heterogeneous catalysis **[29]**. In homogeneous catalysis, a heterobimetallic complex containing an electron deficient metal atom and an electron rich metal atom presents the possibility of Lewis acid activation of a substrate molecule bound to the electron rich metal centre. The heterobimetallic complexes which have such types of properties are usually derived from widely divergent metals **[30]**. Further, the heterobimetallic complexes have the potential to mediate certain chemical reactions of industrial relevance either more efficiently or in different manner to isolated metal centres **[31]**. They exhibit distinct reactivity pattern as compared to their monometallic and homobimetallic complexes.

The heterobimetallic complexes have been successfully used as precursors in the preparation of ceramic materials favouring an intimate mixing of the elements which enable reactions at lower temperature rather than for traditional route for the preparation of purer inaccessible solid state phases **[32]**.

Description of the ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

The present ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone has been derived from the condensation of succinoyl dihydrazine with 2-hydroxy-1-naphthaldehyde. The present ligand has several potential coordination centres such as carbonyl oxygen atoms, naphtholic oxygen atoms, secondary amine nitrogen atoms and azine group nitrogen atoms, all in duplicate which due to symmetry has equal probability of taking part in coordination. This can react with the metal ions in keto, keto-enol and enol forms.

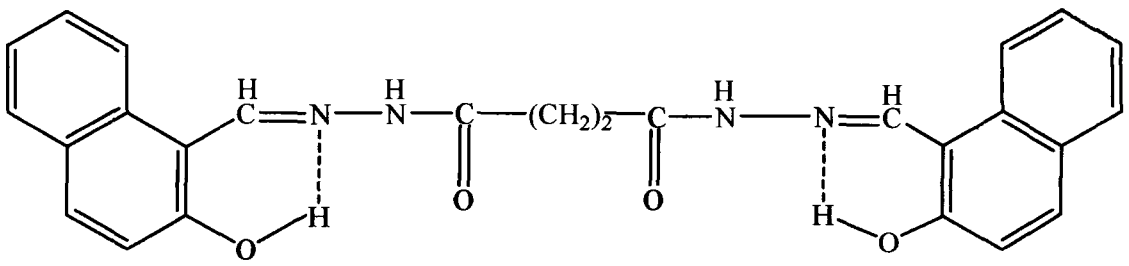
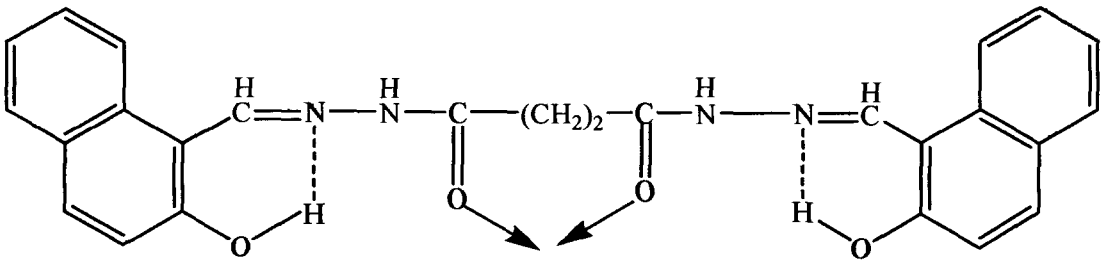


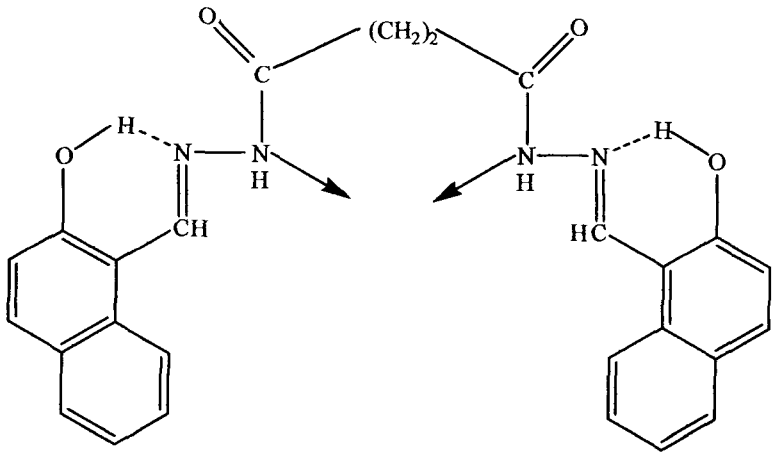
Fig 1.1. Bis(2-hydroxy-1-naphthaldehyde)succinoyl dihydrazone

Thus because of the presence of as many as eight bonding sites and because of its ability to exhibit keto-enol tautomerism in the complexes, it can form bonds to metal ions in several different ways as shown below:

1. It may function as a neutral bidentate ligand coordinating either through two carbonyl oxygen atoms (I) or the two secondary amine nitrogen atoms (II), the OH groups remaining hydrogen bonded in the complexes.

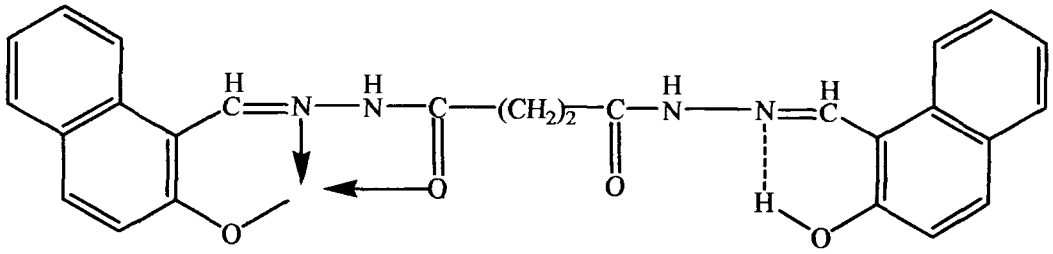


(I)



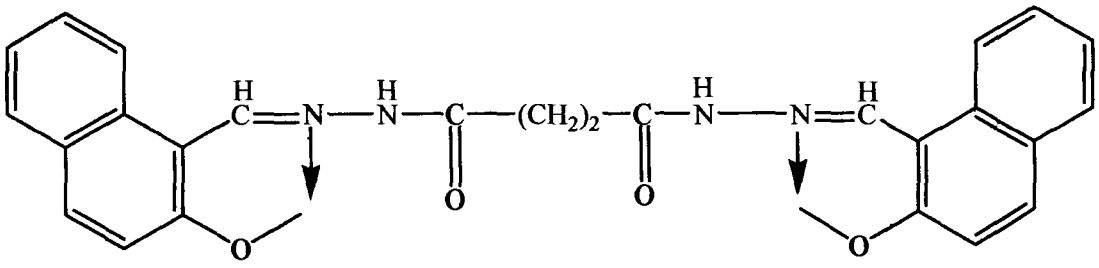
(II)

2. It may function as a monobasic tridentate ligand coordinating through one hydroxyl oxygen, one azine group nitrogen and one >C=O group oxygen atom (III), while the other half of the ligand molecule remains unbonded.



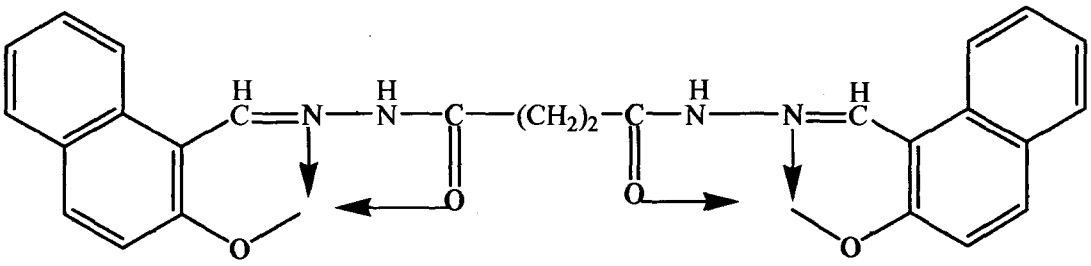
(III)

3. It may function as a dibasic tetradentate ligand coordinating through two hydroxyl oxygen atoms and the two azine group nitrogen atoms (IV), the two carbonyl oxygen atoms remains unbonded.



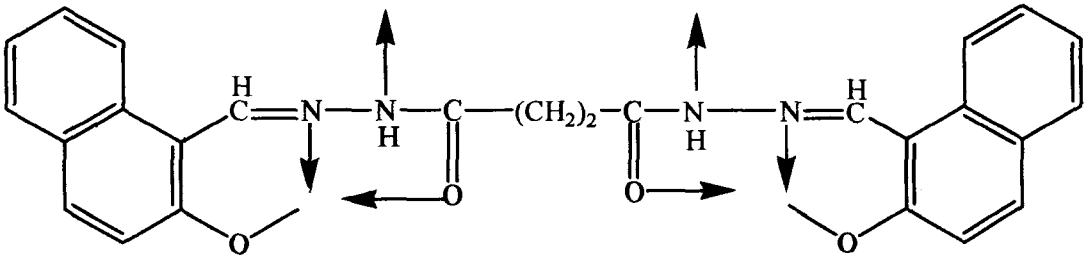
(IV)

4. It may act as a dibasic hexadentate ligand bonding to the metal ion through the two hydroxyl atoms, two azine group nitrogen atoms and the two carbonyl oxygen atoms (V).



(V)

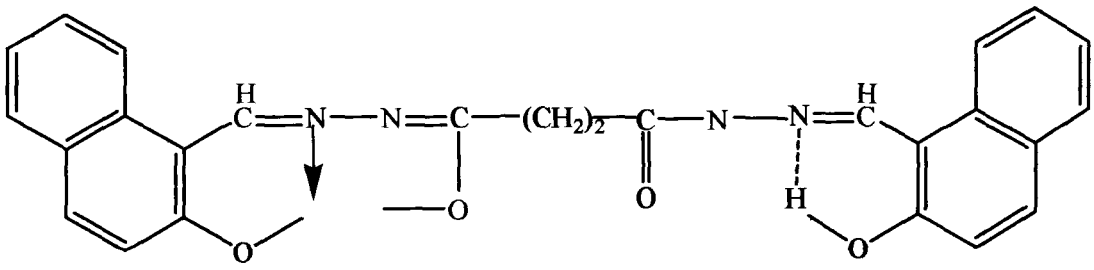
5. It may function as a dibasic octadentate ligand bonding to the same metal ion through all the available bonding sites (VI) but such a probability is ruled out on account of the simultaneous coordination of the secondary amine nitrogen atom and carbonyl oxygen atom to the same metal centre or even to different metal centres due to steric considerations and inductive effect.



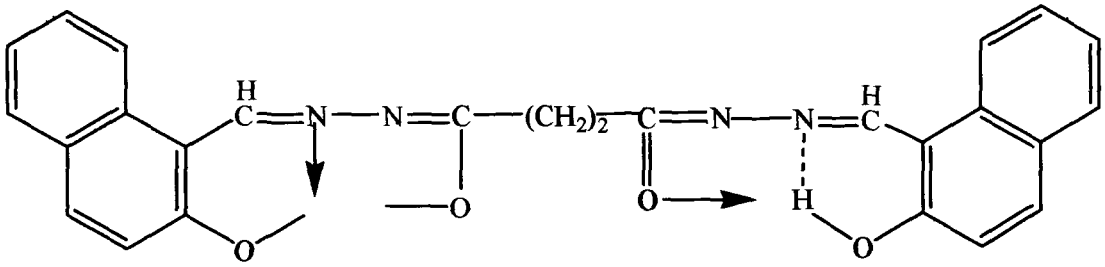
(VI)

6. When the lignad undergoes enolization as shown below, it may afford newer bonding sites. In this form, it can act as dibasic tridentate (VII), dibasic tetradentate (VIII), dibasic pentadentate (IX), and tetrabasic hexadentate (X) ligand bonding to

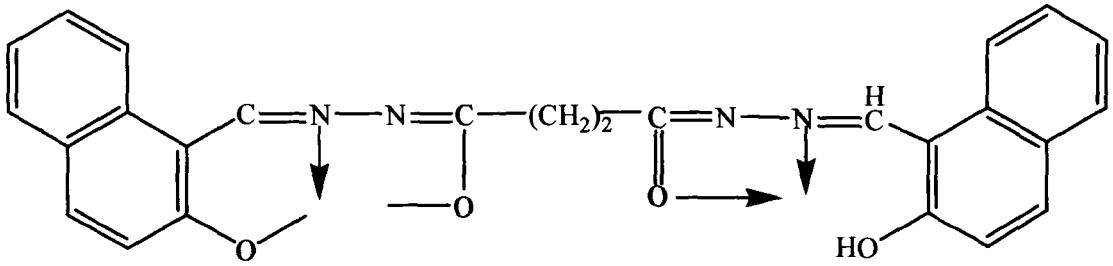
the same or different metal ions. In the enolized form it can act as a binucleating or a polynucleating ligand.



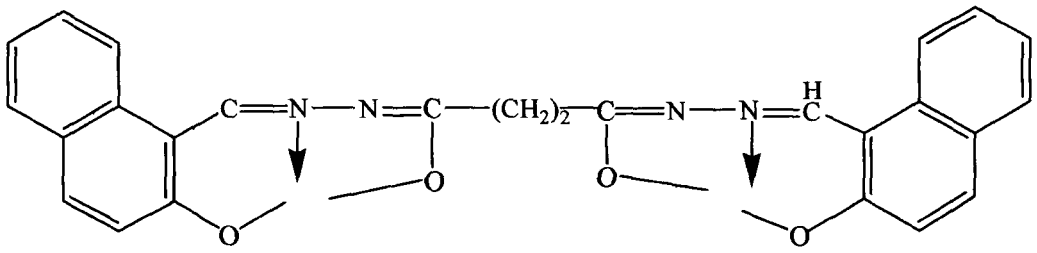
(VII)



(VIII)

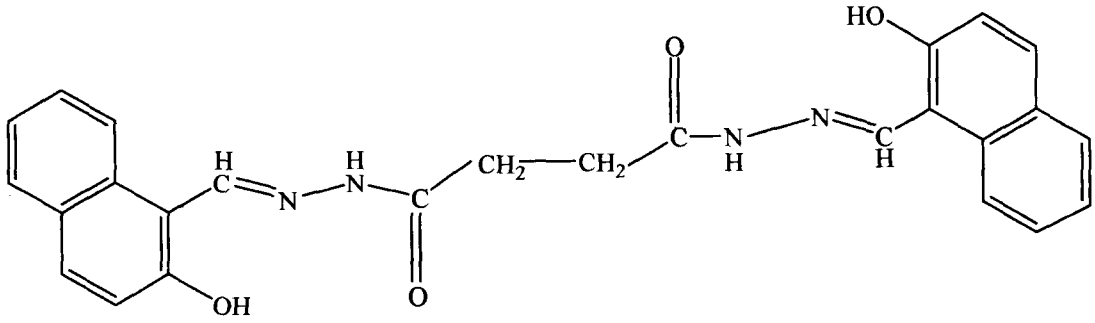


(IX)

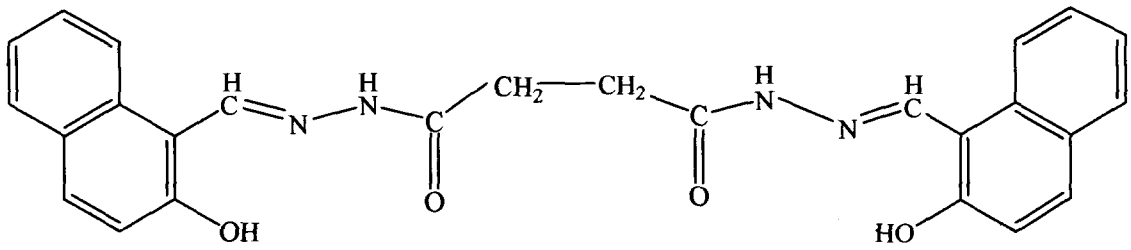


(X)

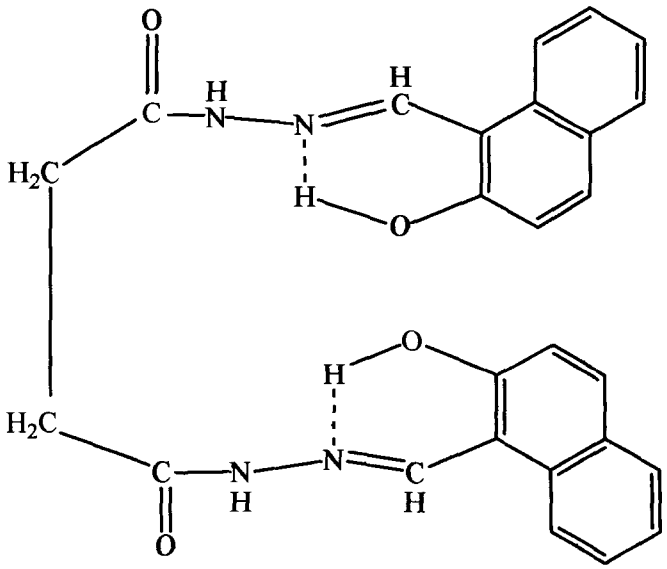
The most essential characteristic feature of the ligand skeleton is that, it possesses the group $-CH_2-CH_2-$ which offers high flexibility to the ligand whereas naphthaldimine fragment is associated with bulky characteristic which may introduce steric crowding in the molecule. The present dihydrazone can exist in the *staggered* configuration (XI) or *cis*-configuration in the uncoordinated state and as well as in the metal complexes. In *cis*-configuration the dihydrazone can adopt either *syn-cis* configuration (XII) or *anti-cis* configuration (XIII).



(XI)



(XII)



(XIII)

All these possibilities can actually be realized in practice if the nature of the metal salt, molar ratio of the metal ion and the ligand, the nature of the counter cation and anion, reaction medium, pH and temperature of the reaction medium are varied.

LITERATURE SURVEY

The dihydrazones are examples of polyfunctional ligands which can bind two metals in close proximity to one another. The work on metal complexes of polyfunctional ligands has recently created much interest among chemists, because the magneto and electro chemical properties of complexes derived from them show promise in developing theories whereby electron transport phenomena can be understood **[33]**. Acyl-, aroyl-, and pyridoyl-, dihydrazones are some of the few examples of ligands which can yield binuclear, heteronuclear and polynuclear complexes of transition and inner-transition metals, possessing interesting magnetic and electrochemical properties **[34]** and which can serve as models in bioinorganic chemistry **[35]**. Acyl-, aroyl-, and pyridoyl-, dihydrazones derived from the condensation of *o*-hydroxyaromatic aldehydes and ketones and acyl- and aroyl- dihydrazines in which two hydrazone groups are separated from each other by methylene chains of varying length or phenyl group, or pyridoyl group and those derived from condensation of monohydrazines with dialdehydes, constitute a special class of molecules. This class of molecules reacts in the keto-enol forms **[36]** depending upon the mode of preparation of the complexes, the nature of the reaction medium, the pH of the reaction medium, the nature of the metal salt and the molar ratio of the metal salt and the ligand employed, the present ligand can act as mono-, di-, tri-, and tetrabasic hexadentate ligand and give rise to polymeric complexes through both ligand bridging due to their flexibility in three-dimensional space and oxo-bridging through the phenolic atoms.

The dihydrazones can be obtained from condensation of acyl-, aroyl-, and pyridoyl-, dihydrazines [$R(CONHNH_2)_2$]; (R = O, $-(CH_2)_n-$, $C_6H_4<$, $C_6H_3N<$) with *o*-hydroxyaromatic aldehydes and ketones. Another category of the dihydrazones can be obtained from condensation of dialdehydes [$R(CR'O)_2$]; (R = O, $-(CH_2)_n-$, $C_6H_4<$, $C_6H_3N<$, R′ = alkyl groups) with monoacyl-, aroyl-, pyridoyl- and quinaldenoyl-, hydrazines. Accordingly, the literature survey is presented under the following two major sections.

1. Complexes of dihydrazones derived from condensation of acyl-, aroyl-, and pyridoyl-, dihydrazines with simple *o*-hydroxyaromatic aldehydes and ketones.

2. Complexes of dihydrazones derived from condensation of dialdehydes with monoacyl-, aroyl-, pyridoyl- and quinaldinoyl-, hydrazines.

Sacconi **[37]** has isolated a seies of diamagnetic dinuclear nickel(II) complexes of dihydrazones obtained from condensation of aliphatic dicarboxylic acid dihydrazides with

salicylaldehyde, 2-hydroxy-1-naphthaldehyde, *o*-aminobenzaldehyde, and *o*-hydroxyacetophenone. He showed that the hydrazones react in their enol forms with $Ni(OAc)_2$ in aq. alc. ammonia as bis-tridentate complexing agents.

Aggarwal and co-workers **[38]** isolated complexes of the compositions $[VO(LH_2)]SO_4$, $[VO(LH_2)]Cl_2$, $[VO(LH_2)py]SO_4$ from reaction of vanadyl sulfate and chloride and metal(II) chloride with bis(acetone)oxaloyldihydrazone, bis(acetone)malonoyldihydrazone and bis(acetone)succinoyldihydrazones in alcoholic medium. The complexes $[VO(LH_2)]SO_4$ and $[VO(LH_2)]Cl_2$ were proposed to have square-pyramidal stereochemistry while the remaining complexes were proposed to have octahedral stereochemistry.

Iskander and co-workers **[39]** isolated the metal (II) complexes of the composition $M(LH_3)X{\cdot}nH_2O$, $M_2(LH_2)X_2{\cdot}nH_2O$, $M(LH_2){\cdot}nH_2O$ and $M(LH_3)_2{\cdot}nH_2O$ (where M = Cu(II), Ni(II) and Co(II); X = Cl^-, Br^-, I^-) from reaction of the metal(II) salts with dihydrazones (LH_4) derived from condensation of salicyaldehyde with acyldihydrazines with the methylene backbone varying from 1 to 5 under different experimental conditions. They assigned a pseudo-octahedral stereochemistry for the nickel(II) complexes $[Ni(LH_3)X]{\cdot}nH_2O$ (X = Cl^-, Br^-, I^-) and $[Ni_2(LH_2)Cl_2]{\cdot}2H_2O$ on the basis of magnetic moment data and spectral studies. The latter complexes change to penta-coordinated state on dehydration. However, five coordinate structure was proposed for the nickel(II) complexes $Ni(LH_2){\cdot}nH_2O$ as against a distorted octahedral structure for the corresponding cobalt(II) analogues. On the other hand, Kapoor and co-workers **[40]** suggested that the nickel(II) complexes $Ni(LH_2){\cdot}nH_2O$ have octahedral stereochemistry. Anomalous magnetic behaviour of the nickel complexes $Ni_2(L){\cdot}nH_2O$ (μ_{eff} values lying in the range 1.65-1.70 BM) is ascribed to arise due to the presence of two magnetically non-equivalent sites in the same unit cell. This is confirmed from electronic spectral study of the complexes as well which show bands characteristic of octahedral and square planar nickel(II) sites in the complexes. All the cobalt(II) complexes are proposed to have octahedral stereochemistry. The copper complexes $Cu(LH_3)X{\cdot}nH_2O$ and $Cu_2(LH_2)X_2{\cdot}nH_2O$ are proposed to have square-pyramidal stereochemistry. The low magnetic moment values than the spin only value is attributed to superexchange interactions through the oxygen bridges. The complex $Cu(LH_2){\cdot}nH_2O$ has been suggested to have square planar stereochemistry.

Narang and Lal **[41]** have described complexes of disalicyaldiminesuccinamide (H_2L) and N,N-bis(*o*-hydroxyacetophenoneimine)succinamide (H_2J) of the types ML, MJ, M(HL)Cl,

$M(HJ)Cl$ and $M'(HL)_2$ (where M = Cu(II), Ni(II), or Co(II). The complexes are proposed to have either octahedral stereochemistry or square planar stereochemistry.

Narang and Lal **[42]** have reported mono and binuclear zinc(II) complexes $Zn(HL)Cl$ and $Zn_2(L\text{-}2H)$ derived from multidentate acyldihydrazone ligands. The reaction medium, zinc salts and ligand geometry are shown to influence the composition and stereochemistry of the complexes. The zinc centres were proposed to have octahedral as well as tetrahedral stereochemistry.

Polymeric metal (II) complexes **[43]** of the type M_2L derived from dihydrazones obtained from condensation of oxaloyldihydrazide, succinoyldihydrazide and phthaloyldihydrazide with salicylaldehyde or *o*-hydroxyacetophenone have been described by the above authors. Copper complexes and few nickel and cobalt complexes are proposed to have square planar stereochemistry while other nickel and cobalt complexes are proposed to have distorted octahedral and square-pyramidal stereochemistry. The anomalously low magnetic moments of some complexes are related to M-M interactions via oxo-bridged structure.

Narang and Lal **[44]** have prepared and characterized the metal(II) complexes $M(H_2J)$, $M(H_2K)$, $M(H_3J)Cl$, $M(H_3K)Cl$, M_2J, M_2K and $M_2(HK)(CH_3COO)$ (where M = Cu(II), Ni(II) and Co(II)) derived from di(salicylaldimine)malonamide (H_4J) and di(*o*-hydroxyacetophenoneimine)malonamide (H_4K) and the zinc(II) complexes ZnH_2L and Zn_2L from a number of multidentate acyldihydrazones (H_4L). The copper complexes are shown to have square-pyramidal and pseudo-octahedral stereochemistry. The cobalt complexes are shown to have square planar, square-pyramidal, mixed octahedral and tetrahedral and distorted octahedral stereochemistry in the solid state whereas zinc complexes have octahedral and tetrahedral stereochemistry.

Narang and co-workers **[45]** synthesized a new series of polymeric cobalt (II) complex of the type $Co_2(L)\cdot nH_2O$ from reaction of metal(II) acetate and dihydrazone (LH_4) where LH_4 is bis(*o*-hydroxyacetophenone)oxaloyldihydrazone, bis(salicylaldehyde)oxaloyldihydrazone, bis(*o*-hydroxyacetophenone)succinoyldihydrazone in the ratio 4:1 (metal:ligand) in ethanol under reflux. The complexes have been proposed to have polymeric structure with strong Co-Co interactions with planar disposition of donor atoms around metal centres.

Sahni and co-workers **[46]** synthesized and characterized complexes of the type $[M(LH_2)]X_3$ (where M = Cr(III), Mn(III), Fe(III) or Co(III); X =Cl^-, NO_3 or OAc) from

reaction of metal (III) salts with N-N-dibenzylidene dipicolinic acid hydrazone (LH_2) in ethanol medium. The ligand acts as a pentadentate unit having coordination sites at pyridine nitrogen, amide oxygen and hydrazinic nitrogens or azomethine nitrogens. In this context, it is important to mention that these authors **[47]** have also claimed that dipicolinic acid dihydrazine behaves as pentadentate ligand. On the otherhand, Dutta and Sarkar **[48]** have argued in favour of neutral tridentate behaviour of this ligand in which it can function either as a (NNN) or as a (ONO) donor.

Kapoor and co-workers **[49]** have studied reaction of vanadyl chloride and dipicolinic acid dihydrazone in presence of acetylacetone or other β-diketones in ethanol and acetic acid. They isolated brown solid complexes of macrocylic ligand bis(β-diketone) dipicolinoyldihydrazones. On the other hand they isolated a non-macrocyclic pyrazole derivative when reaction of vanadyl chloride was carried out with the preformed bis(β-diketone)dipicolinic acid dihydrazone. Similar products **[50]** were also isolated in case of zirconium(IV).

Teotia and Rana **[51]** synthesized complexes $[M(L)\cdot 2H_2O]$ (M = Cu(II), Ni(II) and Co(II)) of the above macrocyclic ligands by treating a methanol solution containing a mixture of acetylacetone and 2,6-dipicolinic acid hydrazide and the appropriate metal chloride. The IR spectra indicated condensation of both the oxygen atoms of acetylacetone with NH groups of dihydrazine. The electronic spectral bands agree reasonably well with the five coordinate geometry.

Kapoor and co-workers **[52]** synthesized a number of metal (II) and metal (III) complexes from reaction of metal (II) and metal (III) salts with dihydrazones obtained from condensation of salicylaldehyde with oxaloyldihydrazine, malonoyldihydrazine and succinoyldihydrazine under different experimental conditions. The trivalent metal ions are found to yield complexes having compositions $[M_2LX_2]\cdot nH_2O$ and $[M_2(LH_2)X_4]\cdot nH_2O$ (M= Cr(III), Fe (III) and Mn (III)) (X= Cl^-, NO_3^-, OAc, OH) while the bivalent metal ions were found to form complexes having compositions $[M(LH_2)]$ and $[ML(H_2O)_4]$ (M= Mn(II) and Fe(II)). The dihydrazones are suggested to function as dibasic and tetrabasic hexadentate binucleating ligands. Iron(III) complexes were characterized by Mossbauer spectroscopy as well. The complexes have been suggested to have distorted octahedral stereochemistry.

Narang and Yadav **[53]** studied reaction of aluminium(III) salts with several dihydrazone ligands in aqueous medium at controlled pH and characterized the resulting complexes by

infrared spectroscopy. The complexes are suggested to be polymeric with dihydrazones coordinated in the keto form.

Narang and Dubey **[54]** have described Zn(II), Cu(II), Ni(II) and Co(II) complexes of solid polymers derived from glyoxal and organic acid dihydrazides. They have discussed the structure of the complexes in light of magnetic moment, electronic and IR spectral studies.

Yacouta and co-workers **[55]** studied the complexation behaviour of uranyl ion with various dihydrazides and their diydrazones obtained from condensation of simple *o*-hydroxyaromatic aldehydes and ketones with dihydrazides. They isolated several monometallic and bimetallic uranyl complexes and characterized them by various physico-chemical data and spectroscopic studies. They also studied the effect of excess acetate ion on complex formation.

Lal and co-workers **[56]**, have prepared several homotrinuclear complexes having general formula $[M_3LCl_2(H_2O)_3]$ (M=Mn(II), Co(II) or Ni(II)) from bis(acetophenone)-2,6-dipicolinoyldihydrazone (LH_4) in alcoholic medium by adjusting pH to ~8 by KOH. The complexes show low μ_{eff} values, much less than those expected for the high-spin metal ions possibly due to metal-metal interaction and anti-ferromagnetic exchange. The complexes are proposed to have mixed six coordinate octahedral and five coordinate square-pyramidal stereochemistry.

Narang and Singh **[57]** have synthesized polymeric complexes $M(L\text{-}2H)\cdot nH_2O$ (where M = Fe(II), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II), L=A,B) from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (A) and bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (B) by solid-solution reaction. All of the complexes were suggested to have distorted octahedral stereochemistry.

Lal and co-workers **[58]** studied the reaction of uranyl acetate with the above dihydrazones (H_4L) in aqueous-alcoholic media and isolated complexes of the type $(UO_2)_2L\cdot 6H_2O$. The dihydrazones coordinate to the metal centre in enol form. They have studied the effect of complexation on the coupling of >C=O vibrations, in an enolized form and of ligand coordination to the uranyl ion as a function of the number of methylene groups by comparing the asymmetric stretching vibrations of the uranyl ion in various complexes recorded under identical conditions.

Lal and Das **[59]** studied reaction of uranyl nitrate and acetate with dihydrazones (H_4L) (where H_4L = disalicylaldehydeoxaloyldihydrazone (H_4A), -malonoyldihydrazone (H_4B), -succinoyldihydrazone(H_4C), -glutoyldihydrazone(H_4D), -adipoyldihydrazone (H_4E), and phthaloyldihydrazone (H_4F) in 3:1 molar ratio in alcoholic medium. The complexes $[(UO_2)_2(H_2L)(NO_3)_2(H_2O)_4]\cdot 2H_2O$ and $[(UO_2)_2(H_2L)(CH_3COO)_2(C_2H_5OH)_2]\cdot C_2H_5OH$ have been isolated and characterized.

Lal and co-workers **[60]** synthesized copper(II) complexes $Cu_2(L)\cdot nH_2O$ and dioxouranium(VI) complexes $[(UO_2)_2(H_2L)(C_2O_4)]\cdot 2nH_2O$ of the above dihydrazones. The $C_2O_4^{2-}$ group is suggested to cooordinate to the uranium centre retaining its D_{2h} symmetry.

Lal and co-workers **[61]** synthesized a series of uranyl complexes of the composition $[UO_2(H_3L)_2]\cdot nH_2O$ from above dihydrazones from reaction of uranyl nitrate with salicylaldehyde and acyl- and aroyl- dihydrazines in 1:4:2 molar ratio in ethanol medium.

Lal and coworkers **[62]** studied reactions of disalicylaldehyde adipoyldihydrazone with uranyl nitrate and uranyl acetate in aqueous and ethanol media under different experimental conditions. The resulting complexes of the compositions $[UO_2(H_2L)(H_2O)]_n$, $[UO_2(H_2L)_2]_n\cdot 3nH_2O$, $[UO_2(H_3L)(CH_3COO)]_n\cdot 3nH_2O$, $[UO_2Zn(L)(H_2O)_2]_n\cdot 2nH_2O$, $[(UO_2)_2(H_2L)(C_2O_4)]\cdot nH_2O$, $[(UO_2)_2(L)(py)_2(H_2O)_4]$, $[(UO_2)_2(HL)(CH_3COO)(H_2O)_3]_3\cdot nH_2O$ $[(UO_2)_3(L)(CH_3COO)_2(H_2O)_2]_n\cdot 2nH_2O$, $[(UO_2)_2(L)(py)_2(H_2O)_2]_n\cdot XnH_2O$, (where py = pyridine or α-, β-, γ-picoline, X = 0, 1) have been isolated and characterized. In the complexes the ligand functions as a bridging monobasic tetradentate, dibasic hexadentate and tetrabasic hexadentate ligand and exhibits keto-enol tautomerism. In the heterobimetallic complexes $[UO_2Zn(L)(H_2O)_2]_n\cdot 2nH_2O$, the uranium and zinc atoms are considered to have hexagonal bipyramidal and tetrahedral stereochemistry respectively.

Lal and co-workers **[63]** have described dioxouranium(VI) and Zn(II) complexes $[M(H_2L)(H_2O)_2]_2\cdot 2nH_2O$ (where M= UO_2^{2+}, Zn^{2+}) of bis(*o*-hydroxynaphthaldehyde) oxaloyldihydrazone (H_4L). The complexes are obtained from reaction of metal acetate with oxaloyldihydrazine in 1:1 molar ratio in ethanol followed by reaction of excess *o*-hydroxynaphthaldehyde under reflux. Dioxouranium(VI) complex is proposed to be eight coordinate involving coordination of dihydrazone in the enolic form with *cis*-configuaration while the zinc complex is proposed to be octahedral involving coordinated dihydrazone in enolic form in the *staggered* configuration. The naphtholic -OH groups are

proposed to be non-coordinated. They **[64]** have, further, synthesized dioxouraninum(VI) complexes $[UO_2(H_2L)]_n \cdot 2nH_2O$ and $[(UO_2)_2(L)(H_2O)_6]_n$ from reaction of uranyl nitrate with preformed dihydrazone bis(*o*-hydroxynaphthaldehyde)oxaloyldihydrazone in 3:1 molar ratio in aqueous and ethanol media, respectively, under reflux. Based on the splitting of the δ NH signal in monometallic complex and δ CH=N in both complexes into quartet as compared to the singlet in free dihydrazone, the complexes are proposed to exist in chair formation with the *anti-cis*-configuration of dihydrazone involving eight and nine coordinated uranium atoms, respectively. The complexes **[65]** $Na_4[(UO_2)_4(L)_2(CH_3COO)_4(H_2O)_4] \cdot 4H_2O$ and $Na_4[(UO_2)_4(L)_2F_4(H_2O)_4]$ obtained from the same ligand have also been described by them.

Patil and Kulkarni **[66]** and others **[67]** obtained complexes of the type $[UO_2L] \cdot nH_2O$ from interaction of uranyl acetate disalicylaldehyde thiocarbohydrazone (H_2L) and established their structure by ^1H NMR and IR spectroscopic studies.

Kapoor and co-workers **[68]** studied reaction of malonoyldihydrazine and phthaloyldihydrazine with β-diketones in presence of the dioxouraninum(VI) cation which appears to function as a metal template. This facilitates condensation of dihydrazide with diketones resulting in the formation of several dioxouranium(VI) complexes of macrocylic ligands. The formation of a macrocyclic ring was confirmed from infrared spectroscopic studies. However, when dioxouranium(VI) nitrate was treated with the condensation product of phthaloyldihydrazine and acetylacetone, an entirely different pyrazole derivative was formed.

Sahoo and co-workers **[69]** have synthesized several first series transition metal complexes from several dihydrazones. The complexes were characterized by elemental analyses, physic-chemical data and spectral studies.

Pandey **[70]** reported a number of organometallic complexes derived from pyridoyldihydrazones. In this study, he showed from IR spectral data that dihydrazones coordinate to the metal centre in keto form through both >C=O and >C=N groups.

Mahale and Havanur **[71]** studied dioxomolybdenum(VI) complexes of the composition $(MoO_2)_2(L)(py)_2$ synthesized from dihydrazones (H_4L) obtained from condensation of the several acyl dihydrazines and substituted salicylaldehydes.

Panda and co-workers **[72]** synthesized heterobimetallic complexes $[MNiM(BTDO)_2X_2(H_2O)_4] \cdot nH_2O$ (where M = Ni(II), Co(II) and Cu(II); X = Cl^-, NO_3^-, n =

0 or 0.5 and BTDO = 1,8-Bis(2'-oxophenyl)-2,3,6,7-tetraza-4,5-dimethyl-1,3,5,7-octatetraene) from the precursor nickel complex nickel[bis(diacetyldihydrazone)]. The metal centres have been proposed to have octahedral stereochemistry.

Gopinathan and co-workers **[73]** have shown that the Schiff base, $((HOC_6H_4CH{=}NNCO)_2CH_2))$ (H_4L) derived from the condensation of salicylaldehyde and malonoyldihydrazine reacts with organotin chlorides to yield binuclear complexes of the type $R_2Sn(L)SnR_2$, where R = CH_3^-, $C_2H_5^-$, $C_4H_9^-$, $C_5H_5^-$, $CH_3CO_2CH_2CH_2$, and $C_6H_5CH_2$. The complexes have vbeen characterized and the structures were assigned on the basis of their elemental analyses, IR, ^1H, ^{13}C, ^{119}Sn NMR spectra and X-ray crystallographic data. They studied the structure of the complex $[(C_2H_5)_2Sn]_2(OC_4H_4CH{=}NNCO)_2CH_2$ by X-ray cryatallography.

Sacconi **[74]** studied the reactions of biacetyl-bis(benzoylhydrazone) with nickel(II) acetate in alcohol in the presence of concentrated ammonia and isolated orange coloured biacetyl-bis(benzoylhydrazonato)nickel(II) complex and studied its reaction with pyridine **[75]**. The formation constant of the complexes formed between biacetyl-bis(benzylhydrazonato)nickel(II) and various alkyl amines **[76]** have been studied. Complexes of lead(II), lead(IV) and tin(IV) of the types [Pb(L)], $[Ph_2Pb(L)]$, $[Sn(L)_2]$, [PhSn(L)Cl] and $[Ph_2Sn(L)]$ have been obtained by mixing methanol solutions of the appropriate metal salts and the ligand **[77]**.

Pelizzi and co-workers **[78]** have studied reaction of copper(II) chloride dihydrate with 2,6-diacetylpyridine-bis(picoloylhydrazone) (LH_2) in refluxing ethanol yielding a dark green crystal of $Cu_2(L)Cl_2{\cdot}H_2O$. IR spectral data indicate coordination of all the three pyridine nitrogens. The ligand behaves as an octadentate bridging (NONNNNNN) donor. The authors have established the square-pyramidal structure of the complex unequivocally by X-ray crystallography. The environment around one Cu(II) is made up of a basal plane consisting of a chloride, two nitrogen atoms from the ligand (LH_2), an oxygen atom from second adjacent ligand molecule and another nitrogen from the same adjacent ligand molecule taking up the axial position. The environment around the second Cu(II) is made up of four nitrogen atoms from the first ligand molecule, while a chloride ion takes up the apical site. Same authors **[79]** have isolated another series of complexes of the type $M(LH_2)Cl_2{\cdot}nH_2O$ (M=Mn(II), Co(II), Ni(II) and Cu(II)) by mixing chloroform solution of LH_2 and ethanolic solution of the metal chlorides in 1:1 molar ratio. Another Mn(II) compound $MnL{\cdot}9H_2O$ was obtained by adding dropwise, a dilute NaOH solution to a warm ethanol-water solution containing LH_2 and $MnCl_2{\cdot}4H_2O$ in (1:1) molar ratio until

pH~ 8.0. The compounds were characterized by magnetic moment data, electronic and IR spectroscopic studies. The complex $Mn(LH_2)Cl_2 \cdot 5H_2O$ was shown to have pentagonal bipyramidal stereochemistry by X-ray crystallography **[80]**. On the basis of similarity of IR spectra of Cu(II), Ni(II) and Zn(II) complexes with that of Mn(II) complexes, a similar pentagonal bipyramidal stereochemistry was also proposed for them with ligand acting as ONNNO donor and chloride or water molecules occupying apical positions. The complex $MnL \cdot 9H_2O$ was also characterized by X-ray crystallography and was shown to have pentagonal bipyramidal stereochemistry.

Curtis and co-workers **[81]** and others **[82]** studied Cu(II) and Ni(II) complexes of acetylacetonebis(picoloylhydrazone) and acetylacetonebis(isonicotinoylhydrazone). They carried out X-ray structural analysis of the copper(II) complex of acetylacetonebis(isonicotinoylhydrazone) obtained from reaction of metal(II) salt, isonicotinoylhydrazine and acetyl acetone and confirmed the square-pyramidal stereochemistry.

Giordano and co-workers **[83]** isolated cobalt(II) and nickel(II) complexes of compositions $[Co(LH_2)(H_2O)(NO_3)]NO_3$ and $[Ni(LH_2)(H_2O)_2](NO_3)_2 \cdot 2H_2O$ from the reaction of metal nitrates with 2,6-diacetylpyridine-bis(benzoylhydrazone) (LH_2) in 95% ethanol. The X-ray crystallographic study confirmed that the metal atoms are in a pentagonal bipyramidal arrangement in the structural unit of the complexes.

Palenik and co-workers **[84]** isolated lanthanum complex of composition $[La(LH_2)(NO_3)_3]$ from the reaction of lanthanum nitrate and the ligand in ethanol at 55 °C in the presence of water. The complex was studied by infrared spectroscopy and X-ray crystallographic studies. They showed lanthanum to be eleven coordinated in these complexes. A decahedral arrangement of the donor atoms of the ligand is proposed around the lanthanum atom in the complexes.

Paolucci and co-workers **[85]** prepared a series of dioxouranium(VI) complexes of 2,6-acetylpyridinebis(4-methoxy benzoylhydrazone) (H_2dapmb). The neutral compound of the composition UO_2(dapmb) was formed in two different crystalline forms, α and β depending upon the experimental conditions. The geometry of $[UO_2(dapmb)]$ which was formed in two forms is very similar, the only significant difference being the difference in the conformation of carbon atoms in a methoxy group. Seven fold coordination of uranium(VI) was established with the five donor nitrogen atoms in the equatorial plane.

Pelizzi and co-workers **[86]** isolated tin(IV) complexes of the composition $[Snpr_2(LH_2)]$ from reaction of n-propyltinchloride in anhydrous acetone, under nitrogen atmosphere with boiling suspension of 2,6-diacylpyridinebis(salicylhydrazone) (LH_4) in dry methanol. X-ray crystal structure study has established that tin atom is seven coordinated in the complex with pentagonal bipyramidal arrangement of ligand atoms. The -OH groups remain uncoordinated.

Teotia and co-workers **[87]** have studied reactions of metal(II) salts (M=Cu(II), Ni(II)) with picolinoyl/isonicotinoylhydrazine in presence of acetylacetone. They isolated complexes of the compositions [M(LH)X] (M = Ni(II), Cu(II), X = Cl^-, Br^- NO_3^- and NCS, LH_2 = acetylacetonebis(picolinoylhydrazone) or acetylacetonebis(isonicotinoylhydrazone). All the complexes have been established to have square-pyramidal stereochemistry. The complexes $[M(LH)X_2]$ [X= Cl^-, Br^- NO_3^- and NCS for M=Cu(III); X = OAc, Cl^-, Br^-, NCS for Mn(III) and OH for Co(III) were also prepared similarly **[88]** by them. These complexes have been suggested to have six-coordinate tetragonal structure.

Paolucci and co-workers **[89]** synthesized several complexes of 2,6-diformylphenolbis(benzoylhydrazone) and its substituted derivatives with the bivalent metal ions (M = Co (II), Ni (II), Cu(II) and Zn(II) and established their molecular structure by various physico-chemical techniques. A fascinating aspect of these ligands is the coordinating and bridging ability of phenolic -OH of the 2,6-formylphenol moiety plus the very subtle behaviour of acidic protons.

Dutta and co-workers **[90]** isolated complexes of the composition [VO(L)] from reaction of $VO(acac)_2$ with acetylacetonebis(benzoylhydrazone) (LH_2) in acetone. The same ligand on reaction with CoX_2 (X = Cl^-, Br^-) in anhydrous medium yield blue coloured tetrahedral polymeric complexes $[Co(LH_2)X_2]$ **[91]**. However, in the presence of lattice water, bromide salt yields pink coloured pseudo-octahedral $[Co(LH_2)Br_2]$ complexes. The dihydrazone reacts with nickel(II) chloride in rectified spirit and yields diamagnetic, orange yellow complex [Ni(L)] **[92]**. However the reaction with anhydrous $NiCl_2$ in warm anhydrous methanol gives a paramagnetic complex $[Ni(LH_2)Cl_2]$ having a *trans*-dichloro pseudo-octahedral structure. When this complex is exposed to moist atmosphere and over KOH, the partial dechlorination occurs giving the complex [Ni(LH)Cl]. This complex is proposed to have a five-coordinate structure. They have also isolated the complexes [Zn(L)], $[Cd(L)]\cdot 2H_2O$ and [Pb(L)] from the interaction of appropriate metal acetate with the ligand in ethanol.

Snow and co-workers **[93]** studied the reaction of bis(acetylacetonato)oxovanadium(IV) with benzoylhydrazine in dry ethanol under dry nitrogen. They isolated bis(acetylacetone benzoylhydrazonato)vanadium (IV). A trigonal prismatic geometry was verified for this complex.

Dutta and co-workers **[94]** showed that the reaction of $VO(acac)_2$ with benzoylhydrazine and related ligands in methanol, ethanol and methyl acetate yielded violet or almost black coloured bis(acetylacetonebenzoylhydrazonato)vanadium(IV) whereas reaction in acetone or methyl ethyl ketone yielded (acetylacetonebenzoylhydrazonato)oxovanadium(IV). While in the former complex, the abstraction of oxo-group has been suggested to occur, in the latter complex it is retained.

Lanthanide complexes **[95]** of the type $[Ln(L)(OH)(H_2O)]$ (Ln = La(III), Pr(III), Nd(III), Sm(III), Gd(III), Ho(III), Er(III)) have been obtained in situ by refluxing biacetyl, benzoylhydrazine and the appropriate metal chloride in ethanol in the presence of a regulated quantity of NH_4OH. The ligand acts as a quadridentate ONNO donor in its enol form.

Pelizzi and co-workers **[96]** have isolated a new series of metal(II) complexes of the type $[M(LH_2)(OH_2)Cl]$ (M = Co(II), Ni(II), Mn(II), Cu(II) and Zn(II)) by mixing ethanol solutions of LH_2 with ethanol solutions of metal(II) chloride in 1:1 molar ratio. With metal(II) acetates, the compounds of the type [ML] are obtained. The ligand reacts with metal centres in keto form in complexes $[MLH_2(OH_2)Cl]Cl$ and enol form in complexes [ML]. Some of the complexes are characterized by X-ray crystallographic method as well. The complexes are shown to have pentagonal bipyramidal stereochemistry.

Dutta and co-workers **[97]** have studied the reaction of $MoO_2(acac)_2$ with benzoylhydrazine and related ligands in different solvents. They isolated the complex (benzoylhydrazine)(benzoylhydrazido)(acetylacetonato)molybdenum(VI) in dry methanol while in ordinary methanol the complexes (acetylacetonato)(*cis*-dioxo)molybdenum(VI)-μ-diol-(benzoylhydrazino)(*cis*-dioxo)molybdenum (VI) dihydrate was isolated. They have shown that in dry methanol acetylacetone and hydrazines condense to give Schiff base complexes whereas no Schiff base formation occurs in ordinary methanol. The Schiff bases derived from acetylacetone and 2-picolinoylhydrazide or isonicotinoylhydrazide are similar to above, but they give complexes of the $[UO_2L]Cl$ (where LH = Schiff base), in which Schiff bases coordinate through both azomethine nitrogen and pyridine nitrogen (in

the case of 2-picolinoylhydrazone) or carbonyl oxygen (in the case of isonicotinoylhydrazone) **[98]**.

On the basis of IR and conductivity data Dey et al **[99]** have reported the formation of $[UO_2(LH_2)](NO_3)_2$ (where LH_2 represents 1,2-dimethylbis(4-methoxybenzoylhydrazone)). Similarly they have reported the formation of $[UO_2(LH_2)(NO_3)]NO_3$ upon acidification of $[UO_2L]$ with HNO_3. Ligands are proposed to coordinate to the metal centres in keto as well as enol forms. Interaction of these complexes with neutral mono and bidentate ligands lead to the formation of $[UO_2L(A)_2]$ and $[UO_2L(AA)]$ (where A = pyridine, picoline, methylamine, aniline, Ph_3PO; AA = en, ph, phen).

Marangoni and co-workers **[100]** synthesized mercury (II) complex with 2,6-diacetylpyridinebis(2-pyridoylhydrazone). They carried out X-ray structural analysis of the complex, and confirmed its pentagonal bipyramidal stereochemistry.

Pelizzi and co-workers **[101]** synthesized nickel(II) complex $[\{Ni(H_2apsh)(OH_2)(I)\}_2C1_2]\cdot 2dmf\cdot 5H_2O$, and cobalt(II) and copper (II) complexes, viz. $[Co(H_2dpsah)(OH_2)_2]Cl\cdot 4H_2O$ of 2,6-diacetylpyridinebis[2-(semicarbozono)propionylhydrazone] (H_4apsh) and 2,6-diacetylpyridinebis[2-(semicarbazono)acetophenoylhydrazone] (H_2dpash) respectively. In the nickel complex, the four atoms of the semicarbazone system are involved in coordination while in the cobalt complex, semicarbazone system does not participate in coordination. They established the structure of the complexes by IR spectroscopy and X-ray crystallography.

Pelizzi and co-workers **[102]** studied the structure of a tetranuclear copper(II) complex $[Cu_2(dappc)(OH_2)_3]_2[Cu_2(dappc)(OH_2)_2(ClO_4)]_2(ClO_4)_6\cdot 2H_2O$ (I) and $[(Cu_2(dapip)Br]_2$ (II) derived from the polyfunctional ligand 2,6-diacetylpyridinebis(2-pyridine carbonylhydrazone) (H_2dappc) and 2,6-diacetylpyridinebis(2-(2-pyridinecarbonylhydrazone phenylacetohydrazone) (H_4dapip) respectively. The structure of compound (I) is built up of complex cations of formula $[Cu_2(dappc)(OH_2)_3]_2^{4+}$ and $[Cu_2(dappc)(OH_2)_2ClO_4]^{2+}\cdot ClO_4$ anions and uncoordinated H_2O molecule while that of the compound (II) consists of neutral unit of formula $[Cu_2(dapip)Br]_2$ and solvating H_2O molecules. In both compounds, two metal atoms for one hydrazone molecule are present and the ligand is bideprotonated in complex (I) and trideprotonated in complex (II).

A monoperoxo complex of Schiff base $(H_5C_6C{=}N\text{-}NHC(S)SCH_2C_6H_5)_2$, ($LH_2$) has been reported by Tarafder et al **[103]**. The complex $[UO_2(O_2)L]$ was prepared by treating uranyl nitrate with the Schiff base dissolved in a solution of KOH in 30% H_2O_2. The Schiff base

behaves as dibasic NNSS tetradentate ligand, while peroxo group is bonded to the metal centre as a bidentate chelating ligand.

Toshev and co-workers **[104]** reported the dioxouranium complex of diacetyl-bis(thio-benzoylhydrazone) in which uranium has a distorted pentagonal bipyramidal structure with the uranyl oxygen atoms at the axial positions.

Pelizzi and co-workers **[105]** synthesized copper complexes of di-2-pyridylketone(phenylsemicarbazone)acetylhydrazone (H_2psah) and studied their structure by X-ray crystallography. They showed that the copper complex $[Cu_2(psah)Cl]\cdot H_2O$ consists of a pair of structurally distinct metal centres with different environments bound to the heptadentate hydrazone ligand and held together by a -N-N- bridge.

Katti and coworkers **[106]** synthesized a number of palladium(II) complexes from a series of phosphorous hydrazide and hydrazones. The complexes were characterized by elemental analyses. The structural assessment was carried out by NMR and IR spectroscopic studies. They established the structure of one complex by X- ray crystallography as well.

Lukyanenko and co-workers **[107]** have determined the complex stability of Na^+, K^+, Rb^+, and Cs^+ ions with bis(benzo-15-crown-5) with acylhydrazide fragments in the linking chain in 95% aqueous methanol. In all cases, the formation of 1:1 complex was observed. The studied bis-crown ethers form more stable complexes than benzo-15-crown-5. The stability of biscrown ether complexes is substantially determined by the length of the linking chain. Bis-crown ether with a glutaric acid residue in the linking chain exhibits striking potassium selectivity. High selectivity and stability of the complexes are due to the increase of their sandwich structure rigidity resulting from the formation of H-bonds between acylhydrazide fragments.

Ji and co-workers **[108]** *studied several dinuclear yttrium(III) and lanthanide(III) picrate* complexes derived from acetylferrocenepyridine-2,6-diformylhydrazone having the stoichiometric formula $Ln_2L_2pic_6\cdot n(1\text{-}C_3H_7OH)\cdot mH_2O$ (pic = picrate anion, Ln = Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, n = 2, m = 4; Ln = Er, Tm, Yb, , n = 0, m =2). These complexes were characterized by EPR, IR, UV, ^{1}H NMR spectra and molar conductance data. It was found that the ligand coordinates in keto form to the lanthanide ions. All the complexes described were found to be 1:6 electrolytes in methanol.

Xianzeng and co-workers **[109]** synthesized zinc(II) complex $[Zn_2L(CH_3COO)_2]\cdot C_2H_5OH$, from a binucleating ligand 2,6-diformylpyridine N-oxidebis(benzoylhydrazone) (L) via template reaction in alcohol. They characterized the complex by X-ray crystallographic studies. The dihydrazone ligand was found to be present in doubly deprotonated form. They established that all the coordinated atoms of the Schiff base ligand and two zinc atoms with the same bond length of 2.24(1) Å. The two acetato ions act as bidentate ligands linking two zinc atoms. Both the zinc atoms have a distorted trigonal-bipyramidal environment. The complex crystallizes in the triclinic space group P1.

Pelizzi and co-workers **[110]** synthesized six complexes of copper(II), nickel(II), and iron(II) from a chiral ligand 2,6-diacetylpyridinebis[DL-hydroxy-(phenyl)acetic]hydrazone (H_4dapm) and characterized them by spectroscopic studies. They established the structure of the nickel complex $[Ni(H_4dapm)\text{-}(H_2dapm)]\cdot 13H_2O$ by X-ray diffraction methods. The complex crystallizes in the monoclinic space group C2/c. The complex has two fold crystallography imposed symmetry with the nickel atom in a distorted octahedral environment consisting of six nitrogen atoms from two ligand molecules. With the help of ^1H NMR spectroscopic studies, the existence of the ligand in three forms i.e the meso DL and the two enantiomeric DD and LL ones were established.

Rana and co-workers **[111]** synthesized several manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) complexes of 2,6-diacetylpyridine(benzylacetone)hydrazone (H_2L). The complexes have been shown to have composition $[M(H_2L)X_2]$ (where M = Mn, Fe, Co, Ni and Cu; X = Cl, Br, NO_3, SCN) and have been characterized by molar conductance, magnetic moment data, infrared, and electronic spectroscopy. The dihydrazone has been shown to function as a tridentate ligand bonding to the metal centre through pyridyl nitrogen and azomethine nitrogen atoms. All the complexes have been proposed to be five coordinate having trigonal bipyramidal stereochemistry in which the dihydrazone donor atoms occupy equatorial position while the anions occupy axial positions.

Paolucci and co-workers **[112]** studied the interactions of potentially binucleating ligand, 2,6-diacetylpyridine-bis(1-phthalazinylhydrazone) (H_2dapz), containing only nitrogen donor atoms, with nickel(II), copper(II), and zinc(II) salts. They showed that depending on the nature of the counter ions, Ni(II) and Cu(II) ions, selectively enter in one of the two compartments present in the ligand. They isolated five series of mononuclear complexes [dapzM], $[H_2dapzMCl_2]$, [HdapzMCl], $[(H_2dapz)_2M][ClO_4]_2$, $[HdapzM][ClO_4]$, from the

reaction of metal acetates, metal chlorides and metal perchlorates, respectively and the ligand. They also studied some interconversion reactions. The complexes were characterized by analytical techniques and spectroscopic methods. Some tentative stereochemical assignments of these compounds are reported on the basis of their physico-chemical properties. Different behaviour has been observed in the case of zinc(II) chloride and perchlorate. Crystal structure analysis on the bisdeprotonated complex $[dapzNi]_2$ shows that the compound is dimeric with the metal ions octahedrally coordinated into the upper compartment and the pyridine nitrogens bridging the two nickel atoms.

Maurya and co-workers **[113]** synthesized binuclear dioxotungsten(VI) complexes of the type $[(WO_2)_2L]$, where L is a flexibly bridged hexadentate tetra anionic Schiff base derived from the condensation of methylene or dithiobissalicylaldehyde with isonicotinoylhydrazine, benzoylhydrazine, *p*-nitrobenzoylhydrazine and furoylhydrazine are reported. The IR and NMR spectral data suggest an oligomeric structure for these complexes in which each tungsten atom achieves a pseudo-octahedral structure via W=O→W bridging. They have shown that the bridging methylene ($-CH_2$) or dithio (-S-S-) group has very little effect on the thermodynamic stability of the complexes.

Lal and co-workers **[114]** synthesized the bimetallic manganese (II, III) and dioxouranium(VI) complexes $[Mn_4(H_2L)(OAc)_4]\cdot 4H_2O$, $[Mn_4(L)_2(H_2O)_8]\cdot 4H_2O$, $K_4[Mn_4(L)_2F_6(H_2O)_2]\cdot 2H_2O$, $[UO_2(H_2O)_4[Mn_4(L)_2(OAc)_4]\cdot 4H_2O$, and $K_4[(UO_2)Mn_3(L)_2F_5(H_2O)_3]$ from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L). The complexes have been characterized by physical and spectral data. IR spectral data indicate that the dihydrazone coordinates to the metal centres in keto as well as in enol forms in the *anti-cis*-configuration in all of the complexes.

Lal and Adhikari **[115]** synthesized the compound $[(MoO_2)_2(L)(H_2O)]\cdot 2H_2O$ from the reaction of $MoO_2(acac)_2$ with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L) in ethanol-acetonitrile in 3:1 molar ratio under reflux. The complex is proposed to be a hexamer in which the ligand is arranged in sets of three parallel planes one above the other. The intra-planer metal atoms are bonded to each other by naphthoxo-bridges whereas the inter-planer metal atoms are bonded to each other by M=O···Mo type bridging. The *anti-cis*-configuration of the dihydrazone moieties leads to the chair conformation of the complexes.

Lal and co-workers **[116]** isolated the homobimetallic complex $[(MoO_2)_2(L)]\cdot 4H_2O$ from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L) in the solid state. It reacts

with Lewis bases pyridine and 3-picoline to form the complexes [{μ_2-O)MoO_2}$MoO_2(H_2L)$]·2D·$4H_2O$ (where D = pyridine (py) (2), 3-picoline (3-pic) (3) and with proton bases salicyloylhydrazine ($sylshH_3$) and isonicotinoylhydrazine ($inhH_3$) to yield the Mo(V) complexes [Mo_2(L)$(sylsh)_2$]·$5H_2O$ (4), and [Mo_2(L)$(inh)_2(H_2O)_2$]·$3H_2O$ (5), respectively. The complexes have been characterized by elemental analyses, molecular weight determinations, molar conductance, magnetic moment, ESR, electronic, infrared, and ^{1}H NMR spectral studies. IR and ^{1}H NMR data indicate that the dihydrazone coordinates to the metal centre in *anti-cis*-configuration in all the complexes. The dihydrazone is present in the enol form in the complexes (1). (4), and (5) but in the keto form in the complexes (2) and (3). The complexes (4) and (5) are paramagnetic to the extent of 3.02 and 3.16 μ_B respectively.

Lal and co-workers **[117]** have synthesized the complexes of the type $[(UO_2)_4(L)_2(H_2O)_8]\cdot 4H_2O$ (1), $K_4[(UO_2)_4(L)_2(OAc)_4(H_2O)_4]\cdot 4H_2O$ (2), and $K_4[(UO_2)_4(L)_2F_4(H_2O)_4]$ (3), from bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (H_4L) and characterized them by elemental analyses, molecular weight determinations, molar conductance, electronic, IR and ^{1}H NMR spectroscopic studies. The dihydrazone coordinates to the metal centre in the *anti-cis*-configuration in enol form in the complexes (1) and (3) which contain water and fluoro groups as co-ligands in the coordination sphere functioning as terminal monodentate ligand. The dihydrazone isomerizes to *syn-cis*-configuration when the bridging bidentate acetate group is introduced into the first coordination sphere in the complex (2). The coordination of both azomethine groups of the dihydrazone to the same metal centre in *anti-cis*- configuration in complexes (1) and (3) leads to coupling between azomethine protons suggesting their chair conformation. However, no such coupling occurs when different hydrazone parts of the dihydrazone coordinates to different metal centres in *syn-cis*-configuration in complex (2) eliminating the possibility of its existence in chair conformation.

Lal and Kumar **[118]** have synthesized an unstable monomeric yellow complex of the type $[(MoO_2)_2(CHsalmlhH_4)(H_2O)_2]\cdot H_2O$ {complex (A)} from the reaction between bis(acetylacetonato)dioxomolybdenum(VI) and disalicyldehyde malonoyldihydrazone (CH_2salmlhH) in ethanol. This is transformed into an intermediate complex $[(MoO_2)_2(CHsalmlhH)(H_2O)]_2\cdot 4H_2O$ {complex (AB)} after sometime. Ultimately a stable brown isomer complex $[(MoO_2)_2(CH_2salmlh)(H_2O)_2]\cdot 4H_2O$ {complex (AB)} is obtained. All the products have been characterized by various physico-chemical techniques, IR and ^{1}H NMR spectroscopic studies.

Lal and co-workers **[119]** isolated the complexes of the composition $[UO_2(H_3salligh)(OAc)]\cdot 3H_2O$ and $[UO_2Zn(salligh)(H_2O)_2]\cdot 2H_2O$, where $H_4salligh$ refers to disalicylaldehydeoxaloyldihydrazone ($H_4saloxlh$), malonoyldihydrazone ($H_4salmlh$), succinoyldihydrazone ($H_4salsuch$), glutaroyldihydrazone ($H_4salgluth$), and phthaloyldihydrazone ($H_4salphth$). The complexes have been characterized by molar conductance and spectral data.

Lal and co-workers **[120]** have synthesized the complexes, $Na_4[(UO_2)_4(L)_2(OAc)_4(H_2O)_4]\cdot 4H_2O$ (1) and $Na_4[(UO_2)_4(L)_2F_4(H_2O)_4]$ (2) from bis(*o*-hydroxynaphthaldehyde)oxaloyldihydrazone ($napoxlhH_4$) and characterized by elemental analyses, molar conductance, electronic, IR and ^1H NMR spectroscopic studies. On the basis of these studies, it is suggested that the fluoro complex exists in chair conformation in which coordination of both azomethine nitrogen atoms of the dihydrazone in *cis*-configuration to the same metal centre leads to coupling between azomethine protons. In the acetato complex, the coordination of two hydrazone parts of the dihydrazone even in *cis*-configuration to different metal centres eliminates the possibility of azomethine proton coupling and thus, its existence in chair conformation. All the complexes involves eight-coordinated uranium atom with the dihydrazone in the enol form.

Lal and co-workers **[121]** have synthesized the monometallic complexes of the type $[Zn_2(H_4L)_2(SO_4)_2]$ (1), $[Zn_2(H_2L)_2(H_2O)_2]$ (2), $K_2[Zn_2(H_2L)_2F_2]$ (2a), and the heterometallic complexes of the type compound $[(UO_2)_2Zn_2(H_2O)_6]$ (3), $[(UO_2)_2Zn_2(L)_2F_4(H_2O)_2]$ (3a), $[Cu_2Zn_2(L)_2(H_2O)_4]$ (4), $K_4[Cu_2Zn_2(L)_2F_4(H_2O)_2]$ (4a), and characterized them by analytical, molar conductance, magnetic moment data, electronic, ESR, IR and ^1H NMR spectroscopic studies. All of the complexes have been proposed to be dimer on the basis of molecular weight determinations. Monometallic complexes have been shown to contain the coordinated dihydrazone in *syn-cis*-configuration while the heterobimetallic complexes contain the coordinated dihydrazone in the *anti-cis*-configuration. In these complexes, copper and zinc metal centres have been shown to be five coordinate square-pyramidal whereas uranium centres have been shown to be eight-coordinate hexagonal bipyramidal

Ma Yongxiang and co-workers **[122]** synthesized the chelates $Na_2[Ln(C_{34}H_{28}N_8O_8)Cl]\cdot nH_2O$ of malonoyl dihydrazone of salicylaldehyde with the lanthanides and characterized them by elemental analyses, IR, UV, molar conductance and TGA. They showed that the ligand coordinates to the central metal ion with one hydrazone unit in the keto form and one chloride ion participates in coordination to the

metal ion. These chelates are 1:2 electrolytes in DMF and are more thermostable than their ligand due to the formation of chelate rings.

Bolgar and co-workers **[123]** synthesized a series of dihydrazone and substituted dihydrazone derivatives of biacetyl and of hydrazine and phenylhydrazine derivatives of 2-acetylpyridine. They studied the reactions of those dihydrazones with $[Ru(bipy)_2Cl_2]$ and isolated the products of the composition $[Ru(bipy)_2(L–L)][PF_6]_2$ (bipy = 2,2′-bipyridine; L–L = biacetyldi(phenylhydrazone) 1a, biacetyldi[methyl(phenyl)hydrazone] 1b, biacetyldi(o-tolylhydrazone) 1c, biacetyldi(methylhydrazone) 1d, biacetyl dihydrazone) 1e, biacetyldi(benzaldehyde azine) 1f, 2-acetylpyridinephenylhydrazone 1g, or 2-acetylpyridinehydrazone 1h). The structures of all the complexes were determined using IR, UV/VIS, NMR and microanalysis. The proton NMR spectra of 1a-1c showed an unusual dependence on probe temperature with broadened aromatic resonances, sharpening at both high and low temperatures in the case of 1b and 1c. No emission was observed for complexes with two hydrazone moieties, whereas it was observed for 1g and 1h with one hydrazone. The molecular structure of 1a was determined by X-ray crystallography and it was shown that a hydrazone phenyl group lies over each of the bipyridyl rings: space group C2/c, a = 25.895(3), b= 10.505 (1), c= 17.431(2) Å, β = 106.03 (2)° and Z= 4.

Khan and co-workers **[124]** synthesized a new class of tetraiminetetraamide macrocyclic (Ph_4[20]tetraene, N_8O_4, and Ph_6[20]tetraene, N_8O_4) complexes through the metal ion controlled reaction of 1,2-diphenylethane-1,2-dione dihydrazone (DPEDDH) with succinic acid $[ML_1X_2]$ or phthalic acid of the composition $[ML_2X_2]$ [M = Co, Ni, Cu or Zn; X = Cl or NO_3]. They elucidated the structure of the complexes on the basis of IR, ^{1}H NMR, EPR and electronic spectral data and conductance, as well as magnetic, properties. An octahedral geometry was assigned for all the complexes, involving coordination of all the imine nitrogens.

Labib and co-workers **[125]** synthesized a series of polyacylhydrazones by condensing diacetyl with oxalic, malonic, succinic, glutaric and adipic dihydrazides and characterized them by conventional spectroscopic studies. They reacted these dihydrazones with copper (II) and nickel(II) acetate to give metallopolymers of general formula $\{[Cu_2(L)(OAc)_2(OH)(H_2O)_2]\cdot yH_2O\}_n$, $\{[Cu(L)(AcO)_2(HO)(H_2O)]\cdot yH_2O\}_n$, $\{[Ni_2(L)(AcO)_2(HO)_2]\cdot yH_2O\}_n$, $\{[Ni(L)(AcO)(HO)]\cdot yH_2O\}_n$, where L refers to the neutral dihydrazone unit. Magnetic susceptibility measurements in the range 4.2-300 K indicated significant antiferromagnetic coupling between the Cu^{II} centers in the metallopolymers.

The results might indicate the presence of two polymer chains crosslinked by bis-μ-acetatocopper (II) bridges. Based on IR, spectral and magnetic measurements, tentative structures of the Cu^{II} and Ni^{II} metallopolymers were proposed. The dihydrazone units in these polymers were found to be coordinated to the metal(II) via the azomethine nitrogen(s) whereas the amide group was found to remain uncoordinated. Each Cu^{II} is penta-cordinated in a distorted square-pyramidal environment and is neutralized by one bridged acetate and a hydroxide ion, while the fifth coordination site is occupied by a water molecule. In the nickel(II) metallopolymers, the metal ions were in a tetrahedral environment and were coordinated to azomethine nitrogen, two bridged acetate oxygens and to the hydroxide ion.

Larin and co-workers **[126]** synthesized the dinuclear copper(II) complexes with 2-hydroxypropiophenone, acyldihydrazones (H_4L) having the composition [$Cu_2L \cdot mPy$], where L ligand contains the polymethylene chain with different lengths (from two to five units). The crystal and molecular structure of the 2-hydroxypropiophenone adipoylhydrazone complex [$Cu_2L.4Py] \cdot Py$ were established by X-ray diffraction analysis. Copper atoms were found to be separated from one another by a distance of 8.212 Å. Their nearest environment was found to have tetragonal pyramidal geometry. The ESR spectra of solutions of the complexes based on acyldihydrazones of succinic, malonic, glutaric, and adipic acids were found to contain seven HFS lines with the constant ~ 40×10^{-4} cm^{-1} from two equivalent copper atoms. The spectra were interpreted as a result of the spin-spin exchange interaction of two unpaired electrons. An increase in the polymethylene chain length of five units prevents exchange interactions. The ESR spectrum of the complex with acyldihydrazone of pimelic acid was found to contain a signal of four HFS lines with $A_{Cu} = 73.4 \times 10^{-4}$ cm^{-1}, which is typical of mononuclear copper(II) complexes.

Andelkovic and co-workers **[127]** synthesized complexes of Zn(II), Pd(II) and Pt(II) with 2′-[1-(2-pyridinyl)ethylidene]oxamohydrazide (Hapsox). The complexes were characterized and their structures were determined. All the complexes were found to be neutral type with two apsox ligands coordinating to Zn(II) and one apsox ligand coordinating to Pd(II) or Pt(II). In each case, the polydentate ligand was coordinated via pyridine and hydrazone nitrogens and α-oxyazine, forming an octahedral geometry around Zn(II), and a square-planar one around Pd(II) and Pt(II). The structure determination was performed by IR, ^1H NMR and ^{13}C NMR spectroscopy, and for the Zn(II) complex by X-ray structure analysis.

Para et al **[128]** synthesized dialdehyde starch dihydrazone DASHZ from the reaction of dialdehyde starch with hydrazine. The metal complexes of Ca, Cd, Co(II), Cu(II), Fe(II), Mg, Mn(II), NI(II), Pb(II), and Zn ions with the dihydrazone ligand DASHZ were isolated. It was found that the nitrogen atoms of the >C=N moiety in dihydrazone as well as the oxygen atom of the fomer pyranose ring were the coordination sites. Metal ions were chelated to a different extent. One mole of a metal ion could coordinate with 3 [Cu(II)] to 50 [Mn(II)] mole of the DASHZ units. The ligand DASHZ and the metal complexes decomposed thermally in four steps but the rates of decomposition of the ligand and chelates in relevant steps were different. Except the complex with Mg, these rates for complexes were lower.

Zhao and co-workers **[129]** synthesized polynuclear manganese(II), cobalt(II)/(III), iron(II)/(III) and nickel (II) complexes of a group of flexible polydentate dihydrazone ligands, based on pyridine-2,6-dipicolinic (A), oxalic (B) and malonic (C) subunits. They reported the structural details for the linear dinuclear complexes $[Ni_2(2poap)_2(H_2O)_2](NO_3)_2{\cdot}2CH_3OH{\cdot}2H_2O$ (1), $[Mn_2(pttp)_2(NO_3)_2(CH_3OH)_2(H_2O)_2](NO_3)_2{\cdot}2H_2O$ (2), and $[Mn_2(mapttp)_2(NO_3)_2(H_2O)_2](NO_3)_2{\cdot}10H_2O$ (3), a square tetranuclear complex $[Co_4(pttp)_4]Br_6{\cdot}9H_2O$, a tetranuclear tetrahedral complex $[Ni_4(pttp)_6](BF_4)_6F_2{\cdot}14H_2O$ (7), and a mixed spin state tetranuclear Ni(II) complex $[(2pyoap)_2Ni_4(CH_3OH)_4]{\cdot}1.5CH_3OH$ (10), with a diamond-like arrangement of metal ions. The paramagnetic metal centres are well separated in each case, leading to weak antiferromagnetic coupling or non-existent spin exchange.

Tirosh and co-workers **[130]** synthesized the cadmium(II) complex $[Cd(C_4H_{10}N_4)_3(ClO_4)_2]$ from the reaction of $Cd(ClO_4)_2{\cdot}H_2O$ with biacetyl dihydrazone in methanol. They established the structure of the compound with the help of X-ray crystallography. The cation was found to be located on a 3 axis and was characterized by an approximate octahedral geometry, with each of the ligands occupying two coordination sites around the metal centre.

Carcelli and co-workers **[131]** synthesized a novel series of lanthanide (III) complexes with two potentially hexadentate ligands containing a rigid phenanthroline moiety and two flexible hydrazonic arms with different donor atom sets (NNN'N'OO and NN'N''N'', respectively. These hydrazones, (2,9-diformylphenanthroline)bis(benzoyl)hydrazone (H_2L^1), (2,9-diformylphenanthroline)bis(2-pyridyl)hydrazone (H_2L^2). They prepared and fully characterized both nitrate and acetate complexes of H_2L^1 with La, Eu, Gd, and Tb.

They presented the X-ray crystal structure of the complex $[Eu(HL^1)(CH_3COO)_2]\cdot 5H_2O$. The stability constants of the equilibria $Ln^{3+} + H_2L^1 = [Ln(H_2L^1)^{3+}$ and $Ln^{3+} + (L^1)^{2-} = [Ln(L_1)^+]$ (Ln = La(III), Eu(III), Gd(III), and Tb(III) were determined by UV spectrophotometric titrations in DMSO at t = 25°C. They also synthesized the nitrate complex of H_2L^2 with La, Eu, Gd and Tb. The X-ray crystal structure of the complexes $[La(H_2L^2)(NO_3)_2(H_2O)](NO_3)$, $[Eu(H_2L^2)(NO_3)_2](NO_3)$ and $[Tb(H_2L^2)(NO_3)_2](NO_3)$ were also established.

Salem **[132]** synthesized a series of acyldihydrazones, H_2L^n from the condensation of ethylpyruvate with oxalic, malonic, succinic, and glutaric and adipic dihydrazides. The author isolated dicopper(II) complexes of the general formula $[Cu(L'^n)\cdot H_2O]\cdot xH_2O$, where L'^n refers to the quadruply deprotonated pyruvic acid dihydrazone ligand and n refers to the number of carbon atoms of the aliphatic spacer between the two acylhydrazone units. The isolated complexes were characterized by elemental analyses, infrared spectra, mass spectra, and variable temperature magnetic susceptibility measurements. Magnetic susceptibility measurements in the range 4.2-298 K indicate significant antiferromagnetic coupling between copper(II) centers and suggest association of the coordinated copper(II) units Cu(ONO) via oxazine oxygen bridges. This leads to a polymeric structure where the dimeric units are connected together with aliphatic spacer. From the best fit values of the mole fraction of paramagnetic uncoupled copper(II) centers (ρ), the degree of association in these polynuclear copper(II) complexes were also estimated.

Elengoz etal **[133]** synthesized the zinc complex tris(biacetyldihydrazone-κ^2N,N′)zinc(II) bis(perchlorate) at 110 K and determined its crystal structure precisely.The metal-organic cation, which is located on a 3 axis, is characterized by an approximate octahedral geometry, with each of the ligands occupying two coordination sites around the metal centre. The title compound, crystallizes in the trigonal space group *P3c1* with two units of the $[Zn(C_4H_{10}N_4)_3]^{2+}$ cationic complex and four ClO_4^- anions in the unit cell. The Zn^{II} atom is located on a 3 axis, while the perchlorate anion is located on a threefold rotation axis. The cation is characterized by perfect 3 symmetry, in which three chelating ligands occupy the octahedral coordination sites of the zinc metal ion. The imine N atoms of the lignd provide the coordination sites to the central metal ion. The conformation about the central C–C bond of the ligand is *cis*, with the two C=N bonds being nearly coplanar to direct the two imine coordinating sites towards the metal centre. The N–Zn–N bond angle involving two coordinating N atoms of a given ligand is 74.33 (11)°. In the free form of

the ligand, the N–N=C–C=N–N backbone was found to adopt a planer *anti* conformation (Hauer etal, 1987).

V. P. Singh and P. Gupta **[134]** synthesized and characterized the complexes of diacetyl salicylaldehydeoxalicacid dihydrazone, $CH_3COC(CH_3)$=NNHCOCONHN=$CHC_6H_4(OH)$, (dsodh) and diacetylsalicylaldehydemalonicaciddihydrazone $CH_3COC(CH_3)$=NNHCOCH_2CONHN=$CHC_6H_4(OH)$, (dsmdh) by elemental analyses, molar conductance, magnetic moment, electronic, ESR and infrared spectra and X-ray diffraction data and were found to have the general compositions [M(L)]Cl, [M′(L)Cl], [M(L′)]Cl and [M′(L′)Cl] (where M=Co(II), Cu(II), Zn(II), Cd(II) and M′ = Ni(II); HL = dsodh and HL′ = dsmdh). With the help of magnetic moments and electronic spectral data they predicted a six-coordinate octahedral geometry for Co(II) and square-planar geometry for Ni(II) complexes. They also found that the ESR spectral data of Cu(II) complexes in DMF solution reveal a tetragonally distorted octahedral geometry. Both ligands bond through >C=O, >C=N and deprotonated phenolate groups in all octahedral complexes and through >C=N and deprotonated phenolate groups in Ni(II) square-planar complexes. The lattice parameters for Cu(dsodh) and Co(dsmdh) correspond to an orthorhombic and Ni(dsodh) corresponds to a tetragonal crystal lattice. The complexes were found to exhibit significant antifungal activity against a number of pathogenic fungi viz. Stemphylium, Myrothecium and Alternaria. The antibacterial activity was studied against *Pseudomonas fluorescence* (gram -ve) *and Clostridium thermocellum* (gram +ve).

C. T. Yang and co-workers **[135]** synthesized the complexes of dioxouranium(VI) with four dipyridoxal hudrazone ligands H_4PL^n and characterized them by various analytical and spectroscopic methods including X-ray crystallography. The ligands and the UO_2^{VI} complexes were also tested for cytotoxicity. They found that the solid-state structure of $[(UO_2)_4(PL')_2(H_2O)_4]\cdot 12H_2O$ is a cyclic tetramer.

M. F. Iskander and co-workers **[136]** synthesized and characterized two series of dicopper(II) complexes derived from bis(N-salicylidine)dicarboxylicaciddihydrazides (H_4L^n) of general formula $[Cu_2(L_n)\cdot xH_2O]\cdot yH_2O$ and $[Cu_2(H_2L^n)Cl_2\cdot xH_2O]\cdot yH_2O$ where n refers to the number of carbon atoms in the aliphatic spacer between the two N-salicylideneacylhydrazine units. Magnetic susceptibility measurements for neutral dicopper(II) complexes $[Cu_2(L^n)\cdot xH_2O]\cdot yH_2O$ indicate significant antiferromagnetic coupling between copper(II) centers. The –2J values obtained from the Bleany–Bowers equation are within the range 121–223 cm^{-1}, suggesting association of the coordinated copper(II) units Cu(ONO) via phenoxy bridges. This leads to a polynuclear structure in

which the dimeric units are connected with the aliphatic spacer. From the best-fit values of the mole fraction of paramagnetic uncoupled copper(II) centers (ρ), the degree of association in these polynuclear copper(II) complexes were estimated. The chloro dicopper(II) complexes $[Cu_2(H_2L^n)Cl_2 \cdot xH_2O] \cdot yH_2O$ with n = 0, 2 and 3 also show strong antiferromagnetic exchange coupling (-2J = 215–423cm^{-1}), suggesting a polynuclear structure in which the copper(II) is in a distorted square-pyramidal environment, bound in the equatorial plane with a monoanionic ONO tridentate acylhydrazone unit and the μ-phenoxy oxygen and the axial site occupied by a chloride. The dicopper(II) complexes with n = 1 and 4 were found to show weak antiferromagnetic exchange coupling (-2J=16–20 cm^{-1}).

N. R. Filipovic et al **[137]** synthesized a new dinuclear complex of Cd(II) with N′,N′²-bis[(1E) -1-(2-pyridyl)ethylidene]propanedihydrazide (H_2L) and its crystal structure was determined. The basic structural unit of the complex was foud to be the binuclear $[Cd_2(H_2O)_2(H_2L)_2]^{4+}$ cation, where each cadmium atom was hepta coordinated by two tridentate H_2L ligands, by means of the NNO chelating system, and one water molecule. A 12-membered macrocycle is defined at the core of the binuclear cation. The complex showed a pronounced cytotoxic activity to murine melanoma B16 cells and human cervical cancer HeLa cells.

V. P. Singh and co-workers **[138]** isolated the metal (II) complexes of the general formula [M(Bsodh)]Cl and [(MBsmdh)]Cl where M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) (HBsodh = benzyl salicylaldehyde oxalic acid dihydrazone and HBsmdh = benzyl salicylaldehyde malonic acid dihydrazone) and characterized them by elemental analyses, molar conductance, magnetic moment, ESR, IR and X-ray diffraction studies. The ligands and their metal complexes were found to exhibit significant antibacterial activity against *Bacilus subtilis* and *Pseudomonas fluorescens*.

L. D. Popov and co-workers **[139]** synthesized the dihydrazone ligand 2,6-diformyl-4-*tert*-butylphenolbis(8-quinolylhydrazone) and its transition metal complexes of the composition $[Cu_2(H_2L)Cl]Cl_2$, $[Ni_2(H_2L)Cl_3]$ and $[Mn_2(H_2L)Cl_3]$, where H_2L is the monodeprotonated form of the hydrazone. They studied the conformations of the bis-hydrazone, geometries of the complexes, and parameters of exchange coupling between the ferromagnetic centres using quantum-chemical calculations. They also compared the calculated results with the results of the physico-chemical study of the complexes.

S. Naskar and D. Mishra **[140]** synthesized a Ni(II) complex of 2,6-diacetylpyridine bis(anthraniloylhydrazone) and characterized it by various physico-chemical methods. The structure of the complex was determined by X-ray crystallography. They also found that in the solid state, the compound exist as a dimer and two coordinated ligand moieties form a double helix around the two metal ions.

R. M. Issa and co-workers **[141]** studied the thermal stabilities of bis(salicylidine)adipic dihydrazone derivatives and their complexes with divalent Mn, Ni, Cu and Zn ions and discussed them in terms of structure and type of metal ions. They also found that, the TG curves display mostly four steps of thermal decomposition.

V. F. Shulgin and co-workers **[142]** synthesized and characterized dinuclear copper(II) complexes with acyldihydrazones of 2-hydroxy-5-nitroacetophenone (H_4L) of the composition $Cu_2(py)_xL{\cdot}mEtOH$. It was found that, in the complexes, the coordination polyhedra of the copper atoms are linked to each other by a polymethylene chain of different lengths, from one to five monomer units. They also established the structure of $[Cu_2L{\cdot}4Mrf]$ complex (where Mrf is morpholine) based on acyldihydrazone of malonic acid by X-ray diffraction.

M. Salavati-Niasari and A. Sobhani **[143]** isolated the monomer transition metal complexes, [ML] (M = Mn(II), Co(II), Ni(II) and Cu(II)) from the reaction of metal acetates with bis(salicylaldehyde)oxaloyldihydrazone (H_2L) in 1:1 molar ratio in ethanol under reflux. It was suggested that, in all of the complexes, the principal dihydrazone ligand coordinate to the metal centres in the *anti-cis* configuration. These metal complexes were entrapped in the nano cavity of zeolite-Y. The new Host-Guest Nano Composite Materials (HGNM) were characterized by chemical analyses and spectroscopic methods. They also reported the catalytic activities for the oxidation of cyclohexane with HGNM.

Da-Yu Wu and co-workers **[144]** isolated three ligands, di(2-pyridylcarbaldehyde)-6,6′-dicarboxylicacidhydrazone-2,2′-bipyridine (H_2L^1), di(2-acetylpyridyl)-6,6′-dicarboxylic acidhydrazone-2,2′-bipyridine (H_2L^2) and di(2-pyridyketone)-6,6′-dicarboxylicacid hydrazone-2,2′-bipyridine (H_2L^3) with flexible bis-terdentate coordination sites and their cobalt complexes. The complexes were obtained via self-assembly and their structures were determined by FT-IR, elemental analyses, ESI-MS and X-ray diffraction method.

