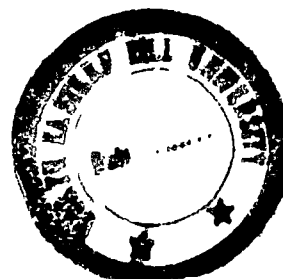


STUDIES ON THE COMPLEXES OF NICKEL (II),  
NICKEL (III), COBALT (II) AND RUTHENIUM (II)  
WITH SOME MONODENTATE LIGANDS

(Abstract)

by

KALI PRASAD SARMA  
DEPARTMENT OF CHEMISTRY  
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Thesis submitted in fulfilment of the requirement of the degree of  
**DOCTOR OF PHILOSOPHY**

to



THE NORTH-EASTERN HILL UNIVERSITY,  
SHILLONG, INDIA

DECEMBER, 1983

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# 1

The thesis deals with the synthesis and study of the physical properties, reactivity and structural aspects of the complexes of nickel(II), nickel(III), cobalt(II) and ruthenium(II) with some monodentate ligands.

Chapter I, describes the synthesis and some of the physical and chemical studies on some ruthenium(II) complexes containing both strong and weak donor ligands. These complexes are of the type  $\text{[Ru(MPh}_3\text{)(C}_6\text{H}_5\text{CHO)}_2\text{Cl}_2\text{]}$  (M = P or As). On the basis of the above studies, it is proposed that the complexes have a distorted square pyramidal structure. To study the ease of substitution of benzaldehyde in  $\text{[Ru(MPh}_3\text{)(C}_6\text{H}_5\text{CHO)}_2\text{Cl}_2\text{]}$ , reactions with some weak donor ligands, viz. pyridine, DMF, DMSO, acetonitrile and carbondisulphide are also described. Some new complexes obtained, are of the type,  $\text{[Ru(MPh}_3\text{)L}_3\text{Cl}_2\text{]}$  (when M = As, L = py or DMF; when M = P, L = DMF) and  $\text{[Ru(}\eta\text{-CS}_2\text{)(PPh}_3\text{)Cl}_2\text{]}$ . Some ruthenium(II) carbonyl complexes of the type  $\text{[Ru(CO)(MPh}_3\text{)}_2\text{Cl}_2\text{]}$  (M = P or As) are also synthesized and structural assignments for the complexes have been made with the help of physical and chemical studies.

Chapter II, describes the synthesis and studies on nickel(II) complexes of the type,  $\text{[Ni(PPh}_3\text{)XCl}_2\text{]}$ ,

$\text{[Ni(OPPh}_3\text{)XCl]}_2$  (X = Cl, Br, SCN or NO<sub>3</sub>). On the basis of physical measurements and chemical reactions, it is proposed that the complexes have a dimeric structure with a distorted tetrahedral environment around the nickel atom with Chloro-bridges. Low value of magnetic moments of these complexes is probably due to antiferromagnetic interaction between two nickel atoms of the dimer through chloro-bridges. Evidence of chloro-bridges is obtained from far infrared spectra too. Reactions of the above mentioned dimeric complexes with triphenylphosphine resulted in the formation of the complexes of the type,  $\text{[Ni(PPh}_3\text{)}_2\text{XCl]}$  (X = Br, NO<sub>3</sub> or NCS). A distorted tetrahedral structures for  $\text{[Ni(PPh}_3\text{)}_2\text{XCl]}$  (X = Br or NO<sub>3</sub>) and a square planar structure for  $\text{[Ni(PPh}_3\text{)}_2\text{(NCS)Cl]}$  is proposed.

Chapter III of the thesis deals with the synthesis of a novel nickel(III) complex, viz.  $\text{[Ni(OPPh}_3\text{)Cl}_2\text{I]}$  by the oxidation of  $\text{[Ni(PPh}_3\text{)}_2\text{I}_2]$  with nitrosyl chloride or chlorine. With the help of magnetic and e. s. r. studies and some chemical reactions the oxidation state of the metal is confirmed to be +3. With the help of other physical measurements a distorted tetrahedral geometry around nickel(II) is proposed. This complex is found to act as a catalyst in the oxidation of triphenylphosphine to

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triphenylphosphine oxide and as an oxidant for the oxidation of cyclohexanol to cyclohexanone.

In Chapter IV, syntheses of some cationic nickel(II) complexes, viz.  $[\text{Ni}(\text{OPPh}_3)_2\text{X}]_2^{+}[\text{Y}_3]_2^{-}$  (when  $\text{X} = \text{Cl}$ ,  $\text{Y}_3 = \text{Br}_3$ ; when  $\text{X} = \text{Br}$ ,  $\text{Y}_3 = \text{Br}_3$  or  $\text{IBr}_2$ ) and their physical and chemical behaviours studied. The presence of trihalide anions is confirmed with the help of uv spectral data, where a very strong band ( $\epsilon \approx 5 \times 10^4$ ) in the u.v. region is observed due to  $\sigma \rightarrow \sigma^*$  transition. Magnetic moments of these complexes correspond to that of nickel(II) tetrahedral complexes. On the basis of various physical studies, these complex cations are proposed to have dimeric structures having distorted tetrahedral environment around nickel(II) with chlorobridges.

Chapter V describes the preparation of nickel(II) thiocyanate by a convenient one-step method and its various physical properties in solid and in solution. Nickel(II) thiocyanate has been used as a precursor for the synthesis of some new and some reported compounds, containing nickel thiocyanate and other donor atoms such as oxygen, nitrogen or phosphorus. New compounds synthesized are,  $\text{NiL}_2(\text{SCN})_2$  ( $\text{L} = \text{OPPh}_3$ ,  $\text{OAsPh}_3$  or  $\text{N}_2\text{H}_4$ ),  $[\text{Ni}(\text{bipy})_3]^{+}(\text{SCN})_2^{-}$ ,  $[\text{NiL}_4(\text{NCS})_2]_2^{+}(\text{NCS})_2^{-}$  (where  $\text{L} = \text{dimethylamine}$  or  $\text{triethyl}$

amine). The physical properties of the above mentioned compounds have been studied to know their structures and mode of bonding of thiocyanate to the metal.

In Chapter VI, complexes of nickel(II) and cobalt(II) containing both strong and weak donor ligands, viz.  $[\text{Ni}(\text{PPh}_3)_2\text{L}_2\text{X}_2]$  and  $[\text{Co}(\text{PPh}_3)\text{LX}_2]$  (L = DMF or DMSO; X = Cl or Br) have been synthesized and characterized with the help of various physical data, including infrared and electronic spectra, magnetic and conductivity measurements. On the basis of physical studies mentioned above, it is proposed that the nickel(II) complexes have distorted trigonal bipyramidal geometry in the solid state and a tetrahedral geometry in solution (when one molecule of DMF or DMSO is lost in the solution) and the cobalt complexes have a distorted tetrahedral geometry around the metal ion.

Part of the work presented in the thesis is published in the following Journals:

Chapter II

1. Reaction of Nitrosylchloride with  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]^{7-}$   
(X = Cl, Br, SCN,  $\text{NO}_3$ )

Kali Prasad Sarma and Raj K. Poddar

Trans. Metal Chemistry, 8, 31-33 (1983).

2. Mixed Ligand Complexes of Nickel(II).

Kali Prasad Sarma and Raj K. Poddar

Trans. Metal Chemistry, 8, 225 (1983).

Chapter III

3. Synthesis and Studies on Dichloriodotriphenylphosphine oxide Nickel(III).

Kali Prasad Sarma and Raj K. Poddar

Polyhedron, 2, 672 (1983).

Chapter V

4. A Convenient Method of Preparing Nickel(II) Thiocyanate and Its Use in Synthesis.

Kali Prasad Sarma and Raj K. Poddar

Trans. Metal Chemistry, (in press).

Chapter VI

5. Mixed ligand Complexes of Nickel(II) and Cobalt(II).

Kali Prasad Sarma and Raj K. Poddar

J. Coordination Chemistry, 12, 237 (1983).

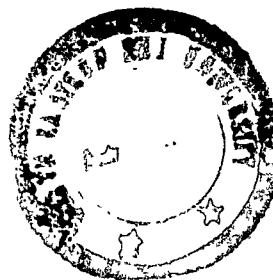
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This is to Certify that Mr. Kali Prasad Sarma has satisfactorily completed all the courses under the requirements of the Pre-Ph. D. programme.

The Courses include:

1. Chemistry of Transition Metals.
2. Advanced Concepts in Physical Chemistry.
3. Highlights of Organic Chemistry.

  
(T. S. B. NARASARAJU)

Head,

Department of Chemistry

Date: ১৫/০৩/১৯. North-Eastern Hill University  
Shillong - 793 003, Meghalaya

C E R T I F I C A T E

I certify that the thesis entitled "Studies on the Complexes of nickel(II), nickel(III), cobalt(II) and ruthenium(II) with some **Monodentate** Ligands" submitted by Mr. Kali Prasad Sarma 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 award of the Ph. D. Degree This work has not been submitted for any Degree of any other university.

Date : 9/12/83

Place: Shillong



( R. K. PODDAR )

Signature of the Supervisor

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*Kaliprasad Sarma*  
(KALI PRASAD SARMA)

Date : 9/12/83

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## P R E F A C E

The work presented in the thesis describes the synthesis and study of the physical properties, reactivity and structural aspects of the complexes of nickel(II), nickel(III), cobalt(II) and ruthenium(II) with some monodentate ligands.

Chapter I describes the syntheses and structural studies on some complexes of ruthenium(II) of mixed donor ligands of the type  $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$  (M = P or As). To study the ease of substitution of benzaldehyde in  $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$ , reactions with some weak donor ligands, viz. pyridine, DMF, DMSO, acetonitrile and carbondisulphide is also discussed.

$[\text{Ru}(\text{CO})(\text{MPh}_3)_2\text{Cl}_2]$  (M = P or As) have also been synthesized. Structural assignments for the complexes have been made with the help of physical and chemical studies.

Chapter II deals with the syntheses and studies on the complexes of the type  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}_2]$ ,  $[\text{Ni}(\text{OPPh}_3)_2\text{XCl}_2]$  (X = Cl, Br, SCN or  $\text{NO}_3$ ) and  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$  (X = Br,  $\text{NO}_3$  or NCS). These complexes seem to have distorted tetrahedral environment except  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]$ , which is square planar.

Chapter III describes the synthesis of a novel nickel(III) complex, viz.  $[\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}]$ . Chemical and physical methods are used to determine the oxidation state of the complex. Catalytic oxidation reactions using the complex have also been discussed.

In Chapter IV, syntheses of some cationic nickel(II) complexes, viz.  $[\text{Ni}(\text{OPPh}_3)_2\text{X}]_2[\text{Y}_3]_2$  (when  $\text{X} = \text{Cl}$ ,  $\text{Y}_3 = \text{Br}_3$ ; when  $\text{X} = \text{Br}$ ,  $\text{Y}_3 = \text{Br}_3$  or  $\text{IBr}_2$ ) and their physical studies are reported.

Chapter V, describes the preparation of nickel(II) thiocyanate by a convenient method. Some of its physical properties have been studied in solid state and in solutions. Nickel(II) thiocyanate has been used as a precursor for the synthesis of some new and some reported compounds. New compounds described are,

$[\text{NiL}_2(\text{SCN})_2]$  ( $\text{L} = \text{OPPh}_3$ ,  $\text{OAsPh}_3$  or  $\text{N}_2\text{H}_4$ ),  
 $[\text{Ni}(\text{bipy})_3](\text{SCN})_2$ ,  $[\text{NiL}_4(\text{NCS})]_2(\text{NCS})_2$  (where  $\text{L} =$   
 dimethylamine or triethylamine).

Chapter VI, deals with the syntheses, physical properties and structural investigation of new nickel(II) and cobalt(II) complexes, namely  $[\text{Ni}(\text{PPh}_3)_2\text{L}_2\text{X}_2]$  and  $[\text{Co}(\text{PPh}_3)_2\text{LX}_2]$  (where  $\text{X} = \text{Cl}$  or  $\text{Br}$ ;  $\text{L} = \text{DMF}$  or  $\text{DMSO}$ ).

(ii)

Particular care has been taken to give due credit to the work reported by other authors in the literature. The author is fully responsible for purely unintentional oversights and errors which could be traced herein.

## CHAPTER I

### STUDIES ON SOME RUTHENIUM(II) COMPLEXES WITH TRIPHENYLPHOSPHINE OR TRIPHENYLARSINE AND OTHER MONODENTATE LIGANDS

#### INTRODUCTION

The chemistry of ruthenium(II) and ruthenium(III) complexes containing mono- tertiary phosphine, arsine or stibine has been evoking interest in inorganic chemists due to their interesting molecular structures and their physical, chemical and catalytic behaviours. Synthesis and studies of ruthenium(II) tertiary phosphine and arsine complexes have gained considerable interest after the synthesis of  $\text{RuCl}_2(\text{PPh}_3)_3$  reported from Wilkinson's group<sup>1</sup>. This compound has been found to have a distorted square-pyramidal structure<sup>2</sup> and is a good catalyst for various homogeneous reactions.<sup>3-5</sup>

Some other ruthenium(II) complexes containing tertiary-phosphine or arsine have also been used as catalysts for a variety of homogeneous reactions, viz. hydrogenation, oxidation, hydroformylation, hydration, polymerization, carbonylation, decarbonylation, dehydrogenation, isomerisation and alkylation.<sup>3-6</sup>

For homogeneous catalysis, the ease with which an organic substrate can enter the coordination sphere of a metal ion is thought to be a key factor in determining the ability of such an ion to catalyse the reactions of the substrate. Hence coordinatively unsaturated metal complexes or complexes which could produce coordinatively unsaturated species in solution either thermally or photochemically could act as good catalysts.<sup>7</sup> Thus, ruthenium(II) or ruthenium(III) complexes having four or five coordination could act as good homogeneous catalysts. Complexes of weak donor ligands having five or six coordination, may also dissociate easily in solution thereby giving four or five coordinated species which could be active species in homogeneous catalysis. A review on the complexes of platinum group of metals with such donor ligands have been reported by Davis and Hartley,<sup>8</sup> wherein they describe the potential of such complexes for homogeneous catalytic reactions. Transition metal complexes containing both strong and weak donor ligands could also act as good catalyst by the dissociation in solution of weakly coordinated ligands in the

complexes. Hence, ruthenium(II) or ruthenium(III) complexes containing tertiaryphosphine or arsine and weak donor ligands and having five or six coordination around the metal could also act as good homogeneous catalyst by the dissociation of weakly coordinated ligand molecules in solution.

Known ruthenium(III) complexes containing triphenylphosphine or triphenylarsine and some weak donor ligands are of the type  $[\text{RuX}_3(\text{iPh}_3)_2\text{L}]$ <sup>1,9-14</sup> (where X = Cl or Br; M = P or As; L =  $\text{CH}_3\text{OH}$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $(\text{CH}_3)_2\text{CO}$ ,  $\text{CH}_3\text{CHO}$ ,  $\text{C}_6\text{H}_5\text{CHO}$ ,  $\text{CH}_3\text{NO}_2$ ,  $\text{OAsPh}_3$ ,  $\text{CS}_2$ ,  $\text{D}_2\text{F}$ ,  $\text{DMSO}$ ,  $\text{THF}$ ,  $\text{RCN}$  (R =  $\text{CH}_3$ ,  $\text{C}_2\text{H}_5$ ,  $n\text{-C}_3\text{H}_7$ ,  $\text{CH}_2=\text{CH}$ ,  $\text{C}_6\text{H}_5$ )). Some other complexes containing triphenylphosphine or triphenylarsine and weak donor ligands are of the type  $[\text{RuX}_3(\text{iPh}_3)_2\text{L}_2]$ <sup>11,12</sup> (X = Cl or Br; M = P or As and L = py,  $\alpha$ -picoline,  $(\text{CH}_3)_2\text{S}$  or  $\text{L}_2 = \text{bipy}$ , o-phen) also.

Some of ruthenium(II) complexes containing triphenylphosphine or triphenylarsine and other weak or strong donor ligands giving a distorted octahedral geometry around ruthenium(II) are also known. Such complexes have the composition of the type  $[\text{RuX}_2(\text{iPh}_3)_2\text{L}_2]$ <sup>1,11,12,15-17</sup> (where X = Cl or Br, M = P or As; L = CO, CS, py,  $\text{NH}_3$ ,  $\text{CH}_3\text{NH}_2$ ,  $(\text{Et})_2\text{NH}$ ,  $(\text{Et})_3\text{N}$ ,  $\text{N}_2\text{H}_4$ ,  $\text{C}_6\text{H}_5\text{NH}_2$  and  $\text{RCN}$  (R =  $\text{CH}_3$ ,  $n\text{-C}_3\text{H}_7$ ,  $\text{CH}_2=\text{CH}$ ), and  $[\text{RuCl}_2(\text{iPh}_3)_2\text{L}_3]$ <sup>16,17</sup> (M = P or As, L = py,  $\text{C}_6\text{H}_5\text{NH}_2$ ,  $o\text{-RC}_6\text{H}_4\text{NH}_2$  (R = Cl,  $\text{CH}_3$ )). In all the cases reported above, the geometry around ruthenium(II) is distorted octahedral.

If such complexes in solutions can lose preferably two weakly coordinated ligands, then these could be good catalysts for homogeneous reactions. If ruthenium(II) complexes could be synthesized containing triphenylphosphine or triphenylarsine and weak donor ligands having four or five coordination around ruthenium(II), there is a greater potential of such complexes to act as homogeneous catalyst.

In this chapter some ruthenium(II) complexes containing triphenylphosphine or triphenylarsine and benzaldehyde are reported having five coordination around ruthenium(II). These are of the type  $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})\text{Cl}_2]$  (M = P or As). The substitution of benzaldehyde in these complexes by other weak donor ligands like pyridine, DMF, DMSO,  $\text{CS}_2$ ,  $\text{CH}_3\text{CN}$  have been tried out to find out the case with which ruthenium(II) complexes containing triphenylphosphine or triphenylarsine and the above mentioned ligands could be obtained. Various physical studies have been made to establish the geometry of the complexes so obtained. Complexes thus obtained have not been tried for their homogeneous catalytic behaviours. Studies along this line is being taken up.

Some carbonyl complexes of ruthenium(II) of the type  $\text{Ru}(\text{CO})(\text{MPh}_3)_2\text{Cl}_2$  (M = P or As) have been obtained by the decarbonylation of benzaldehyde and some of their physical and chemical studies reported.

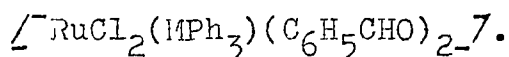
EXPERIMENTAL

All the chemicals used were of reagent grade. Ruthenium trichloride hydrate was supplied by Aurora-Malthey Limited, Calcutta.  $\text{[RuCl}_2(\text{PPh}_3)_2\text{]}_n^{18}$ ,  $\text{[RuCl}_2(\text{PPh}_3)_3\text{]}^{19}$  and  $\text{[RuCl}_2(\text{AsPh}_3)_2\text{]}^{17}$  were prepared according to reported methods.

PREPARATIONS

1.  $\text{[RuCl}_2(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{]}_2$  (M = P or As)

To a solution of ruthenium trichloride hydrate ( $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ ) (0.1 g) in n-butanol (10 ml), benzaldehyde (2 ml) was added. A solution of triphenylphosphine (0.5 g) or triphenylarsine (0.6 g) in n-butanol (5 ml) was added to the hot solution of ruthenium trichloride mentioned above. The resulting solution was then refluxed for about 30 min or 2 hrs, in case of triphenylphosphine or triphenylarsine respectively. The reacted solution was cooled overnight when brownish-yellow crystalline compound in case of triphenylarsine and light green compound in case of triphenylphosphine was obtained. The compound was separated by centrifugation and washed first with methanol and then with diethylether and dried under vacuum. The compounds were analysed for



2.  $\text{[RuCl}_2(\text{CO})(\text{AsPh}_3)_2\text{]}_2$ 

(i) To a clear solution of ruthenium trichloride hydrate (0.1 g) in n-butanol (10 ml) and benzaldehyde (2 ml) mixture, a solution of triphenylarsine (1 g) in n-butanol (5 ml) was added and the mixture was refluxed for about 20 hrs.

Initially, benzaldehyde complex was formed which went into solution and finally an orange solution was obtained which on cooling yielded a yellow compound. The mother liquor upon concentration under reduced pressure and cooling yielded more of the yellow compound, which was centrifuged washed first with acetone and then with ether and dried under vacuum. It was analysed for  $\text{[Ru}(\text{CO})(\text{AsPh}_3)_2\text{Cl}_2\text{]}_2$ .

(ii)  $\text{[RuCl}_2(\text{CO})(\text{AsPh}_3)_2\text{]}_2$  could be obtained also by boiling under reflux  $\text{[RuCl}_2(\text{AsPh}_3)_2\text{]}_2$  (0.2 g) in benzaldehyde (2ml) and n-butanol (10 ml) mixture for about 8 hrs or by boiling under reflux  $\text{[RuCl}_2(\text{C}_6\text{H}_5\text{CHO})_2(\text{AsPh}_3)_2\text{]}_2$  (0.2 g) and triphenylarsine (0.2 g) in n-butanol (10 ml) for about 10 hours and cooling the orange-red solution obtained.

3.  $\text{[RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{]}_2$ 

(i) To a solution of ruthenium trichloride hydrated (0.2 g) in n-butanol (20 ml) and benzaldehyde (4 ml) mixture, a solution of triphenylphosphine (1.5 g) in n-butanol (10 ml) was added and the mixture was boiled under reflux for 6-8hrs,

when a reddish brown crystalline compound (m.p. 195-200 °C) separated out which was separated by centrifugation and washed first with methanol and then with diethylether and dried under vacuum. It was analysed for  $\text{[RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{]}\cdot 7$ .

3. (ii) The reaction was carried out in a way similar to that in (3i). The refluxing of the reaction mixture was continued for 15-20 hrs, when the red crystalline compound obtained as an intermediate, went into solution and finally a reddish-yellow solution was obtained, which on cooling resulted in the separation of a yellow compound. The compound was separated and washed first with acetone and then with ether. Concentration of the mother liquor resulted in the separation of more yellow compound. The compound was analysed for  $\text{[RuCl}_2(\text{CO})(\text{PPh}_3)_2\text{]}\cdot 7$ .
3. (iii) The compound obtained by the method of reaction 3(ii) could be obtained also by boiling under reflux,  $\text{[RuCl}_2(\text{PPh}_3)_2\text{]}\cdot n$  or  $\text{[RuCl}_2(\text{PPh}_3)_3\text{]}\cdot 7$  (0.2 g) in benzaldehyde (2 ml) and n-butanol (10 ml) mixture for about 8 hrs or by boiling under reflux  $\text{[RuCl}_2(\text{C}_6\text{H}_5\text{CHO})_2(\text{PPh}_3)_2\text{]}\cdot 7$  (0.2 g) and triphenylphosphine (0.2 g) in n-butanol (10 ml) for about 10 hrs and cooling the reddish-yellow solution obtained.

$\text{[Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2\text{]}\cdot 7$  obtained according to method 3(i) is reddish brown whereas according to 3(ii) and 3(iii) is yellow.

Reactions of  $\text{[Ru(MPh}_3\text{)(C}_6\text{H}_5\text{CHO)}_2\text{Cl}_2\text{]}$  (M = P or As) With

- (i) L = Pyridine, N,N-Dimethylformamide (DMF) and Dimethylsulphoxide (DMSO)

$\text{[Ru(MPh}_3\text{)(C}_6\text{H}_5\text{CHO)}_2\text{Cl}_2\text{]}$  (0.2 g) was taken with L (0.5 ml) and heated on a water-bath for about 1 hr., when a clear solution was obtained. To the cold solution, methanol was added in the case of DMF or DMSO and diethylether in case of pyridine reaction and the mixture was kept overnight when crystalline compound separated out. It was centrifuged, washed with ether and dried under vacuum. The compounds obtained had the composition,  $\text{[RuCl}_2\text{(MPh}_3\text{)L}_3\text{]}$  (where M = P or As and L = pyridine or DMF) and  $\text{[RuCl}_2\text{(DMSO)}_4\text{]}$ .

- (ii) Carbondisulphide

$\text{[Ru(MPh}_3\text{)(C}_6\text{H}_5\text{CHO)}_2\text{Cl}_2\text{]}$  (0.2 g) was taken in carbon disulphide (15 ml) along with triphenylphosphine or triphenylarsine (0.5 g), depending on the complex taken and the mixture was boiled under reflux for about 5 hrs., when crystalline compound separated out. It was centrifuged, washed with ether and dried under vacuum. In case of triphenylphosphine, a reddish-brown crystalline compound of the composition  $\text{[RuCl}_2\text{(PPh}_3\text{)(CS}_2\text{)}\text{]}$  was obtained, whereas the triphenylarsine complex reaction

product did not contain either  $\text{CS}_2$  or CS group. It had the composition  $\text{RuCl}_2(\text{AsPh}_3)_2$ . In case the reactions with carbondisulphide were carried out without taking extra triphenylphosphine or triphenylarsine, generally the starting compound was obtained.

(iii) Acetonitrile

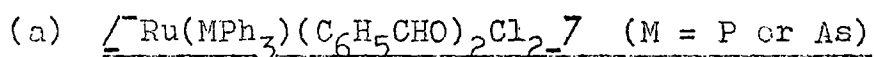
$\text{[Ru}(\text{MPh}_3)_2(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2\text{]}^-$  (0.2 g) was taken with acetonitrile (15 ml) and boiled under reflux for about 4 hrs., when the solution turned yellow. Concentration of this solution under reduced pressure resulted in the separation of a yellow compound which was centrifuged, washed with ether and dried under vacuum. The compounds obtained did not have stoichiometric composition. These were analysed for  $\text{[RuCl}_2(\text{MPh}_3)_x(\text{CH}_3\text{CN})_y\text{]}^-$  (where  $1 \leq x \leq 2$  and  $2 \leq y \leq 3$ ).

Reactions of  $\text{[Ru}(\text{MPh}_3)_2(\text{CO})\text{Cl}_2\text{]}^-$  with Pyridine

$\text{[Ru}(\text{MPh}_3)_2(\text{CO})\text{Cl}_2\text{]}^-$  (M = P or As) (0.2 g) was taken with pyridine (1 ml) and heated on a water bath when a clear yellow solution was obtained. After cooling the solution, ether was added when yellow compound precipitated out, which was centrifuged, washed with ether and dried under vacuum. The compounds had the composition  $\text{[RuCl}_2(\text{CO})(\text{MPh}_3)(\text{py})_2\text{]}^-$ .

Carbon, hydrogen and nitrogen analyses were obtained from the Microanalytical Laboratory, I.I.T., Kanpur. Sulphur and chloride estimations were carried out according to standard methods<sup>19</sup> gravimetrically after decomposing the complexes using  $\text{KNO}_3$ , KOH mixture. Infrared spectra were recorded in KBr as pellets in the region  $4000\text{-}600\text{ cm}^{-1}$  on a Perkin-Elmer 297 infrared spectrophotometer, and on Perkin-Elmer 580 spectrophotometer in the region  $600\text{ to }250\text{ cm}^{-1}$  for some complexes. Visible electronic spectra were recorded in chloroform in the region  $800\text{ to }350\text{ nm}$  on a Beckmann-26 spectrophotometer. Proton magnetic resonance spectra were recorded on a Varian EM-390 90 MHz spectrometer in  $\text{CDCl}_3$ , with TMS as reference. Magnetic susceptibility measurements were carried out using a Gouy balance at room temperature. Mercury tetrathiocyanate cobaltate(II) was used as calibrant. All the melting points are uncorrected. The conductivity measurements were made using an Elico type CM 82 conductivity bridge in nitrobenzene.

## RESULTS AND DISCUSSION



Ruthenium compounds containing triphenylphosphine or triphenylarsine and benzaldehyde have the composition  $\text{[Ru(MPh}_3\text{)}_2(\text{C}_6\text{H}_5\text{CHO)}_2\text{Cl}_2\text{]}^+$  (M = P or As). Benzaldehyde is easily oxidised to benzoic acid. As the reactions were carried

Table I. 1. Some Physical and Analytical Data of  
New Ruthenium(II) Complexes

Compound	Colour	M.P. °C	%C (calc.)	%H (Calc.)	%N (Calc.)	%Cl (Calc.)
$[\text{Ru}(\text{AsPh}_3)_2(\text{benz})_2\text{Cl}_2]$	Brownish Yellow	183-92	55.23 (55.65)	3.94 (3.91)	-	10.15 (10.29)
$[\text{Ru}(\text{PPh}_3)_2(\text{benz})_2\text{Cl}_2]$	Light Green	175-82	59.21 (59.44)	4.44 (4.18)	-	10.73 (10.99)
$[\text{Ru}(\text{CO})(\text{AsPh}_3)_2\text{Cl}_2]$	Yellow	260-67	54.92 (54.68)	3.85 (3.69)	-	8.38 (8.74)
$[\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2]$	Yellow	270-75	61.49 (61.32)	4.36 (4.14)	-	10.05 (9.81)
$[\text{Ru}(\text{AsPh}_3)(\text{py})_3\text{Cl}_2]$	Reddish Brown	198-200	54.95 (55.30)	3.95 (4.20)	6.12 (5.87)	9.62 (9.93)
$[\text{Ru}(\text{AsPh}_3)(\text{DMF})_3\text{Cl}_2]$	Reddish Brown	205-10	46.05 (46.43)	4.69 (5.16)	6.41 (6.03)	9.76 (10.19)
$[\text{Ru}(\text{PPh}_3)(\text{DMF})_3\text{Cl}_2]$	Yellowish Brown	215-20	50.06 (49.62)	5.12 (5.51)	6.11 (6.43)	11.24 (10.87)
$[\text{Ru}(\text{TC-S}_2)(\text{PPh}_3)\text{Cl}_2]$	Reddish Brown	225-30	44.91 (44.7)	2.76 (2.94)	12.66 (12.56)	13.70 (13.92)
$[\text{Ru}(\text{CO})(\text{py})_2(\text{AsPh}_3)\text{Cl}_2]$	Yellow	208-210	52.73 (52.41)	3.42 (3.77)	4.54 (4.22)	11.12 (10.69)
$[\text{Ru}(\text{CO})(\text{py})_2(\text{PPh}_3)\text{Cl}_2]$	Yellow	180-85	55.67 (56.13)	3.86 (4.03)	4.28 (4.52)	11.69 (11.45)

benz. = benzaldehyde; py = pyridine.

out in the presence of air, the possibility of benzaldehyde getting oxidised to benzoic acid and get coordinated to ruthenium can not be eliminated. However, a similar reaction under nitrogen atmosphere also gave the same products. The p.m.r. of  $[\text{Ru}(\text{AsPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$  in deuterated chloroform showed signals at 10, 7.31 and 7.23 $\delta$ . The signals at 10 and at 7.31 and 7.23 $\delta$  were in the ratio 2:25. The aryl aldehyde proton is normally observed in 10.1 to 9.5 $\delta$  range.<sup>20</sup> In the benzaldehyde complex containing triphenylarsine, proton signal at 10 $\delta$  can unambiguously be assigned due to the proton of the aldehyde functional group of benzaldehyde. The signals at 7.31 and 7.23 $\delta$  are due to the phenyl groups of triphenylarsine and benzaldehyde respectively. The ratio of the proton signals for aldehydic proton and the phenyl protons is same as expected (2:25). Similarly, the triphenylphosphine analogue, viz.  $[\text{Ru}(\text{PPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$  gave proton signals at 10, 7.5 and 7.23 $\delta$  (figure no. I. 1.). The ratio of 10 $\delta$  to 7.5 and 7.23 $\delta$  signals is again 2:25 as expected for two aldehyde protons and 25 phenyl protons. The signals at 7.5 and 7.23 $\delta$  are due to the phenyl groups of triphenylphosphine and benzaldehyde respectively. Thus, the p.m.r. spectra of  $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$  (M = P or As) confirmed the presence of three phenyl groups due to triphenylphosphine or arsine, two phenyl groups and two aldehydic protons due to two benzaldehyde molecules.

