SYNTHESIS, STRUCTURAL ASSESSMENT AND SOME REACTION PROFILES OF PEROXO COMPLEXES OF V, Mo AND UO_2^{2+}, A FLUORO COMPOUND OF Cr,

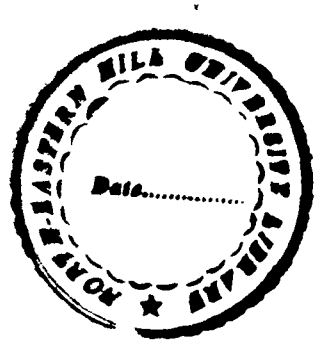
AND

MIXED-LIGAND MOLECULAR COMPLEXES OF THE TYPE M $(acac)_2(dmpz)_n$ [dmpz = 3, 5-dimethylpyrazole, M=Mn, Co, Ni; n=2, M=VO^{2+}; n=1, AND M=UO_2^{2+}; n=4]

ABSTRACT

BY

DEEPA DEY



DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES

SUBMITTED

In fulfilment of the requirement of the Degree of

DOCTOR OF PHILOSOPHY

in

CHEMISTRY

of

NORTH-EASTERN HILL UNIVERSITY

SHILLONG-793003

INDIA

Thesis

SYNTHESIS, STRUCTURAL ASSESSMENT AND SOME REACTION PROFILES OF PEROXO COMPLEXES OF V, Mo AND UO_2^{2+}, A FLUORO COMPOUND OF Cr,

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ABSTRACT

The thesis, consisting of six chapters, deals with the results of investigation on some chosen aspects of the chemistry of peroxo and heteroligand peroxo complexes of vanadium, molybdenum and uranium including peroxo-metal mediated oxidation of Br^- to Br_3^- leading to the synthesis of organic ammonium tribromide, and the synthesis and structural assessment of some mixed-ligand metal acetylacetonate complexes of manganese, nickel, cobalt, uranium and vanadium along with an easy synthesis of pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$ (PFC).

Chapter I provides a brief background of the types of problems selected for the present Ph.D. research. The importance of and the interest in the chemistry of dioxygen, in general, and peroxo and heteroligand peroxo compounds of vanadium, molybdenum and uranium in particular are highlighted. Apart from the importance of studies of peroxo-chemistry, attention has been drawn to the study of mixed-ligand metal acetylacetonato complexes. Also emphasised in this chapter is the importance of chromium(VI) reagents as useful oxidants for organic substrates and some need for further studies. Scope of work in the chosen topics has been highlighted.

Chapter II presents details of the methods adopted for the preparation of starting materials, elemental analyses, and instruments/equipment used for characterisation and structural assessment of the newly synthesised compounds.

Synthesis, characterisation and structural assessment, and reactivity of heteroligand peroxovanadate and heteroligand peroxomolybdate constitute the basis of chapter III. Heretofore unreported dioxo diperoxo-μ-peroxotetrakis(3,5dimethylpyrazole)divanadium(V), $[V_2O_2(O_2)_3(dmpz)_4]$,and oxodiperoxo-bis(3,5-dimethylpyrazole)molybdenum(VI), $[MoO(O_2)_2(dmpz)_2]$, have been synthesised from the reaction of V_2O_5 with 30% H_2O_2 at pH 2 followed by addition of 3,5-dimethylpyrazole, and the reaction of $(NH_4)_6Mo_7O_{24}.4H_2O$ with 30% H_2O_2 at pH 5 followed by the addition of powdered 3,5-dimethylpyrazole, respectively. The compounds have been characterised from the results of elemental analyses, determination of molar conductance in water and methanol in case of $[V_2O_2(O_2)_3(dmpz)_4]$ and in water for $[MoO(O_2)_2(dmpz)_2]$, IR, Laser Raman and UV-Vis spectroscopies, TG and DSC experiments. In both the cases peroxide (O_2^{2-}) is bonded in a side-on (C_{2v}) fashion. Vibrational spectra of the compounds also show the co-ordination of 3,5-dimethylpyrazole through tertiary nitrogen atom, i.e. the pyridine nitrogen of the pyrazole nucleus. Two well resolved LMCT (O_2^{2-}—M) bands due to $\pi_h^* \rightarrow d_\sigma^*$ at *ca.*214nm and due to $\pi_v^* \rightarrow d_\sigma^*$ at *ca.*326nm have been observed in the electronic spectra of the compounds.

Oxidation of some organic substrates have been carried out separately with both the reagents to ascertain their efficacy as oxidising agents. The reagents are expected to be environmentally favorable owing to the presence of non toxic metals and peroxide.

Chapter IV describes an improved synthesis of $(NH_4)_2[UO_2(O_2)F_2].H_2O$, and $K_2[UO_2(O_2)F_2(H_2O)]$ along with the synthesis of new μ-peroxo-dimeric compounds of uranium, $A_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ ($A=NH_4^+$, K^+ or Na^+). $(NH_4)_2[UO_2(O_2)F_2].H_2O$, and $K_2[UO_2(O_2)F_2(H_2O)]$ have been synthesised by the reaction of $UO_3.4H_2O$ with 30% H_2O_2 in the presence of the corresponding bifluoride, AHF_2. Whereas the general synthesis of $A_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ has been based on the reaction of $UO_2(NO_3)_2.6H_2O$ with 30% H_2O_2 at pH 10 maintained by addition of the corresponding hydroxide. One of the significant features of the new syntheses of the fluoro-peroxo uranium compounds is the redundancy of the use of hydrofluoric acid. All the compounds were characterised by elemental analyses, IR spectroscopy and TG, DSC studies.

Chapter V provides evidences for the peroxo-vanadium mediated generation of Br_3^-. This is believed to be important in understanding the nature of the intermediate involved in the reactions catalysed by vanadium bromoperoxidase (V-BrPO). Tribromide thus generated *in situ* from bromide oxidation by vanadium-peroxo complexes was trapped in aqueous solution by a heavy cation, *viz.,* tetrabutylammonium ion. The tribromide has been characterised by elemental analyses, IR, UV-Vis spectroscopies and solution electrical conductance measurements. The major concern in the present context was to investigate its efficacy as an environmentally friendly brominating agent. Bromination of some selected organic substrates has thus been carried out to ascertain its efficacy. The major advantage of the new protocol lie in the ease of synthesis of the reagent and redundancy of the hazardous chemicals like Br_2 and HBr, and the ease in maintaining stoichiometry of the reagent.

Chapter VI, indeed the concluding chapter of the thesis provides information regarding the synthesis of mixed-ligand metal acetlyacetonato complexes starting from the corresponding metal-acetlyacetonato dihydrate as the precursors. The synthesis has been based on the reaction of $M(acac)_2.2H_2O$ (M=Mn, Ni, Co or UO_2^{2+}) with 3,5-dimethylpyrazole resulting to the formation of $M(acac)_2(dmpz)_2$ (M= Mn, Ni or Co) $UO_2(acac)_2(dmpz)_4$. The vanadium analog $VO(acac)_2(dmpz)$ was obtained by the reaction of $VOSO_4.H_2O$ with acetylacetone and 3,5-dimethylpyrazole in ethanol. The compounds were isolated in good yields, and were characterised by elemental analyses, IR, UV-Vis and ESR spectroscopies, TG and DSC studies. Apart from the mixed ligand metal acetylacetonate complexes, an easy synthesis of pyridinium fluorochromate (PFC), achieved by the reaction of CrO_3 with NH_4HF_2 and pyridine, has been reported.

The results of studies described in chapter V and chapter VI in part have been published, the work described in chapter IV is under revision, while the manuscripts based on the contents of chapter III and chapter VI in part are now being prepared.

Chapter IV

Inorg.Synth.(under revision)

Chapter V

Tetrahedron Letter, 1998, **39,** 8163.

Chapter VI

J Fluorine Chemistry, 1997, **81**, 211.

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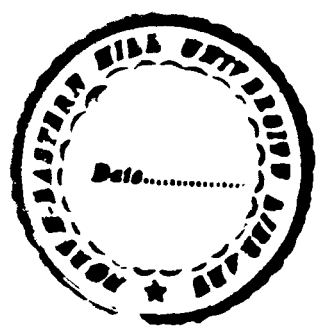

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DEDICATED

TO

KARGIL HEROES

Declaration

THE NORTH-EASTERN HILL UNIVERSITY

Month : August, Year : 1999

I, Miss Deepa Dey hereby declare that the subject matter of the thesis is the record of work done by me, that contents of this thesis did not form the basis of the award of any previous degree to me or to the best of my knowledge to anybody else, and that the thesis has not been submitted by me for any other research degree in any other University/ Institute.

This is being submitted to the North-Eastern Hill University for the degree of **DOCTOR OF PHILOSOPHY in Chemistry**.

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ACKNOWLEDGMENT

With immense pleasure I take this opportunity to place on record my heartfelt gratitude to my research guide, Professor Mihir K.Chaudhuri, FASc, FNA, now in Indian Institute of Technology, Guwahati for his invaluable guidance, tireless efforts, constant encouragement and supervision which enabled me to succeed in this endeavor.

I am grateful to Professor M.K.Mahanti, Head, Department of Chemistry, North-Eastern Hill University, Shillong for accepting to supervise me in the absence of Professor Chaudhuri, enabling me to complete the research work and for rendering valuable suggestions and help.

I am greatly indebted to my laboratory seniors for their suggestions, cooperation and inspiration over all these years.

My thanks are due to the Faculty members of Chemistry Department, NEHU, the Dean, School of Physical Sciences, the Head, RSIC, NEHU. I also wish to thank all the non-teaching staff members of the Department of Chemistry and the technical staff of RSIC, NEHU for their assistance I have received during tenure of research.

I feel very happy to acknowledge the help, inspiration and good wishes of all those who stood by me during the period of my Ph.D. work.

I am thankful to the authorities of Assam Rifles for providing me with hostel facilities and permitting me to carry out the research work.

Senior Research Fellowship (SRF) received from Council of Scientific and Industrial Research(CSIR), New Delhi and Departmental Fellowship under the UGC

Special Assistance Programme(SAP), enabling me to carry out the work smoothly is greatly acknowledged.

My heartfelt gratitude goes to my parents for their constant support, encouragement and affection. It is because of their continued help that I have been able to reach this stage. My thanks are also due to my sister, brother, brother-in-law, sister-in-law and other members of the family.

Finally, I convey my gratefulness to all INANIMATE and ANIMATE entities of the whole universe.

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CHAPTER I

INTRODUCTION

[Background and Scope of Work]

The research work included in the present thesis can broadly be divided into two parts, of which the first part deals with the peroxo chemistry of metals *viz.,* vanadium, molybdenum and uranium. The second part of the thesis records work related to metal-fluoro and mixed ligand metal-acetylacetonato chemistry with chromium, uranium, vanadium, manganese, nickel and cobalt being the metals involved.

The capability of molecular oxygen in acting as a reagent in biochemical and industrial processes has attracted biochemists and industrial chemists alike in their pursuit in studying various aspects of oxygen transport and in the development of homogeneous analogs for heterogeneously catalysed reactions. With the isolation, characterisation and study of reaction of stable dioxygen complexes, it has become possible to get information about bonding, structure and reactivity of co-ordinated dioxygen. Further the interactions

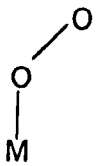
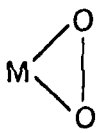
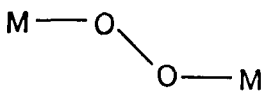
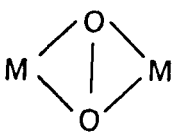
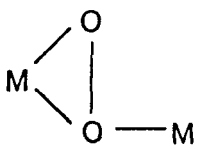
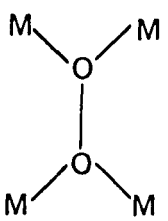
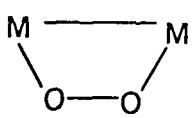
of dioxygen and its reduced forms with transition metal ions represent an important class of reactions in chemical catalysis and bioinorganic chemistry.

The term oxygen refers only to uncoordinated O_2 molecule. As a generic designation dioxygen implies either co-ordinated or free O_2 entity in any of its oxidation states[1] *viz.*, O_2^+, O_2, O_2^- and O_2^{2-}. Vaska rationalised metal-peroxide complexes as the one in which the co-ordinated dioxygen resembled a peroxide (O_2^{2-}) anion.[1]

Peroxo group binding to metals may range from symmetrical bidentate to a terminal monodentate position, including all possible angles in between. Figure.1 summarises the different kinds of co-ordination modes of dioxygen with transition metals.

In identifying the different types of peroxo complexes, both vibrational and electronic spectrocopies play vital role. Single crystal X-ray crystallography plays an important role in solving the structure but when single crystals are difficult to obtain, both vibrational and electronic spectroscopies play a crucial role in elucidating the structure of the compounds. Peroxo-metal complexes are expected to show three vibrations designated as ν_1(O–O stretching), ν_2(symmetric metal-peroxide stretch) and ν_3(asymmetric metal-peroxide stretch). These vibrations occur at *ca.* 880 cm^{-1}, *ca.* 500 cm^{-1} and *ca.* 600 cm^{-1}, respectively.[10]

Electronic spectroscopy helps in assigning the nature of electronic interaction of O_2 with metal ions in catalysis, in biosystem[11a] and in synthetic products. The highest

Structural Type	Structural Designation (Vaska's Classification)	Example	Ref
	η^2(superoxo)	$[Co(CN)_5(O_2)]^{3-}$	2
	η^2(peroxo)	$[V(O_2)_4]^{3-}$	3
	η^2(superoxo)	$[Cu(O_2)(HB(3\text{-}^tBu\text{-}5\text{-}^iPrpz)_3)]$	4
	η^1:η^1(both peroxo and superoxo)	$\{[Cu(TMPA)]_2(O_2)\}^{2+}$	5,6
	η^2:η^2(peroxo)	$[Cu(HB(3,5\text{-}^iPrpz)_3]_2(O_2)$	7
	η^1:η^2(peroxo)	$[(PO_4)W_4O_4(O_2)_8]^{3-}$	8
		$[Mo_4O_{12}(O_2)_2]^{4-}$	8
		$[Ir_2I_2(CO)_2(\mu\text{-}O_2)(Ph_2PCh_2PPh_2)]$	9

TMPA=tris[(2-pyridyl)methyl]amine

Figure 1 : Structural Classification of Dioxygen Complexes

occupied level in free peroxide ion is the degenerate π_g^* set. On complexation with metal ion the degeneracy of π_g^* is lifted, resulting in two π^* levels defined as π_h^* and π_v^*.[11b] Where π_h^* and π_v^* are horizontal and vertical plane with respect to a plane containing metal and dioxygen. The π_h orbital in the M-O_2 plane forms a σ-bond to the metal and is stabilised to a greater extent then π_v^* which can only form a π-bond with the metal.

Dioxygen complexes are classified in two groups (i) containing only dioxygen ligands or in some cases may contain water molecules and (ii) heteroligand dioxygen complexes where in addition to dioxygen the complex contains one or more monodentate or polydentate ligands.

Peroxide has been known to react with a number of metals including vanadium. Incidentally, the chemistry of vanadium is currently a subject of extensive research partly because of its increasingly recognised biochemical importance.[12-14] The interaction of vanadium with peroxide is known for a long time, leading to the formation of peroxovanadates over nearly the entire pH range. From biochemical point of view, the most interesting aspect of peroxovanadium chemistry, is its biochemical activity in an environment of various heteroligands. And heteroligands are believed to play an important role in stabilising and isolating peroxovanadium compounds. A variety of heteroligands combine with vanadium in the presence of peroxide to afford heteroligand peroxovanadium compounds. Some of these compounds seem to have specific importance including biomodelling and biomimicking.[15,16] Vanadate and peroxide have been shown to mimic insulin activity with maximal effects at least as great as insulin.[15] More recently,

Crans and co-workers have isolated a new bisperoxovanadium compound containing imidazole as an heteroligand with equal or greater insulinomimetic activity.[15] Of the few compounds so far tested positive as potential insulin mimics some were also synthesised in this laboratory[17] a few years ago.