Lal and co-workers **[145]** synthesized the complexes $[(UO_2)(CH_2L)(H_2O)_4]{\cdot}4H_2O$, $[M_4(H_2L)_2(H_2O)_4]{\cdot}4H_2O$ (M = Zn, Cu), $(M')_2[(UO_2F)(CH_2L)(H_2O)_2]$ [M′ = K, Na], $M'[(UO_2)_2(CH_2L)(OAc)(H_2O)_2]$ [M′ = K, Na], $K_4[(MF)_2(CH_2L)_2]{\cdot}4H_2O$ [M Zn, Cu] from

the reaction of appropriate metal salts with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone (CH_2LH_4) under different experimenatal conditions in ethanol/methnol media. The complexes have been characterized by elemental analyses, molecular weight, molar conductance, magnetic and EPR data. The structural assessment of the complexes has been carried out on the basis of electronic, infrared, ^1H NMR and ^{13}C NMR sprectral studies.

Lal and co-workers **[146]** synthesized and characterized zinc(II), copper(II), nickel(II) and manganese(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone. In their study, they have shown that the reaction of different salts of the same metal with sterically crowded dihydrazone bis(2-hydroxy-1-naphthaldehyde)malonoyldihydrazone (CH_2LH_4) in ethanol/aqueous media gives complexes of different stereochemistry. While the reaction of Zn(II) and copper(II) sulfate with dihydrazone yields tetrahedral complexes, the zinc(II) and copper(II) chlorides give square-pyramidal and distorted octahedral complexes respectively. On the other hand, nickel(II) sulfate and chloride, both gave high-spin octahedral complexes. They also investigated the reaction of these complexes with KF. All of the products were characterized by analytical, magnetic moment and molar conductance data. The structures of the complexes have been established by spectroscopic studies.

Lal and co-workers **[147]** synthesized the monomer molybdenum(VI) complex $[MoO_2(napoxlhH_2)]\cdot 2H_2O$ (1) from the reaction of $MoO_2(acac)_2$ with bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone ($napoxlhH_4$) in 1:1 molar ratio in ethanol under reflux. This complex on reaction with pyridine /3-picoline/4-picoline yielded the dimer molybdenum(VI) complex $[Mo_2O_4(napoxlhH_2)(A)_2]\cdot 2H_2O$ (A = py (2), 3-pic(3), 4-pic(4)), whereas the reaction with isonicotinoyl hydrazine ($inhH_3$) and salicyloyl hydrazine ($sylshH_3$) led to the reduction of the metal centre yielding monomeric molybdenum(V) complexes $[Mo(napoxlhH_2)(hzid)]\cdot 2H_2O$ (where $hzidH_3$ = $inhH_3$ (5) and $sylshH_3$ (6)). The complexes have been characterized by elemental analyses, molecular weight determinations, molar conductance data, magnetic moment data, electronic, IR, ESR and ^1H NMR spectroscopic data.

M. K. Singh and co-workers **[148]** studied the reaction of bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone ($naohH_4$) with manganese(II) acetate in methanol followed by addition of KOH to get the complex $[Mn^{IV}(naoh)(H_2O)_2]$. They also studied the reaction of activated ruthenium(III) chloride with $naohH_4$ in methanol to get the complex $[Ru^{III}(naohH_4)(H_2O)Cl_2]$ and characterized them by elemental analyses, IR,

electronic, ESR and cyclic voltammetric studies. They observed the replacement of aquo by heterocyclic nitrogen donor in these comolexes when the reaction was carried out in presence of heterocyclic nitrogen donors such as pyridine, 3-picoline or 4-picoline.

From the survey of literature presented above, it is evident that although mono and bimetallic complexes of various types of dihydrazones have been synthesized and characterised, in some detail, those derived from dihydrazones containing bulky fragments in their molecular skeleton have much less been studied. Further, the heterobimetallic complexes of such dihydrazones are almost non-existent. In view of limited number of investigations on metal complexes of dihydrazones containing bulky fragments in their molecular skeleton, the project has been undertaken. It is quite possible to extend and develop such a study, with the help of variety of metal ions into a major field, but because of time factor, it has been restricted to monometallic, homobimetallic and heterobimetallic complexes of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone with zinc(II), nickel(II) and molybdenyum(VI). Part of the work is under consideration for publications.

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CHAPTER II

EXPERIMENTAL

The present chapter deals with the experimental details regarding the synthesis of the ligand, methods of analyses, physico-chemical techniques and the instruments employed for the characterization of the ligand as well as the complexes. The procedures for the preparation of the complexes are given in respective chapters.

Materials

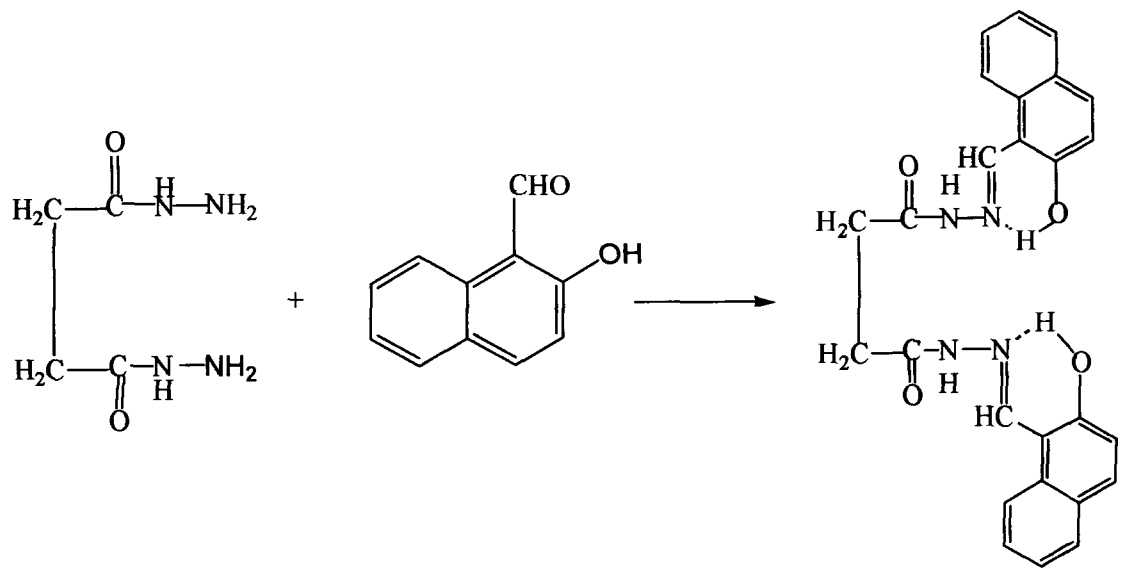
The metal salts, ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$), nickel acetate tetrahydrate ($Ni(OAc)_2{\cdot}4H_2O$), zinc acetate dihydrate ($Zn(OAc)_2{\cdot}2H_2O$), diethyl succinate ($((CH_2)_2(CO_2Et)_2$, hydrazine hydrate ($N_2H_4{\cdot}H_2O$), 2-hydroxy-1-naphthaldehyde ($C_{10}H_6(OH)(CHO)$,) were E-Merck, Qualigens, Hi-Media or equivalent grade reagents and were used without further purification. Acetyl acetone, pyridine, 1-picoline, 2-picoline, 3-picoline, were Lanchaster or equivalent grade reagents. Bis(acetylacetonato)dioxomolybdenum(VI) ($MoO_2(acac)_2$ was prepared by literature method **[1]**.

The organic solvents viz., ethanol, methanol, diethyl ether, dimethyl sulphoxide (DMSO) and dimethyl formamide (DMF) were used after purification by standard literature methods.

Preparation of the Ligand:

The ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) was prepared in two steps. In the first step, succinoyl hydrazine (SDH) was prepared by reacting diethyl succinate with hydrazine hydrate in 1:2.5 molar ratio. In the second step, succinoyl dihydrazine thus obtained was allowed to react with 2-hydroxy-1-naphthaldehyde in 1:2.2 molar ratio in ethanol to get the ligand.

Succinoyldihydrazine (1.00 g, 6.84 mmol) in dilute ethanol solution was allowed to react with 2-hydroxy-1-naphthaldehyde (2.59 g, 15.04 mmol) in ethanol solution under reflux for 30 minutes. The yellow precipitate thus obtained was purified by washing with hot ethanol and dried over anhydrous $CaCl_2$. Yield:0.72 g.



Succinoyldihydrazine 2-hydroxy-1-naphthaldehyde Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

The purity of the hydrazides and the hydrazone were established by C, H, N analyses. The elemental analysis data and the melting point of the hydrazides and the hydrazone are given in Table 2.1.

Table 2.1. Melting point and C, H, N analyses of succinoyldihydrazine and bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Sl. No.	Hydrazide/Hhydrazone	Formula	Melting Point (°C)	Analysis: Expt. (Calc)			Reference
				C	H	N	
1.	Succinoyl dihydrazine	$C_4H_{10}O_2N_4$	167	33.31 (32.85)	6.90 (6.83)	38.71 (38.36)	4
2.	Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone	$C_{26}H_{22}O_4N_4$	254	69.19 (68.72)	4.82 (4.84)	12.65 (12.33)	—

Estimation of Metal(s)

The estimation of various metals was done by following standard procedures **[2]** as given below.

Estimation of Molybdenum

Molybdenum content of the complexes was determined by the following procedure.

About 0.40 g of the complex was accurately weighed in a 250 mL capacity conical flask. To this, 100 mL water and 1.00 g of NaOH were added. The solution was boiled for 2 hours. This decomposed the complex which passed into solution. The solution was neutralized with 0.1M H_2SO_4 using methyl red indicator. This precipitated the ligand which was filtered and rejected. The filtrate was then further acidified with few drops of 0.1M H_2SO_4. Subsequently 5 mL of 2M ammonium acetate solution was added to it and the solution was diluted to 100 mL. The resulting solution was boiled and then oxine solution in dilute acetic acid was added to it until the supernatant liquid became perceptibly yellow. The solution was further boiled and stirred for 3 minutes. This yielded precipitate which was filtered through a sintered glass crucible (G-4). The precipitate was washed several times with water until free from oxine and dried to constant weight at 130–140 °C, and is weighed as $MoO_2(C_9H_6ON)_2$.

Estimation of Nickel

The nickel content of the complexes was estimated gravimetrically as nickel dimethyl glyoximate.

In a typical procedure, an accurately weighed amount of the nickel compound (0.40 g) was taken in a silica crucible and moistened with 4 or 5 drops of conc. H_2SO_4 and 1 or 2 drops of conc. HNO_3. The crucible was gently heated on a low flame. The process was repeated 3 or 4 times. Finally, the crucible was strongly heated to burn off the organic part. The residue was dissolved in a hot (70-80 °C) dilute solution of hydrochloric acid (1:40). To this was added the requisite amount of 1% solution of dimethylglyoxime reagent in ethanol followed by the dropwise addition of aqueous ammonia, until the solution was faintly alkaline whereupon nickel dimethyl glyoximate was precipitated. The whole was heated on a boiling water bath *ca* 30min, and the precipitate was allowed to settle for *ca* 2 hours, while cooling at the same time. Quantitative precipitation of nickel dimethylglyoximate was checked by adding a few drops of dimethyl glyoxime reagent solution. The precipitate was filtered on a weighed sintered Gooch crucible (G-4), washed several times with cold water until free from chloride. The crucible along with the precipitate was dried, to constant weight at 110–120 °C. The precipitate was weighed as nickel dimethylglyoximate ($Ni(C_4H_7O_2N_2)_2$).

Estimation of Zinc

Zinc content of the zinc complexes were estimated gravimetrically as zinc 8-hydroxyquinaldinate.

In a typical procedure, an accurately weighed amount of the zinc (0.40 g) compound was taken in a silica crucible and moistened with 4 or 5 drops of conc. H_2SO_4 and 1 or 2 drops of conc. HNO_3. The crucible was gently heated on a low flame. The process was repeated 3 or 4 times. Finally, the crucible was strongly heated to burn off the organic part. The residue was dissolved in a hot (70–80 °C) dilute solution of hydrochloric acid (1:40). To this was added, aqueous ammonia solution, until a white precipitate of zinc hydroxide just appears. The precipitate of zinc hydroxide was redissolved with a drop of acetic acid solution. To this was added the requisite amount of 8-hydroxyquinaldine reagent in dilute acetic acid. A slight excess of the reagent was then added followed by the addition of 2–3 drops of concentrated ammonia solution so that the pH is maintained at 5.5, whereupon zinc is precipitated as zinc 8-hydroxyquinaldinate. The whole was digested on a water bath at 60-80 °C for *ca* 15min, and then the precipitate was allowed to settle for *ca* 10-20mins, while cooling at the same time. Quantitative precipitation of zinc 8-hydroxyquinaldinate was checked by adding a few drops of 8-hydroxy quinaldine reagent solution. The precipitate was filtered on a weighed sintered Gooch crucible (G-4), washed several times with cold water until free from chloride and 8-hydroxyquinaldine. The crucible along with the precipitate was dried, to constant weight at 130-140 °C. The precipitate was weighed as zinc 8-hydroxyquinaldinate ($Zn(C_{10}H_8ON)_2$) **[2].**

Physico-Chemical Measurement

CHN Analysis: Elemental analyses (C, H, N) were performed by Perkin Elmer 2400 CHNS/O Analyzer 11.

Water, ethanol, pyridine, 3-picoline and 4-picoline molecules were determined by heating the samples in an electric oven at 110°C or 180°C or 220°C respectively, or in the temperature range 80–250°C, and determining the weight loss. Water molecules were identified by passing the vapours through a test tube containing anhydrous copper sulfate which turned blue, while pyridine, 3-picoline and 4-picoline molecules were determined by passing the vapours through a test tube containing (a) a solution of sodium hydroxide and iodine; (b) a solution of $CHCl_3$ containing a drop of 5M NaOH solution and (c) a test tube containing cyanogen bromide solution followed by treatment with phloroglucinol solution which turned green-violet and blue respectively in case of 3-picoline and 4-picoline molecules **[3]**.

Infra red Spectra: Infrared spectra in the range 4000–400/500 cm^{-1} were recorded on either BX-III/FT-IR Perkin-Elmer spectrophotometer or Nicolet-Impact 410 FT-IR Spectrophotometer with samples investigated as KBr discs.

NMR Spectra: The ^{1}H and ^{13}C Nuclear Magnetic Resonance Spectra were recorded on a Bruker AC-F 300MHz and AMX 400 High Resolution Multinuclear FT-NMR Spectrometer in DMSO-d_6. Tetramethyl silane (TMS) was used as an internal standard.

Magnetic Susceptibility: Room temperature magnetic susceptibility measurements were made on Sherwood Magnetic Susceptibility Balance MSB-Auto.

Electronic Absorption Spectra: To record the electronic spectra a Perkiin Elmer Lambda 25 spectrophotometer was made use of. Electronic spectra of the complexes were recorded in DMF solution.

Conductance: All conductance measurements were made at 1 kHz using Wayne Kerr B905 Automatic Precision Bridge. This LCR meter has 0.01 ns resolution and measures conductance with an accuracy of 0.05%. A dip-type conductivity cell having platinized platinum electrodes was used. The cell constant was determined using a standard KCl solution.

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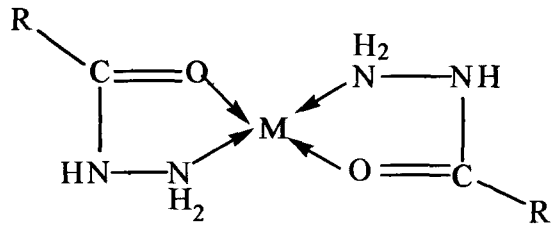
CHAPTER III

Synthesis, Characterization and Structural Assessment of Monometallic Molybdenum(VI) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

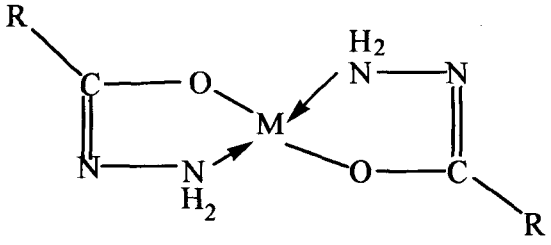
Introduction

The ligand bis(2-hydroxy-1-naphthaldehyde)succinoyl dihydrazone (H_4nsh) contains two hydrazone groupings joined together through two $-CH_2-$ groups. Thus it is the combination of succinoyldihydrazone and 2-hydroxy-1-naphthaldehyde fraction. Hence, it is relevant to briefly review the various types of complexes formed by acyl-, aroyl- and pyridyl- dihydrazines and their hydrazone derivatives with aldehydes and ketones.

The mono acyl hydrazine and mono aroyl hydrazines $RCONHNH_2$ (R = alkyl or aroyl) form 1:1, 1:2 and 1:3 (metal:ligand) complexes with metal ions **[1-5]**. They coordinate to the metal ions in keto form (I) **[6]** or in enol form (II) **[7]**, functioning as a neutral bidentate ligand or monobasic bidentate ligand.

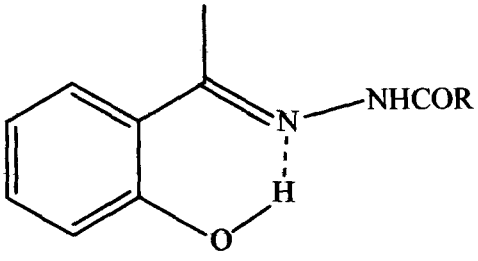


(I)

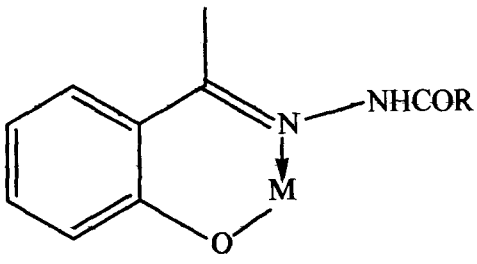


(II)

The Schiff bases (III) derived from mono acyl and mono aroyl hydrazines and hydroxy aldehydes and ketones form 1:1 and 1:2 (metal:ligand) complexes and function either as a monobasic bidentate (IV) **[8]**, monobasic tridentate (V) **[3]** in keto form **[3, 9]** or dibasic tridentate (VI) in enol form **[10, 11]** and yield dimeric or polymeric chelates in which they coordinate to metal ion through >C=O and >C=N groups besides bonding through –OH group.



(III)



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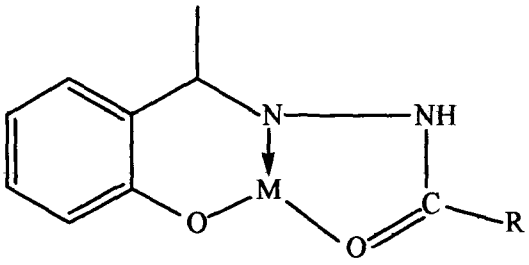
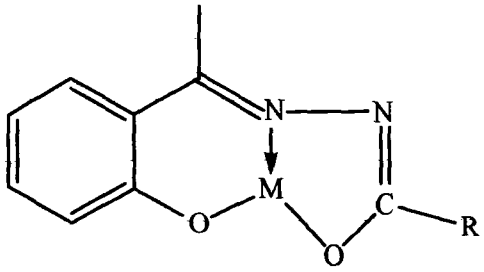


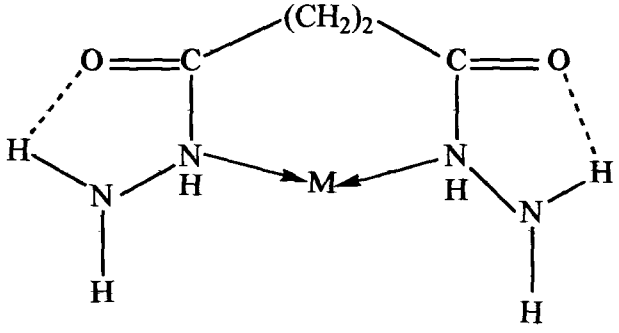
(V)



(VI)

Thus the acyl hydrazines and acyl hydrazones show keto-enol equilibrium in their complexes and are likely to yield different kinds of chelates depending upon the pH of the reaction medium.

Organic acid dihydrazides **[12, 13]** derived from aliphatic dicarboxylic acids containing two $-CONHNH_2$ groups have been reported to coordinate through two imine nitrogen (>NH) even in the presence of potentially stronger coordinating >C=O and $-NH_2$ groups. It has been suggested that strong intramolecular hydrogen bonding, as shown below (VII), probably makes them unavailable for coordination **[14, 15]**.

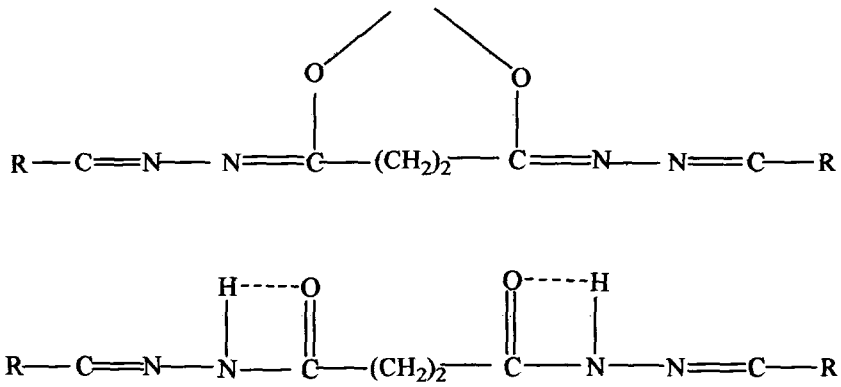


(VII)

However the dipicolinic acid dihydrazide has been reported to coordinate to the metal centre as a neutral pentadentate ligand through pyridoyl nitrogen, two >C=O and two –NH_2 groups **[16]**. It appears that in this ligand, the presence of pyridoyl nitrogen atom makes >C=O and –NH_2 groups more reactive.

Maki and coworkers **[17]** synthesized and characterized dioxouranium(VI) complexes of some dicarboxylic acid hydrazides in ethanol medium in the presence or absence of NaOAc. The dihydrazides were found to coordinate in a tetradentate fashion in the enol form except adipic acid hydrazide which coordinated in the keto form. The existence of dihydroxo-bridges for the complexes isolated in the presence of NaOAc or basic medium (N_2H_4) was also established.

However, when the terminal –NH_2 groups of the dihydrazides are condensed with aldehydes and ketones, the resulting Schiff bases (VIII), in which the above type of hydrogen bonding is likely to disappear, possess >C=O and >C=N groups instead of >C=O and –NH_2 groups in the dihydrazides.

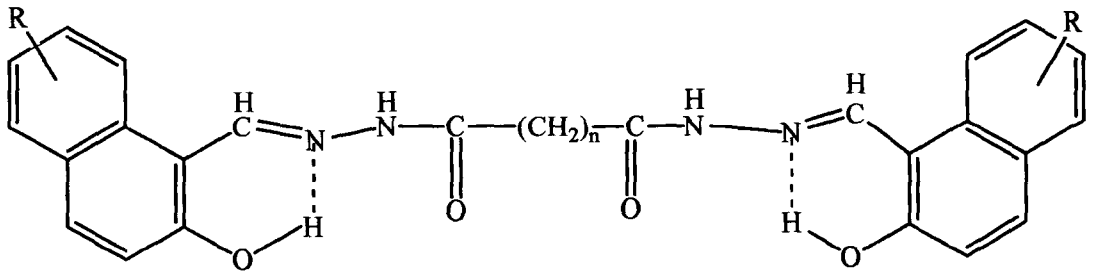


(VIII)

Aggarwal and coworkers **[18]** synthesized 1:1 (metal:ligand) neutral and cationic complexes from the reaction of first row transition metal ions with dihydrazones derived from condensation of acyl dihydrazines and simple aldehydes and ketones. In their study, they have shown that the dihydrazones behave either as a dibasic tetradentate ligand or as a neutral bidentate ligand coordinating through carbonyl oxygen and azomethine nitrogen atoms.

On the other hand , if the dihydrazones are derived from the condensation of acyl-, aroyl-, and pyridoyl dihydrazines with *o*-hydroxy aromatic aldehydes and ketones, they possess –OH groups in addition to >C=O and >C=N groups **[19, 20]**. In such dihydrazones the

possibility of existence of newer hydrogen bonding in the solid state as shown in (IX) cannot be ruled out.



(IX)

Thus, it is evident that the mono acyl and mono aroyl hydrazines coordinate to the metal ions either in the keto form or enol form and in addition, they offer several alternate bonding sites and can act as potential multidentate coordinating or chelating ligands resulting in the formation of complexes having different stoichiometries under different experimental conditions. The molecular model of the dihydrazones indicates their flexible nature in the space due to which they are able to offer planar as well as tetrahedral set of donor atoms depending upon the preferred stereochemical disposition of the metal valences, nature of the R-groups and the bonds formed in the coordination process. The various donor sites in the ligand can bind either to the same metal atom or to different metal atoms leading to a monomeric or a polymeric structure of the complexes **[19]**. However, polymerization may also arise due to oxo-bridged structures **[20, 21]**

A survey of literature has disclosed that few complexes of the first row transition metal ions, dioxouranium (VI) and dioxomolybdenum (VI) with the dihydrazones derived from the condensation of salicylaldehyde and related *o*-hydroxy aromatic aldehydes and ketones with malonoyl dihydrazine and other acyl dihydrazines, aroyl dihydrazines and pyridoyl dihydrazines have been reported. Further, it has been found that some isolated studies on metal complexes of dihydrazones derived from condensation of 2-hydroxy-1-naphthaldehyde with oxaloyl- and malonoyl-dihydrazones are available in the literature, yet the literature survey has failed to locate any systematic study on the metal complexes of the dihydrazones containing bulky naphthyl fragment in their molecular structure. In view of the significant role played by molybdenum in biological systems and absence of work on metal complexes of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone, the monometallic complexes of dioxomolybdenum(VI) from the title dihydrazone have been synthesized in alcoholic media and are described in the present chapter. The composition

of the isolated complexes has been judged mainly from the elemental analyses and thermoanalytical data. The structures of the dioxomolybdenum (VI) complexes have been discussed with the help of molar conductance, magnetic moment, ESR, electronic, ^{1}H NMR, ^{13}C NMR and IR spectral data.

Preparation of the complexes

The complexes were prepared by the following general methods.

1. Preparation of the complex $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1)

The dihydrazone ligand (H_4nsh) (1.00 g, 2.2 mmol) was suspended in ethanol (100 mL) and stirred for half an hour at about 70°C to give a homogeneous suspension. To this was added a solution of bis(acetylacetonato)dioxomolybdenum(VI) ($MoO_2(acac)_2$) (0.80 g, 2.45 mmol) in ethanol (40 mL), maintaining the molar ratio at 1:1.1. The reaction mixture was refluxed for 3 hours which precipitated the orange coloured compound. The compound thus obtained was filtered, washed several times with hot ethanol, and then with ether and dried over anhydrous $CaCl_2$. Yield: 0.63 g.

2. Preparation of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2A.2C_2H_5OH$ (where A = pyridine (py, 3.2); 2-picoline (2-pic, 3.3); 3-picoline (3-pic, 3.4); 4-picoline (4-pic, 3.5))

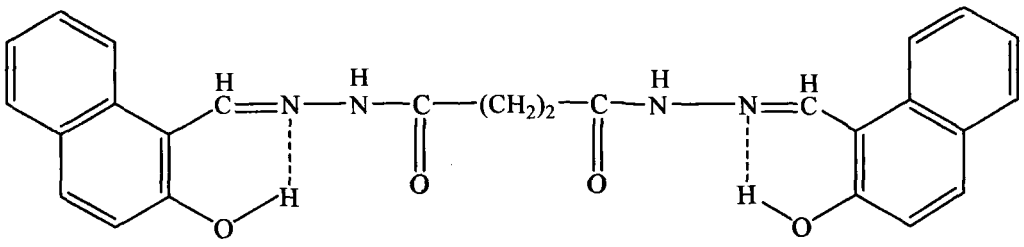
The complex $[(\mu\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1) (1.00 g, 1.67 mmol) was suspended in ethanol (100 mL) accompanied by gentle stirring for 10 minutes at 60-70°C. To this suspension, pyridine (1.40 mL, 16.7 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 3 hours which precipitated the orange coloured compound. The compound thus obtained was filtered, washed with hot ethanol and then with ether and dried over anhydrous $CaCl_2$. Yield: 0.70 g

The complexes (3.3), (3.4) and (3.5) were also prepared in the same manner using 2-picoline, 3-picoline and 4-picoline instead of pyridine. Yield: 0.71 g (3.3); 0.73 g (3.4); 0.72 g (3.5).

Results and Discussion

The ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) is a polyfunctional ligand containing $CH_2\text{-}CH_2$ group flanked by keto groups in addition to other functional groups like amide, azomethine and phenol, each in duplicate. It has been derived from the condensation of succinoyl dihydrazine with 2-hydroxy-1-naphthaldehyde. In this ligand, two hydrazone groupings are joined to each other through

methylene chain containing two methylene units. This ligand can react with the metal ions in keto, keto-enol and enol forms.



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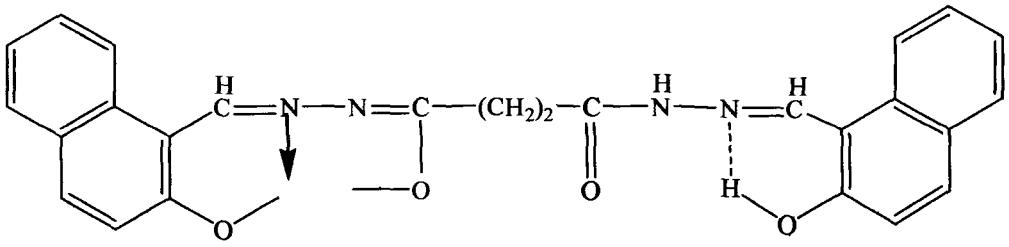

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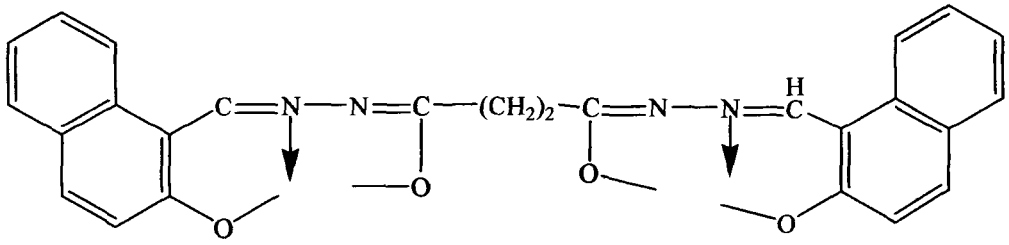


(III)

Fig. 3.1. Keto (I), keto-enol (II) and enol (III) forms of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Thus, because of the presence of as many as eight bonding sites and because of its ability to exhibit keto-enol tautomerism in its complexes, it can coordinate to the metal centre as a monobasic bidentate ligand coordinating through one phenolate oxygen and one azomethine group nitrogen atom; as a monobasic tridentate or dibasic tridentate ligand coordinating through one phenolate oxygen, one azine group nitrogen and one carbonyl oxygen atom while the other half of the molecule remains unbounded; as a neutral bidentate ligand coordinating either through two carbonyl oxygen or the two secondary amine nitrogen atoms with the –OH groups remaining hydrogen bonded in the complexes; as a dibasic tetradentate ligand coordinating through two hydroxyl oxygen atoms and the two azine group nitrogen atoms; as a dibasic hexadentate ligand bonding to the same metal ion through two hydroxyl oxygen atoms, two azine group nitrogen atoms and the

two carbonyl oxygen atoms. Further, this ligand may undergo enolization affording newer bonding possibilities leading to the formation of binuclear or polynuclear complexes. However the above possibilities of bonding depends on the nature of the metal salt, the concentration of the metal ion and ligand, reaction medium, the pH of the reaction medium and the temperature maintained in the preparation of the complexes.

In this chapter, the monometallic Mo(VI) complexes derived from the reaction of bis(acetylacetonato)dioxomolybdenum(VI) ($MoO_2(acac)_2$) with bis(2-hydroxy-1-naphthaldehyde)succinoyl dihydrazone in 1.1:1 molar ratio have been described. The complexes described in the present chapter together with their molecular formula, colour, decomposition point, percentage yield, molar conductance and analytical data are set out in Table 3.2. The electronic spectral data for the complexes are set out in Table 3.3.

When $MoO_2(acac)_2$ is allowed to react with H_4nsh in 1.1:1 molar ratio either as such or in presence of pyridine bases, the complexes of following composition are obtained.

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1)

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py.2C_2H_5OH$ (3.2)

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-pic}).2C_2H_5OH$ (3.3)

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3\text{-pic}).2C_2H_5OH$ (3.4)

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic}).2C_2H_5OH$ (3.5)

The complexes were formed according to the following reaction.

$MoO_2(acac)_2 + H_4nsh$

↓ absolute ethanol

$[(MoO_3)_2(H_4nsh)_2].2C_2H_5OH$

↓ pyridine bases

$[(MoO_3)_2(H_4nsh)_2]2A\cdot 2C_2H_5OH$

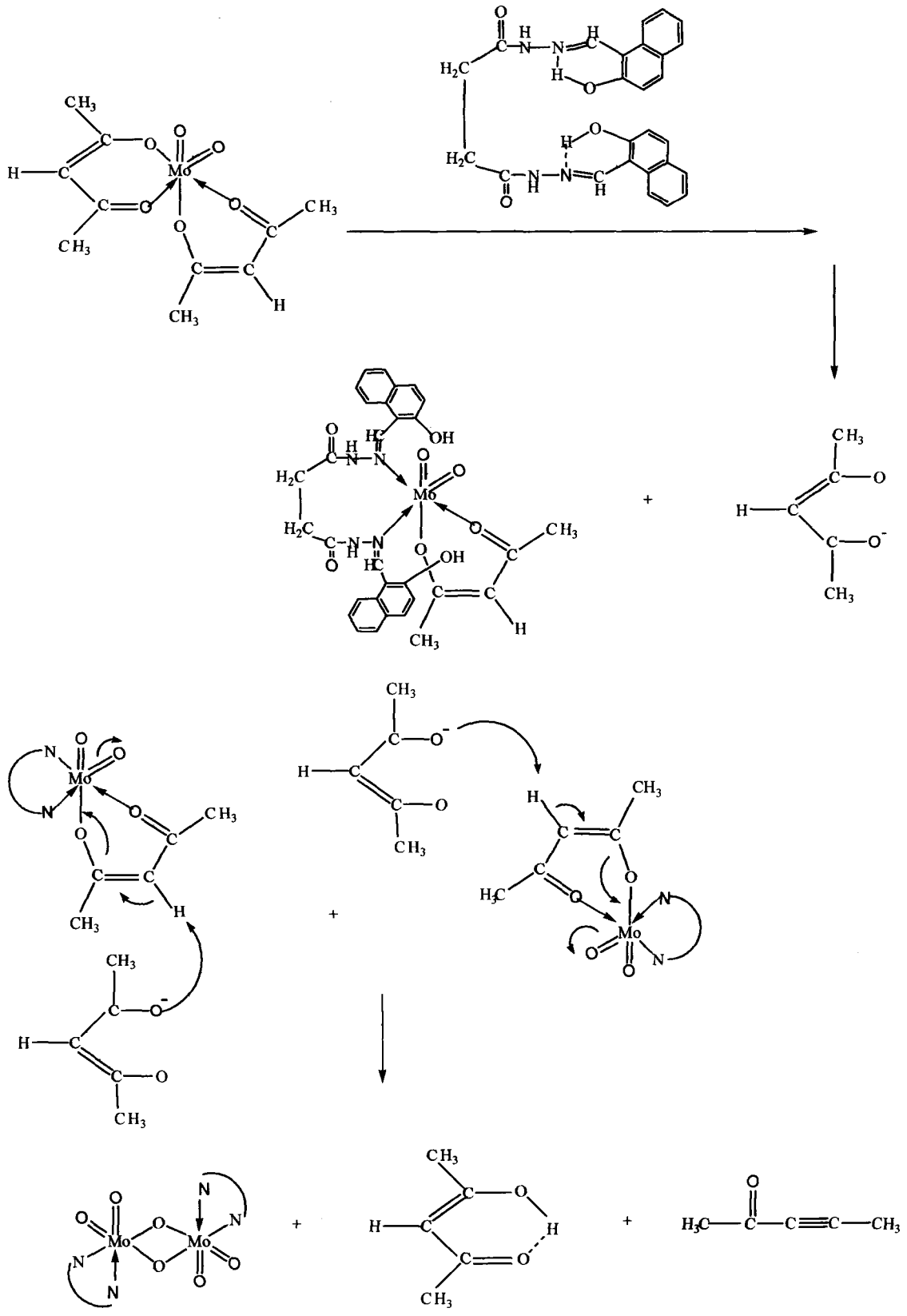
(where A = pyridine (py, 3.2); 2-picoline (2-pic, 3.3); 3-picoline (3-pic, 3.4); 4-picoline (4-pic, 3.5))

The composition of the complexes has been deduced on the basis of the data obtained from elemental analyses and thermoanalytical data.

The complexes described in this chapter are either orange or orange-yellow in colour. All of the complexes are air stable solid powders and decompose without melting above 300 °C.

All of the complexes are insoluble in water and other common organic solvents such as ethanol, methanol, acetone, benzene, acetonitrile, chloroform and ether. But all of the complexes are soluble in highly coordinating solvents like DMSO and DMF.

It is imperative to mention that the formation of the complex (3.1) to (3.5) shows that they contain an additional oxo-group generated during the course of the reaction. It is imperative to mention that the present complexes have been isolated in absolute ethanol. In order to see the role of water in the formation of the complexes the same reaction was carried out in rectified spirit. The resulting yellow coloured complexes were found to contain coordinated ligand to the metal, but as dibasic tetradentate through both the naphtholate oxygen atoms and both the azomethine nitrogen atoms. This ruled out the possibility of water molecules absorbed from open atmosphere (the reaction was carried out in open air) to function as a nucleophile in the reaction medium giving rise to oxo-bridging in the complexes. Now, the only option left was the abstraction of oxygen atom from the acetylacetone group bonded to Mo centre which might function as a nucleophile in the reaction. The probable mechanism for the reaction might be shown as under: (Scheme 1).



Scheme1. Mechanism showing the generation of oxo-groups from acetyl acetone in the complexes

Thermal Studies

Detailed thermogravimetric studies **[22]** of the complexes (3.1), (3.2), (3.4) and (3.5) were carried out manually by heating the samples at a particular temperature for 30 minutes in the temperature range 60–250 °C and at an interval of 5 °C in an electric oven and estimating the weight loss. The vapours evolved were identified by passing them through separate test tubes containing: anhydrous copper sulfate, sodium hydroxide and iodine, $CHCl_3$ solution containing a drop of 5M NaOH solution and cyanogen bromide solution.

The weight loss of the complexes occurs in two prominent steps, i.e. 75–80 °C and 120–150 °C. The vapours evolved in these two temperature ranges in none of the complexes turned anhydrous copper sulfate to blue ruling out the possibility of presence of water molecules in the complexes. The vapours evolved in the temperature range 75–80 °C in all of the complexes gave a yellow precipitate with a solution of sodium hydroxide and iodine confirming that they originate from ethanol molecules present in the lattice structure of the complexes. Further, the weight loss occurring in the temperature range 75–80 °C corresponds to two molecule of ethanol lending credence to the suggested number of ethanol molecules present in the lattice structure of these complexes.

The complexes (3.2), (3.4) and (3.5) show further weight loss in the temperature range120–150 °C. The vapours evolved from complex (3.2) in this temperature range turned the colour of $CHCl_3$ solution containing a drop of 5 M NaOH solution to red and this confirms that the vapours originated from pyridine molecules. Similarly, the vapours evolved from the complexes (3.4) and (3.5) in this temperature range turned the colour of cyanogen bromide solution to green-violet and blue respectively, on treatment with phloroglucinol solution. This suggests the presence of 3-picoline and 4-picoline molecules in the complexes (3.4) and (3.5) **[22]**, respectively. The weight loss in this temperature range corresponds to two molecules of pyridine/3-picoline/4-picoline in the complexes (3.2), (3.4) and (3.5) lending credence to the suggested number of pyridine/3-picoline/4-picoline molecules per metal centre present in the lattice structure of these complexes.

The loss of pyridine, 3-picoline and 4-picoline molecules at such high temperature may indicate their presence in the coordination sphere around the molybdenum centre **[23]**, but the classification of solvent molecules on the basis of thermogravimetric analysis alone as being held in the lattice or being coordinated to the metal centre needs utmost caution in view of the fact that the loss of solvent molecules at considerable high temperatures might occur due to hydrogen bonded network in the solid state of the complexes that might

permeate the lattice **[24]**. The IR spectra of the complexes do not show any new band in the region 1000–1100 cm^{-1} characteristic of ring nitrogen-to-metal bonding, ruling out the possibility of coordination of pyridine, 3-picoline and 4-picoline molecules to the molybdenum centre **[25]**. This evidence further suggests that the pyridine, 3-picoline and 4-picoline molecules are part of the lattice structure of the complexes **[24]**.

Molar Conductance

The molar conductance values for the complexes (3.1) to (3.5) at 10^{-3} M dilution in DMSO solution lie in the range 2.16–2.81 $ohm^{-1}cm^2mol^{-1}$ (Table 3.2).

Molar conductance values for the complexes of different electrolyte types depend on the nature of the solvent. Some of the molar conductance (Λ_M) values reported at 10^{-3} M dilution for the complexes of different electrolyte types in aqueous and non-aqueous solvents are given in Table 3.1.

A comparison of the molar conductance data for the complexes (3.1) to (3.5) with the literature values suggests that these complexes are non-electrolyte in DMSO **[26]**.

Table 3.1. Molar Conductance values at 10^{-3} M dilution for the complexes of different Electrolyte types in Aqueous and Non-aqueous Solvents.

Sl. No.	Solvent	Electrolyte Type ($ohm^{-1}cm^2mol^{-1}$)			
		1:1	1:2	1:3	1:4
1.	Water	95	225–270	380–452	Above 520
2.	Acetonitrile	120–160	220–300	340–420	500–?
3.	Acetone	100–140	160–200	270–?	360–?
4.	Nitromethane	75–95	150–180	220–260	Above 320
5.	Nitrobenzene	20–30	50–60	70–82	90–100
6.	Methanol	80–115	160–220	290–350	450–?
7.	Ethanol	35–45	70–90	120–?	160–?
8.	DMSO	35–70	–	109–?	–
9.	DMF	65–90	130–170	200–240	300–?

Magnetic Moment and ESR

The room temperature magnetic moments of the complexes (3.1) to (3.5) were measured as powdered solid samples. The μ_B values for the complexes indicate that they are

diamagnetic. This fact suggests the presence of molybdenum in +6 oxidation state in these complexes with d^0 electronic configuration. This also suggests that the reduction of the molybdenum centre does not occur under the influence of the ligand.

The ESR spectrum of the complex (3.1) was recorded as a representative example. The complex was found to be ESR silent suggesting that the molybdenum is present in +6 oxidation state in these complexes.

Electronic Spectra

The electronic spectra of the complexes were recorded in the region 800-290 nm in DMSO at 10^{-3} M dilution. The important electronic spectral bands for the dihydrazone ligand (H_4nsh) and the monometallic Mo(VI) complexes isolated in the present study along with their molar extinction co-efficient have been given in Table 3.3. The electronic spectra of the ligand and the complexes (3.1), (3.2) and (3.3) are shown in Fig. 3.7 to 3.10.

The free ligand, H_4nsh shows bands at 317 and 363 nm. These bands are assigned to intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition. The position of the bands given in Table 3.3 is the average position of the absorbtion bands. The essential features of the electronic spectra of the complexes are almost the same. Each ligand band is split into two components which show that the two hydrazone parts of the free dihydrazone molecule are in different planes. In the electronic spectra of the complexes, the average position of the ligand bands, although remains almost unshifted yet are slightly blue shifted. This indicates that bonding between dihydrazone and the metal centre, although weak, yet are significant. The electronic spectra of all of the complexes, in addition to the intraligand bands, show an absorption band in the region 421–423 nm. Mo(VI) complexes do not show any band in the visible region because Mo(VI) has a $4d^0$ configuration **[27, 28]**. Hence, these bands may be assigned to ligand-to-metal charge transfer transition. This is also confirmed from very high molar extinction co-efficient (2490–3310 $dm^3mol^{-1}cm^{-1}$) of these bands. The splitting of the charge transfer band into two components in all of the complexes suggests that there is a transfer of charge from two hydrazone parts to the metal centre existing in the different planes. These results are consistent with the results reported **[29, 30]** for dioxomolybdenum complexes.

Nuclear Magnetic Resonance Spectroscopy

In the present study ^1H and ^{13}C NMR spectroscopies have been used to derive information

regarding bonding mode of the ligand towards the metal centre and to conclude the stereochemistry of the complexes thereform.

The dihydrazones are polyfuctional ligands which can adopt either *staggered* configuration or *anti-cis* configuration or *syn-cis* configuration **[31, 32]** in the metal complexes. The present ligand may provide two types of coordination chambers (N_2O_2 or O_2O_2 chambers) if it coordinates to the metal centre in the *anti-cis* configuration. However, it may provide only one type of coordination chambers (two NO_2 chambers) if it coordinates to the metal centre in either *staggered* configuration or *syn-cis* configuration. The N_2O_2 coordination chamber originates from azomethine nitrogen atoms and naphtholate oxygen atoms of the naphthaldimine fraction of dihydrazone while O_2O_2 coordination chamber originates from carbonyl group and naphtholate oxygen atoms provided the latter acts as a bridging group. On the other hand, when the dihydrazone coordinates to the metal centre in either *syn-cis* configuration or *staggered* configuration, the different dihydrazone parts would be symmetrically bonded to different metal centres through naphtholate oxygen atoms, carbonyl oxygen atoms and azomethine nitrogen atoms making up NO_2 donor set. Such a difference in bonding mode of dihydrazone would be reflected in the spectral properties of the complexes.

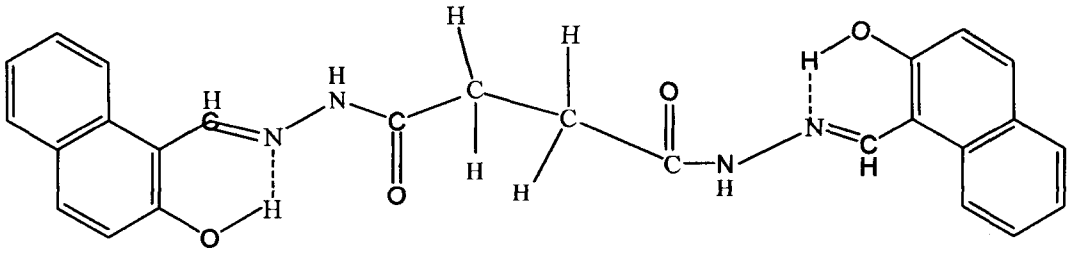


Fig. 3.2. *Staggered* configuration of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

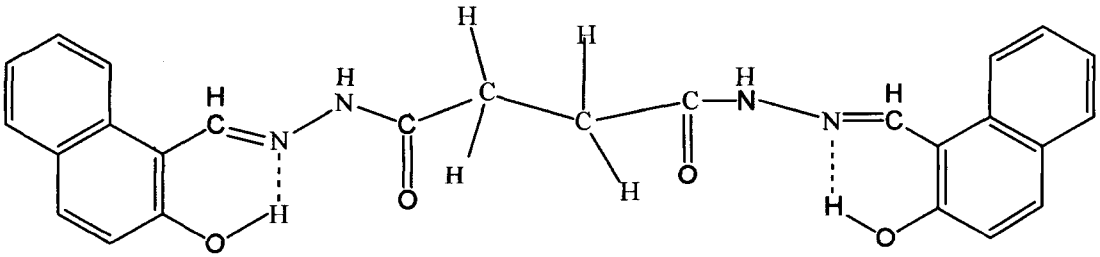


Fig. 3.3. *Syn-cis* configuration of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

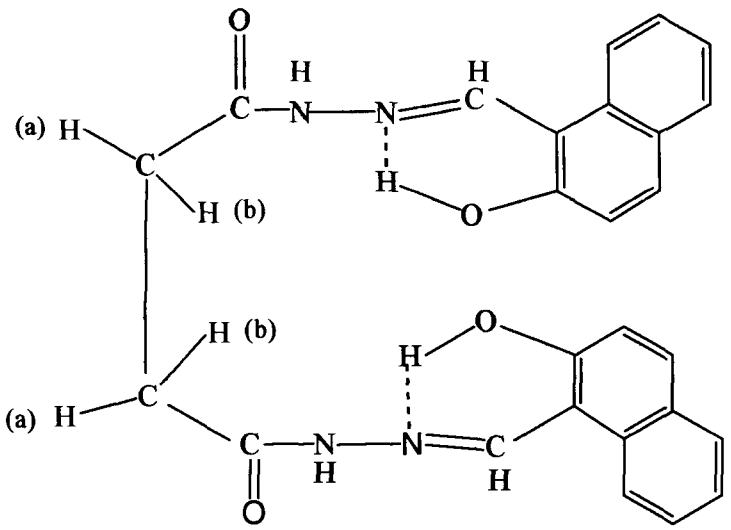


Fig. 3.4. *Anti-cis* configuration of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

^{1}H Nuclear Magnetic Resonance Spectroscopy

The complexes (3.1) to (3.5) have been characterized by proton nuclear magnetic resonance (^{1}H NMR) spectroscopy. The ^{1}H NMR spectra for bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) and the complexes (3.1), (3.2) and (3.5) are shown in Fig. 3.11 to 3.14. The ^{1}H NMR spectral data for the dihydrazone and the metal complexes are given in Table. 3.4.

The ^{1}H NMR spectrum of H_4nsh has been recorded in DMSO-d_6 ($(CD_3)_2SO$) as it is insoluble in other common organic solvents. The assignment of the signals has been made to various types of protons in the light of literature records **[33]**. It is desirable to discuss the important features of the ^{1}H NMR spectrum of the ligand before we proceed to describe the ^{1}H NMR spectral features of the metal complexes.

Two proton signals observed in the region δ 11.61–12.73 ppm have been assigned to δ (OH) protons while the other two proton signals in the region δ 9.99–11.14 ppm down field of TMS have been assigned to δ (NH) protons, respectively. The signals in the region δ 8.60–9.05 ppm have been assigned to azomethine (-CH=N) protons, whereas a multiplet in the region δ 7.19–8.23 ppm to naphthyl protons. Further, the two signals observed at δ 2.66 and δ 2.53 ppm respectively are assigned to methylene protons **[34]**. The two

methylene protons appear at different fields which is consistent with their different chemical environment in the ligand.

The signal at δ 2.66 ppm is attributed to arise from the methylene proton (a) close to carbonyl oxygen, while the signal at δ 2.53 ppm is attributed to arise from the methylene proton (b) (Fig. 3.4.) distant from carbonyl oxygen.

The signals in the region δ 11.61–12.73 ppm and δ 8.60–9.05 ppm appear as two doublets, while the signals in the region δ 9.99–11.14 ppm appear in the form of two resonances only. If the dihydrazone exists in *syn-cis* configuration or *staggered* configuration, the δ OH, δ NH and δ-CH=N- resonanes should appear as a singlet. On the other hand, if δ OH, δ NH and δ-CH=N- resonances show multiplicity, the dihydrazone would exist in the *anti-cis* configuration. The appearance of δ OH, δ-CH=N- and δ NH poroton resonanes in the form of two doublets and two signals, respectively, rules out the possibility of existence of dihydrazone either in *staggered* configuration or *syn-cis* configuration. In other words, this suggests the existence of dihydrazone in the *anti-cis* configuration. The factor which is responsible for the existence of dihydrazone in the *anti-cis* configuration is provided by strong intramolecular and intermolecular hydrogen bonding existing in the molecules which inhibits free rotation of hydrazone groupings around the C–C bond.

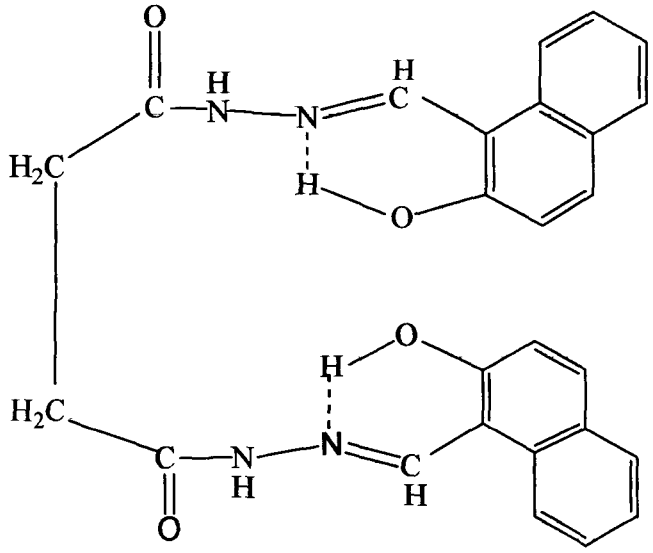


Fig. 3.5. *Anti-cis* configuration of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

As a result of *anti-cis* configuration of the ligand, one of the hydrazone groupings attains axial position while the other hydrazone grouping remains in the equatorial plane. Consequently, the equatorial protons appear upfield as compared to axial protons. Further, coupling between the axial and the equatorial protons occur which ultimately leads to splitting of their singals. Concequently, the δ (OH) and δ (- CH=N -) signals appear in the form of two doublets while the δ (NH) signal appears in the form of two resonances only. The position of the doublets is given in Table. 3.4 with coupling constant 'J' equal to 152 Hz for the – OH protons and 62 Hz for azomethine protons, respectively. At this stage, it is pertinent to mention that stereospecific long range coupling has been reported for hydrazones **[35, 36]**

The essential features of the ^{1}H NMR spectra of the Mo(VI) monometallic complexes (3.1) to (3.5) are similar to that of the uncoordinated dihydrazone. The only significant difference in the ^{1}H NMR spectra of the complexes (3.1) to (3.5) as compared to that of the free dihydrazone is that the δ (-CH=N-) signals show an average downfield shift by δ 0.66–0.44 ppm. This suggests the involvement of nitrogen atom of the azomethine group in coordination to the metal centre **[37]**.

The two proton doublets observed at δ 11.61 and δ 12.63 ppm in the free ligand also remains almost unchanged in their essential feature in the complexes (3.1) to (3.5) and retains almost at the same position. This suggests the non-coordination of naphtholic –OH group through oxygen atom to the metal centre. It appears that, the naphtholic –OH groups which are free from intramolecular hydrogen bonding in the free ligand, again get involved in a new kind of intramolecular hydrogen bonding in the metal complexes.

The two resonances in the region δ 9.99–11.14 ppm in the free ligand were assigned to δ (NH) protons. The positions of these signals also remain unchanged in the complexes (3.1) to (3.5) and appear in the region δ 9.99–11.16 ppm. This rule out the possibility of involvement of N- atom of secondary –NH group in coordination. Such a feature associated with the ^{1}H NMR spectra of the complexes in the δ (OH) and δ (NH) region indicate that the conformation of the dihydrazone remains unaltered on complexation.

The naphthyl proton multiplet appears in the region δ 8.47–7.13 ppm in the complexes (3.1) to (3.5). The complexes (3.2) to (3.5) show an easily identifiable additional resonance in the region δ 8.58–8.64 ppm which are not present in complex (3.1). This signal is attributed to *ortho* protons of pyridyl ring of pyridine, 2-picoline, 3-picoline and 4-picoline molecules. This signal is downfield shifted as compared to its position in the

respective free pyridine, 2-picoline, 3-picoline and 4-picoline molecules **[38]**. This downfield shift of *ortho* proton signals of pyridyl ring dismisses the possibility of its involvement in coordination to the molybdenum centre.

It appears that, in the metal complexes, the lone pair of electrons on nitrogen atom of pyridyl ring of pyridine, 2-picoline, 3-picoline and 4-picoline molecules are repelled by the metal centre and hence become more concentrated on the nitrogen atom. This increases the electron density on nitrogen atom which, in, turn increases its electronegativity and consequently, the more electronegative nitrogen atom withdraws electrons towards itself from the adjacent bonds. This withdrawal of electron is maximum from the *ortho* position while it decreases with increasing distance from the nitrogen atom. As a result, the *ortho* proton signals are maximum downfield shifted and appear in the region δ 8.44–8.61 ppm as compared to their position in free pyridine and picoline molecules. The signals due to *meta* and *para* protons of pyridine, 2-picoline, 3-picoline and 4-picoline molecules appear merged with the signals due to naphthyl protons. Hence, they are not clearly visible in the ^{1}H NMR spectra of the complexes (3.2) to (3.5). A new signal in the region δ 3.03–3.04 ppm is observed in the ^{1}H NMR spectra of the complexes (3.3) to (3.5). This signal is assigned to methyl protons of 2-picoline, 3-picoline and 4-picoline molecules. This signal appears at δ 2.55, δ 2.32 and δ 2.37 ppm in free 2-picoline, 3-picoline and 4-picoline molecules, respectively **[38]**. Thus, the signal due to methyl protons are also downfield shifted in these complexes as compared to their position in free 2-picoline, 3-picoline and 4-picoline molecules. This downfield shift of methyl proton signals further rules out the possibility of coordination of ring nitrogen of pyridyl ring of 2-picoline, 3-picoline and 4-picoline molecules to the metal centre. This may be explained in the same way as has been done in case of *ortho* protons of pyridine and picoline molecules and hence further discussion on the subject is redundant.

Further, these complexes do not show any signal in the downfield region which can be assigned to pyridinium or 2-picolinium or 3-picolinium or 4-picolinium ions. This excludes the possibility of presence of pyridine, 2-picoline, 3-picoline and 4-picoline molecules as pyridinium or 2-picolinium or 3-picolinium or 4-picolinium ions in the metal complexes.

In the ^{1}H NMR spectra of the complexes (3.1) to (3.5) a singlet, a quartet and a triplet are observed in the region δ 1.04, δ 3.02–3.03 and δ 4.32–4.34 ppm respectively. These signals are assigned to methyl, methylene and –OH protons of ethanol molecule **[38]**. The

positions of these signals indicate that the ethanol molecules are present in the lattice structure of the complexes.

Carbon- 13 Nuclear Magnetic Resonance Spectroscopy

Only the dioxomolybdenum (VI) complexes $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ (3.2), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-}pic)\cdot 2C_2H_5OH$ (3.3), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3pic)\cdot 2C_2H_5OH$ (3.4) and $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-}pic)\cdot 2C_2H_5OH$ (3.5), have been characterized by ^{13}C NMR spectroscopy. Due to poor solubility in DMSO, the ^{13}C NMR spectrum of the complex $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)]\cdot 2C_2H_5OH$ (3.1) was not properly resolved and was not worth analyzing. The ^{13}C NMR spectra of H_4nsh and the complexes (3.2) and (3.4) have been shown in Fig. 3.15 to 3.17, respectively. The chemical shift δ (in ppm from TMS) and the chemical shift change Δ δ (in ppm) accompanying the coordination of the ligand to the metal centre in the complexes are set out in Table 3.5. The assignments **[39]** for the ligand have been deduced taking into account the shift in the resonances of the naphthyl ring carbon atoms caused by the substituents, azomethine group, and naphtholic –OH group **[40]**. The numbering scheme for the carbon atoms in the ligand and the complexes are shown in Fig. 3.6. The carbon atoms in the axial and the equatorial positions have been designated by the letters 'a' and 'b', respectively.

Majority of the signals in the ligand and the complexes appear as pair. Only few signals appear as a singlet. The appearance of a few signals as singlets may be attributed to the overlapping of signals due to nearby carbon atoms. The effect of coordination of the metal ions on some carbon resonances (Table 3.5) of naphthyl ring results in a downfield shift while other carbon resonances exhibit an upfield shift.

The signals due to C(2) carbon atom appear at δ 195.32 and 187.24 ppm respectively. These signals shift upfield by δ 0.47, δ 0.89 and δ 0.71 ppm, respectively in the complexes (3.2), (3.3) and (3.4). The shift to higher field of these signals rules out the possibility of coordination of >C=O group to the metal centre.

The signals due to C(3) carbon atom in the uncoordinated dihydrazone appear at δ 160.81 and 159.86 ppm, respectively. These signals get downfield shifted in the complexes (3.2) to (3.5) and appear in the range δ 167.08–177.64 ppm, giving a chemical shift change of 16.12, 9.66, 10.16 and 11.36ppm in the complexes (3.2) to (3.5). This downfield shift is observed because these carbon atoms are closer to the coordinated azomethine nitrogen atom.

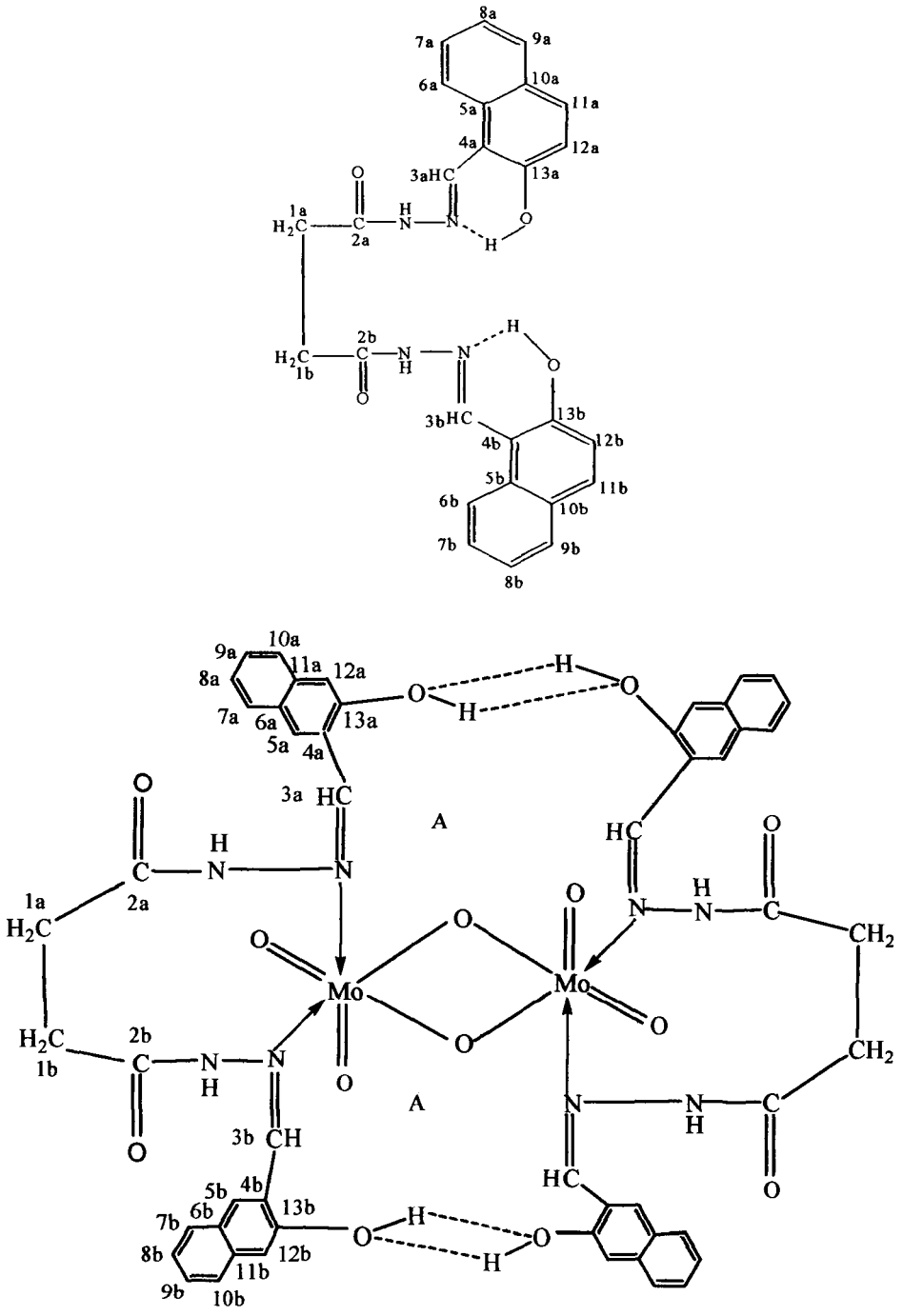


Fig. 3.6. Numbering scheme of the carbon atoms in H_4nsh and (μ_2-O)$_2$[[$(MoO_2)_2(H_4nsh)_2$].2A.2C_2H_5OH (where A = pyridine, (3.2), 2-picoline (3.3), 3-coline (3.4), 4-picoline(3.5))

The signals due to C(13) carbon atoms which appears at δ 167.48 and 167.22 ppm in the free ligand get upfield shifted by δ 8.34–8.37 ppm in the complexes (3.2) to (3.5). This upfield shift is attributed to the non-coordination of naphtholic –OH to the metal centre and is due to drainage of electron density from oxygen atom of naphtholic –OH to C(13) carbon atom due to breaking of hydrogen bonding in the coordinated ligand.

Some new signals have been observed in ^{13}C NMR spectra of the complexes (3.2), (3.3), (3.4) and (3.5) (Table 3.5) which are not present in the ^{13}C NMR spectra of the free ligand. Hence, these signals are assigned to various carbon atoms of pyridine, 2-picoline, 3-picoline and 4-picoline molecules and also to the carbon atoms of ethanol molecules which are present in the lattice structure of the complexes.

In the free pyridine molecule, the signals due to (C2, C6) carbon atoms appear at δ 123.75 ppm, while in the free 2-picoline, 3-picoline and 4-picoline molecules, these signals appear in the region δ 146.93 – 158.00 ppm. The signal due to methyl carbon atom in 2-picoline, 3-picoline and 4-picoline appear in the region δ 18.36 – 24.30 ppm **[38]**. The signal due to C2, C6 carbon atoms in pyridine appeared at δ 127.61ppm in the complex (3.2), while in the remaining complexes this signal appeared in the region δ 151.36–153.52 ppm. Thus, the C2, C6 carbon atoms in pyridine are shifted downfield by 3.86 ppm in complex (3.2), while in substituted pyridine i.e., 2-picoline, 3-picoline and 4-picoline these signals are downfield shifted by δ 1.94–3.25 ppm in the complexes (3.3), (3.4) and (3.5). This suggests non-coordination of pyridyl nitrogen atoms to the metal centre.

It is imperative to mention that due to non-coordination of pyridyl nitrogen atoms to the metal centre, the lone pair of electrons on nitrogen atom are repelled away from the metal and become more concentrated on the nitrogen atom. This increases the electronegativity of nitrogen atom and hence the more electronegative nitrogen atom withdraws electrons from the surrounding carbon atoms. This causes downfield shift of the resonances due to adjacent carbon atoms. For the same reason, the signal due to methyl carbon atoms also show downfield shift in the metal complexes as compared to that in the free molecules.

In the free ethanol molecule, the signal due to $-CH_2$ and $-CH_3$ carbon atoms appear at δ 57.79 and 18.13 ppm, respectively. The signals appearing in the region δ 54.00–57.00 and δ 18.40 – 18.85 ppm, respectively, in the ^{13}C NMR spectrum of the complexes (3.2) to (3.5) have been assigned to $-CH_2$ and $-CH_3$ carbon atoms of ethanol molecule. The position of the ethanol signals in the complexes is upfield shifted as compared to those in

the free ethanol molecule. This suggests the presence of ethanol molecule in the lattice structure of the complexes.

Further, the signal appearing in the region δ 28.69–26.40 in the complexes (3.1) to (3.5) are assigned to C(1a) and C(1b) carbon atoms of methylene group. These signals appear at δ 28.69 and 27.34 ppm in the uncoordinated dihydrazone. They show upfield shift of about δ 1.02 ppm in the complexes (3.2) to (3.5). The upfield shift of this signal in all of the complexes indicates that the electron density of methylene carbon atoms is increased in the coordinated dihydrazone as compared to that in the uncoordinated dihydrazone.

Infrared Spectroscopy

The IR spectrum of the ligand H_4nsh is very much complicated due to overlapping of bands arising from several groups occurring in the same region. However, some of the important bands have been selected for the location of bonding sites of the ligand. The solution spectra of the ligand could not be investigated due to its insolubility in most of the common organic solvents. Hence it was not possible to eliminate the effect of intramolecular hydrogen bonding by comparing the solid state spectra of the complexes with the solution spectrum of the ligand.

The characteristic IR spectral bands for bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) and its monometallic molybdenum(VI) complexes are given in Table 3.6. The IR spectrum of H_4nsh and the complexes (3.1), (3.2) and (3.5) are shown in Fig. 3.18 to 3.21. The IR spectral feature of the complexes on comparison with that of the free ligand suggests that the dihydrazone is present in keto form in all of the complexes (3.1) to (3.5).

OH + NH stretching vibrations

The present ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone shows broad bands in the region 3500–3300 cm^{-1} with peaks at 3423, 3244 and 3051 cm^{-1} assignable to ν(OH + NH). This band is similar to that observed in salicylaldehyde and *o*-hydroxy acetophenone **[41]** indicating the presence of intramolecular hydrogen bonding between naphtholic –OH hydrogen and the >C=O and >C=N groups.

The IR spectra of the complexes (3.1) to (3.5) are complicated in the region 3500–3000 cm^{-1} due to overlapping of bands arising from stretching vibrations of secondary –NH group, lattice and coordinated water molecules and naphtholic –OH group. Further complicacy is added as the IR spectra of the ligand and the complexes are recorded in KBr

pellets which are moisture sensitive. Hence, the bands in this region might have contribution from bands arising due to presence of water molecules absorbed by KBr pellets as well.

The ν(NH) band appearing at 3244 cm^{-1} in the free ligand remains almost unshifted in the complexes (3.2) to (3.5). This rules out the possibility of coordination of >NH group to the metal centre.

Amide bands

Amide bands arise due to mixed vibration and approximate contributions from various modes in amide frequencies **[39]** as given below.

1672 cm^{-1}(vs)	Amide I	80% C=O stretrching
1633 cm^{-1}(vs)		
1540 cm^{-1}(m)	Amide II	80% C=O stretching
1321 cm^{-1}(m)	Amide III	40% C–N stretching
		30% N–H stretching
		20% CH_3–C stretching
751 cm^{-1}(m)	Amide V	N–H out of plane bending
671 cm^{-1}(m)	Amide IV	40% O=C–N stretching
585 cm^{-1}(m)	Amide VI	C=O out of plane bending

In view of such an interpretation of the amide bands, it is difficult to assign a particular amide band to pure stretching or bending vibrations. However, based on the interpretation of Mashima **[42]** and Nagano **[43]**, the effects of coordination to amide bands of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone are discussed below.

A comparison of the amide I bands of the ligand and the complexes reveals that the amide I band appearing at 1672 cm^{-1} in the free dihydrazone remains either unshifted in position as in complexes (3.1), (3.4) and (3.5) or shifts to lower frequency by about 6 cm^{-1} as in the complexes (3.2) and (3.3). Almost unaltered position and intensity of the amide I band in the complexes (3.2), (3.4) and (3.5) rules out the possibility of coordination of >C=O group to the metal centre. Further, the shift of amide I band to lower frequency by 6 cm^{-1} in the complexes (3.2) and (3.3) may also be related to non-coordination of >C=O group

to the metal centre as it still falls in the region in which the >C=O group in amide complexes has been shown to remain uncoordinated. Thus, the >C=O groups of the dihydrazone donot take part in bonding to the metal centre in these complexes. Similar results have been established in the dihydrazone metal complexes by Pelizzi and co-workers by X-ray crystallography **[44]**.

The free dihydrazone shows a weak band at 1540 cm^{-1} which is attributed to arise due to mixed contribution of amide II and ν(C–O) (naphtholic) bands **[45]**. This band shifts to higher frequency and appears in the region 1557–1566 cm^{-1}. Such a high shift of this band in the complexes indicates the non-coordination of naphtholic oxygen to the metal centre. This fact is further supported by the presence of –OH signals in the ^1H NMR spectra of the complexes. Further, the shift of the band at 1540 cm^{-1} to higher frequency rules out the possibility of coordination of >C=O group to the metal centre.

>C=N Bands

In Schiff bases derived from the condensation of hydrazine and aliphatic aldehydes and ketones, the ν(C=N) band appears in the region 1635–1665 cm^{-1} whereas it appears in the region 1610–1630 cm^{-1} in Schiff bases derived from hydrazine and aromatic aldehydes and ketones **[44]**. Marvell et al **[46]** prepared a number of polymeric salicylidene anilines and found ν(C=N) absorption in the region 1616–1637 cm^{-1} in free base and in the region 1606–1656 cm^{-1} in the metal chelates. The, band observed in the above region in hydrazides and dihydrazide Schiff bases and their transition and non-transition metal complexes have been used by us and other workers **[47, 48]** for the interpretation of the infrared spectra of the complexes of dihydrazone metal complexes.

In the present study, the ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) shows bands at 1633 cm^{-1} and 1593 cm^{-1}. The ν(C=N) band at 1633 cm^{-1} is assigned to stretching vibration of equatorial >C=N group while the band at 1593 cm^{-1} is assigned to the stretching vibration of axial >C=N group. In all of the complexes described in the present chapter, this band appears in the region 1602–1619 cm^{-1}. Thus the average position of the ν(C=N) shifts to lower frequency by 3–7 cm^{-1} in the complexes (3.1), (3.4) and (3.5) while to higher frequency by 6 cm^{-1} in the complexes (3.2) and (3.3), respectively. The negative shift of ν(>C=N) band in the complexes (3.1), (3.4) and (3.5) indicates bonding between azomethine nitrogen atom and metal centre **[49]**. The shift of ν(>C=N) band to higher frequency in the complexes (3.2) and (3.3) may be attributed to the flow of naphthyl ring electron density to the metal centre through azomethine group

[50], thereby increasing the bond order of C=N bond leading to an absorption in a higher frequency region. This indicates coordination of azomethine nitrogen atom to the metal centre in the complexes (3.2) and (3.3). On the other hand the appearance of ν(>C=N) stretching vibration in the form of two bands in the IR spectra of complex (3.1) indicates that the two >C=N groups are not equivalent in this complex . This non-eqivalency of the two >C=N groups suggests that the two azomethine nitrogen-to-metal bonds are of unequal length.

ν(C–O) (naphtholic) Vibrations

In the free dihydrazone a medium intensity band appears at 1281 cm^{-1}. This band is similar to that observed in other ligands containing phenol group. Hence, this band is assigned to ν(C–O) **[51]**. This band remains almost unshifted in position in all of the complexes. Such a feature associated with the ν(C–O) band rules out the possibility of bonding through the naphtholate or carbonyl oxygen atoms to the metal centre.

Aromatic Vibrations

The naphthyl ring shows a weak absorption at about 1600 cm^{-1}. In the present ligand, it appears merged with ν(>C=N) vibration at 1593 cm^{-1}. Even in the metal complexes, it does not show its independent existence, most probably, because of its overlapping with either ν(>C=N) band or amide II band or ν(C–O) (naphtholic) band. The band at 1467 cm^{-1} in the free dihydrazone is characteristic of substitution at α-position of naphthalene **[52]**.

The bands appearing at 1241 cm^{-1}, 1195 cm^{-1} and 1089 cm^{-1} in the present ligand are due to C–H in plane deformation vibration. These bands either remain unshifted or get slightly shifted in the IR spectra of the complexes (3.1) to (3.5). The bands appearing at 824 cm^{-1}, 797 cm^{-1} and 751 cm^{-1} in the present ligand are attributed to arise due to C–H out of plane deformation vibration and vibration due to (OH) vibration of naphtholic portion of the ligand. However, due to complex nature of the spectra in the region 1250–1100 cm^{-1}, it is not possible to identify unambiguously the γ(OH) band in the ligand and as well as in the complexes.

ν(N–N) and ν(C–N) Vibrations

The region below 1200 cm^{-1} in the IR spectra of the hydrazine derivatives is not well defined and it contains bands due to ν(N–N), ν(C–N) and ν(C–H) bending vibrations. The N–N stretching frequency which appears in the region 800–1050 cm^{-1} in the hydrazine

derivatives has been identified and its shift has been found useful in understanding the mode of coordination of nitrogen atoms in coordination. It has been found that the ν(N–N) stretching frequency shows an increase from 885 cm^{-1} in N_2H_4 **[53]** to 973 cm^{-1} in $N_2H_5^+$ **[54]** and 1024 cm^{-1} in $N_2H_6^{2+}$ **[55]** due to protonation which is akin to involvement of lone pair of electrons on nitrogen atom in coordination to the metal centre.

Onyszchuk **[56]** and Sacconi **[57]** observed bands near the above mentioned ranges in the metal complexes containing unidentate and bidentate hydrazine respectively. But the above region in the infrared spectra in no way can be taken as specific for coordination of one or two nitrogen atoms in substituted hydrazine metal complexes. Further, this band appears in the region 986–1014 cm^{-1} in the metal complexes of monosubstituted hydrazines of the type H_2N—NHY **[58]**. But in the metal complexes of N,N-diacyl hydrazines , the ν(N–N) band has been observed in the region 970–1040 cm^{-1} **[59]**. Eliminating the bands due to C–H in plane deformation in the region 900–1050 cm^{-1}, a weak band at 1029 cm^{-1} in the present ligand has been assigned to ν(N–N). This band shifts to higher frequency by 3–20 cm^{-1} in the IR spectra of the metal complexes indicating the involvement of only one nitrogen atom of N–N group in coordination to the metal centre. The C–N vibration appears merged with aromatic vibrations at around 1089 cm^{-1}. This band is shifted to higher frequency in the metal complexes. Because of the complex nature of the spectra in this region, we have refrained from drawing any conclusion from the position of this band regarding the involvement of >C=O group in coordination or otherwise.

Ethanol Bands

On comparing the IR spectra of the ligand with that of the complexes (3.1) to (3.5), a medium to strong intensity band observed in the region 1062–1070 cm^{-1} is assigned to C–O stretching vibration of ethanol molecule **[60]**. The position of this band remains almost unshifted as compared to its position in free ethanol. This suggests that the ethanol molecules are present in the lattice structure of the complexes.

νMoO_2^{2+} Bands

The metals containing dioxo groups such as UO_2^{+}, MoO_2^{2+}, WO_2^{2+}, ReO_2^{2+} exhibit strong bands in the region 1000–850 cm^{-1} due to antisymmetric and symmetric stretching vibrations. The *cis*-dioxo groups show two such bands while the *trans*-dioxo metal complexes show only one band.

The complexes (3.1) to (3.5) exhibit two very strong to medium intensity bands in the region 950–895 cm^{-1} indicating the presence of *cis*-MoO_2^{2+} groupings in these complexes **[61]**. Further, the band of medium intensity in the region 778–792 cm^{-1} is assigned to the stretching vibration of the doubly bridged Mo_2O_2 moiety **[62]**.

Conclusion

The present ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone is a tetrabasic octadentate ligand yet it functions as a neutral bidentate ligand in the complexes bonding to the metal centre through two azomethine nitrogen atoms only and molybdenum is present in the complexes as MoO_3 unit. All of the complexes are diamagnetic consistent with the +6 oxidation state of the metal. All of the complexes show a ligand-to-metal charge transfer transition in their electronic spectra. The appearance of azomethine proton signal in the ^1H NMR spectra of all of the complexes in the form of two signals as that of the uncoordinated dihydrazone ligand suggests that the conformation of dihydrazone remains unchanged on coordination to the metal centre.

All of the complexes are suggested to be dimeric. The molybdenum centres are joined to one another by oxo-bridging. Both the metal centres are suggested to have octahedral stereochemistry in which one of the azomethine nitrogen atoms occupies the equatorial position and the other azomethine nitrogen atom occupies the axial position. One of the oxo groups attached to the molybdenum centre occupies one of the axial position and the other occupy the equatorial position. The remaining two equatorial positions are occupied by bridging oxygen atoms.

On the basis of the various physico-chemical and spectral studies, the complexes are suggested to have the structure as shown in Fig.3.22

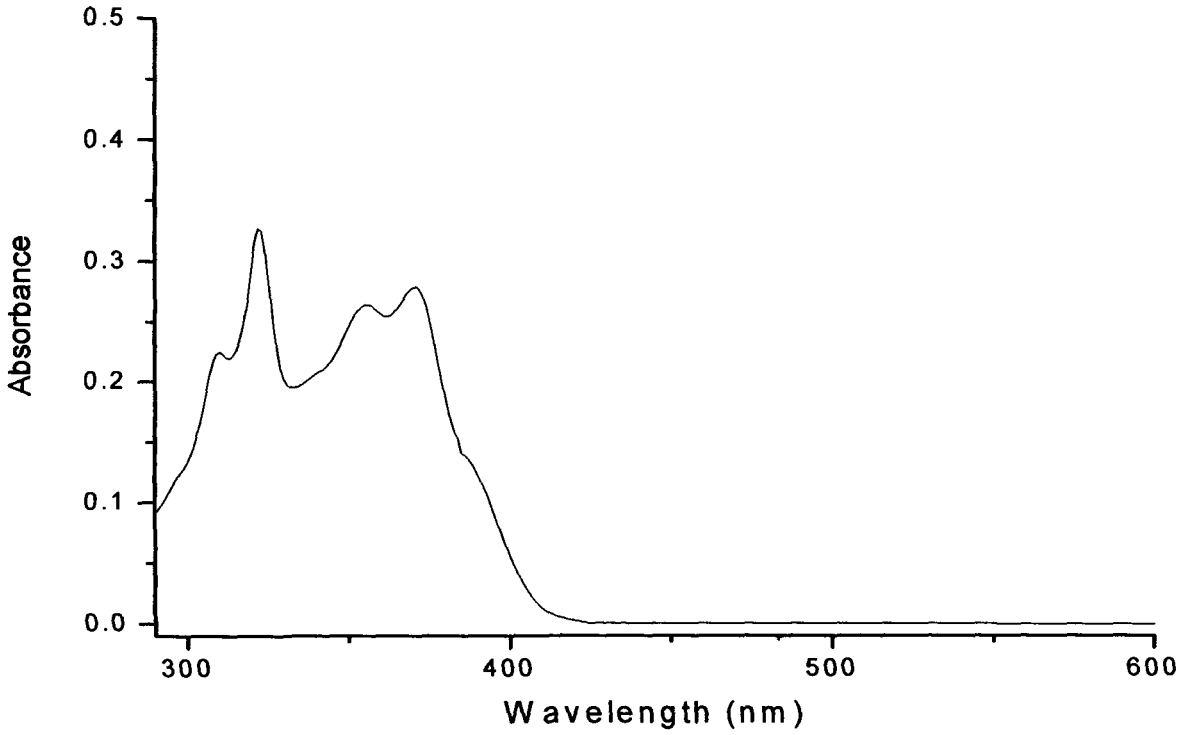


Fig. 3.7. Electronic spectrum of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) in DMF.

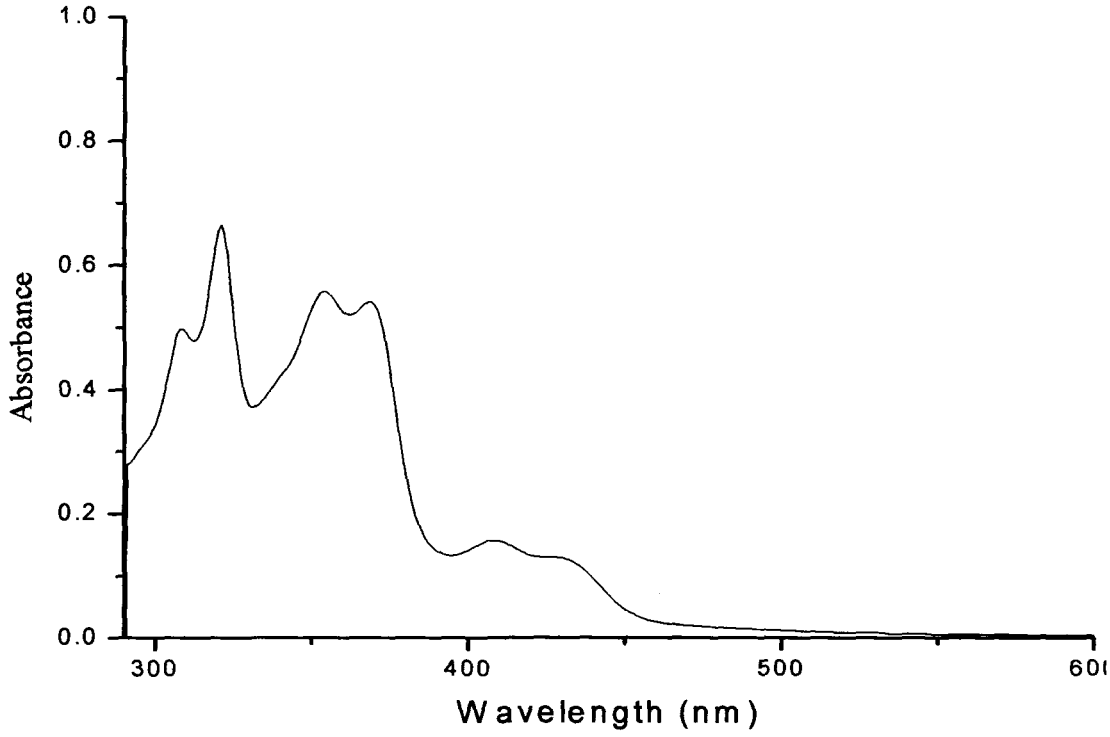


Fig. 3.8. Electronic spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1) in DMF.