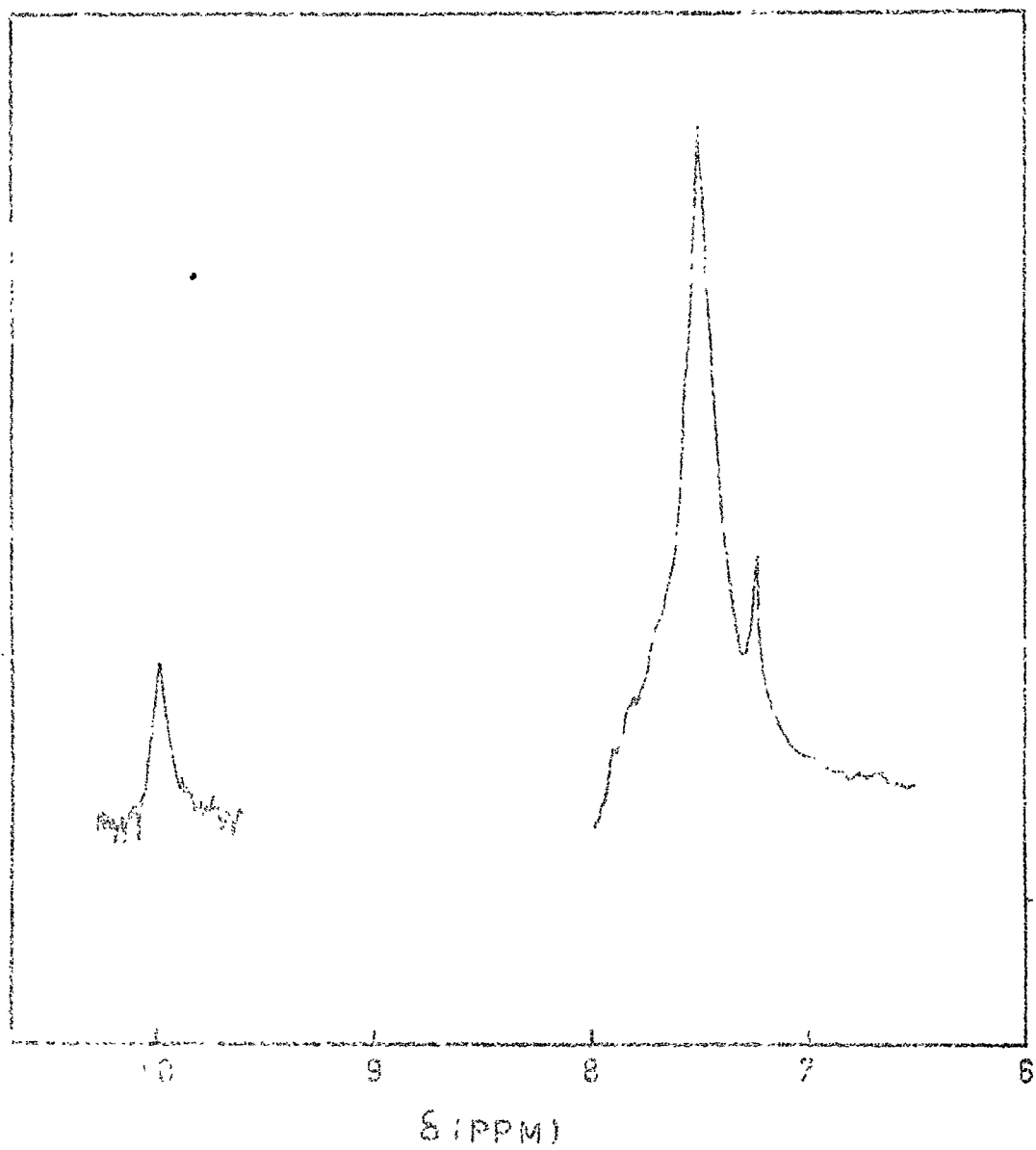


Fig. 1. NMR spectrum of  $[\text{RuCl}_2(\text{PPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2]$   
in  $\text{CDCl}_3$

The infrared spectra of the two complexes discussed above showed all the bands due to triphenylphosphine or triphenylarsine and benzaldehyde. The infrared spectrum of  $[\text{Ru}(\text{AsPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$  is given in figure no. I. 2. Among the important infrared bands due to benzaldehyde are three bands of medium intensity at 1615, 1595 and 1575  $\text{cm}^{-1}$ ; bands at 1450, 1220 and 670  $\text{cm}^{-1}$ .  $\nu_{\text{CO}}$  for free benzaldehyde occurs at 1698  $\text{cm}^{-1}$ . Due to coordination of benzaldehyde to the metal, the stretching frequency of  $\nu_{\text{CO}}$  goes down and one of the bands around 1600  $\text{cm}^{-1}$  could be due to  $\nu_{\text{CO}}$  of benzaldehyde coordinated to ruthenium. Other infrared bands are present in free benzaldehyde too but with a slight shift in the position. A strong band at 330  $\text{cm}^{-1}$  was observed for  $[\text{Ru}(\text{AsPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$ . Triphenylarsine also shows absorption around 330  $\text{cm}^{-1}$ . Hence this band can not be assigned unambiguously, however, it may be due to the coupled vibrations of  $\nu_{\text{Ru-Cl}}$  and the characteristic vibrations of triphenylarsine.<sup>17</sup> The complexes discussed above are diamagnetic, thereby confirming the oxidation state of ruthenium to be +2. These complexes are penta-coordinated and an evidence of which is obtained from electronic absorption spectra in chloroform. The electronic spectra (figure no. I. 3.) show one absorption band in the region 760 to 810 nm and another absorption around 410 nm. The band around 800 nm is observed in ruthenium(II)

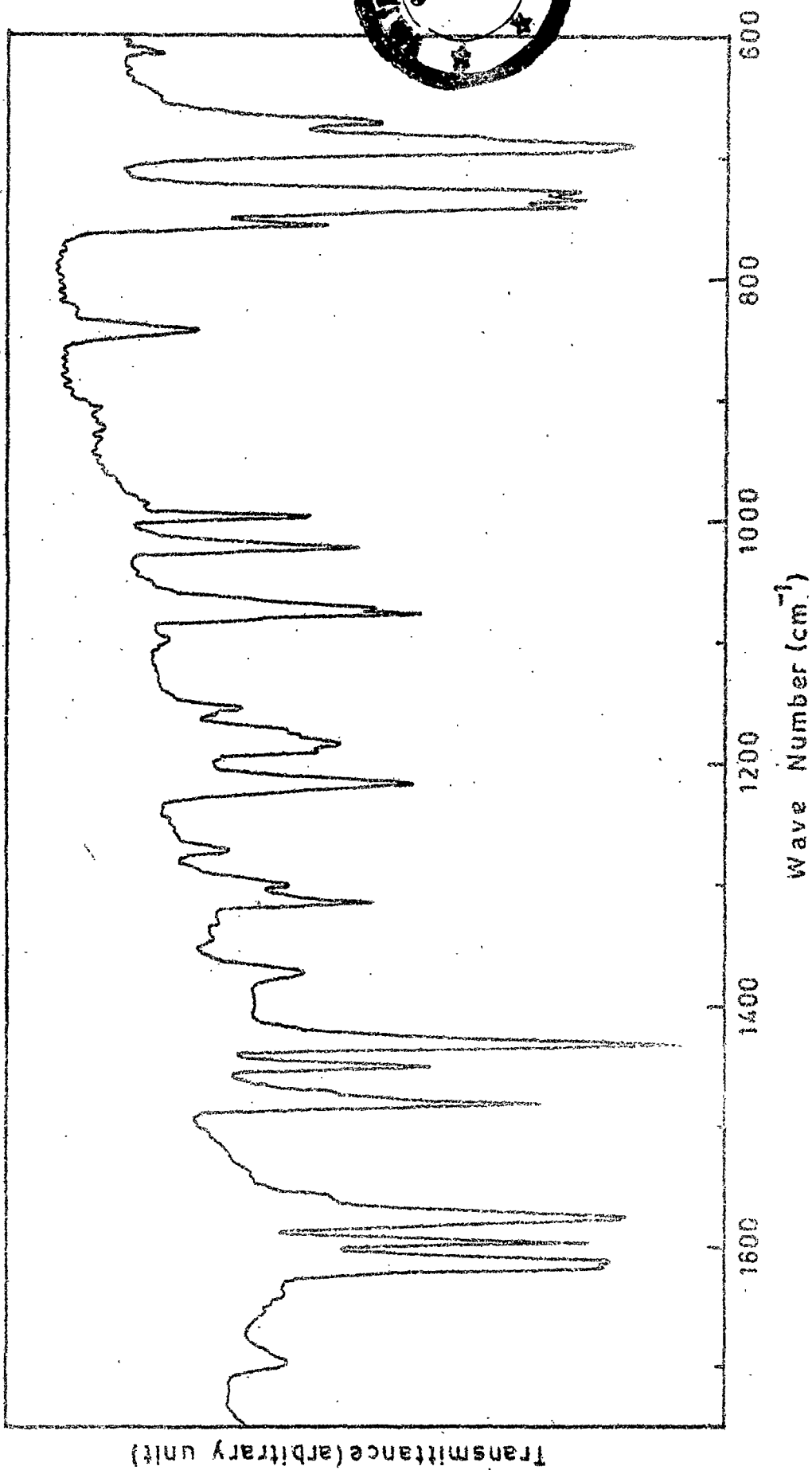


Fig 1.2. infrared Spectrum of  $[\text{RuCl}_2(\text{AsPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2]$  in KBr.

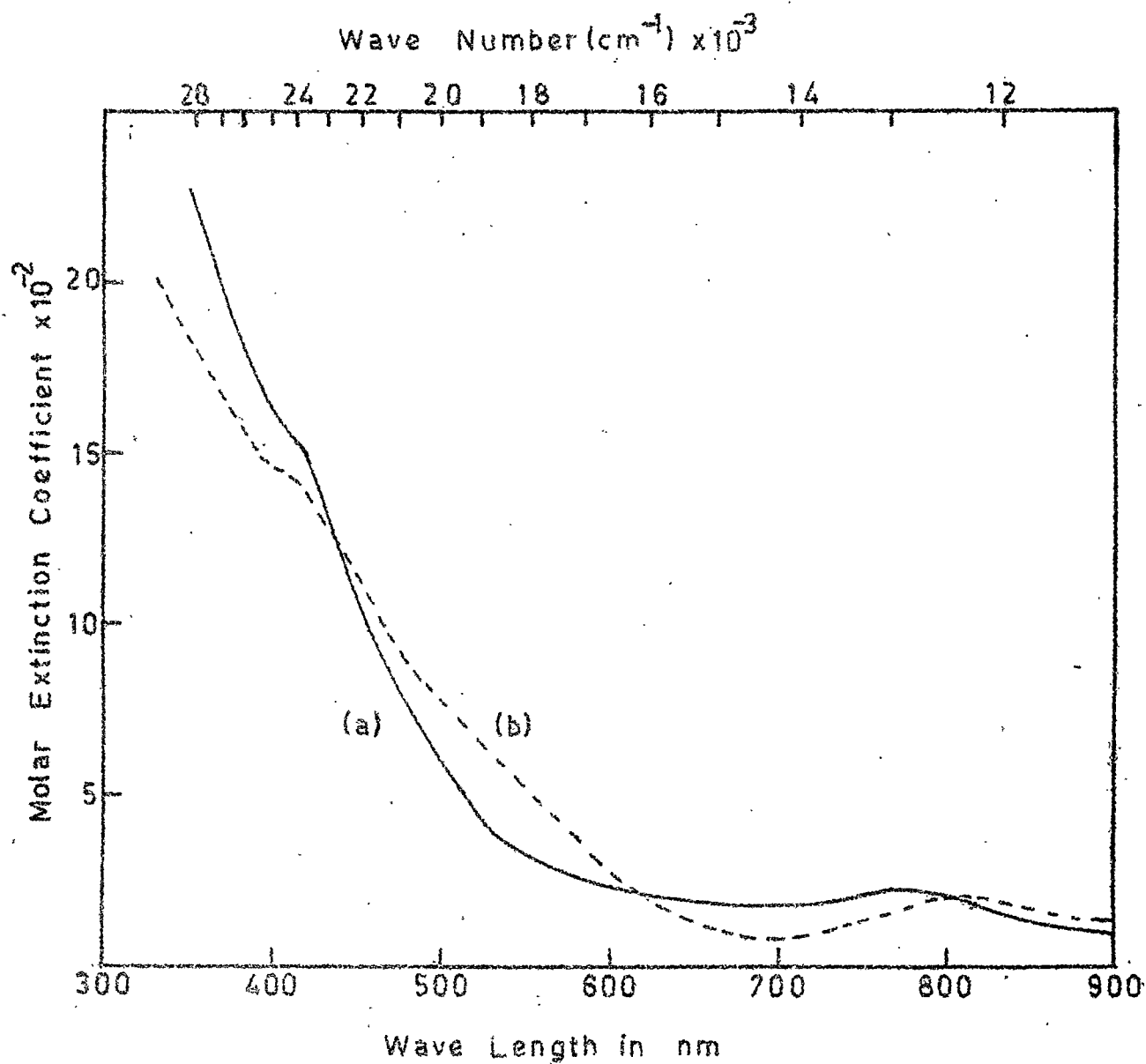


Fig. 1.3. Electronic Spectra of (a)  $[\text{RuCl}_2(\text{PPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2]$   
(b)  $[\text{RuCl}_2(\text{AsPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2]$  in Chloroform.

Table I. 2. Electronic Absorption and Important Infrared Spectral Data of Ruthenium(II) Complexes

Compound	Electronic Spectral Bands		Important Infrared Absorptions in $\text{cm}^{-1}$
	$\lambda_{\text{max}}$	in nm ( $\epsilon_{\text{max}}$ )	
$[\text{Ru}(\text{AsPh}_3)(\text{benz})_2\text{Cl}_2]^{+7}$	810 (220) 520 sh 410 (1460)		1615 m 1595 m 1575 m 1450 m 1218 m 670 m 330 s
$[\text{Ru}(\text{PPh}_3)(\text{benz})_2\text{Cl}_2]^{+7}$	765 (225) 420 (1500)		1615 m 1597 m 1580 m 1452 m 1220 m 675 m
$[\text{Ru}(\text{CO})(\text{AsPh}_3)_2\text{Cl}_2]^{+7}$	-		1940 s
$[\text{Ru}(\text{CO})(\text{PPh}_3)_2\text{Cl}_2]^{+7}$	-		1940 s
$[\text{Ru}(\text{AsPh}_3)(\text{py})_3\text{Cl}_2]^{+7}$	450 (1105) 390 (2300)		1445 m
$[\text{Ru}(\text{AsPh}_3)(\text{D.F})_3\text{Cl}_2]^{+7}$	510 (250) 405 (1050)		1640 s 1360 m
$[\text{Ru}(\text{PPh}_3)(\text{D.F})_3\text{Cl}_2]^{+7}$	550 (240) 415 (1250)		1642 s 1358 m

(Table I. 2..... contd..../-)

Table I. 2. Electronic Absorption and Important  
(contd.) Infrared Spectral Data of  
Ruthenium(II) Complexes

Compound	Electronic Spectral Bands $\lambda_{\max}$ in m ( $\epsilon_{\max}$ )	Important Infra- red Absorptions in $\text{cm}^{-1}$
$[\text{Ru}(\text{PPh}_3)(\pi\text{-CS}_2)\text{Cl}_2]$	-	1192 m 1112 m 1075 m-w 995 m-s
$[\text{Ru}(\text{CO})(\text{py})_2(\text{PPh}_3)\text{Cl}_2]$	-	1962 m-s 1945 m-s 1442 m
$[\text{Ru}(\text{CO})(\text{py})_2(\text{AsPh}_3)\text{Cl}_2]$	-	1952 m 1940 s 1923 n 1445 n

benz. = benzaldehyde; py = pyridine

D: F = dimethylformamide.

pentacoordinated square-pyramidal complexes, viz.

$[\text{RuCl}_2(\text{PPh}_3)_3]$  and  $[\text{RuCl}_2(\text{AsPh}_3)_2]$ .<sup>17</sup> Electronic absorption band in this region is generally not observed for octahedrally coordinated complexes of ruthenium(II). Hence, the benzaldehyde complexes seem to have distorted square-pyramidal structure.

The diamagnetic behaviour thus suggests that the six electrons in ruthenium(II) are probably distributed as  $(d_{xz}, d_{yz})^4, d_{xy}^2$ . The band around 800 nm could be assigned to  $d_{xy} \longrightarrow d_z^2$  and around 400 nm to  $(d_{xz}, d_{yz}) \longrightarrow d_z^2$  transitions. The complexes are non-conducting in nitrobenzene, thereby confirming non-ionic type of structure for the complexes.

(b)  $[\text{Ru}(\text{MPh}_3)_2(\text{CO})\text{Cl}_2]$

The reaction of ruthenium trichloride, benzaldehyde and triphenylphosphine in n-butanol for a period of about 6-8 hrs yielded a reddish-brown crystalline compound of the composition  $[\text{Ru}(\text{PPh}_3)_2(\text{CO})\text{Cl}_2]$ . It is diamagnetic in nature and shows a strong and sharp infrared absorption at  $1980 \text{ cm}^{-1}$  assignable to  $\nu_{\text{CO}}$  (terminal). The compound is same as reported by Poddar, where it has been obtained by a different method and a dimeric chloro-bridged octahedral structure around ruthenium(II) is proposed.<sup>21</sup>

Prolonged reaction ( $\sim 20$  hrs) of ruthenium trichloride benzaldehyde and triphenylphosphine or triphenylarsine resulted

in the formation of yellow compound of the composition  $\text{[Ru(CO)(MPh}_3)_2\text{Cl}_2\text{]}^-$  (M = P or As). These compounds could as well be obtained by the reaction of  $\text{[RuCl}_2(\text{PPh}_3)_3\text{]}^-$ ,  $\text{[RuCl}_2(\text{PPh}_3)_2\text{]}^-$  or  $\text{[RuCl}_2(\text{AsPh}_3)_2\text{]}^-$  with benzaldehyde in n-butanol or by the reaction of  $\text{[RuCl}_2(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{]}^-$  with corresponding triphenylphosphine or arsine in n-butanol.

Formation of these carbonyl containing complexes is due to the extraction of a carbonyl group from a benzaldehyde molecule, either coordinated to the metal or free (present in the reaction medium). The infrared spectra of these yellow carbonyl complexes show a strong and sharp band at  $1940\text{ cm}^{-1}$  assignable to  $\nu_{\text{CO}}$  (terminal), and all other bands due to triphenylphosphine or triphenylarsine.  $\text{[Ru(CO)(PPh}_3)_2\text{Cl}_2\text{]}^-$  has been reported by James et al.,<sup>22</sup> where  $\nu_{\text{CO}}$  is reported at  $1931$  and  $1921\text{ cm}^{-1}$  in nujol and at  $1940\text{ cm}^{-1}$  in dichloromethane. Yellow  $\text{[Ru(CO)(PPh}_3)_2\text{Cl}_2\text{]}^-$  obtained by us may be same as reported by James et al.

#### Reactions of $\text{[Ru(MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2\text{]}^-$ (M = P or As)

##### with Donor Solvents

Reactions of  $\text{[Ru(MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2\text{]}^-$  (M = P or As) with donor solvents were carried out to find out the ease of substitution of coordinated benzaldehyde. Donor solvents used were pyridine, N,N-dimethylformamide (DMF), dimethylsulphoxide (DMSO), acetonitrile and carbondisulphide.

Reactions with pyridine or DMF resulted in the formation of six coordinate,  $[\text{Ru}(\text{MPh}_3)_2\text{L}_3\text{Cl}_2]^-$  (L = py or DMF). Although benzaldehyde containing complexes are penta-coordinated, but their reactions with pyridine or DMF yield hexa-coordinated complexes, when two molecules of benzaldehyde in the complexes are replaced by three molecules of pyridine or DMF. Inability to form hexacoordinate complexes may be due to partial blocking of the sixth coordination site by the phenyl groups of the two benzaldehyde molecules and the triphenylphosphine <sup>or arsine</sup> molecule. The infrared spectra of the complexes containing DMF showed a very strong band at  $1640 \text{ cm}^{-1}$  which is due to  $\nu_{\text{CO}}$  of DMF coordinated through the oxygen atom.<sup>12</sup> In the case of pyridine complexes, all bands due to coordinated pyridine were observed besides bands due to triphenylphosphine or triphenylarsine in the infrared region. A medium-sharp band at  $1445 \text{ cm}^{-1}$  characteristic of pyridine was also observed.

Pyridine or DMF containing complexes are diamagnetic thereby confirming that ruthenium is present in +2 oxidation state in low-spin configuration. The electronic absorption spectra of these complexes showed two bands one in the region 450 to 550 nm and other one in the region 415 to 390 nm, the molar extinction coefficient of which is of the order of  $10^2$  to  $10^3$ . These bands may be assigned to  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$  and  $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$  transitions respectively. The values of the molar extinction coefficient ( $\sim 10^3$ ) is relatively high than expected for  $d \rightarrow d$  transitions. However, this

may be due to the mixing of the energy levels with the charge-transfer band(s) in that region.<sup>15</sup> These complexes are non-electrolyte in nitrobenzene thereby confirming non-ionic type of structure.

Reaction of DMSO with  $\text{[Ru(MPh}_3\text{)(C}_6\text{H}_5\text{CHO)}_2\text{Cl}_2\text{]}^-$  resulted in the substitution of all benzaldehyde and triphenylphosphine or triphenylarsine molecules by DMSO and resulting in the formation of  $\text{[RuCl}_2\text{(DMSO)}_4\text{]}^-$ . The DMSO complex showed strong infrared absorptions at 1120 and 1090  $\text{cm}^{-1}$  due to  $\nu_{\text{S=O}}$  of the S-bonded DMSO and was same as reported by Evans et al.<sup>23</sup>

Even on prolonged refluxing ( $\sim 10$  hrs) of the complex  $\text{[RuCl}_2\text{(AsPh}_3\text{)(C}_6\text{H}_5\text{CHO)}_2\text{]}^-$  with carbondisulphide either in the presence of excess triphenylarsine or even otherwise, no compound containing either thiocarbonyl group or carbondisulphide coordinated to ruthenium(II) was obtained. Only the starting compound was recovered after the reaction. Similarly, reaction of  $\text{[RuCl}_2\text{(PPh}_3\text{)(C}_6\text{H}_5\text{CHO)}_2\text{]}^-$  with carbondisulphide without excess triphenylphosphine gave back the starting compound. However, in presence of excess triphenylphosphine, a reddish-brown crystalline compound was obtained which did not contain benzaldehyde molecules but  $\text{CS}_2$  was coordinated to it, the composition of which was close to the formulation  $\text{[RuCl}_2\text{(PPh}_3\text{)(CS}_2\text{)}_2\text{]}^-$ . The infrared spectrum of which shows a band of medium intensity at 1112  $\text{cm}^{-1}$  and a band of medium to

strong intensity at  $995\text{ cm}^{-1}$ , besides all the bands due to triphenylphosphine. These two bands are characteristic of  $\pi\text{-CS}_2$  group coordinated to the metal.<sup>24</sup>

Reaction of  $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$  (M = P or As) with acetonitrile for about 4 hrs, yielded yellow or orange yellow compounds which did not show exact stoichiometric composition. However, infrared spectra showed presence of both acetonitrile and the triphenylphosphine or arsine. Bands at 2920 and 2270  $\text{cm}^{-1}$  were observed for acetonitriles coordinated to the metal. The former absorption could be assigned to  $\nu_{\text{CH}}$  of the aliphatic type and the later to  $\nu_{\text{CN}}$  of the coordinated acetonitrile ( $\nu_{\text{CN}}$  for free acetonitrile is observed at  $2247\text{ cm}^{-1}$ ).<sup>16</sup>

Reactions of  $[\text{Ru}(\text{CO})(\text{MPh}_3)_2\text{Cl}_2]$  (M = P or As) with Pyridine

Reddish-brown or yellow compounds of the composition,  $[\text{Ru}(\text{CO})(\text{MPh}_3)_2\text{Cl}_2]$  (M = P or As), on treatment with pyridine resulted in the formation of  $[\text{Ru}(\text{CO})(\text{MPh}_3)(\text{py})_2\text{Cl}_2]$ , which showed all infrared absorptions due to triphenylphosphine or triphenylarsine and pyridine. A band at  $1444\text{ cm}^{-1}$  characteristic of pyridine was observed. Besides, two or three bands in the region  $1965$  to  $1920\text{ cm}^{-1}$  due to  $\nu_{\text{CO}}$  were also observed.

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(i) nitrosylation, (ii) nitrosyl halide addition, (iii) oxidation of metal ion and (iv) oxidation of the coordinated ligand. A brief review of the reactions under the above four categories is given below.

Peter and Malito<sup>9</sup> found that nitrosyl halides act as a nitrosylating agent for transition metal complexes. The reactions of nitrosyl chloride with metal carbonylate anions, viz.  $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3]^-$  (M = Cr, Mo or W);  $[\text{Mn}(\text{CO})_5]^-$  and  $[\text{Fe}(\text{CO})_4]^{2-}$  gave neutral nitrosyl compounds, viz.  $[\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_2(\text{NO})]$ ,  $[\text{Mn}(\text{CO})_4(\text{NO})]$  and  $[\text{Fe}(\text{CO})_2(\text{NO})_2]$  respectively.

Compounds containing nitrosyl group coordinated to the metal ions have been reported from Agarwala's<sup>10,11</sup> laboratory. Hydrated ruthenium trichloride or rhodium trichloride was treated with nitrosyl halides NOX (X = Cl or Br) in the presence of tertiary phosphine, arsine or stibine. The compounds obtained were of the type,  $[\text{RuCl}_2\text{X}(\text{NO})\text{L}_2]$  and  $[\text{RhClX}(\text{NO})\text{L}_2]$  (X = Cl, when NOCl; and X = Br, when NOBr were used; L =  $\text{PPh}_3$ ,  $\text{AsPh}_3$  or  $\text{SbPh}_3$ ). Nitrosyl group coordinated in the above compounds is as  $\text{NO}^+$ . In a recent study, Pandey et al.<sup>12</sup> have reported the formation of a high spin  $d^5$ , ruthenium(III) complex,  $\text{NH}_4[\text{RuCl}_5(\text{NO})]$  and a  $d^7$  complex,  $[\text{RuCl}_2(\text{NO})(\text{PPh}_3)_2]$ . However, Coombe et al.<sup>13</sup> report that attempts to obtain compounds reported by Pandey et al.<sup>12</sup> were unsuccessful.

## CHAPTER II

REACTIONS OF NITROSYL CHLORIDE WITH  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$ 

(X = Cl, Br,  $\text{NO}_3$  or NCS)

INTRODUCTION

Activation of small inorganic molecules, viz.  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , CO, NO,  $\text{CO}_2$ ,  $\text{SO}_2$ ,  $\text{CS}_2$ , COS, NOCl, NOBr by the complexes of transition metal ions have gained considerable interest during the past two decades.<sup>1-10</sup> Activation of some of the molecules, viz.  $\text{H}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ , CO, NO by the transition metal complexes have been studied in greater details, whereas studies on molecules like nitrosyl halides, NOX (X = Cl or Br) with transition metal complexes are still in a state of infancy. Interest in the study of the reactions of nitrosyl halides with transition metal complexes continues to grow due to different types of reaction products obtained in these reactions. The products of such reactions can be broadly classified into the following four categories, viz.

Most reactions of nitrosyl halides studied are those, where nitrosyl halide gives addition products. Such reactions are reported with various metal ions of molybdenum, tungsten, iron, rhodium, iridium, and platinum. Details of such reactions are presented in Table II.1.

Oxidation of the metal ions to the next higher oxidation state have been reported for Ni(II), Co(II), Mn(II), Mn(III) and Mo(III) in complexes, by nitrosyl halides.  $[M(PEt_3)_2X_3]$  (X = Cl or Br; M = Ni or Co) were obtained by the oxidation of  $[M(PEt_3)_2X_2]$  with nitrosyl halides, NOX (X = Cl or Br).<sup>27</sup> However, an attempt by Jensen et al.<sup>27</sup> to oxidise  $[Ni(PPh_3)_2X_2]$  (X = Cl or Br) by NOX (X = Cl or Br) were unsuccessful. Cyano complexes of Mn(II), Mn(III) and Mo(III) were oxidised to next higher oxidation states of the metals by nitrosyl chloride, where it acted as one electron oxidant.<sup>28</sup>

The oxidation of coordinated triphenylphosphine to triphenylphosphine oxide has been reported by Davis et al.<sup>17</sup>  $[M(NO)Cl_3(OPPh_3)_2]$  (M = Mo or W) are reported by the reactions of  $[M(CO)_4(PPh_3)_2]$  (M = Mo or W),  $Mo(CO)_3(PPh_3)_2Cl_2$  or  $W(CO)_3(PPh_3)_2Cl_3$  with nitrosyl chloride.

Most of the studies of reactions of nitrosyl halides, discussed above, are with the complexes of heavier transition metal ions. Studies with the complexes of first row transition-metal ions are very few. A study of the reactions of

Table II. 1. Addition Products of the Reaction of Nitrosyl Halides, NOX (X = Cl or Br) with Transition Metal Ion.

Sl.No.	Reactions	Compound Obtained	Physical Properties	References
1	$K_2[PtCl_4] + NOCl$	$K_2[Pt(NO)Cl_5]$	IR, Mag.	14
2	$[Pt(NH_3)_4]Cl_2 + NOCl$	$[Pt(NO)(NH_3)_4Cl]Cl_2$	Mag., IR	14
3	$K_2[Pt(NO_2)_4] + NOCl$	$K_2[Pt(NO)(NO_2)_4Cl]$	IR, Mag.	14
4	$[Pt(en)_2]Cl_2 + NOCl$ (en = ethylenediamine)	$[Pt(NO)(en)_2Cl]Cl_2$	IR, Mag.	14
5	$M(CO)_6 + NOX$ (M = Mo or W; X = Cl or Br)	$[M(NO)_2X_2]_n$	IR, Mag.	15, 16
6	$Mo(CO)_4(PPh_3)_2 + NOBr$	$Mo(NO)_2(PPh_3)_2Br_2$	IR, Mag.	16
7	$M_2(CO)_8Cl_4 + NOCl$ (M = Mo or W)	$[M(NO)Cl_3]_n$	IR, Mag.	17
8	$Ni(CO)_4 + NOCl$	$[Ni(NO)Cl_2]_n$	IR, Mag.	18
9	$[Rh(COD)Cl]_2^{(a)} + NOX$ (X = Cl or Br)	$[Rh(NO)X_2]_n$	IR	19
10	$[Ir(COD)Cl]_2^{(a)} + NOCl$	$[Ir(NO)(COD)Cl_2]_n$	IR, NMR	19

Table II. 1..... contd...../

Table II. 1. Addition Products of the Reaction  
(contd..) Nitrosyl Halides, NOX (X = Cl or Br) with  
Transition Metal Ion.

Sl.No.	Reaction	Compound obtained	Physical Properties	References
11	$K_4MnCl_8 + NOCl$	$K_2[Mn(NO)Cl_5]$	IR, cond.	20
12	$Mn_2(C_2H_3O_2)_4^{(b)} + NOCl + OPPh_3$	$[Mn(NO)(OPPh_3)_2Cl_3]$	IR	20
13	$[C_2H_5)_4N]_3Mn_2Cl_9 + NOCl$	$[C_2H_5)_4N]_2[Mn(NO)Cl_5]$	IR, Cond.	20
14	$M(CO)_3(CH_3CN)_3 + L_2 + NOCl$ (M = Mn or W; $L_2$ = diphos, bipy; or phen)	$[M(CO)_2(NO)L_2]Cl$	IR	21
15	$[LM(CO)_2(N_2Ph)] + NOCl$ (L = HBP <sub>2</sub> for M = Mn/W L = C <sub>5</sub> H <sub>5</sub> for M = Mn)	$[LM(NO)(N_2Ph)Cl]$	IR, NMR, Mag.	22
16	$(HBP_{23})^{(c)}Mn(CO)_2NO + NOCl$	$(HBP_{23})Mn(NO)_2Cl$	-	23
17	$Ni(PPh_3)_4 + NOCl$	$[Ni(NO)(PPh_3)_2Cl]$	-	24
18	$Ni(COD)^{(a)}(PPh_3)_2 + NOCl$	$[Ni(NO)(PPh_3)_2Cl]$	-	24

Table II- 1. .... contd...../-

Table II. 1. Addition Products of the Reactions of the  
(contd..) Nitrosyl Halides, NOX (X = Cl or Br) with  
Transition Metal Ion

Sl. No.	Reaction	Compound obtained	Physical Properties	References
19	$\text{Ni(COD)}_2^{(a)} + \text{P(OPh)}_3 + \text{NOCl}$	$\text{[Ni(NO)(P(OPh)}_3)_2\text{Cl}]$	-	24
20	$\text{Ni(COD)}_2^{(a)} + \text{L}_2 + \text{NOCl}$ ( $\text{L}_2 = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ where, n = 1, 2 or 3)	$\text{[NiL}_2\text{(NO)Cl]}$	IR	24
21	$\text{Fe(CO)}_3(\text{PPh}_3)_2 + \text{NOX}$ (X = Cl or Br)	$\text{[Fe(NO)(CO)}_2(\text{PPh}_3)_2\text{X}]$	IR	25
22	$\text{[Ni(PPh}_3)_2\text{]}_2\text{[Fe(CO)}_3\text{(NO)]} + \text{NOCl}$	$\text{[Ni(PPh}_3)_2\text{]}_2\text{[Fe(NO)Cl}_2\text{]}$	IR, Mag., ESR, Cond.	26

(a), COD = 1,5 cyclooctadiene; (b),  $\text{C}_2\text{H}_3\text{O}_2$  = acetato;

(c)  $\text{HBP}_{23}$  = tris-1,pyrazolylborate; IR = Infrared ;

Mag. = Magnetic Susceptibility; NMR = Nuclear Magnetic Resonance

ESR = Electron Spin Resonance; Cond. = Conductivity

$[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br, I,  $\text{NO}_3$  or NCS) with nitrosyl chloride was taken up to find out under which categories these reactions fall, and to study the physical behaviours of the compounds obtained to establish the geometry of the complexes obtained.

In this chapter, reactions of nitrosyl chloride with  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br,  $\text{NO}_3$  or NCS) are reported under two different conditions, whereby compounds of the type  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  and  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$  (X = Cl, Br,  $\text{NO}_3$  or NCS) are obtained. These compounds seem to have a distorted tetrahedral structure with chlorine bridges. Reactions of dimeric chlorobridged compounds with triphenylphosphine gave  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$  (X = Cl, Br,  $\text{NO}_3$  or NCS). Except for thiocyanato complex, which is square planar, others have distorted tetrahedral structure.

### EXPERIMENTAL

All the materials used were of chemically pure or Analar grade.  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br,  $\text{NO}_3$  or NCS) were prepared according to reported methods.<sup>29</sup> Nitrosyl chloride was supplied by Air Products Ltd., London, U.K. and was purified before use.

Reactions of Nitrosyl Chloride with  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$

(X = Cl, Br,  $\text{NO}_3$  or NCS)

- (i) Finely powdered  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br,  $\text{NO}_3$  or NCS) (0.5 g) was suspended in dry cyclohexane (30 ml). Nitrosyl chloride gas was bubbled very slowly with stirring through the suspension for about 20 minutes for all the complexes except thiocyanato complex. For thiocyanato complex, gas bubbling was carried out for only 5 minutes as longer gas bubbling gave impure products. After stopping the gas, the suspension was stirred for about 6 hrs at room temperature, when a change in the colour of the suspended material was observed. Initially the reaction was very vigorous with the evolution of a gas but at the completion of the reaction, no effervescence was observed. The compound obtained was centrifuged, washed several times with warm dry cyclohexane and finally with dry diethyl-ether and dried under vacuum. The analyses corresponded to the formula  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]_2$  (X = Cl, Br,  $\text{NO}_3$  or NCS).
- (ii) In another set of reactions similar to that in (i),  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br,  $\text{NO}_3$  or NCS) (0.5 g) was taken in 30 ml of dry benzene and cyclohexane mixture (1 : 5). Nitrosyl chloride gas was bubbled for about 5 minutes through the suspension very slowly with constant stirring. The suspension was stirred for about 8 hrs

at room temperature, when a change in the colour of the suspended material was observed. The compound obtained was washed first with cyclohexane and benzene mixture, 3 to 4 times and then finally with dry ether and then dried under vacuum. The composition was found to be  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$  or  $\text{NCS}$ ).