Further, with the discovery of vanadium bromoperoxidase, a vanadium(V)-containing enzyme isolated from marine algae, fungi and a lichen,[18-21] peroxo vanadium compounds are becoming increasingly important. The enzyme catalyses the oxidation of halides by hydrogen peroxide and halogenates the organic substrates or in absence of the organic substrates it disproportionates the second molecule of hydrogen peroxide[22] leading to the formation of singlet oxygen.[23] The halogenated organic substrates in turn are important from medicinal point of view because they have antifungal, antibacterial, antiviral (e.g. anti HIV), antiinflamatory and other properties providing chemical defence to marine organisms.[19]

One of such compounds having antimicrobial activity is aeroplysinin-1(Fig2)

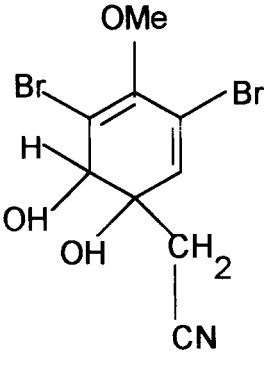


Figure 2

Apart from the peroxovanadium compounds, peroxo molybedenum(VI) compounds have been known for a long time and their catalytic activity has been a topic of considerable interest over the years. Incidentally, the chemistry of molybdenum and vanadium in aqueous solution are quite similar,[24] indeed both the metals exist as oxo species in aqueous solution.

In addition to identifying the nature of such complexes formed in aqueous solution[25,26] at different pH, catalytic oxidations of a variety of organic substrates[27] including alcohols[28] by peroxomolybdenum(VI) system have drawn a considerable attention. A large number of important chemical reactions are catalysed by molybdenum compounds, such as desulphurisation[29] and olefin epoxidation[30] are carried out over molybdenum catalyst.

Like transition metals, actinides too are known to form simple peroxide and heteroligand peroxide complexes. Although the interaction between UO_2^{2+} (uranyl ion) and hydrogen peroxide has been of interest this aspect of uranium chemistry appears to be highly complicated, owing to the formation of a number of different species with a small variation of pH of the reaction solution. For more than a decade our group has been working in the area of peroxo uranium chemistry and reported the synthesis and characterisation of complex peroxouranates having fluoride,[31,32] sulfate, oxalate,[33] carbonate,[34] and amines or amino acids [35] as the co-ligands. As a part of the present Ph.D. work, an improved method of synthesis of peroxouranium containing fluoride as a co-

ligand has been developed. Also accomplished is the synthesis of a dimeric peroxouranate compound.

Apart from what has been discussed about peroxometal complexes, one of the most important aspects of metal peroxo complexes is their reactivity. Co-ordination of peroxide to a metal centre activates peroxide towards the oxidation of a variety of substrates, rendering the metal peroxides important intermediates in biological and chemical catalysis. The reactivity of peroxometal complexes is dependent on many factors such as the identity of the metal atom, the number of the peroxo ligands, and the nature of the remaining ligands in the co-ordination sphere. For instance, peroxo complexes of iron porphyrin compose the active site of catalases and peroxidases,[36] a peroxovanadium(V) intermediate is involved in the activity of vanadium bromoperoxidase,[37] and synthetic peroxo complexes of various metals[8,38,39] catalyse the oxidation of arenes, alcohols, olefins, phosphines, sulfides and halides.[27,40-42]

Peroxovanadium(V) species are involved in several examples of vanadium-mediated reactions, particularly in biological systems. For example, vanadate mediates the oxidation of reduced nicotinamide adenine dinucleotides (NADH, NADPH) in a reaction that may involve superoxide, hydrogen peroxide, and a few radical mediated chain reaction.[43] In addition, vanadyl(IV) ion reduces hydrogen peroxide, which leads to DNA cleavage by hydroxyl radicals.[44] Recently, a number of redox-active transition metal-based nucleases have been shown to cleave DNA and/or RNA with photoactivation[45] or in the

presence of cofactors.[46,47] Phenanthrenequinonediime complexes of Rh(III) are known to recognise and photocleave DNA in a sequence-specific manner,[46,47] and Fe(II)-EDTA[48] its methidium tethered complex,[46] and *bis*(1,10-phenanthroline)Cu^{I} utilise hydrogen peroxide to generate hydroxyl radicals to effect the oxidative cleavage of DNA and RNA.[49,50] Thus it is conceivable that transition-metal complexes with peroxide ligands are likely to be effective nuclease as well. Several vanadium(V)-peroxo complexes have been shown to exhibit antileukemic activities.[51] More recently, Hiort et al. reported the DNA-photocleavage activities of two diperoxovanadium(V) complexes with 1,10-phenanthroline and 4,7-dimethyl 1,10-phenanthroline as ancillary ligands.[52] A mechanism for their photocleavage activities involves singlet oxygen produced from the photolysis of these complexes, and is observed for the first time in vanadium(V).[16]

In the process of our investigation of the reactivity of peroxovanadium(V) systems,[53,54] the oxidation of bromide leading to tribromide was observed. Vanadium bromoperoxidase related biomimetic oxidations of bromide have also been studied in solution by others.[55-60] Consequently, it has become clear that a peroxovanadium(V) intermediate is capable of the catalytic oxidation of bromide. Further, it has been proved by Butler et al. that bromide oxidation by hydrogen peroxide is catalysed by *cis*-dioxovanadium(V). It was also shown by Ramasarma and coworkers,[61] that triperoxodivanadates containing μ-peroxo intermediate are proximal oxidant of bromide in vanadium-catalysed bromoperoxidation.

Other than peroxovanadium compounds, molybdenum peroxides, in particular, have received a considerable attention as reagents for organic transformations.[28,62,63] Specifically notable is molybdenum catalysed epoxidation of propylene by tert-butyl hydroperoxide in Halcon process[64] in which a molybdenum hydroperoxide intermediate is believed to be the active species. A heteroligand oxodiperoxomolybdates containing hmpt (hmpt=hexamethylphosphoric triamide), such as $[MoO(O_2)_2(hmpt)]$, have been used as stoichiometric reagents for a number of organic transformations. A few important examples are the stereospecific conversion of olefins to epoxides,[65-67] enolates to acyloin[68](–C(=O)–CH< → –C(=O)–C(–)(–)–), hydroxylation of cyanide to cynohydrin[69] (>CH–CN → >C(OH)–CN), and naphthalene to naphthol.[70]

Apart from, the importance of peroxo-metal chemistry highlighted above, metal complexes with β–diketonates, particularly involving acetylacetone have been enjoying importance because of their wide applications.[71-82] The metal β-diketonates are a class of unusually volatile metal complexes, surrounded by either a hydrocarbon or fluoro carbon shell, the central metal ion is not as susceptible to the intermolecular forces that characteristically render metal complexes non volatile and insoluble in non-polar solvents but soluble in strongly polar solvents. β–Diketonates derivatives of virtually every metal and metalloid have been synthesised with a wide range of ligands.[83] Metal β–diketonates have found use in fuel additives,[84-87] metal-organic chemical vapour deposition (MOCVD) sources,[88] trace metal analysis by gas chromatography [86,89-93] and numerous

other extraction applications. Only recently has the dissolution of chelating agents in supercritical fluids been explored as a possible route to waste cleanup.[94-100] As mentioned above β–diketonate complexes have many useful appplications, among the most frequently encountered uses are in chemical vapour deposition (CVD) processes that take advantages of the increased volatility of the counter cation, or as complexing agents for the separation of enantiomers. In this method, metal films are formed from volatile metal alkoxides or β–diketonates. Metallisation of microelectronic devices, high quality semiconductor materials for optoelectronic devices, and the preparation of thin films of high temperature superconductors are just a few examples of the areas where CVD has been used.[101] Further, their ability to function as probes for NMR spectroscopic studies has rendered them a useful class of NMR shift reagents.[82] Besides these, metal acetylacetonates constitute a class of good synthons for a variety of compounds.[102,103]

Apart from the importance of and interest in the metal-peroxo and mixed-ligand metal acetylacetonato complexes highlighted above, we have been engaged in developing newer reagents. The search for mild,[104-109] versatile and selective reagents for the operationally simple oxidation of alcohols to carbonyl compounds has long been the objective of many research laboratories. In the process a number of higher valent transition metal oxo derivatives have been successfully used for alcohol oxidation.[104] Of all such reagents chromium(VI) oxidants seem to have been most widely used and studied. Efforts on the development of new reagents and methodologies had led to the introduction of pyridinium fluorochromate (PFC) from our laboratory more than one and half decades

ago.[110] Subsequently its efficacy was ascertained by us [110-112] and others [113-115] and advantages highlighted. Because of its selectivity and controlled acidity, PFC has emerged as the most effective among known chromium(VI) oxidants. Considering its usefulness we decided to improvise an easier alternative synthesis of the reagent. The redundancy of hydrofluoric acid is one of the redeeming features of the new synthesis.

What it follows from the information provided in the foregoing discussion is that there are still a number of issues in the chosen areas that require attention. Accordingly, it was decided to address the following problems as important topics for the present Ph.D.research.

(i) Synthesis of heteroligand peroxo complexes of vanadium and molybdenum, their characterisation and spectroscopic evaluation of structures and their efficacy as oxidising agents. This work has been described in chapter III.

(ii) Newer synthesis of $(NH_4)_2[UO_2(O_2)F_2].H_2O$ and $K_2[UO_2(O_2)F_2(H_2O)]$ without involving hydrofluoric acid and also the synthesis of a dimeric peroxo complex of uranium, is presented in chapter IV.

(iii) Peroxo-vanadium mediated oxidation of Br^- to Br_3^- and trapping of the species by tetrabutylammonium bromide as NBu_4Br_3(TBATB), its characterisation, and especially bromination reactions constituted yet another problem of great importance. Investigation on this has been placed in chapter V.

(iv) The results of studies addressed to the synthesis of mixed-ligand metal acetylacetonato complexes and easy access to pyridinium fluorochromate(PFC), $C_5H_5NH[CrO_3F]$, have been put in chapter VI.

To sum up, the present chapter gives a brief background information pertinent to the topics planned out for the present Ph.D. research and identifies some problems considered imperative to investigate. Chapter II of the thesis describes the methods of preparation of the starting materials as well as the details of the methods of elemental analyses and relevant particulars of instruments/equipment used for physico-chemical studies and structural characterisation.

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CHAPTER II

CHAPTER II

ANALYTICAL METHODS AND THE EQUIPMENT AND INSTRUMENTS USED FOR CHARACTERISATION

The details of the methods used for the quantitative determinations of various constituents, and the relevant particulars of the instruments/equipment used for characterisation and structural assessment of the newly synthesised compounds are described in this chapter.

Preparation of Starting Materials

$UO_3.4H_2O$

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, (5.0 g, 9.96 mmol) was dissolved in water ($100cm^3$), to which pyridine ($10cm^3$) was added where upon a yellow precipitate appeared. This was separated by decantation, washed with water three or four times, twice with acetone and finally dried on a steam-bath to obtain yellow uranium trioxide tetrahydrate, $UO_3.4H_2O$ [Yield : 2.8g, 78%].

3,5-dimethylpyrazole (dmpz)[1]

A methanolic solution of 25cm^3 of hydrazine hydrate (25.0g, 499.40mmol) was added slowly with stirring to a methanolic solution of 25cm^3 of acetylacetone (25.0g, 249.70mmol) in an ice-cold condition. A light yellow solution was obtained. The solution was concentrated to *ca.* 20 cm^3 on a steam-bath and left overnight in a refrigerator. A white crystalline compound was obtained and this was isolated by filtration, washed with water and dried in air. [Yield : 23.5g, 98%].

$UO_2(acac)_2.2H_2O$[2]

$UO_2(NO_3)_2.6H_2O$ (1.0g, 1.99 mmol) was dissolved in *ca.* 15cm^3 of water followed by the addition of 25% aqueous ammonia with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off, washed free from alkali and nitrate, and then mixed with distilled acetylacetone (10cm^3, 100mmol). Stirring was continued for *ca.* 15min during which period the yellow precipitate dissolved completely. The solution was filtered to remove any traces of undissolved impurities and the pH of the solution was found to be 5 or 6. The clear filtrate was concentrated by heating on a steam-bath for 1h and then cooled at *ca* 0°C for *ca.* 2h. The orange yellow crystalline $UO_2(C_5H_7O_2)_2.2H_2O$ thus obtained was separated by decantation, dried on a filter paper, and finally dried *in vacuo* over concentrated H_2SO_4. The compound was recrystallised from dichloromethane [Yield : 0.9g., 90%].

$Ni(acac)_2.2H_2O$

$NiCl_2.6H_2O$ (1g, 4.21 mmol) was dissolved in 100cm^3 water and to this 3cm^3 of 20% NaOH solution was added dropwise while stirring. A green precipitate was produced which was allowed to settle for 10min and washed five or six times with *ca.* 200cm^3 by decantation to make it free form alkali. The precipitate was filtered and then transferred to a 50cm^3 beaker. To this 5 g (50mmol) acetylacetone was added and the suspension was warmed on a steam-bath for 25 min with occasional stirring to get a clear green solution. At this stage, the pH of the solution was recorded to be 5.5 or 6. The solution on cooling at room temperature produced a green microcrystalline product. This was isolated by vacuum filtration, washed with acetone and air dried. The product was recrystallised from acetone [Yield : 0.7g, 57%].

$Mn(acac)_2.2H_2O$

$MnCl_2.4H_2O$ (1g, 5.05mmol) was dissolved in 20cm^3 of water followed by addition of 4cm^3 20% NaOH. A light pink precipitate that formed was allowed to settle for 15min. Then it was washed five or six times with 200cm^3 of water by decantation to make it free from alkali. The precipitate was filtered and then transferred to a 50cm^3 beaker. To this 4 cm^3 (40mmol) of acetylacetone was added and the suspension was warmed on a steam-bath with stirring for 15min. A dark-brown solution was obtained. The pH of the reaction solution at this stage was recorded to be 5.5 or 6. The solution was left at room temperature for 30 min after which a shiny dark green-brown product was formed. The product was filtered and

washed with small volume of acetone to get a shiny yellow compound [Yield: 0.7g, 48%].

$Co(acac)_2.2H_2O$

$Co(CH_3COO)_2.4H_2O$ (1g,4.01mmol) was dissolved in 100cm^3 water. To the clear solution 4cm^3 of 20% NaOH was added with stirring. A red-brown precipitate was formed. The precipitate was allowed to settle for 15min and washed 5 or 6 times with 200cm^3 of water by decantation to make it free from alkali. Then it was separated by filtration and transferred to a 50cm^3 beaker. To the precipitate 4cm^3 (40mmol) of acetylacetone was added and the suspension was warmed on a steam-bath for 20 min while stirring to get a pink solution. The pH was recorded to be 5.5 or 6 at this stage. The solution on cooling at room temperature yielded a pink crystalline product. The product was separated by filtration, washed with ethanol and dried in a vacuum desiccator. The compound was recrystallised from methanol [Yield : 0.5g, 43%].

Elemental Analysis

Vanadium

Vanadium was estimated iodometrically.

An accurately weighed amount (*ca.* 0.1g) of vanadium compound was dissolved in 100cm^3 water and 5cm^3 (5M) H_2SO_4 was added. The solution was boiled for 10min to obtain a light-blue solution. Then approximately 5g potassium persulphate was added followed by the addition of one drop of $AgNO_3$ (0.1M) solution and

boiled for 1h. After this 15cm^3 of H_2SO_4 (5M) was added and the solution boiled for a further period of 30min. The solution was allowed to cool to room temperature and *ca.* 5g of KI was added with stirring. This was kept in the dark for 15 min. The liberated iodine was then titrated with standard $Na_2S_2O_3$ solution using starch as an indicator. The end point was detected by the appearance of light-blue colour.

$$1cm^3 \text{ of } 0.1M\ Na_2S_2O_3 = 0.0051g\ V$$

Molybdenum[3]

Molybedenum was estimated gravimetrically

An accurately weighed amount (*ca.* 0.1g) of the molybdenum compound was dissolved in *ca.* 100cm^3 of water followed by the addition of 25cm^3 of NaOH 20% solution. The solution was boiled for 1h and then cooled to room temperature. The alkali molybdate solution was neutralised with dilute (2.5M) H_2SO_4, to methyl red. To this 5cm^3 2M ammonium acetate solution was added and diluted to *ca* 100cm^3, heated nearly to boiling and then molybdenum was precipitated by the addition of *ca.* 10cm^3 4% 8-hydroxyquinoline (oxine) in dilute acetic acid with vigorous stirring. A yellow precipitate along with the supernatant was then gently boiled, stirred for 5 min and left at room temperature for 15min. The precipitate was filtered through a preweighed G-4 Gooch crucible, washed with *ca.* 150cm^3 hot water to make it free from the reagent, dried to constant weight at 130-140°C and finally weighed as molybdenum oxinate,$MoO_2(C_9H_6NO)_2$.