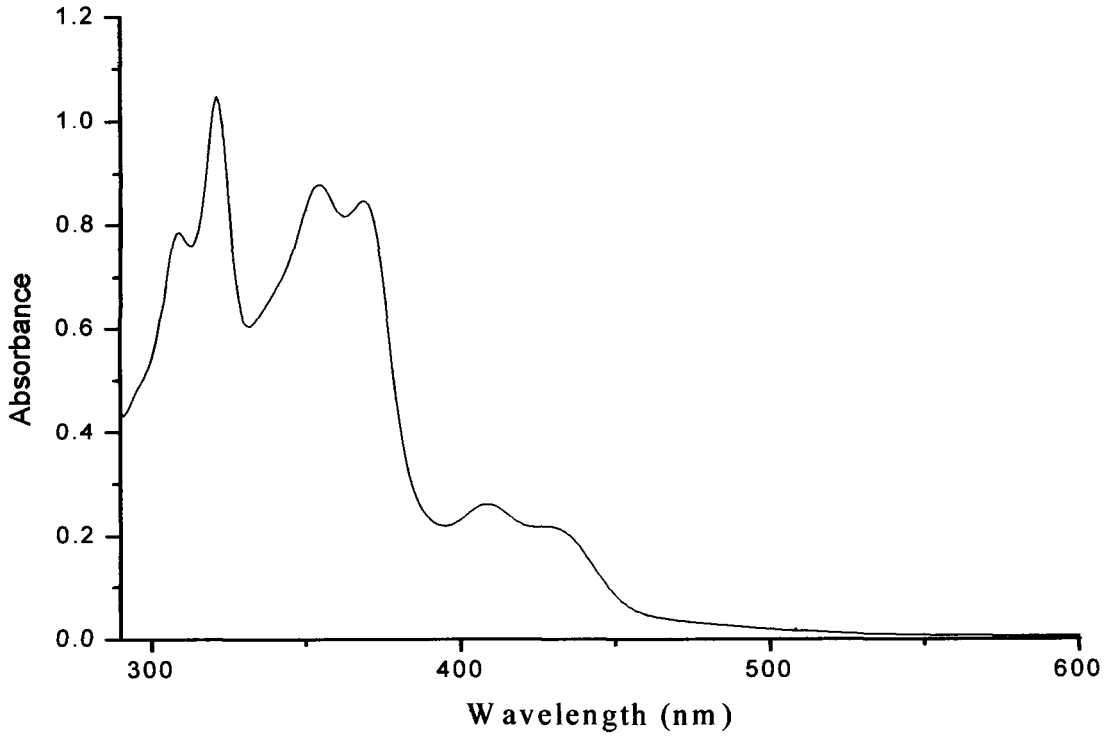


Fig. 3.9. Electronic spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ (3.2) in DMF.

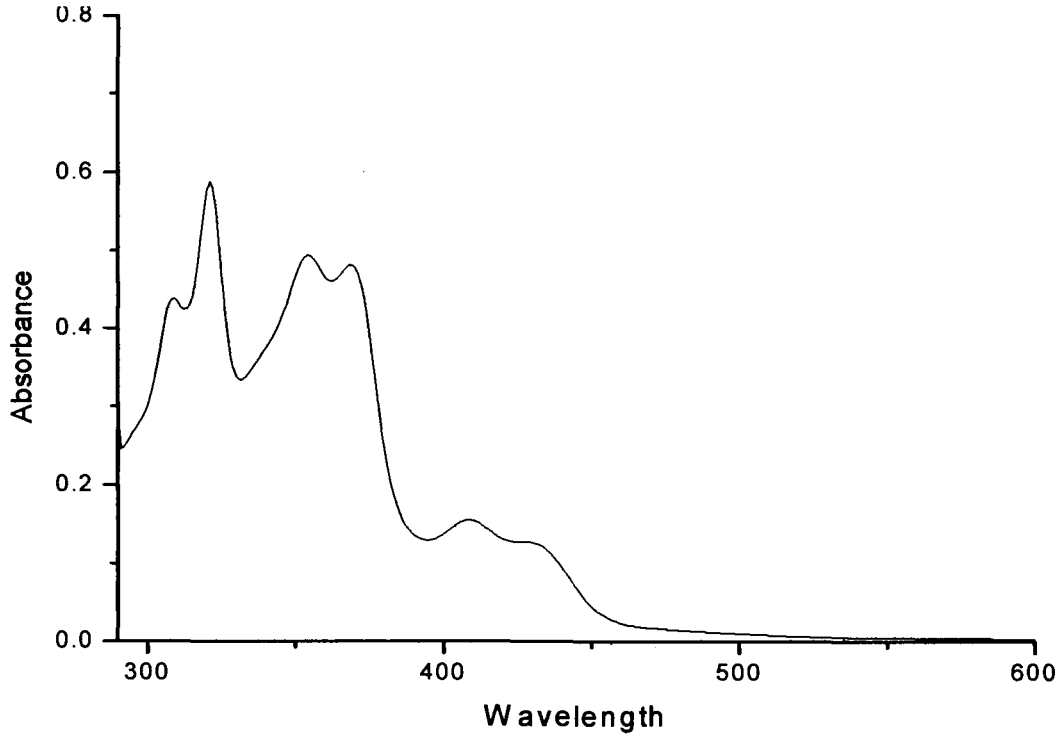


Fig. 3.10. Electronic spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-pic})\cdot 2C_2H_5OH$ (3.3) in DMF.

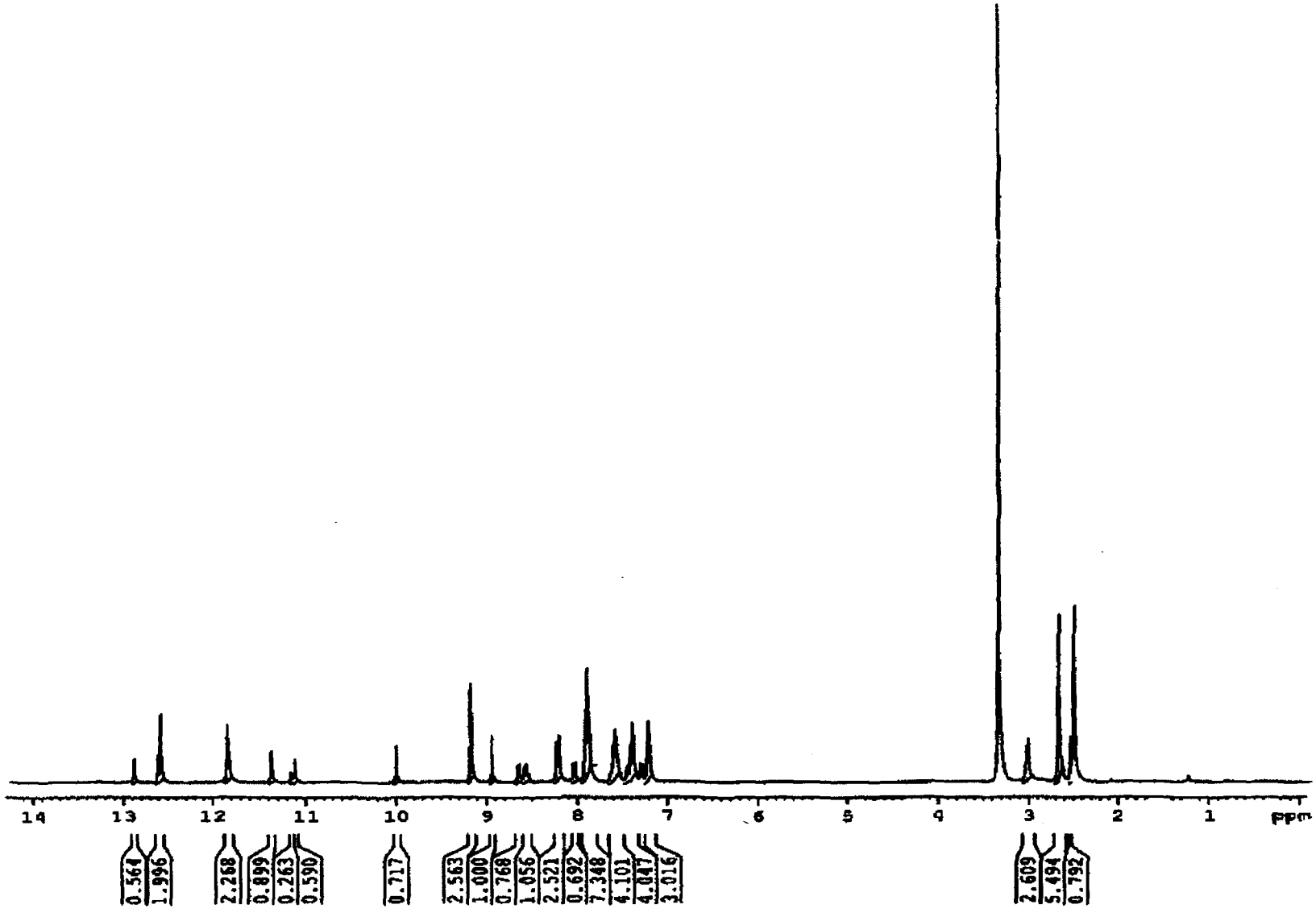


Fig. 3.11. ^{1}H NMR spectrum of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) *in* DMSO-d_6.

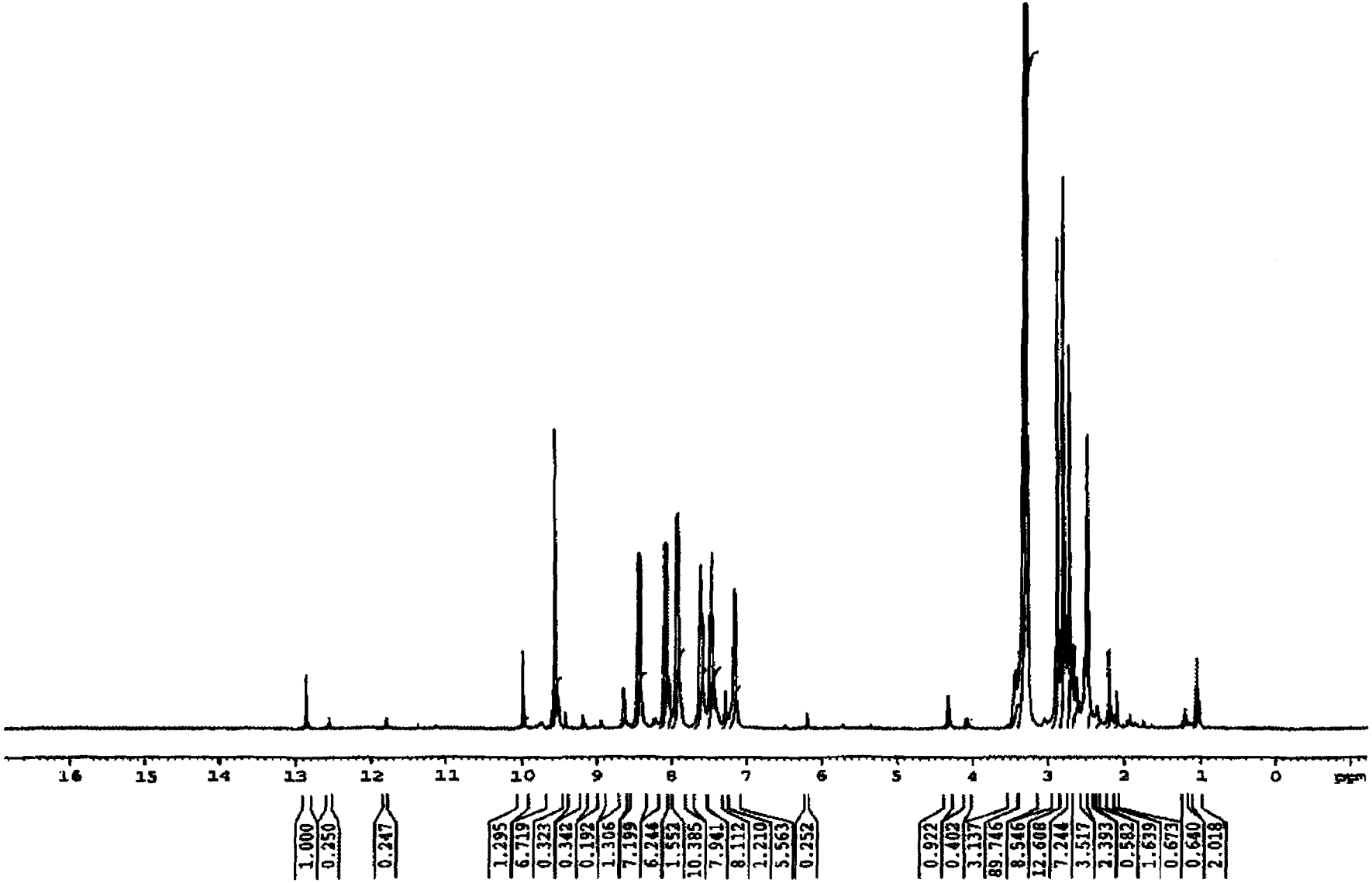


Fig. 3.12. ^{1}H NMR spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1) in DMSO-d_6.

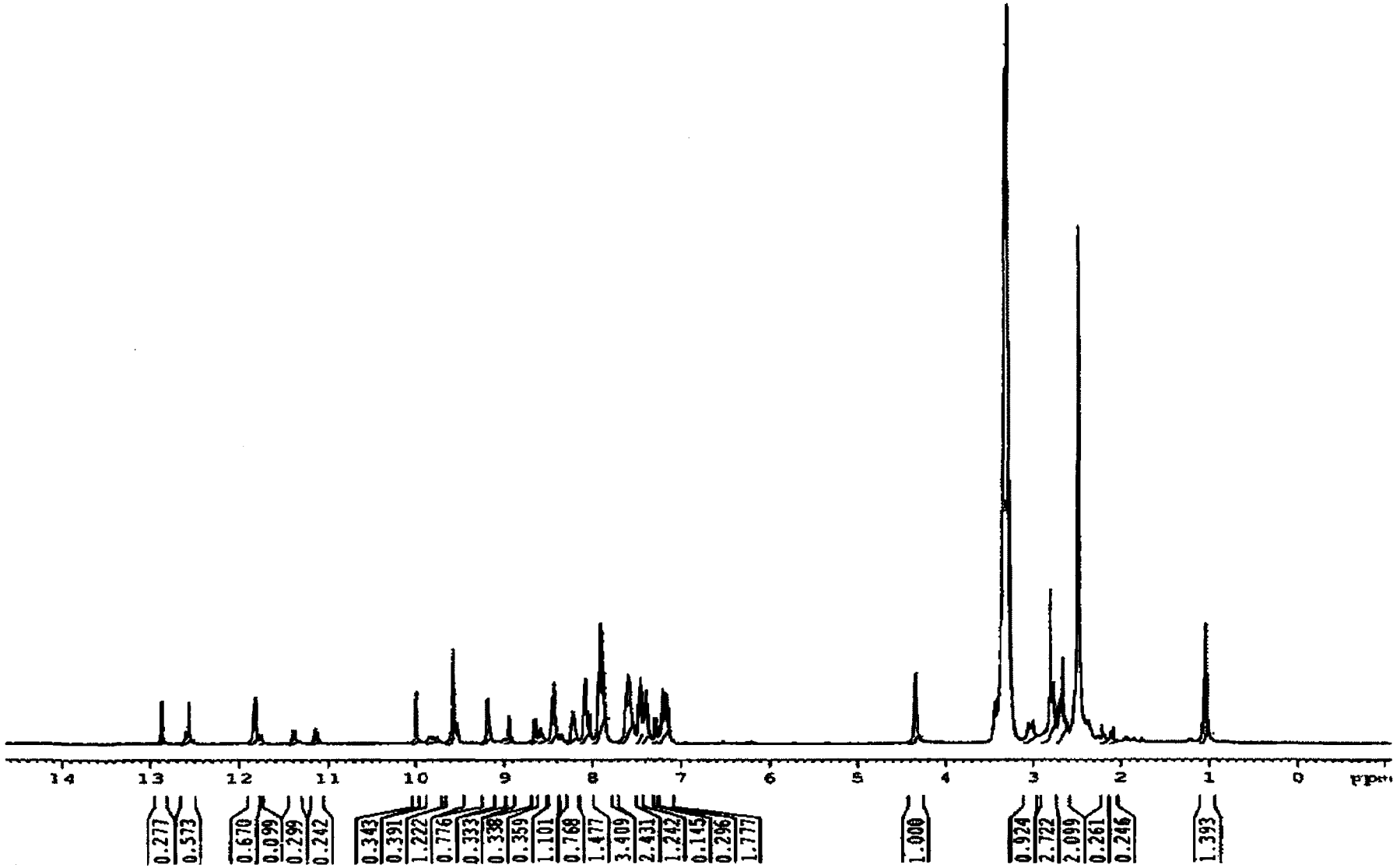


Fig. 3.13. ^{1}H NMR spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ (3.2) in DMSO-d_6.

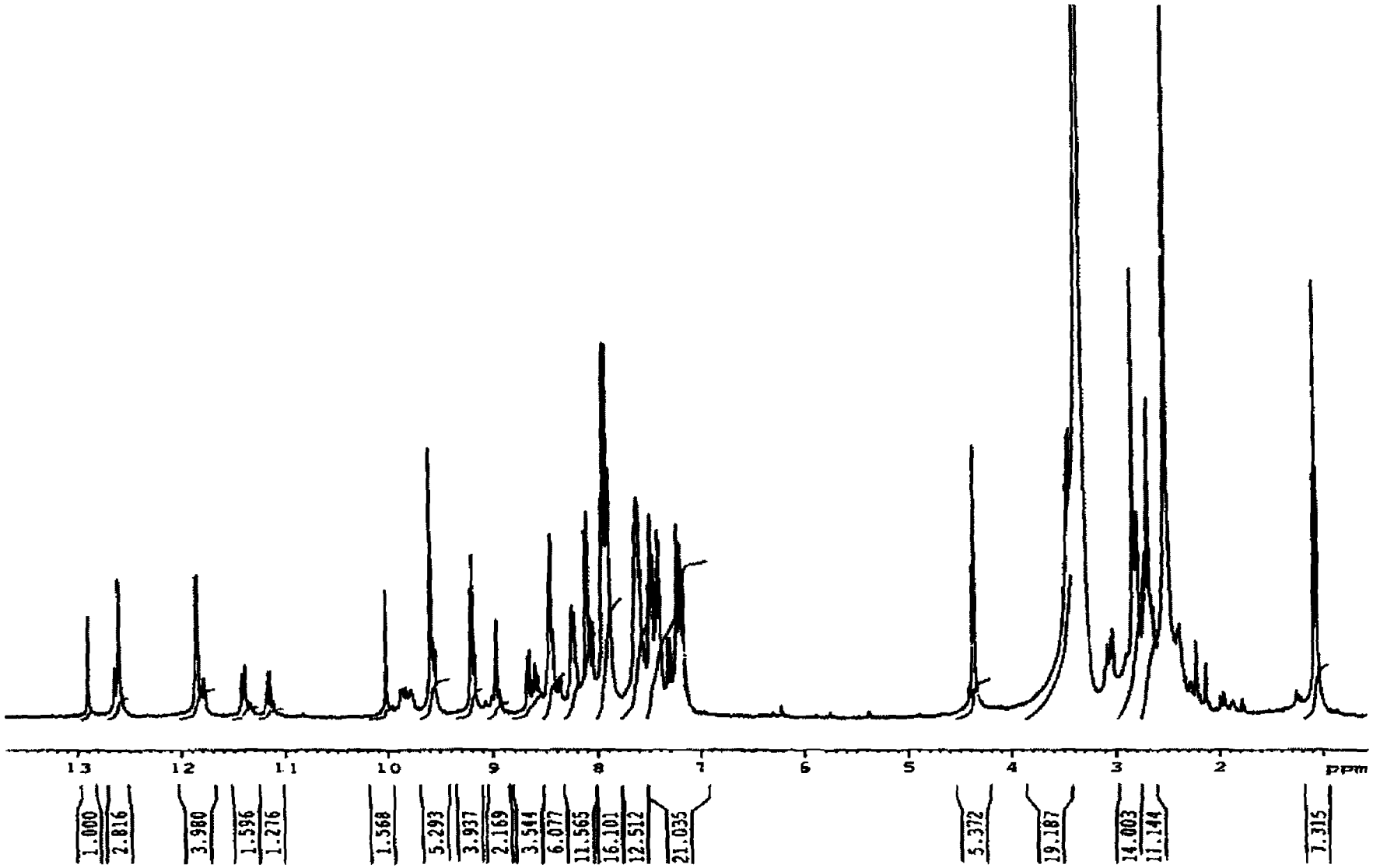


Fig. 3.14. ^{1}H NMR spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic})\cdot 2C_2H_5OH$ (3.5) in DMSO-d_6.

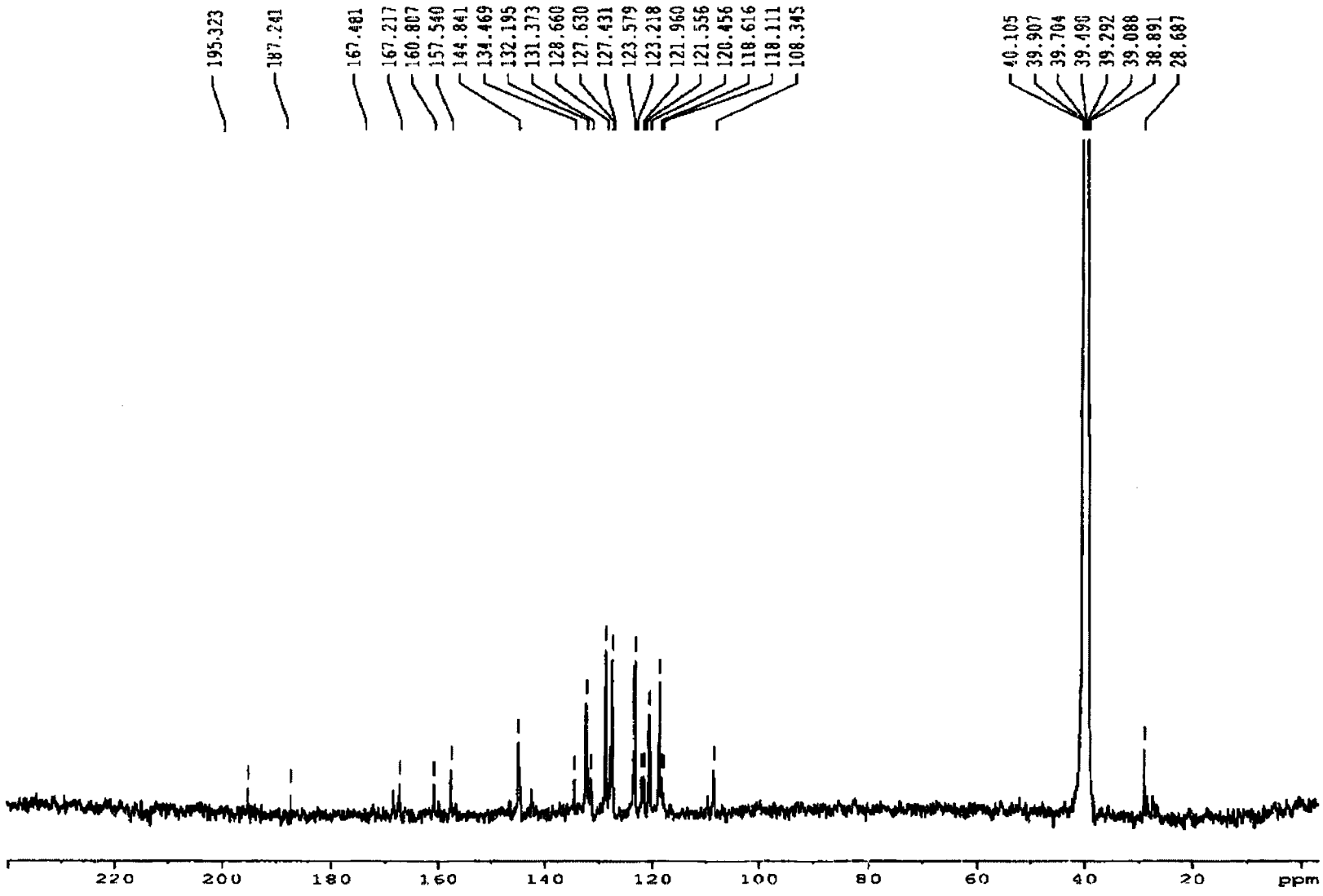


Fig. 3.15. ^{13}C NMR spectrum of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) in DMSO-d_6.

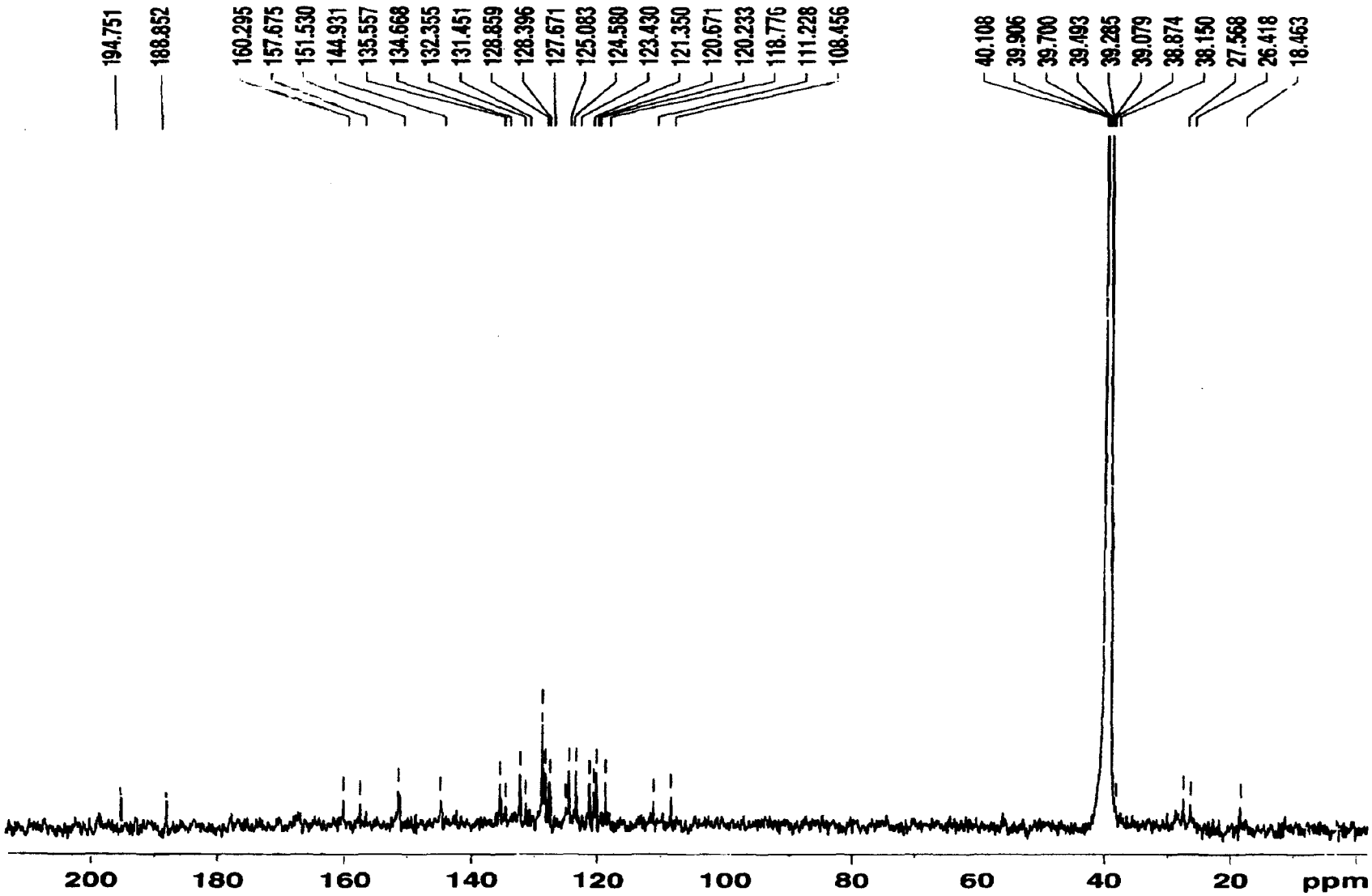


Fig. 3.16. ^{13}C NMR spectrum $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ (3.2) in DMSO-d_6.

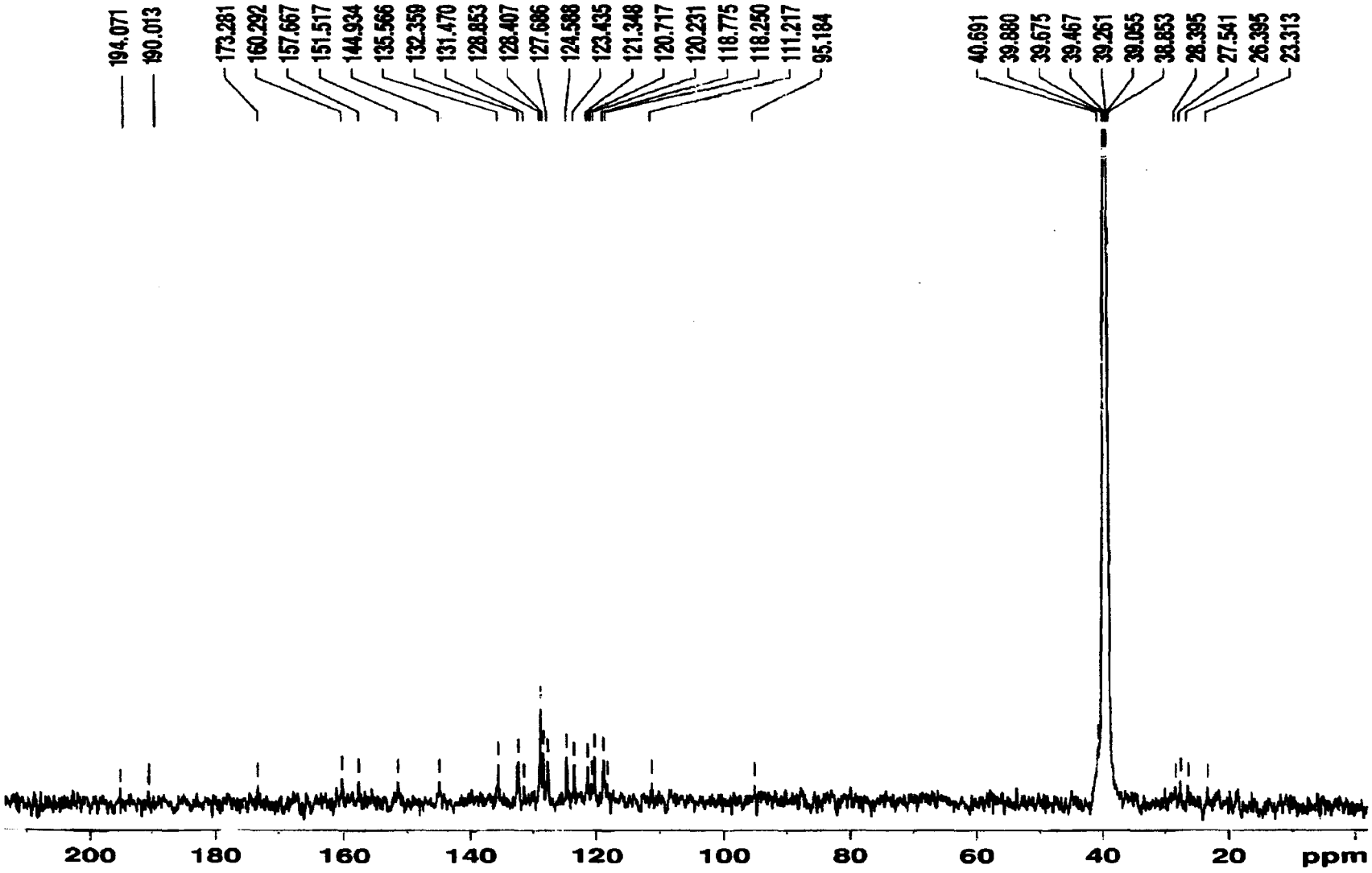


Fig. 3.17. ^{13}C NMR spectrum $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3\text{-pic})\cdot 2C_2H_5OH$ (3.4) in DMSO-d_6.

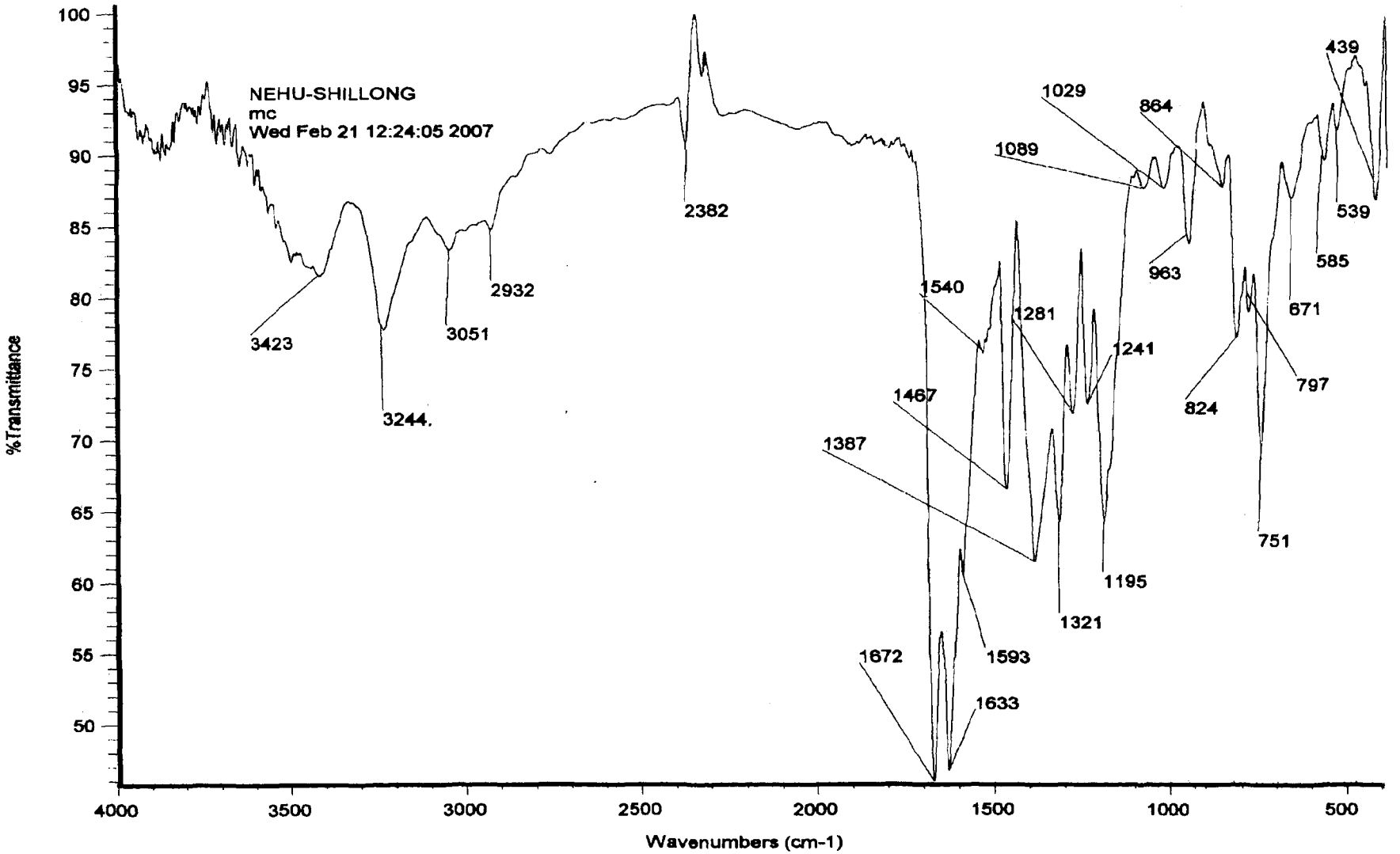


Fig. 3.18. Infrared spectrum of bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) in KBr.

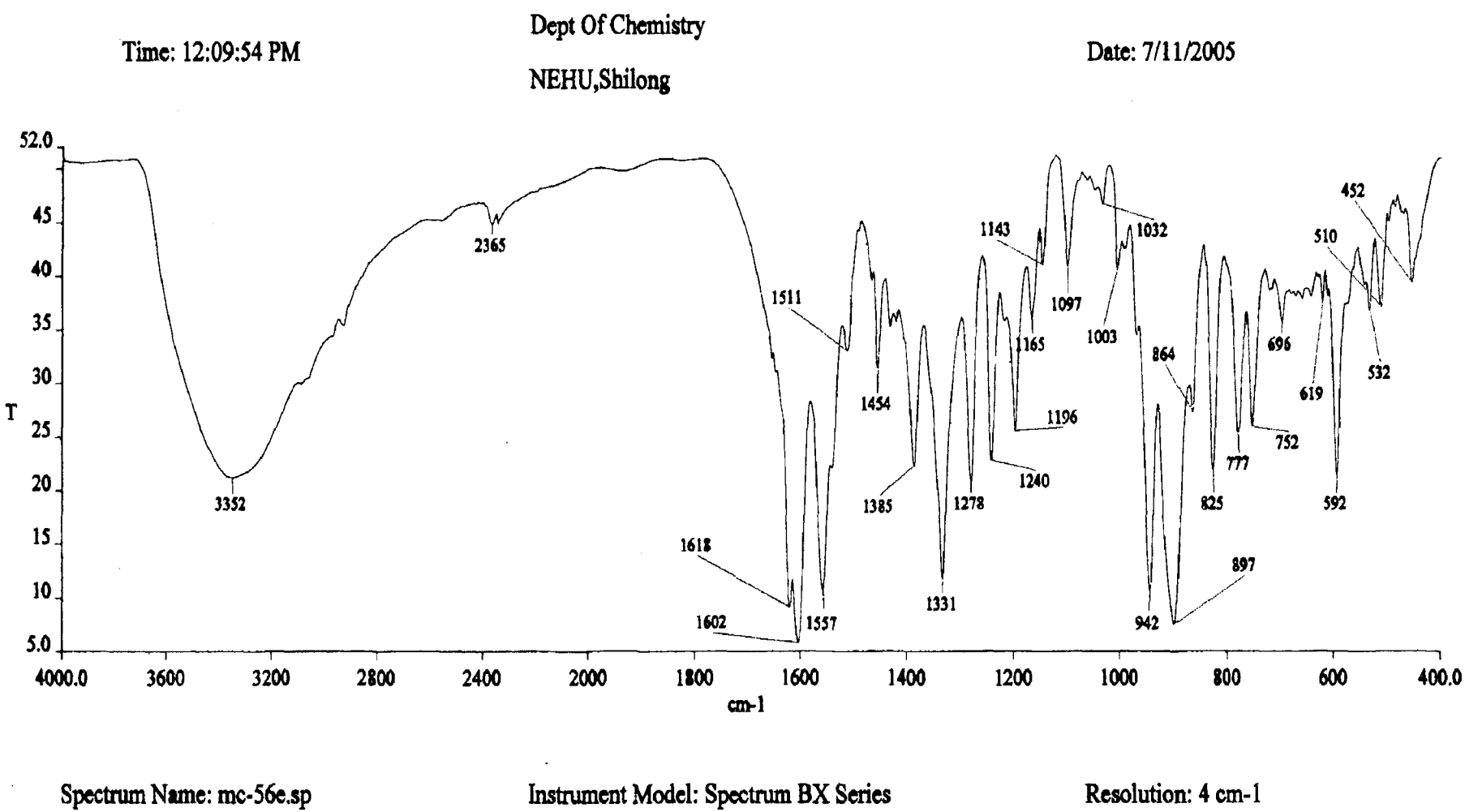


Fig. 3.19. Infrared spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1) in KBr.

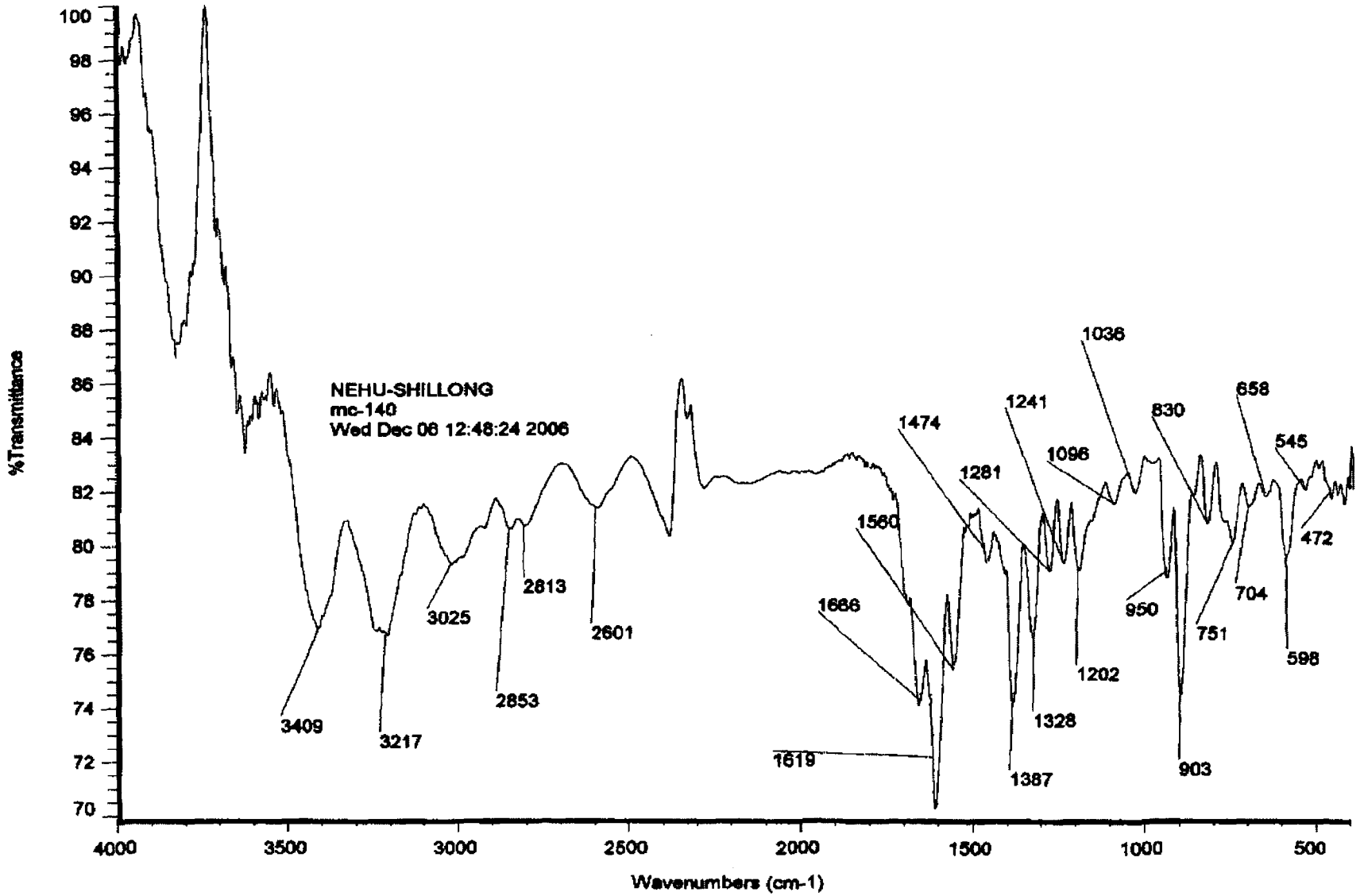


Fig. 3.20. Infrared spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ (3.2) in KBr.

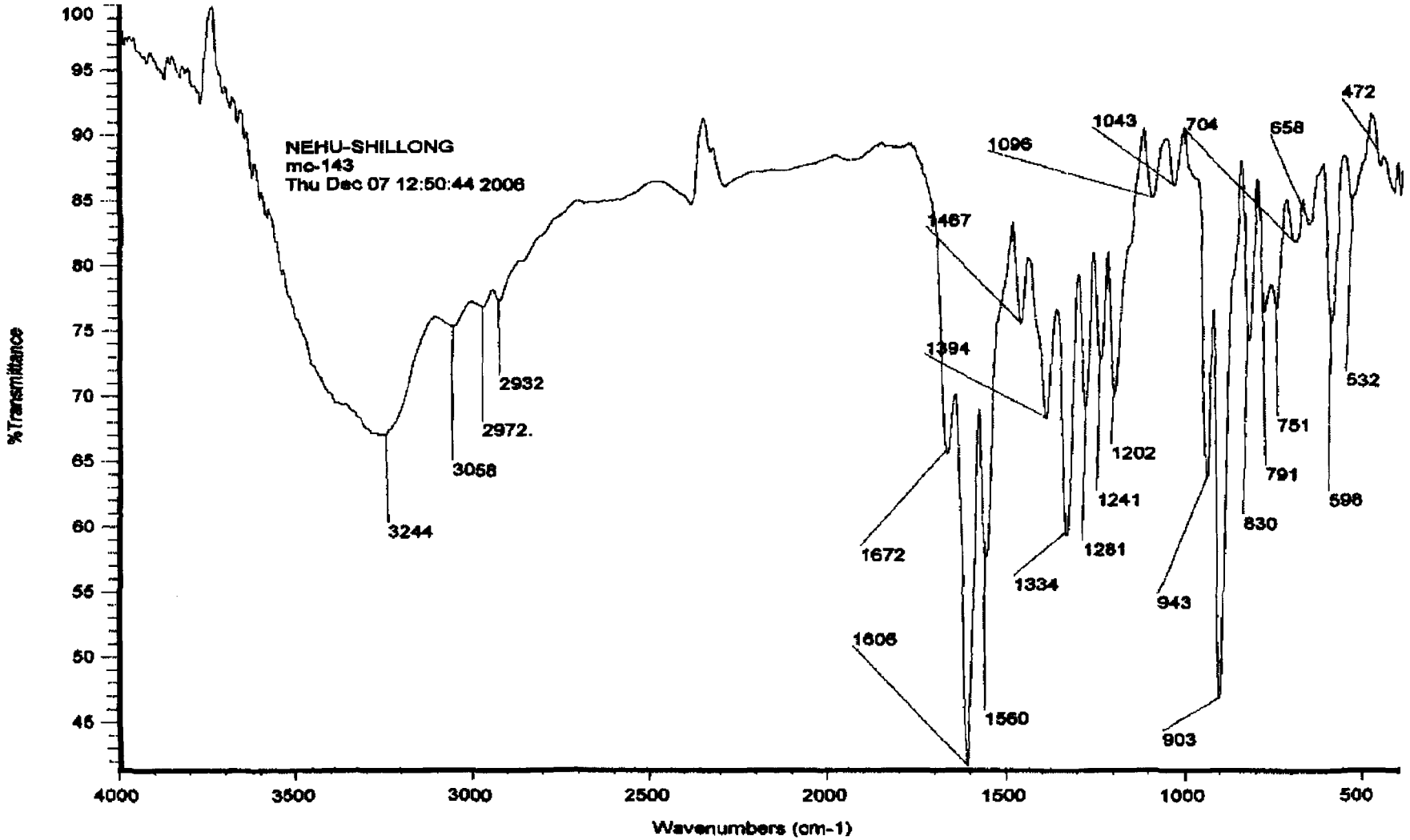


Fig. 3.21. Infrared spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic})\cdot 2C_2H_5OH$ (3.5) in KBr.

Table 3.2: Analytical Data and Physical properties of monometallic Mo(VI) Complexes derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Sl. No	Complex and Colour	D.P (°C)	Yield(%)	Analysis: Found (Calc.) (%)				Molar Conductance (Λ_M) $Ohm^{-1}cm^2mol^{-1}$
				Mo	C	H	N	
3.1	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ Orange	>300	71.00	14.66 (14.89)	52.23 (52.18)	4.32 (4.37)	8.72 (8.69)	2.29
3.2	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ Orange	>300	65.00	13.39 (13.26)	54.81 (54.78	4.60 (4.59)	9.55 (9.68)	3.32
3.3	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-pic})\cdot 2C_2H_5OH$ Orange	>300	62.00	13.15 (13.00)	55.48 (55.36)	4.76 (4.78)	9.46 (9.49)	2.81
3.4	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3\text{-pic})\cdot 2C_2H_5OH$ Orange	>300	60.00	13.14 (13.00)	55.47 (55.36)	4.79 (4.78)	9.51 (9.49)	2.19
3.5	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic})\cdot 2C_2H_5OH$ Orange	>300	63.00	13.17 (13.00)	55.46 (55.36)	4.77 (4.78)	9.49 (9.49)	2.16

Table 3.3 : Electronic spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its monometallic Mo(VI) complexes

Sl. No	Ligand/ Complex	Electronic spectral bands λ_{max} (nm) (ε_{max} ($dm^3mol^{-1}cm^{-1}$))
	H_4nsh	317 (5480), 363 (5420)
3.1	$[(\mu_2\text{-}O)_2\ (MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$	315 (11638), 361 (10990), 423 (2700)
3.2	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$	315 (16330), 362 (15210), 422 (2660)
3.3	$[(\mu\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-pic})\cdot 2C_2H_5OH$	315 (10150), 361 (9720), 421 (2810)
3.4	$[(\mu\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3\text{-pic})\cdot 2C_2H_5OH$	315 (8990), 362 (8620), 421 (2490)
3.5	$[(\mu\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic})\cdot 2C_2H_5OH$	316 (12440), 354 (12040), 421 (3310)

Table 3.4: Structurally significant ^{1}H NMR Spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its monometallic Mo(VI) Complexes

Sl. No	Ligand/ Complex	^{1}H NMR Spectral data (δ-ppm)								
		δ (-CH_2)	δ -naphthyl	δ (-CH=N)	δ (NH)	δ (OH)	CH_3CH_2OH			δ (py/2-pic/3-pic/4-pic)
							δ (CH_3)	δ (CH_2)	δ (OH)	
	H_4nsh	2.66 (s) 2.53 (s)	7.19 – 8.23(m)	9.05 (d, 62 Hz) 8.60 (d, 62 Hz)	9.99 (s) 11.14 (s)	12.73 (d, 152 Hz) 11.61 (d, 152 Hz)	—	—	—	—
3.1	[(μ_2-O)$_2$(MoO_2)$_2$(H_4nsh)$_2$]·2C_2H_5OH	2.66 (s) 2.53 (s)	7.14 – 8.44(m)	9.65 (d, 76 Hz) 9.08 (d, 76 Hz)	9.98 (s) 11.16 (s)	12.71 (d, 148 Hz) 11.60 (d, 148 Hz)	1.04(3 H, t, 6Hz)	**	4.32	—
3.2	[(μ_2-O)$_2$(MoO_2)$_2$(H_4nsh)$_2$]·2py·2C_2H_5 OH	2.66 (s) 2.53 (s)	7.13 – 8.44(m)	9.38 (d, 116 Hz) 9.04 (d, 116 Hz)	9.99 (s) 11.15 (s)	12.72 (d, 148 Hz) 11.61 (d, 148 Hz)	1.04(3 H, t, 6 Hz)	3.03 (2H, q, 10.6 Hz)	4.34 (1H, t, 4Hz)	8.64 (8.61)†
3.3	[(μ_2-O)$_2$(MoO_2)$_2$(H_4nsh)$_2$]·2(2-pic)·2C_2H_5OH	2.66 (s) 2.53 (s)	7.14 – 8.44(m)	9.71 (d, 104 Hz) 9.07 (d, 104 Hz)	9.99 (s) 11.15 (s)	12.71 (d, 148 Hz) 11.61 (d, 148 Hz)	1.04(3 H, t, 6Hz)	3.02 (2H, q, 12 Hz)	4.34 (1H, t, 4Hz)	8.58 (8.48)† 3.03 (2.55)‡
3.4	[(μ_2-O)$_2$(MoO_2)$_2$(H_4nsh)$_2$]·2(3-pic).2C_2H_5OH	2.66 (s) 2.53 (s)	7.14 – 8.45(m)	9.38 (d, 116 Hz) 9.04 (d, 116 Hz)	9.99 (s) 11.15 (s)	12.72 (d, 148 Hz) 11.62 (d, 148 Hz)	1.04(3 H, t, 8Hz)	3.02 (2H, q, 12 Hz)	4.34 (1H, t, 4Hz)	8.61 (8.43)† 3.04 (2.32)‡
3.5	[(μ_2-O)$_2$(MoO_2)$_2$(H_4nsh)$_2$].2(4-pic)·2C_2H_5OH	2.66 (s) 2.53 (s)	7.16 – 8.47(m)	9.71 (d, 98 Hz) 9.08 (d, 98 Hz)	10.01 (s) 11.16 (s)	12.75 (d, 154 Hz) 11.63 (d, 154 Hz)	1.04(3 H, t, 6Hz)	3.02 (2H, q, 11 Hz)	4.37 (1H, t, 6Hz)	8.62 (8.60)† 3.04 (2.37)‡

** merged with –CH_2 proton signals of coordinated Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.

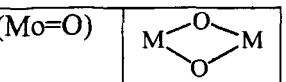
†*ortho* proton signal of pyridine/2-pic/3-pic/4-pic; ‡ Methyl proton signal of 2-pic/3-pic/4-pic

Table 3.5: ^{13}C NMR Spectral Data (in $DMSOd_6$) for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its monometallic Mo(VI) Complexes.

Carbon Atoms	H_4nsh	(3.2)		(3.3)		(3.4)		(3.5)	
		δ^x	$\Delta\delta^x$	δ^x	$\Delta\delta^x$	δ^x	$\Delta\delta^x$	δ^x	$\Delta\delta^x$
C(2a), C(2b)	195.32, 187.24	194.75, 188.85	-0.47	194.61, 189.82	-0.89	194.07, 190.01	-0.71	—	
C(13a), C(13b)	167.48, 167.22	160.30, 157.68	+8.36	160.28, 157.68	+8.37	160.29, 157.67	+8.37	160.32, 157.70	+8.34
C(3a), C(3b)	160.81, 159.86	177.64, 175.28	-16.12	172.92, 167.08	-9.66	173.28, 167.72	-10.16	173.40, 170.40	-11.36
C(11a), C(11b)	144.84, 142.38	144.93, 142.40	-0.06	144.95, 142.36	-0.05	144.93, 144.48	-1.10	144.96, 142.73	-0.24
C(10a), C(10b)	134.47, 132.20	134.67, 132.36	-0.43	132.36, 131.47	+1.42	132.36, 131.47	+1.42	132.44, 131.47	+1.38
C(7a), C(7b)	131.37	132.36, 131.45	-0.53	128.85, 128.39	+2.75	128.85, 128.41	+2.74	128.88, 128.42	+2.73
C(5a), C(5b)	127.63, 127.43	128.86, 128.40	-1.10	127.65	-0.12	127.69	-0.16	127.75	-0.22
C(8a), C (8b)	123.58, 123.22	124.58, 123.43	-0.61	124.47, 123.42	-0.60	124.59, 188.85	-0.47	124.60, 123.44	-0.62
C(9a), C(9b)	121.96, 121.56	121.35, 120.67	+0.75	122.37, 121.34	-0.10	121.35	+0.38	121.37	+0.39
C(6a), C(6b)	118.62, 118.11	118.78	-0.41	118.77, 118.25	-0.14	118.78,123.44	-0.62	118.80	-0.43
C(12a), C(12b)	109.61	111.23	-1.62	111.23	-1.62	111.12	-1.61	111.24	-1.63
C(4a), C(4b)	108.35	108.46	-0.11	108.46	-0.11	108.20	+0.15	108.66	-0.31
C(1a), C(1b)	28.69, 27.34	27.57, 26.42	+1.02	27.57, 26.43	+1.02	27.54, 26.40	+1.05	27.57, 26.42	+1.02

$\Delta\delta^x = \delta^x$ (H_4nsh) - δ^x(complex), 'a' refers to axial carbon atoms and 'b' refers to equatorial carbon atoms. Pyridine: 151.53 (149.94)(C3, C5); 2-picoline: 155.20 (158.00)(C2), 151.36 (149.00)(C6); 3-picoline: 153.52 (150.27)(C6), 151.52 (146.93)(C2); 4-picoline: 151.54 (149.60)(C2, C6)

Table 3.6: Structurally significant Infrared (IR) bands (in cm^{-1}) for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its monometallic Mo(VI) complexes.

Sl. No.	Ligand /Complex	ν(OH + NH)	ν (C =O)	ν(C=N)	Amide II + ν (C -O) (naphtholic)	ν (C–O)	ν (N–N)	ν (Mo=O)	
	H_4nsh	3423 m 3244 m 3051 w	1672 vs	1633vs 1593m	1540 w	1281 m	1029 w	—	—
3.1	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$	3352 m	1671 s	1618 m 1602 s	1557 s	1278 m	1032 w 1003 w	942 m 897 s	778 m
3.2	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$	3409 s 3217s 3025 m	1666 s	1619 s	1560 s	1281 m	1036 w	950 m 903s	791 w
3.3	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-pic})\cdot 2C_2H_5OH$	3409 s 3224 s	1666 m	1619 s	1560 s	1281 m	1036 w	943 m 903 s	792 w
3.4	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3\text{-pic})\cdot 2C_2H_5OH$	3264 s 3058 w	1672 m	1606 s	1566 s	1281 m	1049 w	943 m 903 s	784 m
3.5	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic})\cdot 2C_2H_5OH$	3244 m 3058 w	1672 m	1606 s	1560 s	1281 m	1043 w	943 m 903 s	791 m

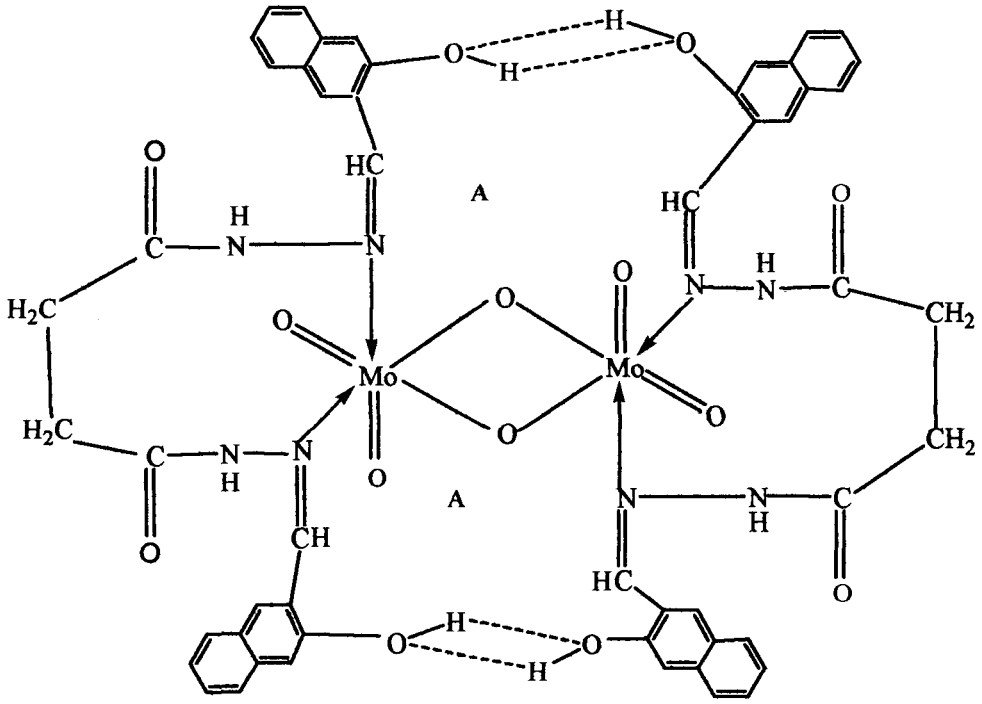


Fig.3.22. Tentative structure for the complexes $[(\mu_2\text{-}O)_2\ (MoO_2)_2(H_4nsh)_2].2A.2C_2H_5OH$ (where A = Pyridine, (3.2), 2-picoline (3.3), 3-picoline (3.4), 4-picoline(3.5))

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CHAPTER IV

Synthesis, Characterization and Structural Assessment of Homobimetallic Molybdenum(VI) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Introduction

The dihydrazone selected in the present study is a polyfunctional ligand containing as many as eight bonding sites such as naphtholate oxygen atoms, azomethine nitrogen atoms, secondary amine nitrogen atoms and carbonyl oxygen atoms, each in duplicate. The molybdenum compounds described in the previous chapter were isolated from the reaction of $MoO_2(acac)_2$ with ligand in 1.1:1 molar ratio in absolute ethanol. To our utter surprise, the dihydrazone behaved as a neutral bidentate ligand coordinated to the metal centre through both the azomethine nitrogen atoms only, in spite of being a multidentate ligand, the remaining coordinating sites were unutilized in the complexes. Hence, it was of interest to carry out the reactions of $MoO_2(acac)_2$ with ligand by keeping $MoO_2(acac)_2$ in large quantity (3:1) and to explore the stoichiometry of the resulting complexes and characterize them by various physico-chemical techniques and spectroscopic studies. It is imperative to mention that the reaction of analogous bis(2-hydroxy-1-naphthaldehyde)oxaloyldihydrazone and malonoyldihydrazone with first row transition metal chlorides and nitrates in 1:3 molar ratio in ethanol yielded metal complexes with 1:1 (metal:ligand) stoichiometry **[1]**. It is important to note that the present ligand contains diazine group and –OH group in its molecular skeleton in addition to azomethine and keto groups. These groups are well known for their binucleating nature **[2-5]**. The diazine group brings the metal ions into close proximity because of its geometric requirement, while the deprotonated –OH group brings metal ions in close proximity through oxo-bridging.

Before we proceed to discuss the synthesis and characterization of molybdenum complexes, it appears appropriate to have a brief review of literature on importance of multimetallic complexes of transition metals in general and molybdenum complexes in particular.

Synthetic dinuclear transition metal complexes provide models for metalloprotein active sites and lend insight toward the design of new catalysts. Dinuclear complexes are of

extensive investigation owing to their biological and industrial application **[6]**. Bimetallic enzymes catalyze diverse reactions ranging from alkaline oxidation to biopolymer degradation **[7]**. Further, the homo-multimetallic molecular complexes are of interest in areas of multimetallic enzymes, homogeneous catalysis and heterogeneous catalysis. Many enzymes in biological systems are homomultimetallic that perform their biological functions by redox cooperativity **[8]**. Ascorbate oxidase enzyme contains eight copper atoms, one normal, three blue and two coupled binuclear sites **[9]**. Ferrodoxins and high potential iron proteins contain clusters of two, three or four iron atoms **[10]**. A tetra manganese complex containing manganese in higher oxidation states present in photosystem II (PS II) in green plants activates CO_2 and H_2O molecules in the presence of sunlight **[11]** converting them to glucose and evolving oxygen. Further, bimetallic cores have been recognized at the active sites of many metalloenzymes **[12]** and model studies with simple dinuclear metal complexes are becoming increasingly important in understanding biological functions of the bimetallic cores **[13]**.

The expanded research in molybdenum complexes is mainly due to its biochemical role in metalloenzymes **[14]** and rather complex chemistry. Molybdenum is the only element of the second transition series, being essential for life; as a constituent of enzymes it participates in redox reactions, e.g., oxidation of aldehydes, xanthine and other purines **[15]**, and reduction of nitrate to molecular nitrogen **[16, 17]**. Molybdenum's biochemical role is based on its ability to facilitate electron exchanges and to form stable complexes with oxygen, nitrogen and sulfur containing ligands. The useful role of molybdenum is not restricted to biological systems only, but it also plays important roles in a variety of chemical reactions such as hydrodesulfurization, oxygen transfer reactions (e.g., olefin epoxidation), and olefin metathesis. The *cis*-dioxo molybdenum compounds display catalytic activities **[18]**, are models for enzymes **[19, 20]** and are useful material precursors **[21]**. Catalytic activity is frequently linked to coordinative unsaturation and the active sites in various molybdenum oxidation catalysts are believed to contain coordinatively unsaturated molybdenum centres **[22, 23, 24]**. In all of these biological and industrial reactions, molybdenum plays the role of a catalytic redox site. Molybdoenzymes consist of two Mo atoms per molecule, suggesting binuclear Mo-sites, joined by one or two oxo-or sulfido- bridges **[25]**.

A close proximity of the metal ions in multimetallic complexes considerably varies the properties of the system which may be significantly different from the properties of the monometallic complexes. The homo multimetallic complexes have the potential to

mediate certain chemical reactions of industrial relevance either more efficiently than, or in a different manner to monometallic complexes. They exhibit distinct reactivity pattern as compared to corresponding monmometallic complexes **[26]**. As a result, the synthesis and characterization of homobimetallic complexes continue to attract attention **[27]**. Especially, the role of *cis*-MoO_2^{2+} unit in the metalloenzymes has led to studies of complexes with ligands containing nitrogen, sulfur or oxygen donors and the analyses of their chemical, spectroscopic and strictural properties **[28]**.

A survey of literature has revealed that, although few homobimetallic complexes of salicylaldehyde and *o*-hydroxy acetophenone dihydrazones with some first row transition metal ions have been synthesized and characterized **[29–40]**, those derived from dihydrazones having bulky fragments in their molecular skeleton have received scant attention only **[41, 42–47]**

The interest in the homo and heteropolymetallic complexes containing two or more metal atoms in close proximity stems from the fact that such complexes are involved in a variety of important biochemical processes **[48, 49]** and are important in the synthesis of solid-state phases of technological and industrial importance favouring an intimate mixing of the elements **[50]**.

In view of the above importance of multimetallic complexes and much less work on the multimetallic complexes of the dihydrazones containing bulky fragments in their molecular skeleton and that the previous chapter describes the synthesis and characterization of monometallic complexes of Mo(VI) derived from the title ligand, it was of interest to synthesize the homobimetallic complexes of the title dihydrazone and characterize the resulting products by various physicochemical and spectral techniques. Accordingly, the present chapter describes the synthesis of homobimetallic complexes of Mo(VI) in ethanolic media and their characterization by various physico-chemical techniques and spectroscopic methods. The stoichiometry of the complexes has been judged mainly from the elemental analyses and thermogravimetric data. The structure of the complexes has been discussed in the light of conductivity, magnetic moment, electronic, IR, ^1H and ^{13}C NMR spectral data

Preparation of the complexes

1. Preparation of $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1)

The dihydrazone ligand (H_4nsh) (1.00 g, 2.20 mmol) was suspended in water-ethanol (5 mL + 95 mL) mixture and stirred for 30 minutes at about 70°C. To this was added a solution of bis(acetylacetonato)dioxomolybdenum(VI) ($MoO_2(acac)_2$) (2.15 g, 6.59 mmol) in ethanol (50 mL), maintaining the molar ratio at 1:3. The reaction mixture was refluxed for 3 hours. The product, thus, obtained was filtered under hot condition, washed several times with hot ethanol, and then with ether and dried over anhydrous $CaCl_2$. Yield: 0.66 g.

2. Preparation of $[(MoO_2)_2(nsh)(A)_2]\cdot C_2H_5OH$ (where A = pyridine (py, 4.2); 2-picoline (2-pic, 4.3); 3-picoline (3-pic, 4.4); 4-picoline (4-pic, 4.5)).

The complex $[(MoO_2)_2(nsh)(H_2O)_2].C_2H_5OH$ (4.1) (1.00 g, 1.21 mmol) was suspended in ethanol (100 mL) accompanied by gentle stirring for 15 minutes at 60–70°C. To this suspension, pyridine (12.77 mL, 6.19 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 3 hours which precipitated the orange coloured compound. The compound, thus, obtained was filtered, washed with hot ethanol and then with ether and dried over anhydrous $CaCl_2$. Yield: 0.70 g.

The complexes (4.3), (4.4) and (4.5) were also prepared similarly using 2-picoline, 3-picoline and 4-picoline instead of pyridine. Yield: 0.75g (4.3); 0.73g (4.4); 0.72g (4.5).

3. Preparation of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(BB)]\cdot C_2H_5OH$ (where BB = 1,10-phenanthroline (phen, 4.6); (2,2′-bipyridine) (bpy, 4.7).

The complex $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1) (1.00 g, 1.27 mmol) was suspended in ethanol (100 mL) accompanied by gentle stirring for 15 mins at 60–70°C. To this was added a solution of 1,10-phenanthroline (0.76 g, 3.83 mmol) in ethanol (50 mL), maintaining the molar ratio at 1:3. The reaction mixture was refluxed for 3 hours which precipitated the light yellow compound. The compound, thus, obtained was filtered under hot conditions, washed with hot ethanol and then with ether and dried over anhydrous $CaCl_2$. Yield: 0.72 g

The complex (4.7), was also prepared in a similar manner using 2,2′-bipyridine instead of 1,10-phenanthroline. Yield: 0.71 g.

Results and Discussion

The complexes isolated in the present study together with their molecular formula, colour, decomposition point, yield, analytical data and molar conductance values are given in Table 4.1. The electronic spectral data for the complexes are given in Table 4.2.

Reaction of the title ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone with $MoO_2(acac)_2$ in 1:3 molar ratio in ethanolic medium under reflux resulted in the formation of the complexes with the following compositions. The composition of the complexes has been decided on the basis of elemental analyses, thermoanalytical data and other spectroscopic data.

$[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1)

$[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ (4.2)

$[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ (4.3)

$[(MoO_2)_2(nsh)(3\text{-pic})_2]\cdot C_2H_5OH$ (4.4)

$[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5)

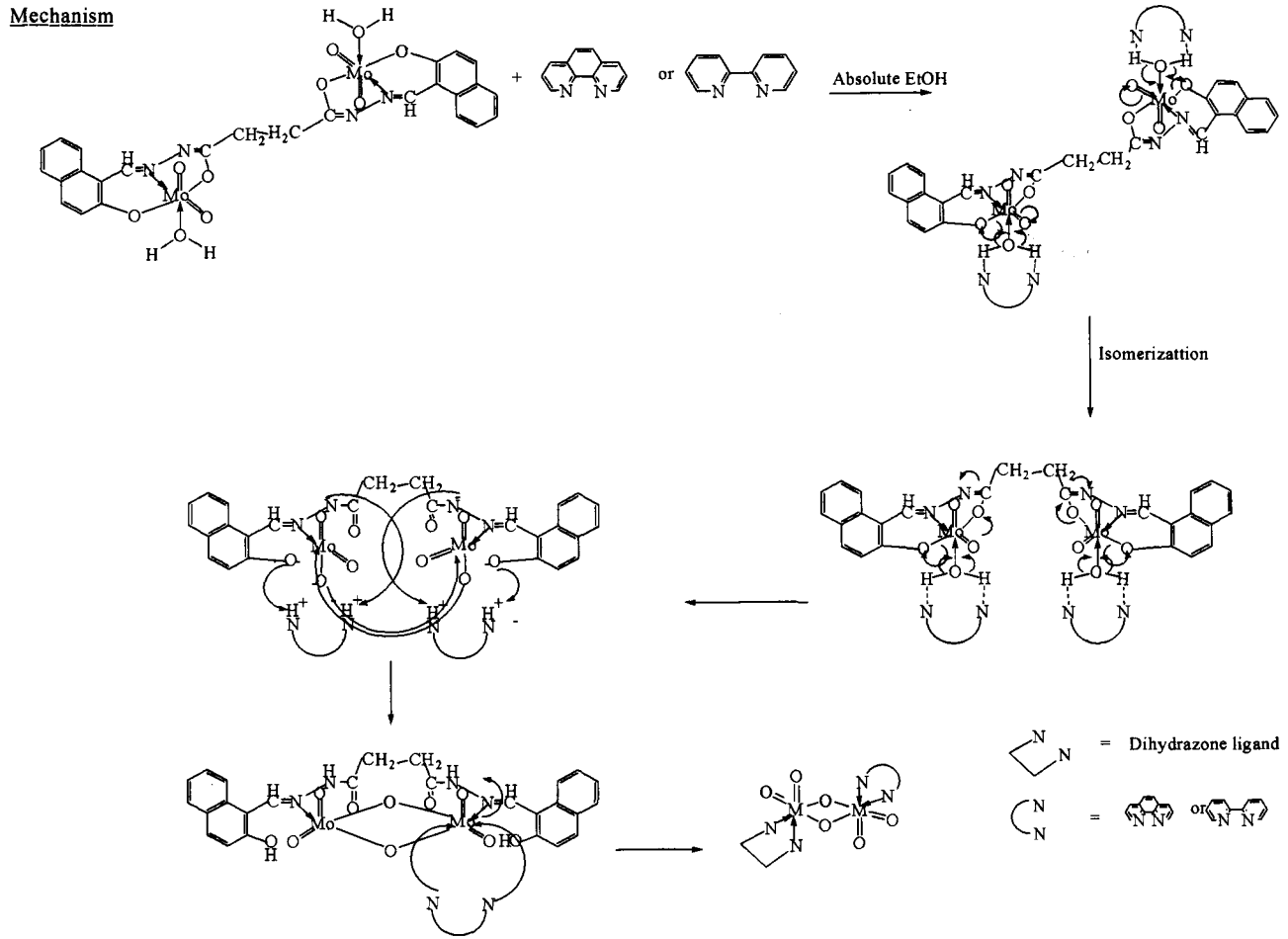
$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$ (4.6)

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$ (4.7)

The complexes are orange, light orange and light yellow coloured, respectively. All of the complexes are air stable solid powders and decompose above 300°C without melting except the complex (4.6) which melts at 217°C. Such a thermal behavior of complex (4.6) indicates appreciable degree of covalent character, whereas in the remaining complexes the metal-ligand bonds have comparatively more ionic character. All of the complexes are insoluble in water and partly soluble in common organic solvents such as ethanol, methanol, acetone, benzene, chloroform, hexane and ether but are soluble in DMSO and DMF.

The stoichiometry of the complexes (4.6) and (4.7) shows that they contain an additional oxo-group generated during the course of the reaction of complex (4.1) with the bidentate nitrogen donor ligands 1,10-phenanthroline and 2,2′-bipyridine, respectively. But in the complex (4.1) to (4.5) which was obtained by the reaction of complex (4.1) with monodentate nitrogen donor ligands viz. pyridine and substituted pyridine molecules no additional oxo-group was found. It is suggested that the bidentate ligands are able to induce the migration of protons from water molecules coordinated to the molybdenum centre in complex (4.1) and consequently generating an oxo-group which binds to molybdenum centre in the complexes (4.6) and (4.7). It is imperative to mention that the

monodentate nitrogen donor ligands are unable to induce the migration of protons from water and consequently, unable to generate an additional oxo-group in the complexes (4.1) to (4.5). The probable mechanism for the generation of the oxo-groups in the complexes (4.6) and (4.7) is shown in Scheme 1. It is suggested that phenanthroline and bipyridine ligands by virtue of their bidenticity are able to simultaneously bind the two hydrogen atoms of water molecules and hence are able to induce the breaking of O-H bond generating oxo-group. Once the bidentate ligands are hydrogen bonded to water molecules, the complex undergoes isomerization to assume *anti-cis* configuration. In this configuration the MoO_2^{2+} groups are brought closer to each other which lead the reaction to completion with eventual coordination of one bidentate phenanthroline or bipyridine molecule to the metal centre and rejection of other. The probable mechanism for the generation of the oxo-groups and consequently the formation of the complexes (4.6) and (4.7) is shown in Scheme 1.



Scheme 1. Mechanism showing the generation of oxo-group from water molecules coordinated to MoO_2^{2+}.

Thermal Studies

The detailed decomposition studies **[51]** of the complexes (4.1), (4.2), (4.4) and (4.5) were carried out in the temperature range 60–250 °C and the vapours evolved were identified by passing them through separate test tubes containing, anhydrous copper sulfate, sodium hydroxide and iodine, $CHCl_3$ solution containing a drop of 5M sodium hydroxide solution and cyanogen bromide solution.

The weight loss occurs in two prominent steps, i.e. 75–80 °C and 200–240 °C in the complexes (4.2), (4.4) and (4.5) while the complex (4.1) showed weight loss in the temperature range 70–80 °C and 160–180 °C.

The vapours evolved in the temperature range 75–80 °C in all of the complexes gave a yellow precipitate with a solution of sodium hydroxide and iodine confirming that they originate from ethanol molecules present in the lattice structure of the complexes. Further, the weight loss in this temperature range corresponds to one molecule of ethanol lending credence to the suggested number of ethanol molecules present in the lattice structure of these complexes. When the vapours in the range 160–80 °C in the complex (4.1) were passed over anhydrous copper sulfate taken in a test tube, it turned blue. This confirmed that the vapours in this range in this complex originated from water molecules. The loss of weight corresponds to two water molecules which suggested their presence in the coordination sphere around the metal centre in this complex **[52]**.

The complexes (4.2), (4.4) and (4.5) showed further weight loss in the temperature range 200–240 °C. The vapours evolved from complex (4.2) in this temperature range turned the colour of $CHCl_3$ solution containing a drop of 5 M NaOH solution to red. This confirmed that the vapours originated from pyridine molecules. Similarly, the vapours evolved from the complexes (4.4) and (4.5) in this temperature range turned the colour of cyanogen bromide solution to green-violet and blue, respectively, on treatment with phloroglucinol solution. This suggests the presence of 3-picoline and 4-picoline molecules in the complexes (4.4) and (4.5) respectively. The weight loss in this temperature range corresponds to one molecule each of pyridine, 3-picoline and 4-picoline per metal centre in these complexes indicating that they are also coordinated to the metal centre **[53]**.

Molar Conductance

All of the complexes have molar conductance values in the region 1.2–4.7 $ohm^{-1}cm^2mol^{-1}$ in DMSO solution at 10^{-3} M dilution. These values suggest that the complexes are non-electrolyte in DMSO **[54]**.

Magnetic Moment

The room temperature magnetic susceptibility measurement of the complexes (4.1) to (4.7) has been carried out in order to decide upon the magnetic behavior of these complexes. These complexes were found to be diamagnetic which indicates that molybdenum is present in +6 oxidation state in these complexes with d^0 electronic configuration. The diamagnetic nature of the complexes also suggests that the reduction of the molybdenum (VI) centre does not take place under the influence of the ligand.

Electronic Spectra

The electronic spectral datra for the homobimetallic dioxomolybdenum(VI) complexes (4.1) to (4.7) are given in Table 4.2. The electronic spectra of the complexes (4.1), (4.2), (4.5) and (4.7) are shown in Fig. (4.2) to (4.5). The ligand bands observed at 317 nm and 363 nm which were assigned to intra ligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions exhibit blue shift on complexation indicating dihydrazone coordination to the metal centre. In addition to the intraliand bands, all of the complexes show a new band in the region 429–436 nm and these bands are assigned to have their origin from ligand-to-metal charge transfer (LMCT) transition.

^{1}H NMR Spectra

All of the complexes were characterized by ^{1}H NMR spectroscopy. The ^{1}H NMR spectral data for the free dihydrazone and the metal complexes are set out in Table 4.3. The ^{1}H NMR spectra of the complexes (4.1), (4.2), (4.5), and (4.7) are given in Figs. (4.6) to (4.9).

^{1}H NMR Spectra of the Complexes (4.1) to (4.5)

Two proton doublets are observed at δ 11.61 and 12.73 ppm while two proton singlets are observed at δ 9.99 and 11.14 ppm in the ^{1}H NMR spectra of the free dihydrazone. These signals are assigned to naphtholic –OH protons and secondary NH protons, respectively. These signals do not appear in the ^{1}H NMR spectra of the complexes (4.1) to (4.5). The absence of signals in the region δ 20–11 ppm in the ^{1}H NMR spectra of the complexes

(4.1) to (4.5) indicates the involvement of the dihydrazone in coordination to the metal centre in the enol form through naphtholic oxygen atoms via deprotonation and carbonyl oxygen via enolization/deprotonation.The azomethine proton signals observed as doublets at δ 9.05 and δ 8.60 ppm in the ^{1}H NMR spectrum of the free dihydrazone exhibit a downfield shift of about 0.32–0.52 ppm in the complexes (4.1) to (4.5). The downfield shift of these signals is attributed to drainage of electron density from the nitrogen atoms of azomethine group to the metal centre **[55]**.

The most crucial feature of the ^{1}H NMR spectra of the complexes (4.1) to (4.5) is the collapse of the doublets corresponding to δ-CH=N signal in the free ligand into a single resonance. This ^{1}H NMR spectral feature of the complexes (4.1) to (4.5) suggests that the dihydrazone, which exists in the *anti-cis* configuration in the free state, attains *staggered* configuration in the complexes (4.1) to (4.5). Similar coordination mode of the related malonoyl dihydrazone to the metal centre has been reported by Gopinathan and co-workers and by Lal et al **[37, 56]**.

The naphthyl proton multiplet appears in the region δ 7.15–8.23 ppm in the complexes (4.1) to (4.5). The complexes (4.2), (4.3), (4.4) and (4.5) show additional resonances in the region δ 7.16 – 8.57 ppm (Table 4.3). These signals are attributed to arise due to *ortho* proton of pyridine, 2-picoline, 3-picoline and 4-picoline molecules. These signals are upfield shifted as compared to their position in free pyridine, 2-picoline, 3-picoline and 4-picoline molecules respectively **[53, 57]**. This upfield shift of the various signals of pyridine, 2-picoline, 3-picoline and 4-picoline molecules is attributed to coordination of pyridyl nitrogen atoms of these Lewis base molecules to the metal centre. As a result of coordination of the pyridyl nitrogen, its electron density decreases which in turn decreases its electronegativity. Consequently the electron density on various bonds of pyridyl ring i.e. C–N, C–C and C–H drifts away from nitrogen atom. This increases the electron density on various carbon atoms and protons. As a result, the electron density on various types of pyridyl protons is increased which results in the upfield shift of the signals due to these protons in the ^{1}H NMR spectra of the complexes (4.2), (4.3), (4.4) and (4.5).

Further, the signal due to methyl protons in 2-picoline, 3-picoline and 4-picoline molecules in the free state appears at δ 2.55, δ 2.32 and δ 2.37 ppm respectively **[58 , 59]**. In the complexes (4.3), (4.4) and (4.5), these signals appear at δ 2.07 ppm and are thus upfield shifted by 0.48, 0.25 and 0.30 ppm, respectively. The upfield shift of methyl proton signals again confirms the coordination of pyridyl nitrogen atoms to the metal

centre due to the same reason as stated above regarding the upfield shift of various signals due to pyridyl protons.

^{1}H NMR Spectra of the complexes (4.6) and (4.7)

The ^{1}H NMR spectra of the complexes (4.6) and (4.7) are significantly different as compared to those of the complexes (4.1) to (4.5). The two proton doublets observed at δ 11.61 and δ 12.73 ppm due to naphtholic –OH protons in the free dihydrazone are upfield shifted in the complexes (4.6) and (4.7) and appear in the region δ 11.60–12.59 ppm. Similarly, the δ NH protons appearing at δ 9.99 and 11.14 ppm are downfield shifted and appear at δ 11.14 in both the complexes. The presence of δ NH signal in these complexes suggests that the dihydrazone is coordinated to the metal centre in the keto form in these complexes.

The azomethine proton signals on an average show a downfield shift by about δ 0.32–0.21 ppm and appear as a doublet in these complexes as against a singlet in the complexes (4.1) to (4.5). Such a feature associated with the δ (-CH=N) signal may be attributed to coordination of the dihydrazone to the metal centre in the *anti-cis* configuration **[60]** in which only the azomethine nitrogen atoms of the dihydrazone molecule are coordinated to the metal centre. As a result of *anti-cis* configuration of the ligand, one of the hydrazone groupings attains axial position while the other hydrazone grouping remains in the equatorial plane. Hence, equatorial protons appear upfield as compared to axial protons. Further, coupling between axial protons and equatorial protons occurs which, ultimately, leads to the splitting of their signal resulting in a doublet for each. It is pertinent to mention that stereospecific long rnage coupling has been reported in hydrazones **[1]**. The appearance of strong bands in the region 1672 cm^{-1} in the IR spectra of the complexes (4.6) and (4.7) suggests that the carbonyl oxygen atoms of the dihydrazone molecule are free in these complexes and do not take part in coordination to the metal centre in these complexes.

The naphthlyl proton multiplet appears in the region δ 7.15–8.23 ppm in these complexes. The signals due to aromatic protons of 1,10-phenanthroline and 2,2′-bipyridine appear merged with the signals due to naphthyl protons and appear in the region δ 7.16–8.57 ppm and hence they do not show their independent existence.

Again the complexes (4.1), (4.3), (4.4), (4.5), (4.6) and (4.7) show a triplet, a quartet and a triplet in the regions δ 1.04, δ 3.45–2.97 and δ 4.36–4.34 ppm, respectively which correspond to methyl, methylene and –OH proton signals of ethanol molecule. A

comparison of the position of these signals with that of free ethanol **[61]** suggests that the ethanol molecules are present in the lattice structure of the complexes.

^{13}C Nuclear Magnetic Resonance Spectroscopy

The dioxomolybdenum(VI) complexes $[(MoO_2)_2(nsh)(H_2O)_2].C_2H_5OH$ (4.1), $[(MoO_2)_2(nsh)(2\text{-pic})_2].C_2H_5OH$ (4.3), and $[(MoO_2)_2(nsh)(4\text{-pic})_2].C_2H_5OH$ (4.5) were characterized by ^{13}C NMR spectroscopy. The ^{13}C NMR spectra of the complexes (4.3) and (4.5) are shown in Fig. 4.10 and 4.11.The chemical shift δ (in ppm from $SiMe_4$) and the chemical shift changes Δ δ (ppm) accompanying the coordination of the ligand in the complexes are set out in Table 4.4. A comparison of the ^{13}C NMR spectra of the ligand and the complexes indicate that the ligand and the complexes have different symmetry. Hence, the spectral features of the complexes (with respect to the number of signals) are entirely different from that of the ligand.