The thiocyanate complex was obtained also by using benzene instead of cyclohexane and benzene mixture.

The mother liquor obtained after removing the products from the above sets of reactions (i) and (ii), upon concentration, yielded triphenylphosphine oxide, which was equimolar to that of the starting material.

Reactions of  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  and  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$   
( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$  or  $\text{NCS}$ )

- (i) A suspension of  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  or  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{NO}_3$ ) (0.5 g) was taken in acetic acid (20 ml). A solution of triphenylphosphine (0.6 g) in acetic acid (5 ml) was added to the above suspension and the mixture was stirred for about 4 hrs at room temperature, when new compounds separated out. The compounds obtained were separated by centrifugation, washed first with acetic acid and then several times with dry diethylether and dried under vacuum. Out of the compounds, thus obtained,  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$  ( $\text{X} = \text{Br}$  or

$\text{NO}_3$ ) are new and  $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$  is same as reported by Venanzi.<sup>29</sup>

- (ii) To a suspension of  $[\text{Ni}(\text{PPh}_3)(\text{NCS})\text{Cl}_2]$  or  $[\text{Ni}(\text{OPPh}_3)(\text{SCN})\text{Cl}_2]$  (0.5 g) in cyclohexane (10 ml), a solution of triphenylphosphine (0.6 g) in cyclohexane (5 ml) was added and the mixture was stirred for about 4 hrs at room temperature. A red crystalline compound separated out which was washed with warm cyclohexane and dried under vacuum. The composition was found to be  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]$ .
- (iii) When  $[\text{Ni}(\text{OPPh}_3)(\text{SCN})\text{Cl}_2]$  and triphenylphosphine were taken in 1:2 molar quantities at room temperature and stirred for 4 hrs,  $[\text{Ni}(\text{PPh}_3)(\text{OPPh}_3)(\text{NCS})\text{Cl}]$  was obtained, which was washed and dried as in (ii) above.
- (iv) Reactions of  $[\text{Ni}(\text{OPPh}_3)\text{XCl}_2]$  (X = Cl, Br or  $\text{NO}_3$ ) with triphenylphosphine oxide under condition similar to that of (i), did not yield any new product. However, if the reactions were carried out under refluxing conditions, the parent compound got decomposed.

### Analyses

Carbon, Hydrogen and nitrogen analyses were obtained from Microanalytical laboratory of Indian Institute of Technology, Kanpur, India. Nickel, Sulphur, Phosphorus and Halogen estimations were done by standard gravimetric methods<sup>30</sup> after

decomposing the compounds using dilute nitric acid. Details of some of the estimations, viz. estimation of nickel and of phosphorous are given below. All the analytical data are given in Table II.2.

#### Estimation of Nickel

Compound containing ~ 30 mg of nickel was decomposed using dilute nitric acid and diluted to 200 ml with water. The clear solution was made alkaline with dilute ammonia, warmed to 80 °C and a solution of dimethylglyoxime (~ 15 ml of 1% solution) added to it in slight excess with constant stirring. The precipitate was digested on a water bath for 30 minutes and tested for complete precipitation. After cooling, the precipitate was filtered through a weighed crucible washed with cold water and dried in an air oven at 120 °C and weighed as Ni(HDMG)<sub>2</sub>.

#### Estimation of Phosphorus

Estimation of phosphorus was carried out by decomposing a weighed amount of the compound in a Parr-bomb crucible. A mixture of sugar, potassium nitrate and sodium peroxide in the ratio of 1:3:20 mg by weight for one mg of phosphorus present in the sample was used as the oxidising agent. The mixture was heated strongly for 15 minutes in the Parr-bomb and cooled. The contents were extracted with water and acidified with dilute sulphuric acid. Concentrated sulphuric

acid (~7 ml) was added to it followed by its evaporation to evolve sulphur trioxide fumes. The residue was extracted with water and filtered if necessary, to remove any insoluble impurities. Phosphorus was estimated in this solution as phosphoammoniummolybdate by the standard method.<sup>30</sup>

### Infrared Spectra

Spectra of the complexes were recorded in KBr or Nujol mull on a Perkin-Elmer model 297 in 4000-600  $\text{cm}^{-1}$  range and on a polytec FIR 30 spectrophotometer in 600-100  $\text{cm}^{-1}$  range. Infrared data in 600-100  $\text{cm}^{-1}$  range are presented in Table II.3.

### Electronic Spectra

The electronic spectra in 800-300 nm range were recorded in acetonitrile or nitrobenzene solvents using a Beckmann-26 spectrophotometer. The solid state reflectance spectra were recorded on a VSU 2-P spectrophotometer. Spectral data are given in Table II.4.

### Magnetic Susceptibility Measurements

These measurements were made using a Gouy balance at room temperature, using mercury tetrathiocyanato cobaltate(II) as calibrant. The results are presented in Table II.4.

Conductivity

Conductivity measurements were made on an Elico type CM 82 conductivity bridge in nitrobenzene.

RESULTS AND DISCUSSION

In the reactions of nitrosylchloride with  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  the following observations were made. (i) No nitrosyl compound was obtained (infrared spectra did not show any absorption in 2000 to 1600  $\text{cm}^{-1}$  region. In the case of the thiocyanato complexes, an absorption around 2100  $\text{cm}^{-1}$  due to  $\nu_{\text{CN}}$  was observed). (ii) No nickel(III) or nickel(IV) compound was obtained (complexes in solution did not act as an oxidising agent, since no product oxidised iodide to iodine). (iii) No addition product of nitrosyl chloride was obtained. (iv) One molecule of triphenylphosphine was displaced from the parent compound and oxidised to triphenylphosphine oxide and one X was replaced by a chlorine atom, when the reactions were carried out in cyclohexane as the solvent. In this process dinuclear chloro-bridged complexes were obtained. (v) Both the molecules of triphenylphosphine coordinated to the parent compound were oxidised to triphenylphosphine oxide and the product obtained contained one molecule of triphenylphosphine oxide coordinated to the metal and one X was replaced by a chlorine atom, when the reaction was carried out using benzene and cyclohexane mixture as the solvent. In this process also,

Table II. 2. Physical Properties and Analytical Data of the Complexes

Compound	Colour	M.P. (a) °C	Found (%) (Calc. %)						N/Br
			Ni	Cl	P	C	H		
$[\text{Ni}(\text{PPh}_3)\text{Cl}]_2$	Light Green	87-90	14.23 (14.97)	17.46 (18.11)	7.84 (7.90)	54.78 (55.10)	3.96 (3.82)	-	
$[\text{Ni}(\text{PPh}_3)\text{BrCl}]_2$	Bluish Green	75-80	12.95 (13.44)	8.62 (8.13)	6.79 (7.10)	49.62 (49.48)	3.54 (3.43)	17.43 (18.32)	
$[\text{Ni}(\text{PPh}_3)(\text{NO}_3)\text{Cl}]_2$	Light Green	130-35	13.86 (14.02)	8.37 (8.48)	7.60 (7.40)	50.97 (51.61)	3.43 (3.58)	3.58 (3.34)	
$[\text{Ni}(\text{PPh}_3)(\text{NCS})\text{Cl}]_2^{(b)}$	Light Brown	110-13	14.37 (14.16)	8.29 (8.56)	6.93 (7.47)	52.18 (52.11)	3.78 (3.61)	3.39 (3.37)	
$[\text{Ni}(\text{OPPh}_3)\text{Cl}_2]_2$	Bluish Green	115-20	14.49 (14.39)	<b>17.86</b> (17.40)	-	52.63 (52.99)	3.96 (3.70)	-	
$[\text{Ni}(\text{OPPh}_3)\text{BrCl}]_2$	Light Green	100-5	12.54 (12.98)	8.22 (7.85)	-	48.20 (47.79)	3.61 (3.34)	16.96 (17.66)	
$[\text{Ni}(\text{OPPh}_3)(\text{NO}_3)\text{Cl}]_2$	Yellowish Green	100	13.04 (13.51)	8.38 (8.17)	-	49.28 (49.76)	3.65 (3.48)	2.57 (3.22)	
$[\text{Ni}(\text{OPPh}_3)(\text{SCN})\text{Cl}]_2^{(c)}$	Light Yellow	90-95	13.27 (13.63)	7.79 (8.24)	7.64 (7.20)	49.65 (50.17)	2.94 (3.48)	2.84 (3.25)	
$[\text{Ni}(\text{PPh}_3)_2\text{BrCl}]_2$	Green	213-16	8.87 (8.40)	5.21 (5.08)	-	62.24 (61.89)	3.92 (4.32)	11.68 (11.44)	
$[\text{Ni}(\text{PPh}_3)_2(\text{NO}_3)\text{Cl}]_2$	Green	215-20	8.32 (8.62)	5.53 (5.21)	-	63.86 (63.51)	4.08 (4.44)	2.32 (2.06)	
$[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]_2^{(d)}$	Reddish Brown	184-90	8.34 (8.67)	5.45 (5.25)	-	65.26 (65.69)	4.61 (4.43)	2.38 (2.07)	

(a) = all compounds decompose; (b) Sulphur, Found = 8.20%; Calc. = 7.72%;

(c) = Sulphur, Found = 7.79%; Calc. = 7.43%; (d) Sulphur, Found = 5.24%; Calc. = 4.73%

similar to that in (iv) dinuclear chloro-bridged compounds were obtained. (vi) From the mother liquor of the reactions described in (iv) and (v) above, triphenylphosphine oxide was obtained.

Dimeric complexes, with halogen bridging react with monodentate ligands, and are found to give monomeric complexes with the breaking of halogen bridges.<sup>31,32</sup> We have observed the formation of  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]_2$ , when  $[\text{NiLXCl}]_2$  (L =  $\text{PPh}_3$  or  $\text{OPPh}_3$ ; X = Cl, Br,  $\text{NO}_3$  or NCS) were treated with excess triphenylphosphine. Except for  $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ , reported by Venanzi,<sup>29</sup> other compounds are new. A reaction of  $[\text{Ni}(\text{OPPh}_3)(\text{SCN})\text{Cl}]_2$  with triphenylphosphine in 1:2 molar ratio gave  $[\text{Ni}(\text{PPh}_3)(\text{OPPh}_3)(\text{NCS})\text{Cl}]_2$ .

Dimeric nature of  $[\text{NiLXCl}]_2$  (L =  $\text{PPh}_3$  or  $\text{OPPh}_3$ ; X = Cl, Br, NCS or  $\text{NO}_3$ ) could not be confirmed by their molecular weight determination, due to low solubility or decomposition in non-donor solvents. However, infrared spectra in low frequency region were very helpful to support the dimeric structure having chlorobridges.

### Infrared Spectra

The infrared spectra of  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  (X = Cl, Br,  $\text{NO}_3$  or NCS) in 4000 to 600  $\text{cm}^{-1}$  region showed all the bands due to triphenylphosphine.  $[\text{Ni}(\text{PPh}_3)\text{NO}_3\text{Cl}]_2$  showed bands at 1500, 1260 and 795  $\text{cm}^{-1}$  [fig. no. II.1] which are

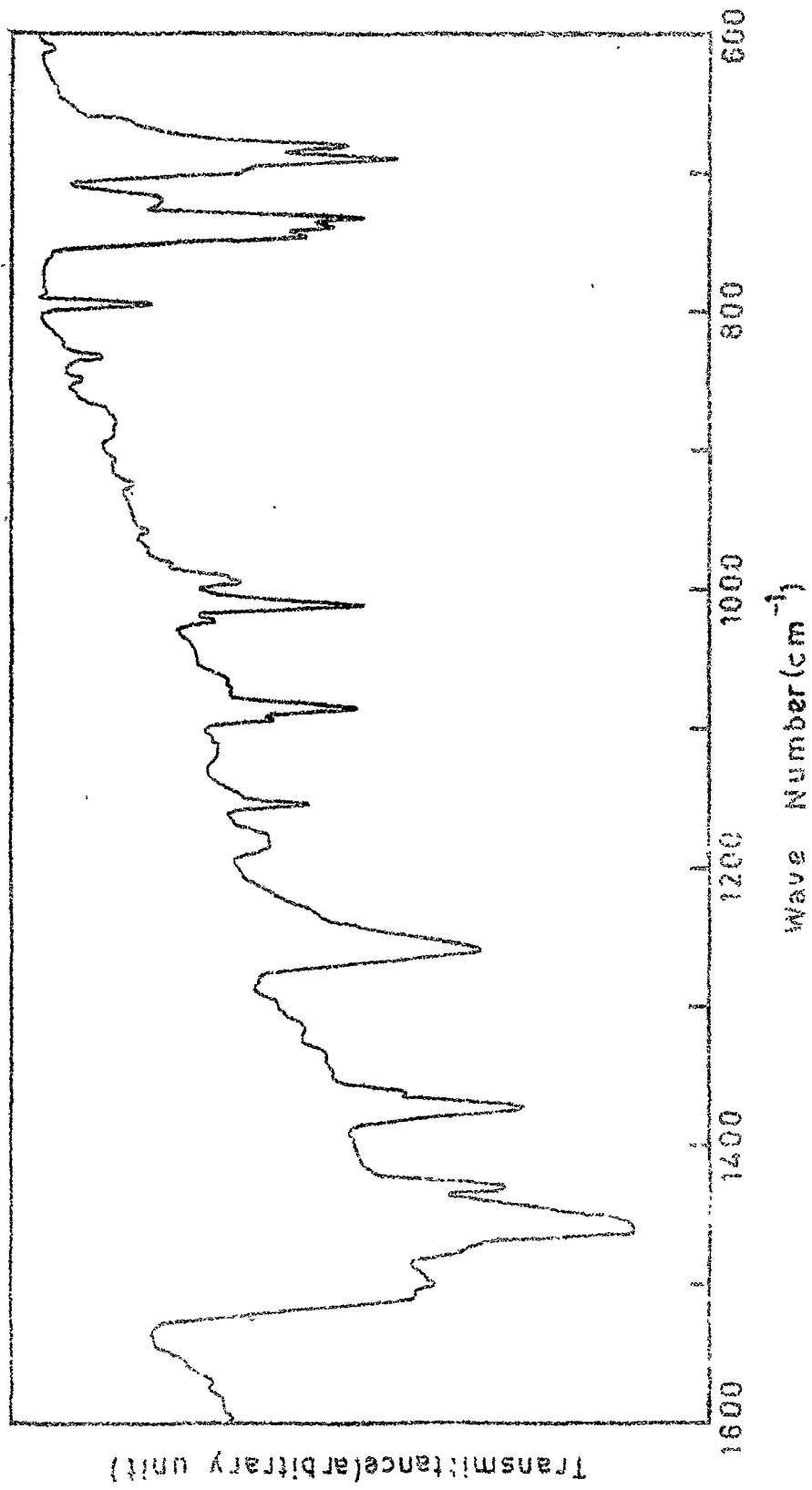


Fig. II-1. Infrared Spectrum of  $[\text{Ni}(\text{PPh}_3)(\text{NO}_3)\text{Cl}]_2$  in nujol.

characteristic of a monodentate nitrate group.<sup>33</sup> The infrared spectrum of  $[\text{Ni}(\text{PPh}_3)(\text{NCS})\text{Cl}]_2$  [fig. no. II.2.] showed one strong and sharp band at  $2080 \text{ cm}^{-1}$  and a medium band at  $865 \text{ cm}^{-1}$  which may be assigned to  $\nu_{\text{CN}}$  and  $\nu_{\text{CS}}$  respectively of an N-bonded thiocyanato group.<sup>33</sup> The absence of a bridging thiocyanato group was confirmed by the absence of any other band around  $2080 \text{ cm}^{-1}$ .

The infrared spectra of  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$  (X = Cl, Br,  $\text{NO}_3$ , NCS) in  $4000$  to  $600 \text{ cm}^{-1}$  region showed all the bands due to triphenylphosphine oxide. A band at  $1180 \text{ cm}^{-1}$  present in triphenylphosphine oxide, due to  $\nu_{\text{P=O}}$  was split into two and were observed in  $1190$ - $1185$  and  $1165$ - $1150 \text{ cm}^{-1}$  regions. In the case of nitrate complex bands at  $1505$ ,  $1275$  and  $800 \text{ cm}^{-1}$  were also observed which are characteristic of a monodentate nitrate group.<sup>33</sup> The infrared spectrum of  $[\text{Ni}(\text{OPPh}_3)(\text{SCN})\text{Cl}]_2$  showed a strong band at  $2100 \text{ cm}^{-1}$  [fig. no. II.3.] also, which could be assigned to  $\nu_{\text{CN}}$  of the S-bonded thiocyanato group. The lack of a band in the region  $870$  to  $780 \text{ cm}^{-1}$  shows the absence of an N-bonded thiocyanate. It is not possible to assign unambiguously  $\nu_{\text{CS}}$  band of the S-bonded thiocyanato group, since triphenylphosphine oxide has absorptions in  $750$  to  $680 \text{ cm}^{-1}$  region. There is a very strong band at  $722 \text{ cm}^{-1}$ , which could be a combination of  $\nu_{\text{CS}}$  (S-bonded SCN) and bands due to triphenylphosphine oxide.

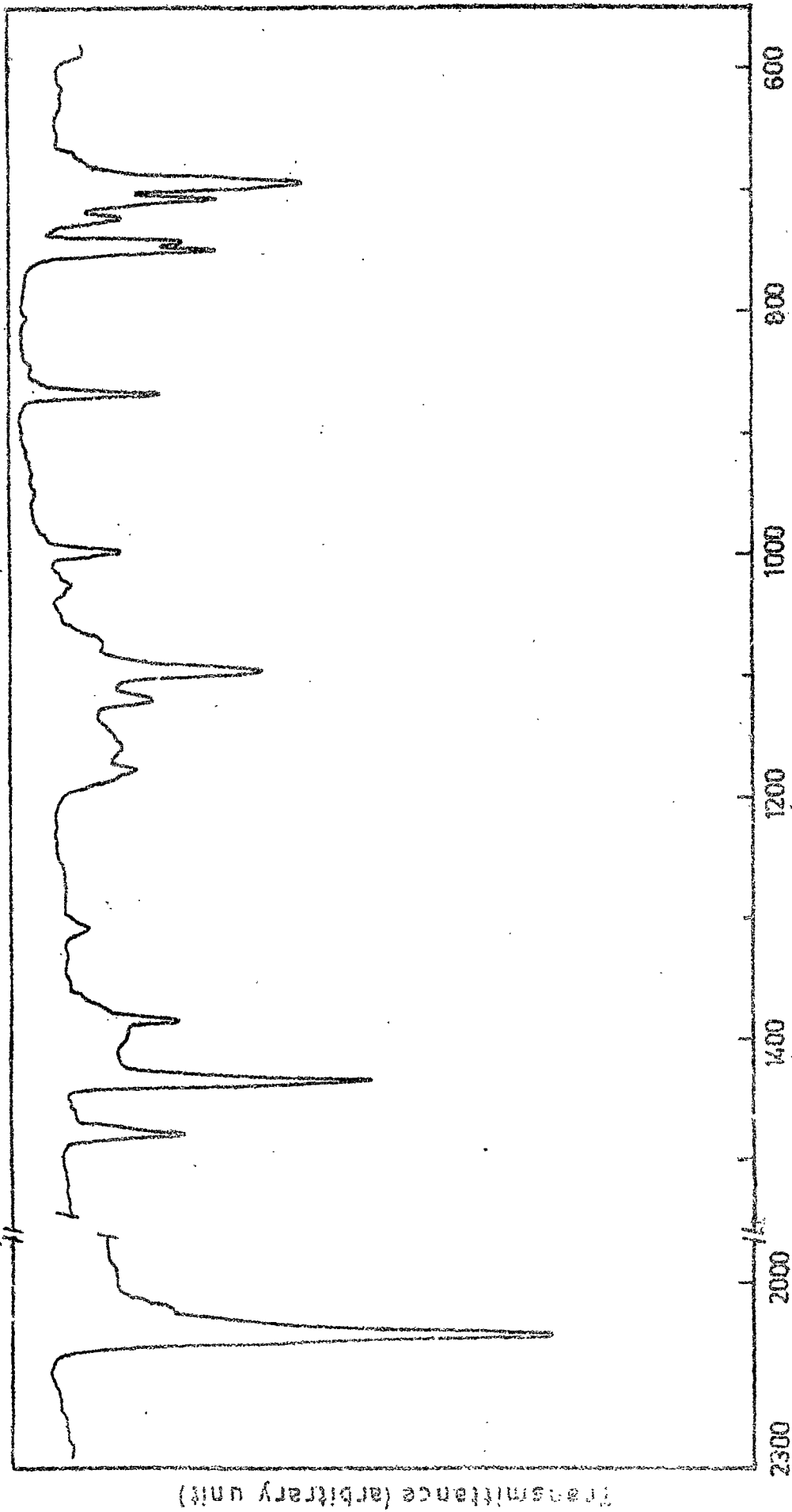


Fig.II.2. Infrared Spectrum of  $[\text{Ni}(\text{PPh}_3)(\text{NCS})\text{Cl}]_2$  in KBr.

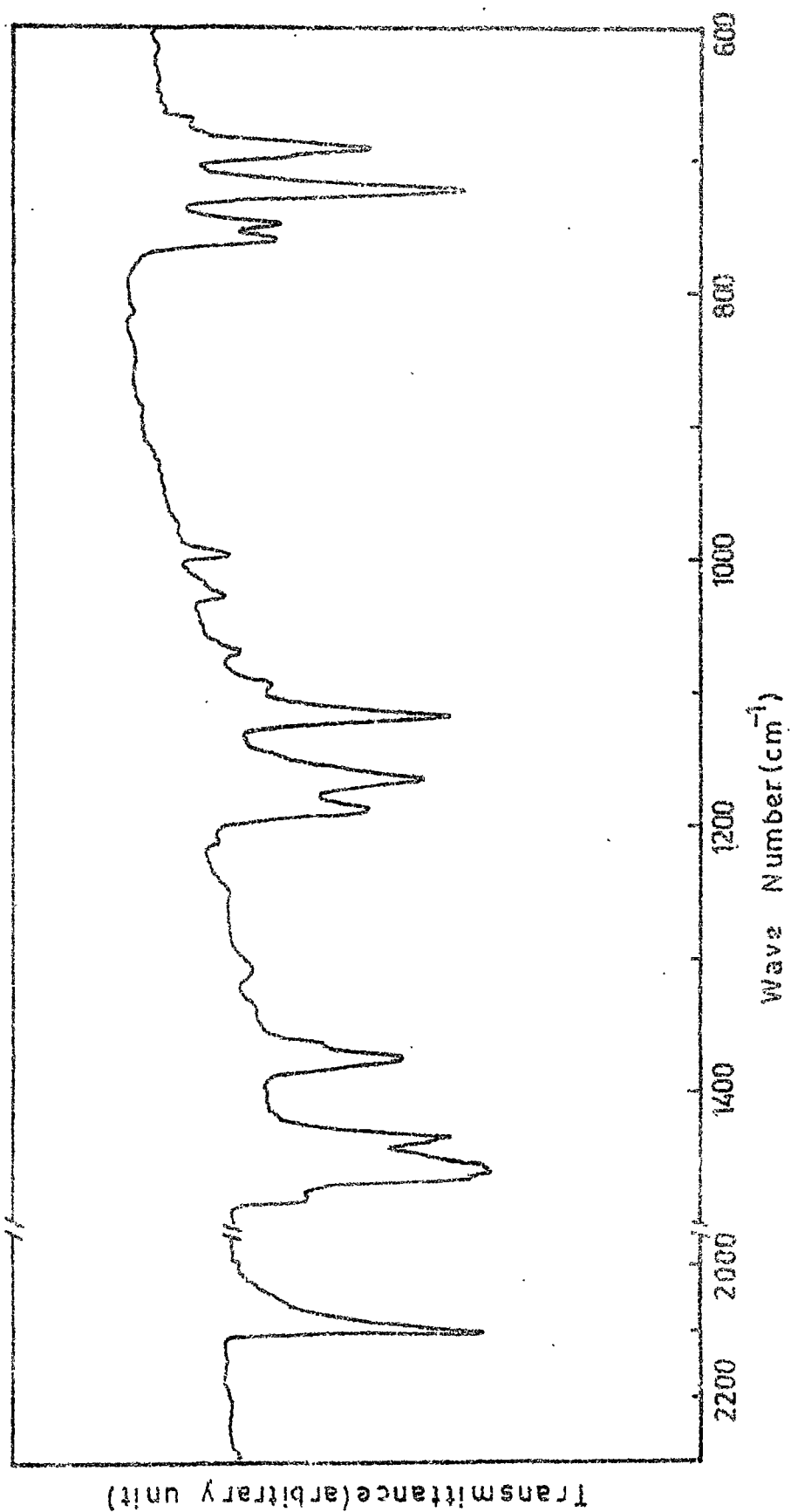


Fig. 11.3. Infrared Spectrum of  $[\text{Ni}(\text{OPPh}_3)(\text{SCN})\text{Cl}]_2$  in nujol.

Infrared spectra of  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$  or  $\text{NCS}$ ) showed all the bands due to triphenylphosphine.

$[\text{Ni}(\text{PPh}_3)_2(\text{NO}_3)\text{Cl}]_2$  has bands at 1522, 1510, 1270 and 805  $\text{cm}^{-1}$  also, due to monodentate nitrate group.<sup>33</sup> The infrared spectrum of  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]_2$  showed a strong band at 2080  $\text{cm}^{-1}$  and a medium band at 867  $\text{cm}^{-1}$  which could be assigned to  $\nu_{\text{CN}}$  and  $\nu_{\text{CS}}$  respectively of the N-bonded thiocyanato group, as in  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2]$ .<sup>33</sup>

The far infrared spectral data of  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$ ) and their assignments are presented in Table II.3. Far infrared spectrum of  $[\text{Ni}(\text{PPh}_3)\text{Cl}_2]_2$  is given in figure no. II.4. The two bands between 280-265 and 240-235  $\text{cm}^{-1}$  are assigned to  $\nu_{\text{Ni-Cl}}$  (bridging) which are absent in the tetrahedral  $[\text{Ni}(\text{PPh}_3)_2\text{Cl}_2]$ .<sup>34</sup> However, in the case of  $[\text{Ni}(\text{PPh}_3)\text{BrCl}]_2$ , these bands could be a combination of  $\nu_{\text{Ni-Br}}$  (terminal) and  $\nu_{\text{Ni-Cl}}$  (bridging). In the case of tetrahedral  $[\text{Ni}(\text{PPh}_3)_2\text{BrCl}]_2$ , having no bridging halogen,  $\nu_{\text{Ni-Cl}}$  and  $\nu_{\text{Ni-Br}}$  are assigned to bands at 345 and 305  $\text{cm}^{-1}$  and at 272 and 247  $\text{cm}^{-1}$  respectively.<sup>35</sup> In the case of thiocyanato complexes, viz.  $[\text{Ni}(\text{PPh}_3)(\text{NCS})\text{Cl}]_2$  and  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]_2$ , bands at 265 and 235  $\text{cm}^{-1}$  and at 355 and 310  $\text{cm}^{-1}$  can be assigned to  $\nu_{\text{Ni-Cl}}$  (bridging) and  $\nu_{\text{Ni-Cl}}$  (terminal), respectively. Besides,  $\delta_{\text{NCS}}$  for the N-bonded thiocyanato and  $\nu_{\text{Ni-N}}$  are observed at 460 and 414  $\text{cm}^{-1}$  respectively for both

Table II.3. Infrared Spectral Data in the Region 600-100  $\text{cm}^{-1}$ 

$\text{[NiCl}_2\text{]}_2$	$\text{[NiBrCl]}_2$	$\text{[NiL(NCS)Cl]}_2$	$\text{[NiLBrCl]}_2$	$\text{[NiL}_2\text{(NCS)Cl]}_2$	Assignments
545 s	545 s	545 s	526 s	512 sh	vibrations due to triphenylphosphine
527 s	524 m	527 m	500 s	520 s	
500 s	513 m	500 m	500 s	500 m	
443 m	441 m	460 m	445 m	460 m	$\delta$ NCS
345 m-s	450 m	447 m	343 m	414 m	$\delta$ P-Ph
307 w		414 w	305 w	355 sh	$\delta$ Ni-N
280 w	270 w*			310 m	$\delta$ Ni-Cl (terminal)
240 m, br	240 m, br*	265 m			$\delta$ Ni-Cl (bridging)
		235 m			$\delta$ Ni-Br (terminal)
170 m	183 m	200 m	272 m	195 w	$\delta$ Ni-P
170 w	170 w	185 m	247 m	185 sh	

L =  $\text{PPh}_3$ ; \* = These bands may be due to a combination of  $\delta$  Ni-Cl (bridging) and  $\delta$  Ni-Br (terminal).

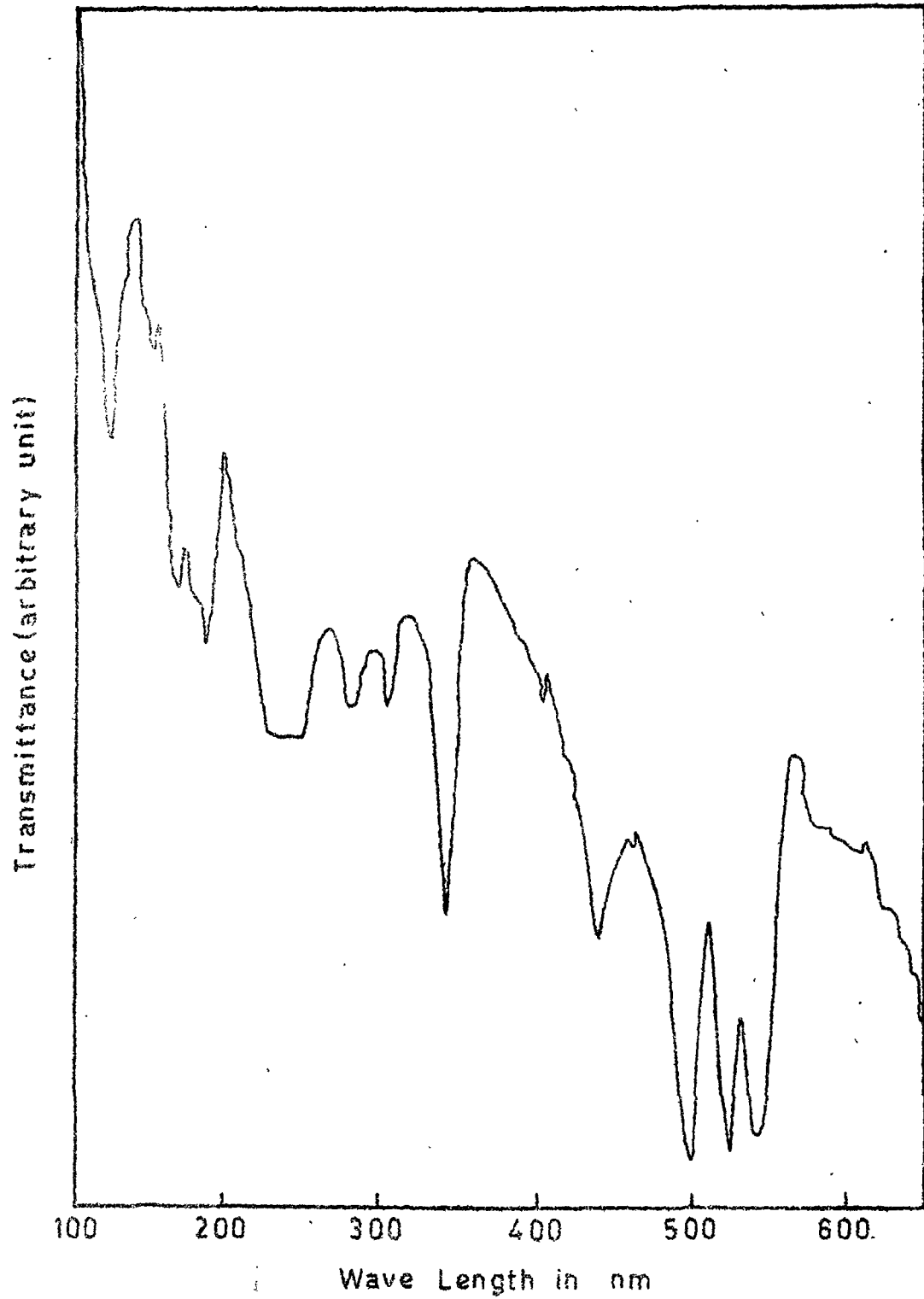


Fig.II.4. Far infrared Spectrum of  $[\text{Ni}(\text{PPh}_3)\text{Cl}_2]_2$ .

the thiocyanato complexes.<sup>33</sup>  $\nu_{\text{Ni-P}}$  has been observed as two bands in 210 to 170  $\text{cm}^{-1}$  region for these complexes.

### Magnetic Moment

The magnetic moments for the complexes  $[\text{NiLXCl}]_2$  (L =  $\text{PPh}_3$  or  $\text{OPPh}_3$ ; X = Cl, Br,  $\text{NO}_3$  or NCS) are in the range 2.5 to 2.8 B.M. (Table II.4.) per nickel atom, at room temperature, which is slightly lower than that of the nickel(II) tetrahedral complexes ( $\sim 3$  B.M.).<sup>36</sup> This could be due to antiferromagnetic interaction between two metal atoms of the dimers. The interaction could occur either directly between the two metal atoms or via chloride bridges in a tetra-coordinated dinuclear structure.<sup>36</sup>

The magnetic moments of  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$  (X = Br,  $\text{NO}_3$ ) are in the range of 3.0 to 3.15 B.M. per nickel atom at room temperature, which is the expected and observed value for the nickel(II) tetrahedral complexes.<sup>29</sup> The compound,  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]$  was found to be diamagnetic similar to  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2]$ , which is due to the square-planar structure of the complex.