Uranium[4]

Uranium was estimated gravimetrically as uranyl oxinate.

An accurately weighed amount of the compound (*ca.* 0.1g) was dissolved in a minimum volume of dilute (6M) nitric acid followed by the addition of dilute ammonia until a yellow precipitate was obtained. The precipitate was filtered off on a Whatman 41 filter paper, washed three or four times with water and finally dissolved in a minimum volume of 1% acetic acid solution. To the resulting solution 5g of ammonium acetate was added, which was then heated to boiling followed by the addition of (*ca.* $10cm^3$) 4% 8-hydroxyquinoline (oxine) solution dropwise, until an orange precipitate appeared. The whole was then heated on a steam-bath for 15min. The precipitate was filtered through a preweighed G-4 Gooch crucible, washed with $100cm^3$ of hot water to make it free from the excess reagent, dried to constant weight at 110 °C and finally dried as uranyl oxinate, $[UO_2(C_9H_6ON)_2.C_9H_7ON]$.

Chromium

Chromium was estimated iodometrically.

An accurately weighed amount of chromium (*ca.* 0.1g) compound was dissolved in water by slight warming. To the chromium(VI) solution thus obtained, 2g of KI was added and kept in the dark for 15min. The liberated iodine was then titrated with standard sodium thiosulphate solution.

$1cm^3$ of 0.1M $Na_2S_2O_3$ = 0.0052g of chromium

Manganese[5]

Manganese was estimated gravimetrically.

To an accurately weighed amount (*ca.* 0.1g) of manganese compound was added *ca.* 100cm^3 5 % NaOH solution and the mixture boiled for 1h to decompose the compound. Hydrated manganese oxide thus formed was filtered out, washed thoroughly with water and dissolved in *ca.* 10cm^3 of concentrated HCl. The dark brown solution so obtained was boiled to get a clear colourless solution. Then it was diluted to 150cm^3 with water followed by the addition of 15g NH_4Cl and 2g diammmonium hydrogen phosphate, $(NH_4)_2HPO_4$. The solution was heated to boiling (90-95°C) and dilute (1:1) ammonia solution was added dropwise with constant stirring until a precipitate of silky appearance was formed. After this, *ca.* 0.8cm^3 (1:1) ammonia solution was added dropwise with stirring to complete the precipitate. Excess of ammonia should be avoided and the temperature of the solution must be maintained at 90-95°C throughout. Heating and stirring was continued for an additional period of 10min until the precipitate became crystalline. At this stage one or two drops of ammonia was added and the precipitate was allowed to settle for 2h at room temperature. The precipitate was filtered through a preweighed G-4 Gooch crucible, washed thoroughly with 1% NH_4NO_3 until free form chloride and dried at 100-105°C to constant weight. Finally, the precipitate was weighed as $MnNH_4PO_4.H_2O$.

Cobalt[6]

Cobalt was estimated gravimetricaly

An accurately weighed amount (*ca.* 0.1g) of a cobalt(II) compound was dissolved in a minimum amount of dilute (1:1) hydrochloric acid. The solution was then treated with 5% NaOH in order to get Co(II) hydroxide. The Co(II) was oxidised to Co(III) by treating with a small amount of 30% H_2O_2 solution. The excess of the reagent was removed by boiling for nearly 30min. It was filtered and Co(III) precipitate thus obtained was, dissolved in warm acetic acid and diluted to 200cm^3. A 10-20cm^3 α-nitroso-β-naphthol reagent solution (4g of α-nitroso-β-naphthol in 100cm^3 of glacial acetic acid and 100cm^3 of hot distilled water) was added with stirring to the warm solution, which was then heated with vigorous stirring until the precipitate coagulated. The precipitate was filtered through a preweighed G-4 Gooch crucible, washed with dilute (1:2) acetic acid and then with hot water. It was dried to constant weight at 130°C and weighed as $Co(C_{10}H_6ONO)_3$.

Nickel[7]

Nickel was estimated gravimetrically

An accurately weighed (*ca.* 0.1g) amount of Ni(II) compound was dissolved in 50cm^3 water and dilute NaOH 20% solution was added dropwise until the precipitation of nickel hydroxide was complete. The solution was boiled for 15min

and the precipitate was allowed to settle for 20min. It was then filtered and dissolved in $5cm^3$ of conc. HCl. The solution was then diluted to $100cm^3$ and heated to 70-80°C. The acid was neutralised with *ca.* $2cm^3$ conc. ammonia solution (25%). Then $11cm^3$ of 1% ethanolic solution of dimethylglyoxime was added to it while stirring. Immediately, dilute (1:1) ammonia was added dropwise until a faint smell of ammonia was obtained. A red precipitate was formed which was warmed on a steam-bath for 20-30min and left at room temperature for 1h. Then it was filtered through a preweighed G-4 Gooch crucible and washed with cold water until free from chloride. The precipitate was dried at constant weight at 110°C-120°C and weighed as $Ni(C_4H_7O_2N_2)_2$.

Peroxide

(a) Permanganometry [8]

Nearly 1g of boric acid was dissolved in $100cm^3$ of water in a conical flask. To this was added an accurately weighed amount (*ca.* 0.1g) of peroxo compound and shaken to dissolve it. The peroxide was then estimated by redox titration with standard $KMnO_4$ solution. The end point was marked by the appearance of a permanent faint pink colour.

$$1cm^3 \text{ of } 0.2M\ KMnO_4 = 0.016g \text{ of } O_2^{2-}$$

(b) Iodometry[9]

To a freshly prepared 2M sulphuric acid solution, containing an appropriate amount of potassium iodide (~2g in $100cm^3$) was added an accurately weighed

amount (*ca.* 0.1g) of a peroxo compound with stirring. The mixture was allowed to stand for *ca.* 15min. in CO_2 atmosphere in the dark. The amount of iodine liberated was then titrated with a standard sodium thiosulphate solution, adding $2cm^3$ of freshly prepared starch solution when the colour of the iodine was nearly discharged

$$1cm^3 \text{ of } 1N\ Na_2S_2O_3 = 0.01701g \text{ of } H_2O_2$$

This method gives the total amount of peroxide plus vanadium present in the compound. On deduction of the contribution of vanadium(V) from the total amount of iodine liberated, the net peroxide content of the compound is evaluated.

Fluoride[10]

An accurately weighed amount (*ca.* 0.1g) of fluoride containing compound of uranium or chromium was dissolved in $150cm^3$ of water. The fluorochromate(VI) compound was boiled with 20-$25cm^3$ of (0.1M) NaOH for *ca.* 30min. Hydrazine monohydrate was then added too the warm solution drop by drop to precipitate the metal as $Cr(OH)_3$. The solution was digested on a steam-bath for *ca.* 15min and filtered to remove $Cr(OH)_3$. In case of fluorouranate(VI), compound was boiled with 20-$25cm^3$ of 25% aqueous ammonia to precipitate the metal quantitatively as ammonium diuranate. The precipitate was filtered and washed with water. To the combined washings and filtrate, two or three drops of bromophenol blue indicator and $3cm^3$ of 10% sodium chloride solution were added and diluted to *ca.* $250cm^3$. Dilute nitric acid (6M) was added to it until the colour just changed to yellow followed by the addition of (0.1M) NaOH solution until the colour changed to blue.

The mixture was then treated with 1cm^3 of conc. HCl and 5g of $Pb(NO_3)_2$ and heated on a steam-bath. After all the lead nitrate had dissolved, 5g crystallised sodium acetate was added to the solution and the solution digested on a steam-bath for about half an hour with occasional stirring and then allowed to stand overnight.

The precipitate was filtered through a Whatman 542 filter paper, washed five or six times with water to make it free from chloride. The precipitate was dissolved in 1% HNO_3 by slight warming. A known excess of standard $AgNO_3$ (0.1M) solution was added and the suspension of AgCl heated almost to boiling and stirred vigorously. The beaker and the content was kept in the dark for 1h. The precipitated AgCl was filtered out and washed with water. The unreacted $AgNO_3$ was titrated with standard KSCN solution using $Fe(NO_3)_3$ as indicator. The end point was marked with the appearance of a faint red- brown colour. The volume of $AgNO_3$ in the filtrate thus found was subtracted from that originally added. The fluoride content was calculated from the volume of $AgNO_3$ solution consumed.

$$1cm^3 \text{ of } 1M\ AgNO_3 = 0.019g \text{ of } F^-$$

Bromide[11]

Bromide was estimated volumetrically following Volhard's method.

An accurately weighed amount (*ca.* 0.1g) of tetrabutyl ammonium tribromide was dissolved in 20cm^3 acetonitrile. Then the solution was treated with 20cm^3 NaOH 20% solution, followed by the addition of 100cm^3 of water. The solution was boiled for 1h and acidified with dilute (1:1) HNO_3. The acidified bromide solution was then

treated with an excess of standard silver nitrate (0.1M) solution. The suspension was heated almost to boiling and stirred vigorously. The beaker along with the suspension was kept in the dark for 30min. The precipitated AgBr was separated out by filtration and washed several times with water. The filtrate and the washings were collected and the unreacted $AgNO_3$ was titrated with standard KSCN solution using $Fe(NO_3)_3$ as indicator. The end point was marked with the appearance of a faint red-brown colour. From the equivalence of standard $AgNO_3$ and standard KSCN solutions, the volume of excess $AgNO_3$ was calculated and this was subtracted from the volume of $AgNO_3$ initially added. The difference is the volume of $AgNO_3$ solution consumed.

$$1 cm^3 \text{ of } 1M\ AgNO_3 = 0.07990g \text{ of } Br^-$$

Carbon, Hydrogen and Nitrogen

The carbon, hydrogen and nitrogen contents were estimated by micro-analytical methods. The results of the analyses were obtained from Micro Analytical Laboratory, Department of Inorganic Chemistry, Indian Association for the Cultivation of Science, Calcutta : 700032, and RSIC, NEHU, Shillong : 793003.

Particulars of Instruments/Equipment Used

pH Measurement

The pH values of the reaction solutions were recorded with a Systronics type 335 digital pH meter and also by using BDH indicator paper.

Solution Electrical conductance

Solution electrical conductance measurement was made by using a Systronic Type 306 digital direct reading conductivity meter and Wayne Kerr Automatic Precision Bridge B 905 conductometer.

Infrared Spectra

Infrared spectra were recorded for KBr pellets on Perkin -Elmer model, 983 spectrophotometer as well as on a Nicolet Impact 410 spectrophotometer.

Laser Raman Spectra

The laser Raman spectra were recorded on a SPEX Ramalog Model 1403 spectrometer. The 4880Å laser line from Spectra Physics Model 165-09 Argon Laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by photon - count processing system. The sample was held in the form of a pellet in KBr. The recording was done at ambient temperature.

Electronic Absorption Spectra

Electronic absorption spectral measurements of freshly prepared solutions were made on Beckman Du 650 spectrophotometer.

Thermal studies

Thermogravimetry (TG) and Differential Scanning Calorimetry (DSC) experiments were conducted with a Delta Series Perkin-Elmer TGA 7

Thermogravimetric Analyser and a DSC 7 Differential scanning calorimeter, respectively, in a constant flow of nitrogen. The samples were heated at a rate of 10°C/min.

ESR Spectra.

The ESR spectra of solids or of solutions were recorded using a Varian E 109 X-band ESR spectrometer fitted with 100 Kc field modulator.

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CHAPTER III

CHAPTER III

Heteroligand Peroxo Compounds of Vanadium and Molybdenum, $[V_2O_2(O_2)_3(dmpz)_4]$ and $[MoO(O_2)_2(dmpz)_2]$, as Newer and Environmentally Acceptable Oxidising Agents for Organic Substrates Synthesis, Characterisation and Investigation of Reaction Profiles

Peroxo compounds represents an important class of reactive intermediates in catalytic oxidation[1-3] and are therefore of importance in biological processes involving oxidation, or conversion of dioxygen species. A variety of peroxo heteroligand complexes of the early transition metals in their high oxidation states are known.[4-6] Molybdenum and vanadium, two of the 'trace elements' essential for living matter [7] are especially interesting in this respect .[6,8,9]

Vanadium has been identified as an essential element for mammals. [7,10-12] However, its actual function does not seem to be completely understood.[13,14]

Peroxovanadium systems in general, constitute an important class of compounds because of their potential as oxidation catalysts [15-21] and biochemical relevance .[1,5,6,15-17] Recent investigations involving vanadium bromoperoxidases[22] and vanadium nitrogenases,[22] both involving V(V), have been very exciting contributions to the current knowledge of biological and catalytic participation of the metal. In addition, a few heteroligand peroxovanadate(V) compounds have shown antitumor,[9] antidiabetic,[23] antileukemic[9] activity and it was emphasised that the heteroligands played an important role[9] to bring about the activity of such a complex species. More recently, Hiort[24] et al . reported the DNA- photocleavage activities of two diperoxovanadium (V) complexes with 1,10-phenanthroline and 4,7-dimethyl-1,10-phenanthroline as ancillary ligands.

Suitable heteroligands are believed to bring about stability to peroxovanadium systems enabling isolation in the solid state. For instance, ImzH[$VO(O_2)_2$Imz] that evaded isolation for a long period was synthesised and crystallographically characterised by Crans[25] et al. only recently. In addition, to this several N,O-donor-peroxo-vanadium(V) complexes have been synthesised and structurally characterised.

For more than one and a half decades our group has engaged its attention to devise synthetic strategies in order to make systematic studies of heteroligand peroxovanadate(V) complexes.[26,27] As a part of the programme, it was considered important to synthesise novel molecular complex peroxovanadium(V) compounds containing N-donor heteroligands and investigate their reactivity.

In addition, to the heteroligand peroxovanadium (V) complexes, there has been a great deal of interest in the studies of peroxomolybdates,[28] and their catalytic activity has been a topic of considerable importance.[15,29,30] Nature has also incorporated molybdenum into a number of important redox enzymes.[31] These include among other aldehyde, sulphite and xanthine oxidase, nitrate reductase and nitrogenase. Nitrate reductase and nitrogenase are important reducing enzymes involved in the nitrogen cycle of plants.

In addition to identifying the nature of peroxomolybdenum complexes formed in aqueous solution [29,30] at different pH, catalytic oxidations of a variety of organic substrates[15] including alcohols[32] by peroxomolybdenum (VI) systems have drawn a considerable attention because of the widespread use of the environmentally acceptable hydrogen peroxide as cooxidant in such systems. Incidentally, it was in our agenda also to develop environmentally acceptable oxidants based on peroxovanadium(V) and peroxomolybdenum(VI) systems. Accordingly, the work was motivated to a considerable extent by the idea that the peroxo-heteroligand metal complexes represent a system that will eventually become a useful model for certain biochemical functions of vanadium and molybdenum as well as that these complexes will undergo or trigger specific catalytic oxidation and oxygen transfer reactions.[33]

The present chapter provides an account of a new heteroligand peroxovanadium(V) complex, dioxodiperoxo-μ-peroxotetrakis(3,5-dimethylpyrazole)divanadium(V), $[V_2O_2(O_2)_3(dmpz)_4]$, and a heteroligand peroxomolybdenum(VI) complex, oxodiperoxo *bis*(3,5-

dimethylpyrazole)molybdenum(VI), $[MoO(O_2)_2(dmpz)_2]$, in terms of their method of synthesis, structure with reference to the mode of co-ordination of ligands, stability, and reactivity with organic substrates.