The assignments for the ligand have been deduced taking into account the shift in the resonaces of naphthyl ring carbon atoms caused by the substituents, azomethine group and naphtholic –OH group **[56]**. The numbering scheme of the carbon atoms in the ligand and the complexes are shown in Fig. 4.1. The carbon atoms in the axial and equatorial position have been designated by the letters 'a' and 'b' respectively.

The signals associated with the carbon atoms near the coordinated sites in the complexes are remarkably shielded in comparison to the free ligand. The effect of molybdenyl ion on carbon resonances of naphthyl ring thus shifts upfield the signals due to C(6), C(7),C(8), and C(9) by at least 1.46–2.44 ppm, while those due to C(3a) and C(11) and C(13) resonances are shifted upfield even more since they are closer to the coordinated oxygen and nitrogen atoms. As a consequence, the signals due to C(2a) and C(2b), which in the free ligand were at δ 195.32 and 187.24 ppm respectively, are upfield shifted and appear at δ 172.26 ppm. The signal at δ 160.00 ppm was assigned to C(13) carbon atom which in the free ligand was observed at δ 167.48 and 167.22 ppm giving a chemical shift change of 7.35 ppm. Similarly, the signal at δ 151.61ppm is assigned to the azomethine carbon atoms which in the free ligand were at 160.81 and 159.86 ppm giving a chemical shift change of 8.73 ppm. The signals at δ 132.41 and 124.65 ppm are assigned to C(10) and C(5) carbon atoms which in the free dihydrazone were at δ 134.47, 132.20 and δ 127.63 and 127.43 ppm giving a chemical shift change of 0.93 and 2.88 ppm, respectively. The signal at δ 108.35 ppm assigned to C(4) carbon atoms in the free ligand remained almost unaltered in position and appeared at δ 108.30 pm in the complexes. Such a small chemical shift

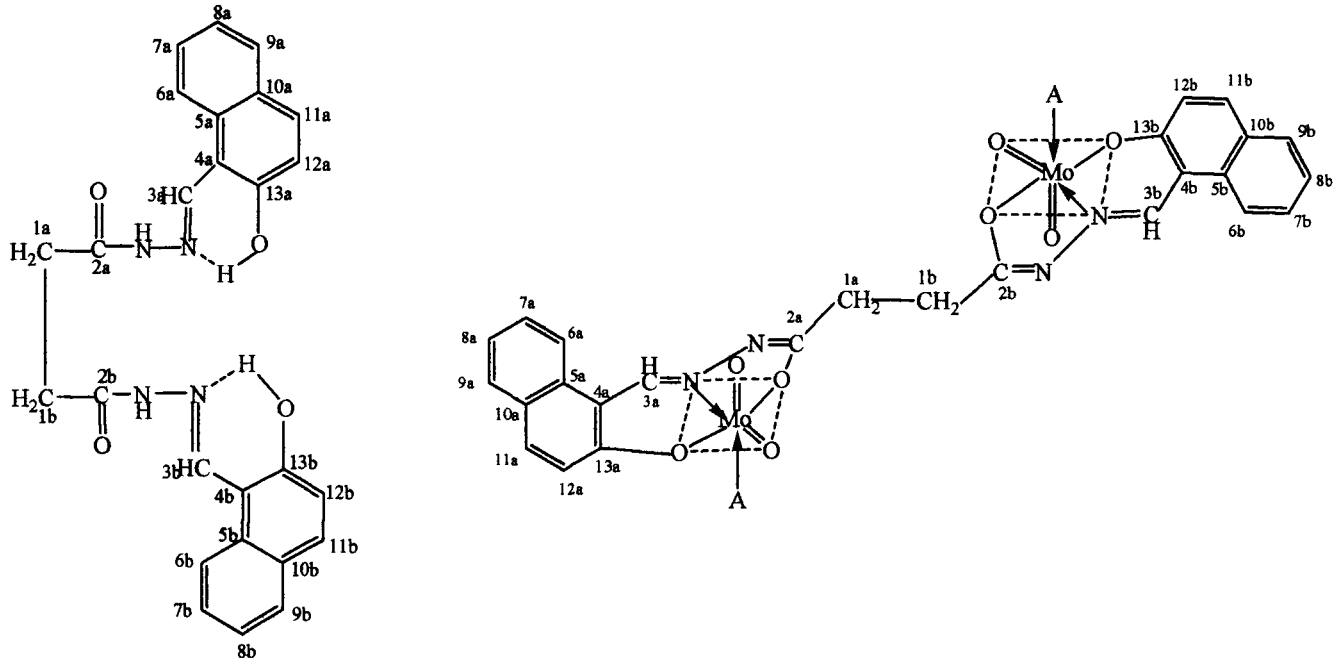


Fig 4.1. Numbering scheme of the carbon atoms in H_4nsh and $[(MoO_2)_2(nsh)(A)_2].C_2H_5OH$ (A = H_2O (4.1), 2-pic (4.3), 4-pic (4.5))

change for C(4) resonance may be attributed to combined effect of drainage of electron density from azomethine nitrogen atom and naphtholate oxygen atoms in opposite direction.

^{13}C NMR spectrum of the ligand shows 13 resonances and all of the signals appear as pairs except the signals due to C(12) and C(4) and C(7) giving rise to 23 resonances in total. Each resonance forms a pair which corresponds to the axial and equatorial carbon atoms. On the other hand, ^{13}C NMR spectra of the complexes shows 13 signals only, each of which corresponds to different carbon atoms (Table 4.4). All of the signals appear as a singlet. Such a feature associated with the ^{13}C NMR spectra of the complexes support the *staggered* configuration of the ligand in coordinated state as deduced from the consideration of ^{1}H NMR spectral features of the complexes.

Infrared Spectra

The IR spectrum of the ligand is highly complicated due to the presence of a large number of groups which absorb in the overlapping regions. However, few bands have been selected in order to observe the effect of complexation. The structurally significant IR spectral bands for the free dihydrazone and the homobimetallic complexes have been set out in Table 4.5. The IR spectra of the complexes (4.1), (4.2), (4.3), (4.5), and (4.6) are shown in Fig. 4.12 to 4.16. A comparison of the IR spectra of the complexes with that of the free ligand H_4nsh suggests that the dihydrazone coordinates to the metal centre in enol form in all of the complexes except the complexes (4.6) and (4.7) in which the ligand coordinates in the keto form.

IR Spectra of the complexes (4.1) to (4.5) in which the ligand is present in enol form.

The bands observed at 3423 and 3244 cm^{-1} in the free dihydrazone due to ν(OH) and ν(NH) stretching vibrations are replaced by a very strong broad band in the region 3150–3600 cm^{-1}. The disappearance of ν(NH) band in this region indicates collapse of amide structure of the ligand on complexation and coordination of the ligand to the metal centre in the enol-form. The strong nature of the band in the region 3150–3600 cm^{-1} indicates that it arises due to ν(OH) of ethanol molecule present in the lattice as well as ν(OH) of moisture absorbed by KBr during pellet preparation.

The strong band at 1672 cm^{-1} assigned to νC=O stretching vibration of carbonyl group in the IR spectrum of the uncoordinated dihydrazone disappears in these complexes. This

again suggests collapse of amide structure of the ligand in these complexes and its coordination to the metal centre through carbonyl oxygen atom in the enol form.

In the free dihydrazone, the ν(C=N) band appears as a couple of bands at 1633 and 1593 cm^{-1}. This band appears as a couple of bands in the region 1623–1602 cm^{-1} in the complexes (4.1) to (4.5) also, thus showing an average shift to lower frequency by 1–4 cm^{-1} respectively. This indicates the coordination of azomethine nitrogen to the metal centre **[62]**. The small shift in νC=N stretching frequency in the complexes is due to the difference of bonded species i.e. from >C=N....H to >C=N→M. The amide III band at 1321 cm^{-1} in the free dihydrazone registers a shift to higher frequency by 7–20 cm^{-1} in all of the complexes showing the involvement of >C=O in coordination.

The free dihydrzone shows a medium intensity band at 1540 cm^{-1} which is attributed to arise due to mixed contribution of amide II and ν(C–O) naphtholic **[1]**. This band shows a considerable shift to higher frequency in the complexes (4.1) to (4.5) and appears in the region 1554–1558 cm^{-1}. Such a high shift of this band indicates bonding through naphtholic oxygen atom via deprotonation to the metal centre **[1]**.

The appearance of a medium to strong intensity band in the region 1554–1558 cm^{-1} in the complexes (4.1) to (4.5) is characteristic of the enolization of the dihydrazone in these complexes and may be assigned to ν(NCO^-) vibration of the newly created NCO^- group owing to enolization of the ligand **[63]**.

The medium intensity band observed at 1281 cm^{-1} in the free dihydrazone is assigned to ν(C–O) (naphtholic). This band shifts to lower frequency by 1–5 cm^{-1} and appears in the region 1276–1278 cm^{-1} in the complexes (4.1) to (4.5). This suggests that the naphtholate oxygen is coordinated to the metal centre **[49]**. The uncoordinated dihydrazone shows a weak intensity band at 1089 cm^{-1} which is assigned to ν(N–N) band. This band shifts to higher frequency by 6–8 cm^{-1} in the metal complexes and appears in the region 1095–1097 cm^{-1}. This indicates the involvement of nitrogen atom of N–N group in coordination to the metal centre **[64]**.

The complexes (4.2) to (4.5) show a new but very weak intensity band in the region 1036–1065 cm^{-1}. This band is assigned to ring breathing mode of pyridine, 2-picoline, 3-picoline and 4-picoline molecules present in the complexes. The presence of this band in the IR spectra of the complexes (4.2) to (4.5) indicates coordination of pyridine, 2-picoline, 3-picoline and 4-picoline to the metal centre **[65]**.

The metal containing dioxo groups exhibit strong bands in the region 1000–850 cm^{-1} due to antisymmetric and symmetric stretching vibrations. The *cis*-dioxo groups show two such bands while the *trans*-dioxo groups show only one band. The complexes (4.1) to (4.5) show two very strong to medium intensity bands in the region 884–956 cm^{-1} indicating the presence of *cis* MoO_2^{2+} grouping in these complexes **[66]**.

IR spectra of the complexes (4.6) and (4.7) in which the ligand is present in keto form.

The IR spectra of the complexes (4.6) and (4.7) show almost similar feature in the region 3000–3500 cm^{-1} as that in the uncoordinated dihydrazone. This indicates the presence of secondary NH and naphtholic –OH group in the complexes. The position of νNH and νOH in these complexes remained almost unchanged as compared to that in the free ligand. This indicates non-coordination of secondary NH and naphtholic –OH to the metal centre. The band at ~3400 cm^{-1} may have contribution due to νOH of lattice ethanol molecules also.

The strong amide I band at 1672 cm^{-1} in the free ligand shifts to higher frequency and appear at 1675 cm^{-1} in the IR spectra of both the complexes. This suggests non-bonding of >C=O group to the metal centre in these complexes.

A couple of strong bands at 1633 and 1503 cm^{-1} assigned to νC=N stretching vibrations undergoes shift to lower frequency by 2–3 cm^{-1}. This indicates coordination of azomethine nitrogen atom to the metal centre **[67]**.

The free dihydrazone shows a medium intensity band at 1540 cm^{-1} which is attributed to arise due to mixed contribution of amide II and ν(C–O) (naphtholic). In the complexes (4.6) and (4.7), this band remains almost unshifted in position and appears at 1541 and 1542 cm^{-1} respectively. Unchanged position of this band in these complexes indicates non-involvement of >C=O and naphtholic –OH in coordination to the metal centre.

The medium intensity band observed at 1281 cm^{-1} in the free dihydrazone arises due to ν(C–O).This band remains almost unshifted in position and appear at 1280 cm^{-1} in both the complexes. Unshifted position of ν(C–O) band in these complexes does not give any conclusive evidence whether >C–O group is involved in bonding or not. However, the ^1H NMR spectral evidences support very clearly the non-coordination of naphtholic oxygen atom in bonding.

The ν(N–N) band observed as a weak band at 1029 cm^{-1} in the IR spectrum of the free dihydrazone shows a positive shift of about 6 and 7 cm^{-1} indicating involvement of one nitrogen atom of the hydrazine group in bonding to the metal centre **[64]**.

1,10-Phenanthroline and 2,2′-Bipyridine Coordination

The 1, 10-phenanthroline complex (4.6) exhibits four medium to strong intensity bands at 1603, 1518, 725 and 636 cm^{-1}. The bands at 1603 and 1515 cm^{-1} are assigned to ν(C=N) and ν(ring) (carbocyclic ring) vibrations respectively. In the IR spectrum of free 1,10-phenanthroline these bands appear at 1615 and 1505 cm^{-1} respectively **[69]**. Thus these bands are shifted to lower frequency on complexation.

The two intense bands, one at 636 cm^{-1} is assigned to the out-of -plane motion of the hydrogen atoms on the heterocyclic rings and the oither at 725 cm^{-1} is assigned to the hydrogen in the centre ring. These two bands are expected because there are two distinct group of hydrogen atoms bound to the heterocyclic rings and two hydrogen atoms to the centre ring **[68, 69]**. A comparison of these bands with the bands at 787 cm^{-1} and 734 cm^{-1} in the IR spectrum of free 1,10-phenanthroline indicates that these bands are shifted to lower frequency upon complexation. Similarly, in the 2,2′-bipyridine complex (4.7), the strong bands observed at 1598 cm^{-1} and 1443 cm^{-1} are assigned to ν(-C=C-) and ν(-C=N-) vibrations **[70]**. In free bipyridine these bands appear at 1578 and 1414 cm^{-1} **[70]**. Thus these bands are shifted to lower frequency upon complexation. Other characteristic bands of free bipyridine are the C–H out-of -plane deformation which appears as a strong band at 758 cm^{-1} and a weak satellite at 739 cm^{-1}. These bands shifts to higher as well as lower frequency on complexation and appear at 758 cm^{-1} and 622 cm^{-1} in the IR spectrum of the complex (4.7). The presence of these bands in the complex (4.6) and (4.7) is indicative of the bidentate N-N coordination of 1,10-phenanthroline and 2,2′-bipyridine to the metal centre **[71, 72]**.

The complexes (4.6) and(4.7) show two very strong to medium intensity bands in the region 884–915 cm^{-1} indicating the presence of *cis* MoO_2^{2+} grouping in these complexes **[66]**.

The band of medium intensity observed in the region 780–796 cm^{-1} in the IR spectra of the complexes (4.6) and (4.7) is assigned to the stretching vibration of the doubly bridged Mo_2O_2 moiety.

Conclusion

In the present chapter it has been shown that the reaction of the dihydrazone ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone with $MoO_2(acac)_2$ in 1:3 molar ratio in ethanol yields homobimetallic molybdenum(VI) complexes $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1). The reaction of this complex with excess of pyridine and substituted pyridine yielded the complexes $[(MoO_2)_2(nsh)(A)_2]\cdot C_2H_5OH$ (A = py (4.2), 2-pic (4.3), 3-pic (4.4), 4-pic (4.5)). The dihydrazone coordinates to the metal centre in the *staggered* configuration. The IR spectra of the complexes show that the ligand functions as a tetrabasic hexadentate ligand in the enol form in all of the complexes. The *staggered* configuration of the dihydrazone ligand in the metal complexes is supported by the unsplit pattern of the azomethine proton signal in the ^1H NMR spectra of the complexes. In the ^1H NMR spectra of the complexes (4.1) to (4.5), the collapse of the two doublets corresponding to δ -CH=N signal into a single resonance suggests that the dihydrazone which exists in *anti-cis* configuration in the uncoordinated dihydrazone, isomerizes to attain *staggered* configuration in the metal complexes. In *staggered* configuration, the different hydrazone parts of the dihydrazone molecule are coordinated to different metal centres. Both the Mo(VI) centres exhibit octahedral stereochemistry in which the ligand donor atoms lie in the equatorial position along with an oxo-group from the MoO_2^{2+} moiety and one of the axial positon is occupied by the other oxo-group and a co-ligand viz. H_2O (4.1), pyridine (4.2), 2-picoline (4.3), 3-picoline (4.4), 4-picoline (4.5).

On the other hand, when the complex $[(MoO_2)_2(nsh)(H_2O)_2].C_2H_5OH$ (4.1) was allowed to react with bidentate ligands 1,10-phenanthroline (phen) and 2,2′-bipyridine (bpy)) in 1:3 molar ratio, the complexes of the composition $[(\mu_2\text{–}O)_2(MoO_2)_2(H_4nsh)(BB)]\cdot C_2H_5OH$ (BB = phen (4.6) and bpy) (4.7)] were obtained. The dihydrazone is coordinated to the metal centre as a neutral bidentate ligand in the keto form through azomethine nitrogen atoms only. The dihydrazone adopts *anti-cis* configuration in these complexes.

On the basis of the results obtained from various physico-chemical and spectral studies and the discussion given above, the suggested structures for the complexes are shown in Fig.4.17 and 4.18.

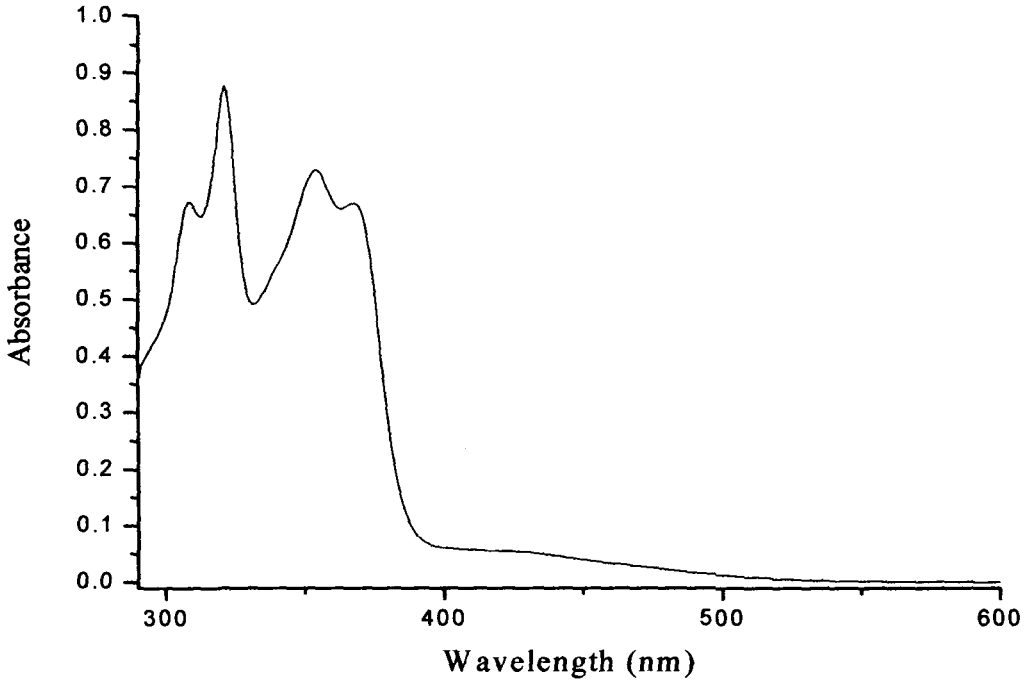


Fig. 4.2. Electronic spectrum of $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$(4.1) in DMF.

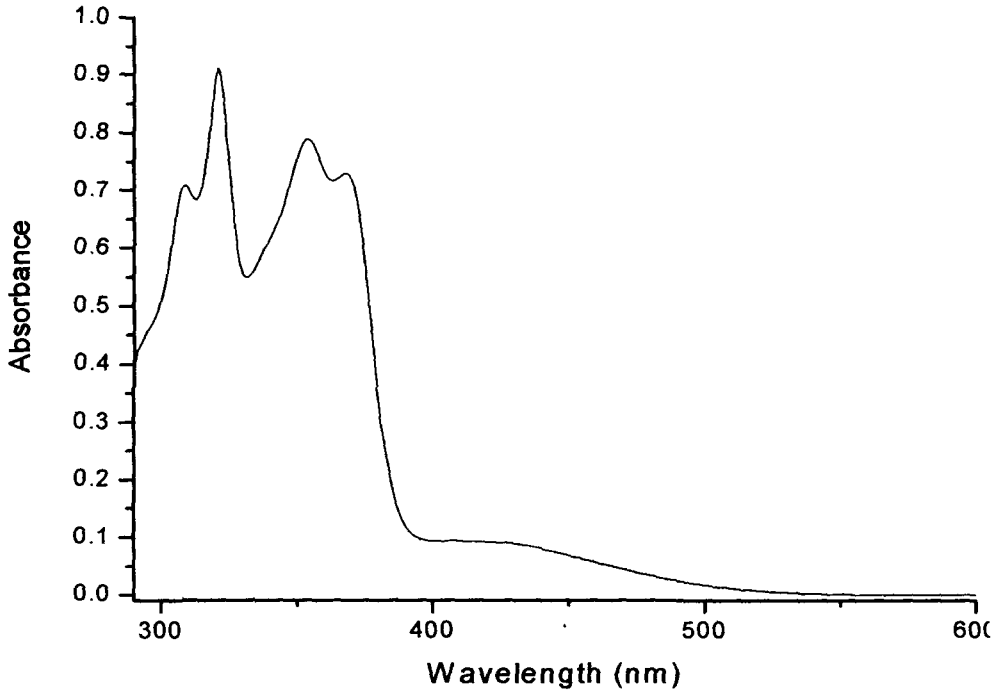


Fig. 4.3. Electronic spectrum of $[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ (4.2) in DMF.

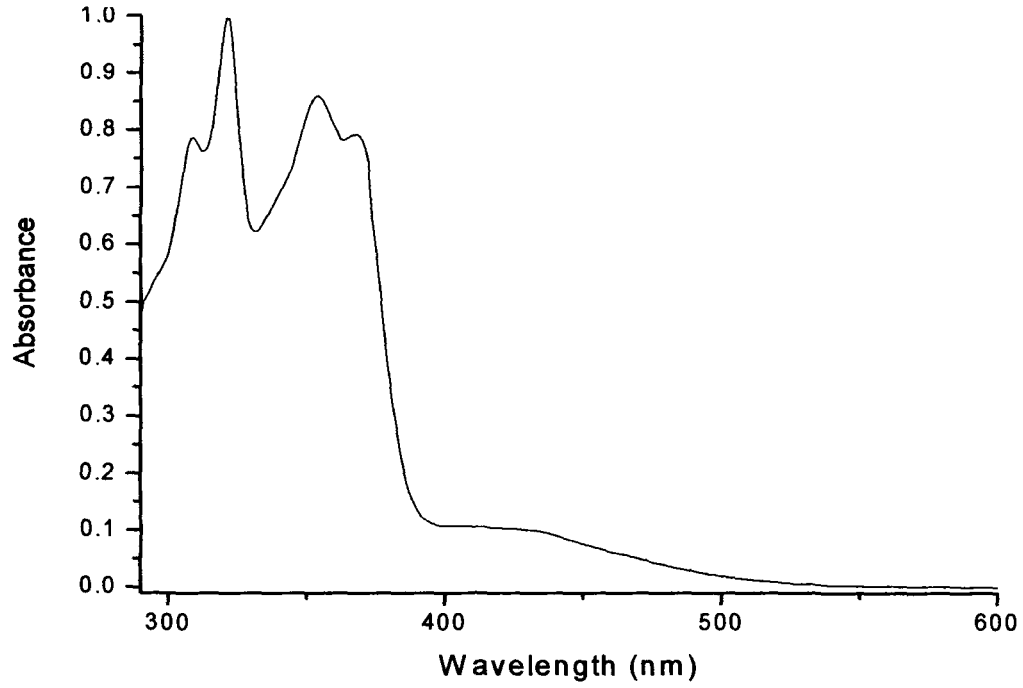


Fig. 4.4. Electronic spectrum of $[(MoO_2)_2(nsh)(4\text{-}pic)_2]\cdot C_2H_5OH$ (4.5) in DMF.

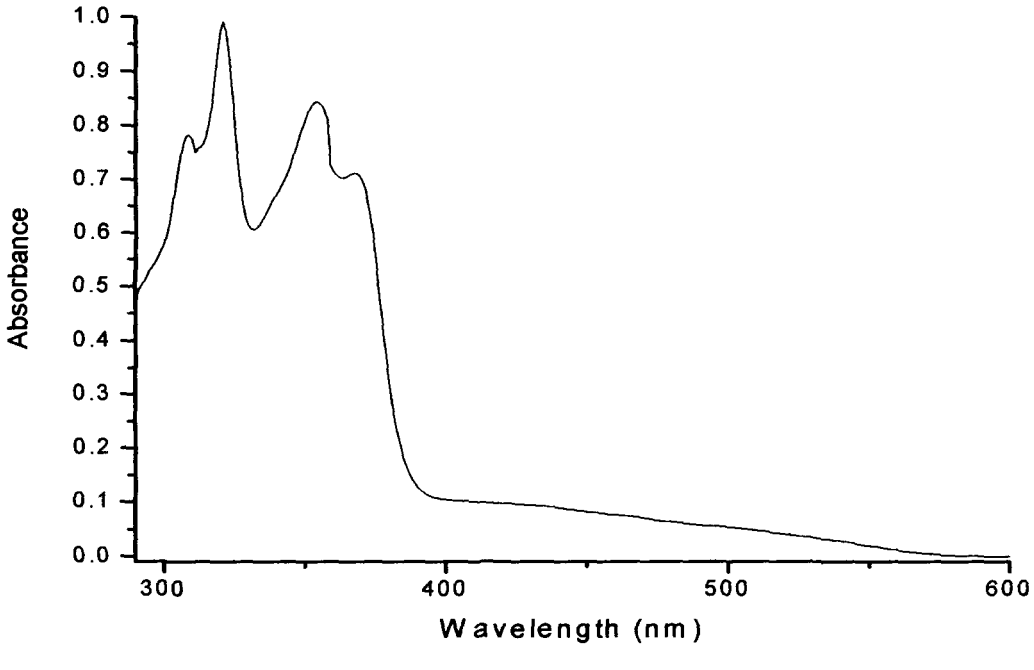


Fig. 4.5. Electronic spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$ (4.7) in DMF.

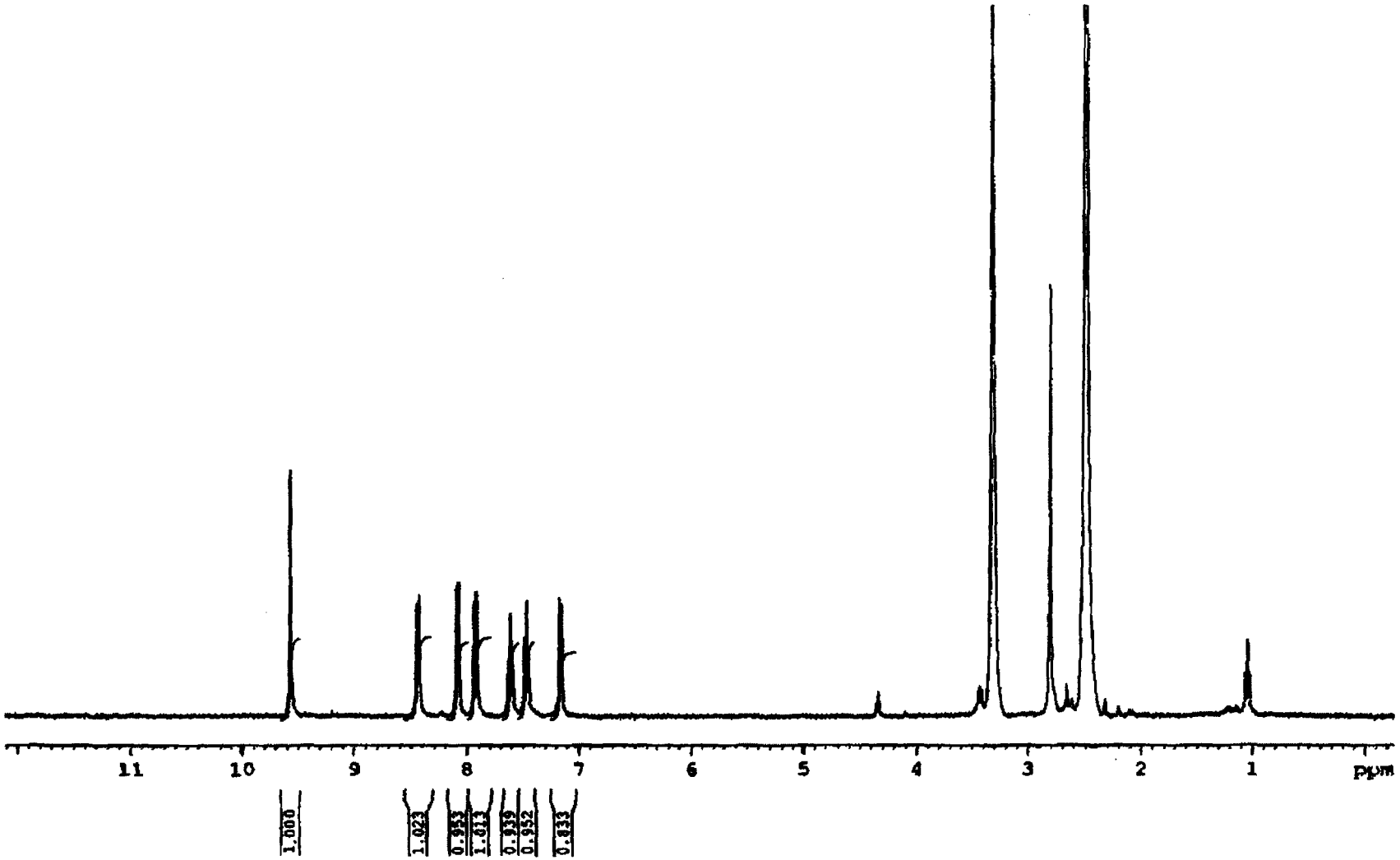


Fig. 4.6. ^{1}H NMR spectrum of $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1) in DMSO-d_6.

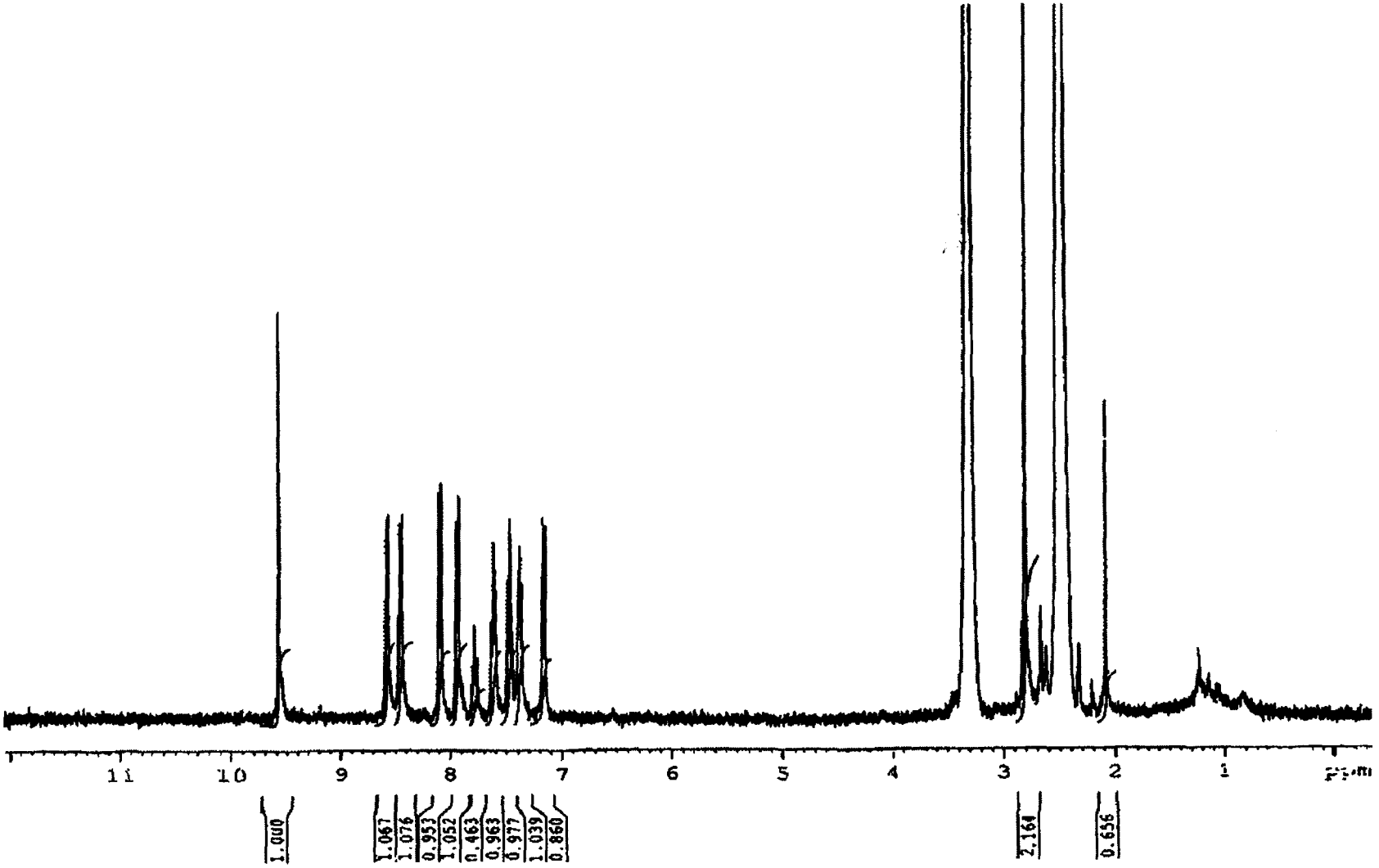


Fig. 4.7. ^{1}H NMR spectrum of $[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ (4.2) in DMSO-d_6.

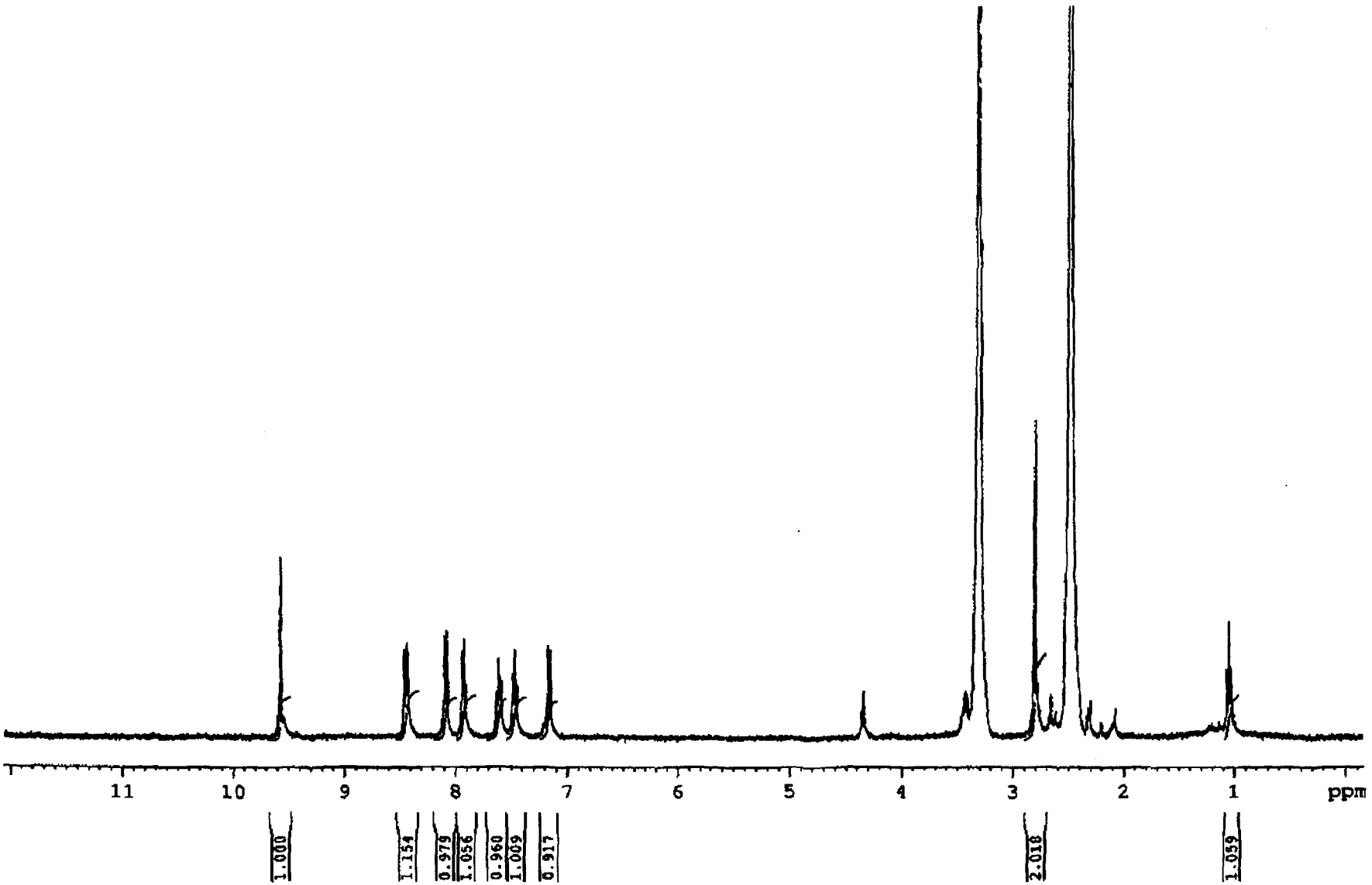


Fig. 4.8. ^{1}H NMR spectrum of $[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5) in DMSO-d_6.

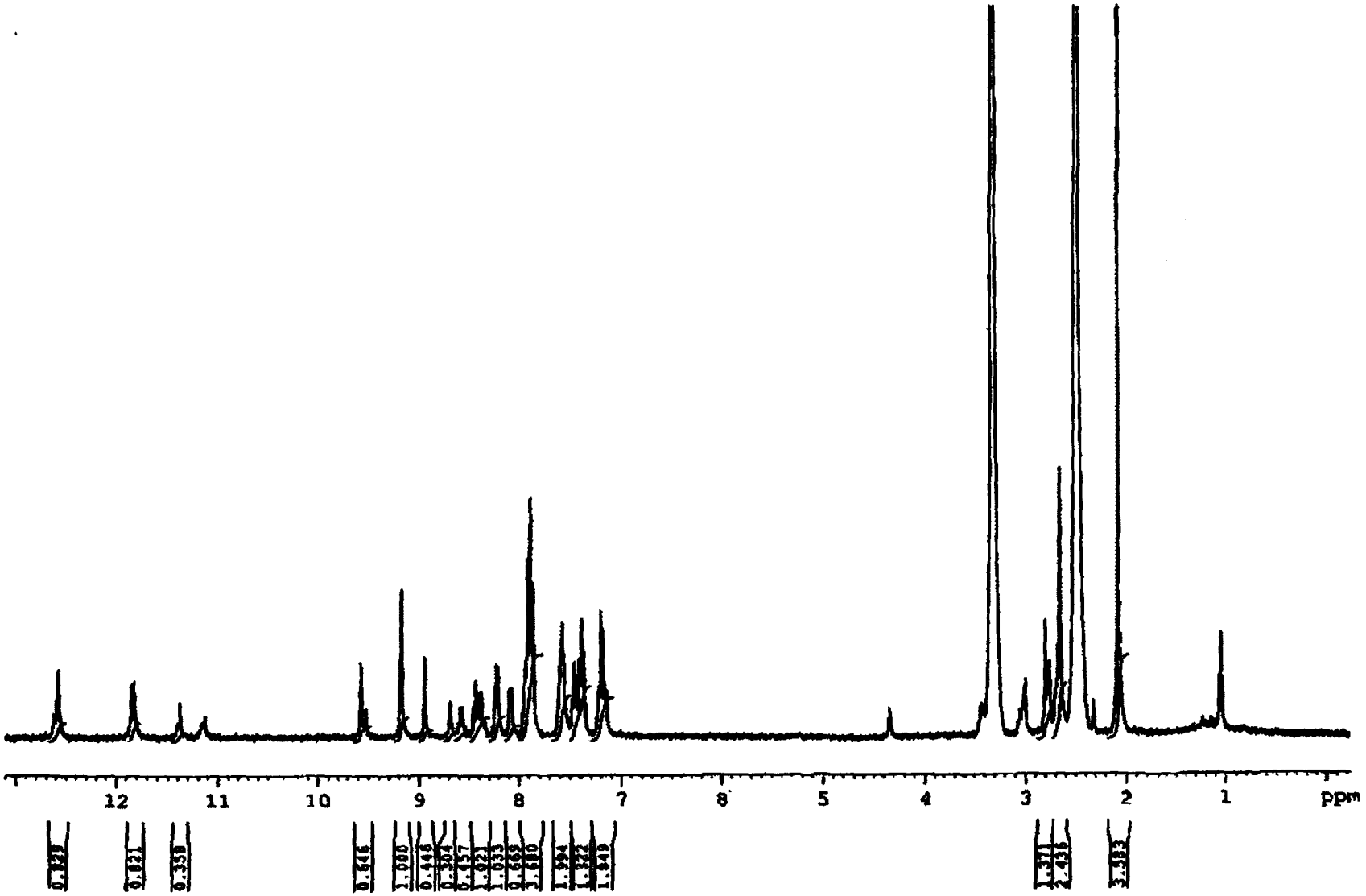


Fig. 4.9. ^{1}H NMR spectrum of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$ (4.7) in DMSO-d_6.

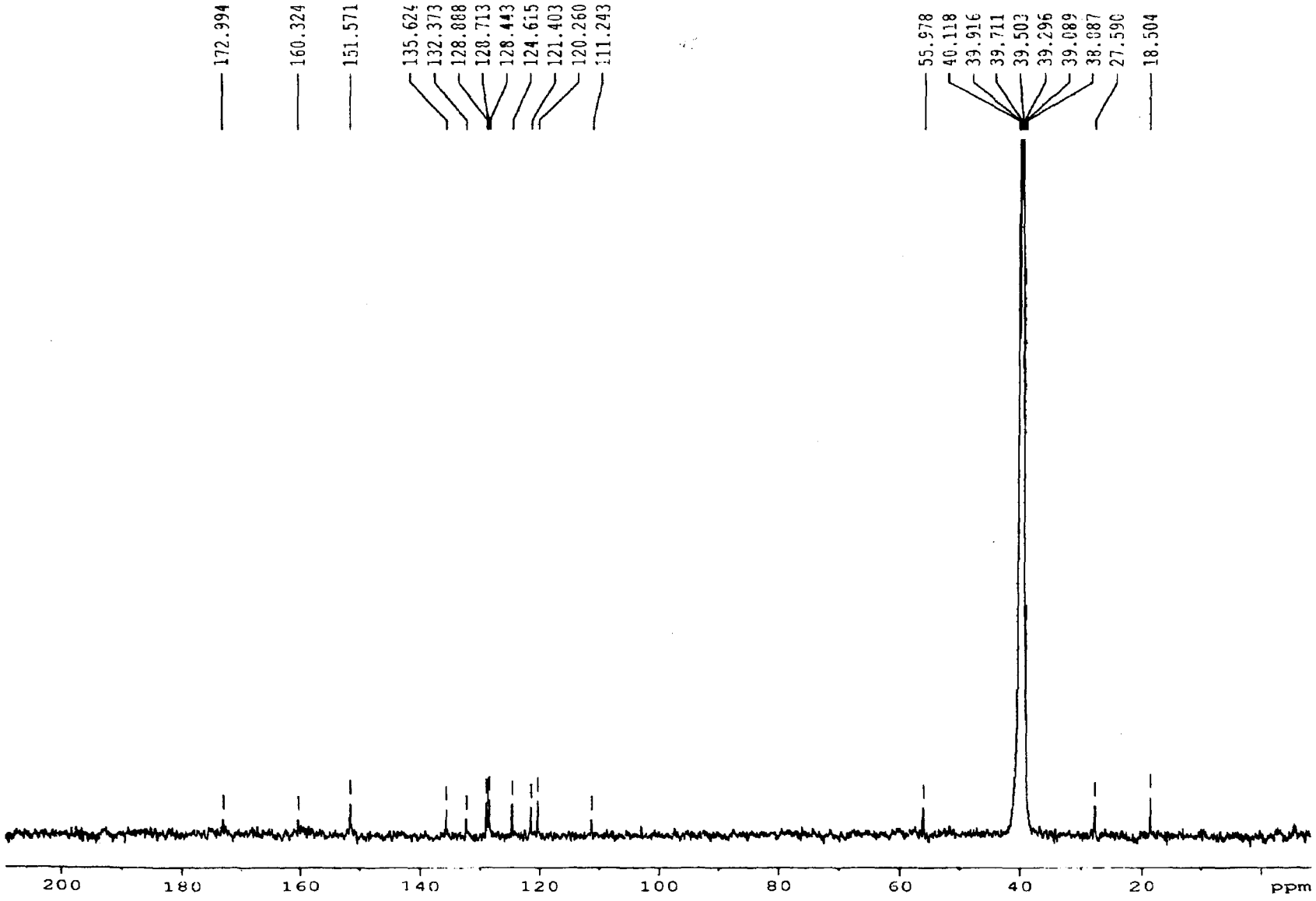


Fig. 4.10. ^{13}C NMR spectrum $[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ (4.3) in DMSO-d_6.

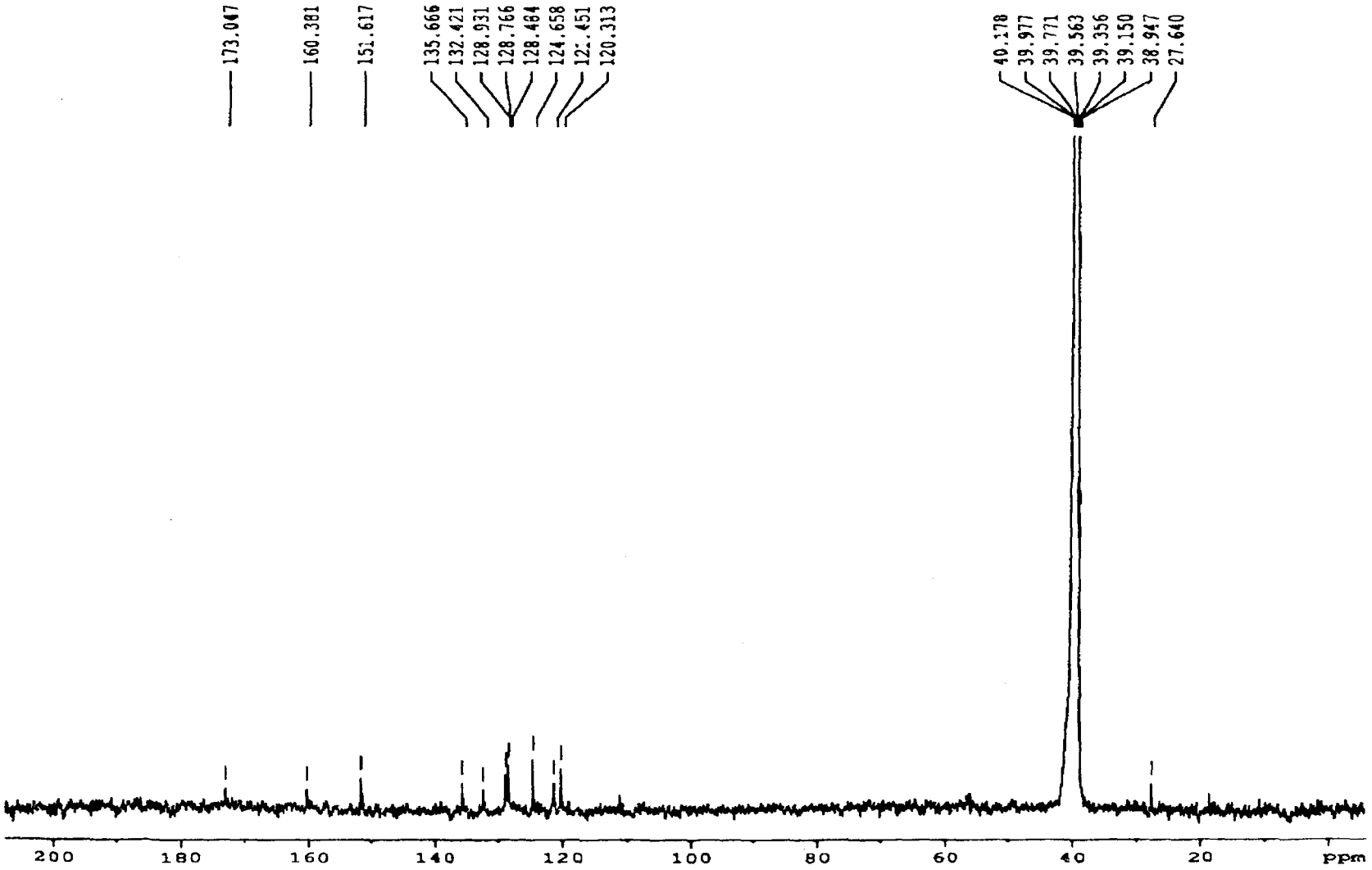


Fig. 4.11. ^{13}C NMR spectrum $[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5) in DMSO-d_6.

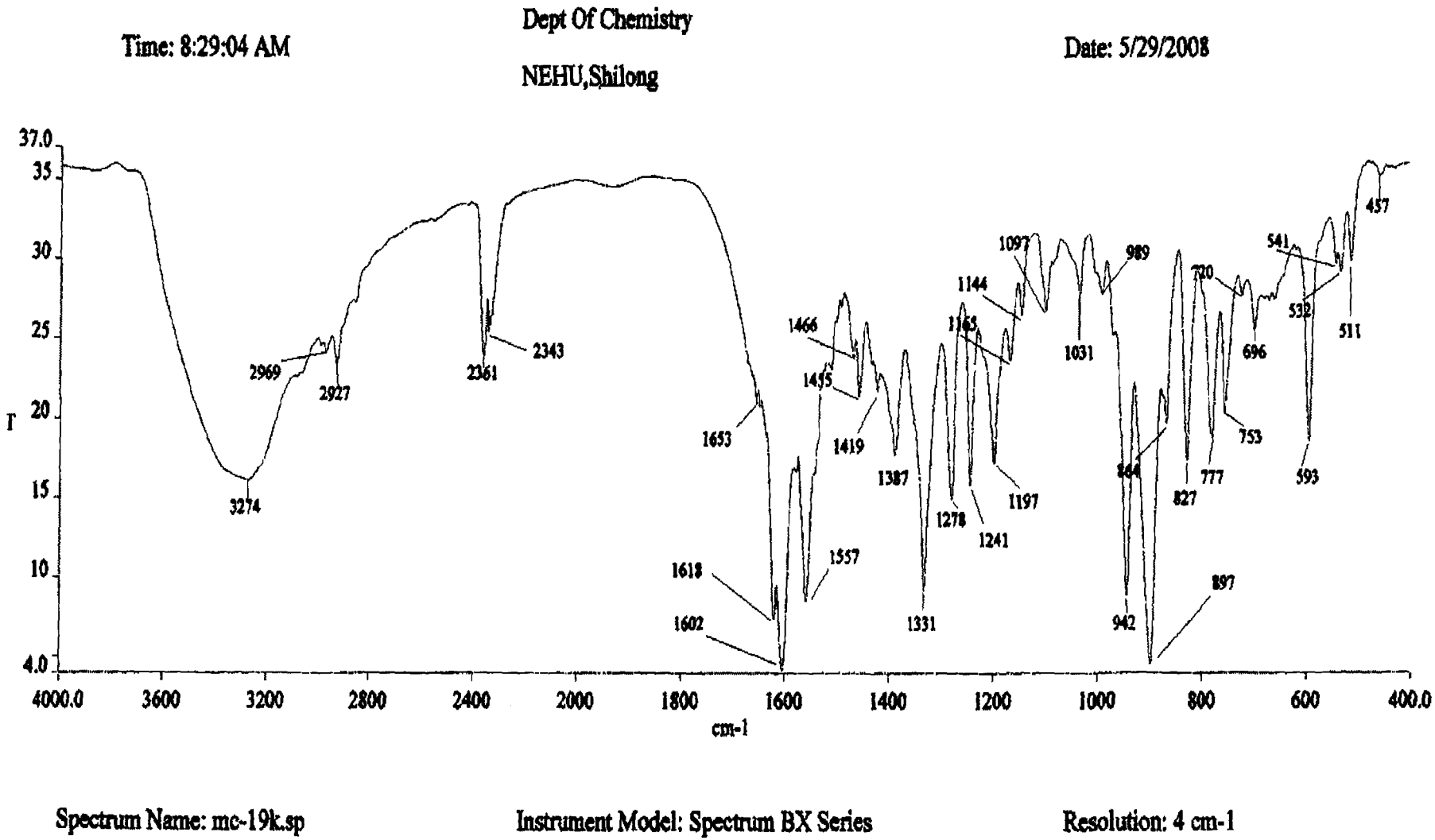


Fig. 4.12. Infrared spectrum of $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1) in KBr.

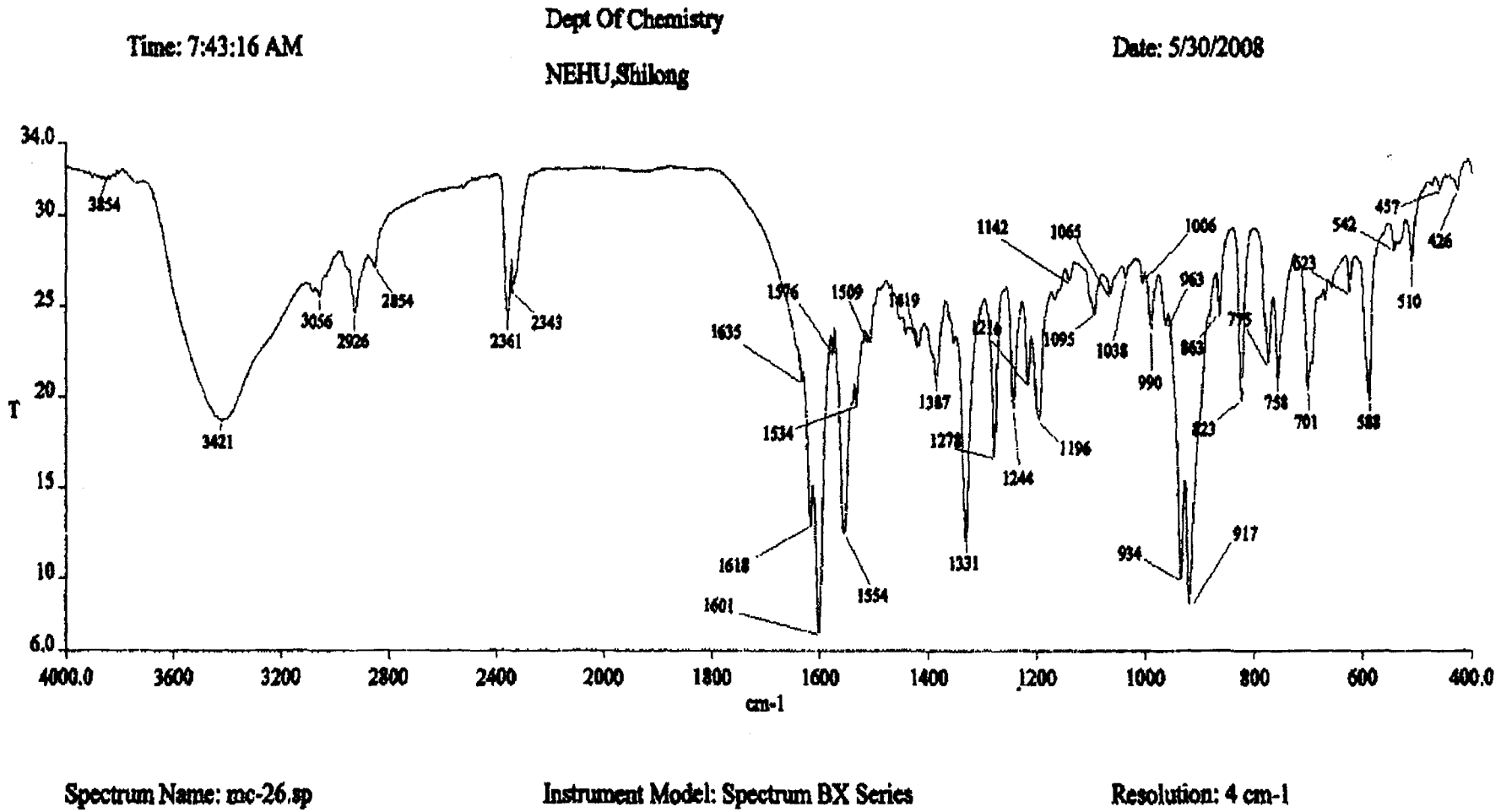


Fig. 4.13. Infrared spectrum of $[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ (4.2) in KBr.

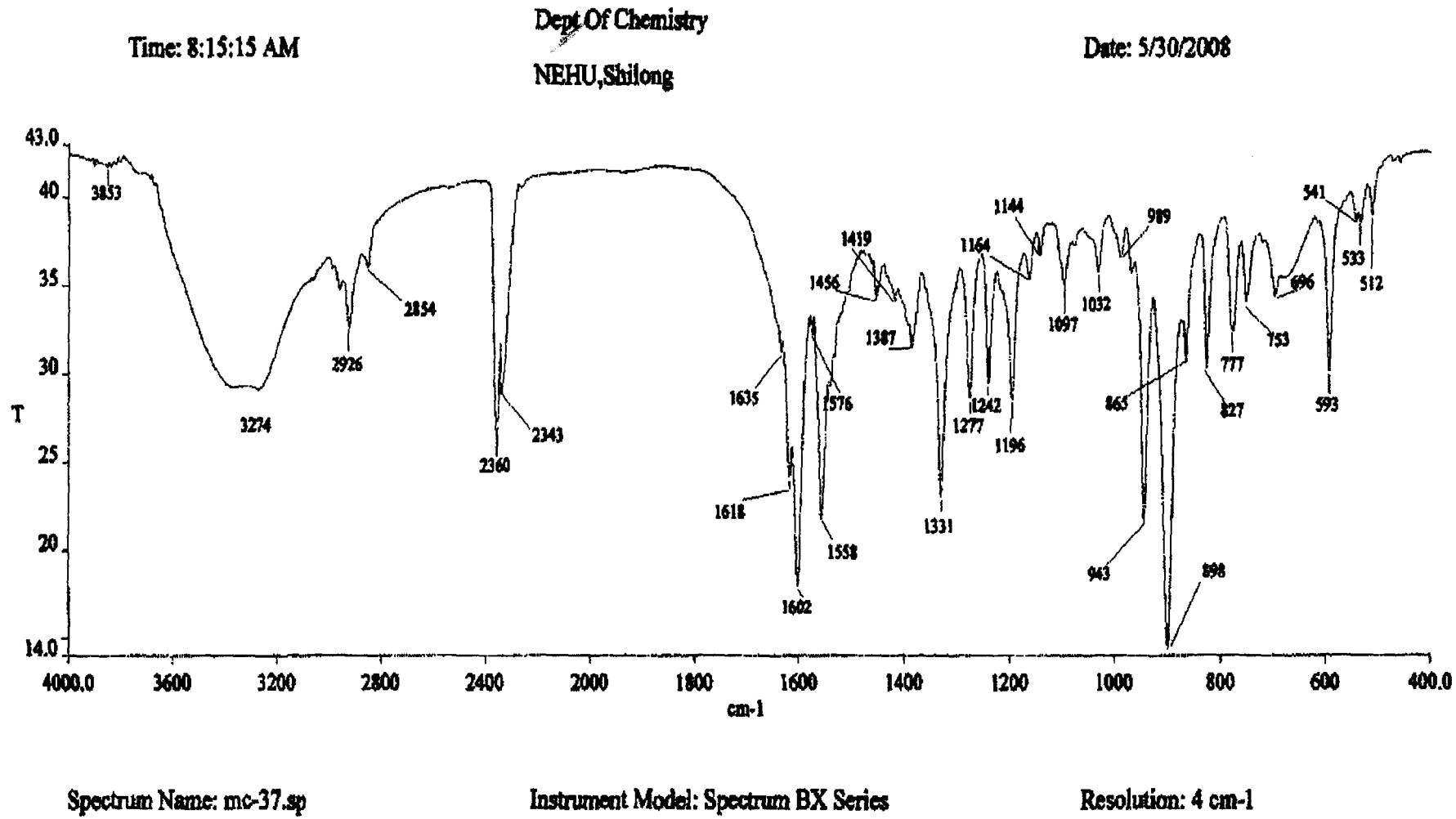


Fig. 4.14. Infrared spectrum of $[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ (4.3) in KBr.

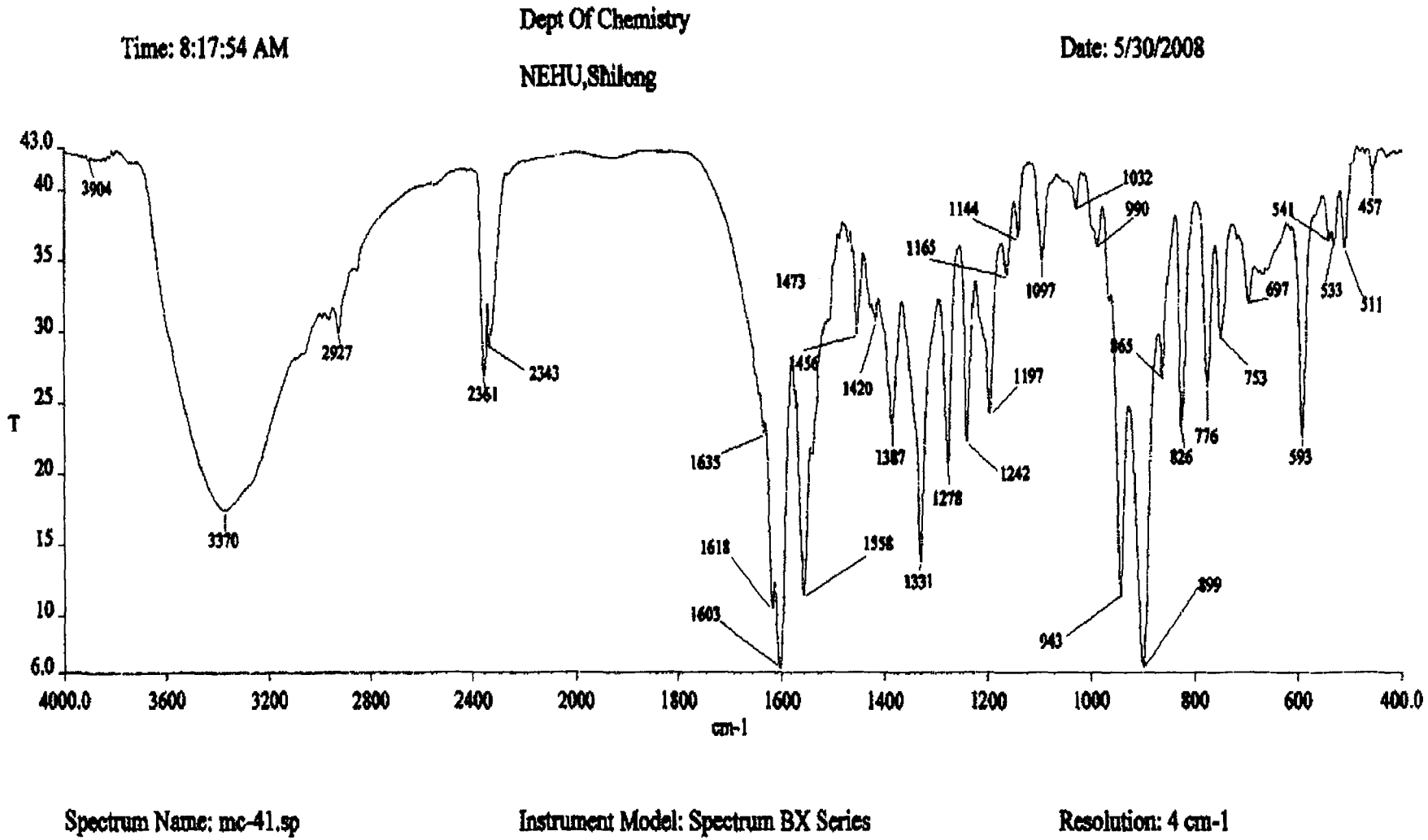


Fig. 4.15. Infrared spectrum of $[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5) in KBr.

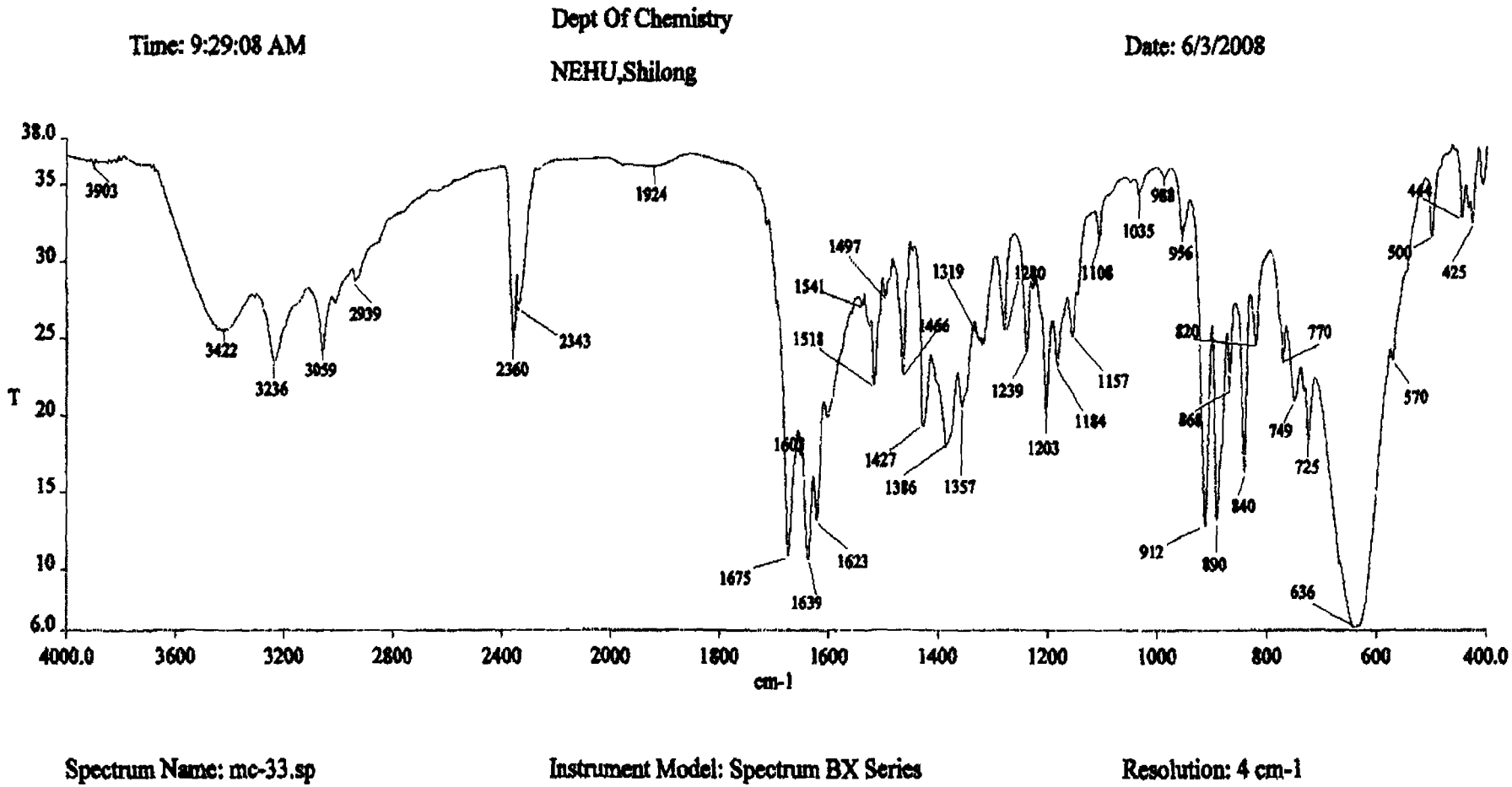


Fig. 4.16. Infrared spectrum of $[(\mu_2\text{–}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$ (4.6) in KBr.

Table 4.1: Analytical Data and Physical properties of homobimetallic Mo(VI) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Sl. No	Complex and Colour	D.P (°C)	Yield(%)	Analysis: Found (Calc.) (%)				Molar Conductance (Λ_M) $Ohm^{-1}cm^2mol^{-1}$
				Mo	C	H	N	
4.1	$[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ Orange	>300	75.00	24.45 (24.34)	42.54 (42.66)	3.53 (3.58)	6.97 (7.11)	4.29
4.2	$[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ Orange	>300	66.00	20.92 (21.07)	50.32 (50.12)	3.72 (3.76)	9.36 (9.23)	3.31
4.3	$[(MoO_2)_2(nsh)(2\text{-}pic)_2]\cdot C_2H_5OH$ Orange	>300	71.00	20.55 (20.44)	51.22 (51.18)	4.11 (4.08)	8.88 (8.95)	2.92
4.4	$[(MoO_2)_2(nsh)(3\text{-}pic)_2]\cdot C_2H_5OH$ Orange	>300	66.00	20.56 (20.44)	51.26 (51.18)	4.12 (4.08)	8.81 (8.95)	3.13
4.5	$[(MoO_2)_2(nsh)(4\text{-}pic)_2]\cdot C_2H_5OH$ Orange	>300	65.00	20.66 (20.44)	51.48 (51.18)	4.05 (4.08)	8.82 (8.95)	4.53
4.6	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$ Light yellow	217	62.00	20.11 (19.81)	49.86 (49.60)	3.72 (3.75)	8.76 (8.68)	2.81
4.7	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$ Light orange	>300	61.00	20.42 (20.31)	48.43 (48.32)	3.87 (3.84)	8.97 (8.90)	2.29

Table 4.2: Electronic spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its homobimetallic Mo(VI) complexes

Sl. No	Ligand/ Complex	Electronic spectral bands λ_{max} (nm) (ε_{max} ($dm^3mol^{-1}cm^{-1}$))
	H_4nsh	317 (5480), 363 (5420)
4.1	$[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$	312 (14814), 361 (13378), 429 (1014)
4.2	$[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$	315 (16024), 361 (15024), 436 (1663)
4.3	$[(MoO_2)_2(nsh)(2\text{-}pic)_2]\cdot C_2H_5OH$	312 (14429), 361 (13168), 431 (920)
4.4	$[(MoO_2)_2(nsh)(3\text{-}pic)_2]\cdot C_2H_5OH$	315 (14814), 361 (14479), 433 (1500)
4.5	$[(MoO_2)_2(nsh)(4\text{-}pic)_2]\cdot C_2H_5OH$	315 (17831), 361 (16550), 433 (1981)
4.6	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$	315 (17887), 362 (18858), 430 (1180)
4.7	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$	315 (19192), 361 (16853), 432 (2036)

Table4.3: Structurally significant ^{1}H NMR Spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its homobimetallic Mo(VI) complexes

Sl. No	Ligand/ Complex	^{1}H NMR Spectral data (δ-ppm)								
		δ (-CH_2)	δ -naphthyl	δ (-CH=N)	δ (NH)	δ (OH)	CH_3CH_2OH			δ (py/2-pic/3-pic/4-pic)
							δ (CH_3)	δ (CH_2)	δ (OH)	
	H_4nsh	2.66 (s) 2.53 (s)	7.19 – 8.23(m)	9.05 (d, 62 Hz) 8.60 (d, 62 Hz)	9.99 (s) 11.14 (s)	12.73 (d, 152 Hz) 11.61 (d, 152 Hz)	—	—	—	—
4.1	$[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$	2.65 (s) 2.80 (s)	7.15 – 8.45(m)	9.57 (s)	—	—	1.04(3H, t)	**	4.32	—
4.2	$[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$	2.66 (s) 2.80 (s)	7.15 – 8.45(m)	9.57 (s)	—	—	1.04(3H, t, 8Hz)	**	**	8.57 (8.613)†
4.3	$[(MoO_2)_2(nsh)(2\text{-}pic)_2]\cdot C_2H_5OH$	2.65 (s) 2.80 (s)	7.15 – 8.45(m)	9.57 (s)	—	—	1.04(3H, t, 8Hz)	3.42(2H, q, 10Hz)	4.34(1H, t, 6Hz)	2.07(2.55)‡
4.4	$[(MoO_2)_2(nsh)(3\text{-}pic)_2]\cdot C_2H_5OH$	2.65 (s) 2.80 (s)	7.15 – 8.45(m)	9.57 (s)	—	—	1.04(3H, t, 8Hz)	3.45(2H, q, 8Hz)	4.34(1H, t, 8Hz)	8.36(8.43)† 2.07 (2.32)‡
4.5	$[(MoO_2)_2(nsh)(4\text{-}pic)_2]\cdot C_2H_5OH$	2.66 (s) 2.80 (s)	7.15 – 8.45(m)	9.57 (s)	—	—	1.04(3H, t, 8Hz)	**	4.37(1H, t, 6Hz)	8.45 (8.60)† 2.07 (2.37)‡
4.6	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$	2.66 (s)	7.15 – 8.45(m)	9.37 (d, 134 Hz) 8.75 (d, 134 Hz)	11.14 (s)	12.59 (d, 102 Hz) 11.60 (d, 102 Hz	1.04(3H, t, 8Hz)	2.97(2H, q, 12Hz)	4.34(1H, t, 4Hz)	—
4.7	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$	2.66 (s) 2.80 (s)	7.15 – 8.45(m)	9.37 (d, 134 Hz) 8.81 (d, 134 Hz)	11.14 (s)	12.20 (d, 242 Hz) 11.61 (d, 242 Hz	1.04(3H, t, 8Hz)	**	4.34(1H, t, 8Hz)	—

*merged with naphthyl proton signals

** merged with –CH_2 proton signals of coordinated Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

†ortho proton signal of pyridine/3-picoline/4-picoline; ‡ Methyl proton signal of 2-picoline/3-picoline/4-picoline

Table 4.4: ^{13}C NMR Spectral Data (im $DMSOd_6$) for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its himobimetallic Mo(VI) Complexes.

Carbon Atoms	H_4nsh	Carbon atoms	(4.1)		(4.3)		(4.5)	
			δ^x	$\Delta\delta^x$	δ^x	$\Delta\delta^x$	δ^x	$\Delta\delta^x$
C(2a), C(2b)	195.32, 187.24	C(2a) = C(2b)	172.26,	+19.07	172.99	+18.34	173.05	+18.28
C(13a), C(13b)	167.48, 167.22	C(13a) = C(13b)	160.00,	+7.35	160.32	+7.03	160.38,	+6.97
C(3a), C(3b)	160.81, 159.86	C(3a) = C(3b)	151.61,	+8.73	151.57	+8.77	151.62,	+8.72
C(11a), C(11b)	144.84, 142.38	C(11a) = C(11b)	135.67	+7.64	135.62	+7.99	135.67	+7.94
C(10a), C(10b)	134.47, 132.20	C(10a) = C(10b)	132.41	+0.93	132.37	+0.97	132.42,	+0.92
C(7a), C(7b)	131.37	C(7a) = C(7b)	128.93	+2.44	128.89	+2.48	128.93,	+2.44
C(5a), C(5b)	127.63, 127.43	C(5a) = C(5b)	124.65	+2.88	124.61	+2.92	124.66,	+2.87
C(8a), C (8b)	123.58, 123.22	C(8a) = C (8b)	121.44	+1.96	121.40	+2.0	121.45	+1.95
C(9a), C(9b)	121.96, 121.56	C(9a) = C(9b)	120.30	+1.46	120.26	+1.50	120.31	+1.45
C(6a), C(6b)	118.62, 118.11	C(6a) = C(6b)	116.49	+1.88	111.24	+7.13	114.30	+4.07
C(12a), C(12b)	109.61	C(12a) = C(12b)	111.30	-1.69	102.95	+6.66	111.11	-1.50
C(4a), C(4b)	108.35	C(4a) = C(4b)	108.30	+0.05		—	107.72	+0.63
C(1a), C(1b)	28.69, 27.34	C(1a) = C(1b)	27.63	+0.39	27.64	+0.43	27.64	+0.38

$\Delta\delta^x = \delta^x$ (H_4nsh) - δ^x(complex), 'a' refers to axial carbon atoms and 'b' refers to equatorial carbon atoms

Pyridine: 151.53 (149.94)(C3, C5); 2-picoline: 155.20 (158.00)(C2), 151.36 (149.00)(C6); 3-picoline: 153.52 (150.27)(C6), 151.52 (146.93)(C2); 4-picoline 151.54 (149.60)(C2, C6)

Table 4.5: Structurally significant Infrared (IR) bands (in cm^{-1}) for bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its homobimetallic Mo(VI) complexes

Sl. No.	Ligand /Complex	ν(OH + NH)	ν (C =O)	ν(C=N)	Amide II + ν (C -O) (naphtholic)	ν (NCO^-)	ν (C–O)	ν (N–N)	ν (Mo=O)	ν (M–O) (naphtholic)	ν (M–O) (carbonyl)
	H_4nsh	3423 m 3244 m 3051 w	1672 vs	1633vs 1593m	1540 w	—	1281 m	1029 w	—	—	—
4.1	$[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$	3274 m	—	1618 m 1602 s	—	1557 w	1278 m	1097 w	942 m 897 s	593 m 541 w 511 w	457 w
4.2	$[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$	3421 s 3056 m	—	1618 s 1602	—	1554 w	1278 m	1095 w	934 s 917 vs	588 m 541 w 512 w	426 w
4.3	$[(MoO_2)_2(nsh)(2\text{-}pic)_2]\cdot C_2H_5OH$	3274 s	—	1618 s 1602s	—	1558 w	1277 m	1097 w	943 m 898 vs	593 m 541 w 512 w	425 w
4.4	$[(MoO_2)_2(nsh)(3\text{-}pic)_2]\cdot C_2H_5OH$	3421 s	—	1617 s 1601s	—	1558 w	1276 m	1097 w	931w 914 s 900s	593 m 541 w	424w
4.5	$[(MoO_2)_2(nsh)(4\text{-}pic)_2]\cdot C_2H_5OH$	3370 m	—	1618 s 1603s	—	1558 w	1278 m	1032 w	943 vs 899 w	593 m 541 w 511 w	419 w
4.6	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$	3422 w 3236 s 3059 w	1675 s	1623 s 1603s	1541 m	—	1280 m	1035 w	912 m 890 s	506 w	446 w 426 w
4.7	$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$	3421 w 3235 s 3079 w	1675 s	1622 s 1598s	1542 w	—	1280 m	1035 w	915 w 884 s	492 w	439 w 426 w

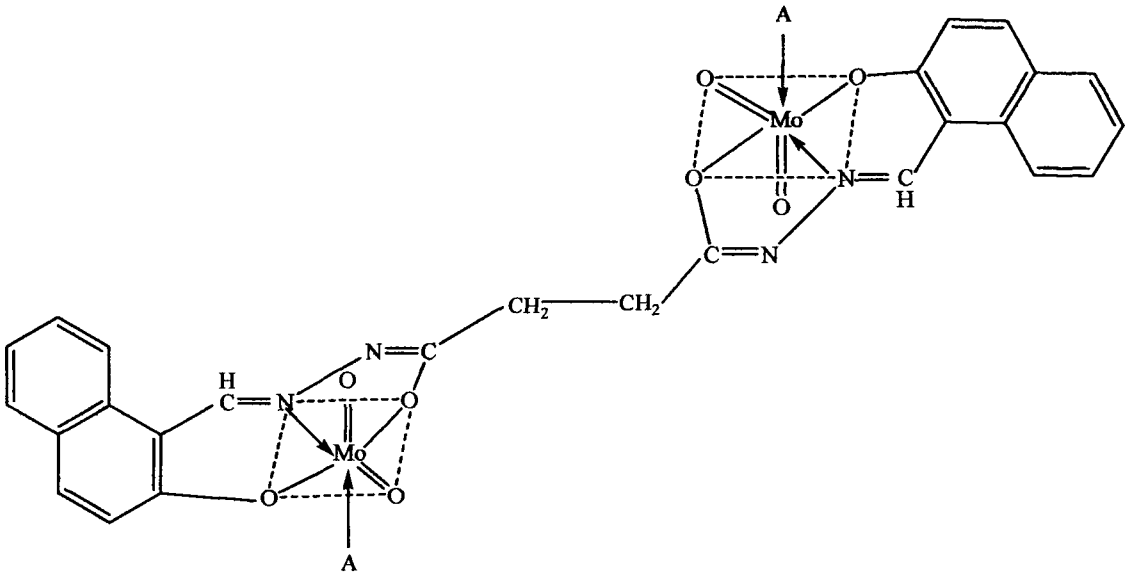
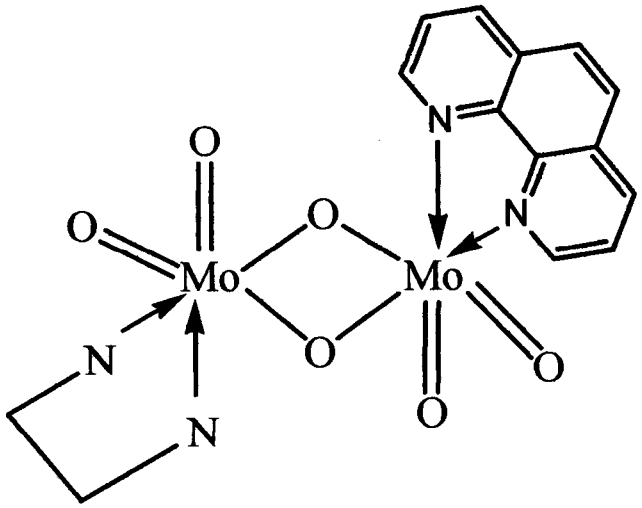
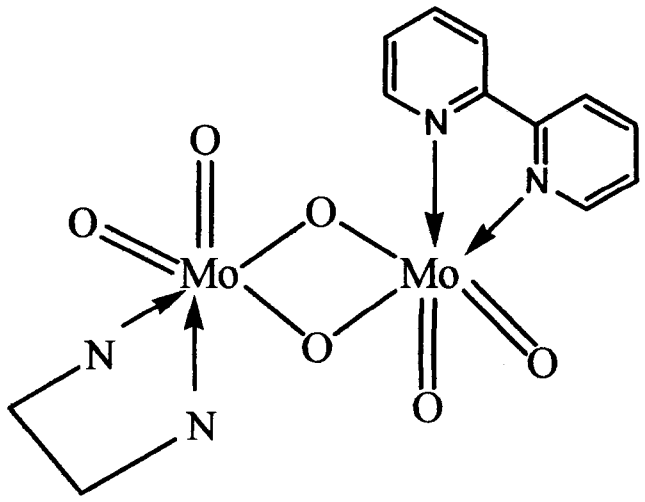


Fig 4.17. Tentative structure of $[(MoO_2)_2(nsh)(A)_2].C_2H_5OH$ (A = H_2O (4.1), py (4.2), 2-pic (4.3), 3-Pic (4.4), 4-pic (4.5)).



(4.6)



(4.7)

Fig. 4.18. Tentative stricture of $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)(BB)].C_2H_5OH$ (BB = 1,10-phenanthroline (4.6), 2,2′-bipyridine (4.7)).

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CHAPTER V

Synthesis, Characterization and Structural Assessment of Zinc(II) Complexes Derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.

Introduction

Third chapter describes the monometallic molybdenum complexes in which polyfunctional dihydrazone is present as a neutral bidentate ligand bonded to the metal centre through two azometh ine nitrogen atoms only while the fourth chapter gives details of the bimetallic molybdenum complexes in which dihydrazone coordinates to the metal centre as a tetrabasic hexadentate ligand through naphtholate and enolate oxygen atoms and azomethine nitrogen atoms. In monometallic complexes, the dihydrazone attains *anti-cis* configuration while in bimetallic complexes with monodentate co-ligands, the dihydrazone coordinates to the metal centre in the *staggered* configuration and with bridging bidentate co-ligands, the dihydrazone coordinates to the metal centre in the *anti-cis* configuration.

Molybdenum discharges its function in biological and industrial catalytic systems by redox cooperativity because it has +6, +5 and +4 potential oxidation states in which the metal can cycle during its reaction. Although in majority of the enzymes such as sulfite oxidase, xanthine oxidase and DMSO reductase etc, the metal occurs alone yet it occurs in combination with iron in the enzyme nitrogenase **[1, 2]**. Molybdenum oxide in combination with other metal oxides is used as efficient and selective catalyst for potential oxidation of light alkanes in petrochemistry **[3]**. A cobalt or nickel or platinum promoted molybdenum catalyst is used in hydrosulfurization and hydrodenitrogenation process **[4]** whereby organo sulfur and nitrogen compounds in petroleum feed stocks are heterogeneously desulfurized and denitrogenated.

Understanding the function of molybdenum in complex biological and catalytic systems is a difficult proposition. In order to understand the function of molybdenum in heterosystems either in biology or catalysis, it is imperative to synthesize and characterize heterometallic complexes containing molybdenum as one component and other metals as second component. The second metal centre present in biological or catalytic systems might also discharge their functions by redox cooperativity. Hence, it is desirable to prepare heterometallic complexes of molybdenum with a simple metal ion from redox

point of view and to characterize them fully and then to undertake the study of heterobimetallic complexes of molybdenum with a redox active metal atom. The chemical information gained in studying the heterometal systems may be transferable to enzyme and catalytic structure functions not readily solvable by studying the enzymes and catalytic systems themselves. From this point of view, zinc was considered as the most suitable candidate because it is the most simple metal ion as it is redox inert and its complexes also have limited options from structure points of view i.e. from tetrahedral to square pyramidal to octahedral to pentagonal bipyramidal. Before we proceed for the preparation of heterobimetallic complexes of Mo and Zn, it is imperative to synthesize and characterize monometallic and bimetallic complexes of zinc which might serve as precursors in the synthesis of heterobimetallic complexes.