$[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  (X = Cl, Br,  $\text{NO}_3$  or NCS) and  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$  (X = Br, NCS or  $\text{NO}_3$ ) are found to be non-conducting in acetonitrile, whereas conductance measurements for  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$  could not be carried out due to their decomposition in acetonitrile or nitrobenzene. Non-conductance

Table II.4. Electronic Absorption Spectral and  
Magnetic Moment Data of the Complexes

Complexes	$\lambda_{\text{max}}$ in nm ( $\epsilon_{\text{max}}$ )	$M_{\text{off}}$ (B.M.)
$[\text{Ni}(\text{PPh}_3)\text{Cl}_2]_2^{(a)}$	640 (103) 595 (105)	2.59
$[\text{Ni}(\text{PPh}_3)\text{BrCl}]_2^{(a)}$	655 sh 625 (105)	2.71
$[\text{Ni}(\text{PPh}_3)(\text{NCS})\text{Cl}]_2^{(a)}$	690 sh 615 (212) 575 sh	2.45
$[\text{Ni}(\text{PPh}_3)(\text{NO}_3)\text{Cl}]_2^{(a)}$	660 (107) 590 sh	2.53
$[\text{Ni}(\text{OPPh}_3)(\text{SCN})\text{Cl}]_2^{(a)}$	655 sh 590 (130) 550 sh	2.83
$[\text{Ni}(\text{PPh}_3)_2\text{BrCl}]_2^{(b)}$	575 (200) 420 (4200)	2.99
$[\text{Ni}(\text{PPh}_3)_2(\text{NO}_3)\text{Cl}]_2^{(b)}$	660 (170) 395 (255)	3.14
$[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]_2^{(b)}$	418 (3300)	Diamag.
$[\text{Ni}(\text{OPPh}_3)\text{BrCl}]_2$	-	2.58
$[\text{Ni}(\text{OPPh}_3)(\text{NO}_3)\text{Cl}]_2$	-	2.51

(a) = in acetonitrile;

(b) = in benzene.

of the compounds show that no ionic species are present in the solution.

### Visible Spectra

The visible spectra of the complexes,  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$ , (X = Cl, Br,  $\text{NO}_3$  or NCS) in acetonitrile show two bands, around 650 and 600 nm (Table II.4.). These bands may be assigned to one of the d-d transitions for Ni(II) tetrahedral system, viz.  ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$ , as in the case of  $[\text{Ni}(\text{OAsPh}_3)_2\text{Cl}_2]$ .<sup>37</sup> In these complexes, the symmetry of the ligand field around the metal ion is lowered from  $\text{Td}$ , which splits the  ${}^3\text{T}_1(\text{P})$  term into one component of two fold degeneracy and another non-degenerate component at different energy levels, thereby giving rise to two bands (or one asymmetrical band with shoulder). The spectra of these compounds in nitrobenzene are similar to that in acetonitrile. The reflectance spectrum of  $[\text{Ni}(\text{PPh}_3)\text{Cl}_2]_2$  (fig. no. II.5), shows a band at 920 nm and two bands at 570 and 620 nm of equal intensity. The band at 920 nm could be due to the  ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{A}_2(\text{F})$  transition and the other two bands could be same as discussed above.

The visible spectra of  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$  (X = Cl, Br,  $\text{NO}_3$  or NCS) in solution show absorptions similar to those of  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$ . However, the intensity of the bands decreases slowly with time due to slow decomposition of the compounds in solution.

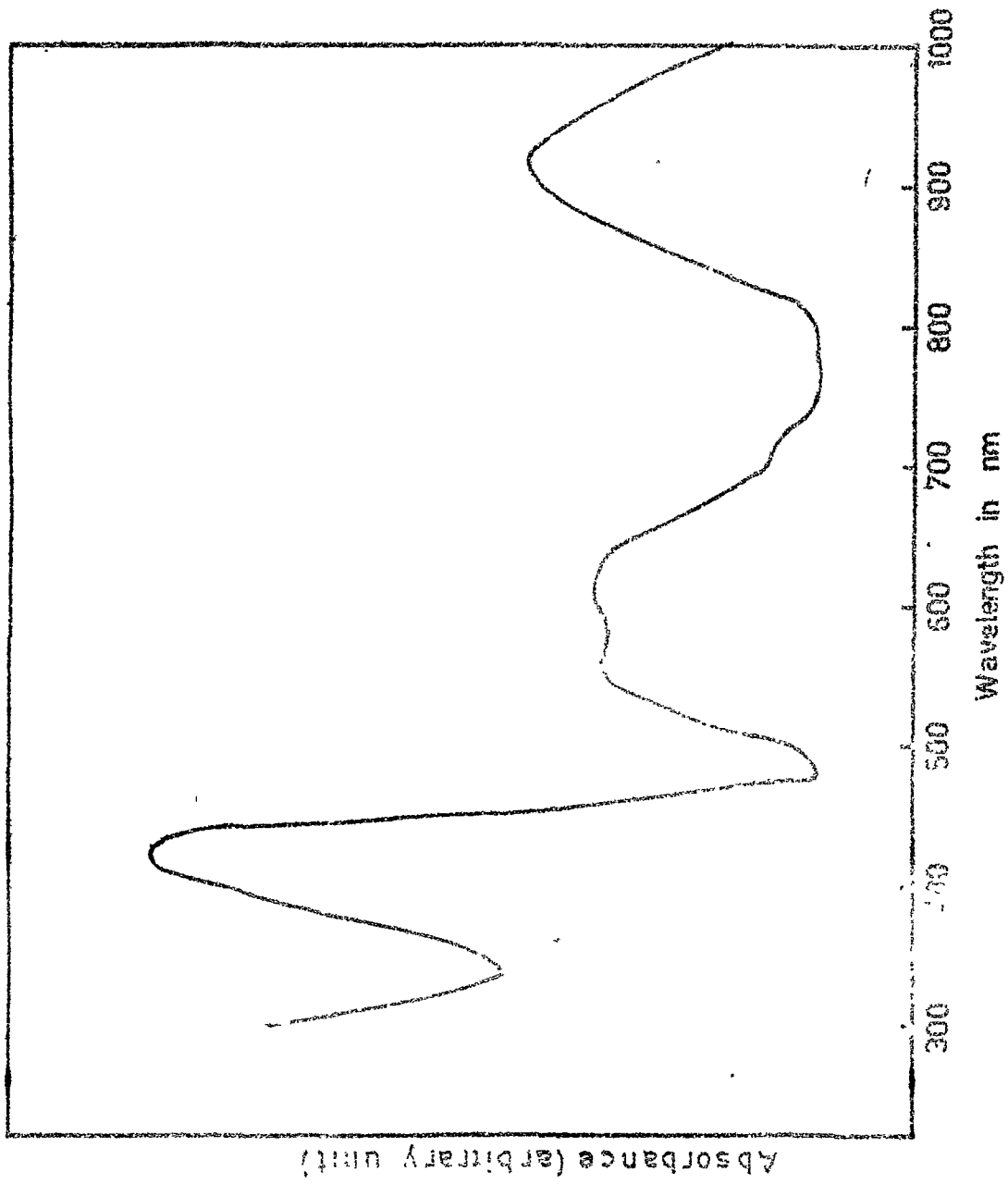


Fig. XI.5. Electronic Reflectance Spectrum of  $[\text{Ni}(\text{PPh}_3)\text{Cl}_2]_2$

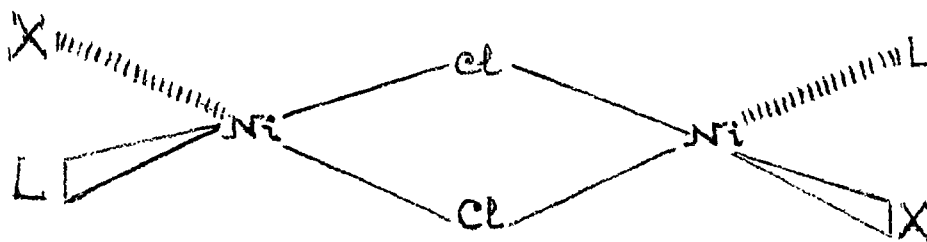
The visible spectral data of  $[\text{Ni}(\text{PPh}_3)_2\text{BrCl}]$  and  $[\text{Ni}(\text{PPh}_3)_2(\text{NO}_3)\text{Cl}]$  in 800-350 nm region are given in Table II.4. These complexes, showed two absorption bands around 600 and 400 nm, which is in conformity with the spectra of  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br, I).<sup>38</sup> The band around 600 nm could be assigned to  ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$  transition for nickel(II) tetrahedral systems.<sup>37</sup> The band around 400 nm is more likely due to charge-transfer. The spectrum of the square planar complex,  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]$  is similar to the reported square planar,  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2]$ ,<sup>38</sup> where only one band at 418 nm is observed, which is likely to be charge-transfer band only. The visible spectra of the complexes in nitrobenzene solvent showed a pattern similar to that in benzene with slight shift of the band position towards higher energy.

The thermogravimetric studies of  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  (X = Cl or Br) also confirm the composition of the complexes. The complexes start decomposing at 80°C and total loss of triphenylphosphine is observed at 460°C and 475°C for X = Cl and X = Br respectively.

The proton n.m.r. spectra for  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  (X = Cl or Br) in acetonitrile at room temperature gave a structureless singlet at 7.57 $\delta$  which is characteristic of the protons of the phenyl groups in triphenylphosphine. The n.m.r. line of the phenyl-proton as well as that of TMS reference are broadened

compared to the n.m.r. of the free ligand which support that paramagnetic  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  is present in solution.

On the basis of above studies the structure of  $[\text{Ni}(\text{PPh}_3)\text{XCl}]_2$  and  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$  or  $\text{NCS}$ ) are proposed to be dimeric bridging through the chlorine atoms, with a distorted tetrahedral arrangement around the nickel atoms as shown below.



where ( $\text{L} = \text{PPh}_3$  or  $\text{OPPh}_3$ ); ( $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$  or  $\text{NO}_3$ ).

The structures of  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$  ( $\text{X} = \text{Br}$  or  $\text{NO}_3$ ) are distorted tetrahedral and  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]$ , a square planar.

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## CHAPTER III

SYNTHESIS AND STUDIES ON DICHLOROiodo TRIPHENYLPHOSPHINE  
OXIDE NICKEL(III)INTRODUCTION

The study of transition metal complexes in uncommon oxidation states has been of increasing interest to inorganic chemists. Such oxidation states are often implicated as transient intermediates in chemical and biochemical redox reactions. To obtain stable compounds containing such oxidation states is of obvious interest. The chemistry of nickel is known in the oxidation state range of -1 to +4, in which the most common, stable and the well studied state is of nickel(II). The higher oxidation states of nickel, viz. +3 and +4 are scarce and have aroused interest in Chemists.

Complexes of nickel(III) have been considered as a recent discovery,<sup>1</sup> however, the first complex of nickel(III), viz.

$[\text{Ni}(\text{PEt}_3)_2\text{Br}_3]^-$  was reported by Jensen<sup>2</sup> in 1936. Though, the chemistry of nickel(III) has not been fully explored, but there has been growing interest in this field during the last fifteen years.<sup>3,4</sup>

A major set-back to the earlier investigations of nickel(III) complexes was the lack of a suitable method of characterization of the 3+ metal centre. Magnetic susceptibilities could only indicate the presence of one unpaired electron on the complex system but not its exact location. Application of electron spin resonance spectroscopy has helped in distinguishing between a  $d^7$  nickel(III) and an electron delocalised over the coordinated ligand(s) in a nickel(II) stabilised radical. Chemistry of trivalent nickel received a great stimulus largely due to the development of methods of its generation, which enabled chemists in synthesising a large number of complexes either in solution or in solid state.

#### Types of Ligands

Depending on the modes of coordination the ligands which form stable complexes with trivalent nickel can be broadly divided into four categories, viz. (i) monodentate, (ii) open chain chelating (polydentate), (iii) macrocyclic and (iv) ligands forming cage type complexes.

Monodentate ligands with which stable complexes of nickel(III) are reported contain F, O, N or P as donor atoms,

although such complexes are very few. Known compounds are  $K_3\text{[NiF}_6\text{]}^{5-}$ ,  $\text{[NO]}^+\text{[Ni(NO}_3\text{)]}_4^{7-}$ ,<sup>6</sup>  $\text{[Ni(PR}_3\text{)]}_2\text{X}_3^{7-}$  (X = Cl or Br, R = Me, Et, n-Pr, n-Bu)<sup>2,7,8</sup> and  $\text{[NiX}_3\text{(PMe}_2\text{Ph)]}_2^{7-}$  (X = Cl or Br).<sup>9,10</sup>  $\text{[Ni(NH}_3\text{)]}_n^{3+}$  has been generated by pulse radiolytic technique.<sup>11</sup>

Open chain chelating ligands stabilizing nickel(III) are mostly bidentate, viz. ethylenediamine,<sup>12,13</sup> propylenediamine,<sup>14</sup> bipyridyl,<sup>15</sup> phenanthrolines,<sup>16</sup> various diphosphines,<sup>17-22</sup> diarsines,<sup>23,24</sup> deprotonated amides,<sup>25-27</sup> peptides,<sup>28-32</sup> oximes<sup>33-35</sup> and dithiocarbamates.<sup>36,37</sup> Some examples of hexadentate ligands containing amino and oximo groups stabilizing nickel(III) are also reported.<sup>38</sup> There has been a considerable progress in the study of the chemistry of nickel(III) compounds with macrocyclic ligands. All the macrocycles studied are of tetraaza type. Reviews on such work has been reported.<sup>3,4</sup> The tetraaza macrocycles of nickel(III) are studied mostly in solution either by electrochemical or by pulse radiolytic technique. Most of tetraaza complexes of nickel(II) exert an unusually high ligand field on the metal ion thus raising the antibonding orbital energies sufficiently, so that the removal of an electron to give a nickel(III) complex is a low energy process.

Sandwich complexes of cyclopentadiene and cage type complexes of carboranes also stabilize trivalent nickel. Examples of such complexes are,<sup>39-42</sup>  $\text{[Ni(cp)]}_2^{+}$ ,  $\text{Ni(cp)(B}_9\text{C}_2\text{H}_{11}\text{)}^{n+}$ ,  $\text{[Me}_4\text{N] [Ni(B}_9\text{C}_2\text{H}_{11}\text{)]}_2^{7-}$ .

### Methods of Generation of Nickel(III)

Three different methods have been used to generate nickel(III) complexes, via oxidation of the nickel(II) analogues. These are (i) chemical oxidation, (ii) electrochemical oxidation and (iii) pulse radiolytic and flash photolytic techniques.

The pulse radiolytic technique is a powerful tool for the generation of nickel(III) in aqueous solution. This is usually not a method for bulk synthesis. The radiolysed solutions are directly investigated by various physicochemical techniques. This technique enables chemists to study the properties of highly unstable intermediates within a short period of time. The major disadvantages of this technique is that due to the very high reactivity of the primary free radicals they also often react with the products. Therefore, experiments with very small conversion to trivalent nickel intermediates can be studied. This technique has been used to study the kinetics of formation and decay of the short-lived nickel(III) complexes of ammonia,<sup>11</sup> ethylenediamine,<sup>13</sup> ethylenediamine tetra acetic acid,<sup>43</sup> glycine<sup>13</sup> and dimethyl glyoxime.<sup>44</sup> Electrochemical oxidation of nickel(II) complexes in aqueous or in non-aqueous solvents has been extensively used to generate nickel(III) complexes. This method of synthesis is usually very neat, since the potential can be precisely set at

the desired value, thus avoiding complicating side reactions. While this method is suitable for bulk synthesis also, it is mostly used to generate nickel(III) in solution which is directly used for further studies such as, esr, without going through isolation and purification. This method has been mostly used to study the nickel(III) complexes of tetraaza macrocycles. Some of the trivalent nickel(III) complexes of bidentate ligands, viz. ethylenediamine,<sup>45</sup> ethylenediamine tetra acetic acid,<sup>46</sup> N,N'-bipyridyl<sup>15</sup> and phenanthrolines<sup>16</sup> have been generated by this method and studied.

The chemical methods of synthesis of trivalent nickel complexes are useful, since complexes can be isolated in solid state too. Thus, various physical studies of the complexes can be made in solid state and in solution too. Nickel(III) complexes have been obtained by the oxidation of their nickel(II) analogues using oxidising agents, such as persulphate, halogens, nitric acid, oxygen, nitrosyl halides, hydrogen peroxide, dinitrogen pentoxide, ferric chloride, thiuramdisulphide, and hexachloro iridium(IV). Many of the complexes thus synthesized and studied include nickel(III) tetraaza complexes. A brief review of the nickel(III) complexes containing monodentate and bidentate ligands obtained by different chemical oxidations has been presented in Table III.1. Macrocyclic tetraaza complexes of nickel(III) obtained by chemical oxidations have not been included in Table III.1, as they have

Table III. 1. Preparations of Nickel(III) complexes using

Chemical Oxidants

Sl. No.	Complexes	Reactants	Oxidising Agent	Physical Properties	Reference
1	$[\text{Ni}(\text{PR}_3)_2\text{X}_3]$ (R = Me, Et, n-Pr or n-Bu; X = Cl or Br)	$[\text{Ni}(\text{PR}_3)_2\text{X}_2]$ i) NOCl or NOBr ii) Br <sub>2</sub>		Mag., Elec., D.M.	2, 7, 8
2	$[\text{Ni}(\text{PMe}_2\text{Ph})_2\text{Br}_3]$	$[\text{Ni}(\text{PMe}_2\text{Ph})_2\text{Br}_2]$	Br <sub>2</sub>	Mag., Elec., X-ray	9, 10
3	$\text{K}_3[\text{NiF}_6]$	$\text{NiSO}_4 + \text{KCl}$	F <sub>2</sub>	Mag.	5
4	$(\text{NO}_2)^+[\text{Ni}(\text{NO}_3)_4]^-$	$\text{NiX}_2$ (X = Cl or NO <sub>3</sub> )	N <sub>2</sub> O <sub>5</sub>	Mag.	6
5	$[\text{Ni}(\text{en})_2\text{Cl}_2\text{Cl}]$ (en = ethylenediamine)	$[\text{Ni}(\text{en})_2\text{Cl}_2]$	Cl <sub>2</sub>	Mag., IR, Cond.	12
6	$[\text{Ni}(\text{en})_2\text{X}_2\text{Y}]$ (X = Br or NO <sub>2</sub> , Y = Br; and X = Cl, Y = Br)	$[\text{Ni}(\text{en})_2\text{X}_2]$	Br <sub>2</sub>	Mag., IR, Cond.	12
7	$[\text{Ni}(\text{pn})_2\text{Cl}_2\text{Cl}]$ (pn = propylenediamine)	$[\text{Ni}(\text{pn})_2\text{Cl}_2]$	Cl <sub>2</sub>	Mag., IR, Cond.	14

Table III. 1. contd../-

Table III. 1. (contd.) Preparations of Nickel(III) Complexes using Chemical Oxidants

Sl.No.	Complexes	Reactants	Oxidising Agent	Physical Properties	Reference
8	$[\text{Ni}(\text{pn})_2\text{Br}]_2(\text{ClO}_4)_2$	$[\text{Ni}(\text{pn})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2$	$\text{Br}_2$	Mag., IR, Cond.	14
9	$[\text{NiLBr}_3]_2$ (L = $\text{R}_2\text{P}(\text{CH}_2)_2\text{PR}_2$ , where R = Me or Et)	$[\text{NiLBr}_2]_2$	$\text{Br}_2$	Mag.	17, 18
10	$[\text{NiLX}_2]_2\text{X}$ (L = $\text{Me}_2\text{P}(\text{CH}_2)_2\text{PMe}_2$ , X = Br or I)	$[\text{NiLX}_2]_2 + \text{HX}$	Air	Mag., Cond.	18
11	$[\text{NiLBr}_3]_2$ (L = $\text{Ph}_2\text{PCH=CHPPH}_2$ , or $\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ , n 2 or 3)	$[\text{NiLBr}_2]_2$	$\text{Br}_2$	Mag., ESR	19, 20
12	$[\text{Ni}(\text{Diphos})_2\text{Cl}_2]_2\text{X}$ (Diphos = $\text{o-C}_6\text{H}_4(\text{PMe}_2)_2$ X = $\text{ClO}_4$ or $\text{PF}_6$ )	$[\text{Ni}(\text{Diphos})_2\text{Cl}_2]_2\text{X}$	$\text{FeCl}_3$	Mag., Cond., ESR.	21, 22

Table III. 1. contd.../-

Table III. 1. (contd.) Preparations of Nickel(III) Complexes using Chemical Oxidants

Sl.No.	Complexes	Reactants	Oxidising Agent	Physical Properties	Reference
13	$\overline{\text{Ni}}(\text{cis-edas})_2\text{Cl}_2$ $\overline{\text{Cl}}$ (edas = $\text{Me}_2\text{AsCH}=\text{CHASMe}_2$ )	$\text{NiCl}_2 + \text{cis-edas}$	$\text{O}_2$	Mag., Elec., NMR, IR, Cond.	23
14	$\overline{\text{Ni}}(\text{Diars})_2\text{Cl}_2$ $\overline{\text{Cl}}$ (Diars = $\text{o-C}_6\text{H}_4(\text{AsMe}_2)_2$ )	$\text{NiCl}_2 + \text{HCl} + \text{Diars}$	$\text{O}_2$	Mag., Cond., ESR.	24
15	$\overline{\text{Ni}}(\text{bi})_2$ $\overline{\text{X}}$ ( $\text{biH}_2 = \text{H}_2\text{NCONHCONH}_2$ )	$\text{K}_2\overline{\text{Ni}}(\text{bi})_2$	$\text{K}_2\text{S}_2\text{O}_8$	Mag., IR, X-ray	25, 26
16	$\overline{\text{Ni}}(\text{Hdpg})_2(\text{py})_2$ $\overline{\text{X}}$ ( $\text{H}_2\text{dpg} = \text{diphenylglyoxime}$ , X = Br or I)	$\overline{\text{Ni}}(\text{Hdpg})_2$ + $\text{pyr}$ + $\text{I}_2$ or $\text{Br}_2$	$\text{I}_2$ or $\text{Br}_2$	ESR	34
17	$\overline{\text{Ni}}\text{L}_3$ $\overline{\text{X}}$ ( $\text{LH} = 2\text{-benzoylpyridine}$ oxime or 2-phenacylpyridine dine oxime)	$\text{NiCl}_2 + \text{NH}_3 + \text{LH}$	$(\text{NH}_4)_2\text{S}_2\text{O}_8$	Mag., Cond., ESR, NMR, IR, UV	35
18	$\overline{\text{Ni}}(\text{Et}_2\text{dtc})_3$ $\overline{\text{X}}$ ( $\text{Et}_2\text{dtc} = \text{N,N-diethylthiocarbamate}$ )	$\overline{\text{Ni}}(\text{Et}_2\text{dtc})_2$	thiuram disulphide	ESR	36
19	$\overline{\text{Ni}}(\text{Bu}_2\text{dtc})_2$ $\overline{\text{I}}$ $\overline{\text{X}}$ ( $\text{Bu}_2\text{dtc} = \text{N,N-di n-butylthiocarbamate}$ )	$\text{Ni}(\text{Bu}_2\text{dtc})_2$	$\text{I}_2$	IR, Mag, ESR	37

Mag. = Magnetic susceptibility, Elec. = Electronic spectrum, DM = Dipole Moment  
Cond. = Conductivity, ESR = Electron Spin Resonance, NMR = Nuclear Spin Resonance.

been discussed in detail elsewhere.<sup>3,4</sup>

From the preceding review on the complexes of trivalent nickel, it is evident that the studies on nickel(III) complexes is in a state of development and the methods of synthesis using chemical oxidants require more work for the systematization and generalizations. With a view to synthesize, nickel(III) complexes containing mono- or bi-dentate ligands using chemical oxidants and to study their physical and chemical behaviours, attempt was made to oxidise nickel(II) tertiaryphosphine complexes, viz.  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{NCS}$  or  $\text{NO}_3$ ) using nitrosyl chloride as oxidant. Except for  $\text{X} = \text{I}$ , in all other cases,  $[\text{NiLXCl}]_2$  ( $\text{L} = \text{PPh}_3$  or  $\text{OPPh}_3$ ) type of compounds were obtained and are described in Chapter II. In the case of  $\text{Ni}(\text{PPh}_3)_2\text{I}_2$ , oxidation with nitrosyl chloride or chlorine resulted in the formation of a nickel(III) complex,  $[\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}]$ . In this chapter synthesis, characterization and study of some physical and chemical properties of the nickel(III) complex are reported.

EXPERIMENTAL

Diiodo bis-triphenylphosphine nickel(II) was prepared according to the method of Venanzi.<sup>47</sup>

Preparation of Dichloroiodo Triphenylphosphine Oxide Nickel(III)

A suspension of powdered  $[\text{Ni}(\text{PPh}_3)_2\text{I}_2]$  (1 g) was taken in dry cyclohexane (50 ml) and nitrosyl chloride was bubbled slowly through the suspension for about 20 minutes while stirring the mixture. Slowly the suspended material went into solution. After discontinuing the bubbling of the gas, the mixture was stirred at room temperature for about 8 hours, when a yellow crystalline compound separated out. During the reaction, colour of the solution changed from dark reddish brown to light red through green. The compound was filtered out and washed several times with dry diethylether and dried under vacuum. M.P., 100-105 °C (decomposes). Analyses :  
 Calculated for  $[\text{Ni}(\text{O}^i\text{PPh}_3)\text{Cl}_2\text{I}]$  : Ni, 10.97; C, 40.37; H, 2.80; P, 5.79; Cl, 13.27; I, 23.74. Found : Ni, 10.95; C, 40.68; H, 3.12; P, 5.80; Cl, 13.57; I, 24.12. Same compound was obtained also when chlorine was used instead of nitrosyl chloride.

The mother liquor, after the separation of the compound, on concentration yielded triphenylphosphine oxide, characterized by m.p. (157 °C) and infrared spectrum ( $\nu_{\text{P=O}}$  at  $1185\text{cm}^{-1}$ ).

2) Preparation of  $\underline{\text{Ni}(\text{PPh}_3)_2\text{ICl}_7}$ .

To a suspension of  $\underline{\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}_7}$  (0.5 g) in acetic acid (20 ml), a solution of triphenylphosphine (0.6 g) in acetic acid (5 ml) was added and the mixture was stirred for about 4 hours at room temperature, when a deep brown crystalline compound separated out. It was centrifuged, washed first with acetic acid and then several times with dry diethylether and dried under vacuum. M.P., 180-184 °C (decomposes). Analysis: Calculated for  $\underline{\text{Ni}(\text{PPh}_3)_2\text{ICl}_7}$  : Ni, 7.87; C, 57.99; H, 4.05; Cl, 4.76; I, 17.02; Found : Ni, 8.0; C, 57.7; H, 4.3; Cl, 5.1; I, 17.1.

Catalytic Oxidation of Triphenylphosphine Using

$\underline{\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}_7}$ .

A solution of  $\underline{\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}_7}$  (0.02 g) and triphenylphosphine (0.5 g) in cyclohexane (40 ml) was boiled under reflux for about 4 hrs while oxygen was bubbled slowly through the solution. The solution was cooled and concentrated under reduced pressure when a compound separated out. It was filtered, washed first with cyclohexane and then with ether several times and dried under vacuum. M.P., 157 °C. Analysis : Calculated for  $\text{C}_{18}\text{H}_{15}\text{PO}$  : C, 77.71; H, 5.40. Found : C, 77.40; H, 5.6.

Estimation of Iodide in presence of Chloride

The total halide content of the compound was obtained by decomposing it with  $\text{KNO}_3$ , KOH mixture, acidifying with dilute nitric acid to make the solution just acidic and then precipitating as silver halide using silver nitrate solution.

Chloride estimation was done by decomposing the compound with dilute nitric acid and heating for about half an hour to oxidize iodide to iodine and get liberated and then precipitating silver chloride by silver nitrate solution. Iodide content was obtained by subtracting chloride content from the total halide content.

Carbon, hydrogen, nitrogen, phosphorous and nickel estimation, infrared spectra, visible spectra, magnetic susceptibility and conductivity measurements were made according to methods reported in Chapter II. A.e.s.r. spectrum was recorded at liquid nitrogen temperature using Varian E 104 Spectrophotometer. The oxidation state of nickel in the +3 complex was determined iodometrically by the reduction of a known amount of the compound with aqueous potassium iodide solution, followed by titration of the liberated iodine with standard sodium thiosulphate solution.

RESULTS AND DISCUSSION

The oxidation product of  $[\text{Ni}(\text{PPh}_3)_2\text{I}_2]^-$  with nitrosyl chloride or chlorine has the empirical formula  $\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}$ . The magnetic moment of which was found 1.68 B.M. at room temperature, characteristic of nickel(III) having one unpaired electron. The oxidation state of the metal in the complex was further confirmed iodometrically according to the method described in the experimental section. Nickel in oxidation state +3 was reduced to +2 by potassium iodide solution. The conductivity measurements of the complex in acetonitrile and nitrobenzene did not show any appreciable conductance, thereby confirming that all the anions are coordinated to the metal ion.

The presence of triphenylphosphine oxide in the complex was confirmed by the infrared study. The spectrum is given in figure no. III. 1. A strong band at  $1180\text{ cm}^{-1}$  is assigned to  $\nu_{\text{P=O}}$  of the triphenylphosphine oxide molecule coordinated to the metal.<sup>48</sup> After decomposing the complex with water, the liberated ligand was isolated and characterised as triphenylphosphine oxide (vide, n.p. and infrared spectrum). The infrared spectrum of the complex in  $600\text{-}100\text{ cm}^{-1}$  region (figure no. III. 2.) shows six bands of which bands at  $548$  and  $520\text{ cm}^{-1}$  are due to triphenylphosphine oxide. The band at  $452\text{ cm}^{-1}$  may be assigned to  $\nu_{\text{Ni-O}}$ , at  $365$  and  $308\text{ cm}^{-1}$  to  $\nu_{\text{Ni-Cl}}$  (terminal) and at  $225\text{ cm}^{-1}$  to  $\nu_{\text{Ni-I}}$  (terminal). These assignments are

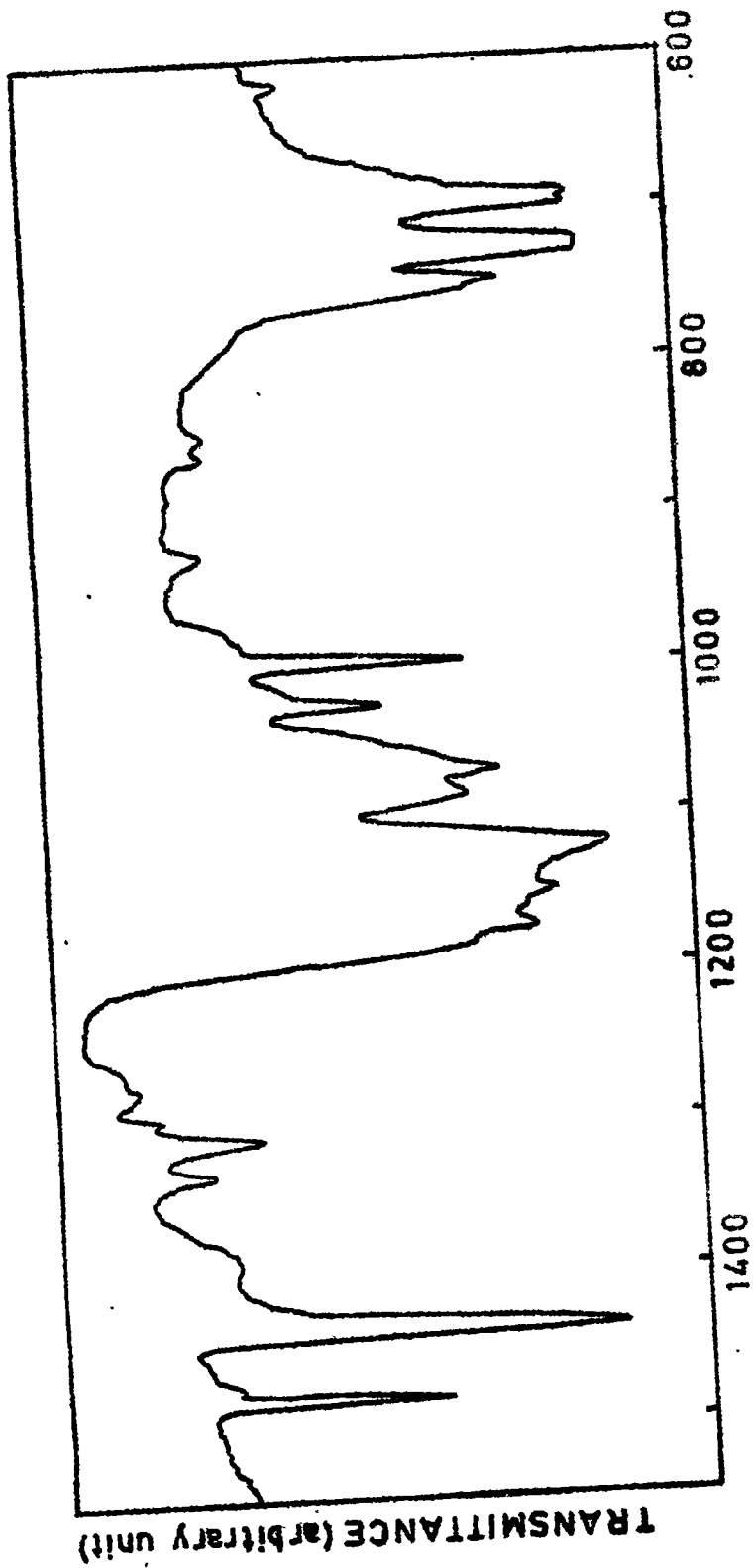


Fig.III.1. Infrared Spectrum of  $[\text{Ni}(\text{OPPh}_3)_2\text{Cl}_2\text{I}]$  in KBr.