EXPERIMENTAL

3,5-dimethylpyrazole was prepared as described in chapter II .All the chemicals and organic solvents used were of reagent grade quality. The details of the instruments/ equipment used for the characterisation of the products are given in chapter II.

Synthesis of $[V_2O_2(O_2)_3(dmpz)_4]$

An aqueous suspension of 1.0g (5.49mmol) V_2O_5 was treated with $5cm^3$ (44.09mmol) 30% H_2O_2 in an ice cold condition. The mixture was stirred occasionally for 20min to obtain a red solution. The pH of the solution was 2 at this stage. To this 2.1g (21.84 mmol) powered 3,5-dimethylpyrazole was added slowly in portions with continuous stirring. After stirring for 15min a yellow solution was obtained, which on further stirring gave a lemon-yellow compound. The product was isolated by vacuum filtration, washed two or three times with a small amount of ethanol and finally dried *in vacuo* over concentrated H_2SO_4. The yield of $[V_2O_2(O_2)_3(dmpz)_4]$ was 2.3g (68%).

Synthesis of $[MoO(O_2)_2(dmpz)_2]$

An amount of 1.0g (0.809mmol) ammonium molybdate(VI) tetrahydrate was dissolved in $5cm^3$ (44.09 mmol) of 30% H_2O_2 in an ice cold condition. The pH of the

solution at this stage was 5. To the resulting solution 1.08g (11.23mmol) of finely powdered 3,5-dimethylpyrazole was added with continuous stirring. A red suspension was obtained. The suspension on keeping overnight in the freeze afforded a yellow microcrystalline product. The product was separated by vacuum filtration, washed twice with water and dried *in vacuo* over concentrated H_2SO_4. The yield of $[MoO(O_2)_2(dmpz)_2]$ was 1g (48%).

Oxidation of Organic Substrates by $[V_2O_2(O_2)_3(dmpz)_4]$

Oxidation of Benzyl alcohol

To the solution of $[V_2O_2(O_2)_3(dmpz)_4]$ (1.62 mmol) in 20cm^3 of dichloromethane, 4.07mmol of benzyl alcohol was added and stirred for 1h. Colour of the solution changed from yellow to orange-red. The resulting solution was extracted with water. The water extract was discarded while the organic layer was collected. This was concentrated and to this 2,4-dinitrophenylhydrazine was added to precipitate the 2,4-dinitrophenylhydrazone of benzaldehyde. [Yield :56%][a] ; M.P=234°C (lit.[34] 237°C).

a= Yield of the 2,4-dinitrophenylhydrazone.

Oxidation of Triphenylphosphine

A dichloromethane (30cm^3) solution of $[V_2O_2(O_2)_3(dmpz)_4]$ (4.07mmol) was stirred for 5min and to this, a solution of triphenylphosphine (3.81mmol) in dichloromethane (10cm^3) was added. The colour of the solution changed immediatly from yellow to orange-red. The solution was extracted with hexane. The hexane extract on evaporation afforded a white coloured compound (*cf.*$O=PPh_3$). The white product was recrystallised from dichloromethane. [Yield :66%] ; M.P=155°C (lit[35] 156-158°C).

Oxidation of Benzoin

To a dichloromethane ($15cm^3$) solution of $[V_2O_2(O_2)_3(dmpz)_4]$ (2.44mmol) a solution of benzoin (3.06mmol) in dichloromethane ($10cm^3$) was added and the mixture stirred for 1h. The colour of the solution changed from yellow to orange-red. The solution was filtered and the filtrate was extracted with hexane. The hexane extract was treated with charcoal and then filtered. The solution was then concentrated and cooled. Yellow coloured needle shaped crystals separated out. [Yieid :70%] ; M.P=94°C (lit.[36] 95°C).

Oxidation of Cyclohexanol

To the solution of $[V_2O_2(O_2)_3(dmpz)_4]$ (4.07mmol) in dichloromethane ($25cm^3$), cyclohexanol (4.1mmol) was added and the reaction mixture stirred for 3h. There was a change in the colour of the reaction solution from yellow to orange during this period. The reaction mixture was extracted with hexane and the extract was evaporated. To this 2,4-dinitrophenylhydrazine was added whereupon orange coloured compound precipitated out. [Yield: 53%][a]; M.P=158°C (lit.[37]160°C).

a=Yield of the 2,4-dinitrophenylhydrazone.

Oxidation of Allyl alcohol

An amount of 4.07mmol of $[V_2O_2(O_2)_3(dmpz)_4]$ was dissolved in $35cm^3$ dichloromethane, to this (6.03mmol) allyl alcohol was added and stirred for 45min. The colour of the solution changed from yellow to orange. The solution was extracted with

hexane and to the hexane extract 2,4-dinitrophenylhydrazine was added to precipitate the 2,4-dinitrophenylhydrazone of acrolein. [Yield :45%][a] ; M.P=168°C (lit.[38] 165°C).

a= Yield of the 2,4-dinitrophenylhydrazone.

Oxidation of n-Butanol

A quantity of 4.07mmol of $[V_2O_2(O_2)_3(dmpz)_4]$ was dissolved in $35cm^3$ dichloromethane. To this 5.54mmol of n-butanol was added and stirred for !h. The resulting solution was extracted with hexane and to the hexane extract 2,4-dinitrophenylhydrazine was added to precipitate 2,4-dinitrophenylhydrazone of n-butanal. [Yield :56%][a] ; M.P=121°C (lit. [39] 123°C).

a= Yield of the 2,4-dinitrophenylhydrazone.

Oxidation of Organic Substrates by $[MoO(O_2)_2(dmpz)_2]$

Oxidation of Benzyl alcohol

A solution of 9.26mmol of benzyl alcohol in $10cm^3$ dichloromethane was added to the solution of 9.24mmol of $[MoO(O_2)_2(dmpz)_2]$ in $15cm^3$ of dichloromethane and refluxed for 3h on a steam-bath. The reaction solution turned violet. The solution was filtered and extracted with hexane. The hexane extract on concentration on a steam-bath followed by addition of a solution of 2,4-dinitrophenylhydrazine afforded a orange colour precipitate of the hydrazone of benzaldehyde. The product was isolated by filtration and recrystallised from dichloromethane and dried *in vacuo* over concentrated H_2SO_4. [Yield=62%][a] ; M.P =235°C (lit.[34]237°C).

a= Yield of the 2,4-dinitrophenylhydrazone.

Oxidation of Triphenylphosphine (PPh_3)

To a solution of 2.72mmol of $[MoO(O_2)_2(dmpz)_2]$ in dichloromethane 2.97mmol of triphenylphosphine was added and stirred for 1h. The colour of the solution changed from yellow to violet. From the violet colour solution, the product was extracted in hexane. The hexane extract on concentration over steam-bath to *ca.* $5cm^3$, and then cooling to room temperature afforded a white product (*cf.*$O=PPh_3$). The product thus obtained was recrystallised from ether. [Yield=72%] ; M.P=155°C (lit.[35] 156-158°C).

Oxidation of Benzoin

A solution of $[MoO(O_2)_2(dmpz)_2]$ 4.07mmol in $20cm^3$ of dichloromethane was stirred to get a clear yellow solution. To this 5.09mmol of benzoin in $20cm^3$ of dichloromethane was added and stirred for 1h. The product was extracted in hexane. The hexane extract on concentration on a steam-bath to $5cm^3$ and then cooling to room temperature afforded a light yellow product(benzil). This was recrystallised from dichloromethane. [Yield:85%] ; M.P=94°C (lit.[36] 94-95°C).

Oxidation of Cyclohexanol

To the solution of 4.08mmol of $[MoO(O_2)_2(dmpz)_2]$ in $25cm^3$ of dichloromethane, 4.1mmol of cyclohexanol was added and the reaction mixture stirred. The reaction mixture was stirred for 3 min. The solution colour changed from yellow to orange in *ca.* 15min followed by precipitation of a solid product. The solution was filtered and the filtrate extracted with water and evaporated under reduced pressure. To the remaining solution,

2,4-dinitrophenylhydrazine was added which led to the precipitation of 2,4-dinitrophenylhydrazone of cyclohexanone.[Yield : 57%][a]; M.P=158°C (lit.[37]160°C).

a= Yield of the2,4-dinitrophenylhydrazone

Oxidation of Allyl alcohol

To 4.34mmol of $[MoO(O_2)_2(dmpz)_2]$ in $25cm^3$ of dichloromethane, 6.50mmol of allyl alcohol was added and the solution stirred for 2h. The colour of the solution changed from yellow to orange. The solution was extracted with hexane and to the hexane extract 2,4-dinitrophenylhydrazine was added. Orange precipitate of 2,4-dinitrophenylhydrazone of acrolein was obtained. [Yield : 46%][a]; M.P=166°C (lit.[38]166°C).

a=Yield of the 2,4-dinitrophenylhydrazone.

Oxidation of n-Butanol

To a vigorously stirred solution of 5.43mmol of $[MoO(O_2)_2(dmpz)_2]$ in $25cm^3$ of dichloromethane, 5.9mmol n-butanol was added. The solution stirred for 2h. The resulting solution was then extracted with hexane. The hexane extract was concentrated and to this 2,4-dinitrophenylhydrazine was added to precipitate the 2,4-dinitrophenylhydrazone of n-butanal.[Yield:53.6%][a]; M.P=122°C(lit.[39]123°C).

a= Yield of the 2,4-dinitrophenylhydrazone.

Oxidation of Geraniol

To the solution of 7.11mmol of $[MoO(O_2)_2(dmpz)_2]$ in $25cm^3$ of dichloromethane, 6.49mmol of geraniol was added. The mixture was stirred and refluxed for 2h. The cold reaction mixture was extracted with ether, and evaporated under reduced pressure,

followed by the addition of 2,4-dinitrophenylhydrazine to precipitate the hydrazone of geranial. [Yield : 51%][a] ; M.P= 107°C (lit.[40] 110°C).

a= Yield of the2,4-dinitrophenylhydrazone.

Results and Discussion

The compound $[V_2O_2(O_2)_3(dmpz)_4]$

The reaction of vanadium with hydrogen peroxide is highly pH dependent, and a small variation of pH of the reaction solution leads to the formation of peroxovanadium complexes of varied composition, implying thereby that pH of the reaction medium is an important parameter for such investigations .[41-43] In the present synthesis, the suitable pH for bringing about co-ordination of both peroxide and 3,5-dimethylpyrazole with oxovanadate(V) centre was ascertained to be 5 or 5.5. Incidentally, this pH was attained spontaneously without any addition of acid or alkali. It is important to mention that the order of addition of the reactants, as mentioned in the experimental section, is necessary to maintain to achieve the success. The compound $[V_2O_2(O_2)_3(dmpz)_4]$ was obtained from the reaction of 3,5-dimethylpyrazole with a solution of V_2O_5 in H_2O_2. However, the compound appears in the solid form after quite some time(vide Experimental). Attempt to precipitate the compound by the addition of ethanol was not successful. This could be due to a very high solubility of the product in the organic solvent.

The compound $[V_2O_2(O_2)_3(dmpz)_4]$, is lemon-yellow microcrystalline product, and is not very stable. The compound is soluble in water as well as in organic solvents at ambient temperature. $[V_2O_2(O_2)_3(dmpz)_4]$ is diamagnetic in nature, as evident from the

results of magnetic susceptibility measurement, in conformity with the view that vanadium occurs in its +5 oxidation state (d^0). The compound was ESR silent. The peroxide estimation was accomplished by redox titrations separately with standard potassium permanganate solution and iodometrically by standard sodium thiosulphate solution. The results obtained thereof clearly suggested the presence of O_2^{2-}:V ratio as 1.5:1 indicating the possibility of a dimeric nature of the complex. The molar conductance of the compound recorded separately in water and methanol gave the values (Table 3.1) indicating rather typical of a non-electrolytic species.[44] Analytical data are listed in Table 3.1.

The significant features of IR spectrum of $[V_2O_2(O_2)_3(dmpz)_4]$ (Fig. 3.1) involve absorptions due to V=O,[45] co-ordinated peroxide[46,47] and co-ordinated 3,5-dimethylpyrazole. The strong band at 986 cm^{-1} has been assigned to ν(V=O) [45] arising from the terminally bonded V=O group. The bands at 881, 644 and 539 cm^{-1} have been assigned to ν(O–O)(ν_1), ν(V–O_2)(ν_3), and ν(V–O_2)(ν_2), respectively, of the co-ordinated peroxide groups (Table 3.2).[46,47] The stretching frequency of the O–O bond is in order and compares well with those reported in the literature. [45-48] In addition, the absortions at 644 and 539 cm^{-1} indicate the bidentate peroxide co-ordination .[49-51] 3,5-dimethylpyrazole behaves as a monodentate co-ordinating ligand and co-ordination is through the pyridine N of the azole ring.[52] The appearance of two strong bands at 1581 and 1304 cm^{-1} corresponding to ν(C–C)+ν(C–N) and ν(C–N)+ν(C–C) modes [53,54] indicates the presence of dmpz in $[V_2O_2(O_2)_3(dmpz)_4]$, (Fig. 3.1), (Table 2). A band at 3317 cm^{-1} due

to ν(N–H) mode [55] further supports the co-ordination of 3,5-dimethylpyrazole *via* its tertiary nitrogen. A band at 313 cm^{-1} due to (V–N)[56] confirms the co-ordination of 3,5-dimethylpyrazole through its tertiary nitrogen atom.

Electronic spectroscopy is very important to study metal-dioxygen interaction.[57] The electronic spectrum of $[V_2O_2(O_2)_3(dmpz)_4]$ (Fig. 3.2) was recorded in water and methanol (Table 3.4). Ideally, the side-on peroxo-metallates are expected to show two LMCT absorption bands due to $\pi_v^* \rightarrow d_\sigma^*$ and $\pi_h^* \rightarrow d_\sigma^*$ transitions.[58] The spectrum of $[V_2O_2(O_2)_3(dmpz)_4]$ exhibited two bands one at 213nm (46,948cm^{-1}; ε=23,590dm^3 $mol^{-1}cm^{-1}$) and the other as a broad band at 322nm (31,055cm^{-1}; ε=1676$dm^3mol^{-1}cm^{-1}$) (Table 3.3). The band at 213nm and 322nm have been assigned to $\pi_h^* \rightarrow d_\sigma^*$and $\pi_v^* \rightarrow d_\sigma^*$ transitions, respectively.[58,59] The bands due to dmpz to vanadium charge-transfer might have been obscured by the peroxide to vanadium charge-transfer band at 213 nm.[60]

In order to throw light on the thermal stability and the decomposition pattern, and also to demonstrate whether dmpz suffers preferential loss on application of heat, thermoanalytical (TG and DSC) study of the compound $[V_2O_2(O_2)_3(dmpz)_4]$ was undertaken. The suitability of $[V_2O_2(O_2)_3(dmpz)_4]$ for thermal studies was envisaged because of the presence of volatile ligands. The thermogravimetric experiment was performed in the range 40-700° C and the DSC experiment at 60-510°C under constant flow of nitrogen. The thermogram (Fig.3.6) of $[V_2O_2(O_2)_3(dmpz)_4]$ reveals that the compound is stable upto 68°C. The weight loss begins at 68.72° C and continues up to 149.31°C with a loss of weight corresponding to the expulsion of one dmpz, N_2, C_2H_2,

CH_4 (calc. 27.04 , obs. 26.712%). After the inflection at 206.86°C the thermogram exhibits a slow rate of weight loss up to 299.01°C followed by a sharp loss between 382.69°C and 682.05°C . The weight loss from 206.82-299.01° C gets along well with the loss of C_2H_2 ,CH_4 (calc. 6.84, obs. 6.6%). The intermediate, presumably $[V_2O_2(O_2)_3(dmpz)(C_4H_4N_2)]$, formed at this stage appears to be unstable and undergoes thermal decomposition finally leading to the formation of V_2O_5.