At this stage it appears pertinent to review the literature related with the importance of zinc particularly in biological systems and technology. Zn(II) is the second most abundant metal in the human body and is a structural or catalytic component of more than 300 enzymes, for example, in carbonic anhydrase, alkaline phosphatase, dehydrogenases, aldoses and alcohol dehydrogenases etc. The enzymes are involved in energy release, sugar metabolism and metabolism of alcohol. Intracellular concentration of free Zn^{2+} are closely controlled by a complex and effective system of zinc transporters and zinc specific solute carriers **[5,6]**, such that the free or loosely bound Zn^{2+} concentration in the cytosol is subfemtomolar **[7]**. Cells that have undergone oxidative stress have been found to contain much higher cytosolic concentration of free Zn^{2+}. In addition, the neurobiology of Zn(II) has become a subject of increasing attention **[8]**.

Further, zinc occurs in combination with copper in the enzyme superoxide dismutase obtained from bovine tissue in which it serves as a structural element. Superoxide dismutase containing Cu and Zn catalyses the transformation of superoxide (O_2^{2-}) into hydrogen peroxide and citrate synthase.

Zinc is present in transferases (e.g. DNA and RNA polymerase) and lysases (carbonic anhydrase). Zinc is also present in non-enzyme zinc finger proteins which have a strong regulatory ability. In many of these systems, the non-redox active Zn^{2+} ion is present as a Lewis acidic centre at which substrates are coordinated, polarized and hence activated **[9]**.

Zn^{2+} is used extensively as an anodic inhibitor for metallic corrosion protection by making protective shield on metal surface. Literature reports point to a synergic action of Zn^{2+} and

polyphosphonates that is explained in terms of metal phosphonate inhibiting films on the metallic surface **[10]**.

Zinc plays important role in sensor technology. In addition to its function in enzymes and zinc finger proteins, zinc influences DNA synthesis and apoptosis (programmed cell suicide e.g. information of limbs and digits in embryos/ and gene expression) **[11]**.

In view of the above importance of zinc in biology and technology and importance of its complexes in synthesis of heterometal systems, the present chapter aims at synthesizing zinc complexes from the title ligand and to characterize them by various physico-chemical and spectral techniques.

Preparation of the Complexes:

1. Preparation of [Zn(H_2nsh)(A)] (where A = H_2O (5.1), pyridine (py, 5.2); 2-picoline (2-pic, 5.3); 3-picoline (3-pic, 5.4); 4-picoline (4-pic, 5.5))

Succinoyl dihydrazine (0.50 g, 3.42 mmol) was dissolved in hot methanol-water mixtutre (40 mL) (90:10). A solution of $Zn(OAc)_2.2H_2O$ (0.75 g, 3.45 mmol) in methanol (50 mL) was added to the above solution accompanied by gentle stirring over a period of 15 minutes. To this was added a solution of 2-hydroxy-1-naphthaldehyde (1.47 g, 8.54 mmol) in methanol (100 mL) drop by drop at *ca* 70 °C over a period of 10 minutes accompanied by gentle stirring. The reaction mixture was refluxed for 1 hour and this precipitated a bright-yellow coloured compound. The compound thus obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.62 g.

In order to prepare the complex (5.2), [Zn(H_2nsh)(H_2O)] (5.1) (1.00 g, 1.81 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 minutes at 50–60 °C. To this suspension, pyridine (1.50 mL, 18.10 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 5 hours which precipitated the yellow coloured compound. The compound thus obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.71 g.

The complexes (5.3), (5.4) and (5.5) were also prepared in the same manner using 2-picoline, 3-picoline and 4-picoline respectively, instead of pyridine. Yield: 0.71g (5.3); 0.69g (5.4); 0.72 g (5.5).

2. Preparation of $[Zn_2(nsh)(A)_2]$ (where A = H_2O (5.6) pyridine (py, 5.2); 2-picoline (2-pic, 5.3); 3-picoline (3-pic, 5.4); 4-picoline (4-pic, 5.5))

The dihydrazone (H_4nsh) (1.00 g, 2.20 mmol) was suspended in methanol (100 mL) and stirred for 30 minutes at 60° C. To this was added a solution of $Zn(OAc)_2.2H_2O$ (1.65 g, 6.63 mmol) in methanol (50 mL) maintaining the molar ratio at 1:3. The reaction mixture was refluxed for 6 hrs, which precipitated a brown compound. The compound, thus, obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.64 g.

In order to prepare the complex (5.7), $[Zn_2(nsh)(H_2O)_2]$ (5.6) (1.00 g, 1.55 mmol) was suspended in methanol (100 mL) by gentle heating at 60° C. To this suspension, pyridine (1.24 mL, 15.42 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 2 hrs. The resulting precipitate was isolated in the usual way.

The complexes (5.8) to (5.10) were also synthesized by essentially following the above procedure using 2-picoline, 3-picoline and 4-picoline instead of pyridine maintaining the metal:base molar ratio at 1:10, respectively. Yield: 0.62 g (5.7); 0.65 g (5.8); 0.62 g (5.9); 0.63 g (5.10).

Results and Discussion

The complexes described in the present chapter together with their molecular formula, colour, decomposition point, percentage yield, analytical data and molar conductance data are set out in Table. 5.1. The electronic spectral data for the complexes are given in Table. 5.2.

On the basis of analytical data, the complexes have been suggested to have the following composition.

$[Zn(H_2nsh)(A)]$ (where A = H_2O, (5.1); pyridine (py, 5.2); 2-picoline (2-pic, 5.3); 3-picoline (3-pic, 5.4); 4-picoline (4-pic, 5.5)).

$[Zn_2(nsh)(A)_2]$ (where A = H_2O, (5.6); pyridine (py, 5.7); 2-picoline (2-pic, 5.8); 3-picoline (3-pic, 5.9); 4-picoline (4-pic, 5.10)).

All of the complexes are yellow in colour and are air stable. The complexes (5.1), (5.3), (5.4), and (5.5) to (5.10) decompose above 300 °C without melting while the complexes (5.2) and (5.5) melt with decomposition at 272 and 274 °C, respectively. All of the complexes are insoluble in water and other common organic solvents such as ethanol,

methanol, acetone, benzene and chloroform, but are soluble in highly coordinating solvents like DMSO and DMF. The complexes (5.1) to (5.10) have molar conductance values in the range 2.4–3.1 $ohm^{-1}cm^2mol^{-1}$ in DMSO solution at 10^{-3} M dilution. These values are consistent with the non-electrolytic nature of these complexes in this solvent **[12]**.

A consistent effort to crystallize the complexes either from saturated solution or by diffusing ether/hexane into saturated solutions in DMSO and DMF in a closed system led to the precipitation of amorphous products. Such behaviour of the complexes with respect to their crystallization prevented their analyses by single crystal X-ray crystallography.

Thermal studies

Thermogravimetric studies of the complexes (5.1), (5.2), (5.4), (5.5), (5.6), (5.7), (5.9) and (5.10) were carried out manually by heating the samples at a particular temperature for 30 minutes in the temperature range 60–250°C at and interval of 5 °C in an electric oven and estimating the weight loss. The vapours evolved were identified by passing them through separate test tubes containing anhydrous copper sulfate, sodium hydroxide and iodine, $CHCl_3$ solution containing a drop of 5 M NaOH solution and cyanogen bromide solution.

In complex (5.1) and (5.6), the weight loss occurs in the temperature range 170–180 °C and the vapours evolved turned anhydrous copper sulfate blue, confirming that they originate from water molecules. The weight loss at 180°C corresponds to one molecule of water in complex (5.1) and two molecules of water in complex (5.6) and this suggests the presence of water molecule in the first coordination sphere of these complexes. However, the complexes (5.2), (5.4), (5.5), (5.7), (5.9) and (5.10) were stable and did not show any weight loss in the temperature range 80–180 °C, ruling out the possibility of presence of water or solvent molecules either in the lattice structure or in the first coordination sphere of these complexes. The complexes (5.2), (5.4) and (5.5), showed weight loss corresponding to one and the complexes (5.7), (5.9) and (5.10) showed weight loss corresponding to two pyridine/ 3-picoline/4-picoline molecule per metal centre at 220°C. The expulsion of these neutral Lewis bases at such a high temperature indicates that they are coordinated to the metal centre. In the systematic thermogravimetric study, the vapours evolved in the complexes (5.2) and (5.7) in the temperature range 200–240 °C turned the $CHCl_3$ and NaOH solution to red which confirmed that the vapours in this complex originate from pyridine **[13]**. Similarly, the vapours evolved in the complexes (5.4), (5.5), (5.9) and (5.10) in this temperature range turned the colour of cyanogen bromide solution

to green–violet and blue respectively on treatment with phloroglucinol solution. This suggested the presence of 3-picoline molecules in the complexes (5.4) and (5.9) and 4-picoline in the complexes (5.5) and (5.10), respectively **[13]**.

Magnetic Moment

All of the complexes are diamagnetic consistent with d^{10} electronic configuration of Zn^{2+} ion in them.

Electronic Spectra

The position of all the characteristic absorption bands along with their molar extinction co-efficients for the dihydrazone as well as the complexes (5.1) to (5.10) have been set out in Table 5.2. The electronic spectra of the complexes (5.1), (5.2), (5.5), (5.6), (5.7) and (5.9) are shown in Fig. (5.1) to (5.6).

The ligand bands observed at 317 nm and 363 nm which arise due to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transition undergo red shift on complexation indicating dihydrazone coordination to the metal centre. All of the complexes show additional strong absorption bands in the region 470–490 nm with molar extinction co-efficient ε_{max} in the region 2247–2522 $dm^3cm^2mol^{-1}$ in the complexes (5.1) to (5.5) and in the region 457–486 $dm^3cm^2mol^{-1}$ in the complexes (5.6) to (5.10) . Such a value of molar extinction co-efficient for these bands indicates that their origin lies in the chare transfer transition from ligand-to-metal (LMCT) which is also responsible for their dark yellow colour **[14]**.

Proton Magnetic Resonance Spectroscopy

All of the complexes were characterized by ^1H NMR spectroscopy. The ^1H NMR spectra of the ligand (H_4nsh) and the complexes were recorded in DMSO because of their insolubility in CCl_4, $CHCl_3$, CH_2Cl_2 and other common organic solvents. The ^1H NMR spectral data for the free dihydrazone and the Zn(II) complexes are set out in Table 5.3. The ^1H NMR spectra of the complexes (5.1), (5.3), (5.5), (5.6), (5.7), and (5.9) are shown in Fig. 5.7 to 5.12 as representative examples.

^1H NMR spectra of the complexes (5.1) to (5.5)

Two proton doublet observed at δ 11.61 and δ 12.73 ppm assigned to δ OH protons in the free dihydrazone **[15]** are downfield shifted on complexation and appear as singlets in the ^1H NMR spectra of all of the complexes. These signals appear in the region δ 12.21–12.88

ppm. The appearance of this signal due to naphtholic –OH protons in the ^{1}H NMR spectra of all of the complexes indicates the presence of –OH group in the complexes. The downfield shift of these signals indicates coordination of naphtholic –OH group to the zinc centre.

The δ (NH) signal (Table. 5.3) which appears in the region δ 9.99–11.14 ppm in the ^{1}H NMR spectrum of the free dihydrazone disappears in all of the complexes. The disappearance of δ NH proton signals in these complexes indicated collapse of amide structure of the dihydrazone and its coordination to the metal centre in the enol form. Such a conclusion drawn from the ^{1}H NMR spectral data of the complexes (5.1) to (5.5) is also supported by the IR spectral evidences which do not show any band characteristic of >C=O group.

The azomethine proton signals which in the free dihydrazone appear in the region δ 8.60–9.05 ppm as doublets exhibit a downfield shift of the order of δ 0.29–0.69 ppm, respectively in the complexes (5.1) to (5.5). The downfield shift of these signals is attributed to the deshielding caused by the coordination of azomethine nitrogen atom to the metal centre.

The multiplet appearing in the region δ 7.19–8.23 ppm in the free ligand was assigned to naphthyl protons. These signals remain almost unshifted in position in all of the complexes and appear in the region δ 7.06–8.23 ppm.

In addition to naphthyl proton signals observed in the region δ 7.06–8.23 ppm in the ^{1}H NMR spectra of the complexes (5.2) to (5.5), some new signals are also observed in the region δ 7.77–7.79 ppm. These new signals are attributed to arise due to *ortho* protons of pyridyl ring of pyridine, 2-picoline, 3-picoline and 4-picoline molecules. These signals are upfield shifted as compared to their position in free pyridine, 2-picoline, 3-picoline and 4-picoline molecules **[16]**. Such a feature associated with pyridine, 2-picoline, 3-picoline and 4-picoline proton signals in the complexes (5.2) to (5.5) suggests that the pyridine ring nitrogen atoms of these heterocyclic molecules are coordinated to the metal centre.

In the ^{1}H NMR spectra of the complexes (5.3), (5.4) and (5.5), a new signal is observed at δ 2.07, δ 2.07 and δ 2.04 ppm (Table. 5.3) respectively. This signal is assigned to methyl protons of 2-pcoline, 3-picoline and 4-picoline molecules, respectively. These signals appear at δ 2.55, δ 2.32 and δ 2.37 (Table 5.3) in free 2-picoline, 3-picoline and 4-picoline molecules, respectively **[17]**. Thus the methyl proton signals are also upfield shifted in the complexes (5.3), (5.4) and (5.5) as compared to their position in free 2-picoline, 3-picoline

and 4-picoline molecules. This upfield shift of methyl proton signals further indicates the coordination of ring nitrogen atom of 2-picoline, 3-picoline and 4-picoline molecules to the metal centre.

Further the signals appearing at δ 2.66 and δ 2.49 ppm in the ^{1}H NMR spectrum of the free ligand were assigned to methylene protons (-CH_2-) of succinoyl fraction of the ligand. These signals either exhibit a upfield shift or remain unchanged in all of the complexes.

^{1}H NMR spectra of the complexes (5.6) to (5.10)

The ^{1}H NMR spectra of the complexes (5.6) to (5.10) are significantly different as compared to those of the complexes (5.1) to (5.5). The two proton doublets observed at δ 11.61 and 12.73 ppm and two proton singlets observed at δ 9.99 and 11.14 ppm due to naphtholic –OH protons and secondary NH protons, respectively, in the ^{1}H NMR spectra of the free dihydrazone do not appear in the ^{1}H NMR spectra of the complexes (5.6) to (5.10). The absence of signals due to δ (OH) and δ (NH) in the ^{1}H NMR spectra of the complexes (5.6) to (5.10) indicates the involvement of the dihydrazone in coordination to the metal centre in the enol form through naphtholate oxygen atoms via deprotonation and carbonyl oxygen atoms via enolization/deprotonation.

The azomethine proton signals observed as doublets at δ 9.05 and δ 8.60 ppm in the ^{1}H NMR spectra of the free dihydrazone exhibit a downfield shift of about 0.72–0.81 ppm in the complexes (5.6) to (5.10). The downfield shift of these signals is attributed to drainage of electron density from the nitrogen atom of azomethine group to the metal centre **[15]**.

The main feature of the ^{1}H NMR spectra of the complexes (5.6) to (5.10) is the collapse of the doublets corresponding to δ -CH=N signal in the free ligand into a single resonance. This ^{1}H NMR spectral feature of the complexes (5.6) to (5.10) suggests that the dihydrazone, which exists in the *anti-cis* configuration in the free State, attains *staggered* configuration in the complexes (5.6) to (5.10). Similar coordination mode of the related malonoyl dihydrazone to the metal centre has been reported by Gopinathan and co-workers and by Lal et al **[14, 18]**.

The naphthyl proton multiplet appears in the region δ 7.07–8.44 ppm in the complexes (5.6) to (5.10). The complexes (5.7) to (5.10) show additional resonances in the region δ 7.72–7.88 ppm (Table 5.3). These signals are attributed to arise due to *ortho* protons of pyridyl ring and methyl protons of pyridine, 2-picoline, 3-picoline and 4-picoline molecules. These signals are upfield shifted as compared to their position in free pyridine,

2-picoline, 3-picoline and 4-picoline molecules, respectively **[19, 20]** and is similar to those in monometallic complexes (5.2) to (5.5) indicating the coordination of these neutral donor molecules to the metal centre. Hence further discussion on this aspect is redundant.

^{13}C Nuclear Magnetic Resonance Spectroscopy

An effort was made to characterize the complexes by ^{13}C NMR spectroscopy. However, all of the complexes gave a featureless spectrum which is most probably due to their poor solubility in DMSO.

Infrared Spectroscopy

Some of the structurally significant IR spectral bands for the free dihydrazone (H_4nsh) and its Zn(II) complexes are set out in Table. 5.4.

The IR spectra of the complexes (5.1), (5.3), (5.4), (5.5) (5.6), (5.7) and (5.10) have been shown in Fig. (5.13) to (5.19). A comparison of the IR spectra of the complexes with that of the free ligand (H_4nsh) suggests that the dihydrazone is coordinated to the metal centre in enol form in all of the complexes.

All of the complexes show a strong band in the region 3420–3500 cm^{-1}. The IR spectra of the complexes are complicated in the region 3000–3530 cm^{-1} because of occurrence of bands due to stretching vibrations of secondary -NH groups, lattice and coordinated water molecules and naphtholic –OH groups. The bands in this region also have contribution from bands arising due to water molecules absorbed by KBr pellets which are moisture sensitive. In order to decide upon whether the bands in this region arise due to water molecules or hydroxo groups, the compounds were heated at 110 and 180 °C, respectively and the vapours evolved were identified by passing through a trap containing anhydrous copper sulfate. The complexes (5.1) and (5.6) showed weight loss corresponding to one water molecule per metal centre at 180 °C. This indicated the presence of one molecule of water in the first coordination sphere around the zinc centre in the complexes (5.1) and (5.6). However, the complexes (5.2) to (5.5) and (5.6) to (5.10) showed no weight loss either at 110 or 180 °C indicating that, in these complexes, the bands in the region 3420–3500 cm^{-1} arise due to moisture absorbed by KBr pellets. Further, in all of the complexes, the band in the region 3000–3530 cm^{-1} have contribution from stretching vibration of naphtholic –OH groups. The position of the band in this region suggests the presence of new type of hydrogen bonding in these complexes.

The ν(NH) band observed at 3244 cm^{-1} in the uncoordinated dihydrazone does not appear in the IR spectrum of all of the complexes. This suggests the destruction of amide structure of ligand in these complexes. The absence of bands due to secondary –NH group in the region 3240–3500 cm^{-1} in combination with the absence of amide I (>C=O) band in all of the complexes suggests collapse of amide structure of the dihydrazone as a result of enolization and its coordination through oxygen atom of >C=O group to the metal centre in the enol form. This is also corroborated by the absence of the very strong ligand band at 1672 cm^{-1} in the IR spectra of the complexes.

In the free dihydrazone, the ν(C=N) band appears as a couple of bands at 1633 and 1593 cm^{-1}. This band appears as a single band in the IR spectrum of the complexes (5.2) to (5.5) while as a couple of bands in the complex (5.1) and the complexes (5.6) to (5.10) in the region 1618 – 1602 cm^{-1} and thus shows either no shift as in the complexes (5.1) to (5.5) or shift to lower frequency by 1–2 cm^{-1} respectively. This indicates the coordination of azomethine nitrogen to the metal centre **[21]**. The small shift in νC=N stretching frequency in the complexes is due to the difference of bonded species i.e. from >C=N..... H to >C=N→M. The amide III band at 1321 cm^{-1} in the free dihydrazone registers a shift to higher frequency by 7–20 cm^{-1} in all of the complexes showing the involvement of >C=O in coordination.

The band of weak intensity at 1540 cm^{-1} in the IR spectrum of the free dihydrazone is assigned to amide II + ν(C–O) (naphtholic). This band shifts to higher frequency in all of the complexes except the complex (5.1) in which it appear at 1508 cm^{-1} while it appears in the region 1542–1559 cm^{-1} in the complexes (5.2) to (5.10). This band in the region 1508–1559 cm^{-1} in all of the complexes is assigned to ν(NCO^-) vibration of the newly formed NCO^- group as a result of enolization of the dihydrazone **[22]**. This is further supported by the absence of -NH band in the IR spectrum of all of the complexes. The assignment of this band in the region 1508–1553 cm^{-1} remains quite tentative unless confirmed by isotopic substitution study.

A band of medium intensity observed at 1281 cm^{-1} due to ν(C–O) vibration in the free ligand, shifts to higher frequency by 2–7 cm^{-1} and appears in the region 1284–1288 cm^{-1} in the IR spectra of all the complexes. The shift of ν(C–O) band to higher frequency indicates the coordination of naphtholic OH group to the metal centre in the complexes.

The ν(N–N) band observed at 1029 cm^{-1} in the IR spectra of the free dihydrazone shifts to higher frequency by 1–21 cm^{-1} in the complexes (5.1) to (5.5) and appears in the

region 1030–1050 cm^{-1}. However in the homobimetallic complexes (5.6) to (5.10) this band shifts to higher frequency by 55–56 cm^{-1} .The magnitude of shift of this band is consistent with the involvement of only one nitrogen atom of >N – N< group in bonding to the metal centre **[23]**.

All of the complexes show a new band in the region 528–539 cm^{-1}. This band is tentatively assigned to ν(M–O) **[24]** due to coordinated naphtholic –OH group. However, the complexes (5.6) to (5.10) show an additional weak band in the region 468 – 473 cm^{-1} which is assigned to ν(M–O) (enolate). The presence of this band indicates bonding between enolate oxygen and zinc centre. On the other hand this band is absent in the IR spectra of the complexes (5.1) to (5.5) ruling out the possibility of coordination of carbonyl oxygen to zinc centre. A new non-ligand band observed in the region 870 – 873 cm^{-1} in the IR spectra of the complexes (5.6) to (5.10) is assigned to the stretching vibration of the tetra-atomic species [M<O>M] resulted form involvement of naphtholate oxygen atom in bridge formation. The presence of this band indicates that the Zn(II) atoms are tethered together through naphthoxo bridging **[25].**

Further, all of the complexes show a new weak intensity band in the region 1003–1010 cm^{-1}. This band is assigned to ring breathing mode of pyridine, 2-picoline, 3-picoline and 4-picoline molecules in the complexes (5.2) to (5.5) and (5.7) to (5.10). The presence of this band in these complexes further indicates the coordination of pyridine, 2-picoline, 3-picoline and 4-picoline molecules to the metal centre **[26]**.

Conclusion

In this chapter, monometallic and homobimetallic Zn(II) complexes derived from the dihydrazone ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh) have been described.

In case of monometallic complexes, it has been found that $Zn(OAc)_2.2H_2O$ reacts with H_4nsh which is produced in situ by the reaction of succinoyl dihydrazine and 2-hydroxy-1-naphthaldehyde in methanol to give the Zn(II) complex [Zn(H_2nsh)(H_2O)] (5.1). The reaction of complex (5.1) with pyridine bases in methanol gave Zn(II) complexes of composition [Zn(H_2nsh)(A)] (where A = pyridine (py) (5.2), 2-picoline (2-pic) (5.3), 3-picoline (3-pic) (5.4), 4-picoline (4-pic) (5.5)). On the other hand the reaction of the title ligand with $Zn(OAc)_2.2H_2O$ in 1:3 molar ratio in methanol led to the formation of homobimetallic Zn(II) complex [Zn_2(nsh)(H_2O)$_2$] (5.6). The reaction of this complex with pyridine and substituted pyridine bases in methanol yielded the complexes [Zn_2(nsh)(A)$_2$]

(where A = pyridine (py) (5.7), 2-picoline (2-pic) (5.8), 3-picoline (3-pic) (5.9), 4-picoline (4-pic) (5.10)).

From the physico-chemical and spectroscopic studies presented and discussed in this chapter, it is evident that the present dihydrazone which is a polybasic multidentate ligand acts as a dibasic tetradentate ligand in all of the monometallic complexes while as a tetrabasic hexadentate ligand in the homobimetallic complexes. The dihydrazone coordinates to the metal centre in enol form in all of the complexes.

The azomethine proton signal in the uncoordinated dihydrazone and all of the monometallic complexes appears in the form of two resonances only. Such a feature associated with the ^{1}H NMR spectra of the complexes suggests that the dihydrazone is coordinated to the metal centre in the *anti-cis* configuration. On the other hand in the homobimetallic complexes the azomethine proton signal appears as a single resonance indicating that the dihydrazone coordinates to the metal centre in the *staggered* configuration. In the monometallic complexes, the different hydrazone parts of the dihydrazone coordinate to the same metal centre in *anti-cis* configuration. In the homobimetallic complexes, the different hydrazone parts of the dihydrazone molecule are coordinated to different metal centres in the *staggered* configuration. The two zinc(II) metal centres are tethered together by naphthoxo bridging in homobimetallic complexes. The Zn(II) centres are proposed to have five coordinate square-pyramidal stereochemistry in all of the complexes.

The tentative structures of the complexes are shown in Fig. 5.20 and Fig. 5.21

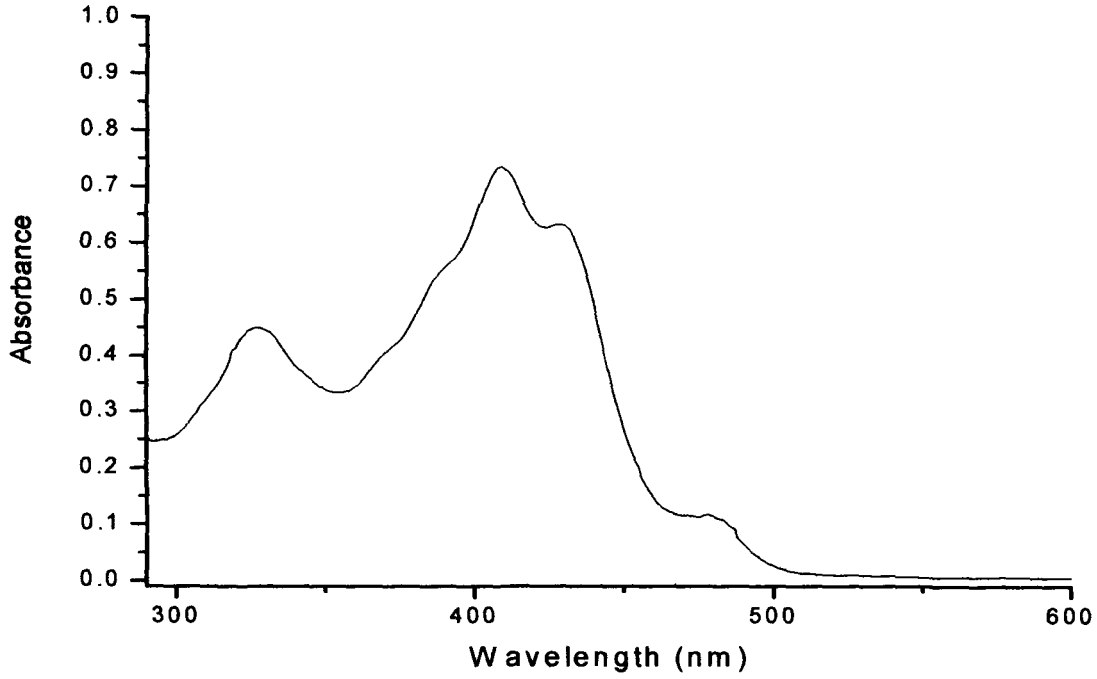


Fig. 5.1. Electronic spectrum of [Zn(H_2nsh)(H_2O)] (5.1) in DMF.

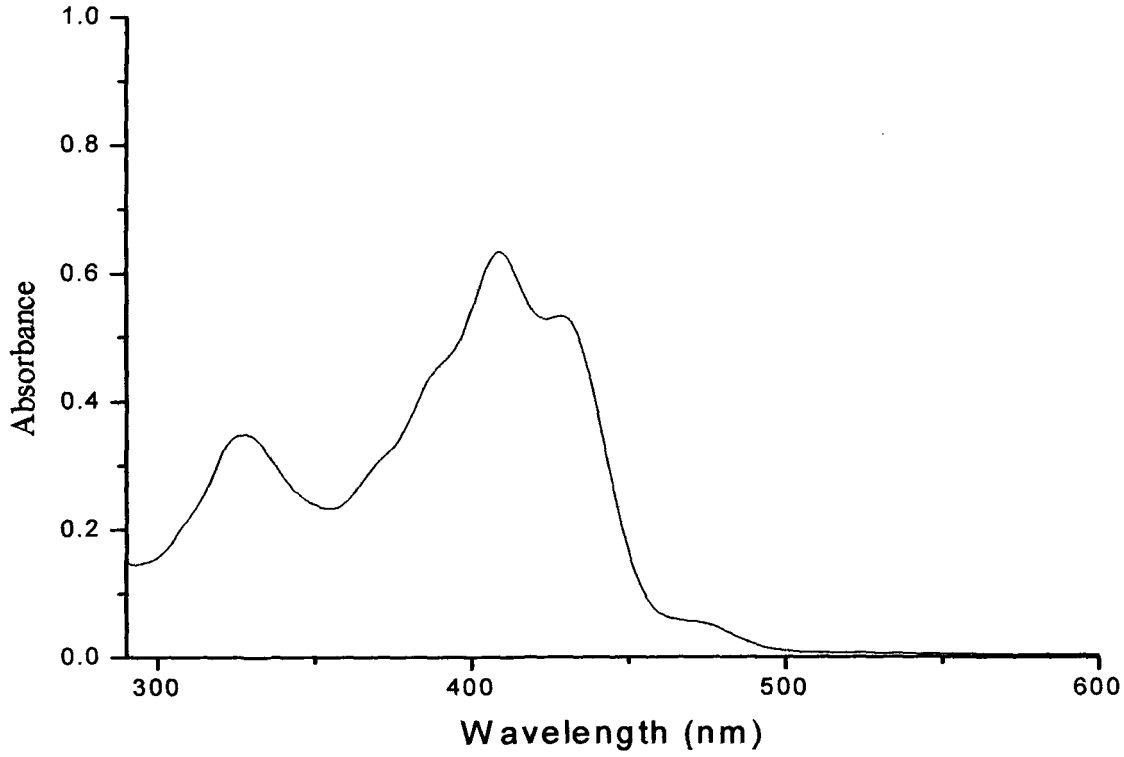


Fig. 5.2. Electronic spectrum of [Zn(H_2nsh)(py)] (5.2) in DMF.

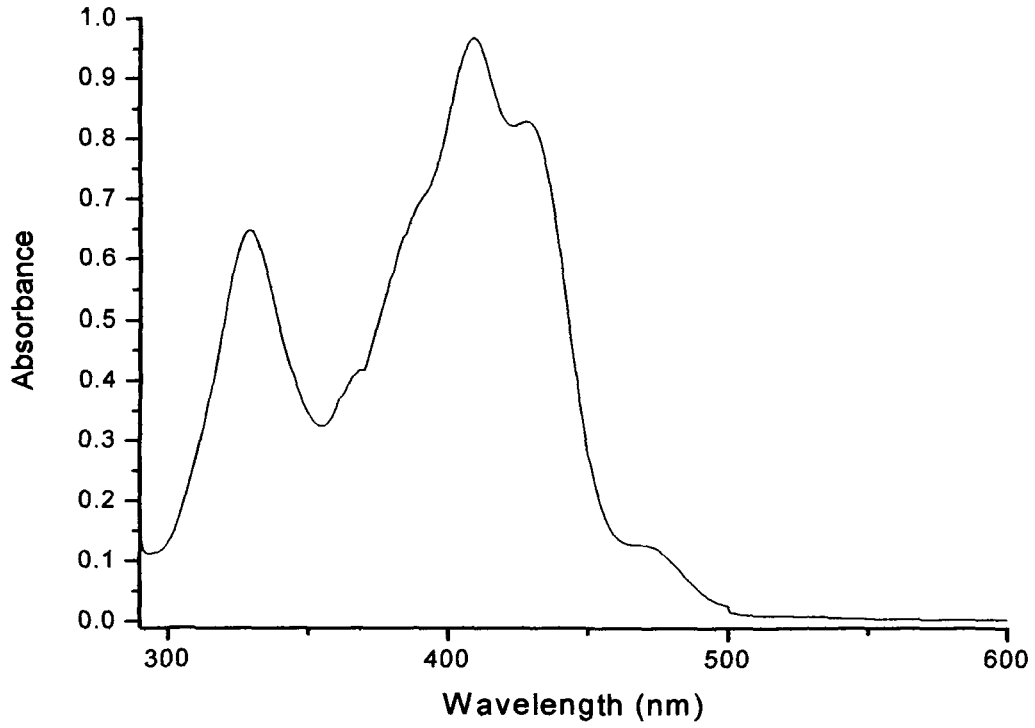


Fig. 5.3. Electronic spectrum of [Zn(H_2nsh)(4-pic)] (5.5) in DMF.

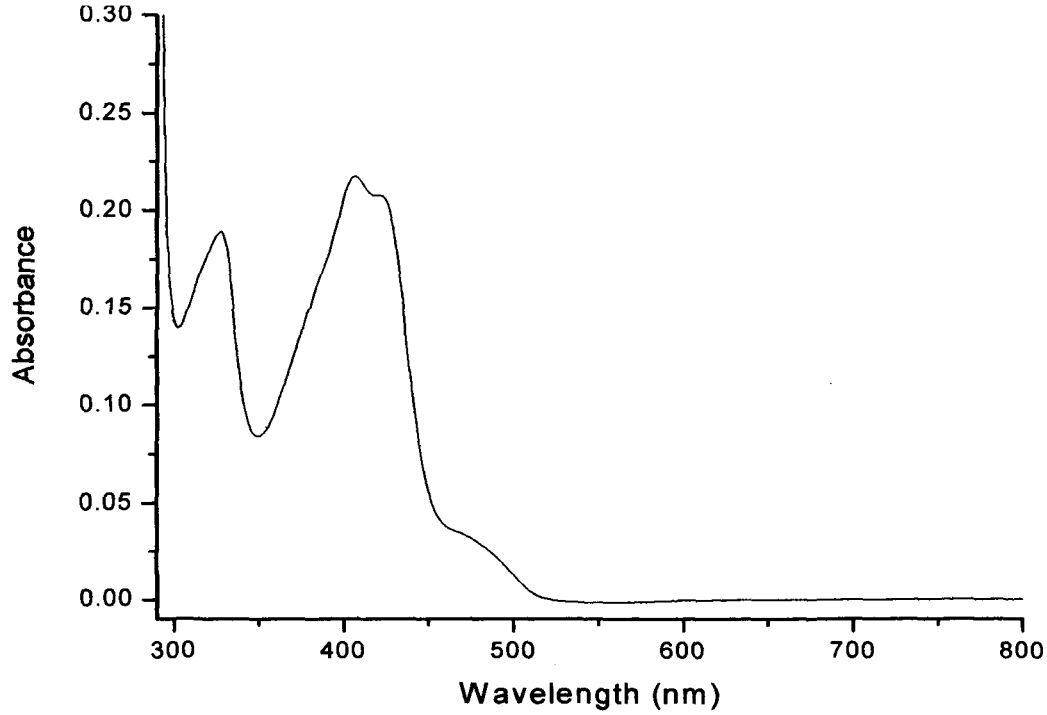


Fig. 5.4. Electronic spectrum of [Zn_2(nsh)(H_2O)$_2$] (5.6) in DMF.

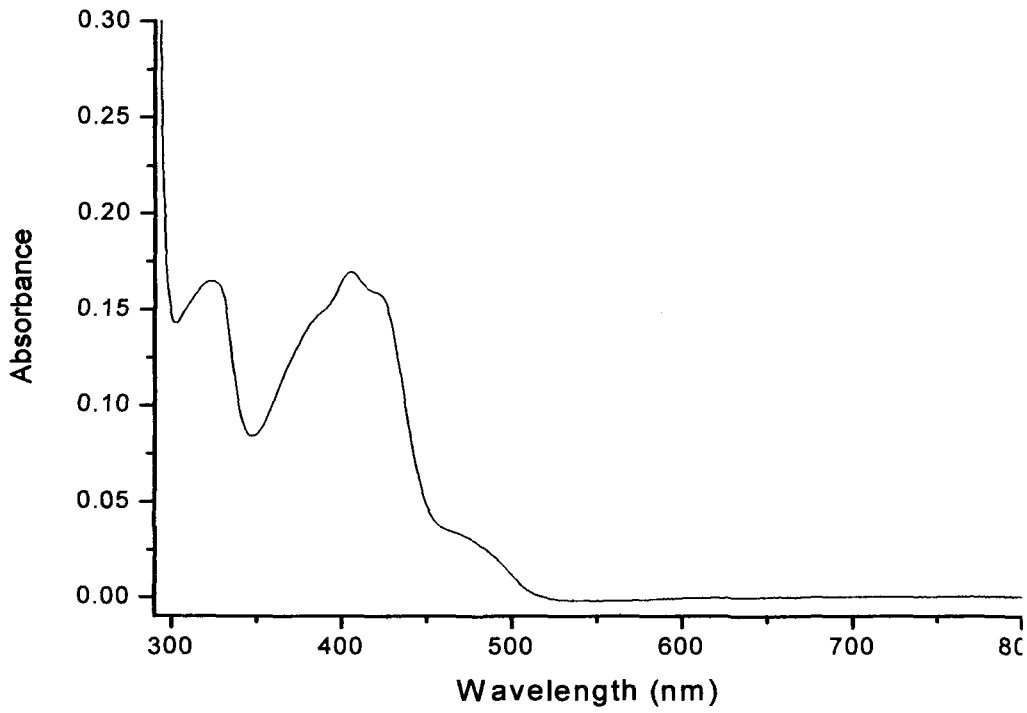


Fig. 5.5. Electronic spectrum of $[Zn_2(nsh)(py)_2]$ (5.7) in DMF.

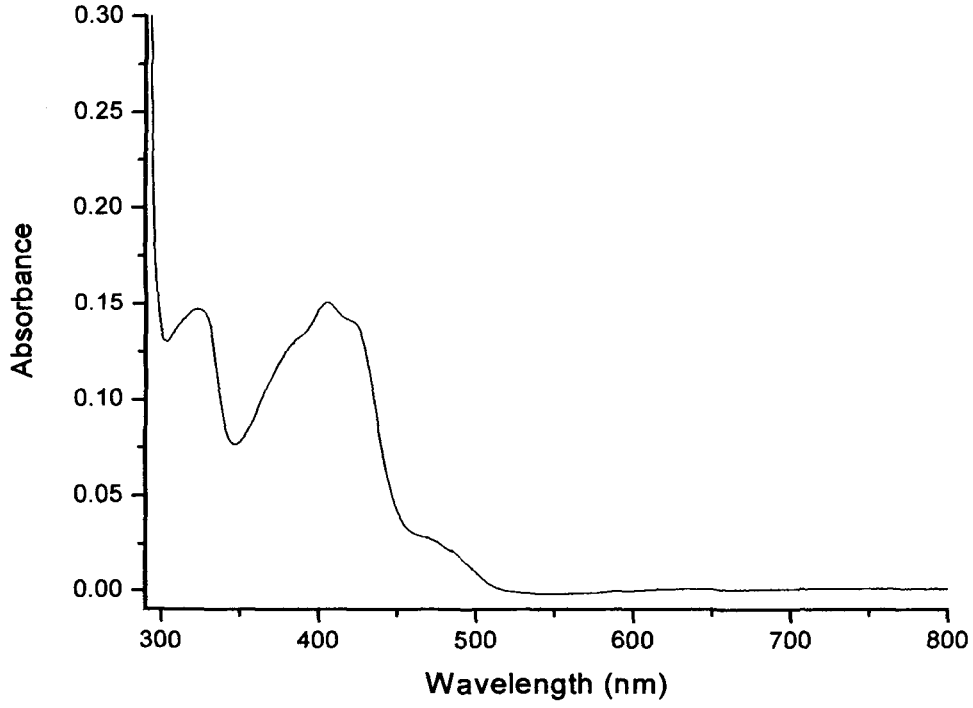


Fig. 5.6. Electronic spectrum of $[Zn_2(nsh)(3\text{-pic})_2]$ (5.9) in DMF.

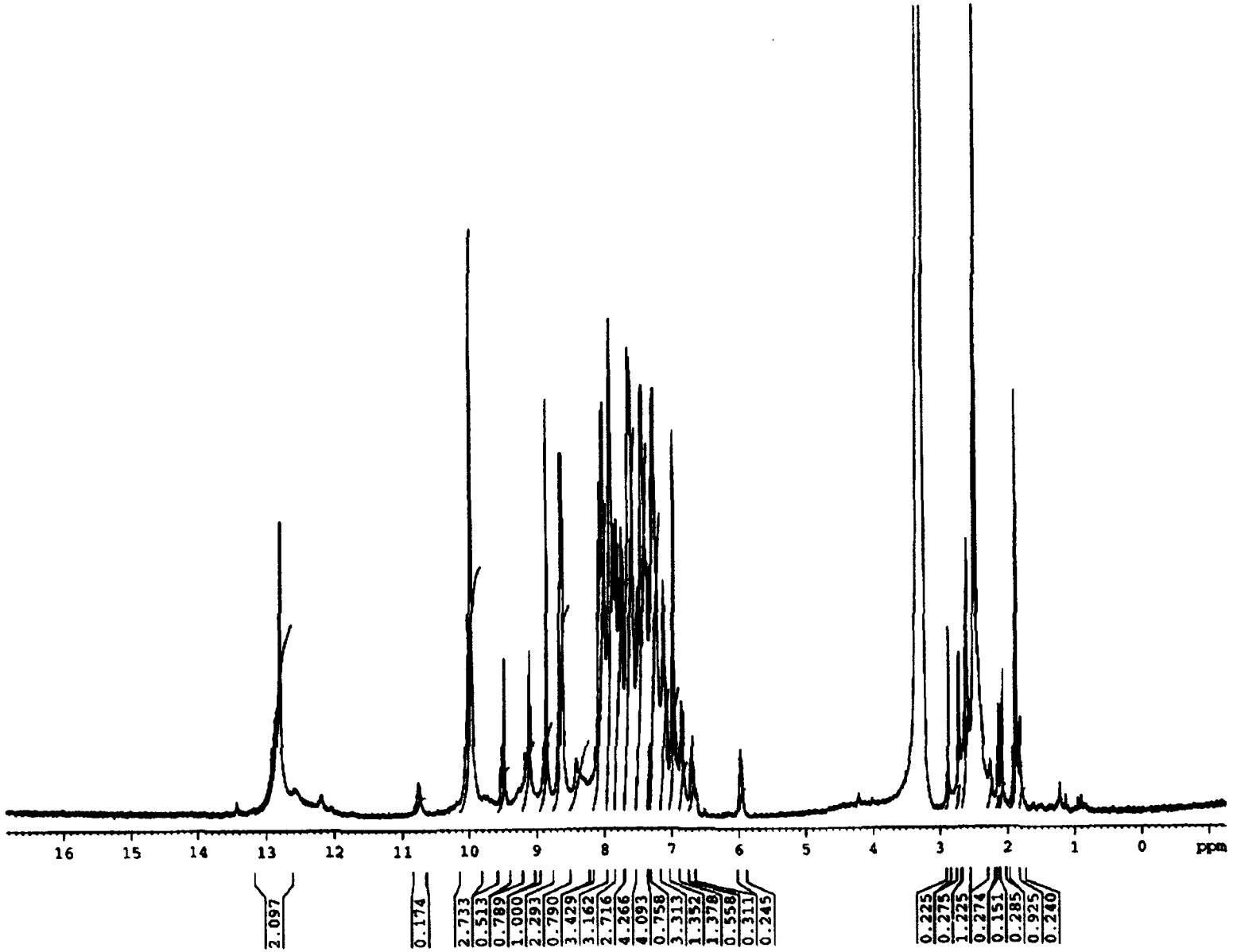


Fig. 5.7. ^{1}H NMR spectrum of $[Zn(H_2nsh)(H_2O)]$ (5.1) in DMSO-d_6.

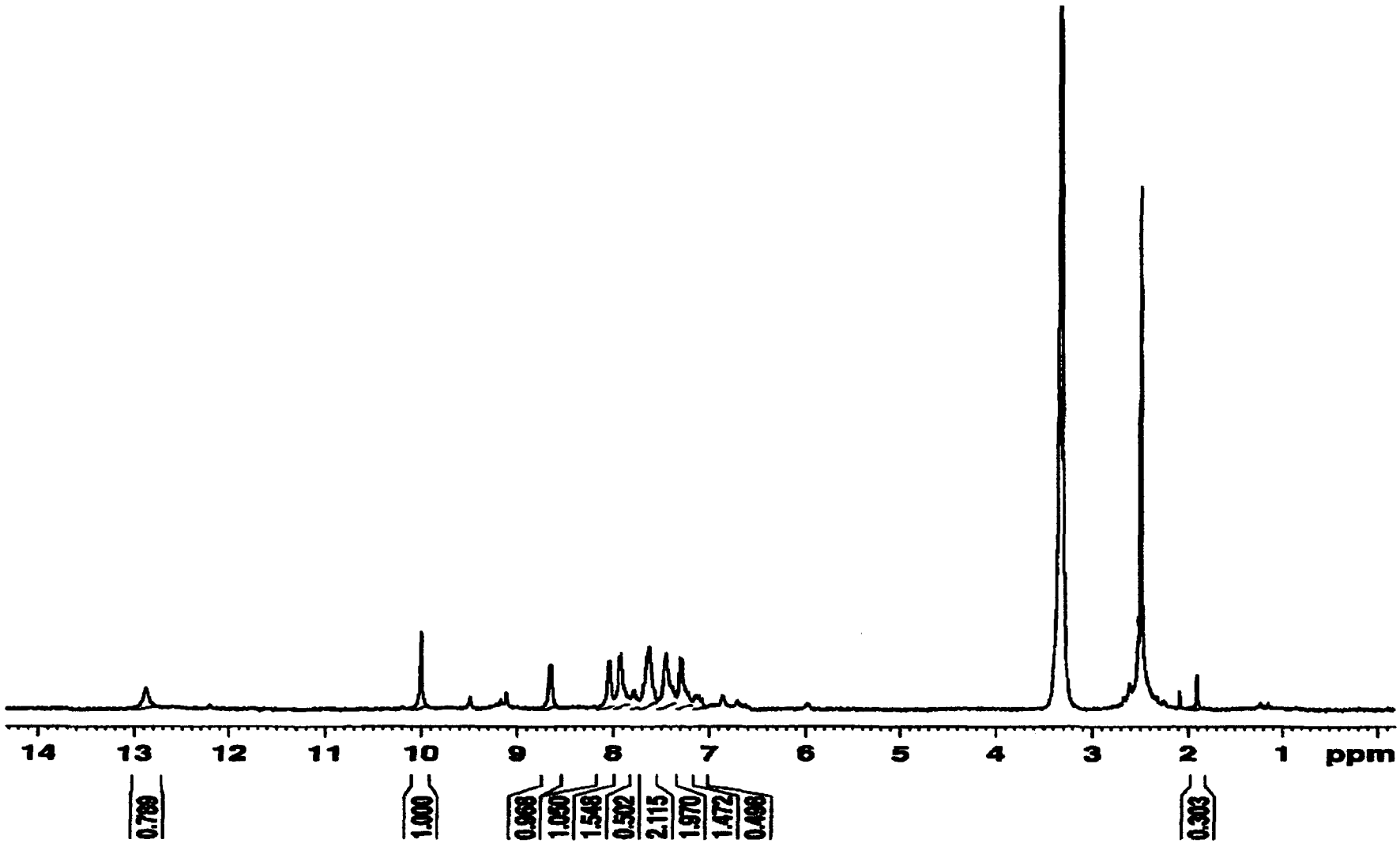


Fig. 5.8. ^{1}H NMR spectrum of [Zn(H_2nsh)(2-pic)] (5.3) in DMSO-d_6.

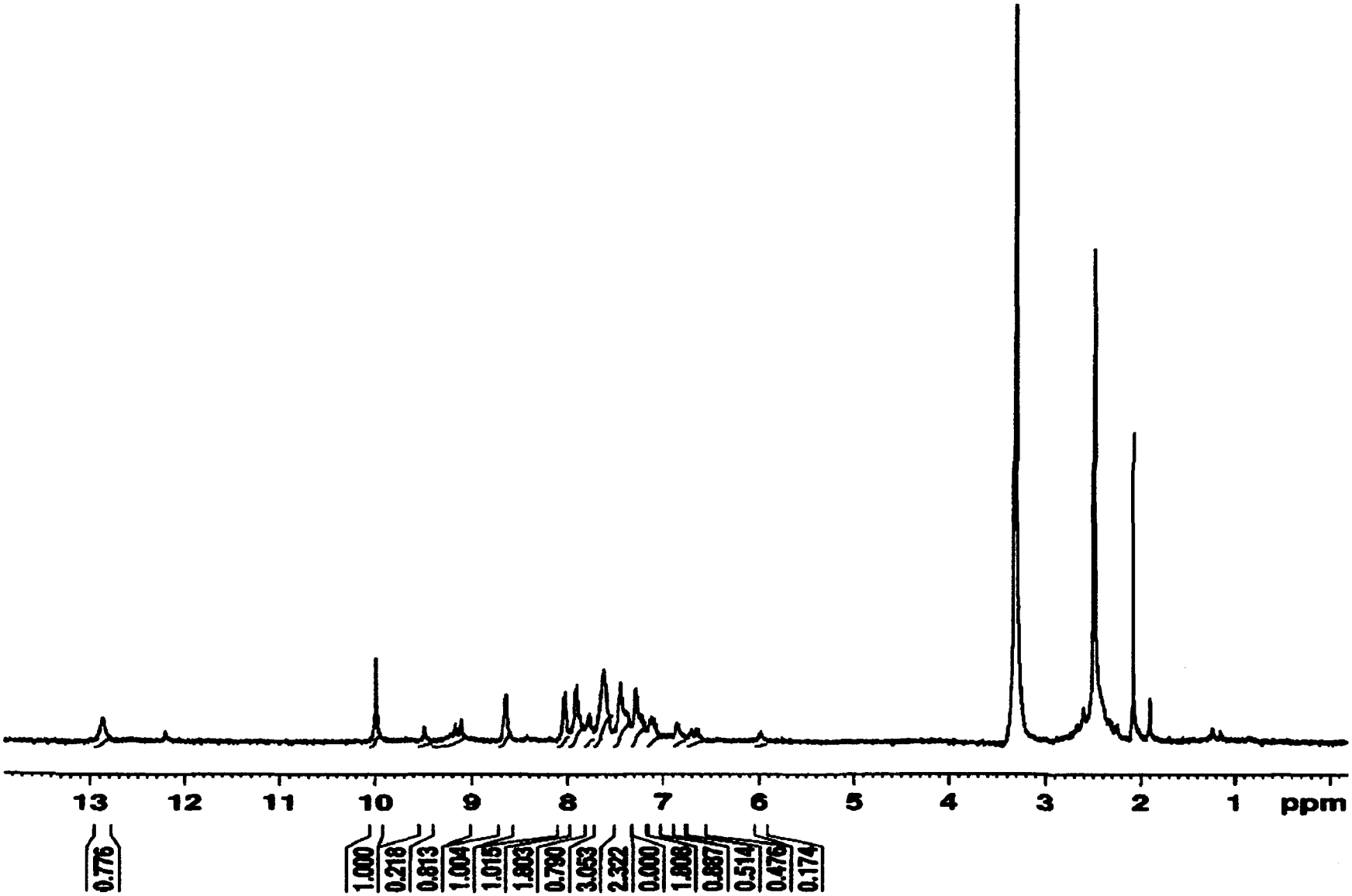


Fig. 5.9. ^{1}H NMR spectrum of [Zn(H_2nsh)(4-pic)] (5.5) in DMSO-d_6.

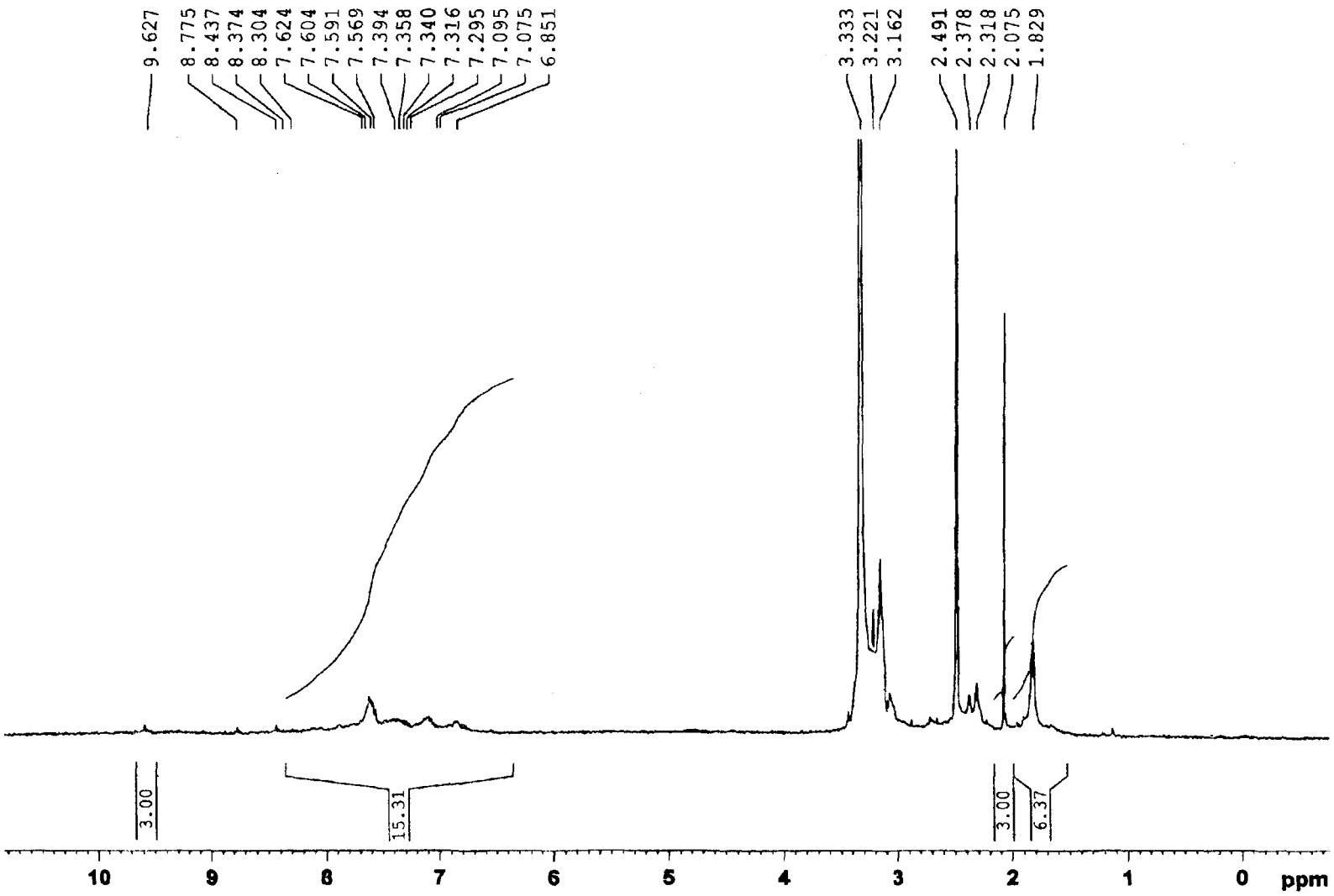


Fig. 5.10. ^{1}H NMR spectrum of [Zn_2(nsh)(H_2O)$_2$] (5.6) in DMSO-d_6

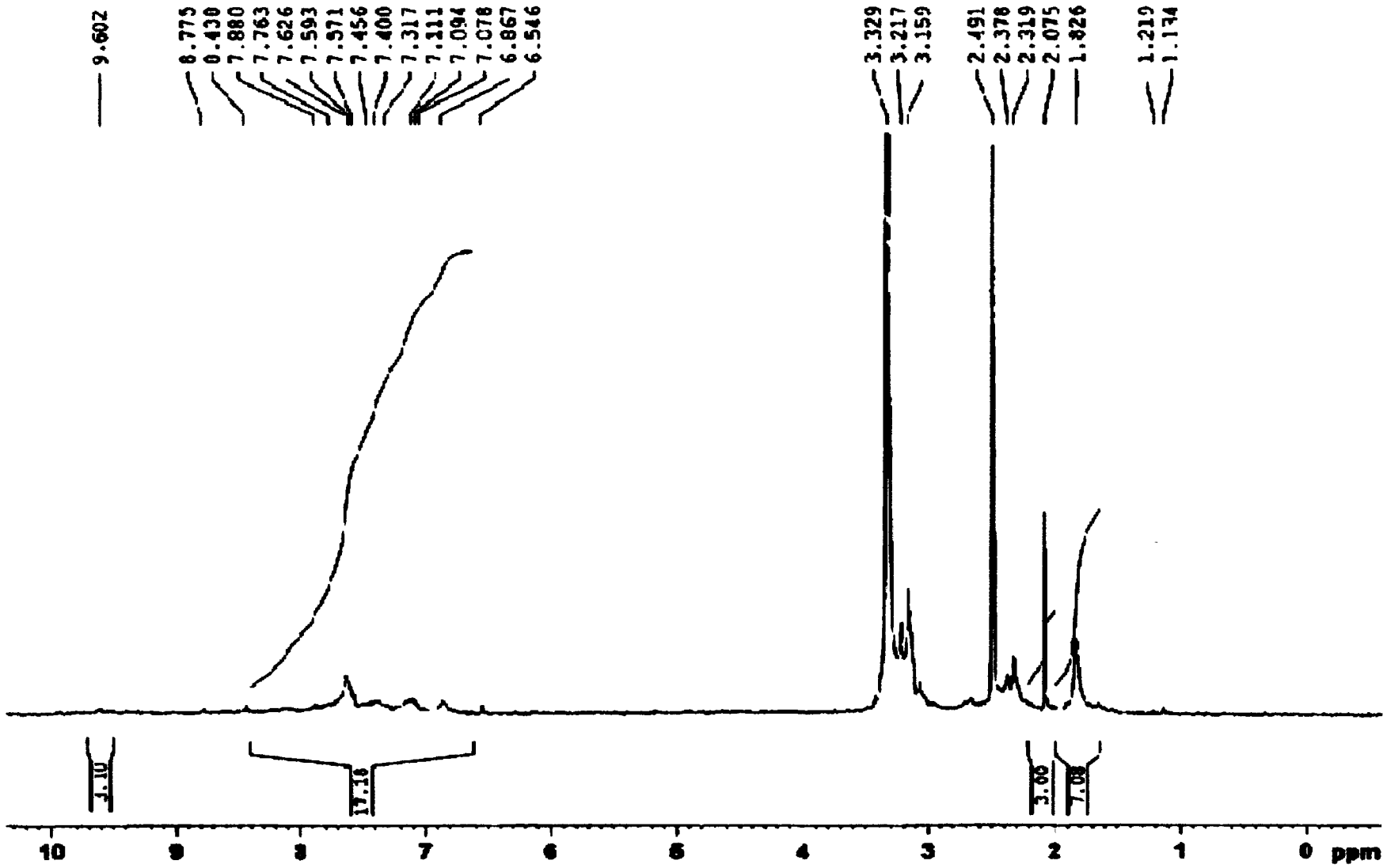


Fig. 5.11. ^{1}H NMR spectrum of [Zn_2(nsh)$(py)_2$] (5.7) in DMSO-d_6.

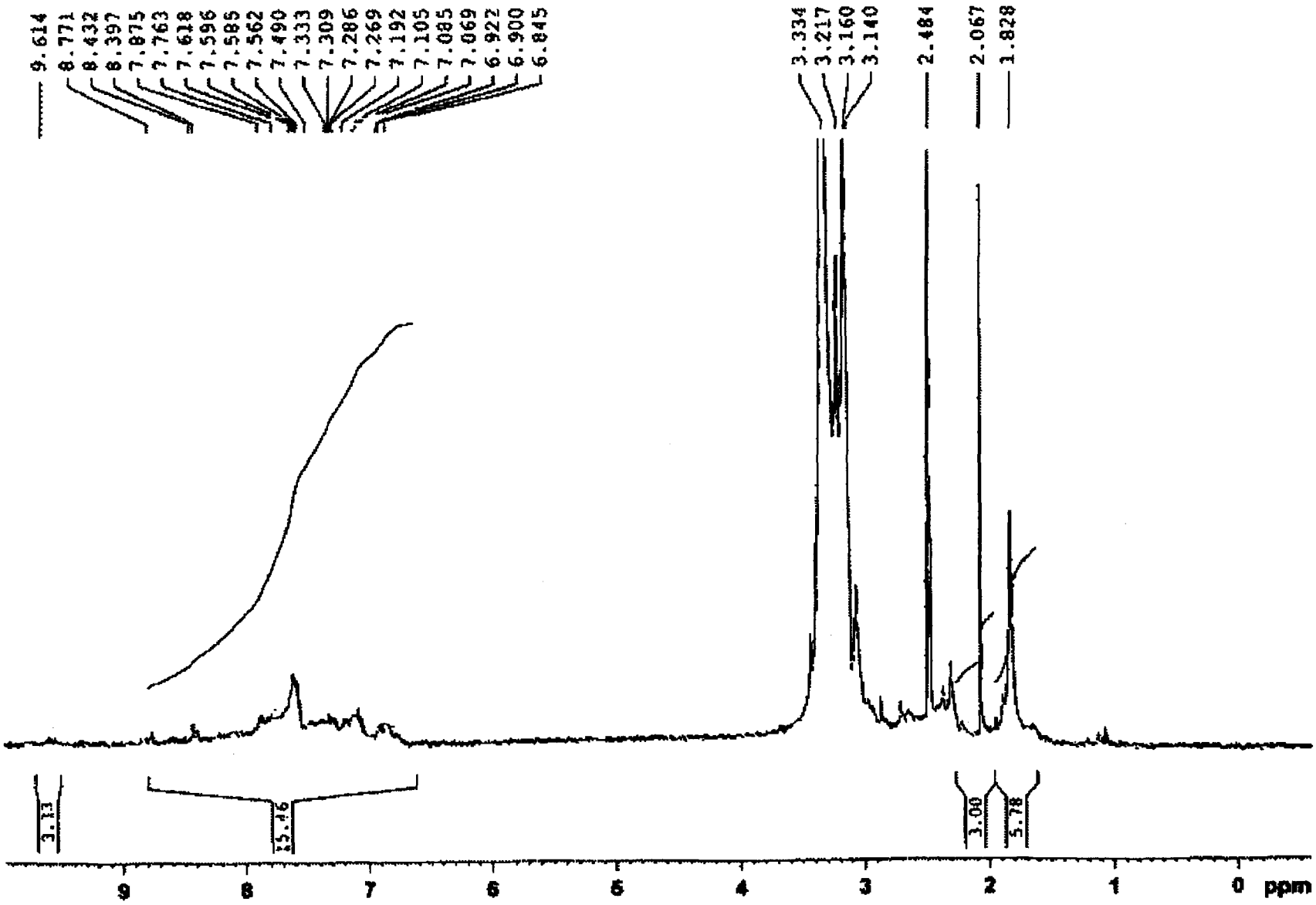


Fig. 5.12. ^{1}H NMR spectrum of $[Zn_2(\ \ nsh)(3\text{-pic})_2]$ (5.9) in DMSO-d_6.

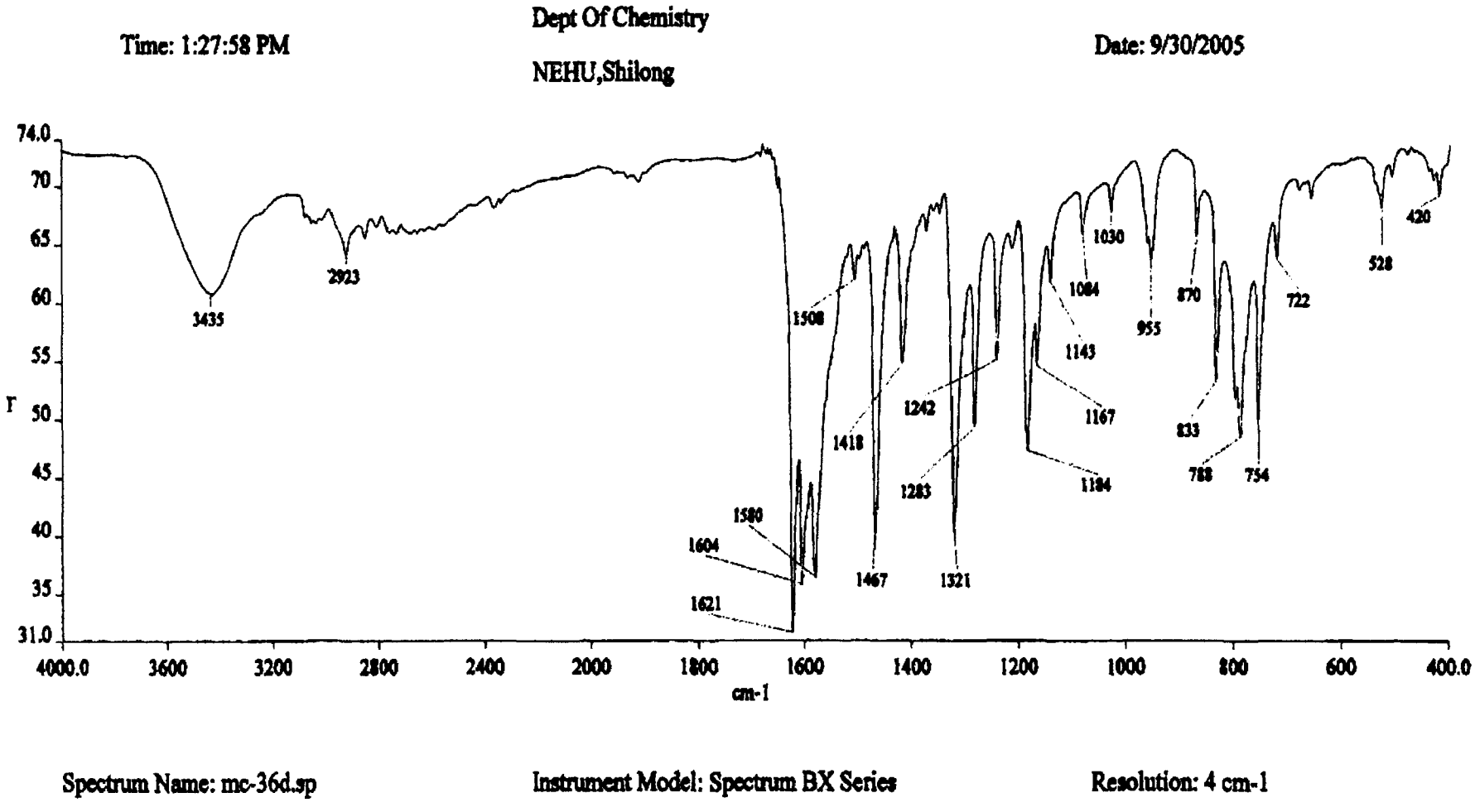


Fig. 5.13. Infrared spectrum of $[Zn(nshH_2)(H_2O)]$ (5.1) in KBr.

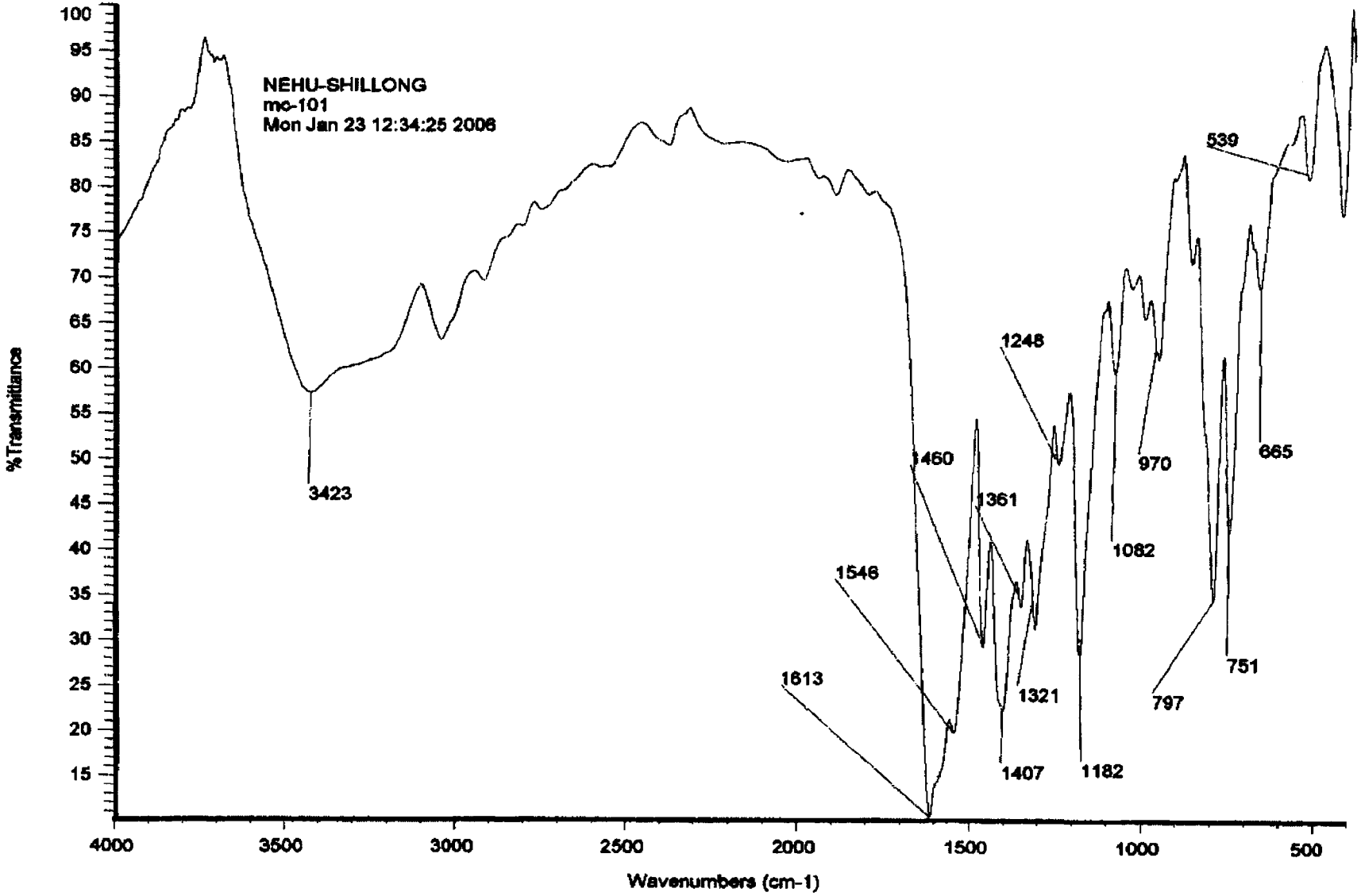


Fig. 5.14. Infrared spectrum of [Zn(nshH$_2$)(2-pic)] (5.3) in KBr.

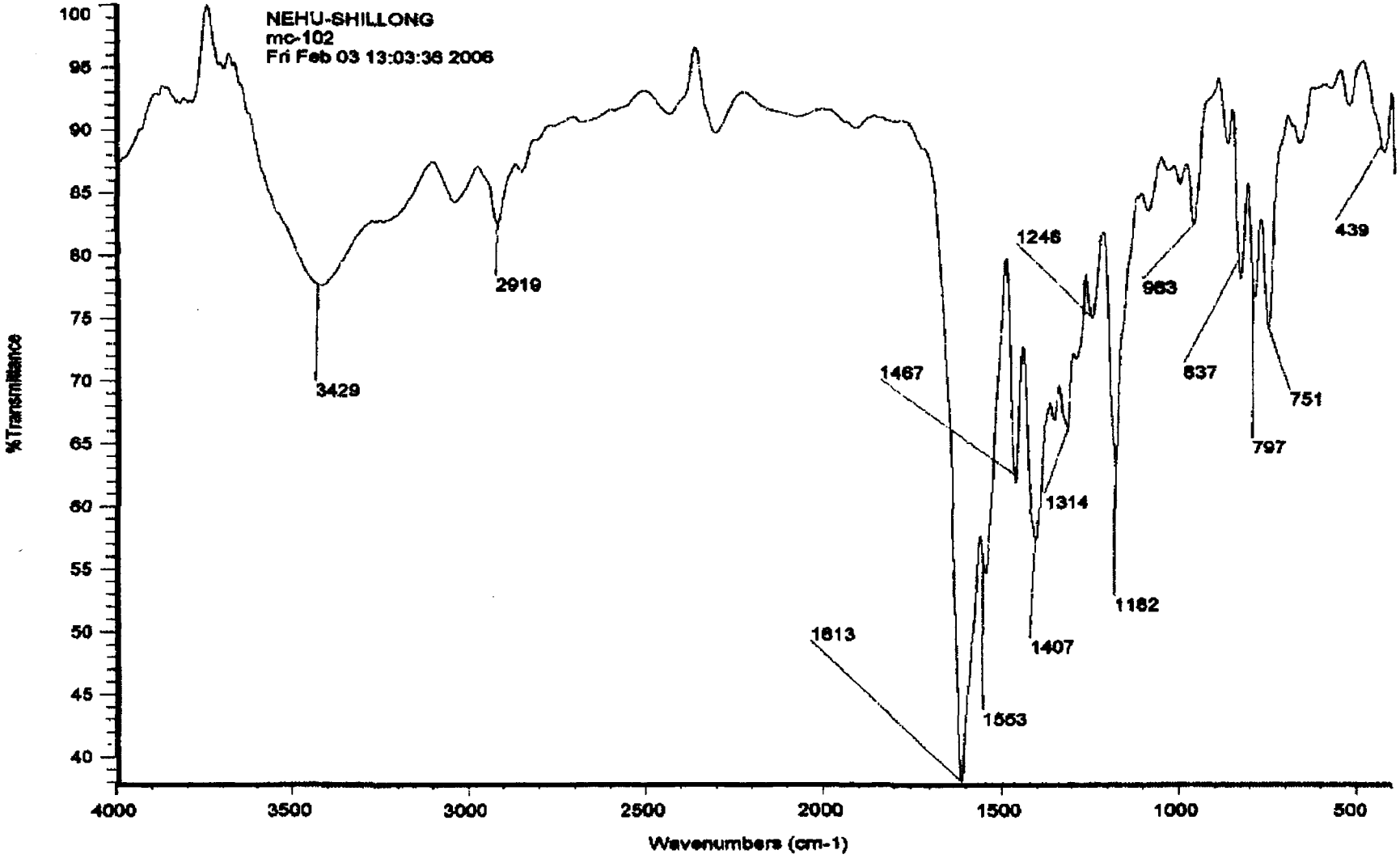


Fig. 5.15. Infrared spectrum of [Zn(nshH$_2$)(3-pic)] (5.4) in KBr.

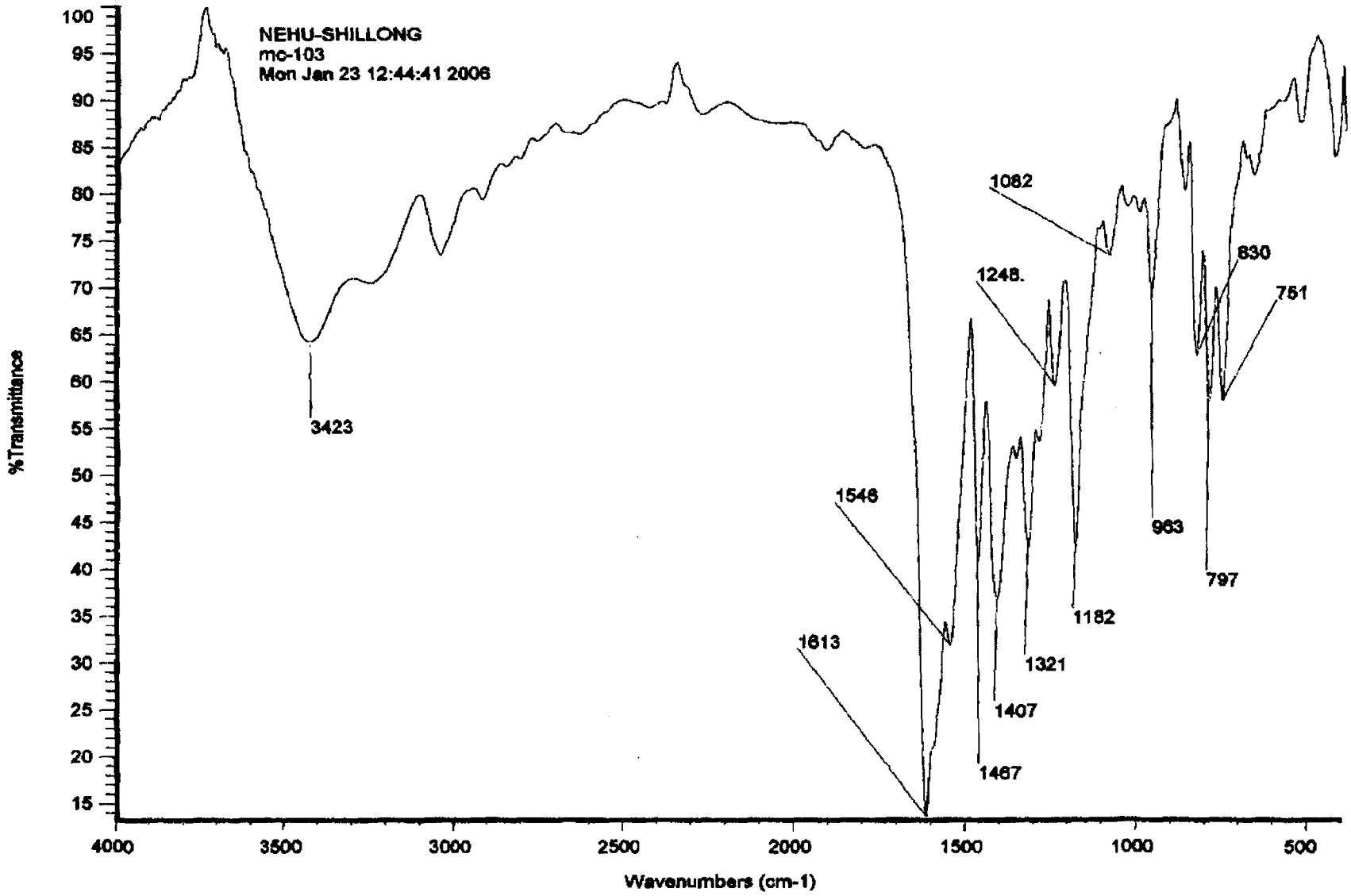


Fig. 5.16. Infrared spectrum of [Zn(H_2nsh)(4-pic)] (5.5) in KBr.

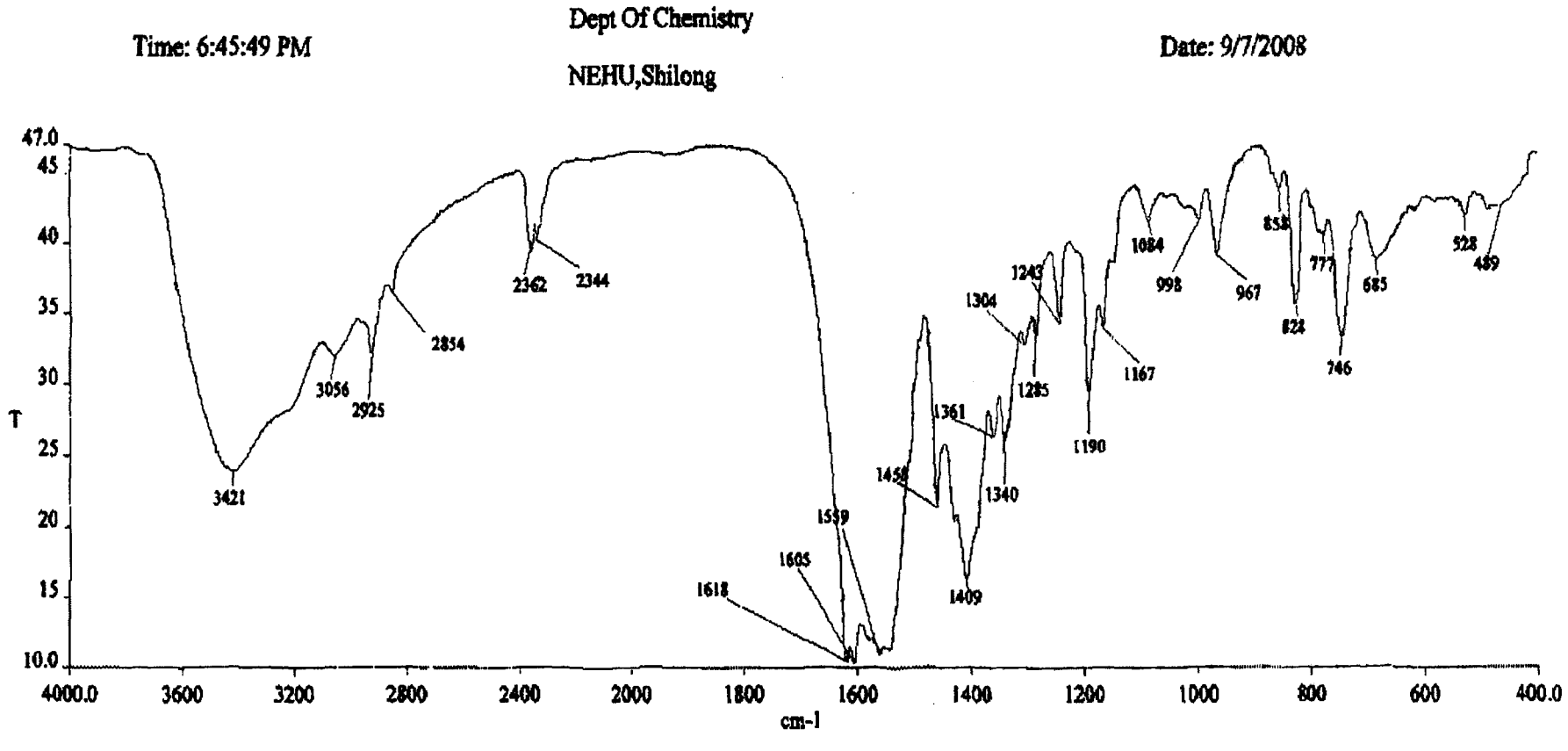


Fig. 5.17. Infrared spectrum of $[Zn_2(nsh)(H_2O)_2]$ (5.6) in KBr.

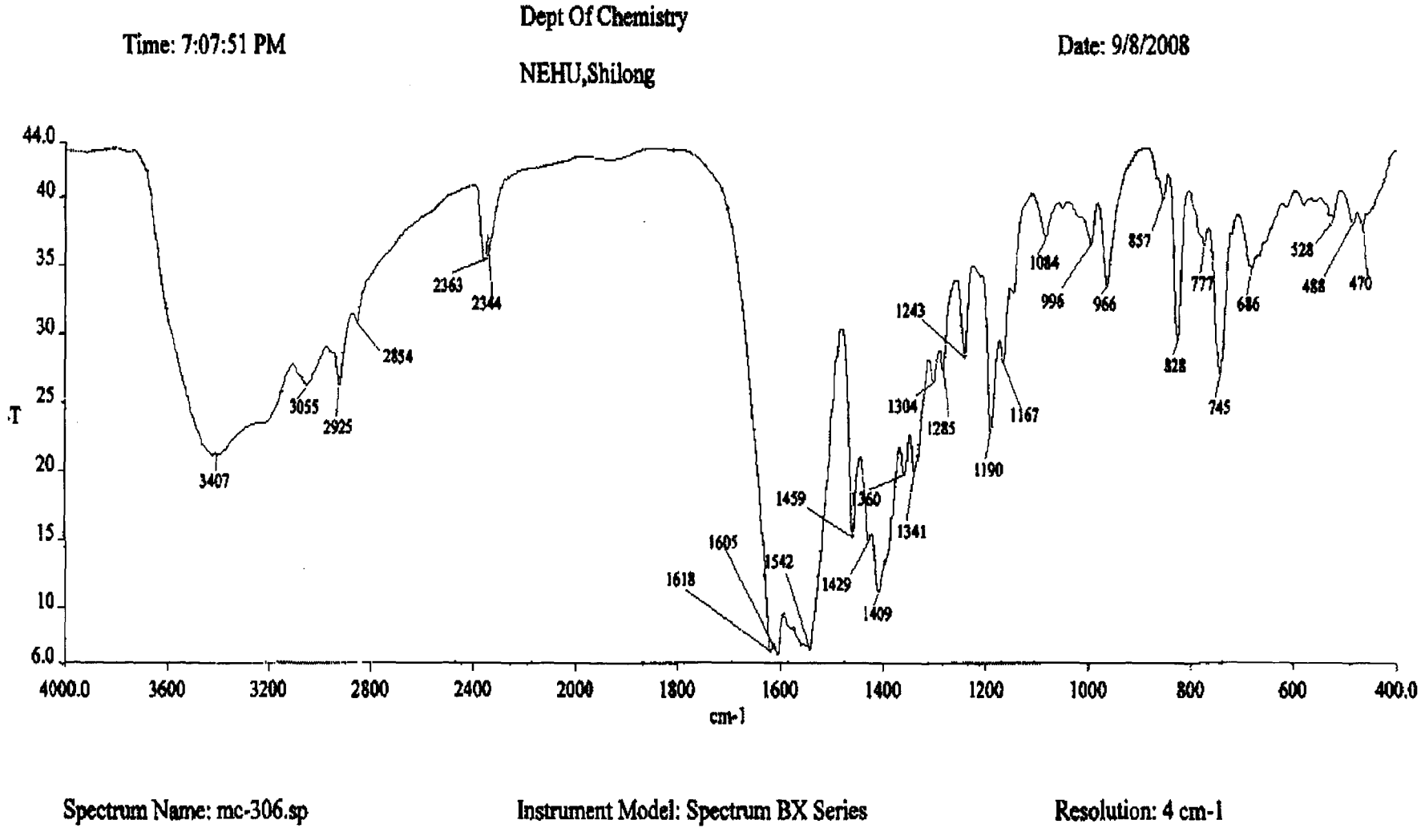


Fig. 5.18. Infrared spectrum of $[Zn_2(nsh)(py)_2]$ (5.7) in KBr.