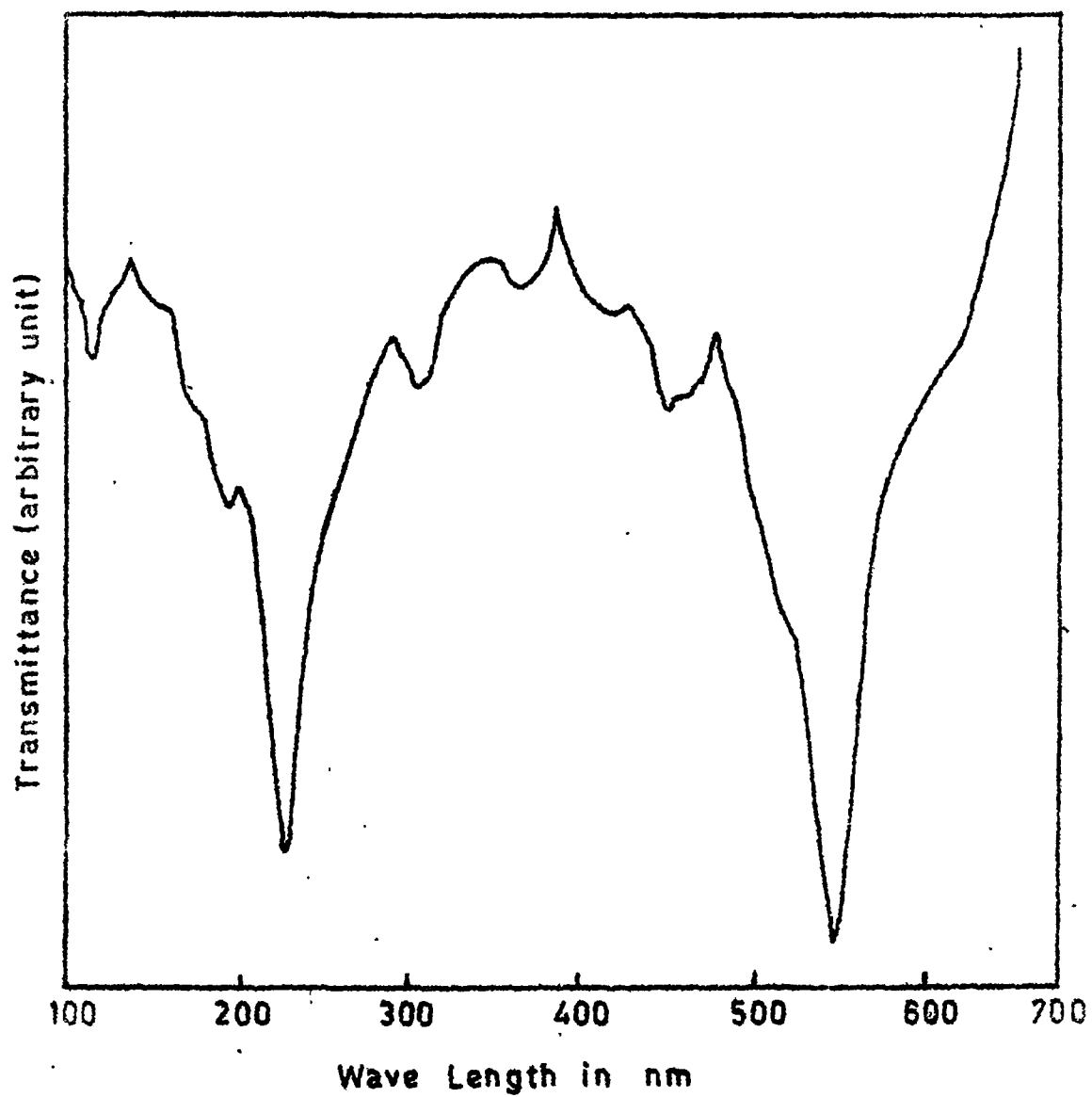


Fig. III.2. Far infrared Spectrum of  $[\text{Ni}(\text{OPPh}_3)\text{Cl}_2]$

made in accordance with that of isotopically labelled nickel complexes, viz.  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{Br}$  or  $\text{I}$ ).<sup>49</sup>

The electron spin resonance spectrum of a powdered sample of the complex at liquid nitrogen temperature (figure no. III.3) shows two absorption lines from which the  $g$  values calculated are,  $g_{\perp} = 2.085$  and  $g_{\parallel} = 2.430$ . If we choose the  $z$  coordinate such that it bisects the  $\text{ClNiCl}$  angle and  $x$  and  $y$  coordinates perpendicular to the above, then a possible configuration is  $(d_{x^2-y^2})^2(d_z)^2(d_{xz})^2(d_{yz})^{\dagger}$ . Following the detailed treatment of  $d^7$  system with the above configuration,<sup>50,51</sup> we can predict  $g_{zz} > g_{yy}$ , which is observed experimentally too. Due to the lack of availability of all the  $d-d$  transitions, it is not possible to interpret, the e.s.r. data quantitatively. On the basis of observed  $g$  values, we can make a tentative assignment of  $25,000 \text{ cm}^{-1}$  ( $\epsilon = 70$ ) band to  $d_{x^2-y^2} \longrightarrow d_{yz}$  and  $16,000 \text{ cm}^{-1}$  ( $\epsilon = 13$ ) band to  $d_z \longrightarrow d_{yz}$  transition. Thus the complex has a tetrahedral geometry with tetragonal distortions.

A reaction of the complex with triphenylphosphine in acetic acid resulted in the formation of a dark brown crystalline compound of the composition  $[\text{Ni}(\text{PPh}_3)_2\text{ClI}]$ , a nickel(II) complex. The magnetic moment of this complex is 3.31 B.M. at room temperature. Similar magnetic moment values are observed for nickel(II) tetrahedral complexes.<sup>47</sup> This complex does not contain triphenylphosphine oxide coordinated to nickel(II) as evidenced by the infrared spectrum. The strong band at

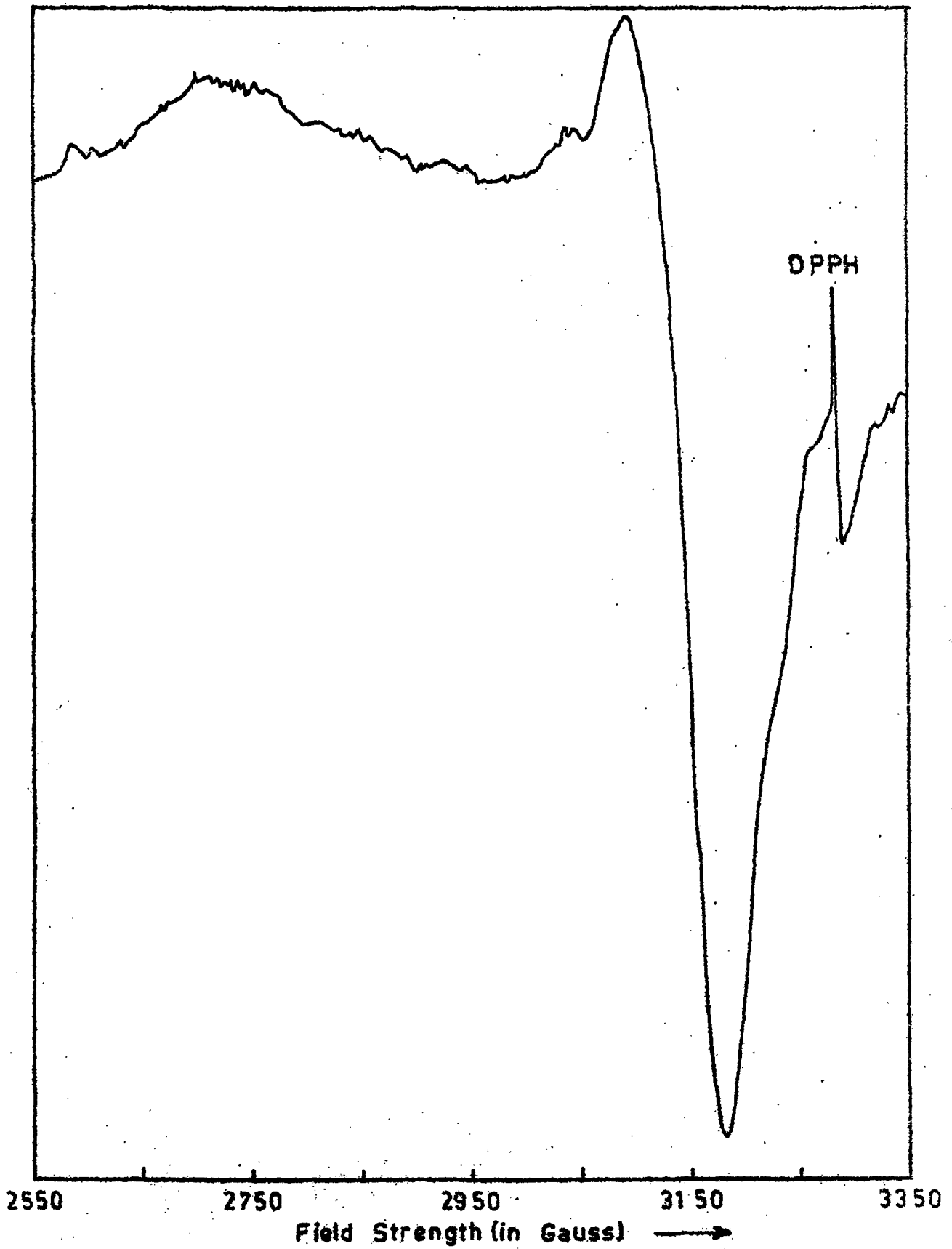


Fig. III.3. ESR Spectrum of  $[\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}]$   
at liquid nitrogen temperature

1180  $\text{cm}^{-1}$  due to  $\nu_{\text{P=O}}$  of the phosphine oxide is absent in the spectrum. The conductivity measurement of this complex in acetonitrile does not show any conductance thereby confirming that all the anions are coordinated to the metal ion. The complex shows absorptions in the visible region at 18,200 sh, 22,000 and 23,800  $\text{cm}^{-1}$  which is similar to those of  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br, I).<sup>52</sup> The band at 18,200  $\text{cm}^{-1}$  could be assigned to  ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$  transition of nickel(II) tetrahedral complexes, whereas the other bands may be due to charge-transfer. Thus  $[\text{Ni}(\text{PPh}_3)_2\text{ICl}]$  has a distorted tetrahedral environment around nickel(II).

The nickel(III) complex,  $[\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}]$  is found to act as a catalyst in the oxidation of triphenylphosphine to triphenylphosphine oxide. The catalytic oxidation reactions using the complex and triphenylphosphine in varying proportions (upto 1:25) in cyclohexane or nitrobenzene gave quantitative yield of the corresponding oxide, which was characterised by melting point (158 °C) and infrared spectrum (absorption at 1185  $\text{cm}^{-1}$  due to  $\nu_{\text{P=O}}$  of the phosphine oxide). The complex is found to oxidize cyclohexanol to cyclohexanone in pyridine.

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## CHAPTER IV

STUDIES ON  $[\text{Ni}(\text{OPPh}_3)_2\text{X}]_2$   $[\text{Y}_3]_2$ (X = Cl, Y<sub>3</sub> = Br<sub>3</sub>; X = Br, Y<sub>3</sub> = Br<sub>3</sub> or IBr<sub>2</sub>)INTRODUCTION

Our interest in the syntheses and studies of nickel(III) complexes has led to the study of a nickel complex viz.  $[\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}]$  described in Chapter III. Oxidation of the nickel(II) complex,  $[\text{Ni}(\text{PPh}_3)_2\text{I}_2]$  by chlorine or nitrosyl chloride resulted in the formation of the above mentioned compound. Chlorine or nitrosyl chloride acted as oxidising agents for the oxidation of nickel(II) to nickel(III) with simultaneous oxidation of triphenylphosphine to the corresponding oxide. Similar to chlorine, bromine is also an oxidising agent which is expected to oxidise the metal and the coordinated ligands. With a view to obtain nickel(III) complex, reaction of bromine with nickel(II) complexes, viz.  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br, I, NCS) were carried out.

However, the results of bromine oxidation were different and oxidation of only the coordinated ligand, triphenylphosphine to the corresponding oxide was achieved and the compounds obtained were of the type  $[\text{Ni}(\text{OPPh}_3)_2\text{X}]_2[\text{Y}_3]_2$  (when  $\text{X} = \text{Cl}$ ,  $\text{Y}_3 = \text{Br}_3$ ; when  $\text{X} = \text{Br}$ ,  $\text{Y}_3 = \text{Br}_3$  or  $\text{IBr}_2$ ). Compounds obtained had a nickel(II) complex cation and a trihalide anion.

Although, the first polyhalide anion was reported in 1819<sup>1</sup>, however, a careful thorough reexamination of the methods of preparation, physical properties and reactions in solution and in solid state of the polyhalides were carried out by Cremer and Duncan<sup>2</sup> in early twentieth century. A polyhalide anion may be defined as an addition product of a halide ion acting as a Lewis base with one or more halogen or interhalogen molecules acting as Lewis acids. Such an ion can be assigned the generalised formula  $\text{X}_m\text{Y}_n\text{Z}_p^-$ , where X, Y and Z represent either identical or different halogen atoms. For all the well defined species of this type,  $m + n + p$  is an odd number that can be 3, 5, 7 or 9.

Not all metals are capable of forming polyhalide salts. In order to form a polyhalide salt, the cation must have a large radius and a small charge.<sup>3</sup> The best known and the most stable of the metal poly-halogen salts are those of Cesium and Rubidium. The condition of large cationic size and low

charge are admirably fulfilled in tetra-alkyl ammonium salts,  $\text{NR}_4^+$  or  $\text{AsPh}_4^+$  and the polyhalides of these cations are well known.<sup>3</sup> Poly-valent cations apparently do not yield salts with the trihalides. However, salts of magnesium, zinc, cobalt, nickel and beryllium with the tetrachloroiodate(III) ion are known.<sup>3</sup> Few other transition metal polyhalide salts are also known, viz.  $\text{Ni}(\text{ClF}_2)_2^4$ ,  $\text{Ni}(\text{ClF}_4)_2^4$ ,  $[\text{Ni}(\text{NH}_3)_4]^{2+}[\text{I}_7]^{5-}$ ,  $[\text{Co}(\text{NH}_3)_6]^{2+}[\text{I}_3]^{5-}$  and  $[\text{Co}(\text{NH}_3)_6]^{2+}[\text{I}_7]^{5-}$  and the polyhalide salts of  $[\text{Co}(\text{en})_2\text{Cl}_2]^{3+}$  (en = ethylene diamine).<sup>3</sup> In this chapter, trihalides of the nickel(II) complex cations of the type  $[\text{Ni}(\text{OPPh}_3)_2\text{X}_2]^{2+}[\text{Y}_3]^{5-}$  (when X = Cl, Y<sub>3</sub> = Br<sub>3</sub>; X = Br, Y<sub>3</sub> = Br<sub>3</sub> or IBr<sub>2</sub>) and their physical and chemical studies are reported.

### EXPERIMENTAL

$[\text{Ni}(\text{PPh}_3)_2\text{X}_2]^{2+}$  (X = Cl, Br, I, NCS) were prepared according to the method of Venanzi.<sup>6</sup>

#### Reaction of Bromine with $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]^{2+}$

$[\text{Ni}(\text{PPh}_3)_2\text{X}_2]^{2+}$  (X = Cl, Br, I, NCS) (0.6 g) was taken with dry benzene and cyclohexane mixture (1:6 ratio ~ 30 ml) in a two necked round bottom flask and stirred for about 30 minutes. Bromine (0.2 ml) was taken with cyclohexane (20 ml) in a dropping funnel, and was added dropwise to the suspension

of the compound in benzene cyclohexane mixture, with constant stirring. Bromine addition was completed in about 2 hrs and the mixture was stirred for 10-15 hrs more. First, a pasty mass was obtained which ultimately turned to orange yellow solid compound with the supernatant liquid also turning yellow. The compound obtained was centrifuged, washed with dry cyclohexane several times and dried under vacuum. The compounds obtained have the composition  $\text{Ni}(\text{OPPh}_3)_2\text{XBr}_3$  (where X = Cl, Br or I). In case of the reaction of  $\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2$  with bromine, compound obtained did not seem to have a stoichiometric composition.

Reaction of Triphenylphosphine with  $\text{Ni}(\text{OPPh}_3)_2\text{X}_2\text{Y}_2$

- (i) To a suspension of  $\text{Ni}(\text{OPPh}_3)_2\text{X}_2\text{Y}_2$  (0.1 g) in acetic acid (5-7 ml), triphenylphosphine (0.4 g) was added and the mixture was stirred at room temperature for about 4 hrs. The compound thus obtained was centrifuged, washed with acetic acid and finally with dry diethyl ether and dried under vacuum.  $\text{Ni}(\text{PPh}_3)_2\text{IBr}_2$  was obtained when  $\text{Ni}(\text{OPPh}_3)\text{Br}_2\text{IBr}_2$  was used, whereas  $\text{Ni}(\text{OPPh}_3)_2\text{X}_2\text{Br}_2$  (X = Cl or Br) resulted in the formation of  $\text{Ni}(\text{PPh}_3)_2\text{Br}_2$ .
- (ii) A reaction similar to that of (i) was carried out using dry cyclohexane (6-10 ml). The compound was washed with cyclohexane and dried under vacuum.

$[\text{Ni}(\text{OPPh}_3)_2\text{IBr}]$  was obtained when  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}]_2$  and  $[\text{IBr}_2]$  was used and  $[\text{Ni}(\text{OPPh}_3)_2\text{X}]_2$  and  $[\text{Br}_3]$  (X = Cl or Br) resulted in the formation of  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}_2]$ .

Carbon, Hydrogen and Nickel analyses, infrared spectra, electronic spectra, magnetic susceptibility and conductivity data were obtained according to methods reported in Chapter II. The analyses of halide contents were obtained from National Chemical Laboratory, Pune. These data are given in Tables IV.1. and Table IV. 2. Total reducible halogen content in the polyhalides was estimated by iodometric titration. The compound was taken in water, acidified with acetic acid, potassium iodide added and stirred in dark at room temperature ( $\sim 20^\circ\text{C}$ ) for about 15 min to liberate iodine completely. The liberated iodine was titrated against standard sodium thiosulphate solution.

## RESULTS AND DISCUSSION

The reaction of bromine with  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br or I) gave compounds of the stoichiometric composition,  $[\text{Ni}(\text{OPPh}_3)_2\text{XEr}_3]$ , where X = Cl, Br or I. Looking at the composition, one would like to call these complexes to have distorted octahedral environment around nickel(IV) ions. Nickel(IV) octahedral complexes are reported to have diamagnetic behaviour, however, in the presence of a weak crystal field,

Table IV. 1. Analytical and Some Physical Data of the Complexes

Compound	Colour	M.P. °C	Molar Conductance		Found (%) (Calc. %)				
			at 20 °C in 1 cm <sup>2</sup> mol <sup>-1</sup>	Aceto- nitrile	C	H	Ni	Br	I/Cl
$[\text{Ni}(\text{OPPh}_3)_2\text{Br}]_2(\text{IBr})_2$	Yellow	145-7	248	32	43.6 (44.0)	2.8 (3.1)	6.3 (6.0)	24.0 (24.4)	13.5 (12.9)
$[\text{Ni}(\text{OPPh}_3)_2\text{Br}]_2(\text{Br}_3)_2$	Yellow	105-8	440	36	46.4 (46.2)	3.1 (3.2)	7.0 (6.3)	34.6 (34.2)	-
$[\text{Ni}(\text{OPPh}_3)_2\text{Cl}]_2(\text{Br}_3)_2$	Yellow	108-10	262	38	47.9 (48.5)	3.5 (3.4)	6.2 (6.6)	26.6 (26.9)	3.7 (4.0)
$[\text{Ni}(\text{PPh}_3)_2\text{IBr}]_2$	Dark Brown	158-61	-	-	55.1 (54.7)	4.1 (3.8)	6.9 (7.4)	10.6 (10.1)	16.7 (16.1)

Table IV.2. Magnetic Moment and Electronic Spectral Data of the Compounds

Compound	$\lambda_{\max}$ in nm ( $\epsilon_{\max}$ ) in acetonitrile	$\lambda_{\max}$ in nm ( $\epsilon_{\max}$ ) in nitrobenzene	$\mu_{\text{eff}}$ (B.M.)
$[\text{Ni}(\text{OPPh}_3)_2\text{Br}_2][\text{Br}_2]$	630 450 sh 370 (340) 256 (33,000)	465 (60)	3.40
$[\text{Ni}(\text{OPPh}_3)_2\text{Br}_2][\text{Br}_3]$	700 sh 642 (85) 605 sh 460 (45) 370 (640) 268 (34,700)	465 (54)	-
$[\text{Ni}(\text{OPPh}_3)_2\text{Cl}_2][\text{Br}_3]$	700 sh 645 (52) 605 sh 460 sh 370 (350) 268 (47,000)	465 (21)	2.94
$[\text{Ni}(\text{PPh}_3)_2\text{IBr}]$	620 510 sh 370 270 sh 247		

magnetic moment corresponding to four unpaired electrons may be expected. Compounds obtained, have magnetic moment in the range 3 to 3.4 B.M. (Table IV.2.), corresponding to two unpaired electrons, expected for tetrahedral or octahedral nickel(II) complexes. Hence the complexes obtained should contain nickel(II) ions in it.

Considering that the complexes contain nickel(II) ions, the only possibility of explaining the composition of the compounds is by assuming it to contain a monohalide and a trihalide anion. The presence of trihalide anion is confirmed by the ultra-violet spectral studies of these compounds (to be discussed later). As we know that the polyhalide anions are stabilized by low charge and big size cation, it is expected here also that the compounds should have an ionic nature with a cation and a counter polyhalide anion. Assuming a tetrahedral geometry around the nickel(II) ion, a composition of the type  $[\text{Ni}(\text{O}^-\text{PPh}_3)_2\text{X}_2]^{+}[\text{Y}_3]^{-}$  is the likely possibility. In such cases, the conductivity measurements would help in knowing the nature of the compounds. The molar conductance of 1:1 electrolytes (viz.  $\text{R}_4\text{P}^{+}[\text{X}_3]^{-}$ ) in  $10^{-3}$  M acetonitrile<sup>8</sup> solution at 25 °C is reported  $\sim 160 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ . The molar conductance obtained for these compounds are about  $260 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$  at 20°C, which is very close to the expected value for 1:2 electrolytes in acetonitrile. The molar conductance value for  $[\text{Ni}(\text{O}^-\text{PPh}_3)_2\text{Br}_2](\text{Br}_3)^{-}$  is higher ( $440 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ ). The molar conductance in nitrobenzene for these compounds is of the order of  $35 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ , a value lower than expected for 1:2 electrolyte. It could be due to incomplete ionization in nitrobenzene.

The coordinated triphenylphosphine molecules of  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  (X = Cl, Br or I) have been oxidised by bromine to give  $[\text{Ni}(\text{OPPh}_3)_2\text{X}_2][\text{Br}_3]$ . Presence of triphenylphosphine oxide is confirmed by the infrared spectra, where a band of medium intensity in the region  $1155$  to  $1165 \text{ cm}^{-1}$  is observed, assignable to  $\nu_{\text{P=O}}$ <sup>9</sup>. Infrared spectrum of  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}_2][\text{Br}_3]$  is given in figure no. IV. 1. Besides, a band around  $1090 \text{ cm}^{-1}$  due to triphenylphosphine was replaced by a band at  $1120 \text{ cm}^{-1}$  characteristic of triphenylphosphine oxide and its complexes.

The absorption bands in the visible region for these compounds could be assigned assuming a distorted tetrahedral environment around the metal ion. The absorption around  $600 \text{ nm}$  could be due to  ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$  transition of the tetrahedral  $d^8$  systems.<sup>10</sup> Visible spectrum of  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}_2][\text{Br}_3]$  is given in figure no. IV.2. Splitting of  ${}^3\text{T}_1(\text{P})$  state could be explained due to large distortion in the symmetry around the metal ion from  $\text{T}_d$ .

In the light of above discussions, the following formulations for  $\text{Ni}(\text{OPPh}_3)_2\text{Br}_4$  are possible, viz.,  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}_2][\text{Br}_3]$  or  $[\text{Ni}(\text{OPPh}_3)_2(\text{Br}_3)_2\text{Br}_2]$ . However, as no examples of covalently bonded  $\text{Er}_3^-$  or any other polyhalide ions are known, the former formulation is preferred over the later. Besides the ultraviolet spectrum of the compound in acetonitrile (figure no. IV. 3b.) shows an absorp-

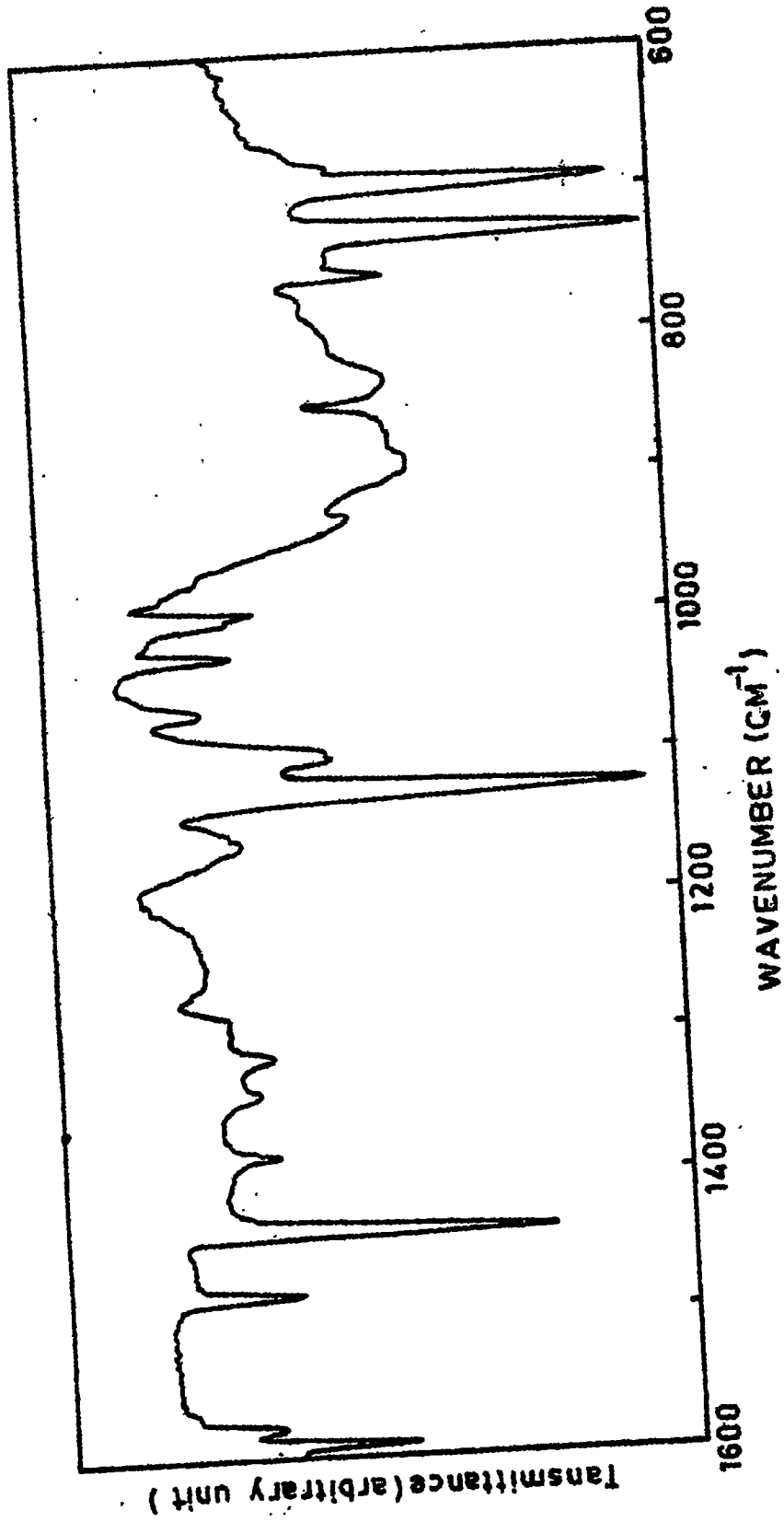


Fig. IV.1. Infrared Spectrum of  $[\text{Ni(OPh)}_3]_2\text{Br}_2$  in KBr.

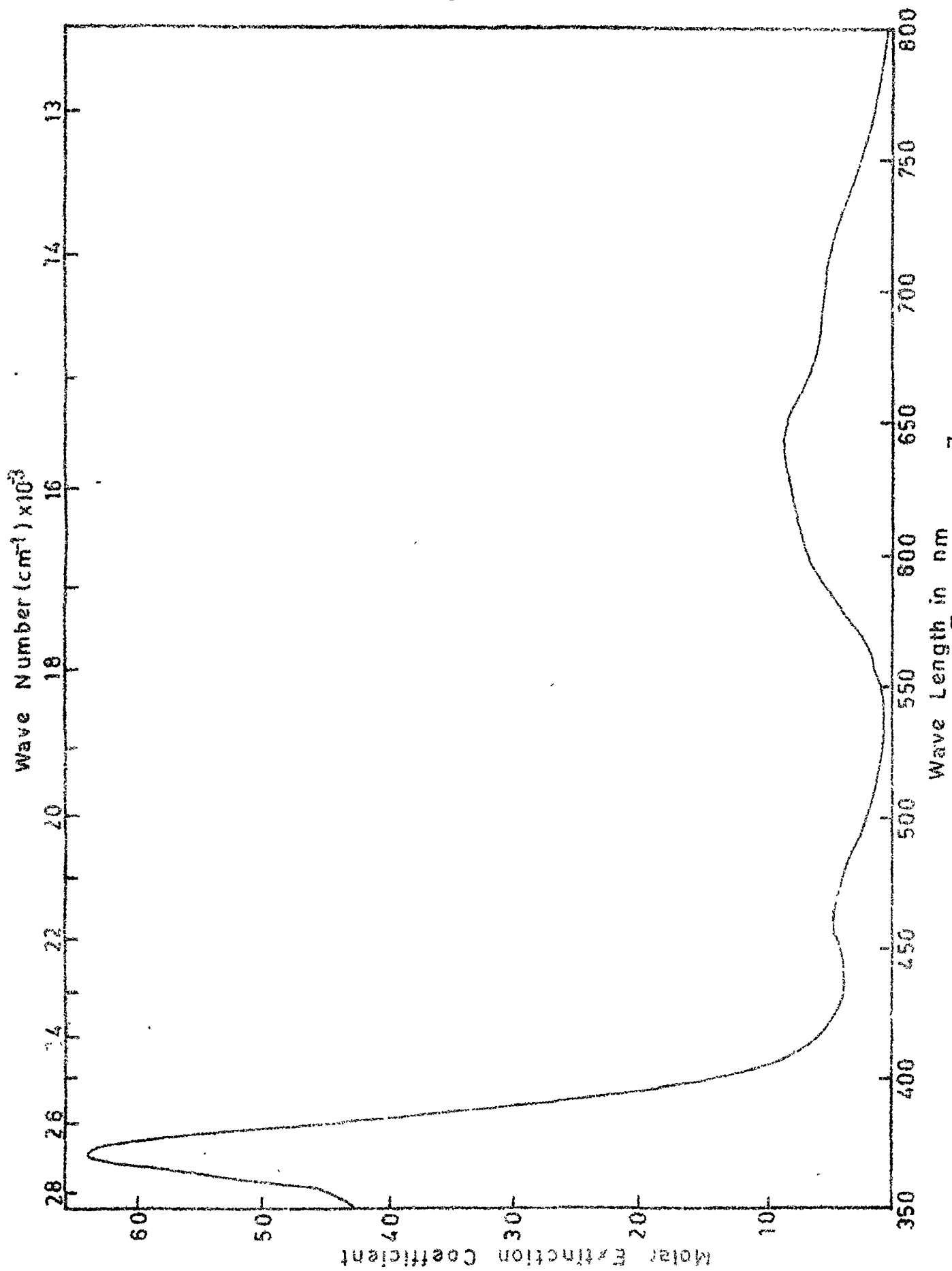


Fig. IV.2. Electronic Spectrum of  $[\text{Ni}(\text{OPPh}_3)_2 \text{Br}] \text{Br}_3$  in Acetonitrile.