The corresponding DSC shows a sharp endotherm at 133.238° C attributable to the loss of one dmpz as observed in TG . In addition , an exotherm appearing at 362° C could be correlated to the event at 299-382° C observed in the TG experiment (*cf.* the loss of C_2H_2 and CH_4).

The compound $[MoO(O_2)_2(dmpz)_2]$

Metal-peroxide interaction leading to the formation of a variety of peroxo-metal species in solution offers a rather complex[29,30] but rewarding area of investigation . And molybdenum is no exception as a to this metal. Indeed , there have been ample evidences of peroxomolybdates having been investigated by several researchers,[21,62,63] though with varying nature of interest. Molybdenum, more specifically MoO_3, has been known to react with hydrogen peroxide and depending upon the reaction strategies, species of different composition were synthesised.[28]

For the present work, the reaction of ammonium molybdate tetrahydrate, with 30% hydrogen peroxide was conducted at pH 5.5 (natural, attained spontaneously) in the

presence of a stipulated amount of 3,5-dimethylpyrazole (dmpz) (vide experimental) leading to the synthesis of $[MoO(O_2)_2(dmpz)_2]$, in a reasonably good yield.

The compound $[MoO(O_2)_2(dmpz)_2]$ is yellow in colour and stable for a couple of months. A sample, retained for a longer period, slowly loses the active oxygen content. The peroxide content was determined by redox titrations with standard potassium permaganate solution. The analytical results suggest the presence of $Mo:O_2^{2-}$ ratio as 1:1.8. An aqueous solution of $[MoO(O_2)_2(dmpz)_2]$ registered a molar conductance value of $68.22\Omega^{-1}$ cm^{-1} mol^{-1} (Table 3.1). The value indicates to a non-electrolytic nature of the compound.[44] Analytical data are listed in Table 3.1.

The vibrational spectra of $[MoO(O_2)_2(dmpz)_2]$ (Fig3.4) show bands due to the presence of co-ordinated peroxide [46,47] (O_2^{2-}) and 3,5-dimethylpyrazole.[55] Appearance of a strong band at 953 cm^{-1} has been assigned to Mo=O stretching (Table 3.3). The absorptions at 882, 592 and 665 cm^{-1} are due to $\nu(O-O)(\nu_1)$, $\nu(Mo-O_2)(\nu_2)$ and $\nu(Mo-O_2)(\nu_3)$, respetively.[46,47] The vibrational spectrum evidences that the ligand 3,5-dimethylpyrazole behaves as a monodentate co-ordinating ligand and binds the metal through the tertiary N atom of the ring.[52] The appearance of two strong bands at 1568 and 1273 cm^{-1} assigned to $\nu(C-C)+\nu(C-N)$ and $\nu(C-N)+\nu(C-C)$ also indicates [53,54] the presence of 3,5-dimethylpyrazole in $[MoO(O_2)_2(dmpz)_2]$. A band at 3323 cm^{-1} due to $\nu(N-H)$ mode [55] suggests this nitrogen atom is rather free from co-ordination supporting indirectly the co-ordination of 3,5-dimethylpyrazole involving its tertiary nitrogen atom. In

addition the band at 303 cm^{-1} due to (Mo–N)[56] further points to the possibility of co-ordination of 3,5-dimethylpyrazole through its tertiary nitrogen atom.

The complementary Raman signals due to ν (Mo=O), ν(O–O)(ν_1), ν(Mo–O_2)(ν_3), ν(Mo–O_2)(ν_2) and ν(Mo–N) have been observed at 956 cm^{-1}, 886 cm^{-1}, 674 cm^{-1}, 595 cm^{-1} and 320 cm^{-1}, respectively. The IR and Raman spectra strongly support the identity of the complex.

The electronic spectroscopy of transition metal dioxygen complexes is rather complicated as shown by Lever and Gray.[57] It is relevant to note that the side-on peroxometallates are expected to give just two absorption bands (LMCT) due to $\pi_v^* \rightarrow d_\sigma^*$ and $\pi_h^* \rightarrow d_\sigma^*$ transitions.[58] The latter transition involving a comparatively higher energy than the former is rarely observed.[57,59] Incidentally, the compound [$MoO(O_2)_2(dmpz)_2$] showed clearly distinguishable electronic spectral features exhibiting the two predicted LMCT bands. The lower energy less intense band at 332 nm and the higher energy more intense band at 216 nm have been assigned to $\pi_v^* \rightarrow d_\sigma^*$ and $\pi_h^* \rightarrow d_\sigma^*$ transitions, respectively.[58] Based on these results it is hoped that the compound might serve as a good probe for studying the detailed interactions involved in metal-dioxygen systems.

In order to understand the thermal stability and the decomposition pattern, thermogravimetric(TG) and differential scanning calorimetric (DSC) experiments were performed on the compound [$MoO(O_2)_2(dmpz)_2$]. The temperature range covered for TG was 30–530°C where as DSC measurement was conducted over the temperature range of

50–520°C under a constant flow of nitrogen. The thermogram(TG) shows that the compound is stable upto 93°C. The weight loss initiates at 93.84°C and continues upto 229.9°C. The loss of weight at this step corresponds to the expulsion of one molecule of 3,5-dimethylpyrazole (calc.26.08, obs. 23.663%). The intermediate at this stage is suggested to be $MoO(O_2)_2$(dmpz). The thermogram then exhibits a weight loss in the temperature range 229.9-357.57°C corresponding to the loss of one peroxo ligand (calc.8.69, obs. 6.106%) leading to the formation of [MoO_3(dmpz)] The thermogram exhibits a weight loss in the temperature range 357.57-499.95°C corresponding to the loss of second molecule of dmpz (calc. 26.08, obs. 26.929%) leading to the formation of MoO_3 as the end product. The IR of the residue matches correctly with the spectra of MoO_3.[61] The corresponding DSC shows an exotherm at 107.234°C attributable to the loss of one dmpz as observed in the TG experiment.

Peroxometallates are, in general, anticipated to be potential oxygen donors to a variety of substrates. In order to investigate the reactivity profile of the compound, oxidation involving some selected organic substrates were carried out. The results (vide Experimental) indicate clearly that the peroxomolybdates like the peroxovanadates described earlier in this chapter, reacted to bring about oxidations or transformations depending on the nature of the substrates. Thus, triphenylphosphine, benzyl alcohol, benzoin, cyclohexanol, allyl alcohol, geraniol, n-butanol were converted to triphenylphosphine oxide, benzaldehyde, benzil, cyclohexanone, acrolein, geranial, butanal, respectively, in moderate to good yields (Table 3.6 and 3.7). The products have been characterised by melting point determination, infrared spectroscopy and preparation of

2,4-dinitrophenylhydrazone of the corresponding aldehyde and ketone and then comparing with the literature melting points. The characterisation data of the organic products match well with the literature values.

Table 3.1 : Analytical data and Solution Electrical Conductance of $[V_2O_2(O_2)_3(dmpz)_4]$and of $[MoO(O_2)_2(dmpz)_2]$

Compound	MolarConductane (Ω^{-1} cm^2 mol^{-1})	Element	Found (%)	Calc.(%)
$[V_2O_2(O_2)_3(dmpz)_4]$	70(H_2O)	V	16 58	16 59
	85(CH_3OH)	O_2^{2-}	15 62	15 63
		C	39 25	39 12
		H	5 30	5 21
		N	18 32	18 24
$[MoO(O_2)_2(dmpz)_2]$	68 22(H_2O)	Mo	27 40	26 07
		O_2^{2-}	16 79	17 38
		C	32 39	32 63
		H	4 58	4 35
		N	14 15	15 22

Table 3.2 : Structurally Significant IR Bands of $[V_2O_2(O_2)_3(dmpz)_4]$

Compound	Band Position (cm^{-1})	Assignment
$[V_2O_2(O_2)_3(dmpz)_4]$	3317	ν(N–H)
	1581	ν(C–C)+ν(C–N)
	1304	ν(C–N)+ν(C–C)
	986	ν(V=O)
	881 815	ν(O–O)
	644	ν_3(V–O_2)
	539	ν_2(V–O_2)
	313	ν(V–N)

Table 3.3 : Structurally Significant IR and Raman Bands of $[MoO(O_2)_2(dmpz)_2]$

Compound	IR (cm^{-1})	Laser Raman (cm^{-1})	Assignment
$[MoO(O_2)_2(dmpz)_2]$	3323		ν(N–H)
	1568		ν(C–C)+ν(C–N)
	1273		ν(C–N)+ν(C–C)
	953	956	ν(Mo=O)
	862	886	ν_1(O–O)
	665	674	ν_3(Mo–O_2)
	592	595	ν_2(Mo–O_2)
	326	320	ν(Mo–N)

Table 3.4 : Electronic Spectral Data of $[V_2O_2(O_2)_3(dmpz)_4]$

Compound	Wavelenght (nm)	Wavenumber (cm^{-1})	ε ($dm^3mol^{-1}cm^{-1}$)	Assignment
$[V_2O_2(O_2)_3(dmpz)_4]$	322(inH_2O)	31,055	1676	$\pi_v^* \rightarrow d_\sigma^*$
	213(inH_2O)	46,948	23,590	$\pi_h^* \rightarrow d_\sigma^*$
	333(inCH_3OH)	30,030	2619	$\pi_v^* \rightarrow d_\sigma^*$
	213(inCH_3OH)	46,948	27,597	$\pi_h^* \rightarrow d_\sigma^*$

Table 3.5 : Electronic Spectral Data of $[MoO(O_2)_2(dmpz)_2]$

Compound	Wavelenght (nm)	Wavenumber (cm^{-1})	ε ($dm^3mol^{-1}cm^{-1}$)	Assignment
$[MoO(O_2)_2(dmpz)_2]$	332	30,120	903	$\pi_v^* \rightarrow d_\sigma^*$
	216	46,296	11,260	$\pi_h^* \rightarrow d_\sigma^*$

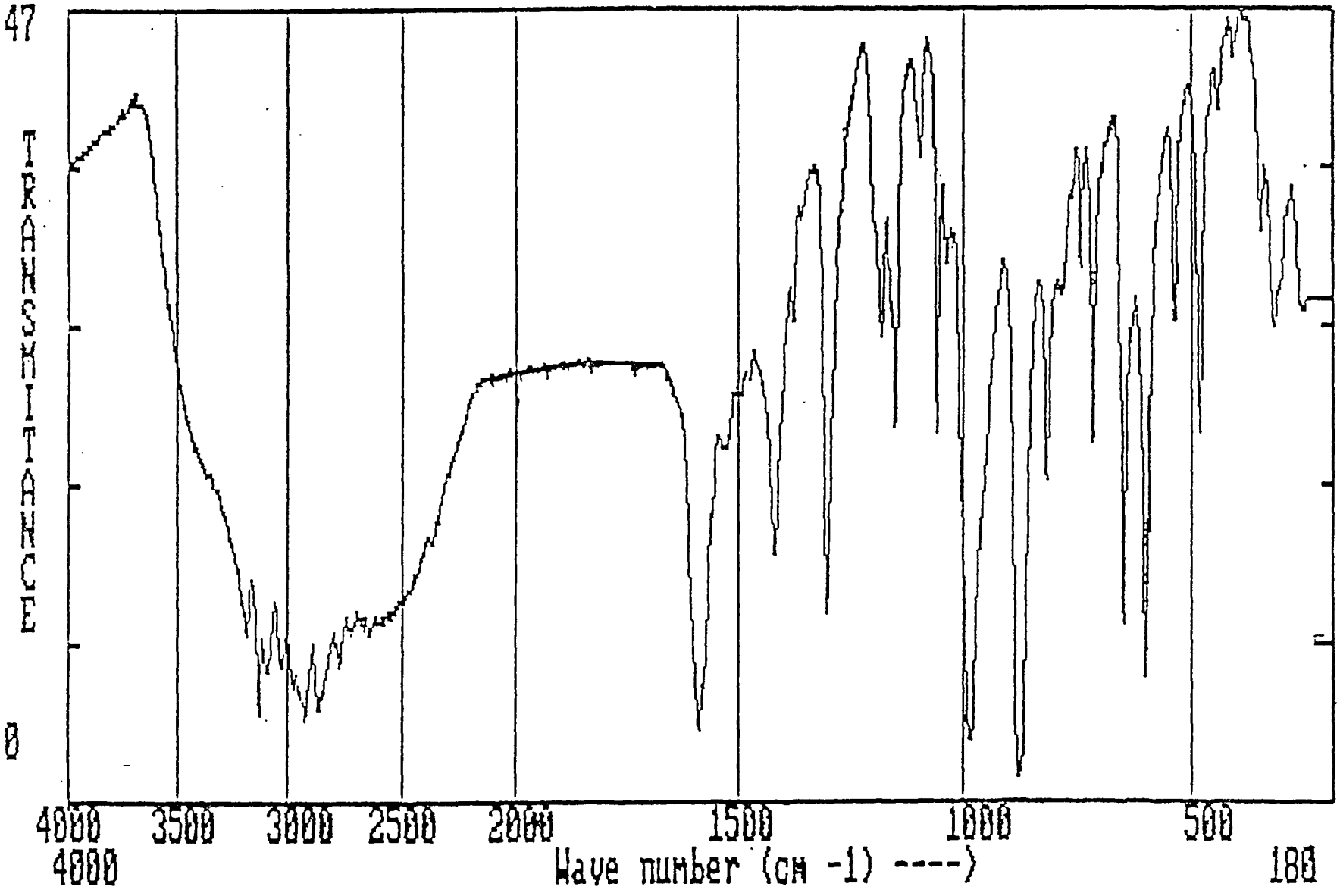
Table 3.6 : Oxidation of Organic Substrates by $[V_2O_2(O_2)_3(dmpz)_4]$

Substrate	Substrate: Oxidant	Solvent	Reaction time (min)	Product	Yield (%)	M.P (°C)
Benzyl alcohol	1:1.25	CH_2Cl_2	60	Benzaldehyde	56	234[a]
n-Butanol	1:1.1	CH_2Cl_2	60	n-Butanal	50	121[a]
Allyl alcohol	1:1.5	CH_2Cl_2	45	Acrolein	45	168[a]
Cyclohexanol	1:1	CH_2Cl_2	120	Cyclohexanone	53	158[a]
Benzoin	1:1.25	CH_2Cl_2	60	Benzil	70	94
Triphenylphos-phine	1:1.1	CH_2Cl_2	1	Triphenylphos-phine oxide	66	154