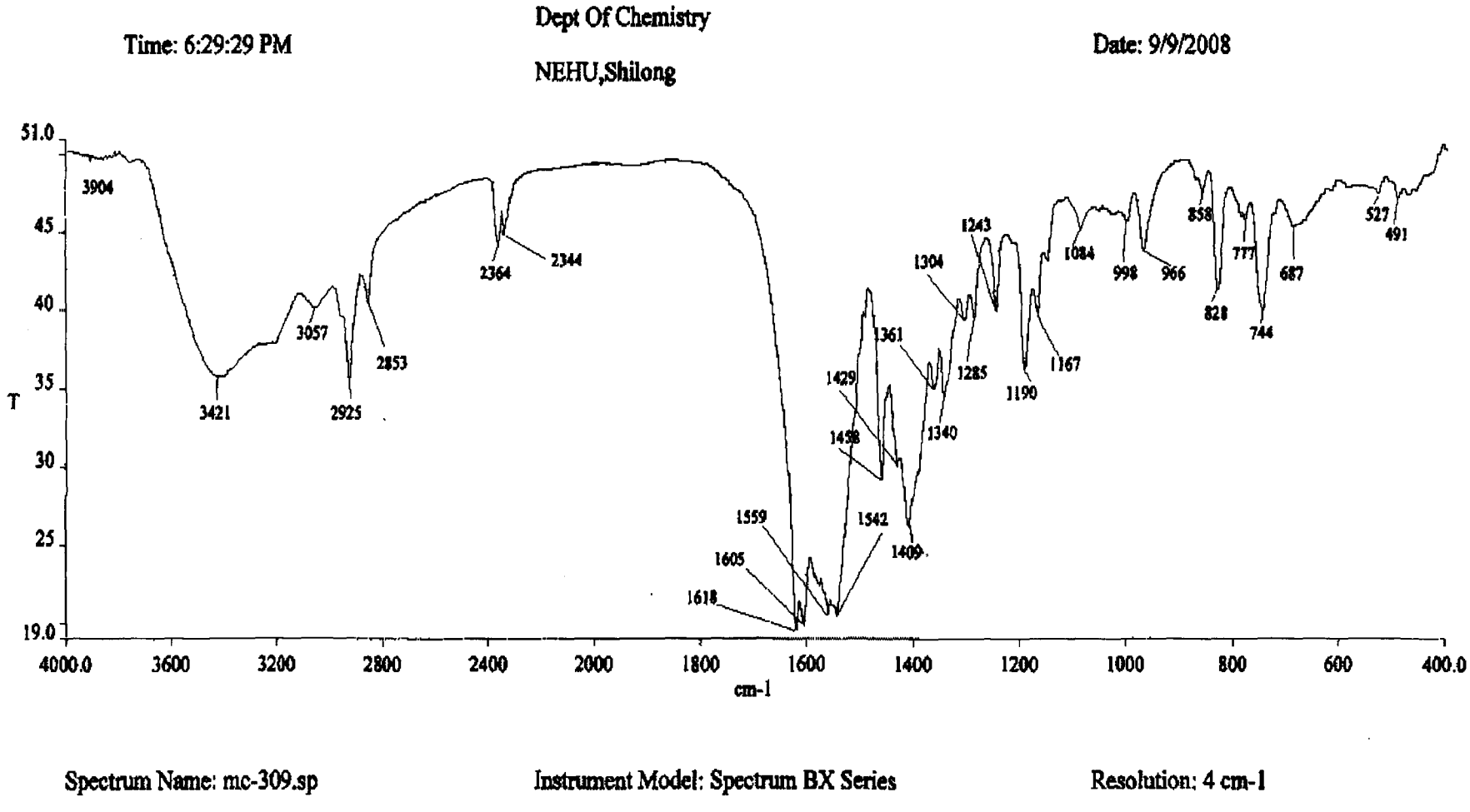


Fig. 5.19. Infrared spectrum of $[Zn_2(nsh)(4\text{-pic})_2]$ (5.10) in KBr.

Table 5.1: Analytical Data and Physical properties of monometallic Zn(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Sl. No	Complex and Colour	Magnetic Moment μ_B (BM)	D.P (°C)	Yield(%)	Analysis: Found (Calc.) (%)				Molar Conductance (Λ_M) Ohm^{-1}cm^{2}mol^{-1}
					Zn	C	H	N	
5.1	[Zn(H_2nsh)(H_2O)] yellow	Dia	>300	72.00	12.29 (12.20)	58.34 (58.28)	4.12 (4.14)	12.41 (10.45)	3.1
5.2	[Zn(H_2nsh)(py)] Yellow	Dia	272	65.00	11.02 (10.95)	62.31 (62.37)	4.21 (4.22)	11.68 (11.73)	2.9
5.3	[Zn(H_2nsh)(2-pic)] yellow	Dia	>300	62.00	10.85 (10.70)	62.88 (62.91)	4.43 (4.45)	11.42 (11.46)	2.5
5.4	[Zn(H_2nsh)(3-pic)] yellow	Dia	>300	63.00	10.83 (10.70)	62.89 (62.91)	4.42 (4.45)	11.44 (11.46)	2.3
5.5	[Zn(H_2nsh)(4-pic)] yellow	Dia	274	62.00	10.86 (10.70)	62.87 (62.91)	4.43 (4.45)	11.48 (11.46)	2.4
5.6	[Zn_2(nsh)(H_2O)$_2$] Yellow	Dia	>300	68.00	21.08 (21.19)	50.55 (50.59)	3.57 (3.59)	8.98 (9.08)	2.97
5.7	[Zn_2(nsh)(py)$_2$] yellow	Dia	>300	64.00	17.39 (17.69)	58.83 (58.48)	3.79 (3.82)	11.15 (11.36)	2.92
5.8	[Zn_2(nsh)(2-pic)$_2$] yellow	Dia	>300	63.00	17.08 (17.04)	59.26 (59.47)	4.22 (4.20)	10.98 (10.95)	2.59
5.9	[Zn_2(nsh)(3-pic)$_2$] yellow	Dia	>300	62.00	17.11 (17.04)	59.25 (59.47)	4.18 (4.20)	10.99 (10.95)	2.47
5.10	[Zn_2(nsh)(4-pic)$_2$] yellow	Dia	>300	61.00	17.09 (17.04)	59.29 (59.47)	4.23 (4.20)	10.94 (10.95)	2.58

Table 5.2: Electronic spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its Zn(II) complexes

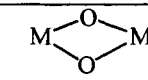
Sl. No	Ligand/ Complex	Electronic spectral bands λ_{max} (nm) (ε_{max} ($dm^3mol^{-1}cm^{-1}$))
	H_4nsh	317 (5480), 363 (5420)
5.1	$[Zn(H_2nsh)(H_2O)]$	327 (8850), 408 (14520), 432 (12386), 479 (2272)
5.2	$[Zn(H_2nsh)(py)]$	327 (8908), 409 (14595), 431 (12547), 480 (2247)
5.3	$[Zn(H_2nsh)(2\text{-pic})]$	326 (10931), 409 (19419), 430 (16557), 473 (2302)
5.4	$[Zn(H_2nsh)(3\text{-pic})]$	327 (11191), 409 (19620), 428 (16857), 472 (2522)
5.5	$[Zn(H_2nsh)(4\text{-pic})]$	330 (12973), 408 (19379), 431 (16436), 474 (2462)
5.6	$[Zn_2(nsh)(H_2O)_2]$	325 (2982), 405 (3274), 426 (2901), 480 (457)
5.7	$[Zn_2(nsh)(py)_2]$	327 (6163), 404 (7035), 423 (6763), 485 (846)
5.8	$[Zn_2(nsh)(2\text{-pic})_2]$	323 (4239), 406 (4355), 424 (4020), 483 (669)
5.9	$[Zn_2(nsh)(3\text{-pic})_2]$	324 (3773), 404 (3869), 424 (3568), 482 (528)
5.10	$[Zn_2(nsh)(4\text{-pic})_2]$	322 (5011), 404 (4911), 423 (4561), 482 (744)

Table 5.3: Structurally significant ^{1}H NMR Spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its Zn(II) Complexes

Sl. No	Ligand/ Complex	^{1}H NMR Spectral data (δ-ppm)					
		δ (-CH_2)	δ -naphthyl	δ (-CH=N)	δ (NH)	δ (OH)	δ (py/2-pic/3-pic/4-pic)
	H_4nsh	2.66 (s) 2.53 (s)	7.19 – 8.23(m)	9.05 (d, 62 Hz) 8.60 (d, 62 Hz)	9.99 (s) 11.14 (s)	12.73 (d, 152 Hz) 11.61 (d, 152 Hz)	—
5.1	[Zn(H_2nsh)(H_2O)]	2.88 (s) 2.49 (s)	7.06 – 8.08(m)	9.73 (d, 154 Hz) 8.99 (d, 154 Hz)	—	12.80 (s) 12.21 (s)	—
5.2	[Zn(H_2nsh)(py)]	2.61 (s) 2.49 (s)	7.07 – 8.04(m)	9.74 (d, 62 Hz) 8.88 (d, 62 Hz)	—	12.88 (s) 12.21 (s)	7.77 (8.613)†
5.3	[Zn(H_2nsh)(2-pic)]	2.49 (s) 2.07 (s)	7.07 – 8.04(m)	9.74 (d, 62 Hz) 8.88 (d, 62 Hz)	—	12.87 (s) 12.21 (s)	7.78(8.48)† 2.07(2.55)‡
5.4	[Zn(H_2nsh)(3-pic)]	2.49 (s) 2.07 (s)	7.12 – 8.04(m)	9.58 (d, 62 Hz) 8.89 (d, 62 Hz)	—	12.87 (s) 12.21 (s)	7.79(8.44)† 2.07 (2.32)‡
5.5	[Zn(H_2nsh)(4-pic)]	2.49 (s) 2.04 (s)	7.16 – 8.04(m)	9.74 (d, 62 Hz) 8.90 (d, 62 Hz)	—	12.85 (s) 12.21 (s)	7.79(8.60)† 2.04 (2.32)‡
5.6	[Zn_2(nsh)(H_2O)$_2$]	2.49 (s) 2.07 (s)	7.07 – 8.44(m)	9.63 (s)	—	—	—
5.7	[Zn_2(nsh)(py)$_2$]	2.49 (s) 2.07 (s)	7.07 – 8.44(m)	9.60 (s)	—	—	7.88 (8.613)†
5.8	[Zn_2(nsh)(2-pic)$_2$]	2.49(s) 2.07 (s)	7.07 – 8.44(m)	9.62 (s)	—	—	7.72(8.48)† 2.08(2.55)‡
5.9	[Zn_2(nsh)(3-pic)$_2$]	2.48 (s) 2.07 (s)	7.12 – 8.43(m)	9.61 (s)	—	—	7.88(8.44)† 2.08 (2.32)‡
5.10	[Zn_2(nsh)(4-pic)$_2$]	2.49(s) 2.07 (s)	7.16 – 8.44(m)	9.54 (s)	—	—	7.79(8.60)† 2.04 (2.37)‡

†ortho proton signal of pyridine/3-picoline/4-picoline; ‡ Methyl proton signal of 2-picoline/3-picoline/4-picoline

Table 5.4: Structurally significant Infrared (IR) bands (in cm^{-1}) for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its Zn(II) complexes.

Sl. No	Ligand/Complex	ν(OH + NH)	ν(C=O)	ν(C=N)	Amide II + ν(C–O) (naphtholic)	ν(NCO^-)	ν(C—O)	ν(N—N)	ν(M—O)	Other bands	
	H_4nsh	3423 m 3244 m 3051m	1672 vs	1633 vs 1593m	1540 m	—	1281m	1029 w	—	—	—
5.1	[Zn(H_2nsh)(H_2O)]	3435 m	—	1621s 1604 w	—	1508 w	1283 w	1030 w	528 w	—	—
5.2	[Zn(H_2nsh)(py)]	3436 m	—	1613 s	—	1547 w	—	1050 w	532 w	1010 w (py)	—
5.3	[Zn(H_2nsh)(2-pic)]	3423 m	—	1613 s	—	1546 w	—	1050 w	539 w	1010 w (2-pic)	—
5.4	[Zn(H_2nsh)(3-pic)]	3429 m	—	1613 s	—	1553w	1284 m	1050 w	533 w	1003 w (3-pic)	—
5.5	[Zn(H_2nsh)(4-pic)]	3423 s	—	1613 s	—	1546 w	1288 m	1043 w	539 w	1010 w (4-pic)	—
5.6	[Zn_2(nsh)(H_2O)$_2$]	3421 m 3056 w	—	1618 s 1605 w	—	1559 w	1285 w	1084 w	528 w	—	872 w
5.7	[Zn_2(nsh)(py)$_2$]	3407 m 3055 m	—	1618 vs 1605 s	—	1542 w	1285 w	1084 w	528 w	1052 w (py)	870 w
5.8	[Zn_2(nsh)(2-pic)$_2$]	3400 m 3053 m	—	1617 vs 1604vs	—	1543 w	1285 w	1084 w	530 w	1053 w (2-pic)	871 w
5.9	[Zn_2(nsh)(3-pic)$_2$]	3421 m 3056 m	—	1618 vs 1605 vs	—	1559 w	1285 w	1085 w	529 w	1052 w (3-pic)	871 w
5.10	[Zn_2(sh)(4-pic)$_2$]	3421 m 3057 w	—	1618 vs 1605vs	—	1546 w	1288 w	1084 w	527 w	1053 w (4-pic)	873 w

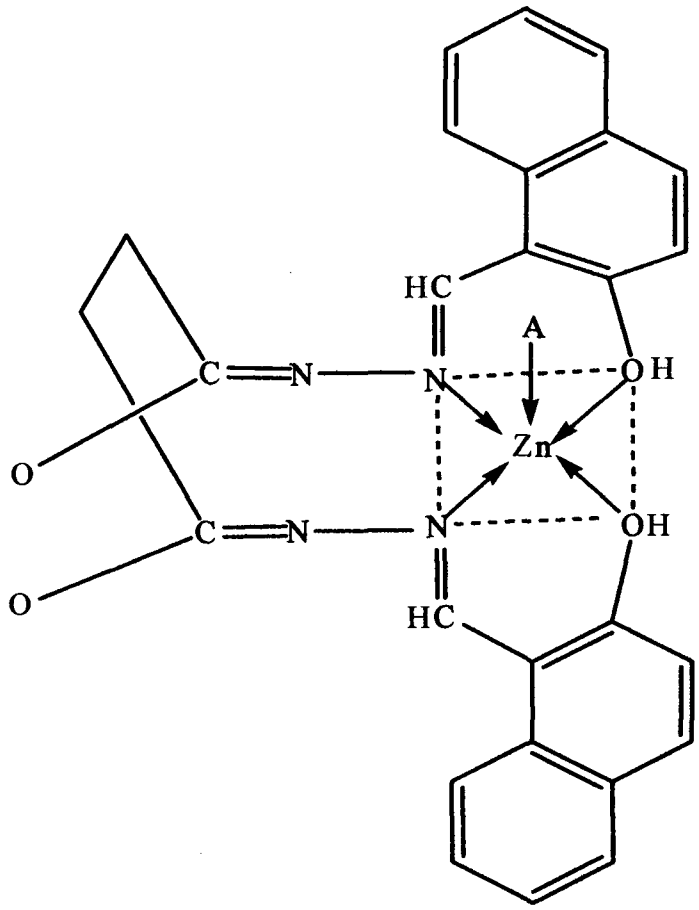


Fig. 5.20. Tentative structure of the complex [Zn(H_2nsh)(A)] (A = H_2O (5.1), py (5.2), 2-pic (5.3). 3-pic (5.4), 4-pic (5.5)).

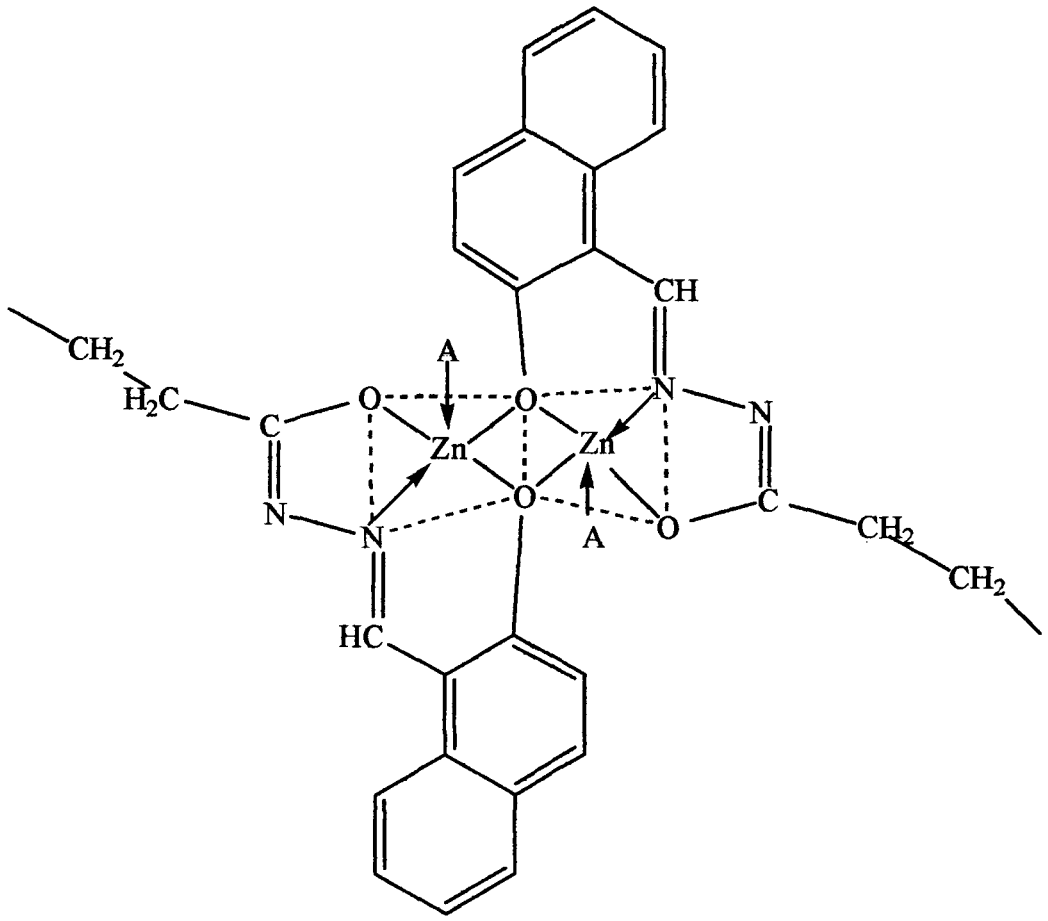


Fig. 5.21. Tentative structure of the complex $[Zn_2(nsh)(A)_2]$ (where A = H_2O (5.6), pyridine (py, 5.7), 2-picoline (2-pic, 5.8), 3-picoline (3-pic, 5.9), 4-picoline (4-pic, 5.10))

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CHAPTER VI

Synthesis, Characterization and Structural Assessment of Ni(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Introduction

The first two chapters describe the synthesis and characterization of monometallic and homobimetallic Mo(VI) complexes of the title dihydrazone respectively, while the third chapter describes the synthesis and characterization of zinc complexes of the same ligand. Nickel is another metal ion from the first transition series which has been selected for the synthesis of its complexes with the title dihydrazone and their characterization. Its selection is based on the consideration that a nickel or cobalt promoted molybdenum catalyst is important in industrial catalysis; particularly in the hydrosulfurizaton process **[5]** whereby organo sulfur compounds in petroleum feed stocks are heterogeneously desulfurized with dihydrogen. Moreover nickel is also present in six types of metalloenzymes namely ureases, hydrogenases, methyl coenzyme M reductase, carbon monoxide dehydrogenase, acetyl coenzyme A synthase and nickel superoxide dismutases **[1]**. Urease, the only nickel containing metallohydrolase catalyses the hydrolysis of urea to ammonia and carbon dioxide **[2]**. The microbial urease from klebsiella aerogenes has been found to contain two nickel(II) ions which are 3.5 Å apart within the dinuclear active site **[2]**. Further nickel occurs in heterobimetallic enzymes such as jack bean urease **[3]** and hydrogenase enzyme **[4]** in which nickel is present in combination with iron.

In addition nickel plays a prominent role in several areas of material chemistry. Some topical interplay between nickel coordination chemistry and material science exists in the use of Ni-containing alkoxides for the synthesis of ceramic materials by MOCUD and sol-gel processes, in the preparation of nanoscopic dendrimers incorporating Ni, the construction of 3D hyrid inorganic-organic porous materials with Ni coordination units and the fabrication of supported Ni catalysts and Ni nano-structures through nano-technology and paramagnetic high magnetism, culminating in the recent discovery of the first single molecule magnets based on Ni(II) centres **[6]**.

A survey of literature reveals that few complexes of Ni(II) ion with the dihydrazone ligand derived from the condensation of salicylaldehyde and related *o*-hydroxy aromatic

aldehydes and ketones with malonoyl dihydrazine and other acyl dihydrazines, aroyl dihydrazines and pyridoyl dihydrazines have been reported **[7, 8, 9, 10,]**, yet it has failed to locate any study on metal complexes of the dihydrazone ligand containing succinoyl fragment and bulky naphthyl fragment in its molecular skeleton.

In view of such an importance of nickel and its relation to hetero molybdenum systems and the fact that the previous chapters describe the synthesis and characterization of zinc and molybdenum complexes derived from the title dihydrazone ligand, it was of interest to study the monometallic and the homobimetallic Ni(II) complexes with the title ligand which might serve as precursors in the synthesis of heterobimetallic systems comprising of nickel and molybdenum. Accordingly, the synthesis and characterization of monometallic and homobimetallic Ni(II) complexes with the title dihydrazone by various methods in methanol are described in this chapter. The composition of the isolated complexes has been judged mainly from the analytical data. The structures of the complexes have been discussed with the help of molar conductance, magnetic moment, electronic and infrared spectral data.

Preparation of the complexes:

1. Preparation of $[Ni(H_2nsh)(H_2O)_2]$ (6.1)

Succinoyl dihydrazine (0.90 g, 6.16 mmol) was dissolved in hot methanol-water mixture (50 mL, 90:10). A solution of $Ni(OAc)_2.4H_2O$ (1.50 g, 6.02 mmol) in methanol (50 mL) was added to the above solution accompanied by gentle stirring for a period of 10 minutes. The resulting solution was refluxed for 15 minutes. To this was added a hot solution of 2-hydroxy-1-naphthaldehyde (2.70 g, 15.70 mmol) in methanol (100 mL). The reaction mixture was refluxed for 1 hour which precipitated a yellow-brown compound. The complex, thus, obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.72 g.

2. Preparation of $[Ni(H_2nsh)(A)_2]$ (where A = pyridine (py, 6.2); 2-picoline(2-pic, 6.3); 3-picoline(3-pic, 6.4); 4-picoline (4-pic, 6.5).

The complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1) (1.00 g, 1.86 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 minutes at 50-60°C. To this suspension, pyridine (1.50 mL, 18.10 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 3 hours which precipitated the light brown compound.

The compound, thus, obtained was filtered, washed repeatedly with hot methanol and then with ether and dried over anhydrous $CaCl_2$. Yield: 0.70 g

The complexes (6.3), (6.4) and (6.5) were also prepared in the same manner using 2-picoline, 3-picoline and 4-picoline instead of pyridine and maintaining the metal:base ratio at 1:10 respectively. Yield: 0.75 g (6.3); 0.77g (6.4); 0.78g (6.5).

3. Preparation of $[Ni_2(nsh)(H_2O)_4]$ (6.6)

The dihydrazone (H_4nsh) (1.00g, 2.20 mmol) was suspended in methanol (100 mL) and stirred for 30 minutes at 60 °C. To this was added a solution of $Ni(OAc)_2.4H_2O$ (1.65 g, 6.63 mmol) in methanol (50 mL) maintaining the molar ratio at 1:3. The reaction mixture was refluxed for 3 hours, which precipitated a brown compound. The compound, thus, obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.65 g.

4. Preparation of $[Ni_2(nsh)(A)_4]$ (where A = pyridine (py, 6.7); 2-picoline(2-pic, 6.8); 3-picoline(3-pic, 6.9); 4-picoline (4-pic, 6.10)

The complex $[Ni_2(nsh)(H_2O)_2]$ (6.6) (1.00 g, 1.55 mmol) was suspended in methanol (100 mL) by gentle heating at 60° C. To this suspension, pyridine (1.24 mL, 15.42 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture was refluxed for 2 hours. The resulting precipitate was isolated in the usual way. The complexes (6.7) to (6.10) were also synthesized by essentially following the above procedure using 2-picoline, 3-picoline and 4-picoline instead of pyridine maintaining the metal: base molar ratio at 1:10, respectively. Yield: 0.61 g (6.7); 0.65 g (6.8); 0.67 g (6.9); 0.64 g (6.10).

Results and Discussion

The complexes described in the present chapter together with their molecular formula, colour, decomposition point, percentage yield, analytical data, magnetic moment and molar conductance data are set out in Table 6.1. The electronic spectral data for the complexes have been shown in Table 6.2. The composition of the complexes has been deduced on the basis of elemental analyses as given below.

$[Ni(H_2nsh)(A)_2]$ (A = H_2O (6.1), py (6.2), 2-pic (6.3), 3-pic (6.4) and 4-pic (6.5))

$[Ni_2(nsh)(A)_4]$ (A = H_2O (6.6), py (6.7), 2-pic (6.8), 3-pic (6.9) and 4-pic (6.10))

The complexes are brown, yellow, light brown and dark yellow in colour. All of the complexes are air stable and decompose above 300 °C without melting. All of the complexes are insoluble in water and common organic solvents such as ethanol, methanol, chloroform, benzene, hexane, and ether. However, all of the complexes are soluble in DMF and DMSO.

Thermal studies

The detailed weight loss studies of the complexes have been carried out in the temperature range 80–250 °C and the vapours evolved have been identified by passing through a trap containing anhydrous copper sulfate and a test tube containing sodium hydroxide solution and chloroform **[11]**. There was no weight loss observed in the temperature range 80–120 °C in any of the complexes ruling out the possibility of presence of water molecules in the lattice structure of the complexes. However, the complexes (6.1) and (6.6) showed weight loss corresponding to two and four water molecules respectively at 180°C suggesting the presence of two and four water molecules in the first coordination sphere around the metal centre in these complexes. On the other hand, the complexes (6.2) to (6.5) and (6.7) to (6.10) showed weight loss corresponding to two and four pyridine/2-picoline/3-picoline/4-picoline molecules in the temperature range 200–240°C. The expulsion of these neutral electron donor molecules at such a high temperature indicates that they are coordinated to the metal centre. Further, in the complexes (6.2) and (6.7) the vapours evolved in the temperature range 200–240 °C turned the solution of chloroform and sodium hydroxide red. This confirmed that the vapours from these complexes originated from pyridine **[12]**. Similarly, the vapours evolved from the complexes (6.4), (6.5), (6.9) and (6.10) in this temperature range turned the colour of cyanogen bromide solution to green-violet and blue respectively on treatment with phloroglucinol solution. This further confirmed the presence of 3-picoline molecules in the complexes (6.4) and (6.9) and 4-picoline molecules in the complexes (6.5) and (6.10), respectively.

Molar Conductance

The molar conductance values of the complexes (6.1) to (6.10) in DMSO solution at 10^{-3} M dilution falls in the range 2.62–3.13 $ohm^{-1}cm^2mol^{-1}$ suggesting that they are non-electrolytes in this solvent **[13]**.

Magnetic Moment

The μ_B (BM) values for the complexes (6.1) to (6.10) are set out in Table 6.1. The effective electronic configuration of nickel(II) is $3d^8$ and exhibits a magnetic moment higher than that expected for two unpaired electrons in an octahedral and a tetrahedral environment, whereas diamagnetism of the nickel(II) complexes lead to square planar stereochemistry. The effective magnetic moment reported for a high-spin octahedral Ni(II) complexes is in the range 3.00–3.50 BM, while for the tetrahedral complexes it ranges from 3.5 to 4.0 BM. The reason for this deviation is attributed to arise from spin-orbit coupling which causes an orbital contribution in the quenched $^3A_{2g}$ ground state of Ni(II) ion in an octahedral environment and not due to contribution from the orbital angular momentum of the electrons because the orbital angular momentum do not affect the $^3A_{2g}$ state. On the contrary, in case of a tetrahedral Ni(II) complex, the orbital angular momentum contributes strongly to the magnetic moment leading to magnetic moment values as high as 4.0 BM. The paramagnetism of the nickel (II) complexes (6.1) to (6.5) rules out the possibility of square planar structure and tetrahedral structure can be discarded on the basis of the magnitude of the magnetic moment. The complexes (6.1) to (6.5) have magnetic moment values in the region 2.87–3.45 BM which is typical of an octahedral Ni(II) compound **[14]**.

In the homobimetallic Ni(II) complexes (6.6) to (6.10), two Ni(II) ions are present for each ligand molecule and the resulting complexes have magnetic moment values in the region 1.14–1.73 BM i.e. 0.5–0.87 BM per metal(II) ion. Such low values of magnetic moment in the complexes (6.6) to (6.10) certainly rules out low-spin square planar stereochemistry for the complexes. But these values are considerably less than the values reported for spin free nickel (II) complexes indicating a strong metal-metal interaction in the structural unit. Anomalous magnetic moment values in the solid state have been explained on the basis of absorption spectra by proposing a mixed octahedral and square planar stereochemistry in the solid state due to molecular association **[15]**, but the electronic absorption spectra of the complexes described in this chapter are consistent with the tetragonally distorted octahedral stereochemistry. Since, the hydrazine bridges do not cause any lowering of the magnetic moment **[16]**, therefore, it is still reasonable to believe that the lowering of the magnetic moment is due to the presence of oxo-bridged structure and as a result of this Ni(II) complexes attain a tetragonally distorted octahedral stereochemistry.

Electronic Spectra

The electronic spectra of the ligand and its Ni(II) complexes were recorded in DMF solution because of poor solubility of the ligand and the complexes in common organic solvents. The important electronic spectral bands for the dihydrazone ligand (H_4nsh) and the monometallic and homobimetallic Ni(II) complexes along with their molar extinction coefficient are presented in Table 6.2. The electronic spectra for the complexes (6.1), (6.2), (6.4), (6.6), (6.7) and (6.8) have been shown in Fig. (6.1) to (6.6).

The free ligand H_4nsh exhibits a couple of bands in the region 317 nm and 363 nm. The band at 317 nm is assigned to intraligand $\pi \rightarrow \pi^*$ transition while the band at 363 nm is assigned to $n \rightarrow \pi^*$ transition **[17]**.

The electronic spectra of the complexes exhibit two to four bands in the region 300–450 nm. The bands appearing in the region 319–370 nm are attributed to arise due to intraligand transitions which exhibit red shift on complexation. The red shift of the ligand bands gives good evidence of chelation of dihydrazone to the metal centre. All of the complexes show new bands in the region 410–440 nm which has very high molar extinction coefficient. In view of very high molar extinction coefficient of this band, it is assigned to have its origin in the ligand-to-metal charge transfer transition. This band arises most probably from charge-transfer transition from naphtholate oxygen atoms to the metal centre **[18]**. This ligand-to-metal charge-transfer band is strongly influenced by the chemical nature of the ligand within a given stereochemistry and is responsible for the appearance of orange colour of the complexes.

In an octahedral environment, Ni(II) complexes exhibit three bands which are assigned to $^3A_{2g} \rightarrow {}^3T_{2g}$ (F), (ν_1); $^3A_{2g} \rightarrow {}^3T_{1g}$ (F), (ν_2) and $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), (ν_3) transitions, respectively. Since the transition $^3A_{2g} \rightarrow {}^3T_{1g}$ (P), (ν_3) generally occurs in the region 330–400 nm in which the bands due to organic fraction of the complexes arise as well, hence, this region is not useful from the point of view of drawing any conclusion about the stereochemistry around the Ni(II) centre. However, the first two low energy bands observed in the region 500–900 nm in all of the complexes are characteristic of nickel(II) in octahedral environment. The octahedral geometry of Ni(II) complexes is further supported by the value of ν_2/ν_1 ratio which lie in the region 1.498–1.504 **[19]**.

Various ligand field parameters (Table 6.3) viz. Racah inter-electronic repulsion parameter (B), ligand field splitting energy (10Dq), covalency factor (β) and ligand field stabilization energy (LFSE) have been calculated for the Ni(II) complexes.

The ligand field splitting energy (10Dq) and the Racah inter-electronic repulsion parameter (B) were calculated by the equations given by Lever **[20]**.

$^3A_{2g} \rightarrow {}^3T_{2g}$ (F), (ν_1) = 10Dq

$^3A_{2g} \rightarrow {}^3T_{1g}$ (F), (ν_2) = $7.5B + 15Dq - \frac{1}{2}(225B^2 + 100Dq^2 - 180DqB)^{1/2}$

$^3A_{2g} \rightarrow {}^3T_{1g}$ (P), (ν_3) = $7.5B + 15Dq + \frac{1}{2}(225B^2 + 100Dq^2 - 180DqB)^{1/2}$

The Racah interelectronic repulsion parameter (B) was also calculated by the following equation **[21]** and the values obtained were found to be same as calculated from the equations given by Lever.

$B_{Complex} = (2\nu_1^2 + \nu_2^2 - 3\nu_1\nu_2)/(15\nu_2 - 27\nu_1)$

The covalency factor (β) was obtained by the following equation:

$\beta = B/B'$ (B' is the free ion value = 1038 cm^{-1} **[22]**)

The ligand field stabilization energy (LFSE) is expressed by the equation:

LFSE = 12Dq

The percentage lowering of energy of 'P' state in the complexes as compared to its value in the free gaseous ion ($\beta°$) is obtained by the equation:

$\beta° = 100 - (\beta \times 100)$

The energy of first transition for the complexes (6.1) to (6.10) lie in the range 11765–11876 cm^{-1}which is equal to 10Dq. The evaluation of Racah inter-electronic repulsion parameter 'B' from the expression of ν_1 gave values which lie in the range 645–662. These values are very low as compared to the free ion value (1038 cm^{-1}). This indicates that all of the complexes have considerable covalent character. The nephelauxetic ratio, β, for the complexes lie in the range 0.62–0.64. The obtained β value being less than unity suggests the presence of considerable amount of covalent character in the metal–ligand bonds. The percentage lowering of energy of 'P' state in the complexes as compared to its value in the free gaseous ion i.e. $\beta°$ lie in the range 36.32–37.95% which shows a high degree of covalency.

The ν_2/ν_1 values for tetragonal complexes are found significantly higher than the usual range for octahedral complexes and sometimes greater than the theoretical limit of 1.80 for octahedral symmetry. The interaction between $^3T_{1g}$ (P) and $^3T_{1g}$ (F) states **[23]** gradually

lowers the ratio of ν_2/ν_1 from the theoretical value of 1.80 to 1.50–1.70 and values in the range 1.60–1.70 are common for nickel(II) complexes of octahedral symmetry. In the present complexes the ν_2/ν_1 values lie in the range 1.49–1.50 which are slightly lower than the lower limit of usual octahedral complexes but are within the range reported for octahedral nickel(II) complexes **[24]**. These low values indicate a strong interaction between $^3T_{1g}$ (P) and $^3T_{1g}$ (F) states of the complexed nickel(II) ion. The value of ligand field stabilization energy for the complexes lie in the range 40.42 – 40.80 kcal mol^{-1}.

Infrared Spectra

Some of the structurallty significant infrared (IR) spectral bands for the free dihydrazone (H_4nsh) and the nickel (II) complexes are listed in Table 6.4. The IR spectra of the complexes (6.2), (6.3), (6.6) and (6.10) are shown in Fig. (6.7) to (6.10) as representative examples.

A comparison of the IR spectra of the nickel (II) complexes with that of the uncoordinated dihydrazone (H_4nsh) suggests that the dihydrazone is coordinated to the metal centre in enol form in all of the complexes.

The uncoordinated dihydrazone shows a medium intensity broad band centered at 3423 cm^{-1} and a medium intensity band at 3244 cm^{-1}. The band at 3423 cm^{-1} has been assigned to ν(OH) vibration of 2-hydroxy-1-naphthaldehyde part of the dihydrazone, while the band at 3244 cm^{-1} is assigned to arise from secondary -NH group. The IR spectra of the complexes show a weak to medium intensity band in the region 3000–3500 cm^{-1}. This band is attributed to arise due to stretching vibrations of water molecules absorbed by KBr during pellet preparation. However, these bands appear to have contribution from coordinated water molecules in the complexes (6.1) and (6.6). The band in the region 3000–3500 cm^{-1} in the complexes (6.1) to (6.5) also appears to have contribution from the stretching vibration of coordinated naphtholic –OH group. Further, the spectral features of the complexes (6.6) to (6.10) conspicuously indicate the coordination of naphtholic –OH group via deprotonation to the metal centre in these complexes.

None of the complexes shows the band characteristic of νNH vibration. This suggests the destruction of –NH group as a result of enolization of the ligand in the complexes and its coordinaton to the metal centre in the enol form.

The ν(C=O) stretching vibration appears as a very strong band at 1672 cm^{-1} in the infrared spectrum of the uncoordinated dihydrazone. In the infrared spectra of all the complexes,

the amide I band disappears indicating destruction of amide structure of the ligand in these complexes.

The ν(C=N) band appears as a couple of bands in the region 1622–1602 cm^{-1} in the IR spectra of the complexes similar to that in the uncoordinated dihydrazone. This band registers an average downward shift of 2–3 cm^{-1} indicating coordination of dihydrazone through azomethine nitrogen atom to the metal centre **[25]**. This downward shift of ν(C=N) band is attributed to the drainage of electron density from azomethine nitrogen atom to the metal centre. The existence of two ν(C=N) band in the complexes shows that the two azomethine nitrogen groups are inequivalent suggesting that the strength of the two M←N bands are not the same. Further, the difference between the two ν(C=N) stretching frequencies are of the order of 13–18 cm^{-1} which falls in the range in which groups existing in the *anti-cis* configuration have been reported to absorb **[26]**. This suggests that the dihydrazone exist in the *anti-cis* configuration in these complexes.

A band of medium intensity observed at 1540 cm^{-1} in the infrared spectra of the free dihydrazone is attributed to arise due to joint contribution of amide II (ν(C–N) + ν(NH) + ν(C–O) (naphtholic)). This band splits into two bands in the IR spectra of the complexes and appears around 1540 cm^{-1} and 1508 cm^{-1}, respectively. The position of the band at 1540 cm^{-1} remains almost unchanged in the complexes as compared to that in the free ligand. However, the intensity of this band is considerably increased in the complexes comparatively. This may be related to bonding between the naphtholate oxygen atom and metal centre. A weak but intense band at 1508 cm^{-1} in the IR spectra of the complexes is attributed to arise due to stretching vibration of newly created NCO^- group produced as a result of enolization of the ligand **[25]**.

The medium intensity band at 1281 cm^{-1} due to ν(C–O) shifts to higher frequency by 21 cm^{-1} in the complexes (6.1) to (6.5) and appears at ~ 1303 cm^{-1} as a medium intensity band. On the otherhand this band splits into two bands in the complexes (6.6) to (6.10). One of the bands remains almost at the same position in the complexes as compared to that in the free ligand while the other band shifts to higher position by ~21 cm^{-1} and appears around 1303 cm^{-1} as a medium intensity band. Such a feature associated with ν(C–O) band indicates bonding through C–O oxygen atoms to the metal centre **[25]**.

The naphthyl ring shows a weak absorption at about 1600 cm^{-1}. In the present ligand and as well as in the complexes, the band due to naphthyl ring does not show its independent existence, most probably, because of its overlapping with either ν(>C=N–N=C<) band or

amide II band or ν(C - O) (naphtholic) band. The band at 1467 cm^{-1} in the free ligand is characteristic of substitution at α-position of naphthalene ring.

It has been found that the ν(N–N) band appears in the region 1040–970 cm^{-1} in the metal complexes derived from N,N-diacyl hydrazines **[27]**. Eliminating the bands due to C–H in-plane deformation in the region 1050–900 cm^{-1}, a weak band at 1029 cm^{-1} in the present ligand has been assigned to ν(N–N). This band shifts to higher frequency by 14–27 cm^{-1} in all of the metal complexes. This indicates the involvement of nitrogen atom of N–N group in coordination to the metal centre **[28]**. The complexes (6.6) to (6.10) show an additional band in the region 861-897 cm^{-1} and is assigned to have contribution from the band arising from the tetraatomic species [M<O>M] resulted from the involvement of naphtholate oxygen atoms in bridge formation **[29]**.

The complexes (6.2) to (6.5) and (6.7) to (6.10) show a new but very weak intensity band in the region 1076–1045 cm^{-1}. This band is assigned to ring breathing mode of pyridine, 2-picoline, 3-picoline and 4-picoline molecules. The presence of this band in the IR spectra of the complexes (6.2) to (6.5) and (6.7) to (6.10) indicates coordination of pyridine, 2-picoline, 3-picoline and 4-picoline to the metal centre **[30]**.

The antisymmetric and symmetric -OH stretching modes of lattice water appear in the region 3500- 3000 cm^{-1}, while the H – O – H bending mode appears in the region 1630 – 1610 cm^{-1}. Coordinated water molecules besides showing the above two bands also show wagging and rocking modes in the region 900–750 cm^{-1} which are activated by coordination to the metal centre **[31]**.

Since there is no detectable change in the IR spectra of the complexes (6.2) to (6.5) and (6.7) to (6.10) in the above ranges as compared to IR spectrum of the ligand, where modes of lattice and coordinated water should appear and since, there is no loss of water molecules at 110°C, it is suggested that there are neither lattice water nor coordinated water molecules in these complexes. On the other hand the complexes (6.1) and (6.6) show a new band of medium intensity at 687 cm^{-1} and 630 cm^{-1} respectively. These bands are assigned to rocking mode of coordinated water molecules in these complexes.

Conclusion

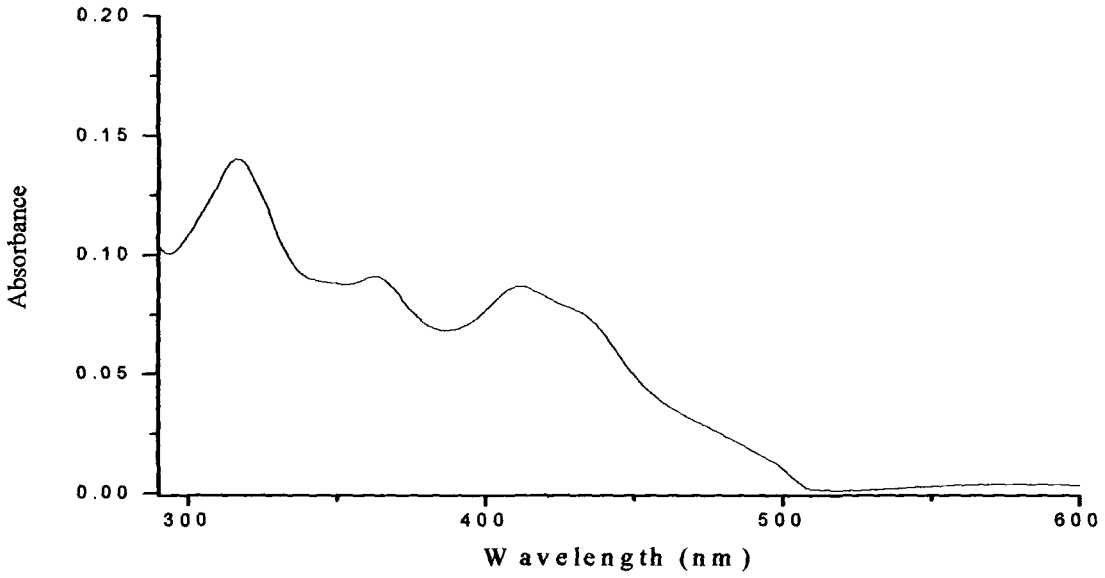
In this chapter, monometallic and homobimetallic Ni(II) complexes derived from the dihydrazone ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone have been described. In all of the complexes, the dihydrazone is present in *anti-cis* configuration in enol form.

The monometallic complexes (6.1) to (6.5) possess μ_{eff} value in the range 2.85–3.45 BM consistent with their octahedral stereochemistry. These values rule out the possibility of any metal-metal interaction between metal atoms in the structural unit of the complexes. The dihydrazone (H_4nsh) coordinates to the metal centre as a dibasic tetradentate ligand in enol form through azomethine nitrogen atoms and deprotonated naphtholic oxygen atoms. In these complexes, the dihydrazone donor atoms are arranged around the Ni(II) centre in the equatorial position while the axial positions are occupied by the co-ligands H_2O/pyridine/2-picoline/3-picoline/4-picoline molecules.

In the homobimetallic complexes (6.6) to (6.10), the magnetic moment values lie in the region 1.14–1.73 BM i.e. 0.57–0.87 per Ni(II) ion which are less than the values reported for spin free Ni(II) complexes indicating a strong metal-metal interaction in these complexes. Electronic spectral studies suggest that all of the homobimetallic complexes have distorted octahedral stereochemistry.

In these complexes the ligand coordinates to the metal centre as a tetrabasic hexadentate ligand. One of the Ni(II) centre is present in N_2O_2 coordination sphere and other Ni(II) centre is bonded to it through naphtholate oxygen atoms via oxo-bridging. Magnetic moment values for these complexes lying in the region 1.14–1.73 BM i.e. 0.57–0.87 BM per Ni(II) ion are less than the values reported for spin free Ni(II) complexes indicating a strong metal-metal interaction in these complexes.

The tentative structures for the complexes have been shown in Fig.6.11 and 6.12.



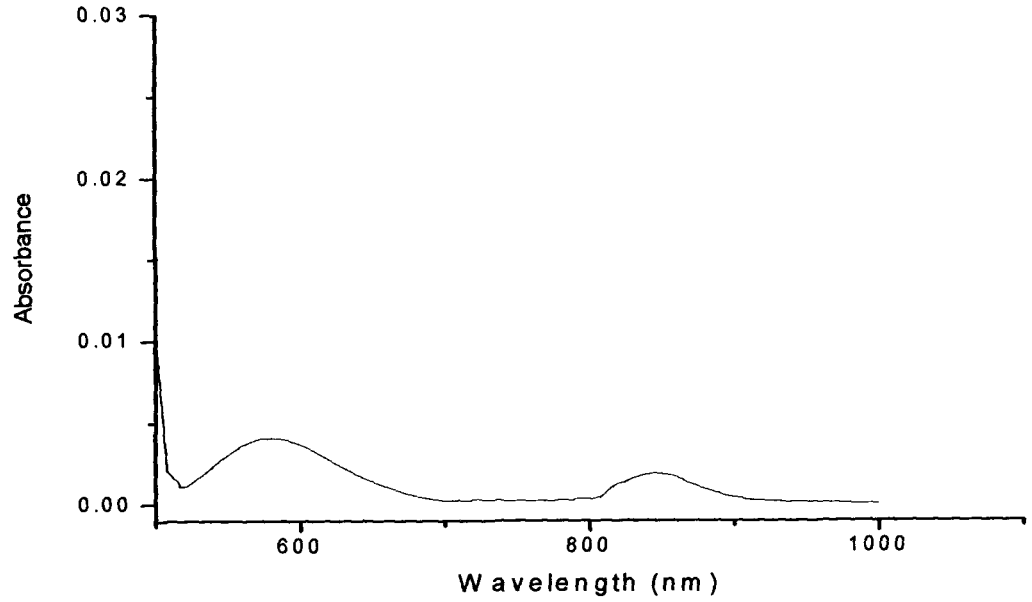


Fig. 6.1. Electronic spectrum of $[Ni(H_2nsh)(H_2O)_2]$ (6.1) in DMF.

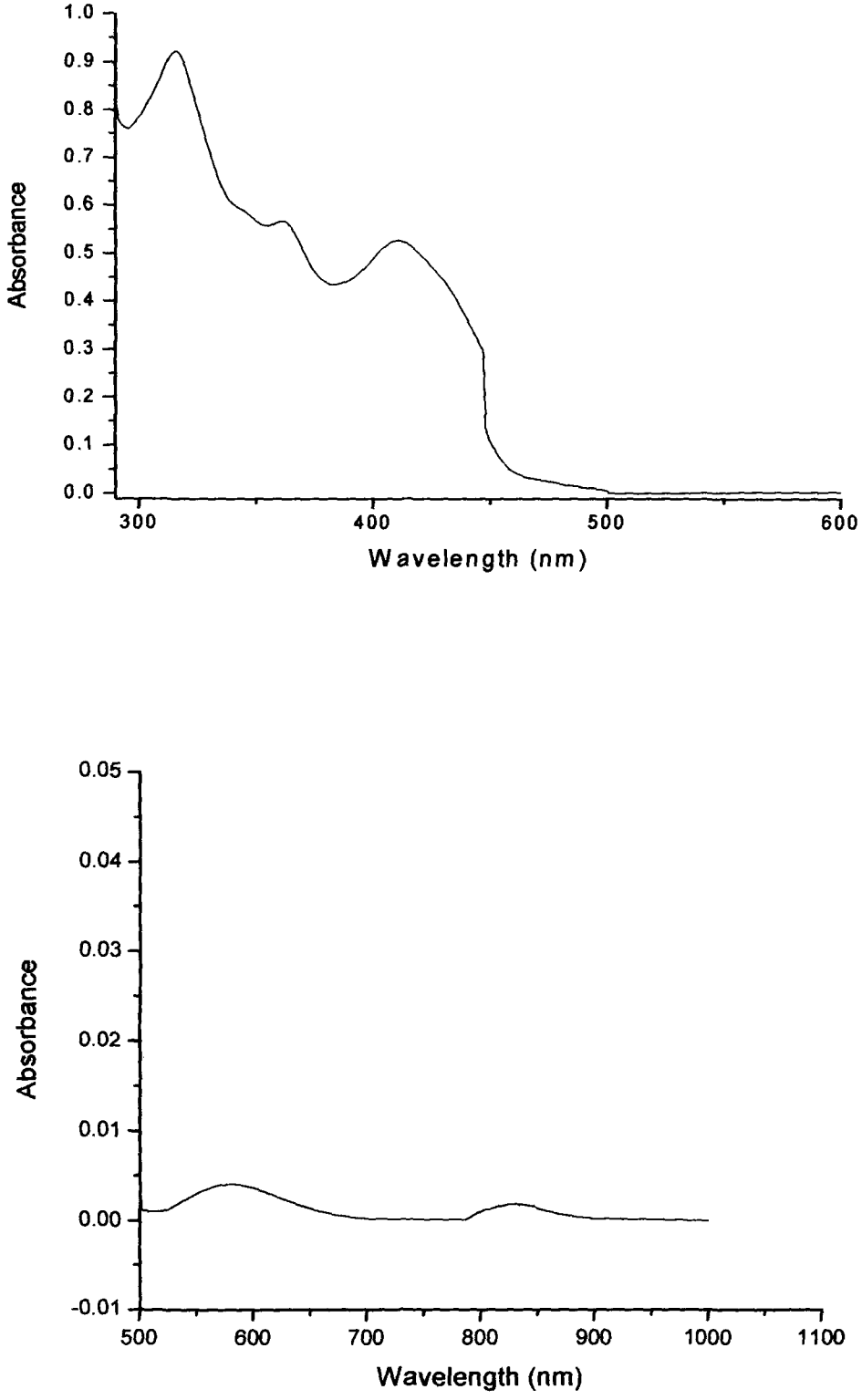


Fig. 6.2. Electronic spectrum of $[Ni(H_2nsh)(py)_2]$ (6.2) in DMF.

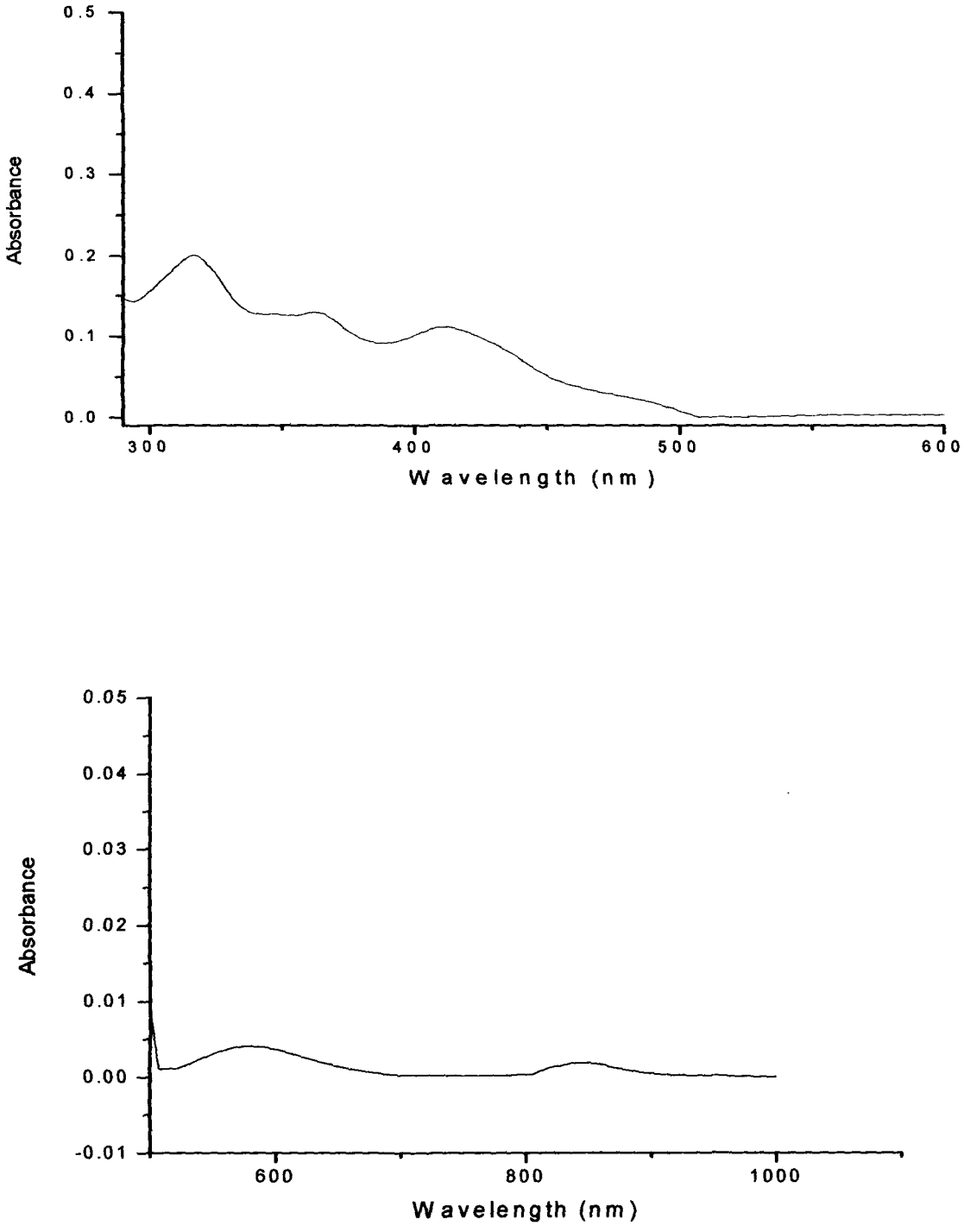


Fig. 6.3. Electronic spectrum of $[Ni(H_2nsh)(3\text{-pic})_2]$ (6.4) in DMF.

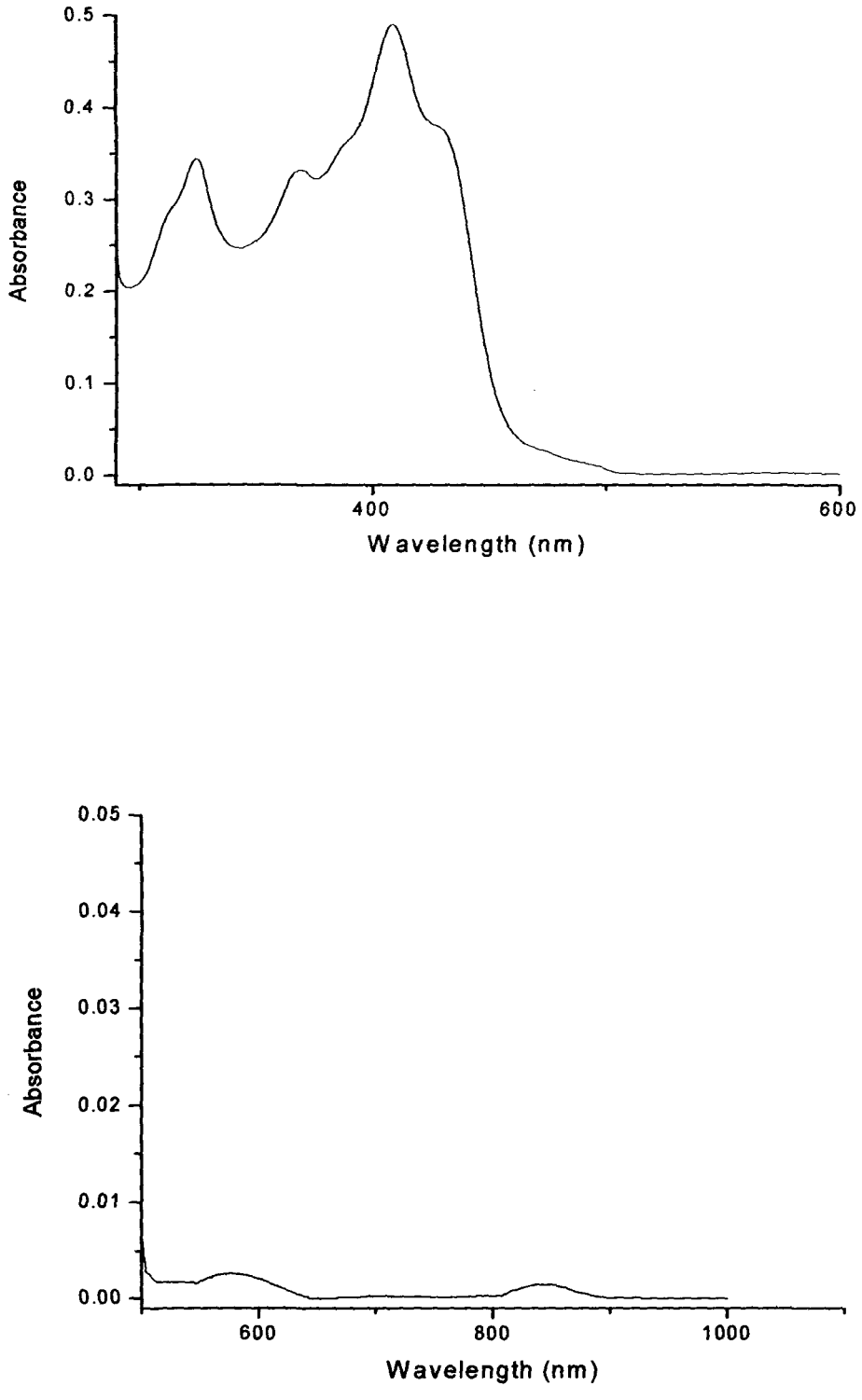


Fig. 6.4. Electronic spectrum of $[Ni_2(nsh)(H_2O)_4]$ (6.6) in DMF.

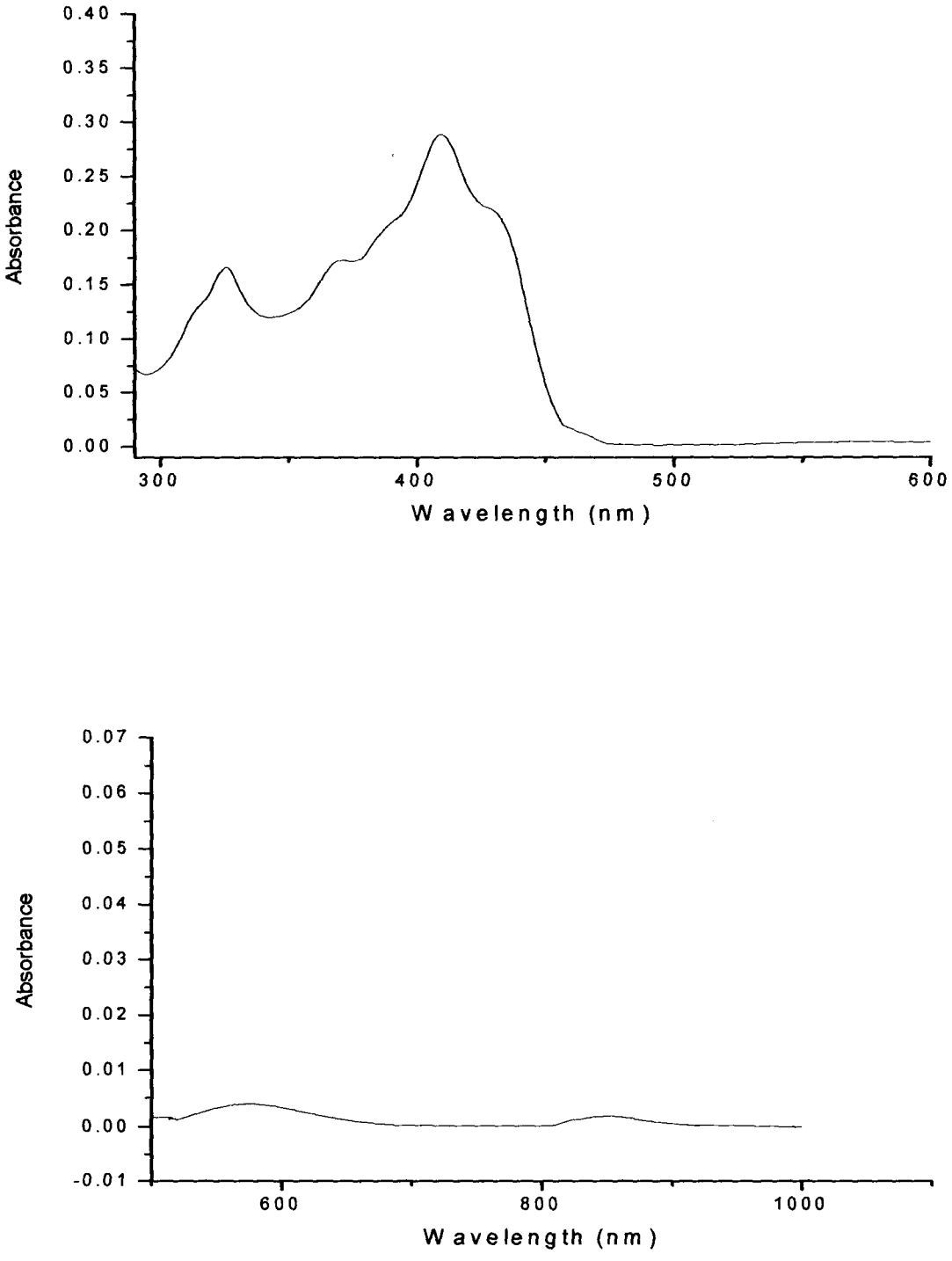


Fig. 6.5. Electronic spectrum of $[Ni_2(nsh)(py)_4]$ (6.7) in DMF.

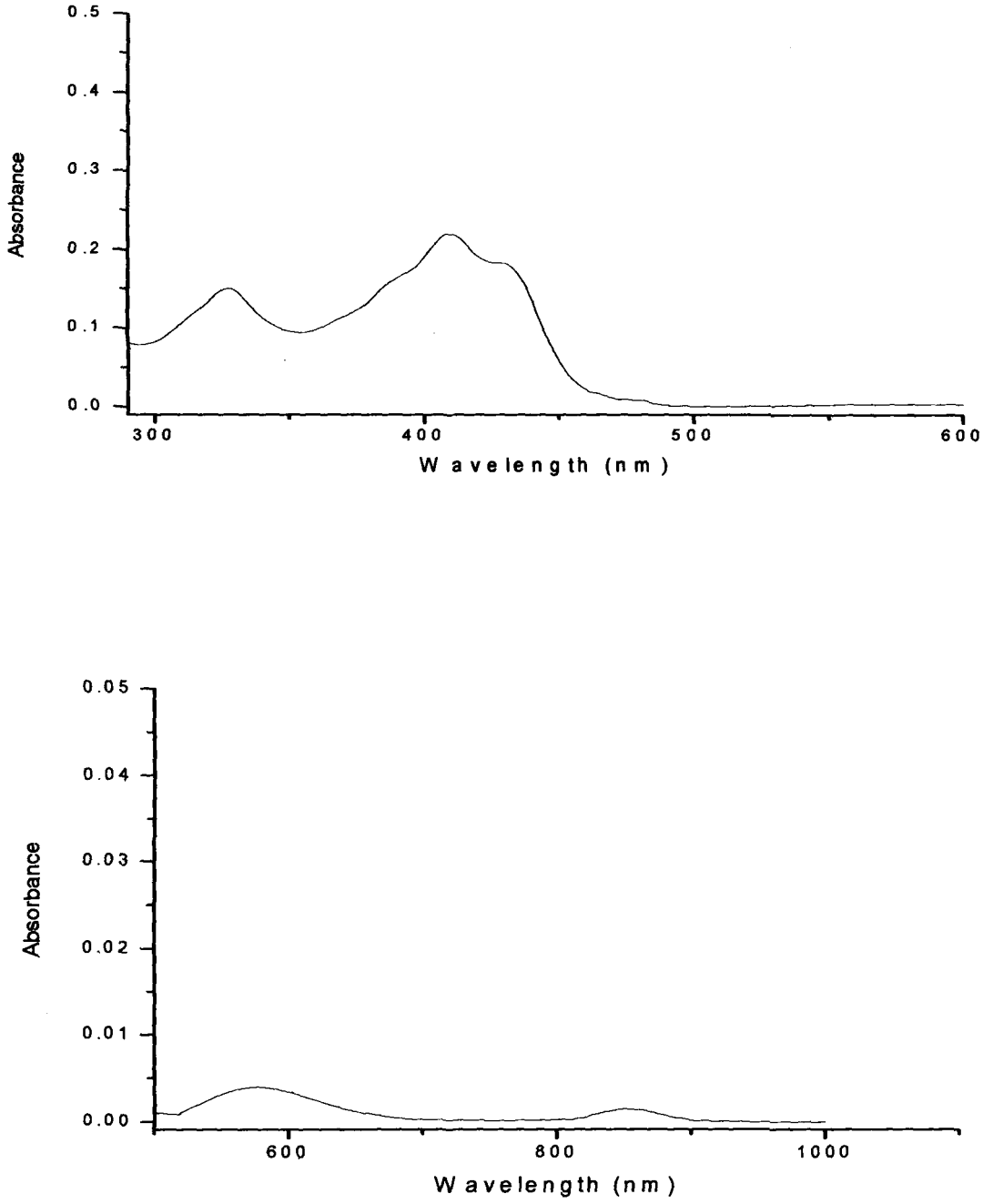


Fig. 6.6. Electronic spectrum of $[Ni_2(nsh)(2\text{-pic})_4]$ (6.8) in DMF

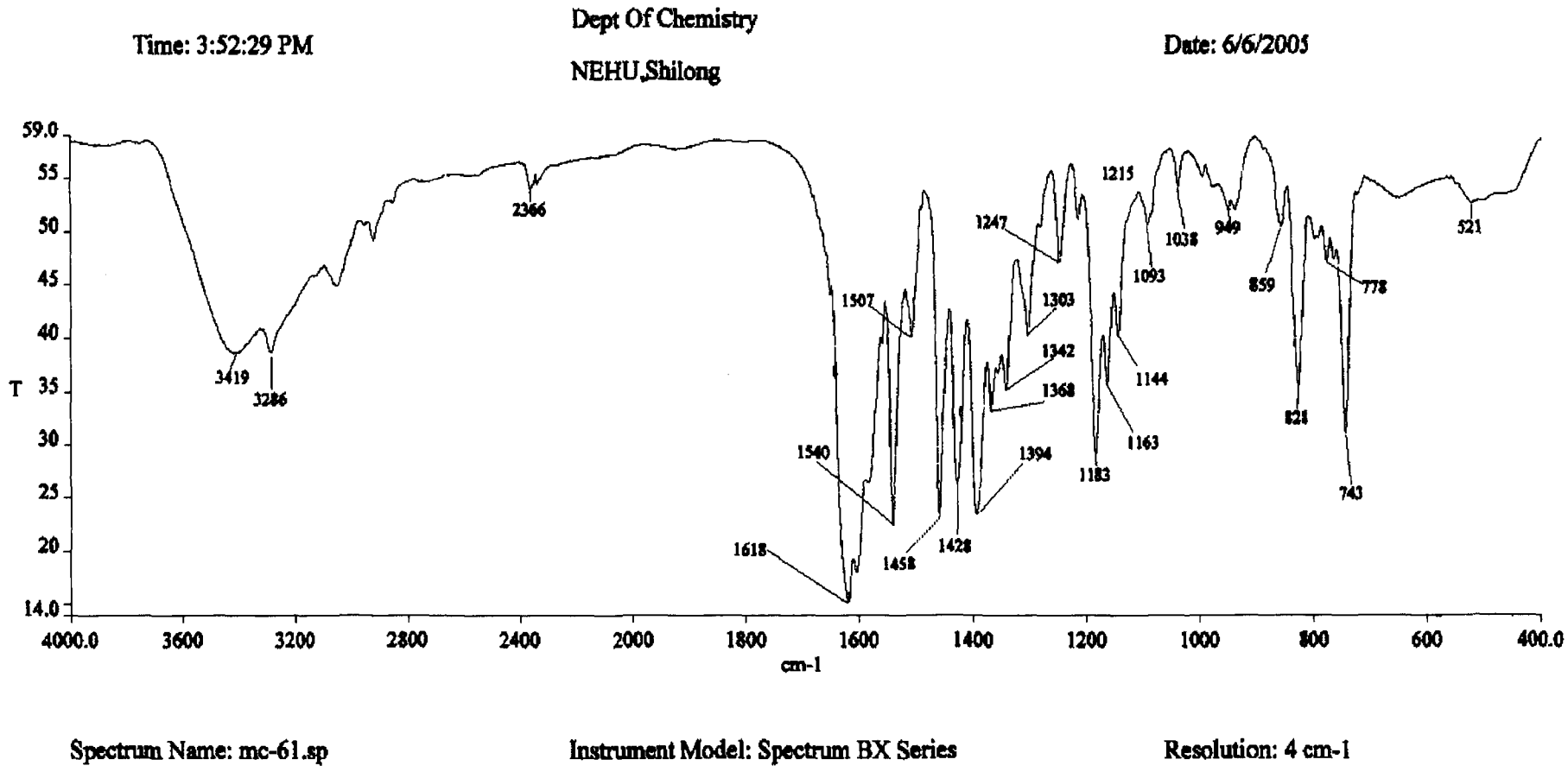


Fig. 6.7. Infrared spectrum of $[Ni(H_2nsh)(py)_2]$ (6.2) in KBr.

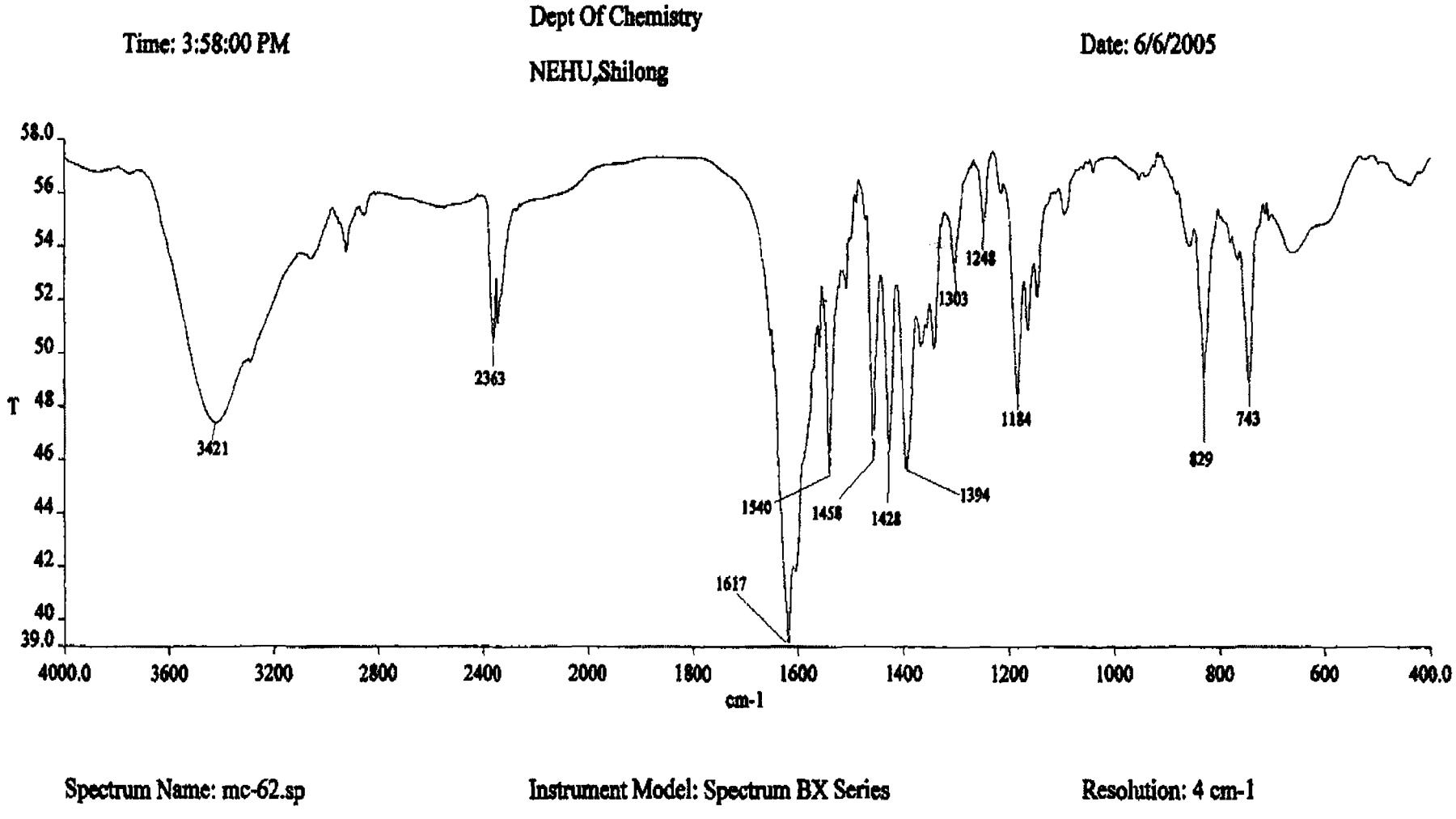


Fig. 6.8. Infrared spectrum of $[Ni(H_2nsh)(2\text{-pic})_2]$ (6.3) in KBr.

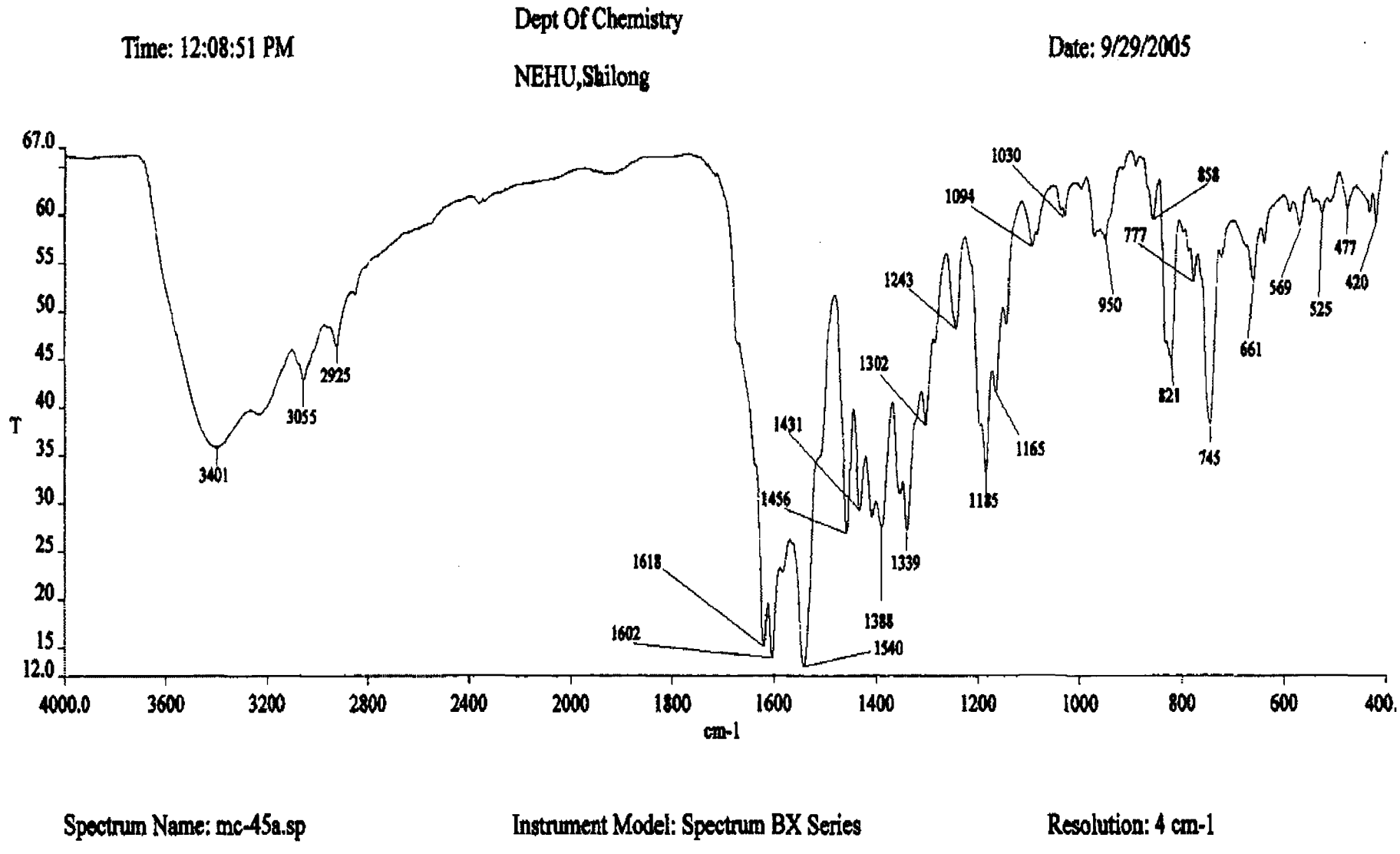


Fig. 6.9. Infrared spectrum of $[Ni_2(H_2nsh)(H_2O)_4]$ (6.6) in KBr.

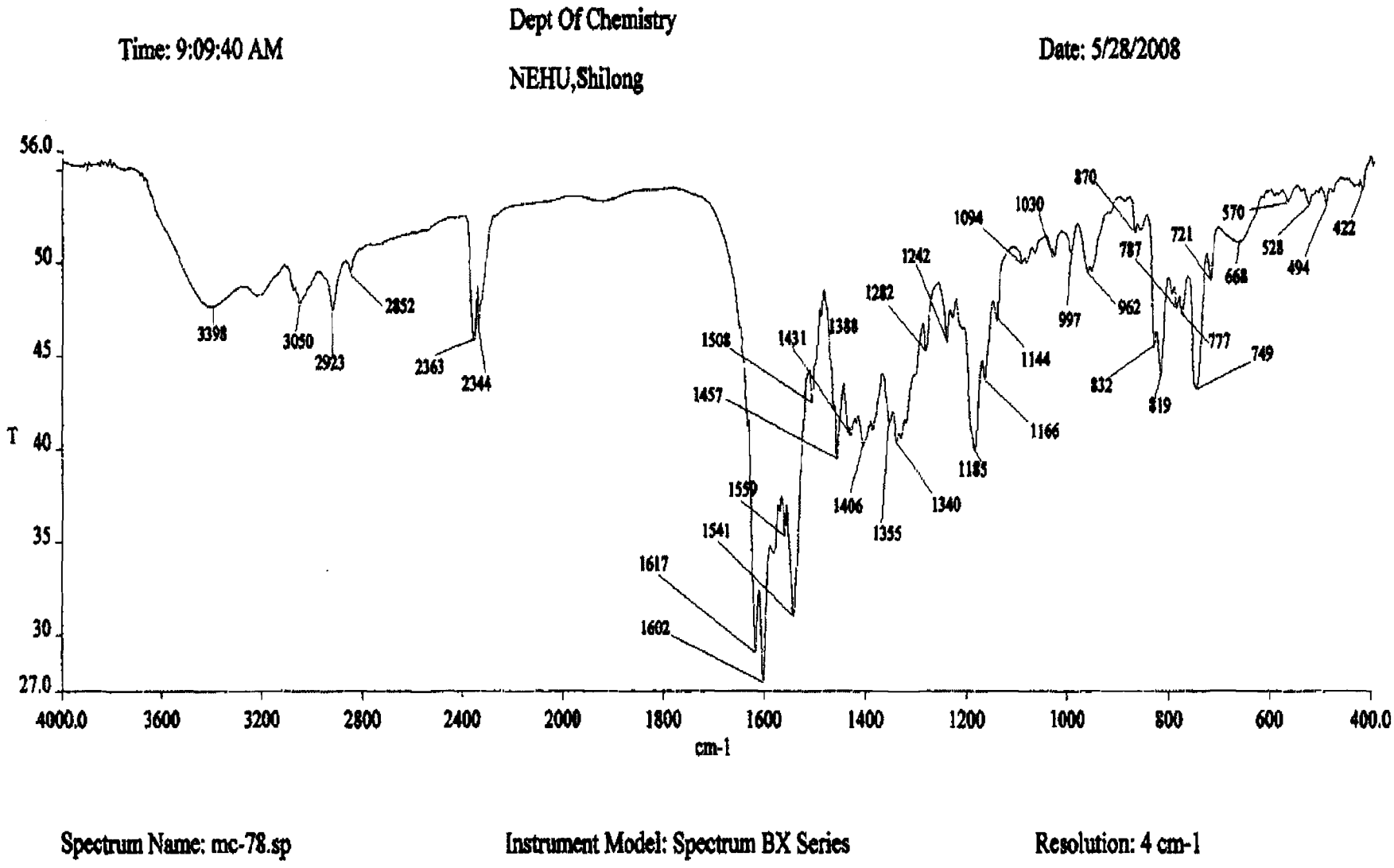


Fig. 6.10. Infrared spectrum of $[Ni_2(H_2nsh)(4\text{-pic})_4]$ (6.10) in KBr.

Table 6.1: Analytical Data and Physical properties of Ni(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.