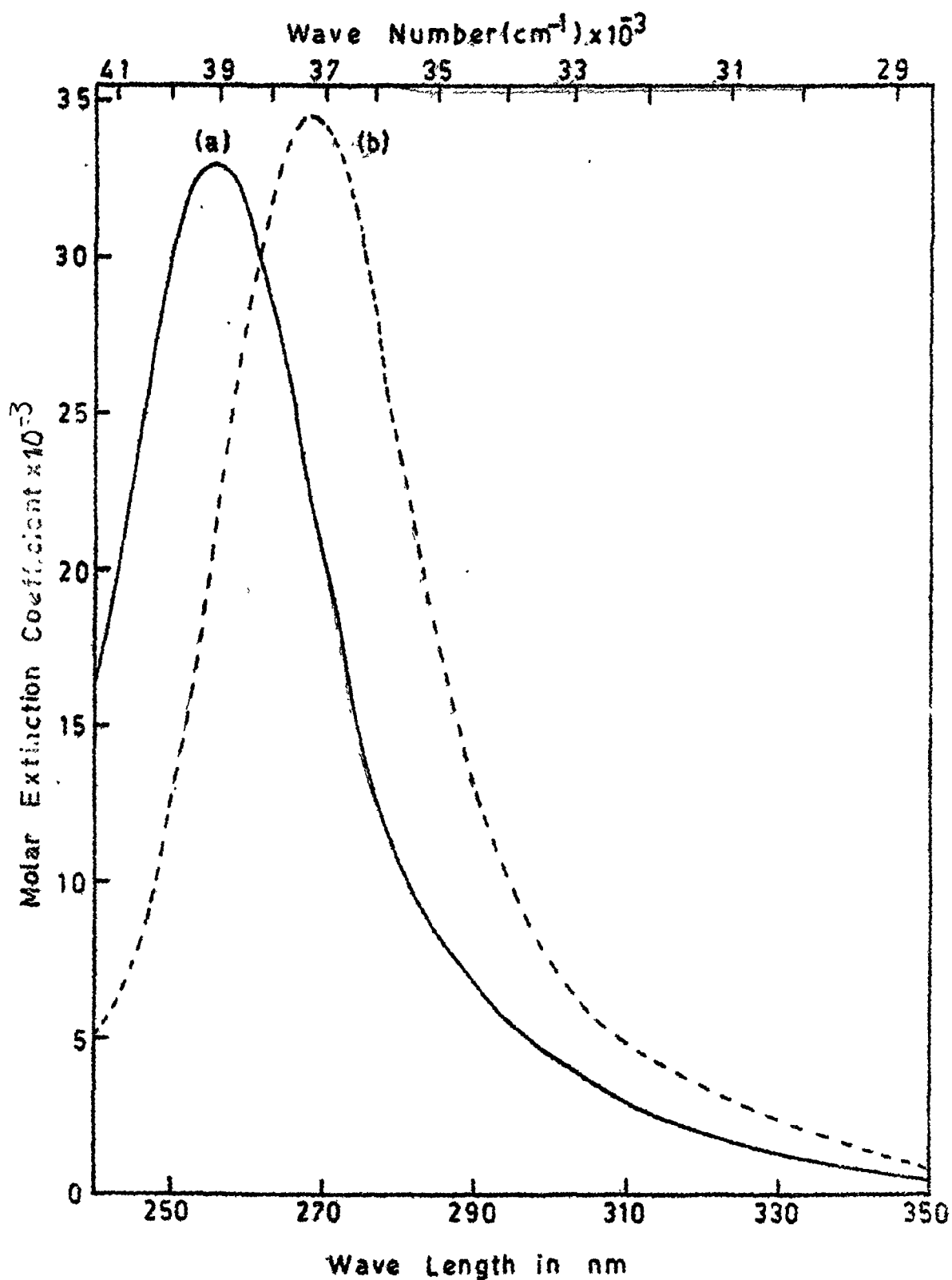


Fig.IV.3. UV Spectra of (a)  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}]\text{IBr}_2$

(b)  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}]\text{Br}_3$  in Acetonitrile.

tion band at 268 nm ( $\epsilon_{\max} = 41,200$ ). A similar band at 269 nm ( $\epsilon_{\max} = 55,000$ ) is reported for the  $\text{Br}_3^-$  ion in acetonitrile.<sup>11</sup> Similarly, for  $\text{Ni}(\text{OPPh}_3)_2\text{ClEr}_3$  and  $\text{Ni}(\text{OPPh}_3)_2\text{IBr}_3$ , the preferred formulations are  $[\text{Ni}(\text{OPPh}_3)_2\text{Cl}]_2[\text{Br}_3]_2$  and  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}]_2[\text{IBr}_2]$  respectively. An absorption band in the u.v. region for the former compound is observed at 268 nm ( $\epsilon_{\max} = 47,000$ ) and for the later (figure IV. 3a.) at 256 nm ( $\epsilon_{\max} = 36,000$ ). The band at 256 nm ( $\epsilon_{\max} = 54,000$ ) is reported for  $[\text{IBr}_2]^-$  ions in acetonitrile.<sup>11</sup> All these absorptions in the u.v. region may be assigned to  $\sigma \longrightarrow \sigma^*$  transition of the trihalide anion.<sup>12</sup>

Total reducible halogen content of  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}]_2[\text{IBr}_2]_2$  and  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}]_2[\text{Er}_3]_2$  are found to be approximately two moles of halogens per mole of the complex, which is in good agreement with the polyhalide ion formulations. Each polyhalide anion liberates one mole of reducible halogen, according to the following :



However, in the case of  $[\text{Ni}(\text{OPPh}_3)_2\text{Cl}]_2[\text{Er}_3]_2$ , reducible halogen content per mole of the complex is about one mole of the halogen.

The cationic complexes of nickel(II), reported above have been reacted with triphenylphosphine in acetic acid and cyclohexane solvents separately and the products obtained are different in both the cases. Acetic acid medium reaction results in

the formation of  $[\text{Ni}(\text{PPh}_3)_2\text{I}]\text{Er}_2$  when  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}]\text{I}[\text{Br}_2]$  is treated and the formation of  $[\text{Ni}(\text{PPh}_3)_2\text{Br}_2]$  when  $[\text{Ni}(\text{OPPh}_3)_2\text{X}]\text{Er}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) is treated with triphenylphosphine. The absence of triphenylphosphine oxide and the presence of triphenylphosphine in the resulting complexes has been confirmed with the help of infrared spectra of these compounds, which do not show bands at  $1160 \text{ cm}^{-1}$  due to  $\nu_{\text{P}=\text{O}}$  and at  $1120 \text{ cm}^{-1}$ , but a new band at  $1090 \text{ cm}^{-1}$  is observed.

$[\text{Ni}(\text{PPh}_3)_2\text{Pr}_2]$  is same as reported by Venanzi.<sup>6</sup>

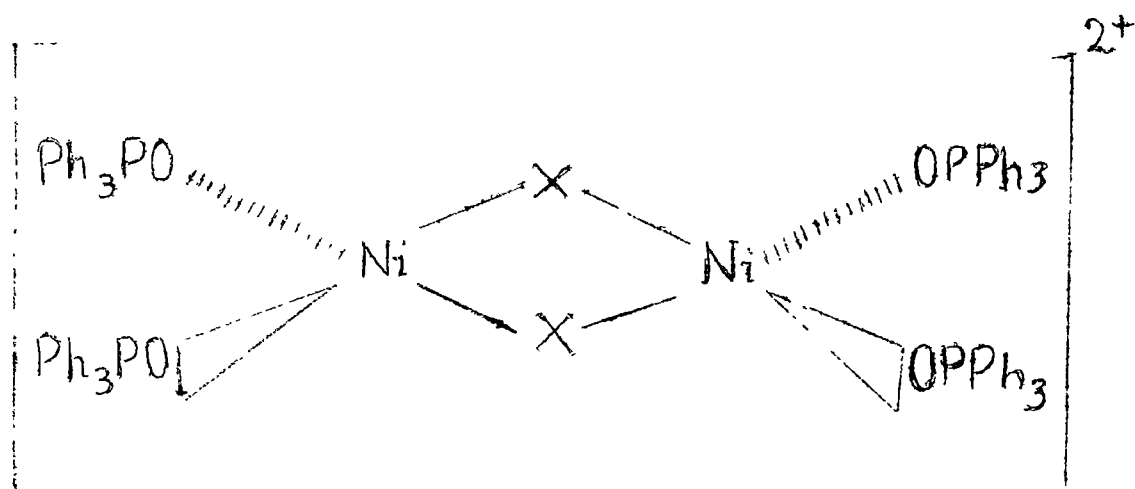
$[\text{Ni}(\text{PPh}_3)_2\text{I}]\text{Br}$  seem to be a new compound. The visible spectrum of this compound shows absorptions around 600 nm which could be due to  ${}^3\text{T}_1(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$  transition as discussed earlier.

Reactions of  $[\text{Ni}(\text{OPPh}_3)_2\text{X}]\text{Y}_3$  with triphenylphosphine in cyclohexane solvent did not replace the triphenylphosphine oxide by triphenylphosphine. Only the polyhalide anion species was converted to the monohalide anion and thus resulting in the formation of  $[\text{Ni}(\text{OPPh}_3)_2\text{I}]\text{Br}$  when  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}]\text{I}[\text{Br}_2]$  was used and formation of  $[\text{Ni}(\text{OPPh}_3)_2\text{Br}_2]$  when  $[\text{Ni}(\text{OPPh}_3)_2\text{X}]\text{Br}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) was used.

$[\text{Ni}(\text{OPPh}_3)_2\text{Er}_2]$  is same as reported by Cotton and Goodgame.<sup>13</sup>

With the help of various physical studies discussed above, the possible geometry around nickel(II) ion in  $[\text{Ni}(\text{OPPh}_3)_2\text{X}_2]^{2+}$  is proposed to be a distorted tetrahedral one, decreasing through halogen bridging as shown below.

Complexes of nickel(II) having similar bridging structures are reported with triphenylphosphine or triphenylphosphine oxide and bridging chlorides!<sup>14</sup>



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## CHAPTER V

A CONVENIENT METHOD OF PREPARING NICKEL(II)  
THIOCYANATE AND ITS USE IN SYNTHESISINTRODUCTION

Compounds containing nickel(II) thiocyanate are prepared mostly by the metathesis between nickel(II) chloride or nitrate with alkali metal thiocyanates.<sup>1</sup> However, in such syntheses if proper precautions are not taken, the final product may be contaminated with impurities originating from starting materials. Use of nickel(II) thiocyanate for such purposes should overcome these difficulties. Methods known for preparing this compound are : (i) treatment of a dilute thiocyanic acid solution with nickel hydroxide or carbonate followed by evaporating the mixture at 150 °C;<sup>2,3</sup> (ii) boiling of aqueous solution of ammonium thiocyanate with a solution of barium hydroxide, followed by addition of an

aqueous solution of nickel sulphate and finally concentrating<sup>3,4</sup> and (iii) metathetic preparation of nickel thiocyanate in ethanol followed by addition of benzene and slow concentration of the solution at atmospheric pressure with final heating to 110 °C in vacuum.<sup>5</sup>

The methods for the preparation of nickel(II) thiocyanates known are generally involving more than one step. Hence to find out a simple, one step preparation of pure nickel(II) thiocyanate was desirable.\* In this chapter, we report a very simple one step method of preparing nickel(II) thiocyanate by treating a solution of nickel(II) chloride or nitrate in acetic acid with a solution of ammonium thiocyanate in the same solvent at room temperature. The compound, thus obtained has been studied for its various physical properties in solid and in solution in different solvents. Besides, this nickel(II) thiocyanate has been used to prepare many compounds containing nickel thiocyanate and other ligands. Some of the compounds reported earlier have been prepared using it as the starting material and some new compounds have also been reported here and their physical properties studied to know their structure and mode of bonding of thiocyanate to the metal.

## EXPERIMENTAL

All the materials used were chemically pure or of Analar grade. Carbon, Hydrogen and Nitrogen analyses were carried out at the Microanalytical Laboratory, I.I.T., Kanpur. Nickel estimation was done according to the method<sup>6</sup> described below.

### Estimation of Nickel

A known quantity of complex containing ~ 25 mg nickel was decomposed using dilute nitric acid, diluted to 100 ml with water and neutralised with ammonia solution. Solid indicator mixture of murexide and  $\text{KNO}_3$  in the ratio 1:100 by weight (~ 50 mg), and 1 M  $\text{NH}_4\text{Cl}$  solution (10 ml) were added to the solution. pH of the solution was obtained at 7 by dropwise addition of conc. ammonia solution. The solution was titrated with standard EDTA solution (0.01 M) until the end point approached. The solution was made strongly alkaline by the addition of ammonia solution (10 ml) and the titration was continued until the colour changed from yellow to violet.

Infrared spectra, electronic spectra, magnetic susceptibility and conductivity measurements were obtained according to the methods described in Chapter II.

PREPARATIONSNickel(II) Thiocyanate, Ni(SCN)<sub>2</sub>

To a solution of 9.5 g (0.04 mole) of nickel chloride hexahydrate in water (10 ml), diluted with glacial acetic acid (100 ml), a solution of 7.6 g (0.1 mole) ammonium thiocyanate in acetic acid (20 ml) was added with a constant stirring at room temperature. An instantaneous reaction took place and a yellow compound separated and the mother liquor turned almost colourless. Stirring was continued for another 2 h. The compound was separated by filtration and washed with water-acetic acid mixture (1:10) for 3 to 4 times and finally dried under vacuum over conc. H<sub>2</sub>SO<sub>4</sub>. Yield 6.3 g (90%).

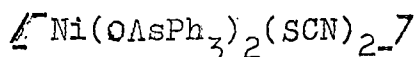
Alternatively, the compound was prepared using nickel nitrate instead of nickel chloride in a similar manner as above. However, the product obtained was not as pure.

Ni(OPPh<sub>3</sub>)<sub>2</sub>(SCN)<sub>2</sub>

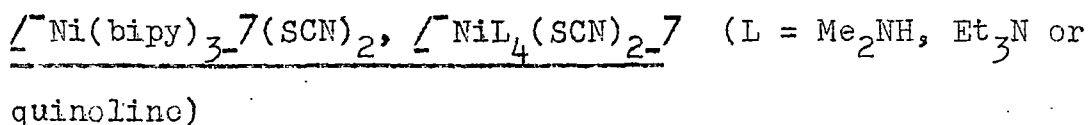
A melt of triphenylphosphine oxide (1g, 0.036 mole) was made by heating in an oil bath to 165 °C to which nickel thiocyanate (0.175 g, 0.01 mole) was added with constant stirring. The stirring was continued for 15 minutes while keeping the mixture at about 165 °C. The contents were cooled, powdered in an agate mortar and then washed several



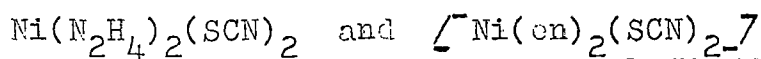
times with benzene to remove unreacted triphenylphosphine oxide and finally dried under vacuum. Yield, 0.71 g (97%).



A solution of nickel thiocyanate (0.175 g, 0.01 mole) in methanol (3 ml) was diluted with acetone (30 ml) and a solution of triphenylarsine oxide (0.7 g, 0.022 mole) in acetone (5 ml) was added and the mixture was boiled under reflux for 2 h. The yellowish green product was separated by centrifugation, washed with acetone and benzene and dried under vacuum. Yield, 0.72 g (88%).

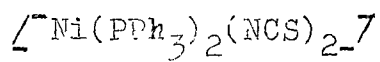


The method was similar to that of  $\text{[Ni(OAsPh}_3)_2(\text{SCN})_2]$ , except that a smaller quantity of acetone (15 ml) was used and nickel thiocyanate and the ligands were taken in 1:3 or 1:4 molar ratio depending on the composition of the complex obtained. The Yield was 80-90%.

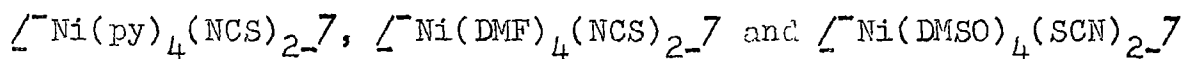


To a solution of nickel thiocyanate (0.175 g, 0.01 mole) in methanol (3 ml), hydrazine hydrate or ethylenediamine (~ 0.02 mole) was added, when immediately compound separated

out. It was centrifuged, washed with methanol and dried under vacuum. The yield was about 90%.



To a suspension of nickel thiocyanate (0.175 g, 0.01 mole) in n-butanol (5 ml) a solution of triphenylphosphine (0.53 g, 0.02 mole) in n-butanol (5 ml) was added and was stirred at room temperature for 1 h. A dark red crystalline compound separated, which was washed with ether and dried under vacuum. Yield, 0.66 g (94%).



Nickel thiocyanate (0.5 g) was taken with pyridine, dimethyl sulphoxide or N,N-dimethyl formamide (5 ml) and heated on a water bath for about 30 min, when a clear coloured solution was obtained. The product separated from the solution on cooling and was centrifuged and washed with acetone and dried under vacuum. The yield was 60-70%.

## RESULTS AND DISCUSSION

Nickel(II) thiocyanate prepared according to the method described in the Experimental Section, was reported earlier by different methods.<sup>2-5</sup> The analytical data of the compound, confirm the composition to be Ni(SCN)<sub>2</sub> (Table V.1.). The

Table V.1. Analytical and Some Physical Data of the Nickel Thiocyanate Complexes

Compound	Colour	M.P. °C	$\mu_{\text{eff}}$ (B.M.)	Found (Calculated) %				Molar Conduc- tance $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$
				C	H	N	S	
$\text{Ni}(\text{SCN})_2$	Yellow	240(dec)	3.26	13.6 (13.7)	15.7 (16.0)	36.1 (36.6)	33.3 (33.6)	
$\text{Ni}(\text{OPPh}_3)_2(\text{SCN})_2$	Yellow	182-5	2.82	62.1 (62.4)	4.3 (4.1)	3.7 (3.8)	8.9 (8.8)	8.3 (8.0)
$\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2$	Yellow- ish green	240-50	3.10	55.3 (55.7)	3.5 (3.7)	3.2 (3.4)	8.3 (7.8)	7.8 (7.2)
$\text{Ni}(\text{bipy})_3(\text{SCN})_2$	Light pink	>300	-	55.6 (55.3)	3.6 (3.2)	12.4 (12.8)	10.9 (11.3)	10.6 (10.4)
$\text{Ni}(\text{Me}_2\text{NH})_4(\text{NCS})_2$	Green	>320	-	33.2 (33.8)	7.5 (7.2)	24.1 (23.7)	17.7 (18.0)	16.3 (16.6)
$\text{Ni}(\text{Et}_3\text{N})_4(\text{NCS})_2$	Green	>320	-	54.3 (53.9)	9.9 (10.4)	14.9 (14.5)	10.8 (11.1)	10.2 (10.1)

(a) = in acetonitrile;

(b) = in nitrobenzene

infrared spectrum in nujol mull or potassium bromide disc shows a strong and sharp band at  $2165\text{ cm}^{-1}$  similar to the band observed by Flint and Goodgame<sup>5</sup> for  $\text{Ni}(\text{SCN})_2$  which is assigned unambiguously to  $\nu_{\text{CN}}$  of the bridging -SCN group. A weak band at  $765\text{ cm}^{-1}$  is assigned to  $\nu_{\text{CS}}$  of the bridging thiocyanato group<sup>5</sup>. Mitchell and Williams<sup>7</sup> reported a band at  $2151\text{ cm}^{-1}$  for  $\nu_{\text{CN}}$  of the bridging -SCN group of  $\text{Ni}(\text{SCN})_2$ . The electronic reflectance spectrum in the region 900 to 300 nm show bands at 650 nm and at 430 nm. The former band is identical to that reported earlier<sup>5</sup>, whilst the band at 430 nm could be due to charge-transfer band. The magnetic moment of the compound is 3.26 B.M., which is close to the value reported by Flint and Goodgame<sup>5</sup>. The structure proposed for nickel thiocyanate in the solid state consists of a tetragonal coordination sphere with four bridging sulphur atoms in the plane with nitrogen atoms in the axial positions<sup>5</sup>.

The infrared and visible spectra of nickel thiocyanate have been recorded in organic solvents to ascertain the mode of coordination of the thiocyanato group in solution and the nature of coordination around the nickel atom. Infrared spectra of nickel thiocyanate in acetonitrile, acetone and methanol show a band around  $2100\text{ cm}^{-1}$  (Table V.2.) which may be assigned to terminal  $\nu_{\text{CN}}$  of the N-bonded thiocyanate. A band around  $800\text{ cm}^{-1}$  in the acetonitrile or acetone solution is characteristic of the  $\nu_{\text{CS}}$  of the N-bonded thiocyanato

Table V. 2. Spectral Data for Ni(SCN)<sub>2</sub>  
in Different Media

Solvent	Electronic Absorption $\lambda_{\max}$ in nm ( $\epsilon_{\max}$ )	Important infra- red bands in $\text{cm}^{-1}$
Solid	650 <sup>(a)</sup> 430	2165 s <sup>(b)</sup> 2120 sh 765 w
Ethanol	727 (3.7) 662 (3.0) 398 (9.6)	
Methanol	725 (4) 660 (4.2) 390 (10) 362 (11)	2110 s 2055 sh
N,N-Dimethyl Formamide	735 (5.7) 675 (6.4) 404 (16.5)	
Dimethyl Sulphoxide	750 br (3) 410 (8)	
Acetone	665 sh (9) 615 sh (10.3)	2150 sh 2105 s 2070 sh 790 m
$\alpha$ -Picoline	685 (4.4) 360	
Acetonitrile	710 sh 610 (16) 370 sh	2100 s 800 m
Pyridine	775 sh 587 (7.9) 360 (18.3)	

s = strong; m = medium; w = weak; br = broad; sh = shoulder

(a) = Reflectance Spectrum; (b) = in KBr or Nujol.

group.<sup>8</sup> However, an analogous band was not observed in methanol solution. Infrared studies of nickel thiocyanate in donor solvents have not been reported earlier, however, infrared spectra of  $[\text{NiL}_2(\text{SCN})_2]$  (L = methanol or ethanol) in nujol provide evidence for a bridging thiocyanato group.<sup>5</sup>

The electronic spectra of nickel thiocyanate have been studied in different organic solvents (fig. no. V.1.) in order to determine the nature of coordination around the metal ion. The spectra in the visible region show two bands around 700 nm and one band around 400 nm (Table V.2.). The molar extinction coefficient for these bands lie in the range 3 to 20, which indicate an octahedral environment around nickel atom. The two bands around 700 nm can be assigned to  ${}^3\text{A}_2(\text{F}) \longrightarrow {}^3\text{T}_1(\text{F})$  and a band around 400 nm to  ${}^3\text{A}_2(\text{F}) \longrightarrow {}^3\text{T}_1(\text{P})$  transitions. Normally in a pure octahedral environment, only one band around 700 nm should be observed, however, due to the lowering of symmetry to  $\text{D}_{4\text{h}}$ , probably due to the formation of  $[\text{Ni}(\text{L}_4)(\text{NCS})_2]$  (L = methanol, ethanol, N,N-dimethylformamide, dimethyl sulphoxide, acetone,  $\alpha$ -picoline, acetonitrile or pyridine), the  ${}^3\text{T}_1(\text{F})$  state is split into two states, one of two fold degeneracy and the other one a singly degenerate state and hence two absorption bands around 700 nm. The visible and uv spectra of nickel thiocyanate in methanol, ethanol and pyridine reported by Kiss and Csokan<sup>9</sup> describes the formation of  $[\text{Ni}(\text{SCN})_2\text{L}_2]$  when no free thiocyanate ions

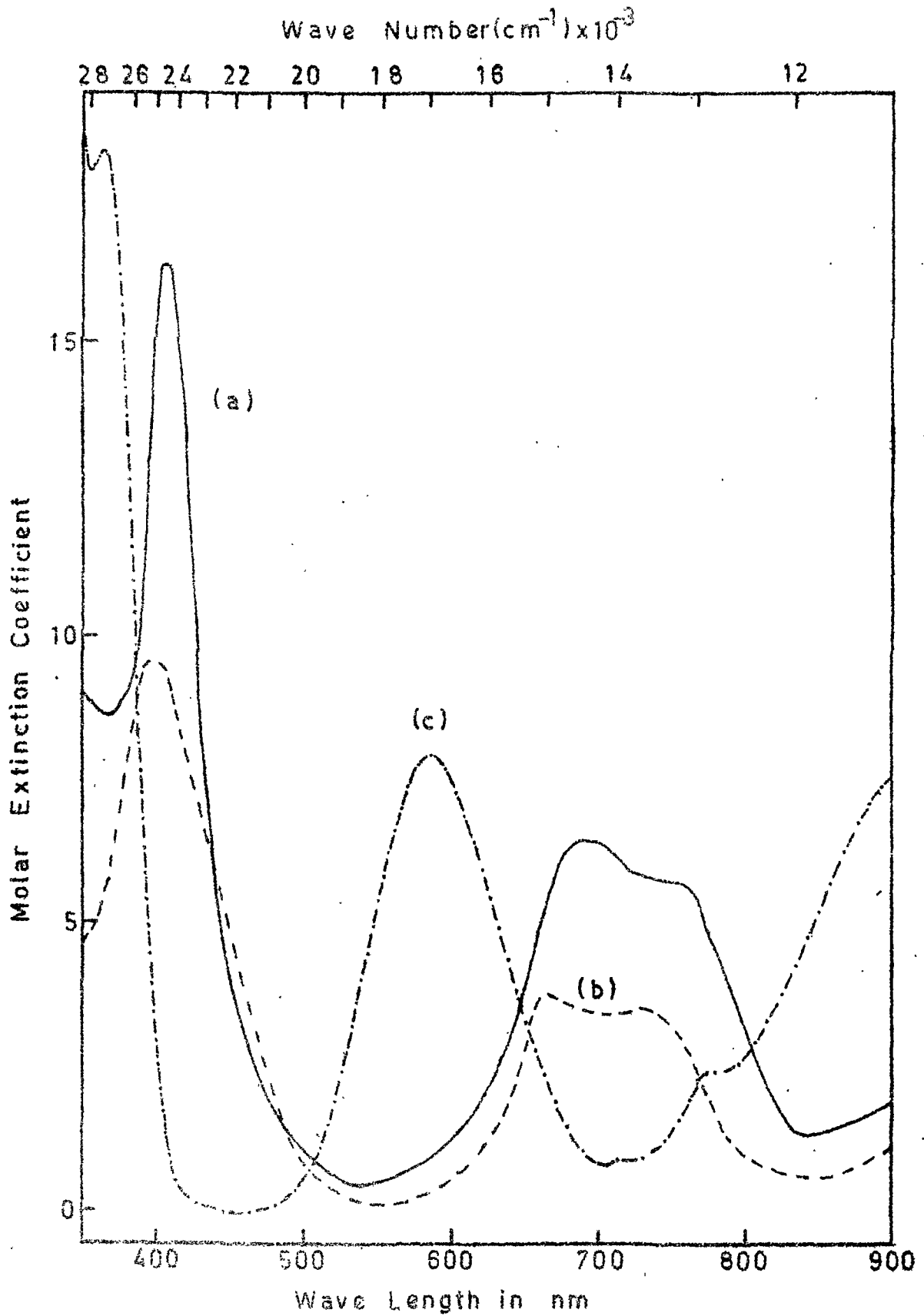


Fig.V.1- Electronic Spectra of Ni(SCN)<sub>2</sub> in  
(a) N,N-dimethyl formamide  
(b) Ethanol (c) Pyridine .

were added and that of  $[\text{Ni}(\text{SCN})_4]^{2-}$  and  $[\text{Ni}(\text{SCN})_4\text{L}_2]^{2-}$  when an excess of free thiocyanate ions were present. We report, here the octahedral coordination around the nickel ion, due to the formation of the species  $\text{NiL}_4(\text{SCN})_2$  (L = solvent molecule). The spectra are similar to the spectra of  $\text{NiL}_4(\text{SCN})_2$  to be discussed later.

Nickel thiocyanate has been used to prepare complexes containing oxygen, nitrogen and phosphorus donor ligands, i.e. triphenylphosphine oxide, triphenylarsine oxide, N,N-bipyridyl, hydrazine, ethylene diamine, dimethylamine, triethylamine, N,N-dimethylformamide, quinoline, pyridine, dimethyl sulphoxide or triphenylphosphine.

The infrared spectra (Table V.3.) of the complexes containing triphenylphosphine oxide or triphenylarsine oxide show a strong band around  $2100 \text{ cm}^{-1}$  which can be assigned to  $\nu_{\text{CN}}$  of the terminal thiocyanato group.<sup>8</sup> Infrared spectrum of  $[\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2]$  is given in figure no. V.2. Terminal thiocyanate can be either an S-bonded or an N-bonded. We propose, here only S-bonded thiocyanato group, as there is no absorption in the region  $780$  to  $860 \text{ cm}^{-1}$  due to  $\nu_{\text{CS}}$  of the N-bonded thiocyanate.<sup>8</sup>  $\nu_{\text{CS}}$  of the S-bonded thiocyanato group should be observed in  $690$  to  $740 \text{ cm}^{-1}$  region.<sup>8</sup> There are several bands in this region due to the presence of phenyl groups in the ligands, hence no absorption can unambiguously be assigned to  $\nu_{\text{CS}}$  of the S-bonded thiocyanate.

Table V. 3. Some Spectral Data of Complexes  
Containing Nickel Thiocyanato Group.

Compound	Electronic Absorption $\lambda_{\max}$ in nm ( $\epsilon_{\max}$ )	Important infra- red bands in $\text{cm}^{-1}$
$\text{Ni}(\text{OPPh}_3)_2(\text{SCN})_2$	660 (a) 415	2100 s 1188 m 1182 m
$\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2$	850 (a) 650 390	2097 s 866 m-s
$\text{Ni}(\text{bipy})_3(\text{SCN})_2$	780 (12) (b) 513 (23)	2045 s 780 s 740 m
$\text{Ni}(\text{N}_2\text{H}_4)_2(\text{NCS})_2$	-	3320 m 3300 m 3210 m 2080 s 972 m 790 m
$\text{Ni}(\text{Me}_2\text{NH})_4(\text{NCS})_2$	610 (5.1) (c) 400 (8.6)	2104 m 2030 s
$\text{Ni}(\text{Et}_3\text{N})_4(\text{NCS})_2$	660 sh (c) 620 (9.2) 425 (20)	2110 m 2030 s
$\text{Ni}(\text{en})_2(\text{NCS})_2$	880 (4.4) (b) 545 (4.4)	2072 s
$\text{Ni}(\text{DMF})_4(\text{NCS})_2$	735 (2.7) (b) 662 (3.1) 392 (9.3)	2108 s 1645 s 790 m
$\text{Ni}(\text{Quin})_4(\text{NCS})_2$	725 (4.8) (b) 660 (5.4) 397 (13)	2100 s
$\text{Ni}(\text{py})_4(\text{NCS})_2$	740 sh (b) 630 (5) 380 (11)	2085 s 800 m
$\text{Ni}(\text{DMSO})_4(\text{SCN})_2$	735 (3.4) (b) 660 (4.3) 400 (10)	2090 s 1020 m 995 s 950 s
$\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2$	-	2080 s 865 m

(a) = Reflectance spectrum; (b) = in MeOH; (c) = in nitrobenzene

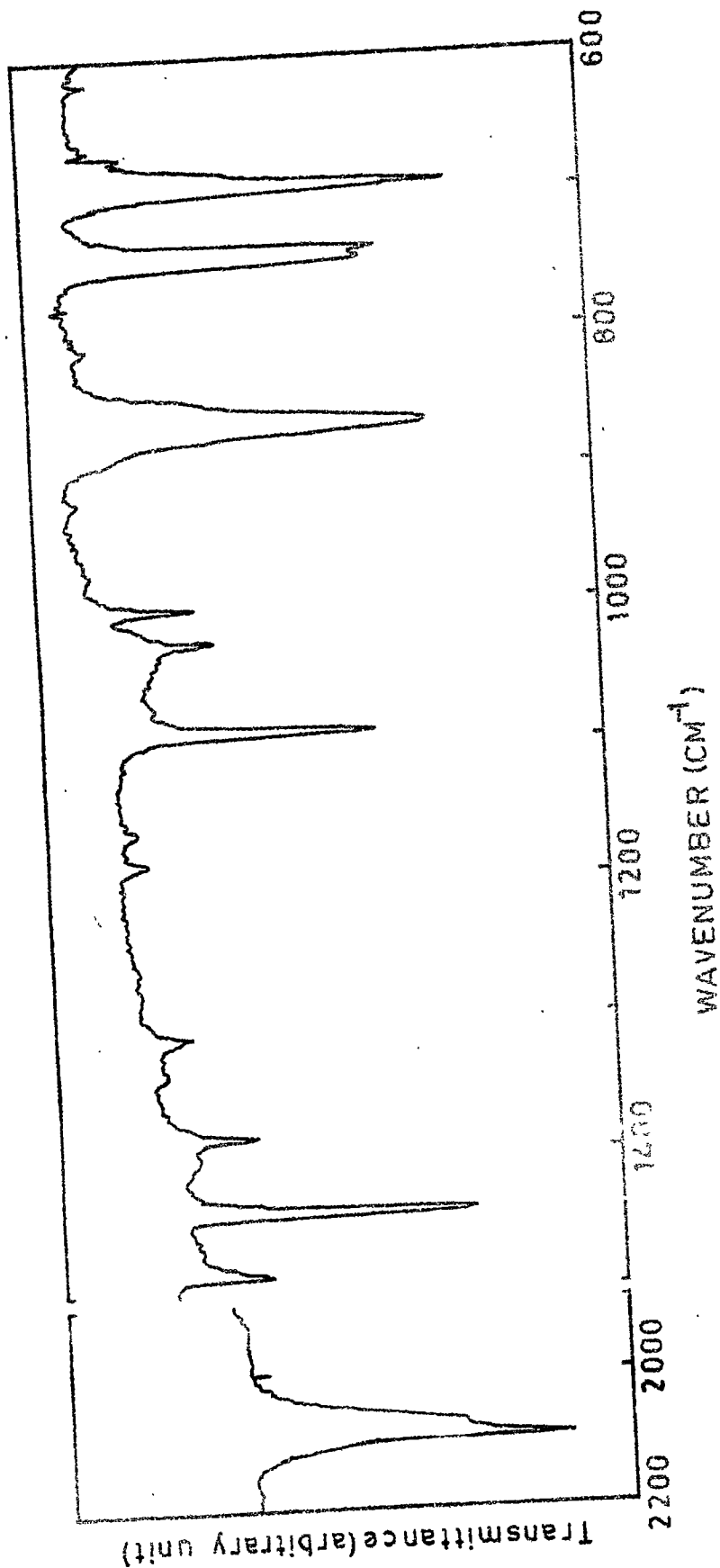


Fig. V.2. Infrared Spectrum of  $[\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2]$  in KBr.