Table 3.7 : Oxidation of Organic Substrates by $[MoO(O_2)_2(dmpz)_2]$

Substrate	Substrate: Oxidant	Solvent	Reaction time (min)	Product	Yield (%)	M.P (°C)
Benzyl alcohol	1:1.25	CH_2Cl_2	60	Benzaldehyde	62	235[a]
n-Butanol	1:1.1	CH_2Cl_2	120	n-Butanal	54	122[a]
Allyl alcohol	1:1.5	CH_2Cl_2	120	Acrolein	46	166[a]
Cyclohexanol	1:1	CH_2Cl_2	30	Cyclohexanone	57	160[a]
Benzoin	1:1.25	CH_2Cl_2	60	Benzil	80	94
Triphenylphos-phine	1:1.1	CH_2Cl_2	60	Triphenylphos-phine oxide	72	155
Geraniol	1:1.1	CH_2Cl_2	120	Geranial	51	107[a]

a= Melting point of 2,4 dinitrophenylhydrazone derivative



3.1. Infrared Spectrum of $[V_2O_2(O_2)_3(dmpz)_4]$

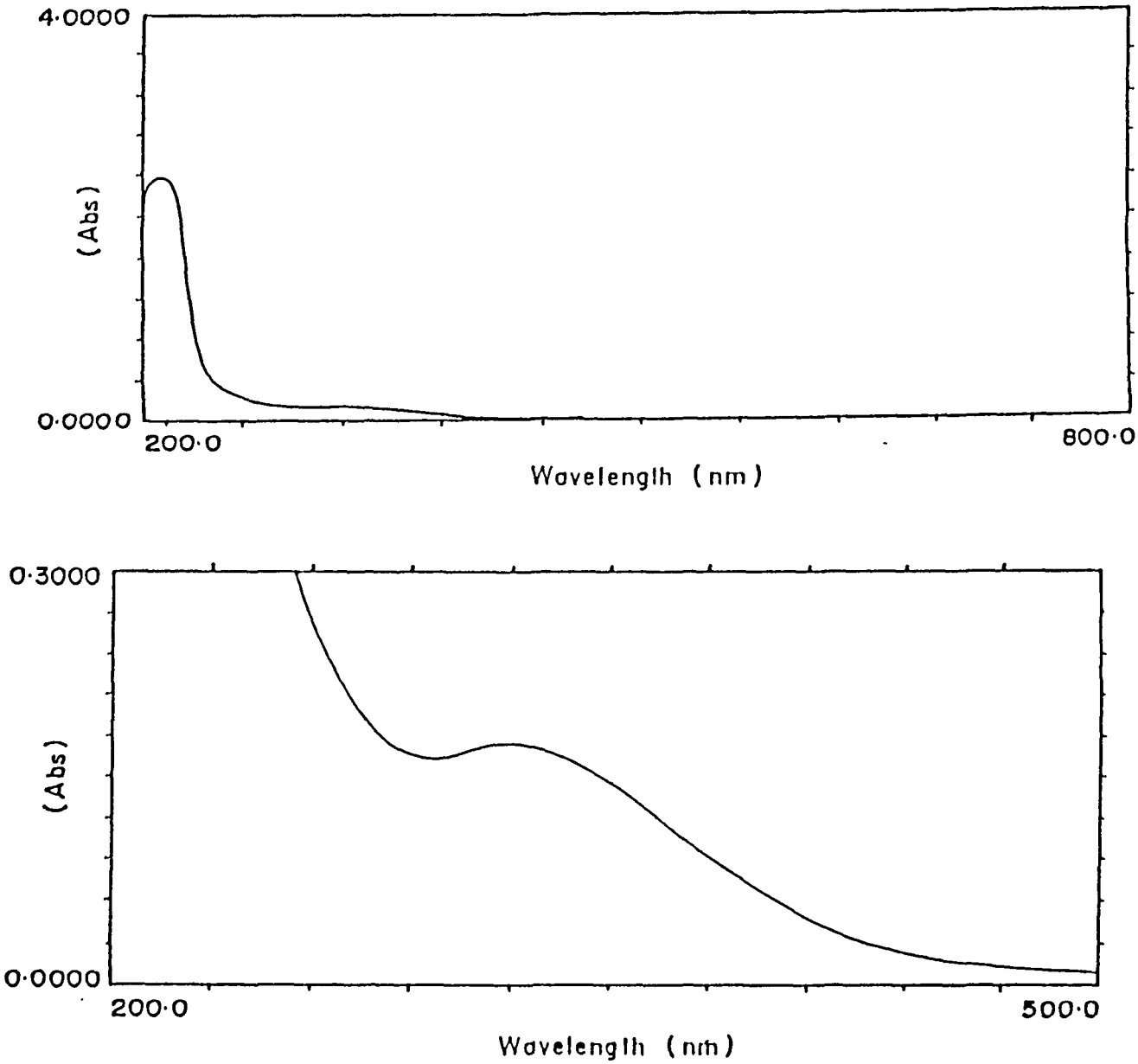
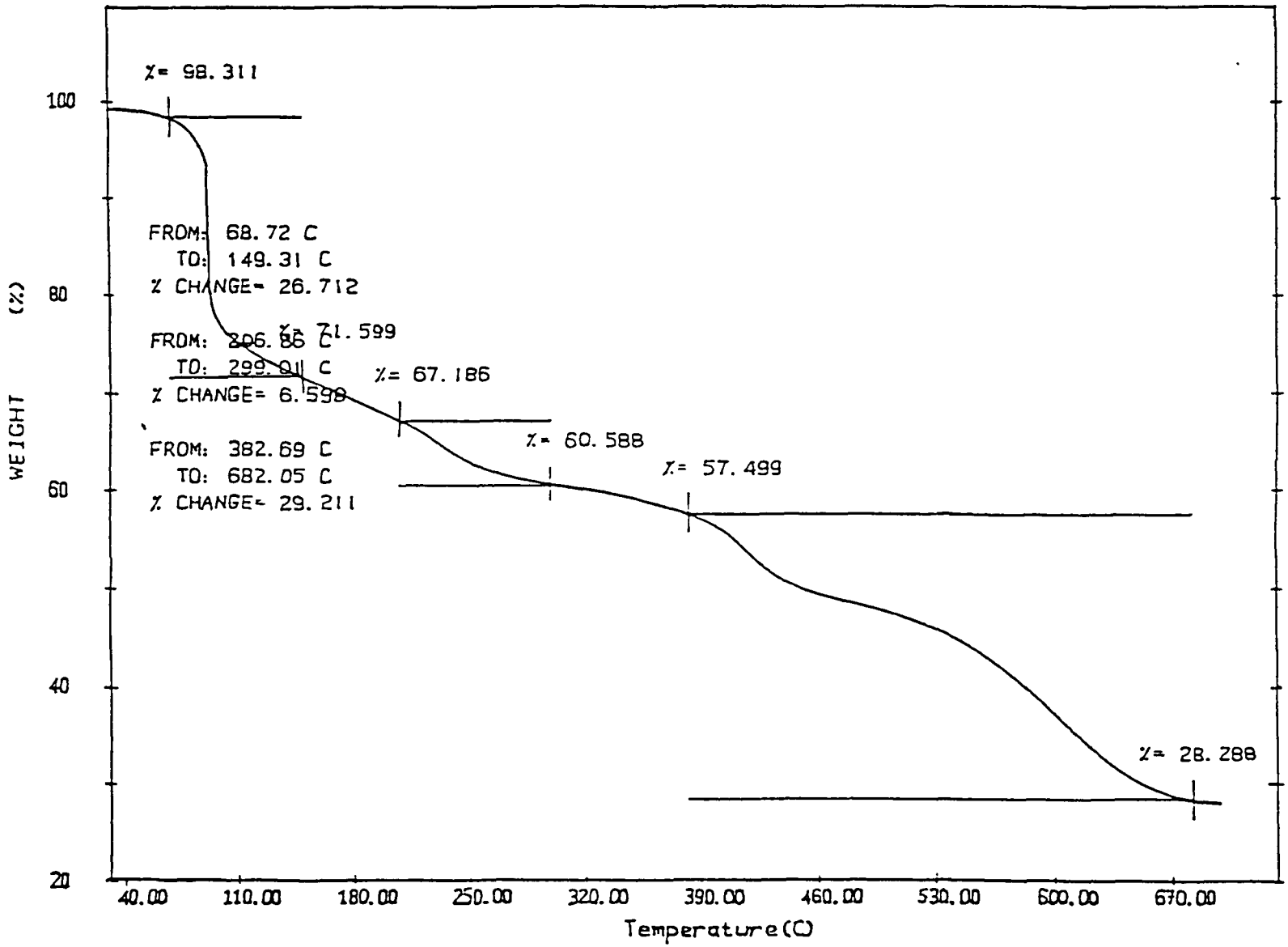
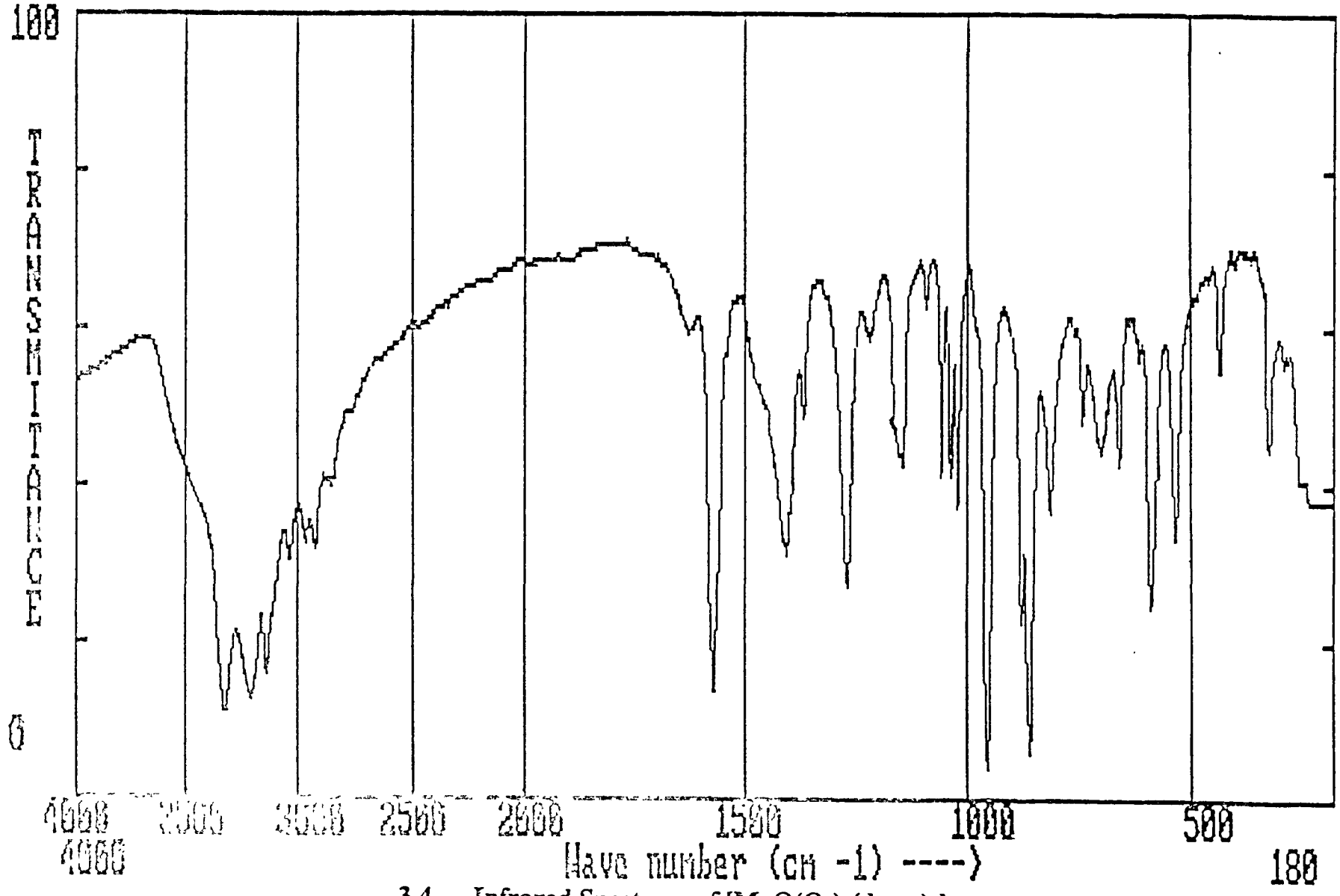


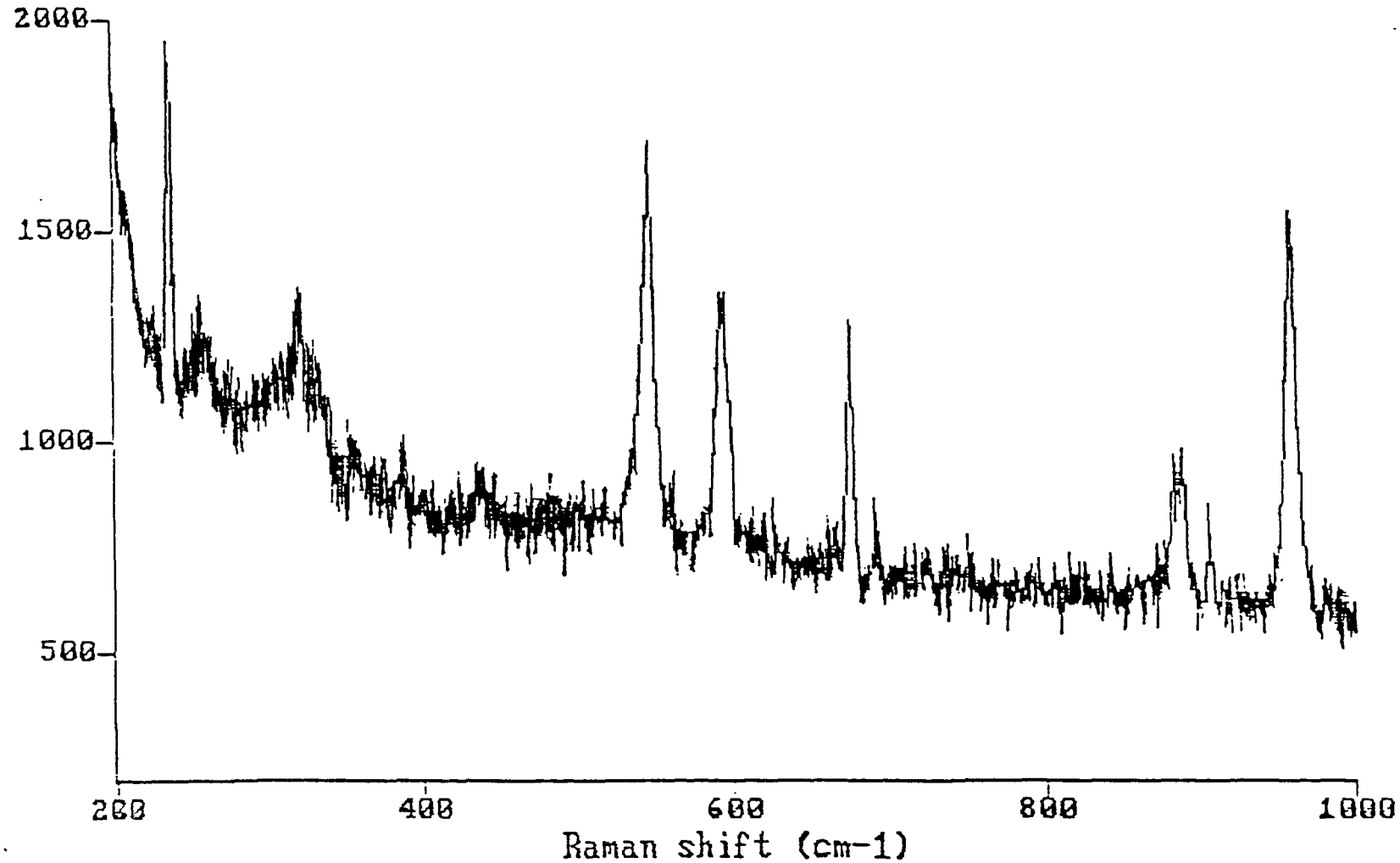
Figure 3.2 Electronic Spectra of $[V_2O_2(O_2)_3(dmpz)_4]$