Sl. No	Complex and Colour	D.P (°C)	Yield(%)	Analysis: Found (Calc.) (%)				Molar Conductance (Λ_M) $Ohm^{-1}cm^2mol^{-1}$	Magnetic Moment μ_B (BM)
				Ni	C	H	N		
6.1	$[Ni(H_2nsh)(H_2O)_2]$ Brown	>300	70.00	10.54 (10.73)	56.94 (57.07)	4.39 (4.42)	10.14 (10.24)	3.13	2.87
6.2	$[Ni(H_2nsh)(py)_2]$ Brown	>300	68.00	8.54 (8.77)	63.74 (64.60)	4.51 (4.52)	12.23 (12.55)	2.81	3.45
6.3	$[Ni(H_2nsh)(2\text{-pic})_2]$ Yellow	>300	65.00	8.04 (8.41)	64.94 (65.44)	4.89 (4.91)	11.94 (12.05)	2.62	2.98
6.4	$[Ni(H_2nsh)(3\text{-pic})_2]$ Brown	>300	63.00	8.09 (8.41)	65.04 (65.44)	4.90 (4.91)	11.96 (12.05)	2.91	3.09
6.5	$[Ni(H_2nsh)(4\text{-pic})_2]$ Dark Brown	>300	65.00	8.11 (8.41)	65.03 (65.44)	4.89 (4.91)	11.98 (12.05)	2.85	3.30
6.6	$[Ni_2(nsh)(H_2O)_4]$ Brown	>300	69.00	17.94 (18.34)	48.64 (48.80)	4.03 (4.10)	8.64 (8.75)	2.97	1.73
6.7	$[Ni_2(nsh)(py)_4]$ Light Brown	>300	62.00	13.04 (13.28)	62.34 (62.48)	4.36 (4.33)	12.54 (12.67)	2.81	1.14
6.8	$[Ni_2(nsh)(2\text{-pic})_4]$ Brown	>300	65.00	12.17 (12.47)	63.94 (63.87)	4.89 (4.93)	11.84 (11.92)	2.72	1.54
6.9	$[Ni_2(nsh)(3\text{-pic})_4]$ Brown	>300	64.00	12.24 (12.47)	63.74 (63.87)	4.88 (4.93)	11.81 (11.92)	2.64	1.39
6.10	$[Ni_2(nsh)(4\text{-pic})_4]$ Light Brown	>300	65.00	12.06 (12.47)	63.91 (63.87)	4.89 (4.93)	11.87 (11.92)	2.81	1.29

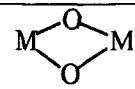
Table6.2: Electronic spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its Ni(II) complexes

Sl. No	Ligand/ Complex	Electronic spectral bands λ_{max} (nm) (ε_{max} ($dm^3mol^{-1}cm^{-1}$))
	H_4nsh	317 (5480), 363 (5420)
6.1	$[Ni(H_2nsh)(H_2O)_2]$	319 (2755), 364 (1815), 410 (1733), 564 (80), 845(37)
6.2	$[Ni(H_2nsh)(py)_2]$	319 (3938), 364 (2579), 413 (2214), 562 (80), 842(36)
6.3	$[Ni(H_2nsh)(2\text{-}pic)_2]$	319 (1428), 366 (1265), 411 (1777), 429 (1386), 564 (37), 847(33)
6.4	$[Ni(H_2nsh)(3\text{-}pic)_2]$	319 (3930), 366 (2534), 410 (2216), 563 (80), 846(37)
6.5	$[Ni(H_2nsh)(4\text{-}pic)_2]$	319 (1838), 362 (1131), 409 (1047), 561 (80), 842(36)
6.6	$[Ni_2(nsh)(H_2O)_4]$	325 (6874), 369 (6653), 420 (8649), 562 (50), 843 (29)
6.7	$[Ni_2(nsh)(py)_4]$	326 (3345), 368 (3442), 421(5091), 564 (81), 848 (35)
6.8	$[Ni_2(nsh)(2\text{-}pic)_4]$	326 (2987), 421(4006), 565 (79), 849 (29)
6.9	$[Ni_2(nsh)(3\text{-}pic)_4]$	326 (5030), 421(7445), 568 (79), 850 (29)
6.10	$[Ni_2(nsh)(4\text{-}pic)_4]$	348 (5058), 420 (7123) 563 (79), 844 (29)

Table 6.3: Ligand field parameters for Ni(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Sl. No.	Complex	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1)		$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2)		Dq (cm^{-1})	ν_2/ν_1	B (cm^{-1})	β	β° (%)	LFSE (kcal mol^{-1})
		nm	cm^{-1}	nm	cm^{-1}						
6.1	$[Ni(H_2nsh)(H_2O)_2]$	845	11834	564	17730	1183.4	1.498	653.57	0.6278	37.22	40.66
6.2	$[Ni(H_2nsh)(py)_2]$.	842	11876	562	17794	1187.6	1.4983	656.09	0.6302	36.98	40.80
6.3	$[Ni(H_2nsh)(2\text{-}pic)_2]$.	847	11806	564	17730	1180.6	1.5017	659.79	0.6338	36.62	40.56
6.4	$[Ni(H_2nsh)(3\text{-}pic)_2]$	846	11820	563	17762	1182	1.5027	662.63	0.6365	36.35	40.61
6.5	$[Ni(H_2nsh)(4\text{-}pic)_2]$.	842	11876	561	17825	1187.6	1.5009	661.81	0.6357	36.43	40.80
6.6	$[Ni_2(nsh)(H_2O)_4]$	843	11862	562	17794	1186.2	1.5001	659.18	0.6332	36.68	40.75
6.7	$[Ni_2(nsh)(py)_4]$	848	11792	564	17730	1179.2	1.5035	662.95	0.6368	36.32	40.51
6.8	$[Ni_2(nsh)(2\text{-}pic)_4]$	849	11779	565	17699	1177.9	1.5025	660.07	0.6341	36.59	40.47
6.9	$[Ni_2(nsh)(3\text{-}pic)_4]$	850	11765	566	17606	1176.5	1.4964	645.98	0.6205	37.95	40.42
6.10	$[Ni_2(nsh)(4\text{-}pic)_4]$	844	11848	563	17762	1184.8	1.4991	656.37	0.6302	36.98	40.70

Table 6.4: Structurally significant Infrared (IR) bands (in cm^{-1}) for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its Ni(II) complexes.

Sl. No	Ligand/Complex	ν(OH + NH)	ν(C=O)	ν(C=N)	Amide II + ν(C–O) (naphtholic)	ν(NCO^-)	ν(C—O)	ν(N—N)		ν(M—O)	Other bands
	H_4nsh	3423 m 3244 m 3051m	1672 vs	1633 vs 1593m	1540 m	—	1281m	1029 w	—	—	—
6.1	[Ni(H_2nsh)(H_2O)$_2$]	3410 m 3291 m	—	1622s 1604	1540 s	1508 w	1306 m 1282 w	1084 w 1039 w	—	555 w 521 w	—
6.2	[Ni(H_2nsh)(py)$_2$]	3419 m 3286 m	—	1618 s 1604 m	1540 s	1507 w	1303 m 1282 w	1038 w	—	521 w	1052 w
6.3	[Ni(H_2nsh)(2-pic)$_2$]	3421 m	—	1617 s 1602 m	1540 s	1508 w	1303 m	1038 w	—	521 w	1053 w
6.4	[Ni(H_2nsh)(3-pic)$_2$]	3420 m	—	1616 s 1602 m	1540 s	1506w	1303 m	1038 w	—	521 w	1070 w
6.5	[Ni(H_2nsh)(4-pic)$_2$]	3435 s	—	1617 s 1604 m	1540 m	1508 w	1303 m	1036 w	—	522 w	1045 w
6.6	[Ni_2(nsh)(H_2O)$_4$]	3401 m 3055 m	—	1618 s 1602 w	1540 vs	1508 w	1302 m 1282 w	1030 w	897 w	569 w 525 w	-
6.7	[Ni_2(nsh)(py)$_4$]	3419 m 3051 m	—	1617 vs 1602 s	1540 vs	1508w	1303 m 1283 w	1093 w	882 w	595 w 528 w	1069 w
6.8	[Ni_2(nsh)(2-pic)$_4$]	3421 m 3055 m	—	1617 vs 1602vs	1540 vs	1508w	1302 m 1281 w	1093 w 1032 w	883 w	589 w 567 w	1076 w
6.9	[Ni_2(nsh)(3-pic)$_4$]	3409 m 3051 m	—	1617 vs 1602 vs	1541 vs	1508w	1302 m 1282 w	1049 w 1003 w	862 w	585 w 532 w	1061 w
6.10	[Ni_2(nsh)(4-pic)$_4$]	3398 m 3050 z	–	1617 vs 1602vs	1541 vs	1508w	1302 m 1282w	1094 w 1030 w	861 w	570 w 528 w	1070 w

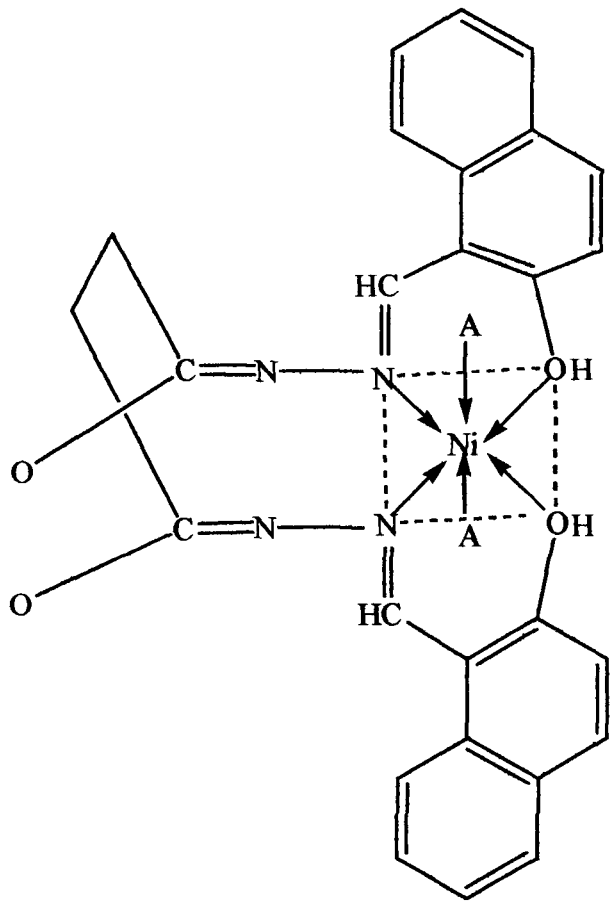


Fig. 6.11. Tentative structure of $[Ni(H_2nsh)(A)_2]$ (where A = water (H_2O) (6.1), pyridine (py, 6.2); 2-picoline(2-pic, 6.3); 3-picoline(3-pic, 6.4); 4-picoline (4-pic, 6.5)

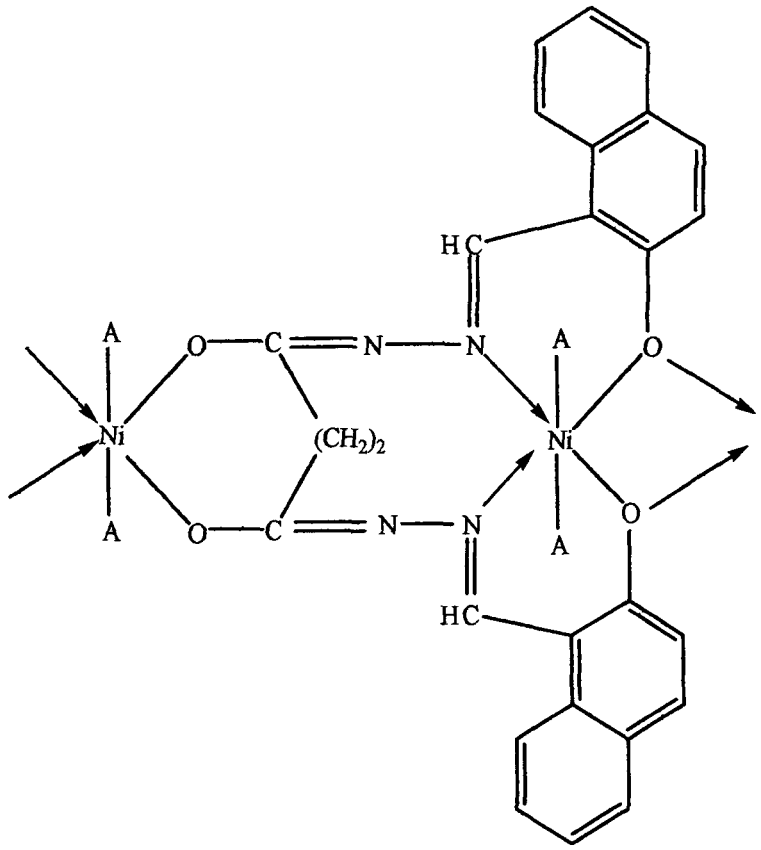


Fig. 6.12. Tentative structure of $[Ni_2(nsh)(A)_4]$ (where A = water (H_2O, (6.6)); pyridine (py, 6.7); 2-picoline(2-pic, 6.8); 3-picoline(3-pic, 6.9); 4-picoline (4-pic, 6.10)

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CHAPTER VII

Synthesis, Characterization and Structural Assessment of Heterobimetallic Ni(II)-Zn(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Introduction

The fifth chapter describes the monometallic and homobimetallic zinc(II) complexes derived form the title ligand, while the sixth chapter describes the corresponding monometallic and homobimetallic Ni(II) complexes. In monometallic zinc(II) complexes, the dihydrazone ligand acts as a dibasic tetradentate ligand coordinating to the metal centre through azomethine nitrogen and protonated naphtholic -OH groups in the *anti-cis* configuration. On the other hand in the homobimetallic Zn(II) complexes, the dihydrazone was found to act as a tetrabasic hexadentate ligand coordinating to the metal centre through naphtholate oxygen atom, enolate oxygen atom and azomethine nitrogen atom in the *staggered* configuration. In contrast, in all of the nickel(II) complexes the dihydrazone is present in the *anti-cis* configuration. Further, the homobimetallic complexes of zinc(II) and nickel(II), both involve naphthoxo-bridging while no such oxo-bridging is present in monometallic complexes. The ligand employed in the present study is a polyfunctional octadentate ligand in which three types of donor atom sets are available. If the dihydrazone coordinates to the metal atoms in *syn-cis* or *staggered* configuration, only one type of donor set i.e. NO_2 will be available for bonding. But if the dihydrazone coordinates to the metal centre in the *anti-cis* configuration, two types of donor sets, i.e. N_2O_2 and O_2O_2 will be available. The O_2O_2 donor set will be available only if the ligand coordinates to the metal centre in *anti-cis* configuration involving naphthoxo-bridging.

In monometallic zinc(II) and nickel(II) complexes both the metal atoms i.e. zinc(II) and nickel(II) are occupying N_2O_2 coordination chamber in respective complexes while in homobimetallic complexes both the zinc atoms occupy only one type of coordination chamber i.e. NO_2 with ligand in *staggered* configuration. In nickel(II) homobimetallic complexes, one nickel(II) atom occupies N_2O_2 coordination chamber while the second nickel(II) atom occupies O_2O_2 coordination chamber. In view of such a behaviour of dihydrazones in monometallic and homobimetallic zinc(II) and nickel(II) complexes, it was interesting to explore the study of the heterobimetallic complexes of these metal ions to examine (i) whether the present ligand would give rise to the formation of

heterobimetallic complexes with the metal ions selected in the present study or not (ii) whether the metal centres in the resulting heterobimetallic complexes would retain their original coordination sphere as in the monometallic complexes or not and (iii) whether the dihydrazone would react with the metal ions in *staggered* or *syn-cis* or *anti-cis* configuration in the resulting heterobimetallic complexes.

Keeping these objectives in mind, it was decided to proceed with the synthesis and characterization of heterobimetallic complexes of the title dihydrazone with the selected metal ions. But before we proceed to study the heterobimetallic complexes, it appears pertinent to review the literature related to the importance of heterobimetallic complexes particularly in biological systems and technology.

The homo and heteropolymetallic complexes containing two or more same or different metal centres in close proximity are involved in a variety of important biochemical processes **[1-3]** and are important in the synthesis of solid state phases of technological and industrial importance favoring an intimate mixing of the elements **[4]**. Further, the metal ions in the enzymes occur either alone or in combination with another atom of their own kind or different kind giving rise to monometallic, homometallic and heterometallic enzymes, respectively. For example, Mo, Zn and Ni are present alone in xanthine oxidase, carbonic anhydrase and bacterial hydrogenase and catalase, respectively, giving rise to monometallic enzymes. On the other hand, copper and manganese are present with more atoms of their own kind and are found in haemocyanin and tyrosinase **[5]** and oxygen evolving complex (OEC) **[6]** in photosystem II respectively, giving rise to multimetallic enzymes. Further, Mo is found in the enzyme nitrogenase **[7]** in combination with iron, whereas Zn and Cu are found together in superoxide dismutase **[8]** and Ni occurs in combination with iron in jack bean urease **[9]** and Ni-Fe hydrogenase enzyme **[10]**. Again Zn occurs in kidney bean phosphatase in combination with iron **[11]**. Zn also occurs in combination with copper in proteins obtained from rat liver **[12]**.The efficacy of heterobimetallic complexes in the asymmetric activation of carbon dioxide and related molecules has been demonstrated **[13]**. In homogeneous catalysis, a heterobimetallic complex containing an electron deficient metal atom and an electron rich metal atom presents the possibility of Lewis acid activation of a substrate molecule bound to the electron rich metal centre. The heterobimetallic complexes which have such types of properties are usually derived from widely divergent transition metals. Further, the heterobimetallic complexes have the potential to mediate certain chemical reactions of industrial relevance either more efficiently than or, in a different manner to isolated metal

centres **[14]**. The heterobimetallic complexes offer an unusual opportunity to study the cooperative interaction between metal ions.

A survey of literature has revealed that although the metal complexes of monoacyl hydrazones, aroyl hydrazones and pyridoyl hydrazones have been studied in some greater detail **[15]**, those of acyl-, aroyl and pyridoyl dihydrazones have received attention in recent years only **[16, 17]**. Further, the reported existence of heterobimetallic complexes derived from dihydrazones as ligands is quite meager **[16, 17, 18, 19]**. Moreover, there is not even a single reported existence of heterobimetallic complexes of dihydrazones containing succinoyl fraction and bulky naphthyl fragments in their molecular skeleton.

In view of the above importance of the bi- or polynuclear and heteropolymetallic complexes, much less work on heterobimetallic complexes of dihydrazones and absence of investigation on heterobimetallc complexes of dihydrazones containing succinoyl and bulky naphthyl fragments in their molecular skeleton, the present chapter describes the synthesis and characterization of heterobimetallic nickel-zinc complexes derived from the title ligand.

The stoichiometry of the complexes has been decided mainly from the elemental analyses data and thermoanalytical data. The structures of the complexes have been discussed in the light of conductivity, magnetic moment, electronic and IR spectral data.

Preparation of the complexes:

1. Preparation of [NiZn(nsh)(B)$_3$] (Where B = H_2O, (7.1); pyridine, (py, 7.2); 2-picoline (2-pic, 7.3)); 3-picoline (3-pic, 7.4)) ; 4-picoline (4-pic, 7.5))

The complex [Zn(H_2nsh)(H_2O)] (5.1) from the fifth chapter was used as a precursor for the preparation of the heterobimetallic complex (7.1).

The complex [Zn(H_2nsh)(H_2O)] (5.1) (1.00 g, 1.81 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 minutes at 60°C. To this was added a solution of $Ni(OAc)_2.4H_2O$ (1.35 g, 5.43 mmol) in methanol (50 mL) drop by drop over a period of 10–15 minutes accompanied by gentle stirring. The reaction mixture thus obtained was refluxed for 5 hours, which precipitated a light brown compound. The compound thus obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.61 g.

In order to prepare the complex [NiZn(nsh)(py)$_3$] (7.2), the complex [NiZn(nsh)(H_2O)$_3$] (7.1) (1.00 g, 1.55 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 minutes at 60°C. To this suspension, pyridine (1.30 mL, 15.52 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture thus obtained was refluxed for 3 hours, which precipitated the orange coloured compound. The compound thus obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.63 g.

The complexes (7.3), (7.4), (7.5) were prepared in a similar way using 2-picoline, 3-picoline and 4-picoline instead of pyridine. Yield: 0.65g (7.3); 0.64 g (7.4); 0.62g (7.5).

2. Preparation of [ZnNi(nsh)(B)$_2$] (Where B = H_2O, (7.6); pyridine, (py, 7.7); 2-picoline (2-pic, 7.8)); 3-picoline (3-pic, 7.9)) ; 4-picoline (4-pic, 7.10))

The complex [Ni(H_2nsh)(H_2O)$_2$] (6.1) from the sixth chapter was used as a precursor for the preparation of the heterobimetallic complex (7.6).

The complex [Ni(H_2nsh)(H_2O)$_2$] (6.1) (1.00 g, 1.86 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for10 minutess at 60°C. To this was added a solution of Zn(OAc)$_2$.2H_2O (1.22 g, 4.56 mmol) in methanol (50 mL) drop by drop over a period of 10–15 minutes accompanied by gentle stirring. The reaction mixture thus obtained was refluxed for 5 hours, which precipitated a light brown compound. The compound thus obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.61 g.

In order to prepare the complex [ZnNi(nsh)(H_2O)] (7.7) the complex [ZnNi(nsh)(H_2O)$_3$] (7.6) (1.00 g, 1.55 mmol) was suspended in methanol (100 mL) accompanied by gentle stirring for 10 minutes at 60°C. To this suspension, pyridine (1.30 mL, 15.52 mmol) was added maintaining the molar ratio at 1:10. The reaction mixture thus obtained was refluxed for 3 hours, which precipitated the orange coloured compound. The compound thus obtained was filtered while hot, washed repeatedly with hot methanol and finally with ether and dried over anhydrous $CaCl_2$. Yield: 0.63 g.

The complexes (7.8), (7.9), (7.10) were prepared in a similar way using 2-picoline, 3-picoline and 4-picoline instead of pyridine. Yield: 0.62g (7.8); 0.64g (7.9); 0.63g (7.10).

Results and Discussion

Synthesis of the pure samples of heterobimetallic complexes is a difficult task in the field of heterobimetallic chemistry. It is important to ensure that the metals are not scrambled giving rise to considerable quantities of other undesired binuclear products. The synthesis of heterobimetallic products is accessible by the strategies developed by Lintvedt et al **[20]** via a monometallic complex intermediate by the use of polyfunctional ligands and Davies et al **[21]** via transmetallation beginning with a complex of discrete molecularity as target and another metal complex as transmetallator. The monometallic complexes synthesized from the title ligand still possesses vacant coordination sites which can be utilized during the course of its reaction with the same or different metal salt taken in excess giving rise to homopolymetallic and heteropolymetallic complexes. Hence, it was of interest to examine the effect of introduction of the second metal ion into the coordination sphere of the monometallic Mo(VI), Zn(II) and Ni(II) complexes described in the third, fifth and sixth chapter.

Accordingly the monometallic complexes $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)]\cdot 2C_2H_5OH$ (3.1) from Chapter III, $[Zn(H_2nsh)(H_2O)]$ (5.1) from Chapter V and $[Ni(H_2nsh)(H_2O)_2]$ (6.1) from Chapter VI have been selected to use as precursors and $Zn(OAc)_2\cdot 2H_2O$, $Ni(OAc)_2\cdot 4H_2O$ and $MoO_2(acac)_2$ have been used as transmetallator for the synthesis of heterobimetallic complexes.

Thus when the precursor Zn(II) complex $[Zn(H_2nsh)(H_2O)]$ (5.1) and Ni(II) complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1) were allowed to react with $MoO_2(acac)_2$ in 1:1.5 molar ratio under reflux, no change in physical appearance of the resulting precipitate was observed. Further, elemental analyses of the precipitates showed that they are devoid of molybdenum. Further, the IR spectra of the precipitates indicated the absence of molybdenum. The ^1H NMR spectral study of the precipitates matched with that of the starting complexes signifying that the zinc and nickel complex did not react with $MoO_2(acac)_2$ at all and remained as such. When monometallic molybdenum complex $[(\mu_2\text{-}O)_2(MoO_2)(H_4nsh)]\cdot 2C_2H_5OH$ (3.1) was refluxed with $Zn(OAc)_2\cdot 2H_2O$ and $Ni(OAc)_2\cdot 4H_2O$ in 1:1.2 molar ratio, again the resulting species were free from molybdenum as ascertained by elemental analyses and IR spectra. This result showed that the metal molybdenum was completely displaced from the complex by Zn(II) and Ni(II). The identity of the precipitates were established to be $[Zn(H_2nsh)(H_2O)]$ and $[Ni(H_2nsh)(H_2O)_2]$, respectively. However, when the complexes $[Zn(H_2nsh)(H_2O)]$ (5.1) and $[Ni(H_2nsh)(H_2O)_2]$ (6.1) were allowed to react with $Ni(OAc)_2\cdot 4H_2O$ and

$Zn(OAc)_2 \cdot 2H_2O$ respectively, in 1:3 molar ratio in methanol, the resulting precipitates were found to contain both nickel and zinc. Hence, the products obtained from these metallation reactions, further, constitute the subject matter of the present chapter.

The complexes described in the present chapter together with their molecular formula, colour, decomposition point, percentage yield, analytical data, magnetic moment and molar conductance data are set out in Table 7.1.

The complexes are brown, orange, yellow and dark brown in colour. All of the complexes are insoluble in water, and common organic solvents such as ethanol, methanol, acetone, chloroform, carbon tetrachloride, benzene and ether but are soluble in highly coordinating solvents like DMSO and DMF. All of the complexes are air stable solid powders and decomposes above 300 °C.

Based on the analytical data, the complexes have been suggested to have the following composition.

$[NiZn(nsh)(B)_3]$ (Where B = H_2O (7.1), pyridine, (py, 7.2); 2-picoline (2-pic, 7.3)); 3-picoline (3-pic, 7.4)) ; 4-picoline (4-pic, 7.5))

$[ZnNi(nsh)(B)_2]$ (Where B = H_2O (7.6), pyridine, (py, 7.7); 2-picoline (2-pic, 7.8)); 3-picoline (3-pic, 7.9)) ; 4-picoline (4-pic, 7.10)).

Thermal studies

The detailed weight loss studies of the complexes (7.1), (7.2), (7.4), (7.5), (7.6), (7.7), (7.9) and (7.10) have been carried out in the temperature range 80–250 °C and the vapours evolved have been identified by passing through a trap containing anhydrous copper sulfate and a test tube containing sodium hydroxide solution and chloroform **[22]**. None of the complexes showed weight loss below 160 °C ruling out the possibility of presence of water molecules in their lattice structure. However, the complexes (7.1) and (7.6) showed weight loss in the temperature range 170–190 °C corresponding to three and two water molecules, respectively. The vapours evolved in the temperature range 170–190 °C in the complexes (7.1) and (7.6) turned anhydrous copper sulfte blue confirming that they originate from the water molecules. This suggests the presence of three and two water molecules in the first coordination sphere around the metal centres in these complexes. On the other hand, the complexes (7.2) to (7.5) and (7.7) to (7.10) showed weight loss at 220–240 °C corresponding to three and two pyridine/2-picoline/3-picoline/4-picoline molecules respectively. The expulsion of these neutral electron donor molecules at such a high

temperature indicates that they are coordinated to the metal centre. Further, in the complexes (7.2) and (7.7) the vapours evolved in the temperature range 200–240 °C turned the solution of chloroform and sodium hydroxide red. This confirmed that the vapours from these complexes originated from pyridine. Similarly, the vapours evolved from the complexes (7.4), (7.5), (7.9) and (7.10) in this temperature range turned the colour of cyanogen bromide solution to gree-violet and blue, respectively, on treatment with phloroglucinol solution. This further confirmed the presence of 3-picoline molecules in the complexes (7.1) and (7.9) and 4-picoline molecules in the complexes (7.5) and (7.10), respectively **[23]**.

Molar Conductance

The molar conductance values for all of the complexes have been recorded in DMSO due to solubility problem in other common organic solvents and have been set out in Table 7.1. The molar conductance values for the complexes (7.1) to (7.10) lie in the range 2.81–3.21 $ohm^{-1}cm^2mol^{-1}$ (Table.7.1). These values fall below the value reported for a 1:1 electrolyte in DMSO. This suggests that, all of the complexes are non-electrolyte in nature **[24]**.

Magnetic Moment

The complexes (7.1) to (7.5) exhibit magnetic moments in the range 2.95–3.15 BM while the complexes (7.6) to (7.10) exhibit μ_{eff} values in the range 3.25–3.42 BM. The μ_{eff} values for nickel(II) complexes have been reported to fall in the regions 3.00–3.30, 3.00–3.45 and 3.45–4.00 BM, respectively having octahedral, 5-coordinate square-pyramidal and tetrahedral geometry, respectively **[25]**. On the other hand the four coordinate square planar nickel(II) complexes have been shown to be diamagnetic. The experimental values of magnetic moment for the complexes rule out their tetrahedral or square planar structure. The magnetic moment values for the complexes (7.1) to (7.5) lie in the range 2.95–3.15 BM which indicates that these complexes have distorted octahedral stereochemistry **[26, 27]**. Literature reports suggest that majority of the five coordinate high spin Ni(II) complexes having square-pyramidal stereochemistry have magnetic moment values lying in the region 3.25–3..29 BM **[28]**. The magnetic moment values for the complexes (7.6) to (7.10) fall in the range reported for high spin square-pyramidal complexes. Thus the complexes (7.6) to (7.10) can be said to have square-pyramidal geometry with considerable amount of distortion.

Electronic Spectra

The important electronic spectral bands along with their molar extinction coefficient are summarized in Table 7.2. The electronic spectra of the complexes (7.1), (7.2), (7.3), (7.5), (7.6), (7.7), (7.8) and (7.10) are shown in Fig. 7.1 to 7.8. In addition to the ligand bands, the complexes show a weak additional band in the region 472–481 nm. This band is similar to the band observed in the precursor Zn(II) complex $[Zn(H_2nsh)(H_2O)]$ and is assigned to have similar origin in nature i.e. charge transfer transition. Accordingly this band is assigned to arise from ligand-to-metal charge transfer transition originating from naphtholate oxygen atom.

The heterobimetallic complexes (7.1) to (7.5) exhibit new bands in the region 931–940 nm (ν_1) and 615–628 nm (ν_2). The position of these bands is typical of an octahedrally coordinated Ni(II) centre and rules out the square planar or tetrahedral structure. A comparison of the position of the bands in the regions 931–940 and 615–628 nm with the corresponding band in the spectra **[29]** of $[Ni(H_2O)_6]^{2+}$ at 1175 and 740 nm and $[Ni(NH_3)_6]^{2+}$ at 935 and 570 nm suggests that ν_1 band bear similarity with that of the nitrogen donor ligands, while the second band ν_2 is intermediate between those observed for oxygen as well as nitrogen donor ligands but approaching towards nitrogen donor ligands. From this observation, it may safely be said that nickel atom is occupying N_2O_2 coordination chamber of the ligand. This suggests that the Zn(II) atom in the complexes (7.1) to (7.5) are displaced by Ni(II) atom. From this observation, it can be said that the Ni(II) occupies N_2O_2 coordination chamber while the zinc(II) occupies O_2O_2 coordination chamber. On the other hand, the complexes (7.6) to (7.10) derived from nickel(II) precursor complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1), exhibit only one band in the region 965–967 nm and is similar in nature to that reported for high spin square-pyramidal Ni(II) complexes **[30, 31]**. Hence these complexes are assigned to have five coordinate square-pyramidal stereochemistry and the band in the region 965–967 nm is assigned to the transition $^3B_1 \rightarrow {}^3E(F)$. A comparison of the position of this band in the region 965–987 nm with the corresponding band in the spectra of $[Ni(H_2O)_6]^{2+}$ at 1175 (ν_1) and $[Ni(NH_3)_6]^{2+}$ at 935 (ν_1) and those in the complexes (7.1) to (7.5) suggests that the ν_1 bands in these complexes is shifted away from the complexes derived from nitrogen donor ligands and towards complexes derived from oxygen donor ligands. It is imperative to mention that in the precursor nickel(II) complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1), the d-d bands appear at 845 and 564 nm. From this observation, it may safely be concluded that the nickel atom in the complexes (7.6) to (7.10) is most probably, coordinated to carbonyl

oxygen atoms via enolization. This suggests that the Ni(II) atom which occupies N_2O_2 coordination chamber in precursor complexes is displaced by Zn(II) atoms in the hetrerobimetallic complexes. Thus it is suggested that in these complexes the nickel(II) occupies O_2O_2 coordination chamber while zinc(II) occupies N_2O_2 coordination chamber.

Various ligand field parameters (Table 7.3) viz. Racah inter-electronic repulsion parameter (B), ligand field splitting energy (10Dq), covalency factor (β) and ligand field stabilization energy for the complexes (7.1) to (7.5) were calculated as described in the previous chapter (Chapter-VI). The calculated values of ν_2/ν_1 (1.49–1.51) lie in the range reported for an octahedral environment around Ni(II) ion **[32]**.

In the electronic spectra of the complexes (7.1) to (7.5), the band in the region 10638–10741 cm^{-1} is attributed to the ν_1 transition $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) and the band in the region 15924 – 16260 cm^{-1} is assigned to ν_2, $^3A_{2g} \rightarrow {}^3T_{2g}$ (F) transition. The low energy band was taken as a 10Dq band in the calculation of ligand field parameters. The calculated values of ligand field parameters (Table 7.3) lie in the range reported for an octahedral environment around a Ni(II) ion **[33]**. The obtained β value being less than unity and the percentage lowering of energy of 'P' state in the complexes as compared to its value in the free gaseous ion i.e. β° (39.78–44.60), suggests the presence of a considerable amount of covalent character of the metal ligand bonds.

Infrared Spectra

Some of the structurallty significant (IR) spectral bands for the free dihydrazone, the precursor Zn and Ni complexes and the heterobimetallic Ni-Zn complexes are listed in Table 7.4. The IR spectra of the complexes (7.1), (7.2), (7.3), (7.5), (7.6), (7.7), (7.8) and (7.10) are shown in Fig. (7.9) to (7.16) as representative examples.

A comparison of the IR spectra of the heterobimetallic complexes with that of the uncoordinated dihydrazone (H_4nsh) suggests that the dihydrazone is coordinated to the metal centre in the enol form in all of the complexes.

In the complexes (7.1), a strong band in the region 3413–3432 cm^{-1} with its centre at 3421 cm^{-1}suggests that it owes its origin in the stretching vibration of water molecule. Further, the complex (7.1) and (7.6) shows weight loss corresponding to three and two water molecules, respectively at 180°C suggesting that they are present in the first coordination sphere around the metal centre. The remaining complexes donot show such a band in this region ruling out the possibility of presence of water molecules in their

structure. The complexes (7.2) to (7.5) and (7.7) to (7.10) show a weak broad band in the region 3000–3500 cm^{-1} which may be assigned to water molecules absorbed by KBr during pellet preparation.

The various amide bands arise from mixed contributions of varying degree from >C=O and >NH group. The contribution from the >NH group is invariably present in amide I, II, III and V bands. Coordination of monoacylhydrazines **[34]** through >C=O and $-NH_2$ groups and monoacyl hydrazones **[35]** through >C=O and >C=N group results in lowering of the group stretching frequencies. In the event of enolozation, the >C=O and >NH groups are destroyed resulting in formation of –C(OH)=N- group in which ν(OH), ν(C–O) and ν(C=N) bands should appear. Reaction with metal ions in enol form results in the formation of –N=C-O and >C=N-N=C< group vibrations **[36]**.

The IR spectra of the complexes donot show any strong band in the region 1630–1700 cm^{-1}.The essential features of the IR spectra of the complexes in this region is similar to that of the precursor Zn(II) complex $[Zn(H_2nsh)(H_2O)]$ (5.1) and Ni(II) complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1). This suggests that the ligand is present in these complexes in the same form as that in the precursor zinc and nickel complex i.e. in the enol form.

The ν(C=N) band appears as a couple of bands in all of the complexes and are similar to that as observed in the precursor Zn and Ni complex. The ν(C=N) bands, on an average, show a negative shift of 3–4 cm^{-1} in metal complexes as compared to those in the free ligand and the precursor zinc and nickel complex. This shows that the azomethine nitrogen atoms are bonded to the metal centre. It is interesting to note that one of the ν(C=N) bands (1593 cm^{-1}) shifts to higher frequency by 8–11 cm^{-1} in all of the heterobimetallic complexes as compared to its position in the in the free dihydrazone whereas the other ν C=N band (1633 cm^{-1}) shifts to lower frequency by ~ 17 cm^{-1}. The shift of one of the ν(C=N) bands to higher frequency and the other band to lower frequency on complexation in these complexes indicates inversion of azomethine group. Consequently, the axial >C=N group attains equatorial position while the equatorial >C=N group attains axial position. The introduction of the positively charged metal ion in the ligand skeleton causes the reversal of azomethine group.

The fact that the ν(C=N) band appears as a couple of bands in the IR spectra of the Ni-Zn heterobimetallic complexes similar to that in the precursor Zn(II) and Ni(II) complex suggests that the two >C=N groups are not equivalent in all of the heterobimetallic complexes just as in case of the precursor Zn(II) and Ni(II) complex. Such an

inequivalency of >C=N groups indicates the coordination of dihydrazone to the metal centre in *anti-cis* configuration. In this configuration the molecule is bent in such a manner that half portion of the dihydrazone remains out of plane of the molecule, while the other half remains in plane **[37]**.

The ν(N–N) band appearing at 1029 cm^{-1} as a weak band in the free dihydrazone appears in the region 1031–1040 cm^{-1} in the heterobimetallic complexes and is similar to those observed in the precursor Zn(II) and Ni(II) complexes. An increase in ν(N–N) band absorption in all the complexes is a clear indication that the increase in double bond character is off-setting the loss of electron density via electron donation to the metal and is a further confirmation of the coordination of the ligand through the azomethine nitrogen atom **[38]**.

The complexes (7.2) to (7.5) and (7.7) to (7.10) show a new but very weak intensity band in the regions 1012–1014 cm^{-1} and 1051–1072 cm^{-1} respectively. These bands are assigned to ring breathing mode of pyridine and substituted pyridine molecules present in the complexes. The presence of this band in the IR spectra of the complexes (7.2) to (7.5) and (7.7) to (7.10) indicates their coordination to the metal centre **[39]**.

A new non-ligand band observed in the region 773–780 cm^{-1} in the IR spectra of all of the complexes is assigned to the stretching vibration of the tetraatomic species [M<O>M] resulted from the involvement of naphtholate oxygen atoms in bridge formation **[40, 41]**.

Based on the literature report **[42, 43]**, it can be said that the ν(M–O)(naphtholate) vibrations may appear in the range 600 – 500 cm^{-1} while ν(M–O)(carbonyl) may appear in the region 480–400 cm^{-1}. The non-ligand bands appearing in the region 525–500 cm^{-1} have been assigned to ν(M–O)(naphtholate) **[44]** while the bands appearing in the region 484 – 420 cm^{-1} have been assigned to ν(M–O)(carbonyl) **[45]**.

Conclusion

In the present chapter, heterobimetallic complexes of zinc and nickel derived from the dihhydrazone ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone have been described. In all of the heterobimetallic complexes, the dihydrazone functions as a bridging tetrabasic hexadentate ligand. The dihydrazone coordinates to the metal centres in *anti-cis* configuration through naphtholate oxygen atoms, azomethine nitrogen atoms and enolate oxygen atoms. All of the complexes possess normal magnetic moment ruling out the possibility of metal-metal interaction in the structural unit of the complexes. It has

been found that the metal ion from the parent monometallic complexes gets displaced from its original position by the second metal ion introduced into the system. Thus the metal ion which occupies N_2O_2 coordination sphere in the parent monometallic complex, occupies O_2O_2 coordination chamber originating from enolate oxygen atoms and oxo-bridged naphtholate oxygen atoms in the heterobimetallic complexes, while the second metal ion entering into the system occupies N_2O_2 coordination chamber. In the complexes (7.1) to (7.5) the equatorial positons around the Ni(II) centre are occupied by azomethine nitrogen atoms and naphtholate oxygen atoms and the axial positons are occupied by the co-ligands viz. H_2O/ pyridine/2-picoline/3-picoline/4-picoline. Thus the Ni(II) core occupies N_2O_2 coordination chamber. The ligand is coordinated to the Zn(II) centre by enolate oxygen atoms and is suggested to exhibit square-pyramidal stereochemistry in which the other coordination sites are occupied by the co-ligands H_2O/ pyridine/2-picoline/3-picoline/4-picoline and the bridged nanphtholate oxygen atoms. The nickel(II) centre is suggested to have distorted octahedral stereochemistry while the zinc(II) centre is suggested to have square-pyramidal stereochemistry.

On the other hand, in the heterobimetallic complexes (7.6) to (7.10), Zn(II) centre is coordinated to azomethine nitrogen atoms and naphtholate oxygen atoms and the fifth coordination site is occupied by the co-ligands H_2O/ pyridine/2-picoline/3-picoline/4-picoline. Thus the Zn(II) core occupies the N_2O_2 coordination chamber. In these complexes the Ni(II) centre is coordinated to enolate oxygen atoms and bridged naphtholate oxygen aroms of the dihydrazone occupying O_2O_2 coordiantion chamber. The other coordination sites around the Ni(II) centre are occupied by the co-ligands H_2O/ pyridine/2-picoline/3-picoline/4-picoline. In these complexes, both the metal atoms are suggested to have square pyramidal stereochemistry.

On the basis of results obtained from various physico-chemical and spectral studies, the tentative structures for the complexes have been suggested as shown in Fig. 7.17 and 7.18.

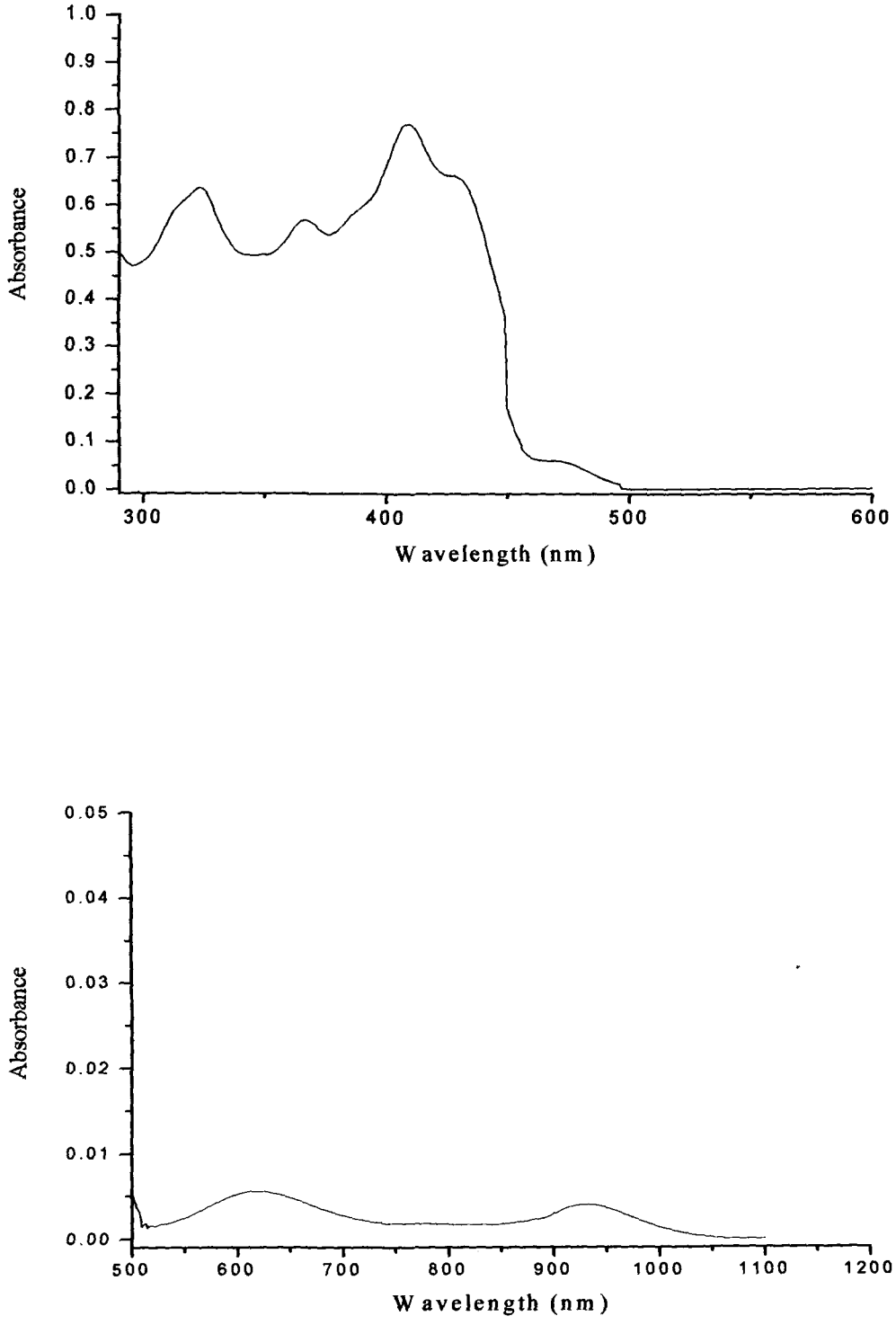
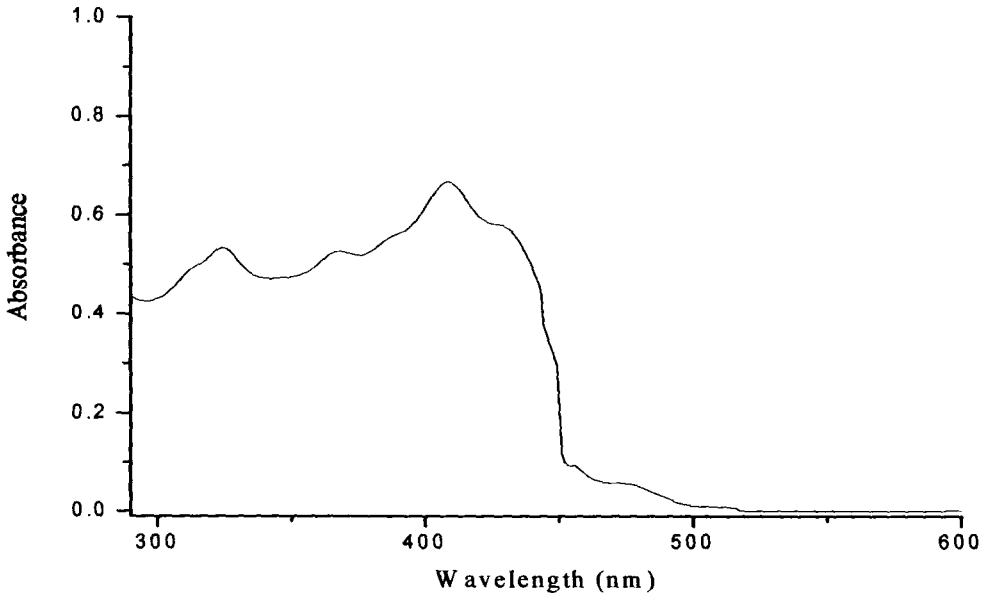


Fig. 7.1. Electronic spectrum of $[NiZn(nsh)(H_2O)_3]$ (7.1) in DMF.



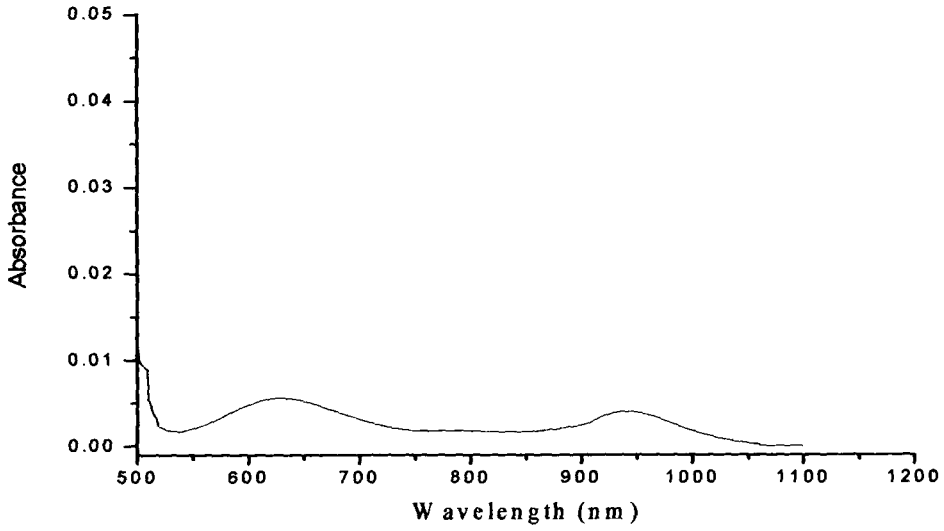


Fig. 7.2. Electronic spectrum of $[NiZn(nsh)(py)_3]$ (7.2) in DMF.

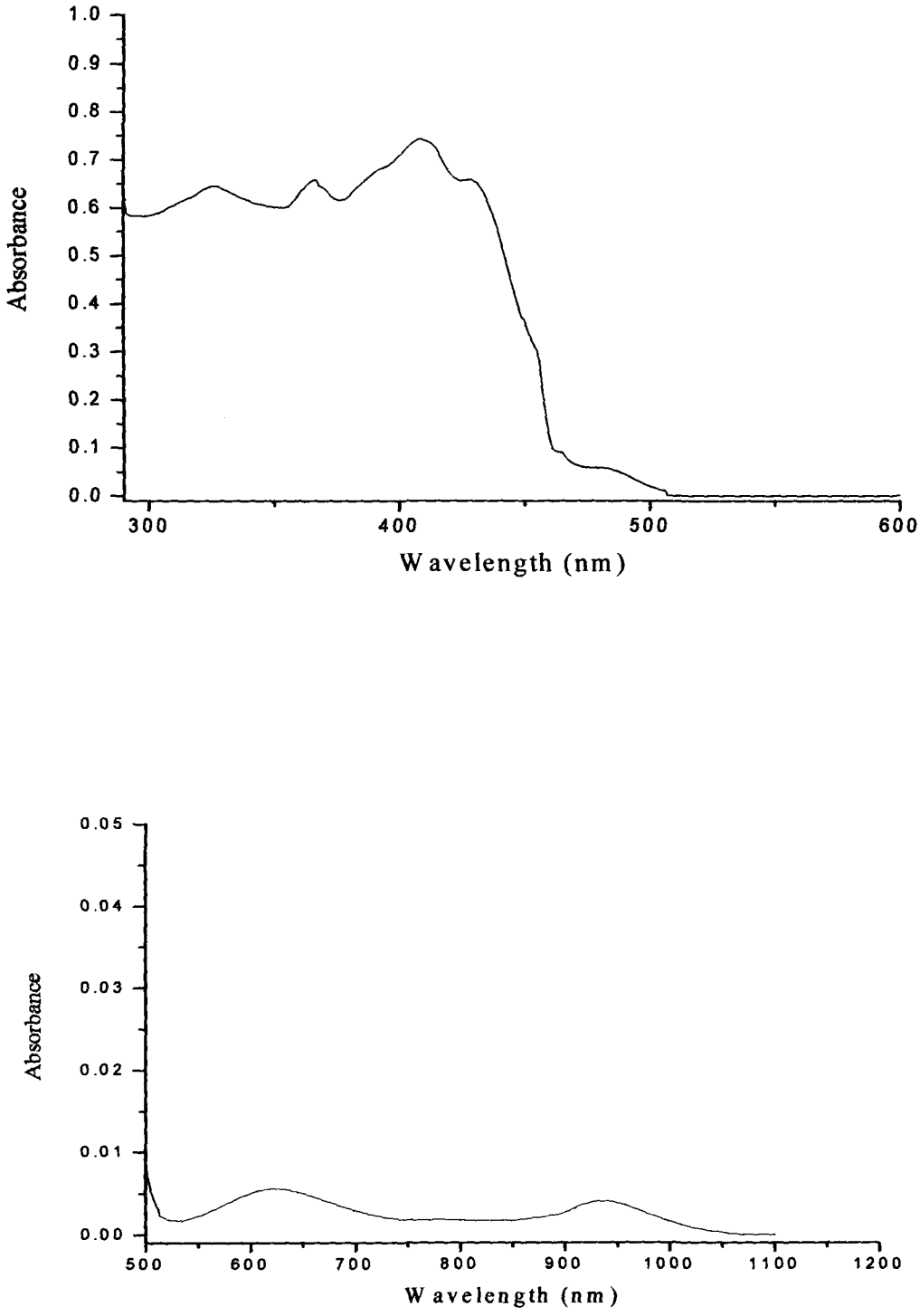
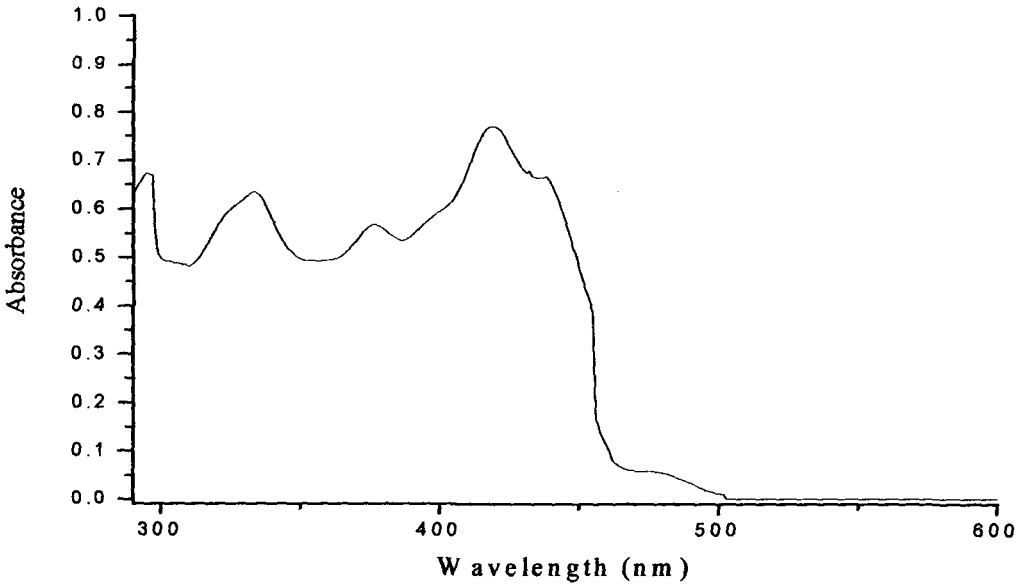


Fig. 7.3. Electronic spectrum of $[NiZn(nsh)(2\text{-pic})_3]$ (7.3) in DMF.



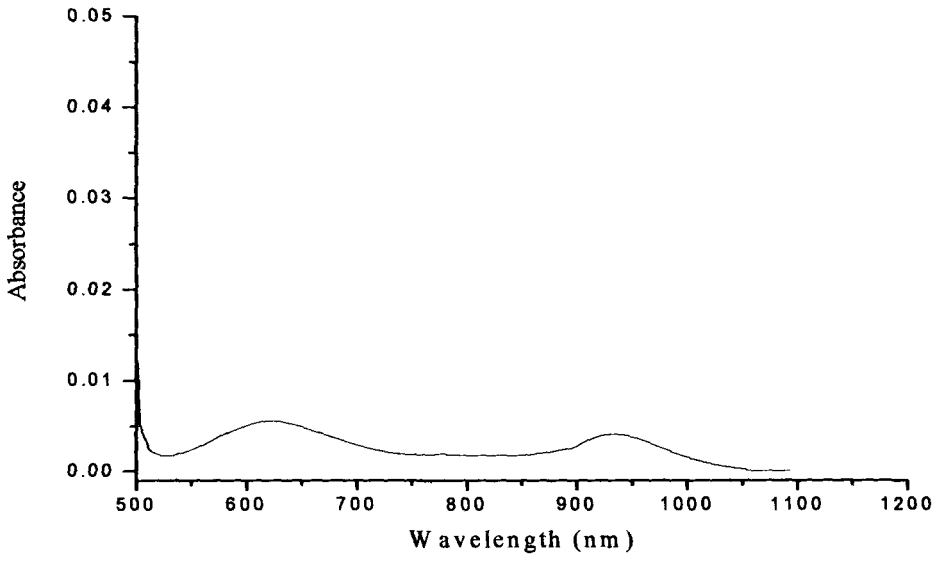


Fig. 7.4. Electronic spectrum of $[NiZn(nsh)(4\text{-pic})_3]$ (7.5) in DMF.

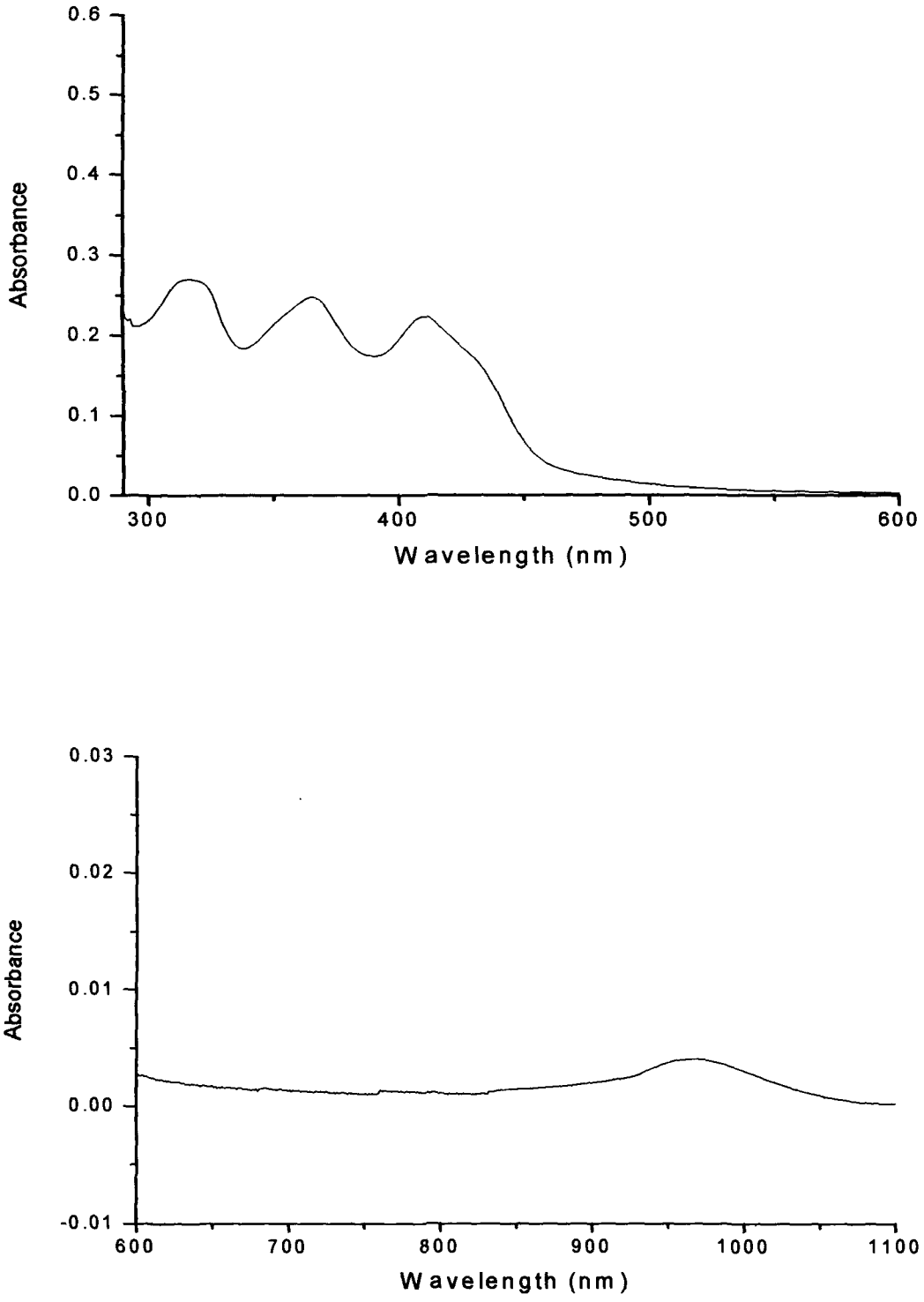


Fig. 7.5. Electronic spectrum of $[ZnNi(nsh)(H_2O)_2]$ (7.6) in DMF.

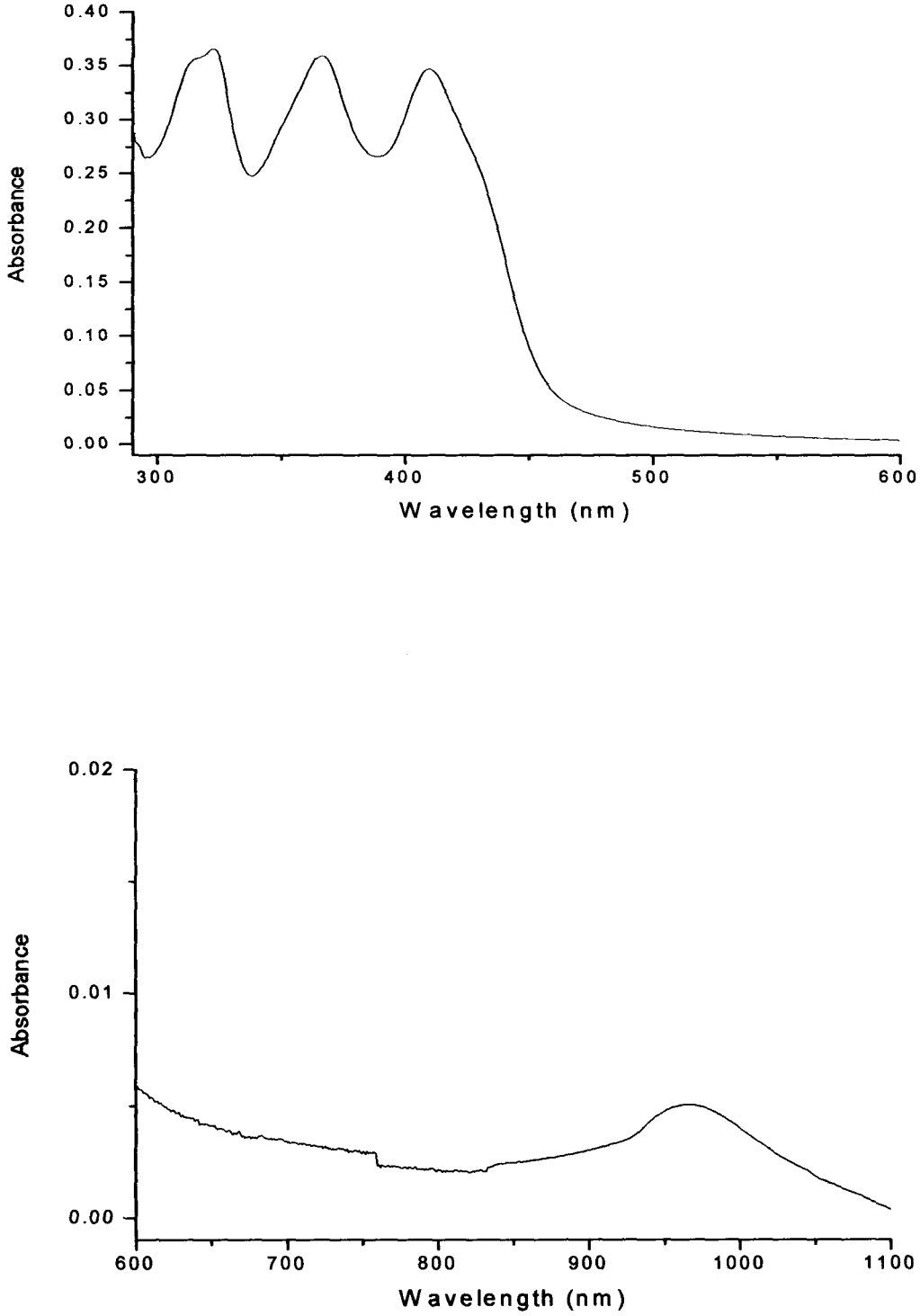


Fig. 7.6. Electronic spectrum of $[ZnNi(nsh)(py)_2]$ (7.7) in DMF.

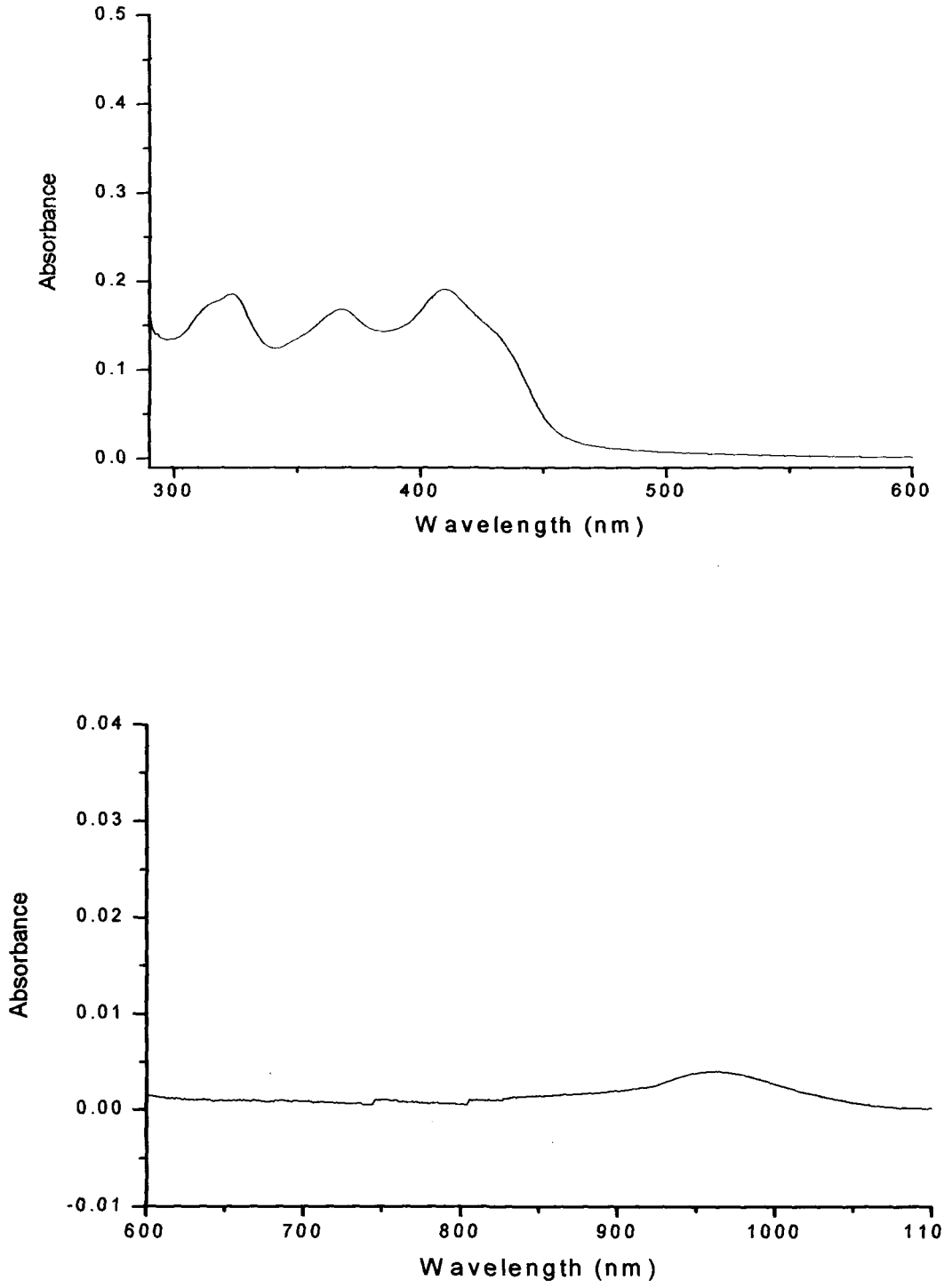


Fig. 7.7. Electronic spectrum of $[ZnNi(nsh)(2\text{-pic})_2]$ (7.8) in DMF.

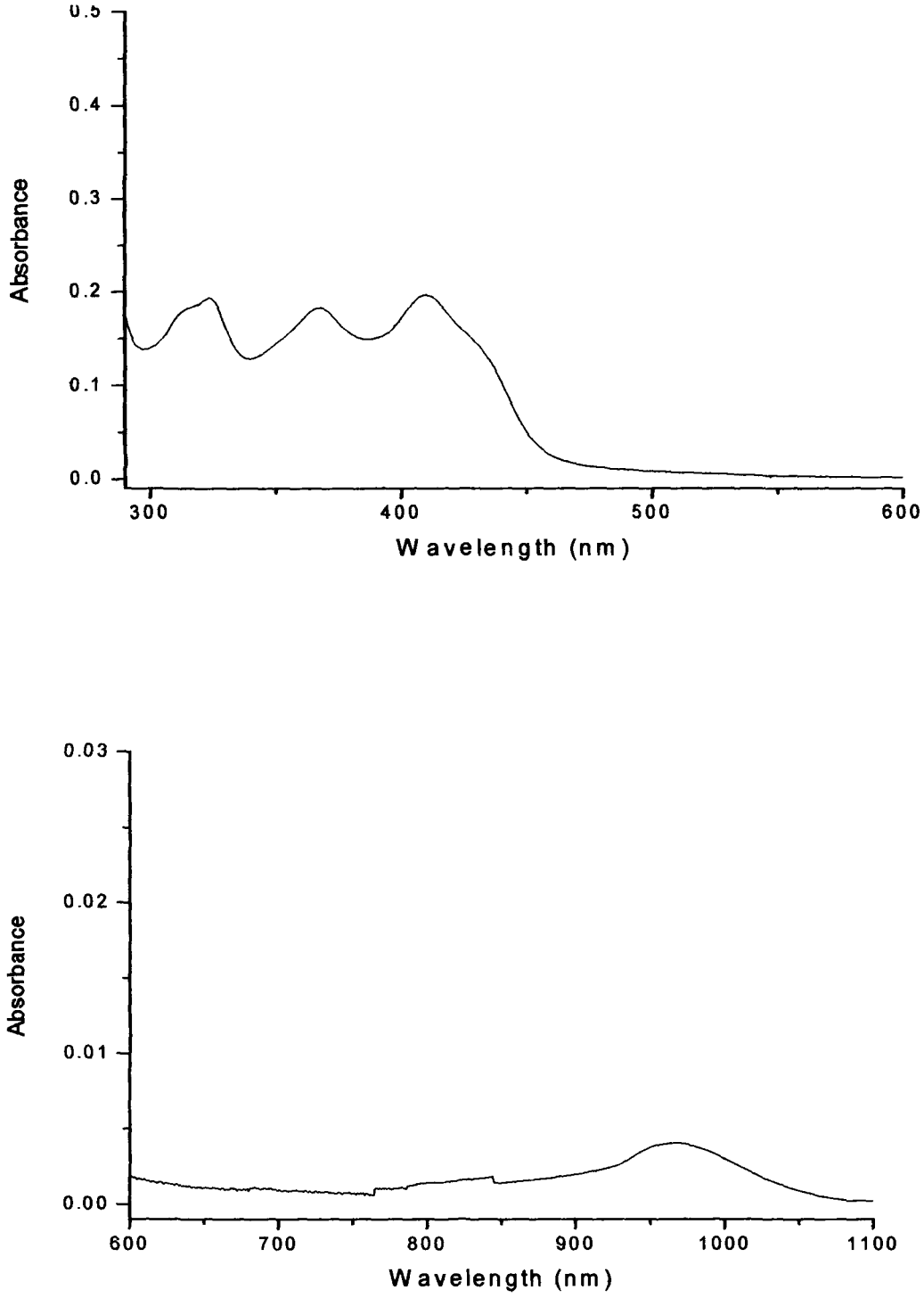


Fig. 7.8. Electronic spectrum of $[ZnNi(nsh)(4\text{-pic})_2]$ (7.10) in DMF.

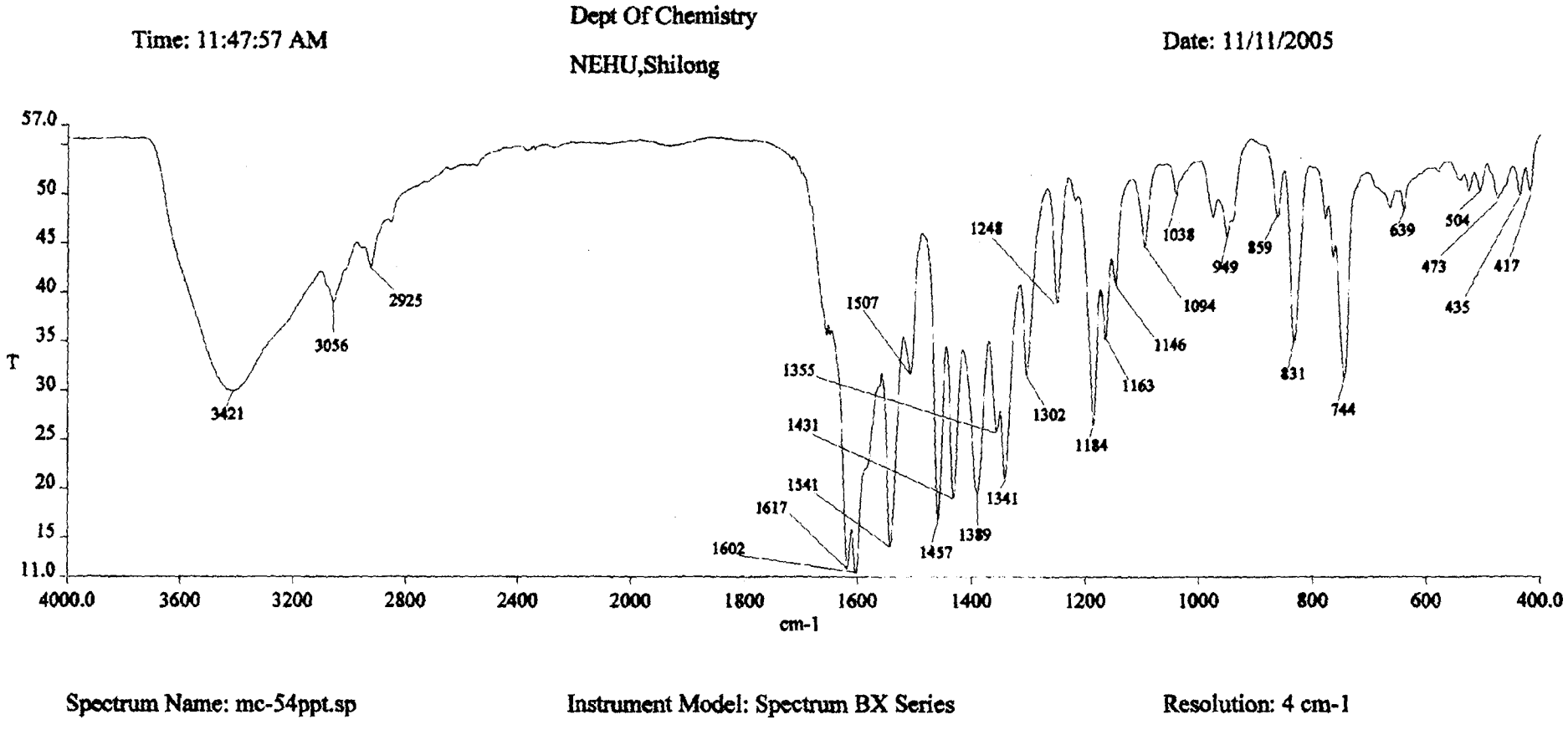


Fig. 7.9. Infrared spectrum of $[NiZn(nsh)(H_2O)_3]$ (7.1) in KBr.

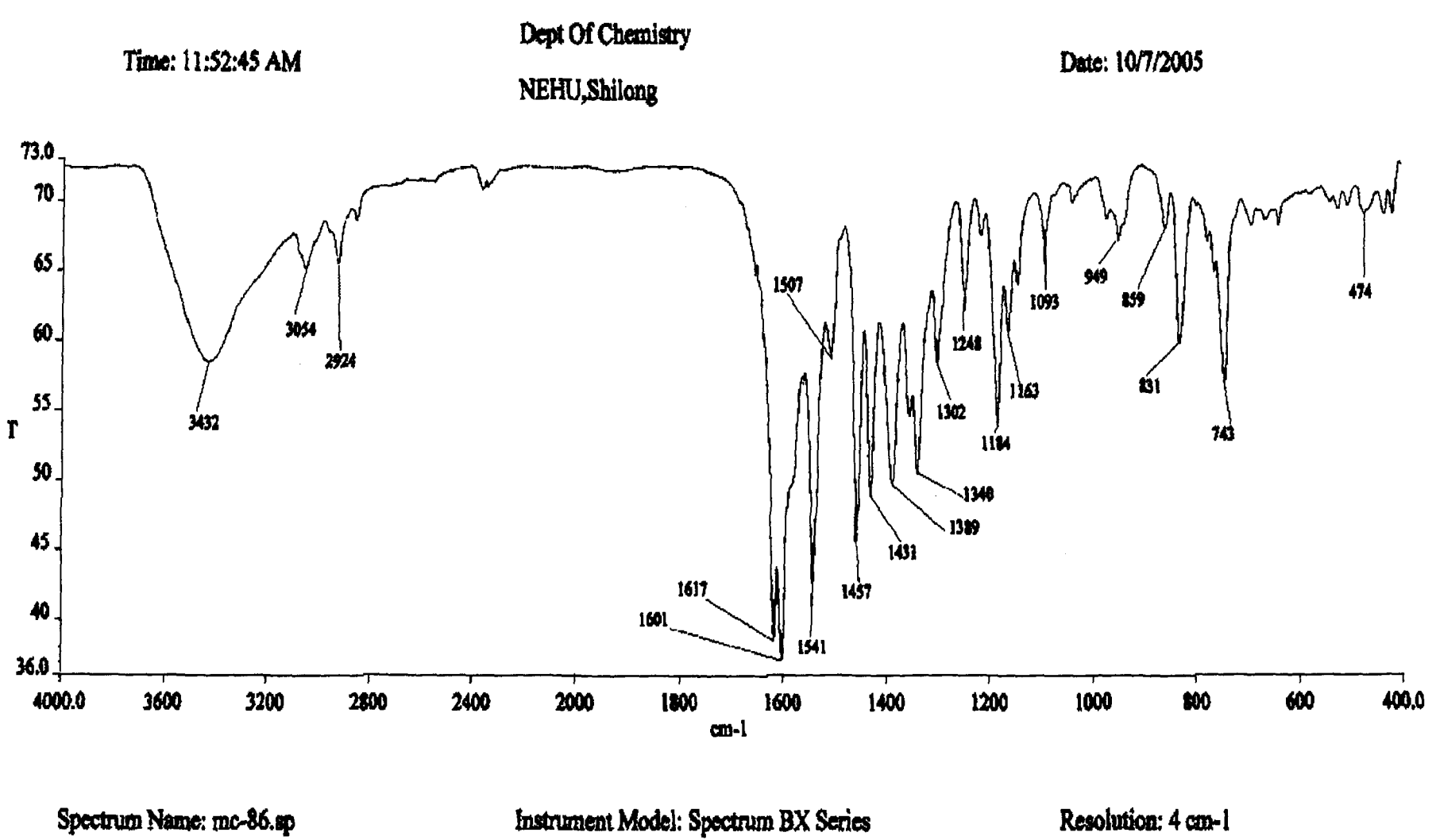


Fig. 7.10. Infrared spectrum of $[NiZn(nsh)(py)_3]$ (7.2) in KBr.

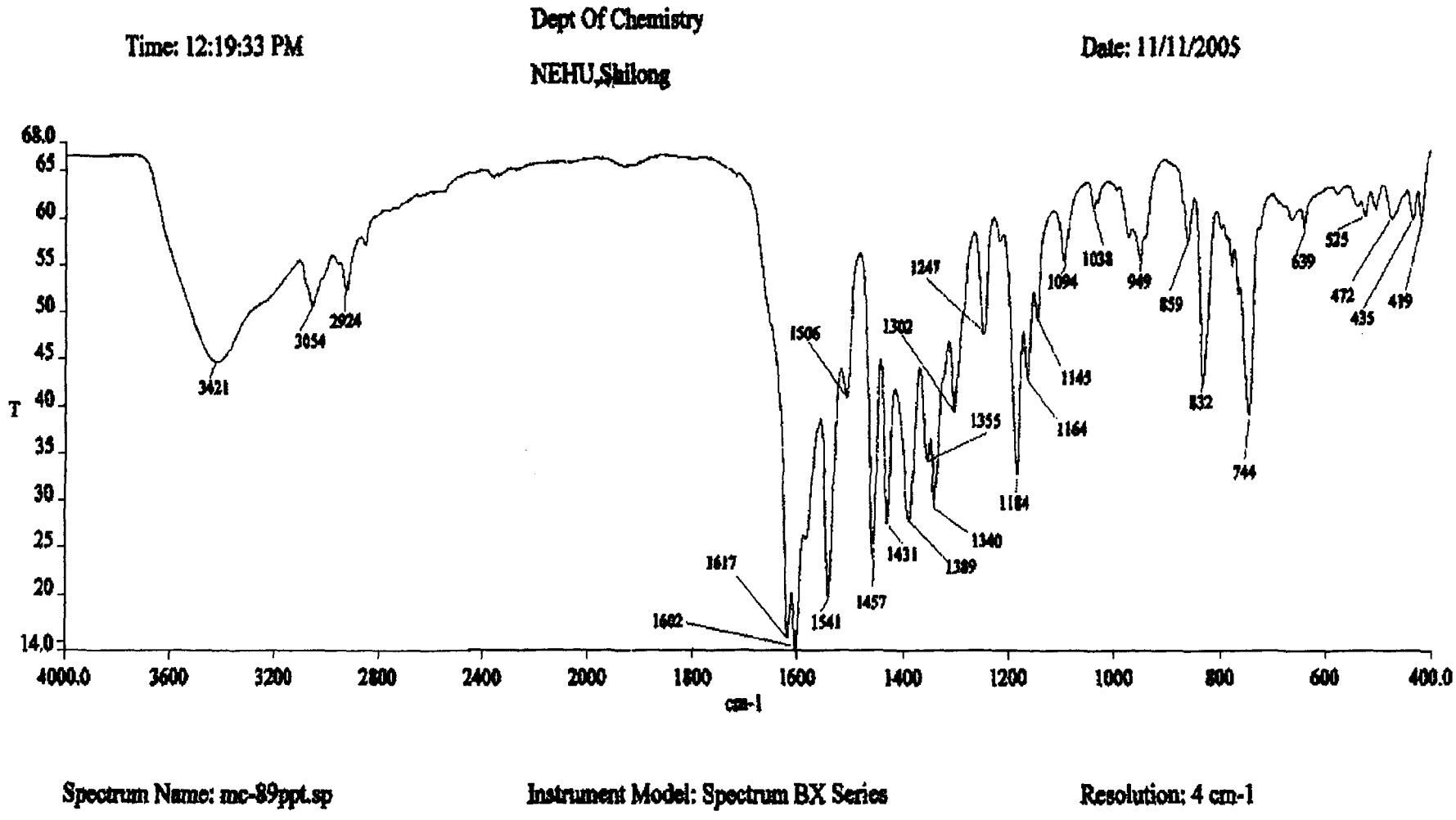


Fig. 7.11. Infrared spectrum of $[NiZn(nsh)(2\text{-pic})_3]$ (7.3) in KBr.

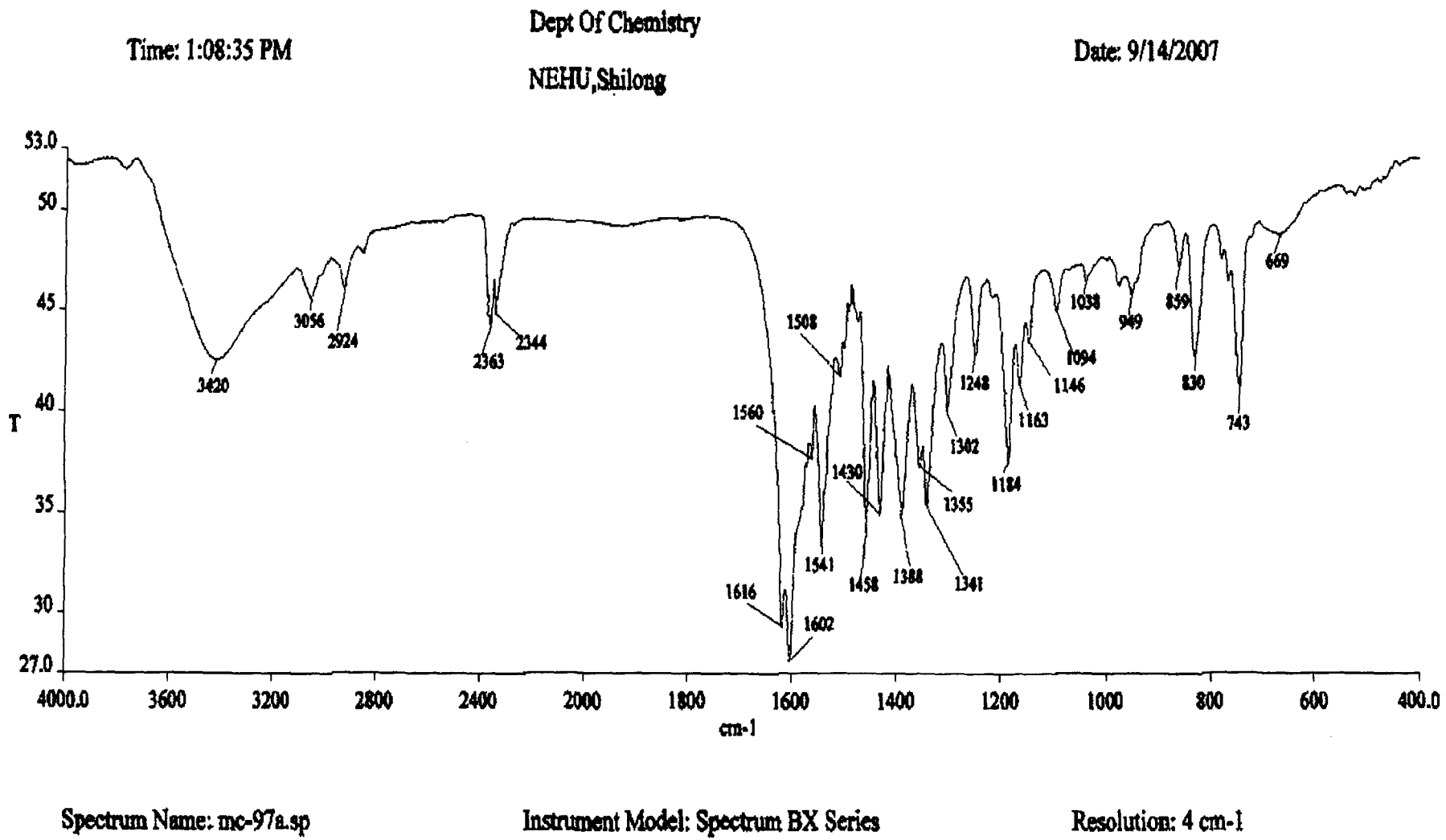


Fig. 7.12. Infrared spectrum of $[NiZn(nsh)(4\text{-pic})_3]$ (7.5) in KBr.