Example of S-bonded thiocyanato complex of nickel(II), viz.  $[\text{Ni}(\text{OPPh}_3)(\text{SCN})\text{Cl}]_2$  having similar infrared absorptions is reported.<sup>10</sup> The infrared bands at  $1185 \text{ cm}^{-1}$  and  $866 \text{ cm}^{-1}$  in the phosphine oxide and arsine oxide complexes are assigned to  $\nu_{\text{P=O}}$  and  $\nu_{\text{As=O}}$  respectively.<sup>8</sup>

$\text{Ni}(\text{OPPh}_3)_2(\text{SCN})_2$  and  $\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2$  have four coordination around the nickel(II) ion. If the complexes are assumed to be monomeric, either a square planar or a distorted tetrahedral geometry is possible. For penta- or hexa- coordination the complexes have to be either dimeric or polymeric respectively, bridging through thiocyanato groups. No evidence of bridging thiocyanato groups is available from infrared (absence of absorption in  $2100\text{--}2200 \text{ cm}^{-1}$  region). Hence penta- or hexa- coordination is not possible in these cases. Square planar complexes of nickel(II) are generally diamagnetic.<sup>11</sup> These complexes have magnetic moments  $\sim 3 \text{ B.M.}$ , which is slightly lower than the moments of tetrahedral nickel(II) complexes.<sup>12</sup> Thus, the possible geometry of these complexes is distorted tetrahedral, which is further supported by their electronic reflectance spectra discussed below. The electronic reflectance spectra show bands around 650 and 400 nm in both the cases. A band at 850 nm is also observed in the arsine oxide complex (fig. no. V.3.). A band similar to this in the phosphine oxide complex, if present beyond 900 nm, could not be observed due to the range of measurement of the

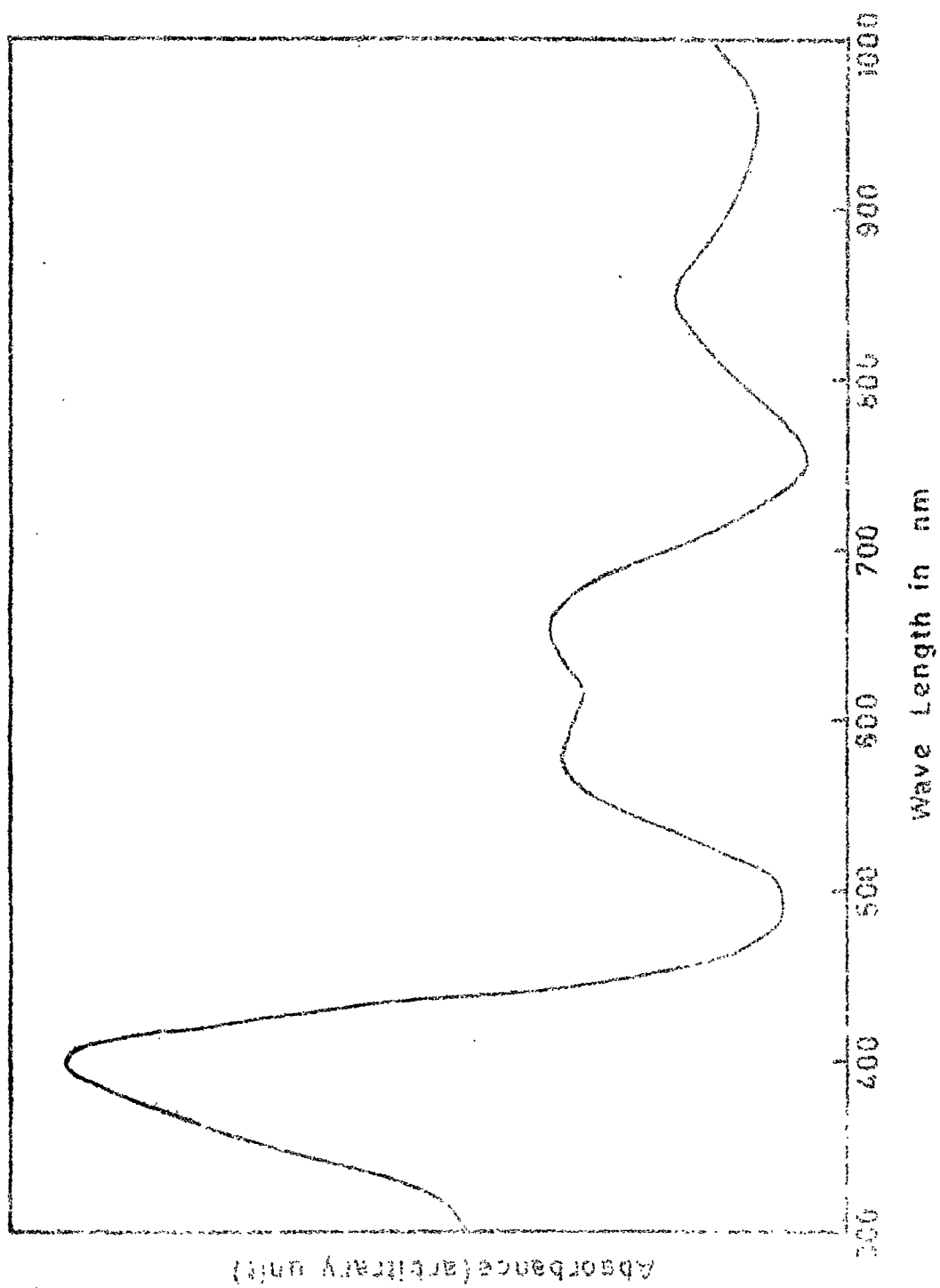


Fig. V.3. Electronic Reflectance Spectrum of  $[\text{Ni}(\text{OAsPh}_3)_2(\text{SCN})_2]$

instrument. The bands at 850 and 650 nm may be assigned to  ${}^3T_1(F) \longrightarrow {}^3A_2(F)$  and  ${}^3T_1(F) \longrightarrow {}^3T_1(P)$  transitions respectively of a nickel(II) tetrahedral system.<sup>13</sup> The band around 400 nm could be due to charge-transfer. The visible spectra in a non-coordinating solvent, like chloroform show only one band around 400 nm. It seems the complexes are decomposing in chloroform. However, spectra of the complexes in a coordinating solvent like N,N-dimethyl formamide is super-imposable with the spectrum of nickel thiocyanate in N,N-dimethyl formamide. It seems in presence of N,N-dimethylformamide, the phosphine oxide or the arsine oxide is liberated and an octahedral species like  $[\text{Ni}(\text{DMF})_4(\text{NCS})_2]^-$  is obtained in the solution.

The complex containing N,N'-bipyridyl with a composition  $\text{Ni}(\text{bipy})_3(\text{SCN})_2$  has molar conductance  $218 \text{ } \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , which is in the range expected for a 1:2 electrolyte in acetonitrile, hence the molecular formula  $[\text{Ni}(\text{bipy})_3]^{2+}(\text{SCN})_2^-$ . The infrared spectrum (fig. no. V.4.) shows a strong band at  $2045 \text{ cm}^{-1}$  besides bands at  $780$  and  $740 \text{ cm}^{-1}$ . All the bands due to bipyridyl are also present. The band at  $2045 \text{ cm}^{-1}$  is assigned to  $\nu_{\text{CN}}$  of the ionic type of thiocyanato group, which is observed at a frequency lower than that of S-bonded or the N-bonded  $\nu_{\text{CN}}$ .<sup>8,14</sup> The band at  $740$  or  $780 \text{ cm}^{-1}$  can not be assigned unambiguously to  $\nu_{\text{CS}}$  due to many absorptions of bipyridyl in  $800$  to  $650 \text{ cm}^{-1}$  region. The electronic spectrum

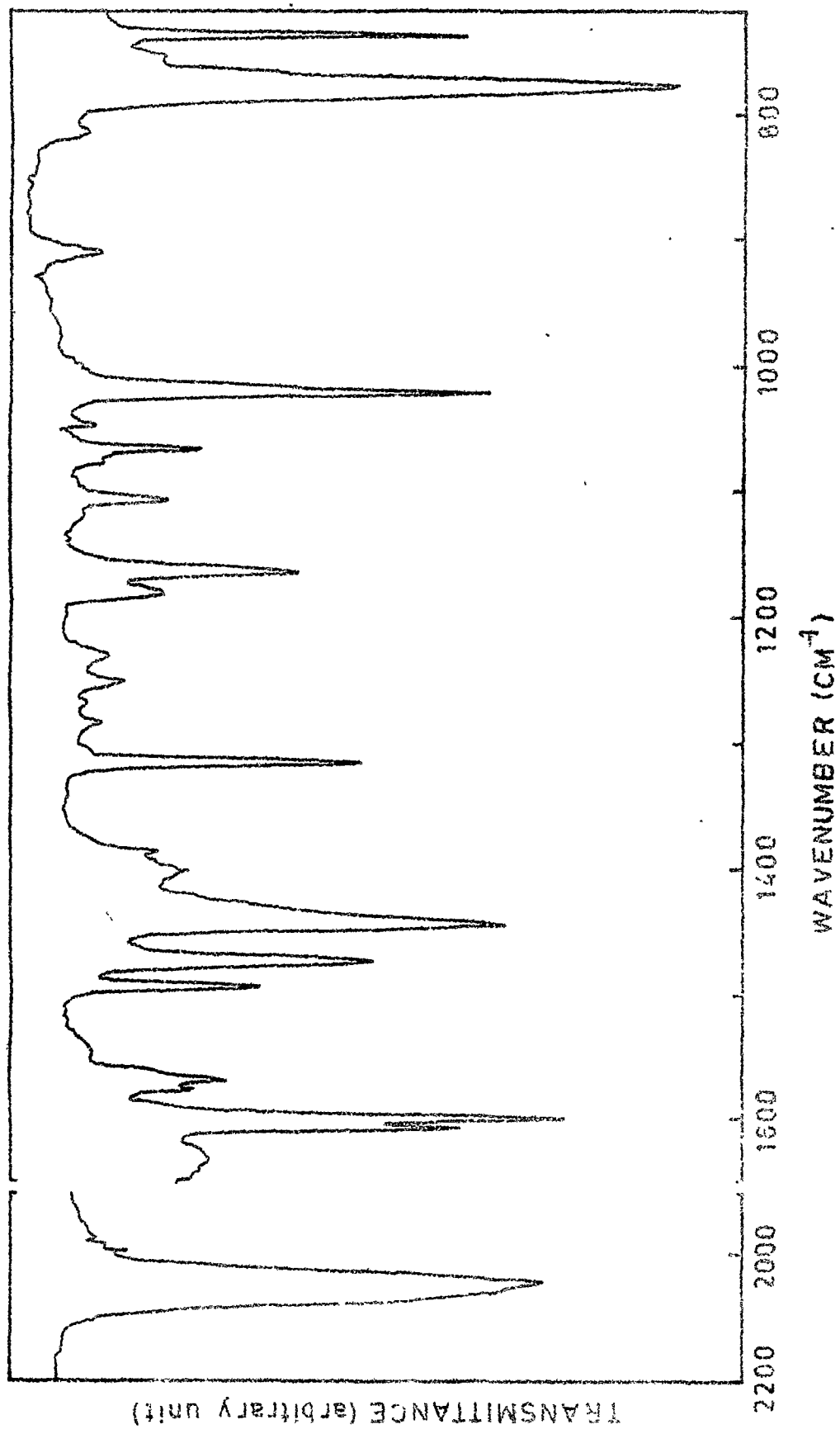


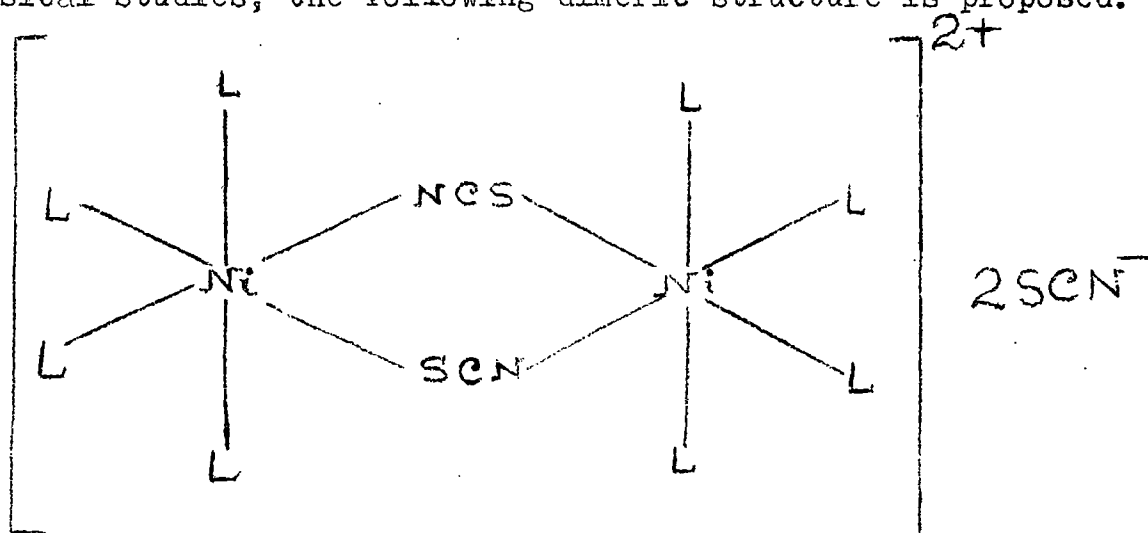
Fig. V.4. Infrared Spectrum of  $[\text{Ni}(\text{bipy})_3](\text{SCN})_2$  in KBr

shows two bands at 780 and 513 nm which may be assigned to  ${}^3A_2(F) \longrightarrow {}^3T_1(F)$  transition in an octahedral system. The splitting of  ${}^3T_1(F)$  state may be due to the lowering in symmetry to  $D_3$ .

A complex of the composition,  $Ni(N_2H_4)_2(NCS)_2$  reported by Ray and Sarkar<sup>15</sup> has molar conductance  $210 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  in water at  $24.5^\circ \text{C}$ . A compound of the same composition obtained by us is insoluble in many organic solvents and water. Hence a conductance measurement and some of the physical studies in solution were not possible. The infrared spectrum shows bands at 3320, 3300 and  $3210 \text{ cm}^{-1}$  which can be assigned to  $\nu_{NH}$  of the hydrazine. Further, a strong band at  $2080 \text{ cm}^{-1}$  and a band of medium intensity at  $790 \text{ cm}^{-1}$  may be assigned to  $\nu_{CN}$  and  $\nu_{CS}$  respectively of the N-bonded thiocyanato group.<sup>8</sup> For ionic thiocyanato group  $\nu_{CN}$  and  $\nu_{CS}$  should have been observed at lower frequencies.<sup>8</sup> A band at  $972 \text{ cm}^{-1}$  can be assigned to  $\nu_{N-N}$  of the hydrazine.<sup>16</sup> This compound may have a polymeric structure having octahedral coordination around nickel atom. Polymerisation may be achieved by the hydrazine ligands bridging between nickel atoms and having N-bonded terminal thiocyanato group. Examples of such polymeric compounds with hydrazine are known.<sup>17</sup>

The complexes of dimethylamine and triethylamine are generally insoluble in most of the organic solvents. The infrared spectra show a band of medium intensity around

2105  $\text{cm}^{-1}$  and a strong band at 2030  $\text{cm}^{-1}$ . The band at 2105  $\text{cm}^{-1}$  may be assigned to  $\nu_{\text{CN}}$  of the bridging thiocyanate group and at 2030  $\text{cm}^{-1}$  due to  $\nu_{\text{CN}}$  of the ionic thiocyanato group. Examples of  $\nu_{\text{CN}}$  of bridging thiocyanato occurring at 2110  $\text{cm}^{-1}$  are known.<sup>18,19</sup> The molar conductance of the compounds assuming the molecular formula  $[\text{L}_4\text{Ni}(\text{NCS})_2\text{NiL}_4]^{2+}(\text{SCN})_2$  in nitrobenzene is found to be of the order of 150  $\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$ , which is normally observed for 1:2 electrolyte systems. The visible spectra of these compounds in nitrobenzene show two bands around 650 nm and one band around 400 nm, which may be assigned to the d-d transitions of distorted octahedral system as discussed earlier. On the basis of the above mentioned physical studies, the following dimeric structure is proposed.



L = Dimethylamine or Triethylamine.

The complexes containing N,N-dimethyl formamide, quinoline, pyridine, dimethyl sulphoxide or ethylene diamine are similar

to the reported compounds<sup>7,20-23</sup>. All these compounds except dimethyl sulphoxide complex have N-bonded thiocyanato group vide infrared (Table V. 3.). N,N-dimethyl formamide is coordinated to nickel through the oxygen atom, as  $\nu_{C=O}$  is shifted to  $1645\text{ cm}^{-1}$  in the complex. The coordination of di-methyl sulphoxide with nickel in its complex is through oxygen atom, as  $\nu_{S=O}$  is shifted towards lower frequency. All these complexes have a distorted octahedral geometry and the electronic spectra in methanol solvent are very much similar, with two bands around 700 nm and one around 400 nm, the assignments of which could be made as above. The complex containing tri-phenylphosphine is a square planar N-bonded thiocyanato complex and is same as reported  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})_2]$ <sup>10,12</sup>.

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## CHAPTER VI

## MIXED LIGAND COMPLEXES OF NICKEL(II) AND COBALT(II)

INTRODUCTION

Dimethylsulphoxide (DMSO) and N,N -dimethyl formamide (DMF) are frequently used as solvents for both organic and inorganic compounds and have considerable amount of interaction with solutes, specially the transition metal salts. DMSO and DMF may be considered as weak donor ligands compared to tertiary phosphines or arsines.<sup>1</sup>

Dimethyl sulphoxide reacts with most of the metal ions to form solvated species and their coordination chemistry is well studied.<sup>2-5</sup> It has long been established that dimethyl sulphoxide exhibits two sites for coordination with metal ions, (i) through soft sulphur atom, and, (ii) through hard oxygen atom. Cotton and Francis<sup>6</sup> have shown that a shift of  $\nu_{SO}$  towards lower energy is an evidence of the coordination through the oxygen atom to the metal ion. The following

transition metal ions have been reported to coordinate through oxygen atom of dimethyl sulphoxides,<sup>2,3,7,8</sup> Ti(IV), Zr(IV), Hf(IV), V(IV), Nb(V), Ta(V), Cr(II), Cr(III), Mo(II), Mo(V), Mo(VI), Mn(II), Re(V), Fe(II), Fe(III), Ru(III), Co(II), Ni(II), Pd(II), Pt(II) and Cu(II). A shift of  $\nu_{SO}$  towards higher energy is observed when coordination takes place through sulphur atom. Dimethyl sulphoxides bonded to the metal through sulphur atoms are known for the transition metal ions,<sup>2,3,9</sup> Cr(0), Mn(I), Re(V), Fe(0), Ir(II), Pd(II) and Pt(II). There are some metal-dimethyl sulphoxide complexes viz.,  $[RuCl_2(DMSO)_4]^-$  and  $[Pd(DMSO)_4]^- (ClO_4)_2$ , where dimethyl sulphoxide molecules are coordinated to the metal through both oxygen and sulphur atoms.<sup>10a,10b</sup> The presence of both O-bonded and S-bonded DMSO is characterized by infrared studies where a absorptions due to  $\nu_{SO}$  are observed both at lower and higher energies compared to that of free DMSO.

The coordination chemistry of N,N-dimethyl formamide is not much studied in comparison to that of dimethyl sulphoxide.<sup>1</sup> DMF has also two potential coordination sites, viz. nitrogen and oxygen atoms. However, bonding through nitrogen atom is not known for transition metal-DMF complexes and bonding only through oxygen atom is reported.<sup>1</sup> The preference of bonding through oxygen atom is due to steric hindrance at the substituted nitrogen atom.<sup>1,11</sup> The complexes

of N,N-dimethyl formamide reported with transition metal ions are with<sup>1,11</sup> Cr(O), Cr(III), Mo(O), Mo(III), Mn(II), Fe(III), Ru(II), Co(II), Ni(II), Pd(II), and Cu(II).

The complexes of N,N-dimethyl formamide with Cobalt(II) and Nickel(II) are of the composition<sup>11</sup>  $[\text{Co}(\text{DMF})_n(\text{ClO}_4)_2]$  ( $n = 4$  or  $6$ );  $[\text{MCl}_2(\text{DMF})_2]$  ( $M = \text{Co}$  or  $\text{Ni}$ );  $[\text{NiBr}_2(\text{DMF})_3]$ ;  $[\text{Ni}(\text{DMF})_6(\text{ClO}_4)_2]$ . The complexes of dimethyl sulphoxide known with Cobalt(II) and Nickel(II) are of the type<sup>2,3</sup>  $[\text{M}(\text{DMSO})_6\text{X}_2]$  (for  $M = \text{Co}$ ,  $X = \text{I}$  or  $\text{ClO}_4$ ; for  $M = \text{Ni}$ ,  $X = \text{Br}$ ,  $\text{I}$  or  $\text{ClO}_4$ );  $[\text{M}(\text{DMSO})_6][\text{MX}_4]$  (for  $M = \text{Co}$ ,  $X = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{NCS}$  or  $\text{NO}_3$ ; for  $M = \text{Ni}$ ,  $X = \text{Cl}$  or  $\text{Br}$ );  $[\text{M}(\text{DMSO})_4\text{X}_2]$  (for  $M = \text{Co}$ ,  $X = \text{NCS}$  or  $\text{NO}_3$ ; for  $M = \text{Ni}$ ,  $X = \text{Br}$ ,  $\text{I}$ ,  $\text{NCS}$  or  $\text{NO}_3$ ). The bonding of DMSO with nickel(II) or cobalt(II) in all these complexes is through the oxygen atom only.

The complexes of nickel(II) and cobalt(II) with strong donor ligand, such as triphenylphosphine are also well known. These are generally of the type  $[\text{M}(\text{PPh}_3)_2\text{X}_2]$  (where  $M = \text{Ni}$  or  $\text{Co}$ ,  $X = \text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{NO}_3$  or  $\text{NCS}$ )<sup>12-14</sup>

Some of the mixed ligand complexes of platinum group of metals, viz. Pd(II) and Ru(II) containing strong donor ligands as tertiary phosphine, diphosphine or carbonyl and weak donor ligand as DMSO or DMF are found to act as good catalysts in the hydrogenation and other reactions.<sup>4,14,15-18</sup>

$[\text{Ru}(\text{PPh}_3)_2(\text{CO})(\text{DMF})\text{Cl}_2]$ ,  $[\text{Me}_2\text{NH}_2][\text{RuCl}_3(\text{DMSO})_3]$  and

$[\text{Pd}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)(\text{DMF})\text{Cl}]^+$  are found to be good catalysts for various hydrogenation reactions.<sup>15-18</sup> The lability of DMF or DMSO molecules coordinated to the metal ions may well be one reason for the catalytic activity of these complexes. Complexes of nickel(II) and cobalt(II) containing both strong and weak donor neutral ligand molecules are not reported. However, some complexes of cobalt(III) containing ethylene diamine and DMSO or DMF reported are of the type  $[\text{Co}(\text{en})_2(\text{DMSO})_2]^{3+}$ ;  $[\text{Co}(\text{en})_2(\text{DMSO})\text{X}]^{2+}$  and  $[\text{Co}(\text{en})_2(\text{DMF})\text{Cl}]^{2+}$ .<sup>2, 19</sup> Synthesis and study of the properties of complexes of nickel(II) and cobalt(II) containing weak and strong donor neutral ligand molecules will be interesting as such compounds may find use as catalysts for various reactions.

A survey of literature shows that complexes of nickel(II) and cobalt(II) containing weak donor ligands as DMF or DMSO and strong donor ligands as triphenylphosphine are not studied. In this chapter, we report the synthesis, characterisation and structural studies of some of such compounds. The compounds presented in this chapter are of the type  $[\text{Ni}(\text{PPh}_3)_2\text{L}_2\text{X}_2]$  and  $[\text{Co}(\text{PPh}_3)\text{LX}_2]$  (where L = DMF or DMSO; X = Cl or Br). The compounds are prepared by two different methods and have been characterized by their elemental analyses and their various physical data, viz. infrared and uv-visible spectral data, magnetic measurement data,

conductivity measurements and thermogravimetric analyses results. Possible structures have also been suggested.

### EXPERIMENTAL

All the solvents, viz. DMF and DMSO were purified and dried according to standard methods.<sup>2,11</sup> Carbon, Hydrogen and Nitrogen analyses were obtained from the Australian Mineral Development Laboratories, Australia, and from the Microanalytical Section, Indian Institute of Technology, Kanpur. Sulphur and Halogen estimations were carried out by standard methods<sup>20</sup> by decomposing the complexes with dilute nitric acid. Nickel estimations were done according to the method described in the Chapter II. Cobalt was estimated according to the method given below.

#### Estimation of Cobalt

A known weight of compound containing ~ 40 mg of cobalt was decomposed by using dilute nitric acid and the solution was neutralised by diluted ammonia. To the solution, 5 ml of mercuric chloride (5%) and 5 ml of ammonium thiocyanate (6%) solutions were added with constant stirring. A deep blue precipitate formed after stirring for about 5 minutes which was allowed to stand for 2 h at room temperature and filtered through weighed sintered crucible, dried at 100 °C and weighed as  $\text{CoHg}(\text{SCN})_4$ .

Infrared spectra, electronic spectra, magnetic susceptibility and conductivity measurements were obtained according to methods given in Chapter II. All these data are given in Tables VI. 1. and VI.2.

### Preparation

The compounds were prepared according to the following methods:-

#### 1. Solution Method:

$\text{MX}_2 \cdot x\text{H}_2\text{O}$  (M = Ni or Co, X = Cl or Br) (0.002 mole) was taken in 20 ml of the solvent (DMF or DMSO). The mixture was heated to  $\sim 100^\circ\text{C}$  for about an hour, when a clear solution was obtained. Triphenylphosphine (0.004 mole) was dissolved in 10 ml of the solvent and was added to the solution of the metal salt and refluxed for about an hour. The solution was concentrated under vacuum at  $50-60^\circ\text{C}$  to about 8 ml and cooled. To the cold solution, dry ether ( $\sim 100$  ml) was added when the complex (blue or green in colour) precipitated out. It was filtered and washed several times with dry ether and dried under vacuum.

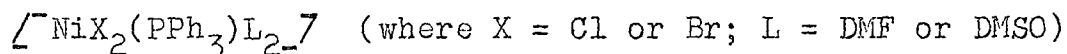
#### 2. Melt Method:

$\text{MX}_2\text{L}_n$  (where M = Ni or Co; X = Cl or Br; n = 3 or 4) were prepared according to the methods reported in the

literature.<sup>1,21</sup> A melt of  $\text{MX}_2\text{L}_n$  (0.002 mole) was prepared by heating the compound to  $80^\circ\text{C}$ , in a small round bottom flask fitted with a guard-tube on a water bath and triphenylphosphine (0.004 mole) was added to it. Heating was continued for about 15 minutes when coloured crystalline compound separated out. It was cooled and washed several times with dry ether to remove the unreacted triphenylphosphine and DMSO or DMF. The compound was dried under vacuum.

The compounds obtained by the above methods are  $\text{[Ni(PPh}_3\text{)}_2\text{L}_2\text{X}_2\text{]}$  (where  $\text{X} = \text{Cl or Br}$ ,  $\text{L} = \text{DMF or DMSO}$ ) and  $\text{[Co(PPh}_3\text{)}_2\text{LX}_2\text{]}$  (where  $\text{L} = \text{DMF or DMSO}$ ,  $\text{X} = \text{Cl or Br}$ ). However,  $\text{[Ni(PPh}_3\text{)}(\text{DMSO})_2\text{Br}_2\text{]}$  and  $\text{[Co(PPh}_3\text{)}(\text{DMSO})\text{Cl}_2\text{]}$  could not be isolated by the solution method. The compounds, except  $\text{[Co(PPh}_3\text{)}\text{LBr}_2\text{]}$  ( $\text{L} = \text{DMF or DMSO}$ ), were recrystallised from dry acetonitrile. The cobalt bromo complexes were recrystallised from dry acetone.

Attempts to prepare the triphenylarsine compounds analogous to the above mentioned triphenylphosphine compounds were unsuccessful by either of the methods and only the compounds containing the solvent (DMF or DMSO) as the ligands were obtained.

RESULTS AND DISCUSSION

On the basis of the analytical data the empirical formula for the nickel complexes is found to be  $[NiX_2(PPh_3)L_2]$  (where X = Cl or Br, L = DMF or DMSO). The physical data of these complexes, as reported in Tables VI.1. and VI.2., suggest that the metal is in +2 oxidation state. The magnetic moment data ( $\mu_{eff} = 3.4$  to  $3.6$  B.M.) are characteristic of nickel(II) in high spin state. These penta-coordinated complexes may have a distorted trigonal bipyramidal geometry in the solid state. In solution, most probably, a tetrahedral geometry is obtained by the liberation of one of the coordinated DMF or DMSO molecule as evidenced by visible spectra (discussed later). Examples of nickel(II) complexes with distorted trigonal bipyramidal structure in the solid state and tetrahedral structure in solution are reported.<sup>22</sup> The conductivity measurements in acetonitrile show that all the complexes are non-electrolytes.

The infrared spectra (Table VI.2.) of the DMF complexes show a very strong band around  $1645\text{ cm}^{-1}$  besides other bands due to DMF and triphenylphosphine. (Infrared spectrum of  $[NiBr_2(PPh_3)(DMF)_2]$  is given in fig. no. VI.1.). The band at  $1645\text{ cm}^{-1}$  can be assigned to  $\nu_{CO}$  of the amide, bonded to the metal through the oxygen atom.  $\nu_{CO}$  of amides on

Table VI. 1. Physical Properties and Analytical Data for the Complexes

Compound	Colour	M.P. °C	$\mu_{\text{eff}}$ (B.M.)	Analysis : Found (Calc.) %				
				C	H	Halogen	Metal	N/S
$[\text{NiCl}_2(\text{DMSO})_2(\text{PPh}_3)_2]$	Blue	175-78d	3.63	43.38 (48.15)	5.15 (4.92)	13.27 (12.95)	11.21 (10.70)	11.83 (11.67)
$[\text{NiBr}_2(\text{DMSO})_2(\text{PPh}_3)_2]$	Green	115-18d	3.58	41.54 (41.43)	4.13 (4.23)	25.32 (25.10)	9.38 (9.21)	10.21 (10.04)
$[\text{NiCl}_2(\text{DMF})_2(\text{PPh}_3)_2]$	Dark Blue	140-45d	3.40	53.59 (53.51)	5.43 (5.38)	13.39 (13.19)	11.25 (10.90)	5.65 (5.20)
$[\text{NiBr}_2(\text{DMF})_2(\text{PPh}_3)_2]$	Dark Green	123-25d	3.42	45.78 (45.91)	4.43 (4.62)	25.83 (25.51)	9.78 (9.35)	4.24 (4.46)
$[\text{CoCl}_2(\text{DMSO})(\text{PPh}_3)_3]$	Blue	70-75d	4.88	51.10 (51.03)	4.39 (4.46)	15.33 (15.09)	12.74 (12.54)	6.29 (6.80)
$[\text{CoBr}_2(\text{DMSO})(\text{PPh}_3)_3]$	Light Blue	112-15d	-	42.76 (42.91)	3.69 (3.75)	28.35 (28.60)	10.42 (10.53)	5.38 (5.72)
$[\text{CoCl}_2(\text{DMF})(\text{PPh}_3)_3]$	Dark Blue	135-40d	4.86	53.85 (54.15)	4.96 (4.72)	15.32 (15.25)	12.34 (12.65)	3.34 (3.00)
$[\text{CoBr}_2(\text{DMF})(\text{PPh}_3)_3]$	Blue	145-48d	-	45.23 (45.46)	3.89 (3.96)	29.01 (28.86)	10.54 (10.62)	2.72 (2.52)

d = decomposes; Figures in the brackets indicate the calculated percentages of the elements present in the compounds.

Table VI. 2. Electronic Absorption, Reflectance and Important Infrared Spectral Data of the Complexes

Complexes	Electronic absorption $\nu_{\max}$ in $\text{cm}^{-1}$ ( $\epsilon_{\max}$ )	Reflectance $\nu_{\max}$ in $\text{cm}^{-1}$	Infrared in $\text{cm}^{-1}$
$[\text{Ni}(\text{PPh}_3)\text{Cl}_2(\text{DMF})_2]_2$	15,625 (75); 16,800 (70)	10,600; 13,000 14,200; 25,000	1640 vs 1370 s 1100 m
$[\text{Ni}(\text{PPh}_3)\text{Br}_2(\text{DMF})_2]_2$	14,600 sh ; 15,625 (81) 26,900(1100);39,000(3150)	10,640; 13,000sh 14,700; 23,000 25,640	1645 vs 1378 s 1110 m 385 m
$[\text{Ni}(\text{PPh}_3)\text{Cl}_2(\text{DMSO})_2]_2$	15,500 (95); 16,900 (92) 27,400 (1320)	10,640; 13,160 14,700; 26,300	1640 m,br 1315 w 996 m 952 m 933 m
$[\text{Ni}(\text{PPh}_3)\text{Br}_2(\text{DMSO})_2]_2$	14,300 (75); 15,430 (97) 16,400 sh	-	1630 m,br 1315 w 995 m 947 m 933 m

Table VI. 2..... contd...../-

Table VI. 2. Electronic Absorption, Reflectance and Important Infrared Spectral Data of the Complexes

Complexes	Electronic Absorption $\nu_{\max}$ in $\text{cm}^{-1}$ ( $\epsilon_{\max}$ )	Reflectance $\nu_{\max}$ in $\text{cm}^{-1}$	Infrared in $\text{cm}^{-1}$
$[\text{Co}(\text{PPh}_3)_2\text{Cl}_2(\text{DMSO})]$	14,700 (580); 15,950 (325) 16,340 (330); 17,030 (335) 17,480 (335); 39,200 (3200)	-	1630 m, br 1315 w 998 m 953 m
$[\text{Co}(\text{PPh}_3)_2\text{Br}_2(\text{DMSO})]$	14,640 (630); 15,380 sh 15,830 (410); 16,220 (380) 16,950 sh	-	1628 m, br 1318 w 995 m 950 m
$[\text{Co}(\text{PPh}_3)_2\text{Cl}_2(\text{DMF})]$	14,700 (460); 15,920 (280) 16,340 (310); 17,000 (270) 17,480 (310); 39,000(7400)	14,000; 15,150sh 16,950; 18,180sh	1640 vs 1375 s 1110 m 377 m
$[\text{Co}(\text{PPh}_3)_2\text{Br}_2(\text{DMF})]$	14,600 (565); 15,380 sh 15,830 (390); 16,220 (345) 16,950 sh	-	1645 vs 1378 s 1110 m 375 m

Vs = very strong; s = strong; m = medium; w = weak; br = broad.