3.3 Thermogram of $[V_2O_2(O_2)_3(dmpz)_4]$



3.4 Infrared Spectrum of $[MoO(O_2)_2(dmpz)_2]$



3.5 Raman Spectrum of $[MoO(O_2)_2(dmpz)_2]$

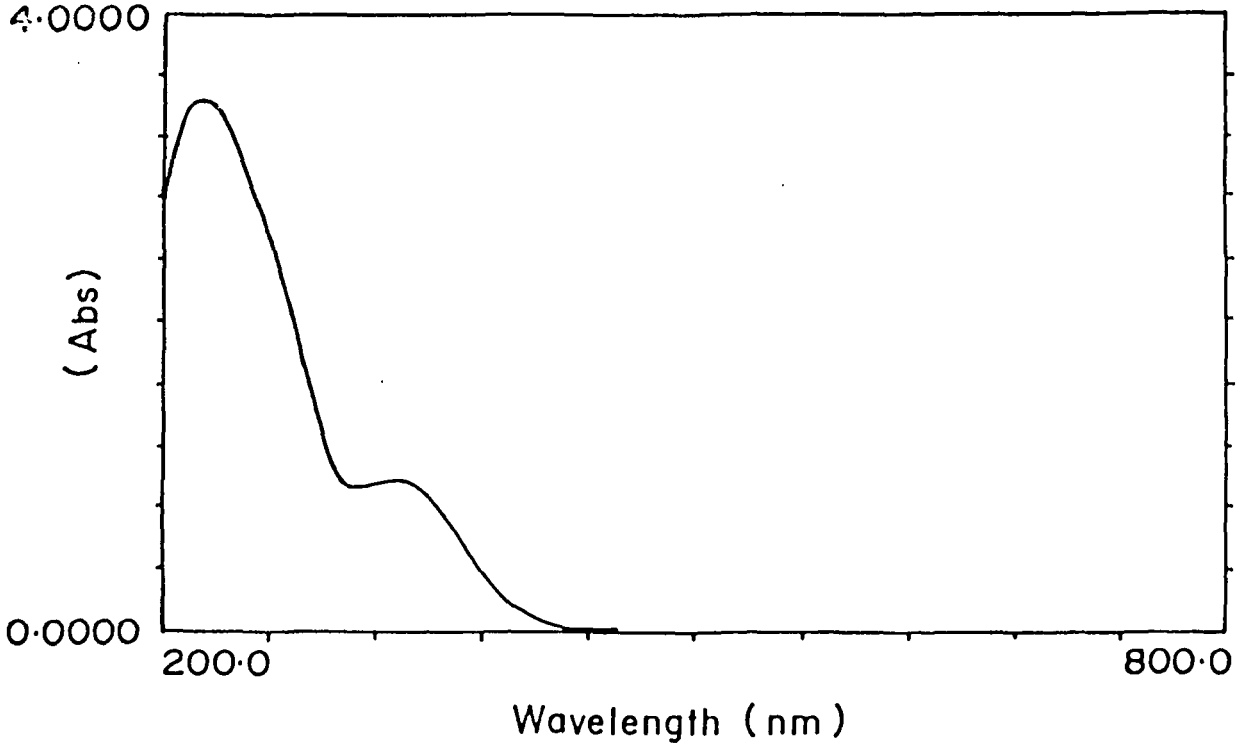
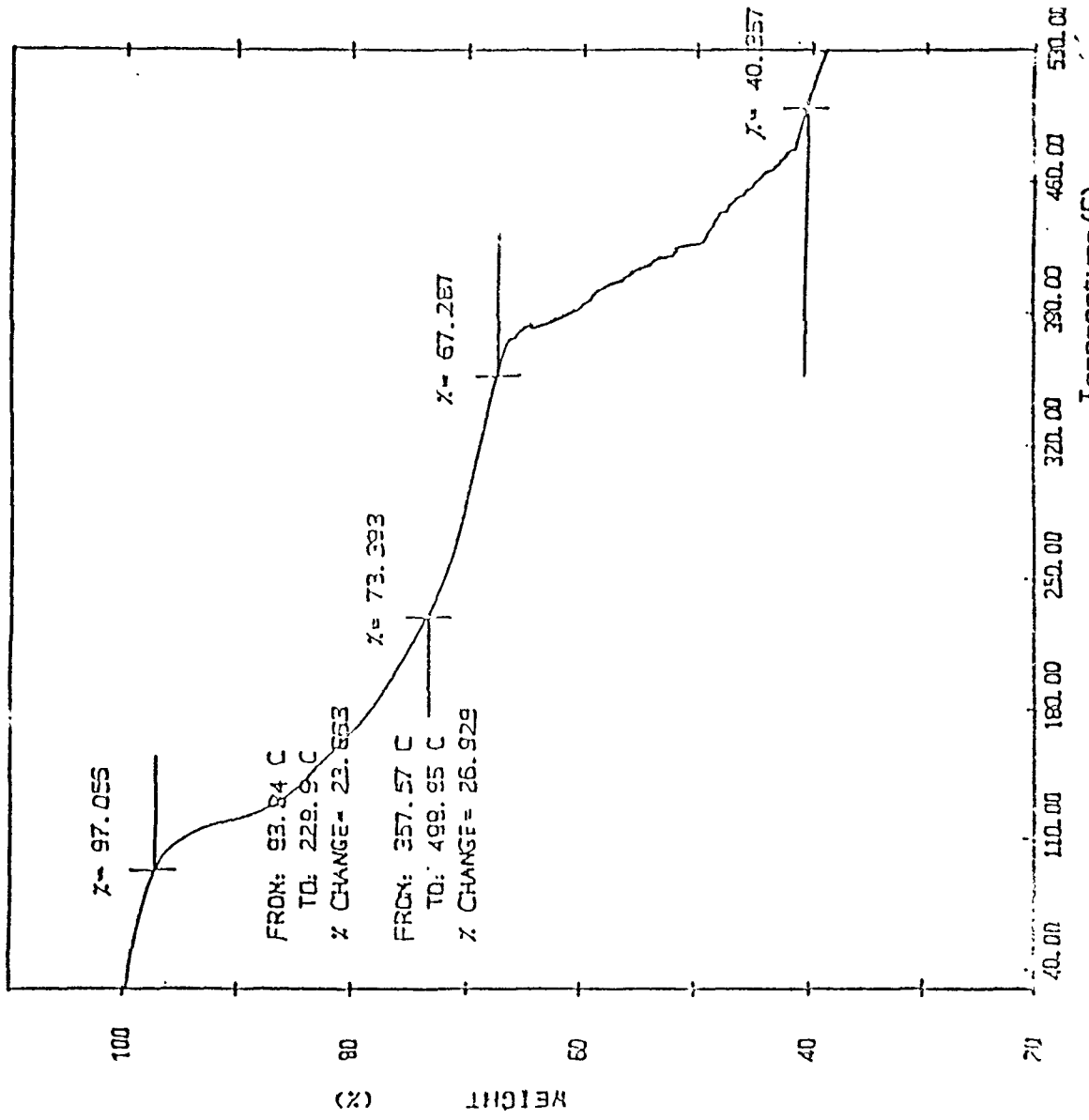


Figure 3.6 : Electronic spectrum of $[MoO(O_2)_2(dmpz)_2]$



3.7 Thermogram of $[MoO(O_2)_2(dmpz)_2]$

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CHAPTER IV

CHAPTER IV

Standardised Synthesis of $(NH_4)_2[UO_2(O_2)F_2].H_2O$ and $K_2[UO_2(O_2)F_2(H_2O)]$ and Synthesis and Structural Evaluation of $A_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ ($A=NH_4^+, K^+$ or Na^+)

For many years,[1-3] studies addressed to the interaction between UO_2^{2+} and hydrogen peroxide have been of interest , though this aspect of uranium chemistry appears to be highly complicated.[3] For instance, synthesis of well defined peroxouranium complex is marred by formation of a host of different species of varying UO_2^{2+}:O_2^{2-} stiochiometry with slight change in reaction solution pH.[1] We have been interested in the peroxo chemistry of uranium and during the past one and a half decades, complex peroxouranates(VI) having fluoride,[4] sulfate and oxalate,[5] carbonate,[6] and amines or amino acids[7] as the coligands have been synthesised and characterised in our laboratory at NEHU, Shillong.

Considering the concern in understanding the activity of bonded peroxide,[8,9] standardised synthesis of a variety of peroxo-metal compounds following a "general route" has been one of our interests. A series of fluoroperoxouranates(VI) was reported from this laboratory in 1985.[5,7] Herein we furnish the standardised synthesis of monoperoxofluoro complexes of UO_2^{2+}.

Further it was ascertained from the literature that in contrast to monoperoxouranates(VI), complexes with UO_2^{2+}:O_2^{2-} ratio of 1:>1 has been far less dealt with. Our concern in this context was to develop a synthetic methodology for peroxouranium(VI) species containing $[U_2O_4(O_2)_3]^{2-}$ and evaluate the mode of co-ordination of the peroxo ligands using vibrational spectroscopy. Such an investigation was undertaken and this chapter includes also the results of our studies on an anionic system $[U_2O_4(O_2)_3(H_2O)_4]^{2-}$ pertaining its synthesis and characterisation.

EXPERIMENTAL

All the chemicals used were reagent grade products. The preparation of $UO_3.4H_2O$ as well as the details of the instruments/equipment used for characterisation of the products are given in chapter II.

Synthesis of diammoniumdifluorodioxomono(peroxo)uranate(VI) monohydrate, $(NH_4)_2[UO_2(O_2)F_2].H_2O$ and

dipotassiumdifluorodioxomono(peroxo)uranate(VI) monohydrate, $K_2[UO_2(O_2)F_2(H_2O)]$

A 1.0g (2.79mmol) sample of $UO_3.4H_2O$ and 2.0g (35.10mmol) of NH_4HF_2 or 2.73g (35.10mmol) KHF_2 were mixed together and the mixture was dissolved in $20cm^3$ of water in a $250cm^3$ polyethylene beaker by slight warming on a steam-bath. The solution was filtered to remove any undissolved residue and cooled to room temperature . To this solution was added $24cm^3$ (211.78mmol) of 30% H_2O_2 with stirring. The pH of the reaction solution was then raised to 6 by dropwise addition of aqueous ammonia (sp.gr. 0.9) or 10% KOH solution whereupon a yellow compound began to appear. On addition of $25cm^3$of ethanol, the complete precipitation of the product was achieved. The yellow product was collected by filtration and washed with ethanol three or four times and finally dried *in vacuo* over concentrated H_2SO_4. The yield of $(NH_4)_2[UO_2(O_2)F_2].H_2O$ was 1.0g (91%) while that of $K_2[UO_2(O_2)F_2(H_2O)]$ was 1.1g (88%).

Synthesis of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$, $K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ and $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$

To 1.0g (1.99mmol) of $UO_2(NO_3)_2.6H_2O$, $30cm^3$ (264.7mmol) of 30% H_2O_2 was added . The mixture was stirred for 2 min followed by dropwise addition of aqueous ammonia (sp.gr.0.9) or a 5% NaOH or a 5% KOH solution. The pH of the solution was held at 10. At this pH an orange coloured solution was obtained. The solution was stirred for another 2 min and then the yellowish orange micro-

crystalline product was obtained by the addition of *ca.* $20cm^3$ of ethanol, with stirring. The product was isolated by filtration and purified by washing three or four times with ethanol. The yield of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ was 0.43g (52.6%), $K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ was 0.58g(67.9%) and that of $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ was 0.60g (72.9%).

Results and Discussion

Uranium(VI) exists as hydrated UO_2^{2+} in aqueous solution and interacts with hydrogen peroxide. The nature of the peroxo species formed depends largely on the pH. Thus, in order to obtain a peroxouranium complex of a particular composition, it is necessary to ascertain the appropriate pH. The first full series of a novel peroxofluorouranate(VI) complexes was reported from the laboratory where the present work has been carried out almost one and half decades ago.[4] The earlier synthesis of $(NH_4)_2[UO_2(O_2)F_2].H_2O$ and $K_2[UO_2(O_2)F_2(H_2O)]$ involved the reaction between alkali-free moist dioxouranate species, $U_2O_7^{2-}$, and hydrofluoric acid in the presence of NH_4F. A direct route to the complex has now been developed based upon the reaction of $UO_3.4H_2O$ and H_2O_2 in the presence of NH_4HF_2 or KHF_2 at pH 6 of the reaction medium maintained by the addition of aqueous ammonia or 10% KOH in the case of the potassium salt. The redundancy of HF is one of the redeeming features of the new synthesis.

$(NH_4)_2[UO_2(O_2)F_2].H_2O$ and $K_2[UO_2(O_2)F_2(H_2O)]$ are yellow microcrystalline compounds stable for months when stored in a plastic vial. For both the compounds,

uranium was determined gravimetrically as uranium oxinate, $[UO_2(C_9H_6ON)_2.C_9H_7ON]$.[10] The peroxide contents were determined by redox titration with standard potassium permaganate solution. Fluoride was estimated as PbClF as described in chapter II. The results of elemental analysis are given in Table 4.1. Both the compounds are sparingly soluble in water but dissolves completely in slightly acidified (H_2SO_4) solution with quantitative liberation of active oxygen. Because of their insolubility in water and in other organic solvents, the electronic spectra were not recorded.

The infrared spectrum of $(NH_4)_2[UO_2(O_2)F_2].H_2O$ (Fig.4.1) has been very informative exhibiting a number of absorptions at the expected regions. The IR bands at 901s and 882s cm^{-1} are believed to have originated from the ν(U=O) [trans O=U=O] modes.[11] The splitting is explained in terms of in-phase and out-of-phase vibrations of the interacting atoms. The band at 856s cm^{-1} is especially important because it owes its origin to ν(O–O) of the co-ordinated peroxide ligand.[12,13] Quite important is also the appearance of a medium intensity band at 353m cm^{-1} due to ν(U–F). The additional bands appearing at 1473 cm^{-1} and 1433 cm^{-1} due to ν_4(N–H) and 1706w cm^{-1} due to $\nu_4+\nu_6$(N–H), while 3171s cm^{-1} due to ν_3(N–H) and 2868m cm^{-1}due to $2\nu_4$(N–H) are all in support[14] of the presence of NH_4^+. The IR spectroscopic evidence for the presence of lattice water[15] in the molecule has been derived from the observance of absorptions at 3421m cm^{-1} and 1640m cm^{-1} attributable to ν(O–H) and δ(H–O–H) modes of vibrations, respectively.

The principal features of the IR spectrum (Fig.4.2) of $K_2[UO_2(O_2)F_2(H_2O)]$ are the absorption due to UO_2^{2+}, chelated O_2^{2-} and coordinated F^- with the corresponding bands being in the expected region [4,12,16,17] (Table.4.1). The observed splitting of the ν(U=O) mode at 904s and 880s cm^{-1} indicates the possibility of a bent [O=U=O] core in the complex or it might as well be due to the in-phase and out-of-phase vibrations of the interacting atoms. The strong and sharp ν(O–O) band at 852s cm^{-1} supports the view that O_2^{2-} is co-ordinated to the UO_2^{2+} centre in a triangular bidentate (C_{2v}) manner .[12,13] In addition, a medium intensity band at 366m cm^{-1} was observed due to ν(U–F) mode. The bands due to the co-ordinated water molecules was observed at 3447s cm^{-1},1635m cm^{-1},750s cm^{-1} and 311m cm^{-1} which owe their origin to ν(O–H), δ(H–O–H), $\rho_r(H_2O)$ and ν(U–OH_2) modes, respectively.[18]

In order to understand the thermal behaviour of $(NH_4)_2[UO_2(O_2)F_2].H_2O$, it was subjected to thermogravimetric (TG) (Fig.4.3) and differential scanning calorimetric (DSC) studies. The temperature range covered in the TG experiment was 50-730°C and for DSC 31-520°C. Both the experiments were conducted under a constant flow of nitrogen. The weight loss begins at 157.6°C and continues up to 272.4°C. The loss of weight at this temperature range corresponds to the loss of one water molecule and two ammonia molecules (calc. 13.19%, obsvd. 13.0%). Immediately followed by this was a continuous loss of weight from 272.4°C to 618.7°C, that correspond to the loss of one hydrogen peroxide molecule, leading to the formation of UO_2F_2. The observed loss for this event is 8.61% as compared with the expected

loss of 8.62%. The corresponding DSC thermogram shows three exotherms at 36°C, 164°C and 194°C which have been attributed to a change in crystallinity (or phase transition) of the compound, and the loss of different constituents as observed in the TG analysis.

The results of replicate synthesis of $K_2[UO_2(O_2)F_2(H_2O)]$ followed by its characterisation are consistent causing us to state that the new method for synthesis of $K_2[UO_2(O_2)F_2(H_2O)]$ is now standardised and can be recommended for adoptation for its preparation.

As mentioned in the introduction section of this chapter , that in contrast to monoperoxouranate(VI), complexes with UO_2^{2+}:O_2^{2-} ratio of 1:>1 has been far less dealt with. Guided by this consideration our interest was particularly drawn to dinuclear " peroxouranium " system with O_2^{2-}:U ratio being 3:2. Accordingly, the reaction of $UO_2(NO_3)_2$. $6H_2O$ with H_2O_2 was carried out in the presence of aqueous ammonia or 5% KOH or 5% NaOH solution (pH=10).