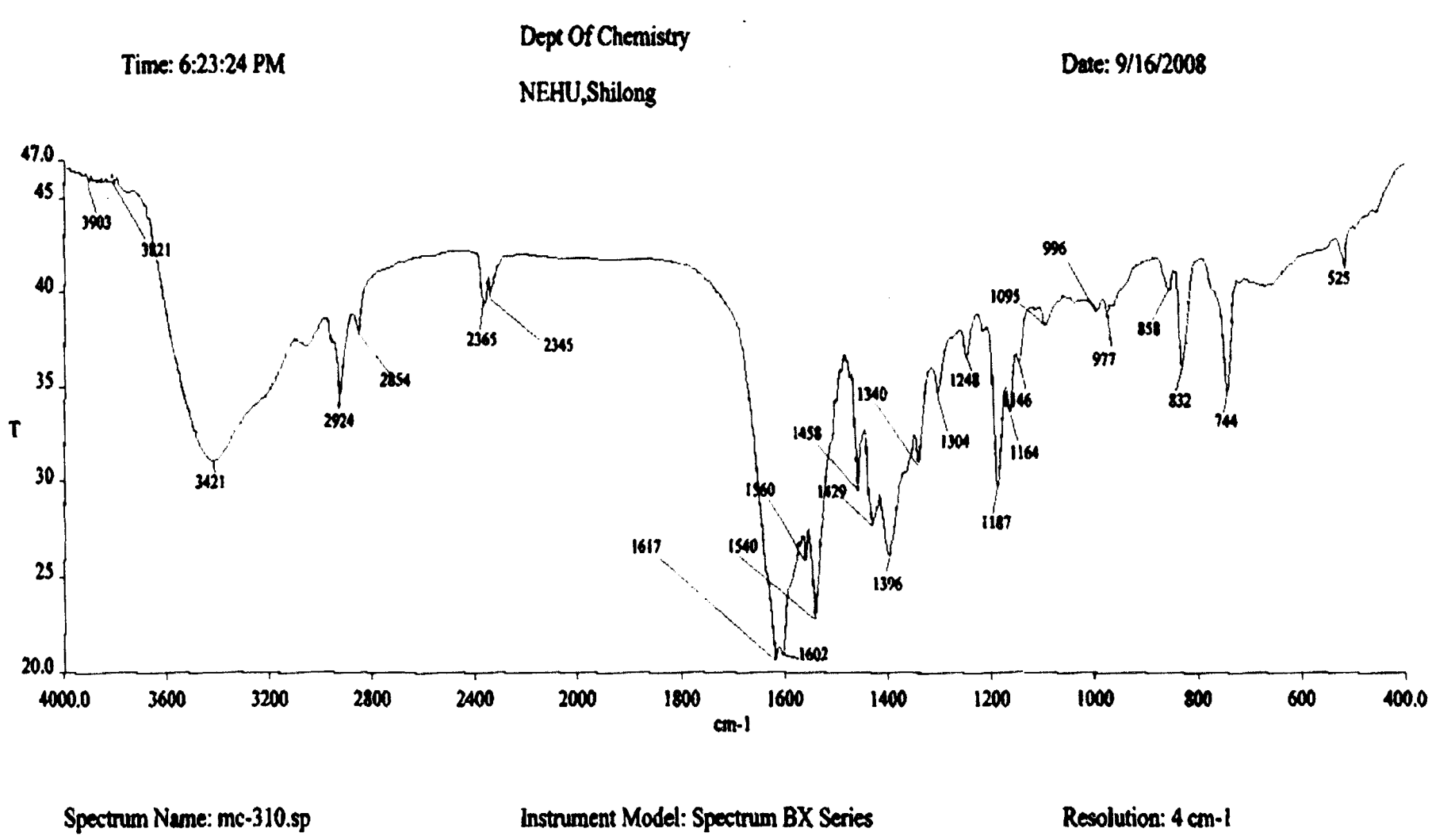


Fig. 7.13. Infrared spectrum of $[ZnNi(nsh)(H_2O)_2]$ (7.6) in KBr

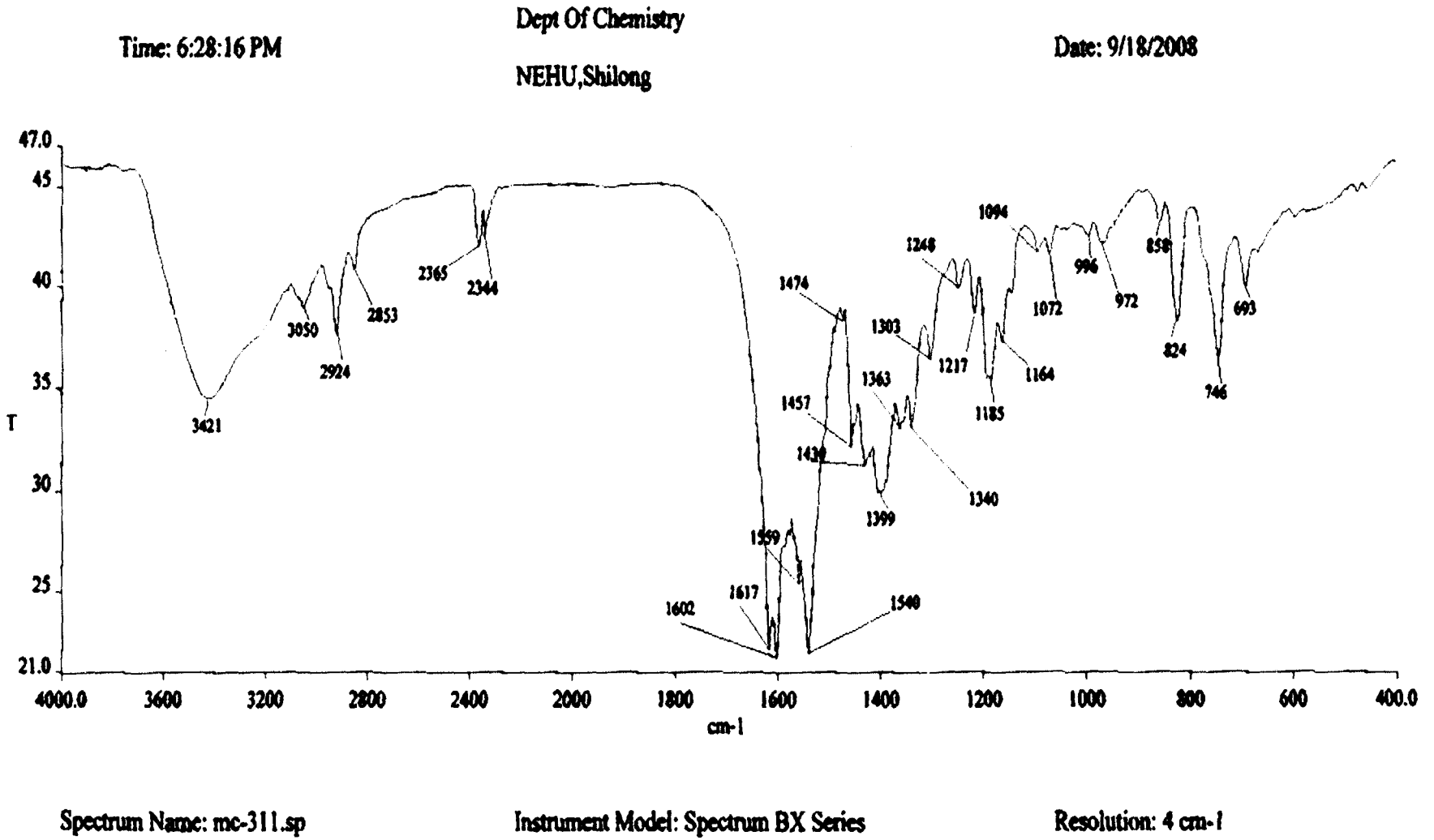


Fig. 7.14. Infrared spectrum of $[ZnNi(nsh)(py)_2]$ (7.7) in KBr.

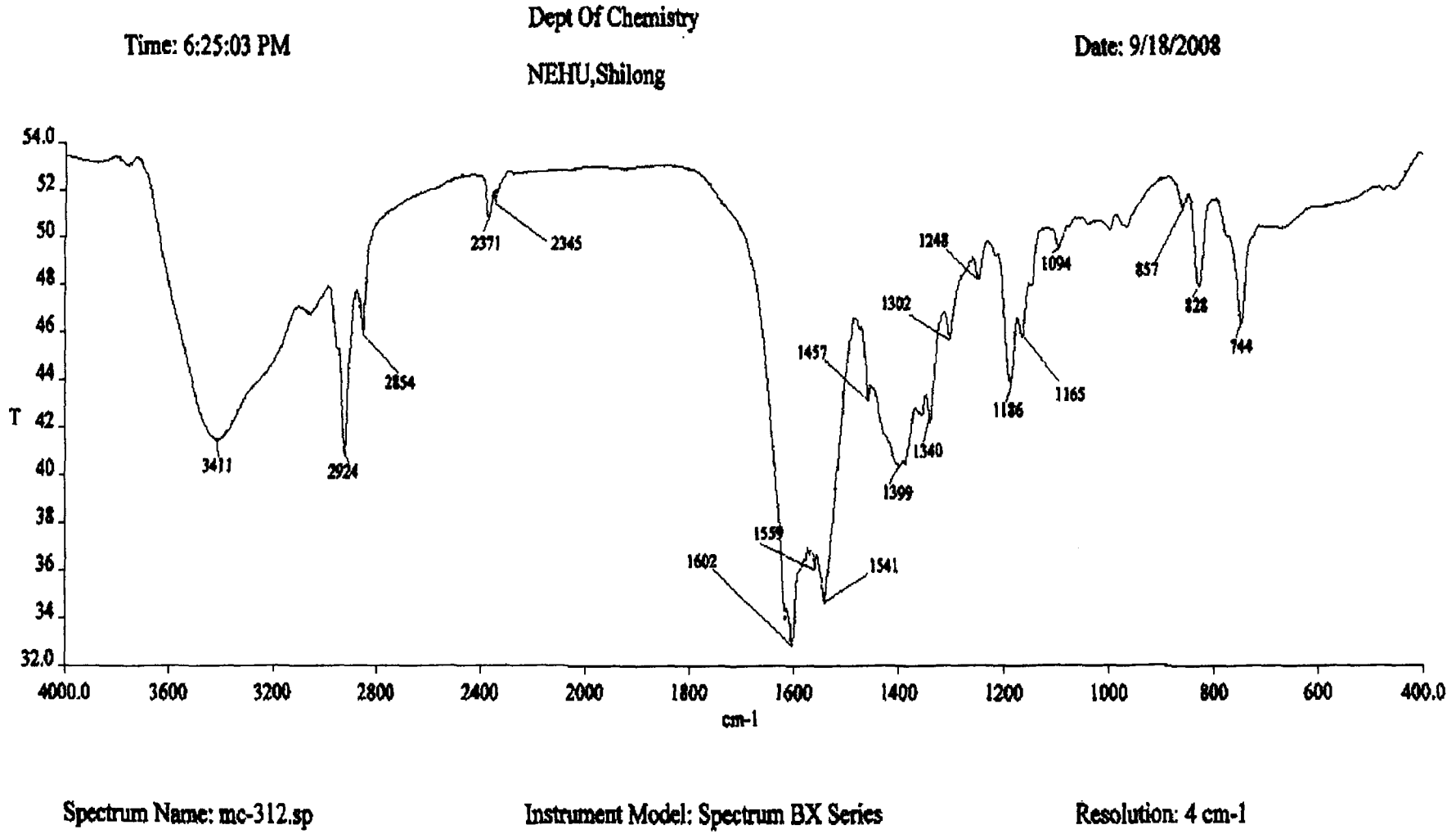


Fig. 7.15. Infrared spectrum of $[ZnNi(nsh)(2\text{-pic})_2]$ (7.8) in KBr.

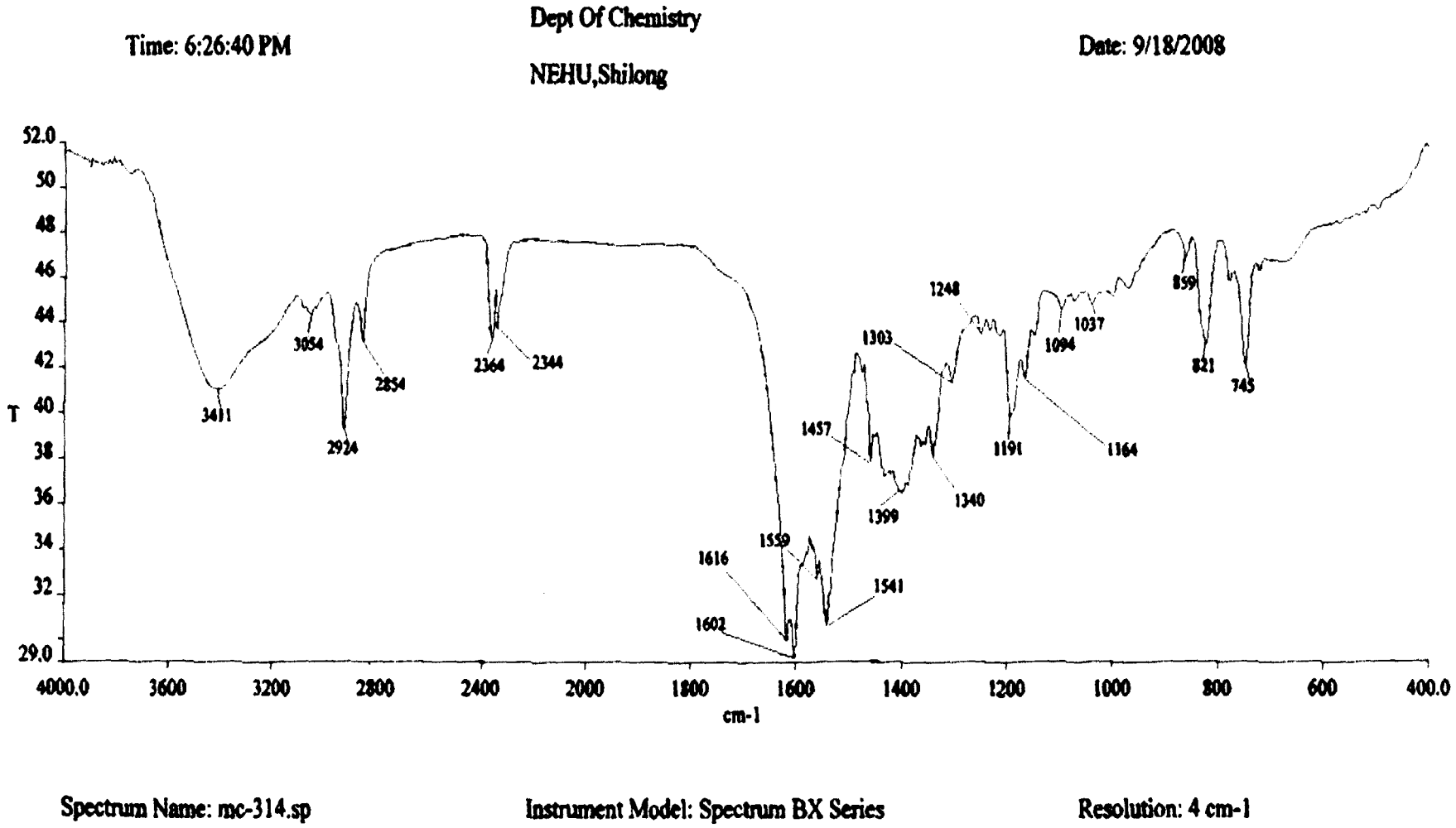


Fig. 7.16. Infrared spectrum of $[ZnNi(nsh)(4\text{-pic})_2]$ (7.10) in KBr.

Table 7.1: Analytical Data and Physical properties of monometallic Ni-Zn Heterobimeatllic Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

Sl. No	Complex and Colour	D.P (°C)	Yield(%)	Analysis: Found (Calc.) (%)					Molar Conductance (Λ_M) $Ohm^{-1} cm^2 mol^{-1}$	Magnetic Moment μ_B (BM)
				Zn	Ni	C	H	N		
7.1	$[NiZn(nsh)(H_2O)_3]$ Brown	>300	65.00	10.16 (10.40)	9.08 (9.34)	49.76 (49.68)	3.83 (3.85)	8.88 (8.91)	3.21	2.98
7.2	$[NiZn(nsh)(py)_3]$ Brown	>300	62.00	8.66 (8.05)	7.08 (7.23)	60.54 (60.66)	4.09 (4.10)	12.14 (12.08)	3.12	3.03
7.3	$[NiZn(nsh)(2\text{-}pic)_3]$ Brown	>300	60.00	7.77 (7.66)	6.52 (6.87)	61.74 (61.89)	4.61 (4.60)	11.45 (11.48)	2.98	3.10
7.4	$[NiZn(nsh)(3\text{-}pic)_3]$ Brown	>300	61.00	7.76 (7.66)	6.68 (6.87)	61.78 (61.89)	4.60 (4.60)	11.47 (11.48)	2.81	2.95
7.5	$[NiZn(nsh)(4\text{-}pic)_3]$ Brown	>300	61.00	7.79 (7.66)	6.55 (6.87)	61.78 (61.89)	4.59 (4.60)	11.52 (11.48)	2.92	3.15
7.6	$[ZnNi(nsh)(H_2O)_2]$ Light brown	>300	61.00	11.01 (10.71)	9.52 (9.61)	51.54 (51.15)	3.61 (3.63)	9.45 (9.18)	3.08	3.25
7.7	$[ZnNi(nsh)(py)_2]$ Light brown	>300	63.00	8.77 (8.92)	8.52 (8.01)	59.24 (59.01)	3.84 (3.85)	11.55 (11.47)	2.98	3.35
7.8	$[ZnNi(nsh)(2\text{-}pic)_2]$ Light brown	>300	60.00	8.77 (8.59)	7.62 (7.71)	59.74 (59.99)	4.21 (4.24)	11.13 (11.05)	3.09	3.40
7.9	$[ZnNi(nsh)(3\text{-}pic)_2]$ Light brown	>300	62.00	8.76 (8.59)	7.67 (7.71)	59.79 (59.99)	4.23 (4.24)	11.12 (11.05)	3.13	3.42
7.10	$[ZnNi(nsh)(4\text{-}pic)_2]$ Light brown	>300	61.00	8.81 (8.59)	7.67 (7.71)	59.78 (59.99)	4.25 (4.24)	11.16 (11.05)	3.08	3.34

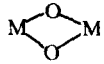
Table 7.2: Electronic spectral data for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its heterobimetallicNi(II)-Zn(II) complexes .

Sl. No	Ligand/ Complex	Electronic spectral bands λ_{max} (nm) (ε_{max} ($dm^3mol^{-1}cm^{-1}$))
	H_4nsh	317 (5480), 363 (5420)
7.1	$[NiZn(nsh)(H_2O)_3]$	322 (12640), 369 (11280), 410 (15420), 472 (1160), 615 (112), 931 (81)
7.2	$[NiZn(nsh)(py)_3]$	326 (10640), 369 (10540), 407 (13300), 478 (1096), 626 (112), 940 (81)
7.3	$[NiZn(nsh)(2\text{-}pic)_3]$	325 (12447), 367 (12698), 407 (14280), 430 (12639), 486 (1026), 622 (108), 935 (78)
7.4	$[NiZn(nsh)(3\text{-}pic)_3]$	326 (10318), 369 (10571), 408 (14064), 477 (1082), 623 (104), 936 (78)
7.5	$[NiZn(nsh)(4\text{-}pic)_3]$	334 (12253), 378 (10941), 421 (14782), 481 (1058), 621 (106), 934 (78)
7.6	$[ZnNi(nsh)(H_2O)_2]$	318 (5392), 367 (4942), 412 (4470), 966 (80)
7.7	$[ZnNi(nsh)(py)_2]$	323 (7328), 366 (7206), 410 (6946), 967(82)
7.8	$[ZnNi(nsh)(2\text{-}pic)_2]$	324 (3643), 368 (3298), 413 (3729), 965 (78)
7.9	$[ZnNi(nsh)(3\text{-}pic)_2]$	323 (7328), 366 (7206), 414 (6946), 967 (80)
7.10	$[ZnNi(nsh)(4\text{-}pic)_2]$	324 (3874), 368 (3660), 410 (3922), 968 (81)

Table 7.3: Ligand field parameters for the heterobimetallic Ni(II)-Zn(II) complexes derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone .

Sl. No.	Complex	$^3A_{2g} \rightarrow {}^3T_{2g}(F)$ (ν_1)		$^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2)		Dq (cm^{-1})	ν_2/ν_1	B (cm^{-1})	β	$\beta°$ (%)	LFSE (kcal mol^{-1})
		nm	cm^{-1}	nm	cm^{-1}						
7.1	$[NiZn(nsh)(H_2O)_3]$	931	10741	615	16260	1074.1	1.51	625.07	0.6022	39.78	36.90
7.2	$[NiZn(nsh)(py)_3]$	940	10638	626	15974	1063.8	1.50	594.16	0.5724	42.76	36.55
7.3	$[NiZn(nsh)(2\text{-}pic)_3]$	935	10695	622	16077	1069.5	1.50	600.8	0.5788	42.12	36.74
7.4	$[NiZn(nsh)(3\text{-}pic)_3]$	936	10684	623	16051	1068.4	1.50	598.21	0.5763	42.37	36.70
7.5	$[NiZn(nsh)(4\text{-}pic)_3]$	934	10707	621	16103	1070.7	1.50	602.77	0.5807	41.63	36.78

Table 7.4: Structurally significant Infrared (IR) bands (in cm^{-1}) for Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone and its heterobimetallic Ni-Zn complexes.

Sl. No	Ligand/Complex	ν(OH + NH)	ν(C=O)	ν(C=N)	Amide II + ν(C–O) (naphtholic)	ν(NCO)	ν(C–O)	ν(N–N)		ν(M–O) (naphtholic)	ν(M–O) (carbonyl)	Other bands
	H_4nsh	3423 m 3244 m 3051m	1672 vs	1633 vs 1593m	1540 m	—	1281m	1029 w	—	—	—	—
	[Zn(H_2nsh)(H_2O)]	3435 m	—	1621 s 1604 m	—	1580 s 1508 w	1283 m	1030 w	—	528 w	420 w	—
	[Ni(H_2nsh)(H_2O)$_2$]	3410 m 3291 m	—	1622 s 1604 m		1540 s 1508 w	1306 m 1282 w	1084 w 1039 w	—	555 w 521 w	—	—
7.1	[NiZn(nsh)(H_2O)$_3$]	3421 m 3056 w	—	1617 s 1602 m	—	1541 s 1507 w	1248 s 1213 w	1038 w	777 w	525 w 504 w	473 w 435 w	—
7.2	[NiZn(nsh)(py)$_3$]	3432 m 3054 w	—	1617 s 1601 m	—	1541 s 1507 w	1248 s 1214 w	1031 w	777 w	525 w 504 w	474 w 435 w	1012 w
7.3	[NiZn(nsh)(2-pic)$_3$]	3421 m 3054 w	—	1617 s 1602 m	—	1541 s 1506 w	1247 s 1214 w	1038 w	777 w	525 w 504 w	472 w 435 w	1012 w
7.4	[NiZn(nsh)(3-pic)$_3$]	3404 m 3056 w	—	1616 s 1602 m	—	1542 s 1506 w	1248 s 1214 w	1038 w	776 w	524 w	—	1013 w
7.5	[NiZn(nsh)(4-pic)$_3$]	3420 m 3056 w	—	1616 s 1602 m	—	1541 s 1508 w	1248 s 1214 w	1038 w	776 w	525 w	—	1014 w
7.6	[ZnNi(nsh)(H_2O)$_2$]	3421 m 3049 w	—	1617 s 1602 m	—	1560 w 1540 s	1248 m 1221 w	1035 w	780 w	525 w	469 w	—
7.7	[ZnNi(nsh)(py)$_2$]	3421 m 3050 w	—	1617 m 1602 s	—	1559 w 1540 s	1248 m 1217 w	1040 w	778 w	502 w	479 w	1051 w
7.8	[ZnNi(nsh)(2-pic)$_2$]	3404 m 3049 m	—	1617 m 1602 s	—	1559 w 1540 s	1248 m 1222 w	1039 w	776 w	518 w	484 w	1053 w
7.9	[ZnNi(nsh)(3-pic)$_2$]	3404 m 3049 w	—	1617 m 1602 s	—	1560 w 1541 s	1248 m 1221 w	1033 w	775 w	510 w	472 w	1069 w
7.10	[ZnNi(nsh)(4-pic)$_2$]	3411 m 3054 w	—	1616 m 1602 s	—	1559 w 1541 s	1248 m 1222 w	1037 w	773 w	522 w	479 w	1072 w

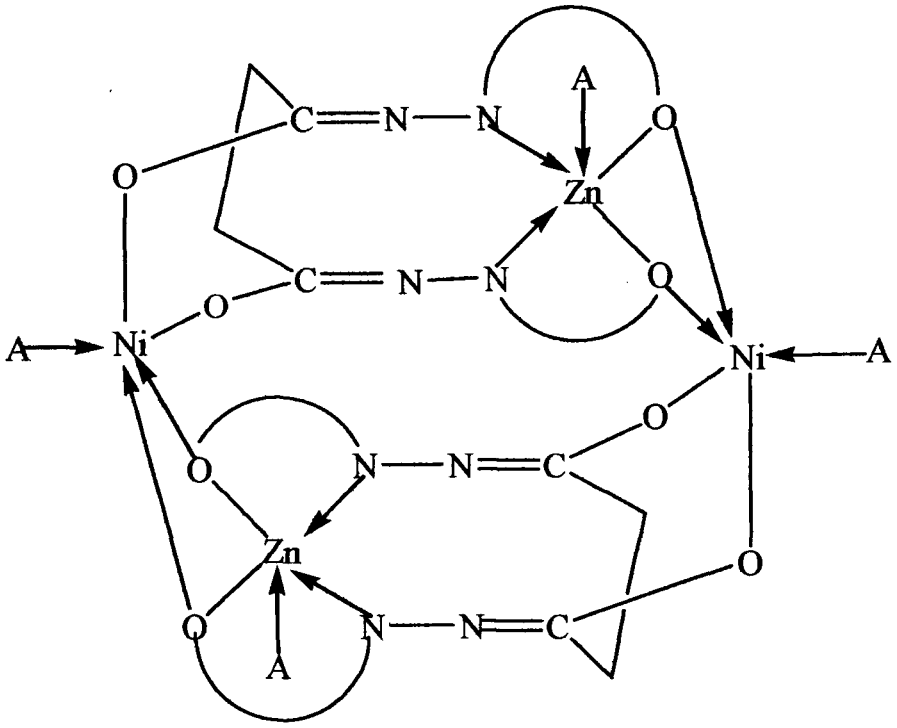


Fig.7.18. Tentative structure of $[ZnNi(nsh)(A)_2]$ where A = H_2O (7.6), pyridine (py, 7.7), 2-picoline (2-pic, 7.8), 3-picoline (3-pic, 7.9), 4-picoline (4-pic, 7.10).

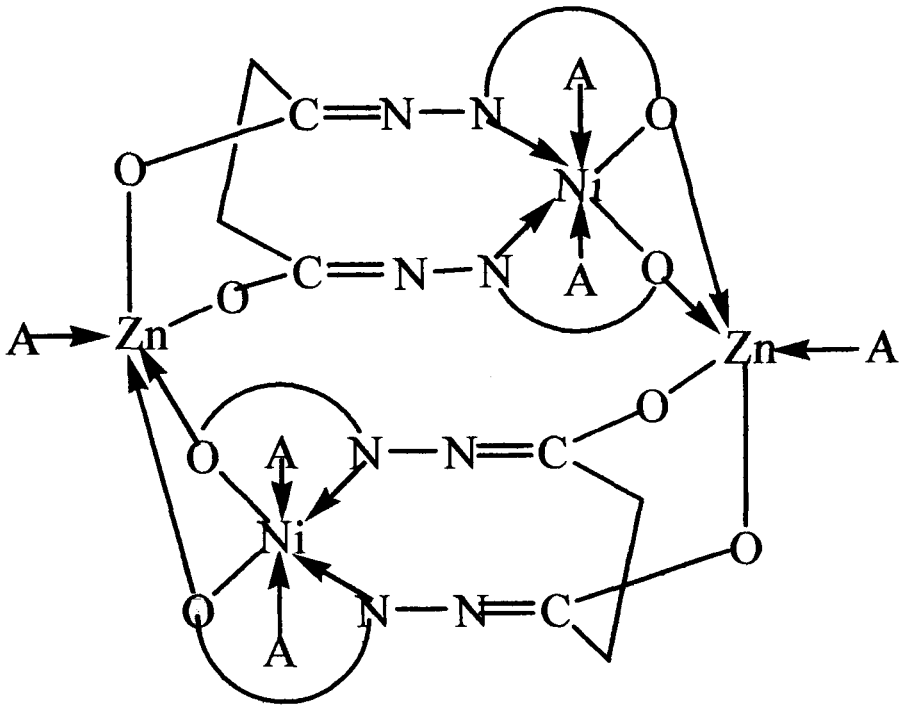


Fig.7.17. Tentative structure of $[NiZn(nsh)(A)_3]$ where A = H_2O (7.1), pyridine (py, 7.2), 2-picoline (2-pic, 7.3), 3-picoline (3-pic, 7.4), 4-picoline (4-pic, 7.5).

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SUMMARY

CHAPTER I

INTRODUCTION AND LITERATURE SURVEY

This chapter presents a brief account of importance of the metal ions selected in the present study i.e. molybdenum, nickel and zinc. It also presents a pertinent literature on the transition and non-transition metal complexes of acyl-, aroyl- and pyridoyl dihydrazines and their dihydrazones derived from their condensation with various aldehydes and ketones and related ligands. An attempt has been made to survey literature on all these ligands up-to-date.

CHAPTER – II

EXPERIMENTAL

In this chapter, the experimental details regarding the preparation of succinoyl dihydrazine and the ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone(H_4nsh) have been described. Procedure for elemental analyses, physico-chemical techniques and instruments used are also described in this chapter.

CHAPTER- III

Synthesis, Characterization and Structural Assessment of Monometallic Molybdenum(VI) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

This chapter deals with the synthesis, characterization and structural assessment of five monometallic molybdenum(VI) complexes derived from the tetrabasic octadentate ligand bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone (H_4nsh).

In the beginning, a brief account of literature survey with respect to coordination behavior of the ligands related to bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone such as acyl-, aroyl- and pyridoyl- dihydrazines and dihydrazones containing hydroxyl groups are discussed.

The following molybdenum complexes have been described in this chapter.

$[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2py\cdot 2C_2H_5OH$ (3.2), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(2\text{-pic})\cdot 2C_2H_5OH$ (3.3), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(3\text{-pic})\cdot 2C_2H_5OH$ (3.4), $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2(4\text{-pic})\cdot 2C_2H_5OH$ (3.5).

The complexes are either orange or orange-yellow in colour. All of the complexes are air stable solid powders and decompose without melting above 300 °C. They are all insoluble in common organic solvents such as ethanol, methanol, acetone, benzene, acetonitrile and ether. But all of them are soluble in highly coordinating solvents such as DMSO and DMF.

Molar conductance values for the complexes (3.1) to (3.5) lie in the range 2.16–2.81 $ohm^{-1}cm^2mol^{-1}$ which are consistent with their non-electrolytic nature in DMSO.

All of the complexes are diamagnetic, consistent with the +6 oxidation state of molybdenum in them. The ESR spectral studies also support the diamagnetic nature of the complexes.

The essential features of the ligand bands in the electronic spectra of the complexes suggests that the ligand is bonded to the metal centre in the same configuration as in the uncoordinated dihydrazone i.e. *anti-cis* configuration.

The electronic spectra of all of the complexes in addition to the intraligand bands exhibit a couple of bands in the region 408–435 nm. These bands are assigned to ligand-to-metal charge transfer transition. The electronic spectra of the complexes suggest that the two hydrazone parts of the ligand are present in different planes either in free state or in the coordinated state.

In the ^1H NMR spectra of the complexes (3.1) to (3.5) two proton signals observed in the region δ 11.61–12.73 ppm has been assigned to δ (OH) protons while the other two proton signals in the region δ 9.99–11.14 ppm downfield of TMS have been assigned to δ (NH) protons, respectively. The signals in the region δ 8.60–9.05 ppm has been assigned to azomethine (-CH=N) protons, whereas a multiplet in the region δ 7.19–8.23 ppm to naphthyl protons. Further, the two signals observed at δ 2.66 and δ 2.52 ppm, respectively are assigned to methylene protons.

The essential features of the ^1H NMR spectra of the complexes are similar to that of the uncoordinated dihydrazone and this suggests that the conformation of the dihydrazone remains unaltered on complexation. The only significant difference in the ^1H NMR spectra

of the complexes (3.1) to (3.5) as compared to that of the free dihydrazone is that the δ(-CH=N) signals show an average down field shift by 0.66–0.44 ppm and this suggests the involvement of azomethine group in coordination to the metal centre. The appearance of δ(OH) and δ(NH) proton signals in the form of doublets in all of the complexes suggests their non-involvement in coordination to the metal centre. This further suggests the existence of dihydrazone in the *anti-cis* configuration in these complexes. The solvent molecules present in the complexes are not bonded to the metal centre.

The complexes (3.2), (3.3), (3.4) and (3.5) have been characterized by ^{13}C NMR spectroscopy and are in good agreement with the findings of ^{1}H NMR spectroscopy.

The uncoordinated dihydrazone show a strong band at 1672 cm^{-1} and is assigned to ν(C=O) stretching vibration. The ν(C=O) band remains either unshifted in positon as in the complexes (3.1), (3.4) and (3.5) or shifts to lower frequency by 6 cm^{-1} as in the complexes (3.2) and (3.3). Such a feature associated with the ν(C=O) band in the IR spectra of the complexes (3.3) to (3.5) rules out the possibility of coordination of >C=O group to the metal centre because the >C=O group absorbs at almost in the same region in the complexes in which uncoordinated >C=O group have been reported to absorb in dihydrazone metal complexes. The ν(C=N) bands observed at 1633 and 1593 cm^{-1} in the free dihydrazone shift to lower frequency by 3–7 cm^{-1} in the metal complexes indicating coordination of N-atom of >C=N group to the metal centre.

In the free dihydrazone, a medium intensity band is observed at 1281 cm^{-1} has been assigned to ν(C-O) stretching vibration. This band remains almost unshifted in position in all of the complexes. Such a feature associated with ν(C-O) band rules out the possibility of bonding through naphtholic oxygen atoms to the metal centre.

The appearance of strong to medium intensity bands in the region 950–895 cm^{-1} in the IR spectrum of the complexes (3.1) to (3.5) clearly indicates the presence of *cis*-MoO_2^{2+} group in these complexes. Further, the band of medium intensity in the region 778–792 cm^{-1} is assigned to the stretching vibration of the doubly bridged Mo_2O_2 moiety.

At the end of the chapter, the tentative structures for the complexes have been suggested.

CHAPTER – IV

Synthesis, Characterization and Structural Assessment of Homobimetallic Molybdenum(VI) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

The present chapter describes the synthesis, characterization and structural assessment of seven homobimetallic molybdenum(VI) complexes derived from bis(2-hydroxy-1-naphthaledyhe)succinoyldihydrazone.

After presenting in brief, the rationality for its relevance in relation to the first chapter, this chapter deals with the importance of multimetallic enzymes in various fields. Subsequently it describes the synthesis of the complexes followed by results and discussion.

The complexes described in this chapter were found to have the following composition:

$[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1), $[(MoO_2)_2(nsh)(py)_2]\cdot C_2H_5OH$ (4.2), $[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ (4.3), $[(MoO_2)_2(nsh)(3\text{-pic})_2]\cdot C_2H_5OH$ (4.4),

$[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5), $[(\mu_2\text{–}O)_2(MoO_2)_2(H_4nsh)(phen)]\cdot C_2H_5OH$(4.6), $[(\mu_2\text{–}O)_2\ (MoO_2)_2(H_4nsh)(bpy)]\cdot C_2H_5OH$ (4.7).

The complexes are orange, light orange and light yellow in colour. All of the complexes are air stable solid powders and decompose above 300 °C without melting except the complex (4.6) which melt at 217 °C. All of the complexes are insoluble in water and common organic solvents such as ethanol, methanol, acetone, benzene, acetonitrile, chloroform and ether. But all of the complexes are soluble in DMSO and DMF.

All of thecomplexesare non-electrolyte in DMSO. All of the complexes are diamagnetic consistent with the presence of molybdenum in +6 oxidation state in these complexes with d^0 electronic configuration.

The electronic spectra of the complexes in addition to the ligand bands exhibit a new band in the region 429–436 nm and these bands are assigned to originate from ligand-to-metal charge transfer transition (LMCT).

The two proton signals observed in each of the region δ 11.61–12.73 ppm and δ 9.99–11.14 ppm downfield of TMS due to naphtholic -OH and secondary -NH protons,

respectively in the ^{1}H NMR spectra of the free dihydrazone are absent in the ^{1}H NMR spectra of the complexes (4.1) to (4.5) indicating collapse of amide structure of the ligand and its involvement in coordination in enol form through naphtholate oxygen atoms via deprotonation and carbonyl oxygen atoms via enolization cum deprotonation. On the other hand, the presence of δ (OH) and δ (NH) proton signals in the complexes (4.6) and (4.7) suggests that the dihydrazone is coordinated to the metal centre in the keto form. The upfield shift of δ (OH) and δ (NH) proton signals rules out the possibility of involvement of >NH and >C=O group in coordination. The most crucial feature of the ^{1}H NMR spectra of the complexes (4.1) to (4.5) is the merger of the doublets corresponding to δ (-CH=N) protons in the free ligand into a single resonance on complexation. This suggests that the dihydrazone, which exist in the *anti-cis* configuration in uncoordinated dihydrazone, isomerizes to attain *staggered* configuration in these complexes. On the other hand, in the complexes (4.6) and (4.7), δ(-CH=N) proton signals appear as doublets indicating that the dihydrazone coordinates to the metal centre in the *anti-cis* configuration in these complexes.

The co-ligand molecules such pyridine and substituted pyridines, 1, 10-phenanthroline and 2,2′-bipyridine are coordinated to the metal centre.

The complexes $[(MoO_2)_2(nsh)(H_2O)_2]\cdot C_2H_5OH$ (4.1), $[(MoO_2)_2(nsh)(2\text{-pic})_2]\cdot C_2H_5OH$ (4.3), and $[(MoO_2)_2(nsh)(4\text{-pic})_2]\cdot C_2H_5OH$ (4.5) have been characterized by ^{13}C NMR spectroscopy. The ^{13}C NMR spectral evidences support the conclusions drawn from ^{1}H NMR spectroscopy regarding coordination of dihydrazone to the metal centre. The ^{13}C NMR signals due to 3-picoline and 4-picoline molecules in the complexes (4.3) and (4.5) have also been assigned.

IR spectra of the complexes support the conclusions drawn from NMR spectroscopy regarding bonding of the ligand to the metal centre.

All of the dioxomolybdenum complexes show two strong to very strong bands in the region 884–956 cm^{-1}. This indicates the presence of *cis*-MoO_2^{2+} group in these complexes.

The tentative structures for the complexes have been proposed at the end.

CHAPTER V

Synthesis, Characterization and Structural Assessment of Zinc(II) Complexes Derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.

The introductory part of this chapter briefly dwells on the importance of zinc(II) and its complexes in various fields like biology and electrochemistry.

This chapter describes the following complexes

$[Zn(H_2nsh)(H_2O)]$ (5.1), $[Zn(H_2nsh)(py)]$ (5.2), $[Zn(H_2nsh)(2\text{-pic})]$ (5.3), $[Zn(H_2nsh)(3\text{-pic})]$ (5.4), $[Zn(H_2nsh)(4\text{-pic})]$ (5.5). $[Zn_2(nsh)(H_2O)_2]$ (5.6); $[Zn_2(nsh)(py)_2]$, (5.7) $[Zn_2(nsh)(2\text{-pic})_2]$ (5.8); $[Zn_2(nsh)(3\text{-pic})_2]$ (5.9), $[Zn_2(nsh)(4\text{-pic})_2]$ (5.10).

All of the complexes are yellow in colour and are air stable. The complexes (5.1), (5.3) and (5.4) decompose above 300 °C without melting while the complexes (5.2) and (5.5) melt with decomposition at 272 and 274°C, respectively. All of the complexes are insoluble in water and other common organic solvents such as ethanol, methanol, acetone, benzene and ether. However, all of them are soluble in DMSO and DMF.

The molar conductance values for the complexes lying in the range 2.3–3.1 $ohm^{-1}cm^2mol^{-1}$ in DMSO solution at 10^{-3} M dilution suggests that they are non-electrolyte in DMSO. All of the complexes are diamagnetic consistent with d^{10} electronic configuration of Zn^{2+} ion in these complexes.

Electronic spectra of the complexes in addition to the intraligand bands show additional strong absorption bands in the region 470–480 nm with molar extinction co-efficient (ε_{Max}) in the region 2247–2522 $dm^3cm^2mol^{-1}$ in the complexes (5.1) to (5.5) and 457–486 $dm^3cm^2mol^{-1}$ in the complexes (5.6) to (5.10) respectively. These bands are attributed to arise due to ligand-to-metal charge transfer transition and are responsible for the dark yellow colour of the complexes.

All of the complexes were characterized by ^1H NMR spectroscopy. The two proton doublets observed at δ 11.61 and δ 12.73 ppm downfield of TMS assigned to naphtholic -OH protons in the ^1H NMR spectrum of the free dihydrazone are downfield shifted on complexation and appear as singlets in the ^1H NMR spectra of the complexes (5.1) to (5.5). The appearance of δ (OH) signals in the ^1H NMR spectra of all of the complexes indicates

the presence of -OH group in the complexes. The downfield shift of these signals indicates coordination of naphtholic –OH group to the zinc centre.The δ (NH) signals which appear at δ 9.99 and δ 11.14 ppm in the ^{1}H NMR spectrum of the free dihydrazone disappears in all of the complexes suggesting collapse of amide structure of the dihydrazone and its coordination to the metal centre in the enol form. However, the ^{1}H NMR spectra of the complexes (5.6) to (5.10) do not show any signal due to δ (OH) and δ (NH). The absence of signals due to δ (OH) and δ (NH) in the ^{1}H NMR spectra of the complexes (5.6) to (5.10) indicates the coordination of dihydrazone to the metal centre in enol form through naphtholate oxygen atoms via deprotonation and carbonyl oxygen atoms via enolization.

The azomethine (>CH=N) proton signal which in the free dihydrazone appear at δ 8.60 and δ 9.05 ppm as doublets exhibit a downfield shift of the order of δ 0.29–0.69 ppm, respectively in the complexes (5.1) to (5.5). The downfield shift of the azomethine proton signal and its appearance in the form of doublets suggests coordination of azomethine nitrogen atom to the metal centre and the existence of dihydrazone in the *anti-cis* configuration in the complexes (5.1) to (5.5). However, the main feature of the ^{1}H NMR spectra of the complexes (5.6) to (5.10) is the collapse of the doublets corresponding to δ-CH=N signal in the free ligand into a single resonance. This ^{1}H NMR spectral feature of the complexes (5.6) to (5.10) suggests that the dihydrazone, which exists in the *anti-cis* configuration in the free state, attains *staggered* configuration in the complexes (5.6) to (5.10). Similar coordination mode of the related malonoyl dihydrazone to the metal centre has been reported by Gopinathan and co-workers and by Lal et al.

The naphthyl proton multiplet appears in the regions δ 7.06–8.23 ppm and δ 7.07–8.44 ppm respectively in the complexes (5.1) to (5.5) and (5.6) to (5.10). In addition to naphthyl proton signals in the region δ 7.06–8.23 ppm and δ 7.06–8.23 ppm in the ^{1}H NMR spectra of the complexes (5.2) to (5.5) and (5.7) to (5.10), some new signals are also observed in the region δ 7.77–7.79 ppm and these signals are attributed to arise due to *ortho* protons of pyridyl ring of pyridine, 2-picoline, 3-picoline and 4-picoline molecules.The complexes (5.3), (5.4), (5.5) and (5.8), (5.9) and (5.10) show a new signal at δ 2.07, δ 2.07 and δ 2.04 ppm assigned to methyl protons of 2-picoline, 3-picoline and 4-picoline molecules. These signals are upfield shifted as compared to their positions in the free molecules. Features associated with the pyridyl protons of pyridine, 2-picoline, 3-picoline and 4-picoline molecules and methyl protons indicates flow of electron density from ring nitrogen atom of these donor molecules.

A comparison of the IR spectra of the complexes with that of the free ligand (H_4nsh) suggests that the dihydrazone is coordinated to the metal centre in enol form in all of the complexes.

The ν(NH) band observed at 3244 cm^{-1} in the uncoordinated dihydrazone does not appear in the IR spectrum of all of the complexes. This suggests the destruction of amide structure of ligand in these complexes. The absence of bands due to secondary –NH group in the region 3240–3500 cm^{-1} in combination with the absence of amide I (>C=O) band in all of the complexes suggests collapse of amide structure of the dihydrazone as a result of enolization and its coordination through oxygen atom of >C=O group to the metal centre in the enol form. This is also corroborated by the absence of the very strong ligand band at 1672 cm^{-1} in the IR spectra of the complexes.

In the free dihydrazone, the ν(C=N) band appears as a couple of bands at 1633 and 1593 cm^{-1}. This band appears as a single band in the IR spectrum of the complexes (5.2) to (5.5) while as a couple of bands in the complex (5.1) and the complexes (5.6) to (5.10) in the region 1618–1602 cm^{-1} and thus shows either no shift as in the complexes (5.1) to (5.5) or shift to lower frequency by 1–2 cm^{-1} respectively. This indicates the coordination of azomethine nitrogen to the metal centre. The small shift in νC=N stretching frequency in the complexes is due to the difference of bonded species i.e. from >C=N..... H to >C=N→M . The amide III band at 1321 cm^{-1} in the free dihydrazone registers a shift to higher frequency by 7–20 cm^{-1} in all of the complexes showing the involvement of >C=O in coordination.

The band of weak intensity at 1540 cm^{-1} in the IR spectrum of the free dihydrazone is assigned to amide II + ν(C–O) (naphtholic). This band shifts to higher frequency in all of the complexes except the complex (5.1) in which it appear at 1508 cm^{-1} while it appears in the region 1542–1559 cm^{-1} in the complex (5.2) to (5.10). This band in the region 1508–1559 cm^{-1} in all of the complexes is assigned to ν(NCO^- vibration) of the newly formed NCO^- group as a result of enolization of the dihydrazone. This is further supported by the absence of -NH band in the IR spectrum of all of the complexes. The assignment of this band in the region 1508–1553 cm^{-1} remains quite tentative unless confirmed by isotopic substitution study.

A band of medium intensity observed at 1281 cm^{-1} due to ν(C–O) vibration in the free ligand, shifts to higher frequency by 2–7 cm^{-1} and appears in the region 1284–1288 cm^{-1} in

the IR spectra of all the complexes. The shift of ν(C–O) band to higher frequency indicates the coordination of naphtholic OH group to the metal centre in the complexes.

A new non-ligand band observed in the region 870–873 cm^{-1} in the IR spectra of the complexes (5.6) to (5.10) is assigned to the stretching vibration of the tetra-atomic species  resulted from involvement of naphtholate oxygen atom in bridge formation. The presence of this band indicates that the Zn(II) atoms are tethered together through naphthoxo bridging.

All of the complexes show a new weak intensity band in the region 1003–1010 cm^{-1}. This band is assigned to ring breathing mode of pyridine, 2-picoline, 3-picoline and 4-picoline molecules in the complexes (5.2) to (5.10). The presence of this band in these complexes further indicates the coordination of pyridine, 2-picoline, 3-picoline and 4-picoline molecules to the metal centre.

The structures for the complexes have been tentatively assigned.

CHAPTER VI

Synthesis, Characterization and Structural Assessment of Ni(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

The introduction part of the chapter describes in brief the rationality for selecting nickel in the present study. Subsequently, it describes the importance of nickel in various fields like industrial catalysis, biology and magnetism.

The following monometallic and homobimetallic Ni(II) complexes have been described in this chapter.

$[Ni(H_2nsh)(H_2O)_2]$ (6.1),$[Ni(H_2nsh)(py)_2]$ (6.2), $[Ni(H_2nsh)(2\text{-pic})_2]$ (6.3), $[Ni(H_2nsh)(3\text{-pic})_2]$ (6.4), $[Ni(H_2nsh)(4\text{-pic})_2]$ (6.5), $[Ni_2(nsh)(H_2O)_4]$ (6.6), $[Ni_2(nsh)(py)_4]$. (6.7), $[Ni_2(nsh)(2\text{-pic})_4]$ (6.8), $[Ni_2(nsh)(3\text{-pic})_4]$ (6.9), $[Ni_2(nsh)(4\text{-pic})_4]$ (6.10).

The complexes are brown, yellow, light brown and dark brown in colour. All of the complexes are air stable solid powders and decompose above 300 °C without melting. All of the complexes are insoluble in water and common organic solvents such as ethanol,

methanol, acetone, benzene, acetonitrile, chloroform and ether, but all of them are soluble in DMSO and DMF.

The molar conductance values for the complexes (6.1) to (6.10) lie in the region 2.62–3.13 $ohm^{-1}cm^2mol^{-1}$ in 10^{-3} M DMSO solution indicating their non-electrolytic nature in this solvent.

The magnetic moment values for the complexes (6.1) to (6.5) lie in the range 2.85–3.45 BM which is typical of an octahedral Ni(II) compound. However, in the homobimetallic Ni(II) complexes (6.6) to (6.10), the magnetic moment values lie in the range 1.14–1.73 BM i.e. 0.57–0.87 BM per Ni(II) ion. These values are considerably less than the values reported for spin free nickel(II) complexes indicating a strong metal-metal interaction in the structural unit.

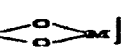
The electronic spectra of the complexes recorded in DMF show red shift of ligand bands that gives good evidence of chelation of dihydrazone to the metal centre. In addition to the intraligand bands, all of the complexes exhibit a new band in the region 410–440 nm which has very high molar extinction co-efficient and is assigned to have its origin in the ligand-to-metal charge transfer transition, most probably, from naphtholate oxygen atoms to the metal centre, All of the complexes show two additional low energy bands in the region 500–900 nm which are characteristic of nickel(II) ion in octahedral coordination.

The band at 1672 cm^{-1} assigned to ν(C=O) stretching vibration in the free dihydrazone disappears in the IR spectra of all the complexes indicating that the ligand H_4nsh is coordinated to the metal centre in the enol form. The bands observed at 1633 and 593 cm^{-1} in the IR spectrum of the free dihydrazone are attributed to ν(C=N) stretching vibrations. These bands, on an average, shift to lower frequency by 2–3 cm^{-1} in all of the complexes indicating coordination of >C=N group to the metal centre.

The ν(C–O) band observed at 1281 cm^{-1} in the free dihydrazone shifts to higher frequency in all of the complexes and appears at ~ 1303 cm^{-1} as a medium intensity band. This indicates bonding through C-O oxygen atoms to the metal centres via deprotonation of the naphtholic –OH group

The complexes (6.2) to (6.5) and (6.7) to (6.10) show a new but very weak intensity band in the region 1076–1045 cm^{-1}. This band is assigned to ring breathing mode of pyridine and substituted pyridine molecules. The presence of this band in the IR spectra of the

complexes indicates coordination of pyridine, 2-picoline, 3-picoline and 4-picoline molecules to the metal centre.

A new non-ligand band observed in the region 861–897 cm^{-1} in the IR spectra of the complexes (6.6) to (6.10) is assigned to the stretching vibration of the tetra-atomic species [] resulted from involvement of naphtholate oxygen atom in bridge formation.

The complexes have been assigned to have distorted octahedral stereochemistry. The tentative structures for the complexes have been proposed.

CHAPTER VII

Synthesis, Characterization and Structural Assessment of Heterobimetallic Ni(II)-Zn(II) Complexes Derived from Bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone

The introductory part of this chapter briefly describes the importance of bimetallic complexes in various fields like homogeneous catalysis, heterogeneous catalysis, multimetallic enzymes and synthesis of solid state phases of inductrial and technological importance.

The following heterobimetallic complexes derived frim bis(2-hydroxy-1-naphthaldehyde)succinoyl dihydrazone have been described.

[NiZn(nsh)$(H_2O)_3$] (7.1), [NiZn(nsh)$(py)_3$] (7.2), [NiZn(nsh)$(2\text{-pic})_3$] (7.3), [NiZn(nsh)$(3\text{-pic})_3$] (7.4), [NiZn(nsh)$(4\text{-pic})_3$] (7.5), [ZnNi(nsh)$(H_2O)_2$] (7.6), [ZnNi(nsh)$(py)_2$] (7.7), [ZnNi(nsh)$(2\text{-pic})_2$] (7.8), [ZnNi(nsh)$(3\text{-pic})_2$] (7.9), [ZnNi(nsh)$(4\text{-pic})_2$] (7.10).

The complexes are brown, orange, yellow and dark brown n colour. All of the complexes are insoluble in water and common organic solvents but are fairly soluble in DMF and DMSO.

All of the complexes are air stable solid powders and decompose without melting above 300°C. None of the complexes show weight loss below 160 °C ruling out the possibility of prexsence of water molecules in the lattice structure of the complexes. However, the complexes (7.1) and (7.6) showed weight loss in the temperature range 170–190 °C corresponding to three and two water molecules respectively. The complexes (7.2) to (7.5) and (7.7) to (7.10) showed weight loss at 220–240 °C corresponding to three and two

molecules of pyridine/2-picoline/3-picoline/4-picoline. The expulsion of these neutral electron donor molecules at such a high temperature indicates the coordination of these molecules to the metal centre.

The molar conductance values for all of the complexes at 10^{-3} M dilution in DMSO solution fall in the region 2.81–3.21 $ohm^{-1}cm^2mol^{-1}$ which suggests that all of the complexes are non-electrolyte in DMSO.

The complexes (7.1) to (7.5) exhibit magnetic moments in the range 2.95–3.15 BM while the complexes (7.6) to (7.10) exhibit μeff values in the range 3.25- 3.42 BM. The μ_{eff} values for nickel(II) complexes have been reported to fall in the regions 3.00–3.30, 3.00–3.45 and 3.45–4.00 BM respectively having octahedral, 5-coordinate square-pyramidal and tetrahedral geometry, respectively. On the other hand the four coordinate square planar nickel(II) complexes have been shown to be diamagnetic. The experimental values of magnetic moment for the complexes rule out their tetrahedral or square planar structure. The magnetic moment values for the complexes (7.1) to (7.5) lie in the range 2.95–3.15 BM which indicates that these complexes have distorted octahedral stereochemistry. Literature reports suggest that majority of the five coordinate high spin Ni(II) complexes having square-pyramidal stereochemistry have magnetic moment values lying in the region 3.25–3..29 BM . The magnetic moment values for the complexes (7.6) to (7.10) fall in the range reported for high spin square-pyramidal complexes. Thus the complexes (7.6) to (7.10) can be said to have square-pyramidal geometry with considerable amount of distortion.

In addition to the ligand bands, the complexes show a weak additional band in the region 472–481 nm. This band is similar to the band observed in the precursor Zn(II) complex $[Zn(H_2nsh)(H_2O)]$ and is assigned to have similar origin in nature i.e. charge transfer transition. Accordingly this band is assigned to arise from ligand-to-metal charge transfer transition originating from naphtholate oxygen atom.

The heterobimetallic complexes (7.1) to (7.5) exhibit new bands in the region and 931–940 nm (ν_1) and 615–628 nm (ν_2). The position of these bands is typical of an octahedrally coordinated Ni(II) centre and rules out the square planar or tetrahedral structure. A comparison of the position of the bands in the regions 931–940 and 615–628 nm with the corresponding band in the spectra of $[Ni(H_2O)_6]^{2+}$ at 1175 and 740 nm and $[Ni(NH_3)_6]^{2+}$ at 935 and 570 nm suggests that ν_1 band bear similarity with that of the nitrogen donor ligands, while the second band ν_2 is intermediate between those observed for oxygen as

well as nitrogen donor ligands but approaching towards nitrogen donor ligands. From this observation, it may safely be said that nickel atom is occupying N_2O_2 coordination chamber of the ligand. This suggests that the Zn(II) atom in the complexes (7.1) to (7.5) are displaced by Ni(II) atom. From this observation, it can be said that the Ni(II) occupies N_2O_2 coordination chamber while the zinc(II) occupies O_2O_2 coordination chamber. On the other hand, the complexes (7.6) to (7.10) derived from nickel(II) precursor complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1), exhibit only one band in the region 965–967 nm and is similar in nature to that reported for high spin square pyramidal Ni(II) complexes. Hence these complexes are assigned to have five coordinate square-pyramidal stereochemistry and the band in the region 965–967 nm is assigned to the transition $^3B_1 \rightarrow {}^3E(F)$. A comparison of the position of this band in the region 965–987 nm with the corresponding band in the spectra of $[Ni(H_2O)_6]^{2+}$ at 1175 (ν_1) and $[Ni(NH_3)_6]^{2+}$ at 935 (ν_1) and those in the complexes (7.1) to (7.5) suggests that the ν_1 bands in these complexes is shifted away from the complexes derived from nitrogen donor ligands and towards complexes derived from oxygen donor ligands. It is imperative to mention that the precursor nickel(II) complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1), the d-d bands appear at 845 and 564 nm. From this observation, it may safely be concluded that the nickel atom in the complexes (7.6) to (7.10) is most probably, coordinated to carbonyl oxygen atoms via enolization. This suggests that the Ni(II) atom which occupies N_2O_2 coordination chamber in precursor complexes is displaced by Zn(II) atoms in the hetrerobimetallic complexes. Thus it is suggested that in these complexes the nickel(II) occupies O_2O_2 coordination chamber while zinc(II) occupies N_2O_2 coordination chamber.

A comparison of the IR spectra of the heterobimetallic complexes with those of the uncoordinated dihydrazone (H_4nsh) suggests that the dihydrazone is coordinated to the metal centre in the enol form in all of the complexes.

The IR spectra of the complexes donot show any strong band in the region 1630–1700 cm^{-1}. The feature of the IR spectra of the complexes in this region is similar to that of the precursor zinc complex $[Zn(H_2nsh)(H_2O)]$ (5.1) and Ni(II) complex $[Ni(H_2nsh)(H_2O)_2]$ (6.1) . This suggests that the ligand is present in these complexes in the same form as that in the precursor zinc complex i.e. in the enol form.

The ν(C=N) band appears as a couple of bands in all of the complexes and are similar to that as observed in the precursor Zn and Ni complex. The ν(C=N) bands, on an average, show a negative shift of 3–4 cm^{-1} in metal complexes as compared to those in the free ligand and the precursor zinc and nickel complex. This shows that the azomethine

nitrogen atoms are bonded to the metal centre. It is interesting to note that one of the ν(C=N) bands (1593 cm^{-1}) shifts to higher frequency by 8–11 cm^{-1} in all of the heterobimetallic complexes as compared to its position in the in the free dihydrazone whereas the other ν C=N band (1633 cm^{-1}) shifts to lower frequency by ~ 17 cm^{-1}. The shift of one of the ν(C=N) bands to higher frequency and the other band to lower frequency on complexation in these complexes indicates inversion of azomethine group. Consequently, the axial >C=N group attains equatorial position while equatorial >C=N group attains axial position. The introduction of the positively charged metal ion in the ligand skeleton causes the reversal of azomethine group.

The fact that the ν(C=N) band appears as a couple of bands in the IR spectra of the Ni-Zn heterobimetallic complexes similar to that in the precursor Zn(II) and Ni(II) complex suggests that the two >C=N groups are not equivalent in all of the heterobimetallic complexes just as in case of the precursor Zn(II) and Ni(II) complex. Such an inequivalency of >C=N groups indicates the coordination of dihydrazone to the metal centre in *anti-cis* configuration. In this configuration the molecule is bent in such a manner that half portion of the dihydrazone remains out of plane of the molecule, while the other half remains in plane.

The complexes (7.2) to (7.5) and (7.7) to (7.10) show a new but very weak intensity band in the regions 1012–1014 cm^{-1} and 1051–1072 cm^{-1} respectively. These bands are assigned to ring breathing mode of pyridine and substituted pyridine molecules present in the complexes. The presence of this band in the IR spectra of the complexes (7.2) to (7.5) and (7.7) to (7.10) indicates their coordination to the metal centre.

A new non-ligand band observed in the region 773–780 cm^{-1} in the IR spectra of all of the complexes is assigned to the stretching vibration of the tetraatomic species [M<O>M] resulted from the involvement of naphtholate oxygen atoms in bridge formation.

The tentative structures for the complexes have been proposed at the end.

APPENDIX - I

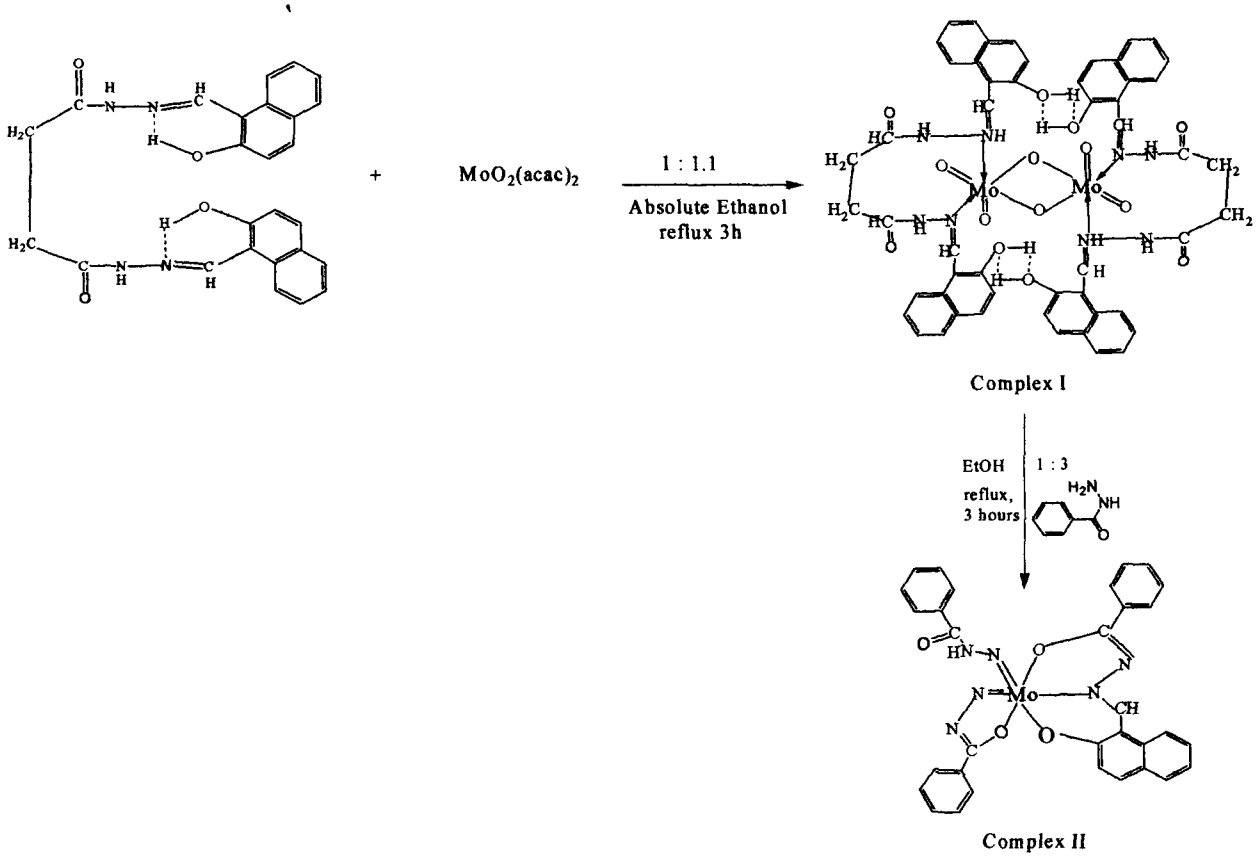
Synthesis and Characterization of a Molybdeum(VI) Complex containing Diazenido(1-) and Hydrazido(2-) Ligands. X-ray Crystal Structure of ([Mo(C_6H_5CON=N)($C_6H_5C(O)$ –NH-N=)($C_{10}H_5OCH$=N-N=COC_6H_5)])

The reaction of the complex $[(\mu_2\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (3.1) with benzoyl hydrazine in 1:3 molar ratio has been studied in ethanol. The resultant product has been characterized by IR, ^1H NMR and single crystal X-ray crystallography and the results are presented.

Experimental:

Reaction of $[(\mu\text{-}O)_2(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (I) with benzoyl hydrazine, $C_6H_5CONHNH_2$.

The complex $(\mu\text{-}O)_2[(MoO_2)_2(H_4nsh)_2]\cdot 2C_2H_5OH$ (I) (1.00 g, 1.62 mmol) was suspended in ethanol (100 mL). To this suspension was added a solution of benzoyl hydrazine (0.66 g, 4.85 mmol) in ethanol (25 mL). The resulting mixture was refluxed for 3 hours. The solution rapidly turned dark red. It was filtered while hot and the filtrate on concentration and standing for one week yielded reddish-brown crystals of the complex (II). M.p. 158 °C. Yield: 70%. Anal. calcd for $C_{66}H_{51}N_{12}Mo_2O_{13}$: Mo,13.59; C, 56.14; H, 3.64; N,11.90. Found: Mo, 13.95; C, 56.76; H, 3.62; N, 12.03. It is soluble in EtOH, MeOH, DMF and DMSO and insoluble in Et_2O, benzene, $CHCl_3$, CH_2Cl_2 and other common organic solvents. IR (KBr) cm^{-1}, 3469m, 3390w (ν O-H); 1600s (ν (>C=N—N=C<)); 1553 m (ν NCO^-); 1484w, 1434w (ν (N=N)). ^1H NMR (DMSO-d_6) δ9.95s(1H,-CH=N), δ7.18 – 8.80m (multiplet, C_6H_5 + $C_{11}H_8O$); δ 6.53s(1H, O-H(CH_3CH_2OH)); δ3.43q(2H, -CH_2(CH_3CH_2OH)); δ1.05 t (3H, -CH_3(CH_3CH_2OH).

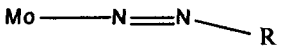


Scheme 1: Reaction showing the formation of complex I and II

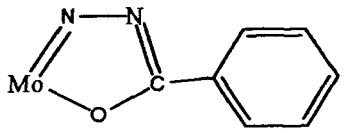
Characterization of complex II

The complex II, benzoyldiazenido(1-)benzoylhydrazido(2-)(2-hydroxy-1-naphthaldehydebenzoylhydrazone)molybdenum(VI) was obtained in 70% yield by the reaction of benzoyl hydrazine with dioxomolybdenum(VI) complex $[(\mu\text{-}O)_2(MoO_2)_2(H_4nsh)_2].C_2H_5OH$ (I) and was characterized by IR, ^1H NMR and single crystal X-ray crystallography. It is soluble in EtOH, MeOH, DMF and DMSO and insoluble in Et_2O, benzene, $CHCl_3$, CH_2Cl_2 and other common organic solvents.

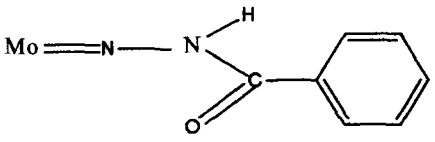
The acyldiazenido and acylhydrazido ligands may be either monodentate when they are bonded to the metal centre through the terminal nitrogen atom or bidentate when they are bonded through the nitrogen and the oxygen atom. In addition, the mode of binding to the metal centre depends on the hydrazide from which it originates as diazenido(1-) or diazenido(3-), hydrazido(1-), or hydrazido(2-). These binding modes [1] are shown in Fig.1. In the present work, one of the benzoyl hydrazine moiety acts as a monodentate ligand and is bonded to the metal centre as diazenido(1-)unit while the other benzoyl hydrazine fragment acts as a bidentate ligand and is bonded to the metal centre as hydrazido(2-)unit. The complex III can be assigned formal charges of $Mo^{6+}(NNHCOC_6H_5)^{2-}(NNCOC_6H_5)^{2-}(C_6H_5CONNCHOC_{11}H_7)^{2-}$.



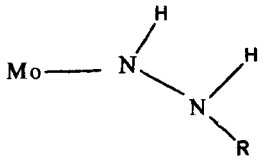
Diazenido(1-)



Diazenido(3-)



Hydrazido(2-)



Hydrazido(1-)

Fig.1. Types of ligation and binding modes of diazenido hydrazido ligands

IR spectrum of the complex II exhibit strong bands in the region 3390–3469 cm^{-1} centered at 3430 cm^{-1}which is attributed to arise from ν(OH) vibrations of lattice water and ethanol

molecules. The C—H stretchings [1] for ethyl group and ligand molecules appear in the region 2859–2932 cm^{-1}. The absence of a strong band in the region 167 –1620 cm^{-1} clearly indicates that the ligand 2-hydroxy-1-naphthaldehydebenzoylhydrazone exists in the enol form in the complex. The appearance of a strong band at 1600 cm^{-1}, characteristic of >C=N-N=C< group in hydrazones produced as a result of condensationn of NH_2 group of benzoyl hydrazine and >C=O group of 2-hydroxy-1-naphthaldehyde and its consequent enolization [2] in the complex. This is also corroborated from the presence of a strong new band at 1553 cm^{-1} which is characteristic of newly formed NCO^- group. A new weak band at ~ 1700 cm^{-1} is present in the complex. This band is observed neither in the IR spectrum of free benzoyl hydrazine nor in that of 2-hydroxy-1-naphthaldehydebenzoylhydrazone. Hence this band is assigned to >C=O group of coordinated diazenido(1-) unit in the complex. The absence of a strong band in the region 900 – 1000 cm^{-1} and any band in the region 1550 – 1650 cm^{-1} characetristic of $-NH_2$ group confirms the condensation of molybdenyl unit with the hydrazide $-NH_2$ group. This view point is corroborated from the appearance of two medium to strong bands at 1484 cm^{-1} and 1434 cm^{-1} in the IR spectra of the complex and these bands were assigned to ν(N=N) vibrations. The strong band observed at 1248 cm^{-1} is assigned to bending vibration of naphtholic C-O group coordinated to the molybdenum centre. The weak intensity bands observed at 1062 and 1029 cm^{-1} are attributed to arise due to ν(N-N)vibration of benzoylhydrazido(2-) unit coordinated to the metal centre and the hydrazone ligand respectively.

In the ^1H NMR spectra of the complex (II), the singlet observed at δ 9.95 ppm is assigned to azomethine proton (-CH=N-) of the 2-hydroxy-1-naphthaldehydebenzoylhydrazone(HNBH). Signals due to aromatic protons of benzoyl hydrazine and 2-hydroxy-1-naphthaldehyde appear in the region δ 7.18 – 8.80 ppm. Further, the signals observed at δ 1.05, δ3.43 and 6.53 are assigned to $-CH_3$, $-CH_2$ and –OH protons of ethanol molecule which are present in the lattice structure of the complex. The signal due to NH proton is not visible even in ^1H NMR spectrum because of its very broad nature due to its coupling with quadrupolar nitrogen nucleus.

X-ray Crystal Structure of

([Mo(C_6H_5CON=N)(C_6H_5C(O)—NH—N=)($C_{10}H_5OCH$=N—N=COC_6H_5)]) (II)

Diffraction quality crystals of the complex(II) were obtained by slow evaporation of an ethanolic solution of the complex. Single crystals of complex II were mounted on a glass fiber and placed on a Oxford Diffraction Xcaliber-S diffractometer (*CrysAlis CCD*) [3]. (Mo Kα, λ = 0.710 73 Å, graphite monochromator). Cell refinement and data reduction were done using *CrysAlis RED* [3]. Intensity data were collected using the ω scan technique. The intensity data were corrected for Lorentz and polarization factors, and an empirical absorption correction based on multi scan using spherical harmonics implemented in SCALE 3 ABSPACK algorithm [3] was applied to the raw data. The structure was solved by using SHELXS97 (Sheldrick, 1997) program and structure refinement was done by using SHELXL97 (Sheldrick, 1997) [4]. Molecular graphics were generated using ORTEP-3 (Farrugia, 1997). Atomic scattering factors were taken from reference 5. The positions and anisotropic thermal parameters of all non-H atoms were refined against F_o^2using full-matrix least-squares techniques. The crystal data and data collection and refinement parameters are summarized in Table 1.

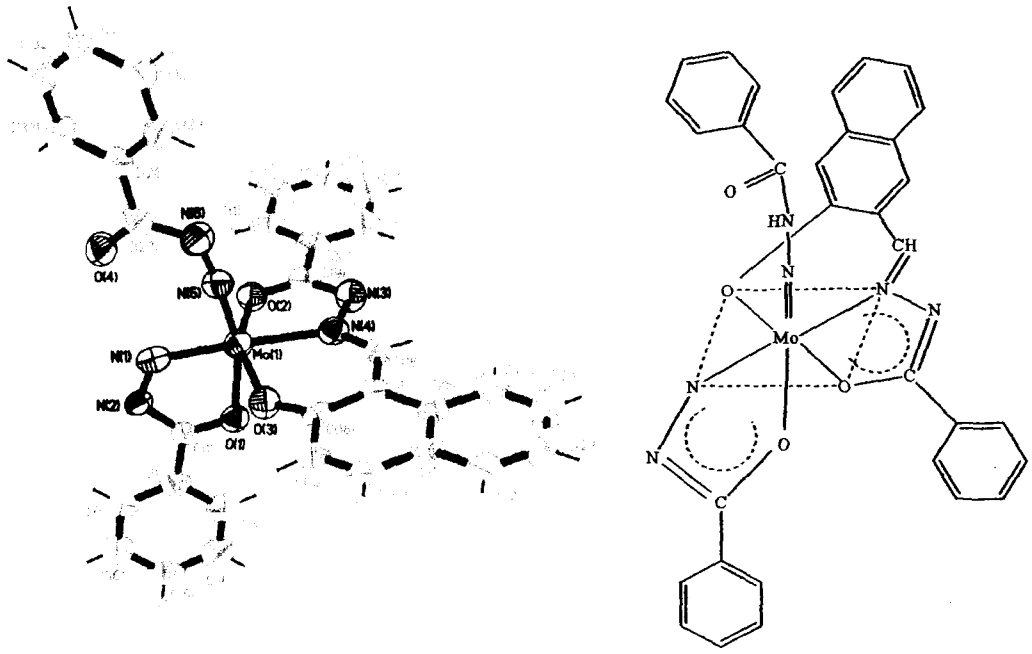


Fig. 2. ORTEP diagram of [Mo(C_6H_5CONN)(C_6H_5CONHN)($C_{10}H_5OCHNNCOC_6H_5$)](II) with atom labeling scheme at 50% probability label

Fig.3. Unit cell structure of C_{66} H_{50} Mo_2 N_{12} O_{13} showing two molecules of [Mo(C_6H_5CONN)(C_6H_5CONHN)($C_{10}H_5OCHNNCOC_6H_5$)], one ethanol and four water molecules

Table 1. Crystallographic and Refinement Data for

$[Mo(C_6H_5CONN)(C_6H_5CONHN)(C_{10}H_5OCHNNCOC_6H_5)]$

Empirical formula	C66 H50 Mo2N12O13
Formula weight	1411.06
Temperature	150(2) K
Diffraction radiation type	MoKα (λ= 0.71073 Å)
Crystal system	Triclinic
Space group	P_1
a, Å	13.162(3)
b, Å	15.683(3)
c, Å	16.667(3)
α, deg	83.567(16)
β, deg	76.674(16)
γ, deg	83.619(16)
V, $Å^3$	3313.8(11)
Z	2
D_{calcd}, Mg m^{-3}	1.414
Cryst. Size, mm	0.33 × 0.26 ×0.21
F(000)	1436
μ, mm^{-1}	0.450
θ_{Max}	25°
hkl range	$-15 \leq h \leq 15, -18 \leq k \leq 18, -19 \leq l \leq 19$
Reflections collected	11580
Reflections unique	30407
Parameters	838
R [I>2σ(I)]	$R_1 = 0.0733$; $wR_2 = 0.1515$
R (all data)	$R_1 = 0.1809$; $wR_2 = 0.1814$
GOF on F^2	0.905
Largest difference peak and hole (e $Å^{-3}$)	+0.802; -0.456

$w = 1/[\sigma^2(F_0^2) + (0.0785P)^2 + (0.00P)]$ where $P = [F_0^2 + 2F_c^2]/3$

Table 2. Selected Bond Lengths (Å) and Angles (deg) for
[Mo(C_6H_5CONN)(C_6H_5CONN)($C_{10}H_5OCHNNCOC_6H_5$)]

Mo(1)-N(5)	1.731(7)	N(5)-N(6)	1.285(8)
Mo(1)-N(1)	1.957(7)	N(2)-C(1)	1.326(9)
Mo(1)-N(4)	2.151(6)	N(3)-C(9)	1.319(9)
Mo(1)-O(1)	2.160(5)	N(4)-(16)	1.296(9)
Mo(1)-O(2)	2.018(5)	C(9)-O(2)	1.304(9)
Mo(1)-O(3)	1.959(7)	C(1)-O(1)	1.268(8)
N(1)-N(2)	1.388(8)	N(6)-C(27)	1.357(10)
N(3)-N(4)	1.406(8)	O(4)-C(27)	1.239(9)
N(5)-Mo(1)-O(3)	98.0(3)	N(5)-Mo(1)-O(1)	163.2(3)
N(5)-Mo(1)-N(1)	89.9(3)	N(5)-Mo(1)-N(4)	101.0(3)
N(1)-Mo(1)-N(4)	164.9(2)	N(1)-Mo(1)-O(2)	95.3(2)
N(1)-Mo(1)-O(1)	73.4(1)	N(1)-Mo(1)-O(3)	107.4(2)
N(4)-Mo(1)-O(3)	81.7(2)	N(4)-Mo(1)-O(3)	73.1(2)
N(4)-Mo(1)-N(5)	101.0(3)	N(4)-Mo(1)-O(1)	95.7(2)
N(6)-N(5)-Mo(1)	175.4(6)		
N(2)-Mo(1)-N(1)	120.4(5)		

Table 3. Comparison of structural features of hydrazido and diazenido ligands

Complex	Bond lengths, Å		Bond angles, (°)	Reference
	Mo-N	N-N	Mo-N-N	
Diazenido(1-)				
$[Mo(N_2C_6H_4OCH_3\text{-}p)_2(S_2N_2C_8H_{18})]$	1.81(1)	1.28(2)	170.4(17) 168.3(19)	[6]
$[Mo(C_6H_5N_2)_2Cl(\mu\text{-}C_3H_7)(C_6H_5NHNH_2)]$	1.79(1) 1.84(2)	1.23(1) 1.24(2)	166.0(1) 170.0(1)	[7]
$[Mo(C_6H_5N_2)_2Cl(\mu\text{-}C_2H_5)(C_6H_5CONHO)]$	1.817 (8) 1.841(8)	1.24 (1) 1.26(1)	171.6 (7) 175.7(7)	[7]
$[Mo_2(NNPh)_4Cl(OMe)_4(PhNHNH_2)_2]$	1.816 (6) 1.829(6)	1.242(8) 1.243(9)	161.0(5) 170.9(5)	[8]
$[Mo(N_2C(O)Ph)NHNHC(O)Ph)(PhC(S)N(Me)O)_2]$	1.758(5)	1.292(7)	168.8(4)	[9]
$([Mo(C_6H_5CON{=}N)(C_6H_5C(O)\text{-}NH\text{-}N{=})(C_{10}H_5OCH{=}N\text{-}N{=}COC_6H_5)])$	1.957(7)	1.388(8)	120.4 (5)	Present work
Hydrazido(2-)				
$[Mo(NNPh_2)_2(S_2CNMe_2)_2]$	1.74(1)	1.31(1)	169.9(8)	[10]
$[Mo(NHNMePh)(NNMePh)(acac)Cl_2]$	1.750(2)	1.301(3)	173.8(2)	[12]
$([Mo(C_6H_5CON{=}N)(C_6H_5C(O)\text{-}NH\text{-}N{=})(C_{10}H_5OCH{=}N\text{-}N{=}COC_6H_5)])$	1.731(7)	1.285(8)	175.4 (6)	Present work
$[MoO(NNMePh)(acac)_2]$	1.789(3)	1.281(4)	175.6(2)	[11]
Hydrazido(1-)				
$[Mo(NHNMePh)(NNMePh)(acac)Cl_2]$	1.948(2)	1.339(3)	142.9(2)	[12]

Discussion of Structure

The ORTEP diagram of complex(II) is shown in Fig.2. Selected bond lengths (Å) and bond angles(°) are set out in Table. 2. The unit cell structure of the complex(II) is shown in Fig.3. The unit cell structure of the complex consists of two molecules of [Mo(C_6H_5CONN)(C_6H_5CONHN)($C_{10}H_5OCHNNCOC_6H_5$)] alongwith one ethanol and four water molecules. The solvent molecules are present in the form of solvent of crystallization. It is interesting to note that the benzoyldiazenido(1-) unit is bonded to the molybdenum(VI) centre through nitrogen and carbonyl oxygen atom via deprotonation whereas the benzoylhydrazido(2-) unit is coordinated to the metal centre only through nitrogen atom. The carbonyl oxygen of benzoylhydrazido(2-) unit remains uncoordinated. The ligand 2-hydroxy-1-naphthaldehydebenzoylhydrazone is bonded to the Mo(VI) centre through one diazene nitrogen (N(4)) atom, the carbonyl oxygen atom (O(2)) of the benzoyl hydrazine unit and the deprotonated hydroxyl oxygen (O(3)) of the 2-hydroxy-1-naphthaldehyde unit. The complex exhibits a distorted octahedral geometry with N(1) and N(4) occupying the axial positions (bond angle, N(1)-Mo(1)-N(4) = 164.9(2)°) and equatorial positions are occupied by one nitrogen (N(5)) and three oxygen atoms (O(1), O(3), and O(2)) respectively.

The group containing N(1), N(2) corresponds to benzoyldiazenido(1-) unit. It forms a five membered chelate ring with the molybdenum centre. The structural parameters for this diazenido(1-) chelate ring are quite different and distinctive. This is, most noticeably, reflected in the Mo(1)-N(1) bond distance (1.957(7)Å), N(1)-N(2) bond distance (1.388(8)Å) and C(1)-N(2) bond distance (1.326(9)Å). These values are very similar to those in another chelated diazenido-diazene complex, [Mo(NHNC(S)Ph)(N_2C(S)(PhC(S)N(Me)O] **[9]**. The short bond lengths are indicative of considerable electron delocalization within the chelate ring. The Schiff base ligand 2-hydroxy-1-naphthaldehydebenzoylhydrazone is acting as a dibasic tridentate ligand and is coordinated to the Mo(VI) centre through the diazene nitrogen atom (N(4)), the carbonyl oxygen atom (O(2)) of the benzoyl hydrazine moiety via enolization and deprotonated hydroxyl oxygen atom (O(3)) of the 2-hydroxy-1-naphthaldehyde moiety. It forms a five membered chelate ring comprising of Mo(1), N(4), N(3), C(9) and O(2) and a six membered chelate ring comprising of Mo(1), O(3), C(18), C(17), C(16) and N(4). The bond lengths, N(3)-N(4) (1.406(8)Å), N(3)-C(9) (1.319(9)Å), C(9)-O(2) (1.304(9)Å), Mo(1)-O(2) (2.018(5)Å), Mo(1)-N(4) (2.151(6)Å), Mo(1)-O(3) (1.959(5)Å), N(4)-C(16) (1.296(8)Å) are comparable to similar structures **[13,14]**. The group containing N(5), N(6) corresponds to benzoylhydrazido(2-) unit. This benzoylhydrazido(2-

)unit exhibits a geometry consistent with molybdenum-nitrogen multiple bonding and extensive delocalization throughout the Mo(1)-N(5)-N(6) group. The Mo(1)-N(5) (1.731(8)Å), and N(5)-N(6) (1.285(8)Å) bond distances in the molybdenum benzoylhydrazido(2-) group are short and comparable to related structures **[9]**. They show significant double bonding and electron delocalization with essentially linear ($Mo{=}N{-}NCOC_6H_5$) entity (bond angle Mo(1)-N(5)-N(6) = 175.4(6)°) **[6]**. Further, the geometry of the benzoylhydrazido(2-) fragment suggests maximum π-interaction between the diazenido ligand π^* orbitals and the molybdenum t_{2g} orbitals [15]. This is supported by the short Mo(1)-N(5) distance (1.731(7)Å) and the wide angle (175.4(6)°)of the Mo(1)-N(5)-N(6) unit for the benzoylhydrazido(2-) ligand as described above.

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List of publications:

1. Synthesis and crystal structure of $[Mn_2(H_2sal)_2(Hsal)_2(H_2O)_4]$. First example of the reductive synthesis of a binuclear manganese(I) salicylate complex.

   Ram A. Lal*, Aka Lemtur, Sanjesh Choudhury, *Mithun Chakrabarty*,Debjani Basumatary, Mahesh K. Singh, Samhita Bhaumik , Arjun K. De Arvind Kumar, Transition Metal Chemistry (2006) 31:423–428.

2. Synthesis and spectroscopic Characterization and of Molybdenum (VI) Complexes Derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.

   Ram A. Lal*, *Mithun Chakrabarty* and Sanjesh Choudhury(communicated).

3. Synthesis , Characterization and Structural Assessment of Zinc(II) Complexes Derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.Ram A. Lal*, *Mithun Chakrabarty* and Sanjesh Choudhury(communicated).

4. Synthesis and Characterization of heterobimetallicNi(II)- Zn(II) Complexes Derived from bis(2-hydroxy-1-naphthaldehyde)succinoyldihydrazone.
   Ram A. Lal*, *Mithun Chakrabarty and* Sanjesh Choudhury and Aziz Ahmed (communicated).

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Fig.7.2. Electronic spectrum of $[NiZn(nsh)(py)_3]$ (7.2) in DMF.

Fig.7.3. Electronic spectrum of $[NiZn(nsh)(2\text{-}pic)_3]$ (7.3) in DMF.

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