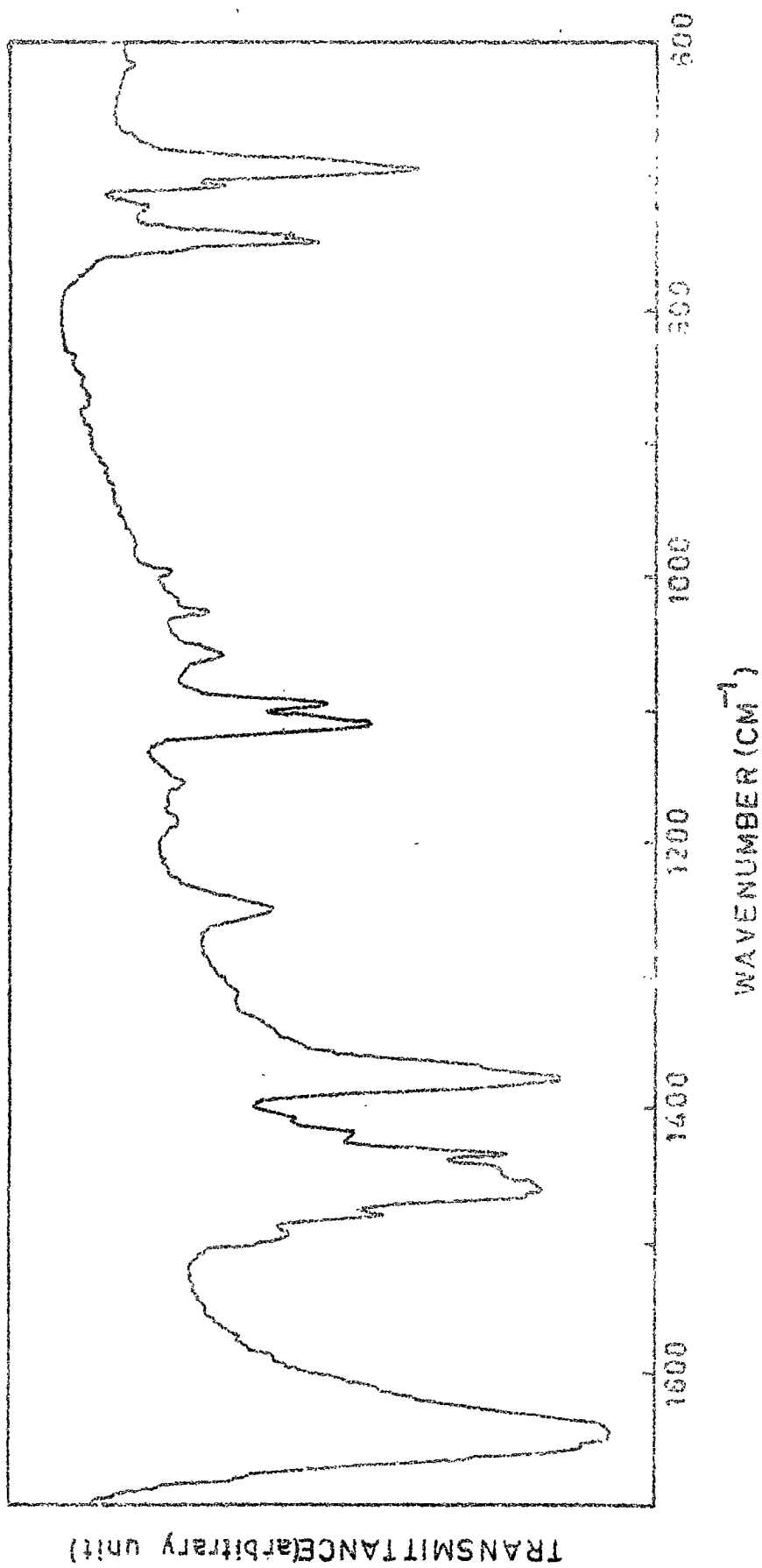


Fig. VI-1. Infrared Spectrum of  $[\text{NiBr}_2(\text{PPh}_3)(\text{DMF})_2]$  in Nujol.

coordination with the metals through oxygen is shifted towards lower energy ( $\nu_{\text{CO}}$  in free DMF is observed at  $1670 \text{ cm}^{-1}$ ).<sup>23</sup> A band of medium intensity around  $385 \text{ cm}^{-1}$  observed in both the complexes could be assigned to  $\nu_{\text{Ni-P}}$ .<sup>24</sup> The infrared spectra of the DMSO complexes show a band around  $995 \text{ cm}^{-1}$  of medium intensity besides other bands due to DMSO and triphenylphosphine. Infrared spectrum of  $[\text{NiBr}_2(\text{PPh}_3)(\text{DMSO})_2]$  is given in fig. no. VI.2. The band at  $995 \text{ cm}^{-1}$  could be assigned to  $\nu_{\text{SO}}$  of the oxygen bonded DMSO. A shift of  $\nu_{\text{SO}}$  to a lower frequency upon coordination of DMSO through oxygen atom is reported for many compounds ( $\nu_{\text{SO}}$  for free DMSO molecule is observed at  $1040 \text{ cm}^{-1}$ ).<sup>25,26</sup> The absence of bands at  $1670 \text{ cm}^{-1}$  and  $1040 \text{ cm}^{-1}$  in the DMF and DMSO complexes respectively suggest the absence of uncoordinated DMF or DMSO, thereby confirming that all the DMF or DMSO molecules are coordinated to the metal.

The reflectance data (Table VI.2.) of the Ni(II) complexes seem to support a distorted trigonal bipyramidal structure in the solid state. The reflectance spectra of the nickel(II) compounds show absorptions around 10,600; 13,000; 14,500; 23,000 and  $25,500 \text{ cm}^{-1}$ . Energy level diagram for high-spin trigonal bipyramidal Ni(II) complexes with a  $D_{3h}$  symmetry have been reported by Ciampolini.<sup>27</sup> According to which the above absorptions could be assigned as follows:-

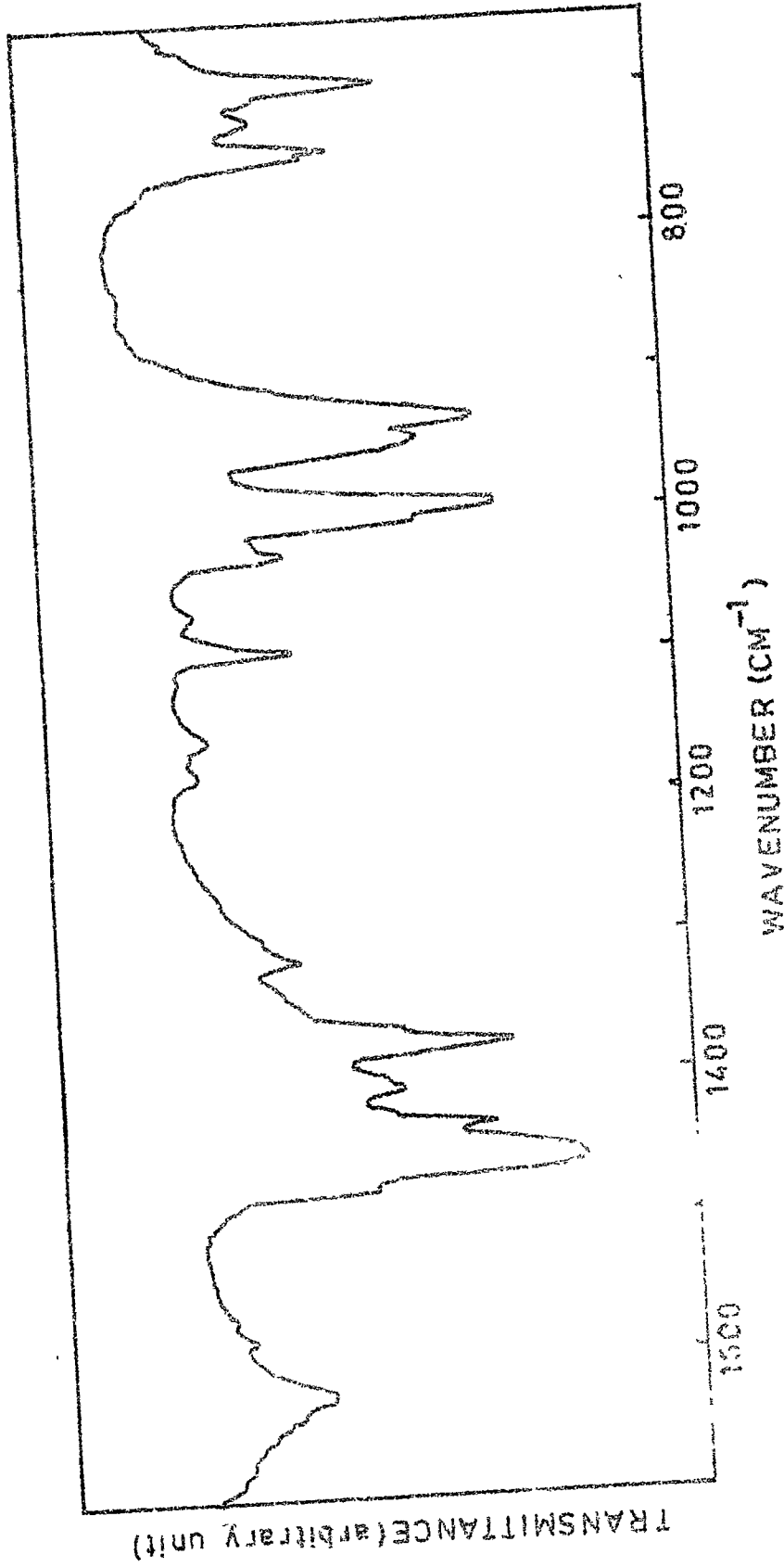


Fig. VI.2. Infrared Spectrum of  $[\text{NiBr}_2(\text{PPh}_3)_2(\text{DMSO})_2]$  in Nujol

10,600 cm <sup>-1</sup>	:::	${}^3E'(F) \longrightarrow {}^3A_2''(F)$
13,000 cm <sup>-1</sup>	:::	${}^3E'(F) \longrightarrow {}^1E''(D)$
14,500 cm <sup>-1</sup>	:::	${}^3E'(F) \longrightarrow {}^3A_2'(F)$
23,000 cm <sup>-1</sup>	:::	${}^3E'(F) \longrightarrow {}^3E''(P)$
25,500 cm <sup>-1</sup>	:::	${}^3E'(F) \longrightarrow {}^3A_2'(P)$

Similar observations have been reported for  $[\text{Ni}(\text{Me}_6\text{tren})\text{Br}_2]\text{Br}$ , a pentacoordinated trigonal bipyramidal compound.<sup>28</sup>

The visible spectral studies of the complexes in solution (acetonitrile) reflect the tetrahedral nature in the solution. An asymmetrical broad band in the region 14,000-17,000 cm<sup>-1</sup> is observed in all the complexes of nickel(II) reported here, which on resolution gives two bands, separated by about 1000 cm<sup>-1</sup> (Table VI.2.). The electronic spectra of  $[\text{NiX}_2(\text{PPh}_3)(\text{DMSO})_2]$  (X = Cl or Br) in acetonitrile are given in fig. no. VI.3. The molar extinction coefficient (between 70 to 100) is in the range for the nickel(II) tetrahedral complexes. The broad band around 15,500 cm<sup>-1</sup> could be assigned to  ${}^3T_1(F) \longrightarrow {}^3T_1(P)$  transition of the tetrahedral systems. The splitting of this band into two could be due to the lowering of symmetry of the ligand field around the central nickel atom.  ${}^3T_1(P)$  term may be split into one component of two-fold orbital degeneracy at one energy and another non-degenerate component at a different energy.<sup>29</sup>

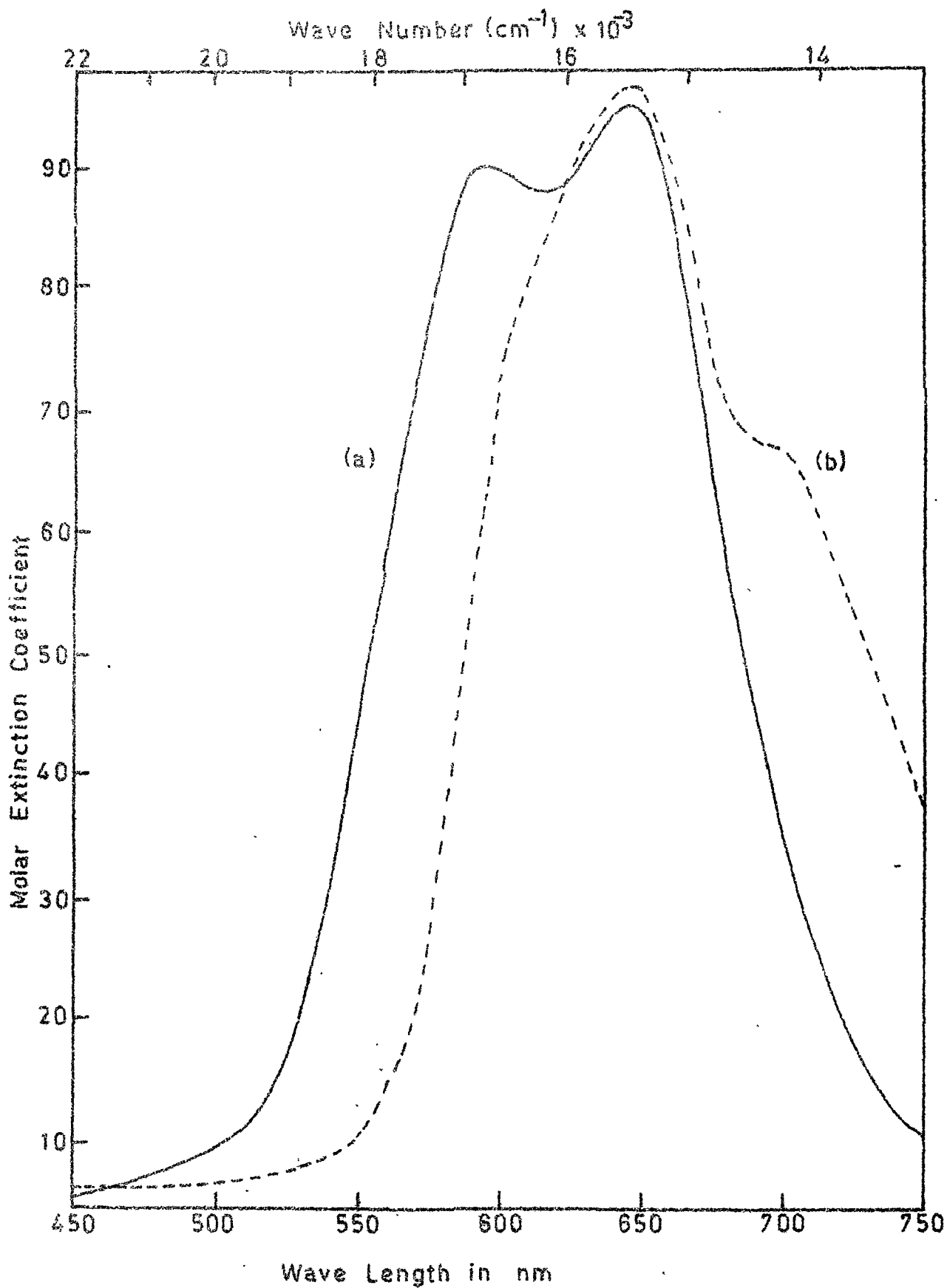
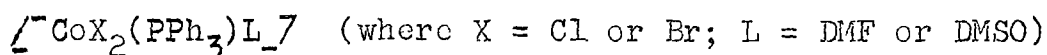
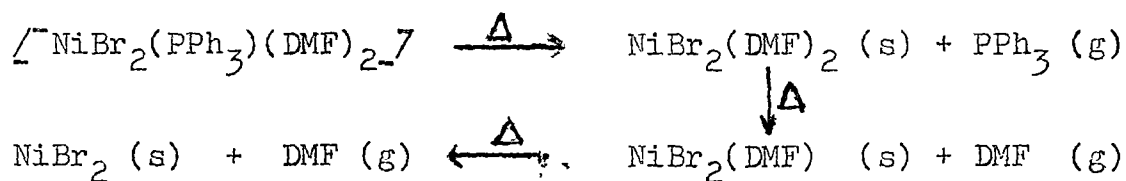


Fig. VI. 3. Electronic Spectra of (a)  $[\text{NiCl}_2(\text{PPh}_3)(\text{DMSO})_2]$   
(b)  $[\text{NiBr}_2(\text{PPh}_3)(\text{DMSO})_2]$  in Acetonitrile.

From the thermogravimetric analysis of  $[\text{NiBr}_2(\text{PPh}_3)(\text{DMF})_2]$  in static air, the complex is found to start dissociating at about  $120^\circ\text{C}$  and complete loss of triphenylphosphine molecule is observed at  $300^\circ\text{C}$ . A horizontal mass level, corresponding to  $\text{NiBr}_2(\text{DMF})_2$  is observed between  $320\text{--}360^\circ\text{C}$ . The loss of one DMF molecule gives an inflection at  $420^\circ\text{C}$  and another inflection at  $560^\circ\text{C}$  corresponds to the loss of the second DMF molecule. The results of thermal dissociation products analysis can be, represented as:-



On the basis of analytical data, the empirical formula for the cobalt complexes is found to be  $[\text{CoX}_2(\text{PPh}_3)\text{L}]$  (where X = Cl or Br; L = DMF or DMSO). The physical data of the complexes as reported in Tables VI.1. and VI.2. suggest that the metal is in +2 oxidation state. The magnetic moment data ( $\mu_{\text{off}}$  4.9 B.M.), is characteristic of cobalt(II) tetrahedral complexes in high spin state. The conductivity studies in acetonitrile conform to the non-ionic structure of these complexes.

The infrared studies give informations similar to that obtained in the nickel complexes. A strong band around  $1640\text{ cm}^{-1}$  and a medium band at  $377\text{ cm}^{-1}$  could be assigned to  $\nu_{\text{CO}}$  of the amide and  $\nu_{\text{Co-P}}$  of the DMF complexes. The infrared spectrum of  $[\text{CoCl}_2(\text{PPh}_3)(\text{DMF})]_7$  is given in fig. n. VI.4. The cobalt complexes containing DMSO show a strong band around  $995\text{ cm}^{-1}$  assigned to  $\nu_{\text{SO}}$  of the O-bonded DMSO. The absence of bands at  $1670\text{ cm}^{-1}$  and  $1040\text{ cm}^{-1}$  in the DMF and DMSO complexes respectively, confirm that the DMF or DMSO molecule is coordinated to the metal. The electronic spectra of these complexes conforms to the distorted tetrahedral structure of the complexes. The electronic spectra of  $[\text{CoX}_2(\text{PPh}_3)(\text{DMF})]_7$  ( $X = \text{Cl}$  or  $\text{Br}$ ) in acetonitrile are given in fig. no. VI.5. The bands in the region  $14,700\text{-}17,500\text{ cm}^{-1}$  are due to the transition  ${}^4\text{A}_2(\text{F}) \longrightarrow {}^4\text{T}_1(\text{P})$  in tetrahedral cobalt(II) systems. Here spin orbit coupling is a smaller perturbation than the low symmetry field and the tetrahedral level  ${}^4\text{T}_1(\text{P})$  splits into components  $\text{B}_2 < \text{A}_2 < \text{B}_1$ . Hence three absorption bands for transition from  ${}^4\text{A}_2(\text{F})$  level to the three singly degenerate  $\text{B}_2$ ,  $\text{A}_2$  and  $\text{B}_1$  states are expected to be observed.<sup>30</sup> However, spin orbit coupling which mixes the  ${}^4\text{T}_1$  and components of  ${}^2\text{G}$  state could be an answer to the type of band observed in the region  $14,700\text{-}17,500\text{ cm}^{-1}$ . The electronic absorption spectrum pattern of the cobalt complexes in the region  $14,700\text{-}17,500$  is very similar to any one of

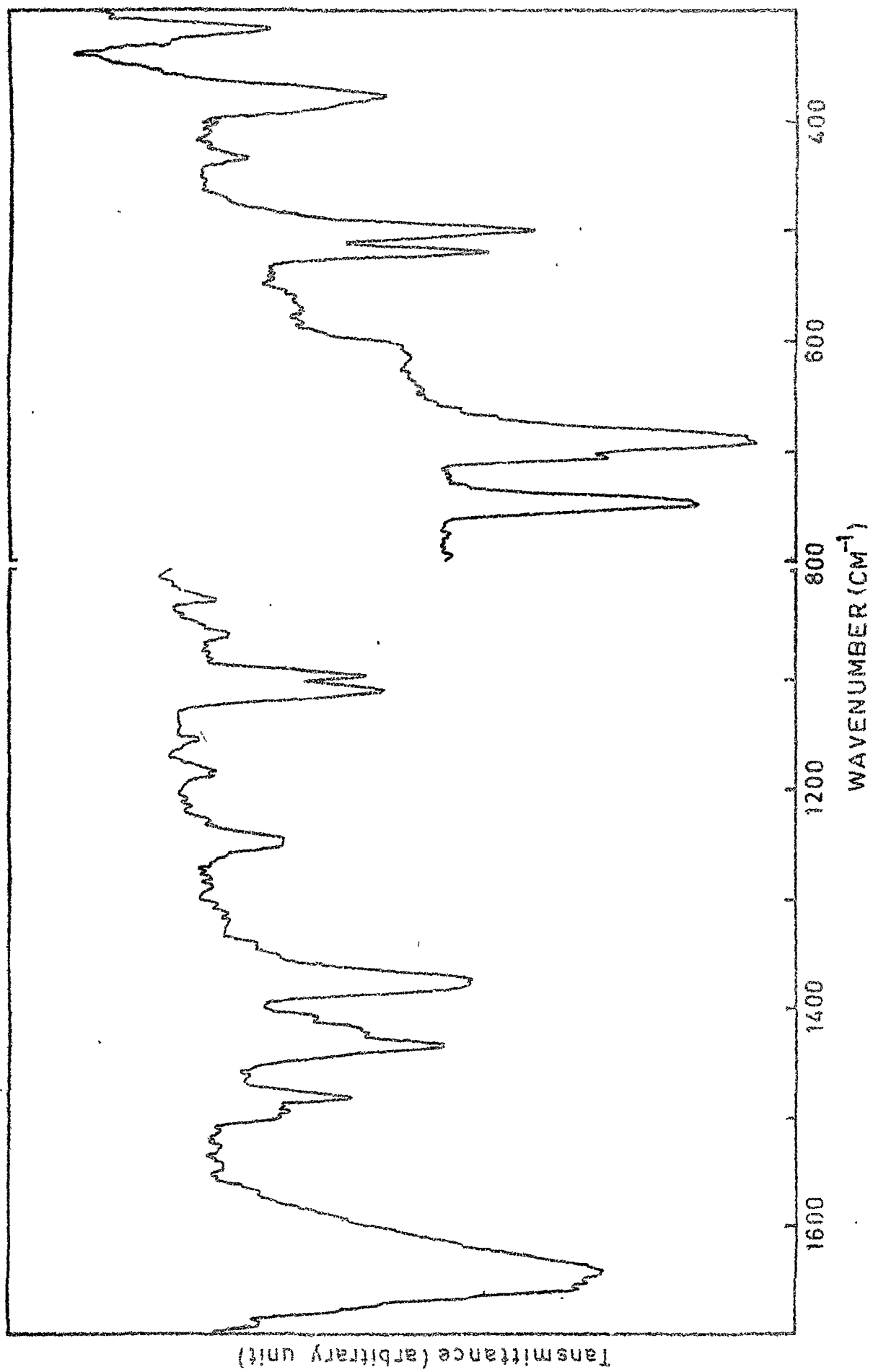


Fig. VI-4. Infrared Spectrum of  $[\text{CoCl}_2(\text{PPh}_3)_2(\text{DMF})]$  in KBr.

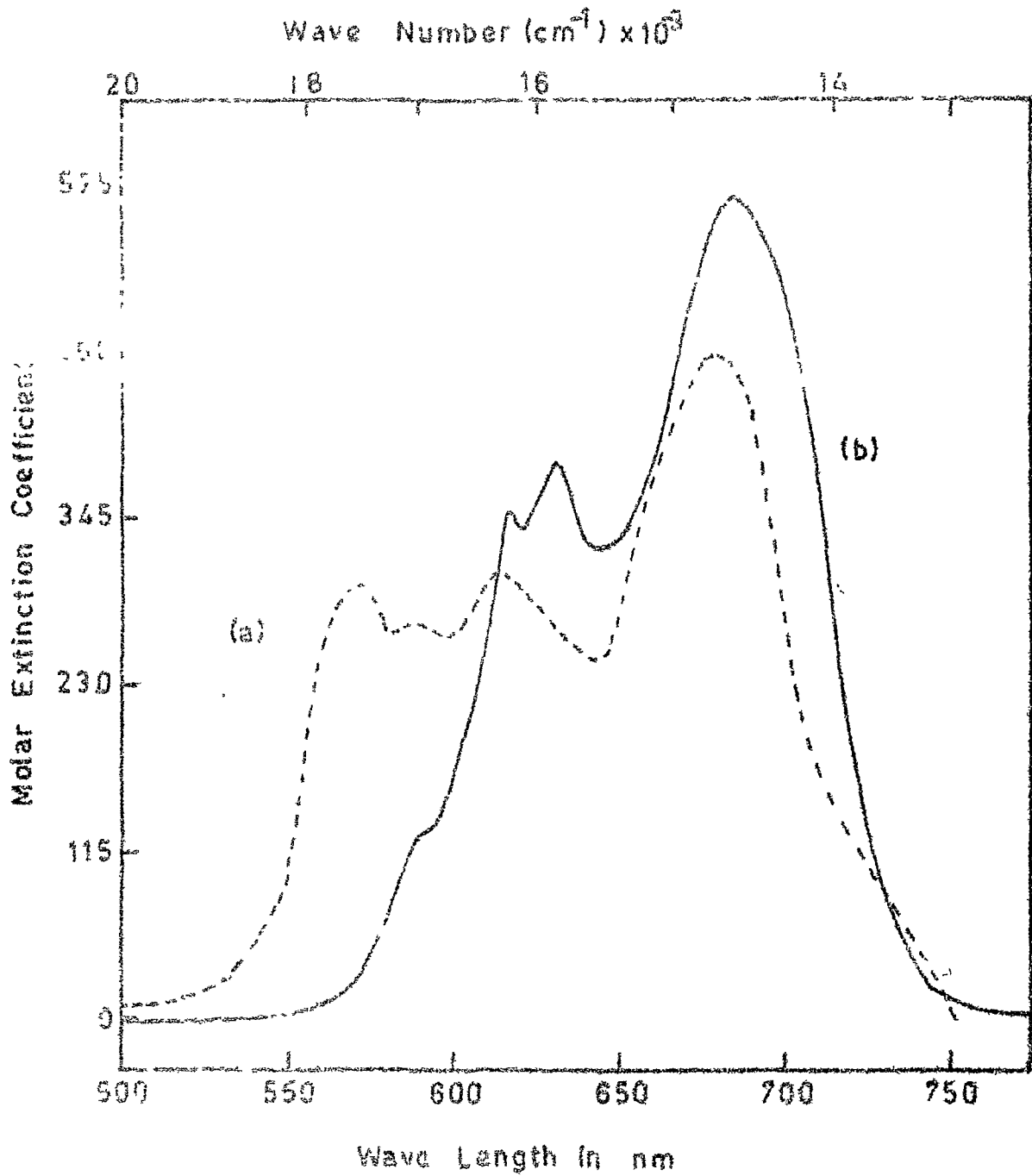


Fig. 11-5. Electronic Spectra of (a)  $[\text{CoCl}_2(\text{PPh}_3)(\text{DMF})]$   
(b)  $[\text{CoBr}_2(\text{PPh}_3)(\text{DMF})]$  in Acetonitrile.

the tetrahedral cobalt(II) complexes.<sup>31</sup> An absorption in the uv region at  $39,000\text{ cm}^{-1}$  with very high molar extinction coefficient could be assigned to metal  $\longrightarrow$  ligand charge transfer band.

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SUMMARY AND SCOPE FOR FURTHER WORK

Transition Metal complexes of monodentate ligands of strong donor, weak donor or of both strong and weak donor ligands are of considerable interest to the chemists, for their interesting structural, synthetic and catalytic behaviours. Present work describes the synthesis and some of physical and chemical studies on the complexes of nickel(II), nickel(III), cobalt(II) and ruthenium(II) having some monodentate ligands.

Ruthenium(II) complexes of the type  $[\text{Ru}(\text{MPh}_3)(\text{C}_6\text{H}_5\text{CHO})_2\text{Cl}_2]$  (M = P or As), containing both strong and weak donor ligands are synthesized. These complexes have penta coordination around ruthenium(II) with a distorted pyramidal structure. Reactions have been carried out to study the ease of substitution of benzaldehyde in the ruthenium(II) complexes by other weak donor ligands. The penta-coordinated ruthenium(II) complexes have a great potential to act as catalyst in homogeneous reactions. Work along this line is being taken up to explore the potential of these complexes as catalysts. Some ruthenium(II) carbonyl complexes of the type  $[\text{Ru}(\text{CO})(\text{MPh}_3)_2\text{Cl}_2]$  (M = P or As) are also synthesized and physical and chemical studies made.

The reaction of nitrosyl chloride with  $[\text{Ni}(\text{PPh}_3)_2\text{X}_2]$  ( $\text{X} = \text{Cl}, \text{Br}, \text{NO}_3$  or  $\text{NCS}$ ) have been carried out under two different conditions whereby complexes of the type  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]_2$  and  $[\text{Ni}(\text{OPPh}_3)\text{XCl}]_2$  are obtained. On the basis of physical measurements and chemical reactions, it is proposed that the complexes have a dimeric structure with a distorted tetrahedral environment around the nickel atom with chloro-bridges. Reactions of the above mentioned dimeric complexes with triphenylphosphine resulted in the formation of the complexes of the type,  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$  ( $\text{X} = \text{Br}, \text{NO}_3, \text{NCS}$ ). A distorted tetrahedral structure for  $[\text{Ni}(\text{PPh}_3)_2\text{XCl}]$  ( $\text{X} = \text{Br}$  or  $\text{NO}_3$ ) and a square planar structure for  $[\text{Ni}(\text{PPh}_3)_2(\text{NCS})\text{Cl}]$  is proposed.

A new nickel(III) complex, viz.  $[\text{Ni}(\text{OPPh}_3)\text{Cl}_2\text{I}]$  has been synthesized by the oxidation of  $[\text{Ni}(\text{PPh}_3)_2\text{I}_2]$  with nitrosyl chloride or chlorine. With the help of magnetic and e.s.r. studies and some chemical reactions, the oxidation state of the metal is confirmed to be +3. With the help of other physical measurements a distorted tetrahedral geometry around nickel(III) is proposed. This complex is found to act as a catalyst in the oxidation of triphenylphosphine to triphenylphosphine oxide and of cyclohexanol to cyclohexanone as an oxidant for the oxidation.

Further work in this line, to synthesize nickel(III) complexes using chemical oxidants will help in systematising the syntheses of nickel(III) complexes. Investigation of the catalytic activity of such nickel(III) complexes will also be interesting.

Nickel(II) complex cations of the type

$[\text{Ni}(\text{OPPh}_3)_2\text{X}]_2^{+}[\text{Y}_3]_2^{-}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) with trihalides ( $\text{Y}_3 = \text{Br}_3^{-}$  or  $\text{IBr}_2^{-}$ ) as the counter anions are synthesized and their physical and chemical behaviours studied. These are some of the very few metal cationic complexes studied which stabilized polyhalides anions. More work along this line can be carried out and the complex cations may be synthesized which will stabilize other bigger polyhalide anions also.

The preparation of nickel(II) thiocyanate by a convenient one step method and its various physical properties in solid and in solution have been studied. It has been used as starting material for preparing many compounds containing nickel thiocyanate and other ligands containing donor atoms such as oxygen, nitrogen or phosphorus. The physical properties of such compounds have been studied to know their structures and mode of bonding of thiocyanate to the metal. Nickel(II) thiocyanate prepared according to this method can be used for the syntheses of other complexes

containing nickel(II) thiocyanate avoiding any impurities due to matatnetical substitution in solution.

Complexes of nickel(II) and cobalt(II) containing both strong and weak donor ligands, viz.  $[\text{Ni}(\text{PPh}_3)_2\text{L}_2\text{X}_2]$  and  $[\text{Co}(\text{PPh}_3)_2\text{LX}_2]$  (L = DMF or DMSO ; X = Cl or Br) have been synthesized and characterised with the help of various physical data, including infrared and electronic spectra, magnetic and conductivity measurements and thermogravimetric analyses. With the help of physical studies, it is proposed that the nickel(II) complexes have distorted trigonal bipyramidal geometry in the solid state and a tetrahedral geometry in solution (when one molecule of DMF or DMSO is lost in the solution) and the cobalt complexes have a distorted tetrahedral geometry around the metal ion. Transition metal complexes containing both strong and weak donor ligands are found to act as good catalyst by the loss of one or two weakly coordinated ligand molecule in the solution. Hence further work on these complexes in this direction will yield more information about their catalytic behaviour too.

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