The complexes are all yellow crystalline solid, stable for months when stored in a plastic vial. Both ammonium and potassium salts are soluble in water but the sodium salt is insoluble. Uranium was estimated gravimetrically as uranyl oxinate[10] as described in chapter II. The peroxide estimation was accomplished by redox titration involving standard potassium permaganate solution. The results obtained thereof clearly suggested the presence of O_2^{2-}:U ratio as 3:2 indicating a dimeric nature of the complex. The molar conductances of 10^{-3}M aqueous solutions of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ and $K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ were 82 and 72

$\Omega^{-1}cm^2mol^{-1}$, respectively. The experimentally obtained values are far too low for the type of compounds as formulated. The exceedingly low molar conductances are indicative of very strong ionic association. However, such a behaviour is not very commonly encountered in co-ordination chemistry. The results of elemental analysis are given in Table.4.1.

The infrared spectra of the complexes revealed structurally very significant informations (Table.4.3). The IR spectrum (Fig.4.4) of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ displayed a strong band at 893s cm^{-1} owing to ν(U=O) stretching mode of trans-linked O=U=O[19] and another band at 800m cm^{-1} attributed to ν(O–O) mode of co-ordinated peroxide.[20] The bands due to peroxide [ν(O–O)]was not observed in these complexes. It is not too surprising because for bridging peroxide the dipole change of the O–O stretching vibration is likely to be small. Thus the band corresponding to this mode is likely to be weak and in some cases the band may not be even observed.[12] This might have been the case with our compounds. The IR features attributed to the NH_4^+ ion were observed at 3166m cm^{-1} and 1405s cm^{-1}. These correlate very well with those observed for the ammonium ion[14] and have been assigned to ν_3 and ν_4 modes of NH_4^+. A very weak band at 1743w cm^{-1} is observed corresponding to $\nu_4+\nu_6$(N–H) mode. The additional bands observed at 3388s(br)cm^{-1}, 1633m cm^{-1}, 720w cm^{-1} and 314m cm^{-1} owe their origins to the ν(O–H) , δ(H–O–H), $\rho_r(H_2O)$ and ν(U–OH_2) modes of water.[18] The

bands at 720w and 373 cm^{-1} owe their origin to the co-ordinated water. The broad nature of ν(O–H) is explained in terms of hydrogen bonding in the molecule.

The general features of vibrational spectrum of the compounds $K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ and $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ (Table.4.3) are the IR signatures (Fig.4.5 and 4.6) at *ca.* 894s cm^{-1}, *ca.* 801m cm^{-1}, *ca.* 600-350(br) cm^{-1}, *ca.*3420s(br) cm^{-1}, *ca.* 1631w cm^{-1} and *ca.*722w cm^{-1}, respectively. A very strong absorption observed at *ca.*894s cm^{-1} was assigned to the ν(U=O) stretching mode of trans-linked O=U=O.[19] The band at *ca.*801m cm^{-1} owes its origin to ν(O–O) of the co-ordinated peroxide ligand.[20] The appearance of a broad, rather weak band at *ca.* 600-350 cm^{-1} in the IR spectrum of the compound lends support to our assignment in favour of $\nu(U–O_2)(\nu_2)$ and $\nu(U–O_2)(\nu_3)$ modes of co-ordinated peroxide. In addition, the absorptions at *ca.*3420s cm^{-1} ,*ca.* 1631w cm^{-1} and *ca.*722w cm^{-1} are assigned to ν(O–H), δ(H–O–H) and $\rho_r(H_2O)$, respectively. The broad nature of ν(O–H) is explained in terms of hydrogen bonding in the molecule. The weak nature of δ(H–O–H) and the presence of a band at *ca.*722 cm^{-1} provide evidence for co-ordination of water molecule to the metal centre.[21,22]

With an objective to understand the thermal stability and the decomposition pattern, thermogravimetric(TG) experiments were performed on $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ (Figure 4.7) and $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ (Figure 4.8). The temperature range covered for TG was 31-840°C. The thermogram of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ shows that compound is stable upto 31°C. The weight loss initiates at 31.2°C and continues up to 193.52°C. The loss of

weight at this step corresponds to the expulsion of eight water molecules and$1/2O_2$ (calc. 19.61%, obs. 19.44%). After this the thermogram exhibits a slow rate of weight loss up to 628°C followed by a sharp loss between 628 and 656°C. The weight loss from 193-628°C gets along well with the loss of two ammonia molecules and $1/2O_2$ (calc. 6.37%, obs. 6.87%). The weight loss in between 628 and 656°C is due to the loss of one hydrogen peroxide (calc. 4.17%, obs. 2.56%), leading to the formation of two units of UO_3 per formula unit of the compound. The DTG shows peaks at 62, 171, 342 and 647°C attributable to loss of eight water molecules, $1/2O_2$, two ammonia molecules and one hydrogen peroxide as described in TG.

The TG experiment on $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ suggests that the weight loss initiates at 31.2°C and continues up to 79.31°C. The loss of weight at this step corresponds to the expulsion of four water molecules (calc. 8.72%, obs. 8.46%). In the temperature range 79.31°C -146.64°C there is a slow weight loss corresponding to the loss of one water molecule (calc. 2.18%, obs. 2.3%). The thermogram then exhibits a sharp weight loss between 146.64°C and 187.53°C due to the loss of three water molecules (calc. 6.54%, obs. 6.11%). Then their is a slow rate of weight loss from 187.53°C which continues up to 760°C, leading to the formation of $Na_2U_2O_7$ (calc. 5.81%, obs. 5.54%) with the loss of one peroxide and $1/2O_2$. The DTG of $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ shows four peaks at 46, 73, 164 and 535°C. The first, second and the third peaks are very intense and sharp compared to the fourth peak at 535°C. The peak at 46°C is attributable to loss of four water molecules in the

corresponding TG curve. The peaks at 73 and 164°C corresponds to the loss of one and three water molecules, and at 535°C the peak is due to the loss of one peroxide and 1/2 O_2, respectively.

Table 4.1 : Analytical Data and Solution Electrical Conductance of $(NH_4)_2[UO_2(O_2)F_2].H_2O$, $K_2[UO_2(O_2)F_2(H_2O)]$ and $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$, $K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ and $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calc. (%)
$(NH_4)_2[UO_2(O_2)F_2].H_2O$	–	U	60.40	60.42
		O_2^{2}	8.79	8.12
		F^-	9.60	9.64
$K_2[UO_2(O_2)F_2(H_2O)]$	–	U	53.07	54.57
		O_2^{2-}	7.06	7.33
		F^-	8.96	8.70
$(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$	82	U	57.90	58.34
		O_2^{2-}	11.48	11.76
$K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$	72	U	54.79	55.48
		O_2^{2-}	11.12	11.18
$Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$	–	U	58.38	57.64
		O_2^{2-}	11.25	11.62

Table 4.2 : Structurally Significant IR Bands of $(NH_4)_2[UO_2(O_2)F_2].H_2O$ and $K_2[UO_2(O_2)F_2(H_2O)]$

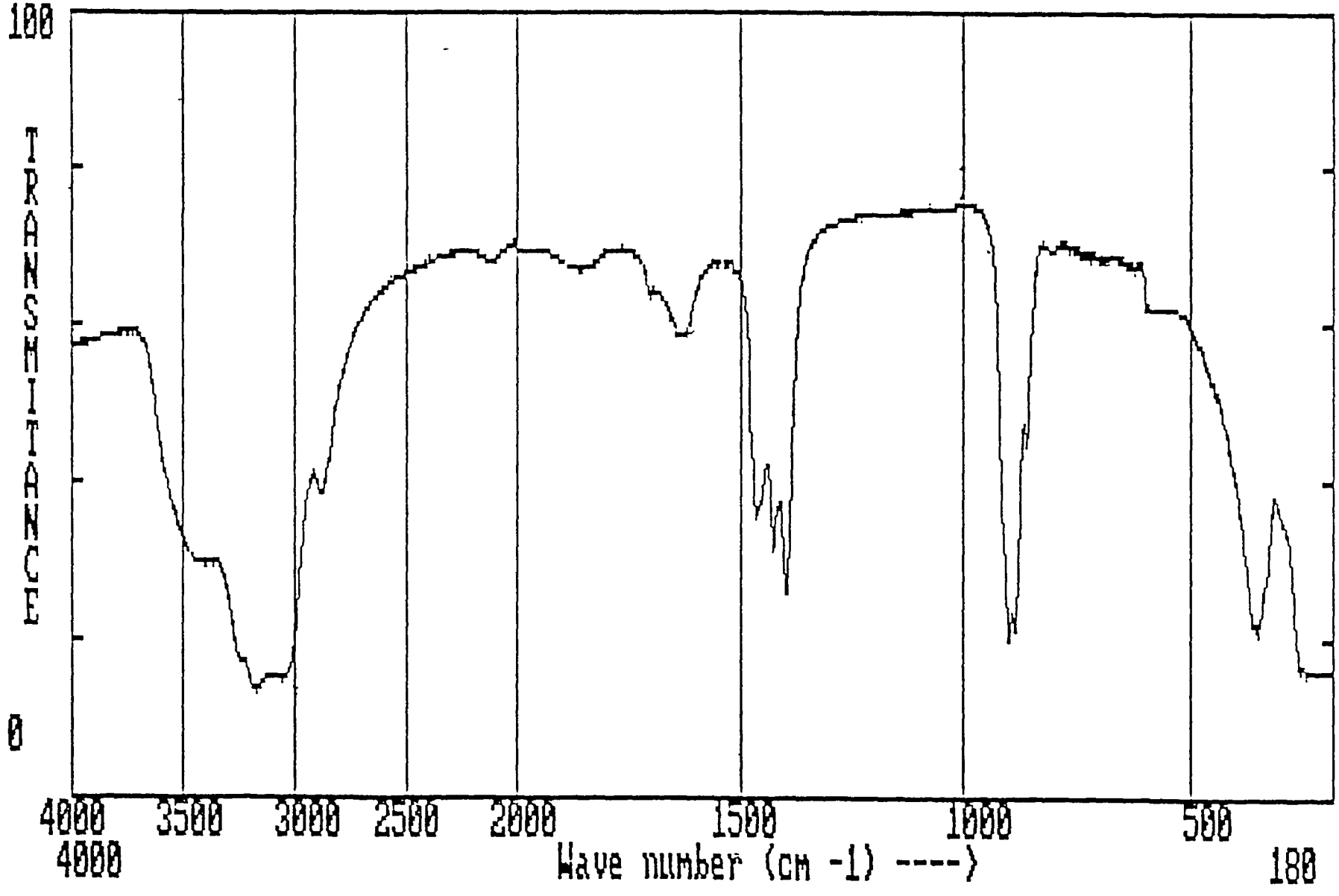
Compound	Band Position(cm^{-1})	Assignment
$(NH_4)_2[UO_2(O_2)F_2].H_2O$	901s 882s	ν(U=O)[transO=U=O]
	856s	ν(O–O)
	353m	ν(U–F)
	3171s	ν_3(N–H)
	3078m	ν_1(N–H)
	2868m	$2\nu_4$(N–H)
	1706w	$\nu_4+\nu_6$(N–H)
	1473 1433	ν_4(N–H)
	3421m	ν(O–H)
	1640m	δ(H–O–H)
$K_2[UO_2(O_2)F_2(H_2O)]$	904s 880s	ν(U=O)[transO=U=O]
	852s	ν(O–O)
	366m	ν(U–F)
	3447s	ν(O–H)

	1635m	δ(H–O–H)
	750s	$\rho_r(H_2O)$
	311m	$\nu(U–OH_2)$

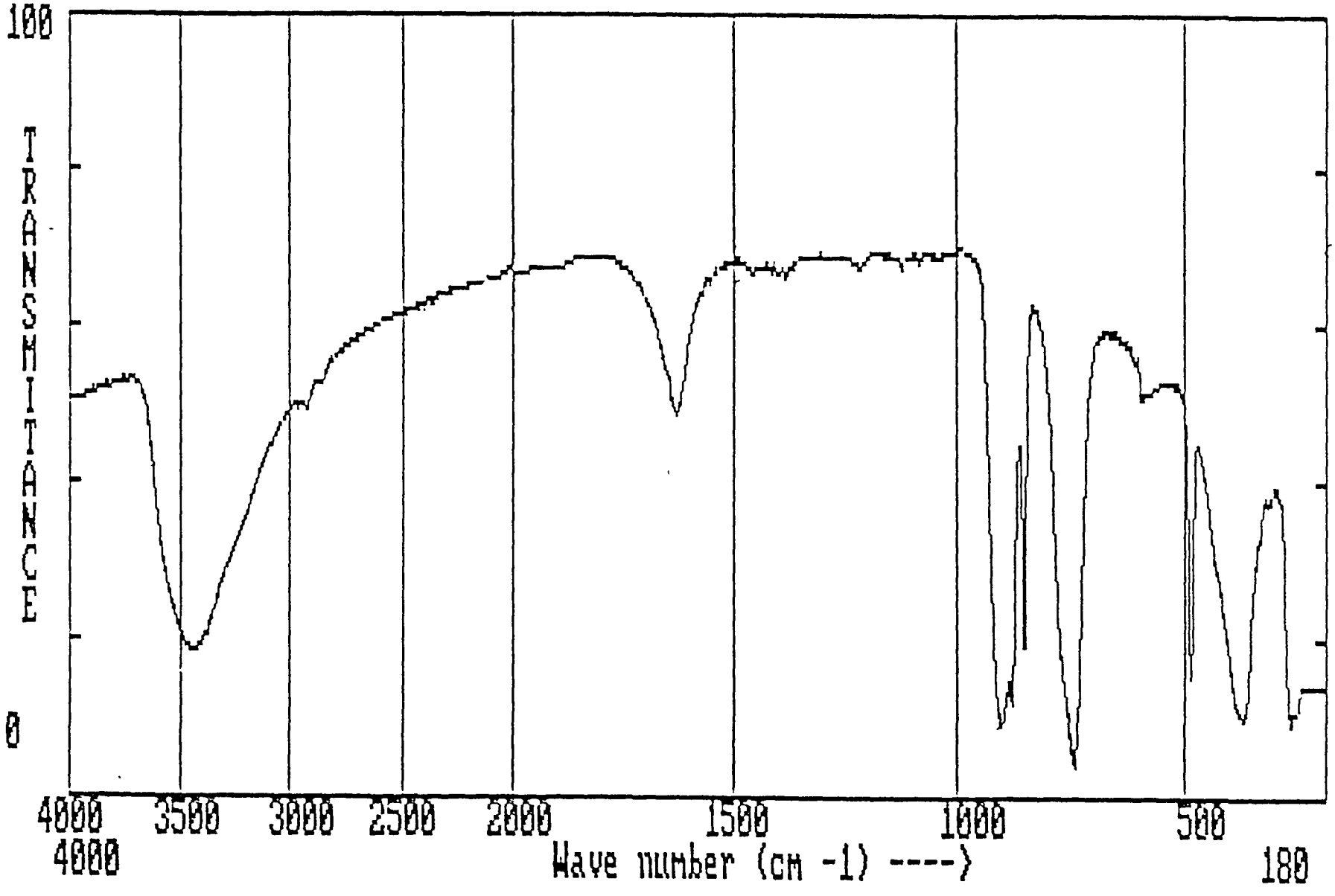
Table 4.3 : Structurally Significant IR Bands of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$, $K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$ and $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$

Compound	Band Position (cm^{-1})	Assignment
$(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$	893s	ν(U=O)[transO=U=O]
	800w	ν(O–O)
	3166m	ν_3(N–H)
	1743w	$\nu_4+\nu_6$(N–H)
	1405s	ν_4(N–H)
	3388s	ν(O–H)
	1633m	δ(H–O–H)
	720w	$\rho_r(H_2O)$
	314m	$\nu(U–OH_2)$
$K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$	893s	ν(U=O)[transO=U=O]
	800m	ν(O–O)
	3418s	ν(O–H)
	1635w	δ(H–O–H)
	723w	$\rho_r(H_2O)$

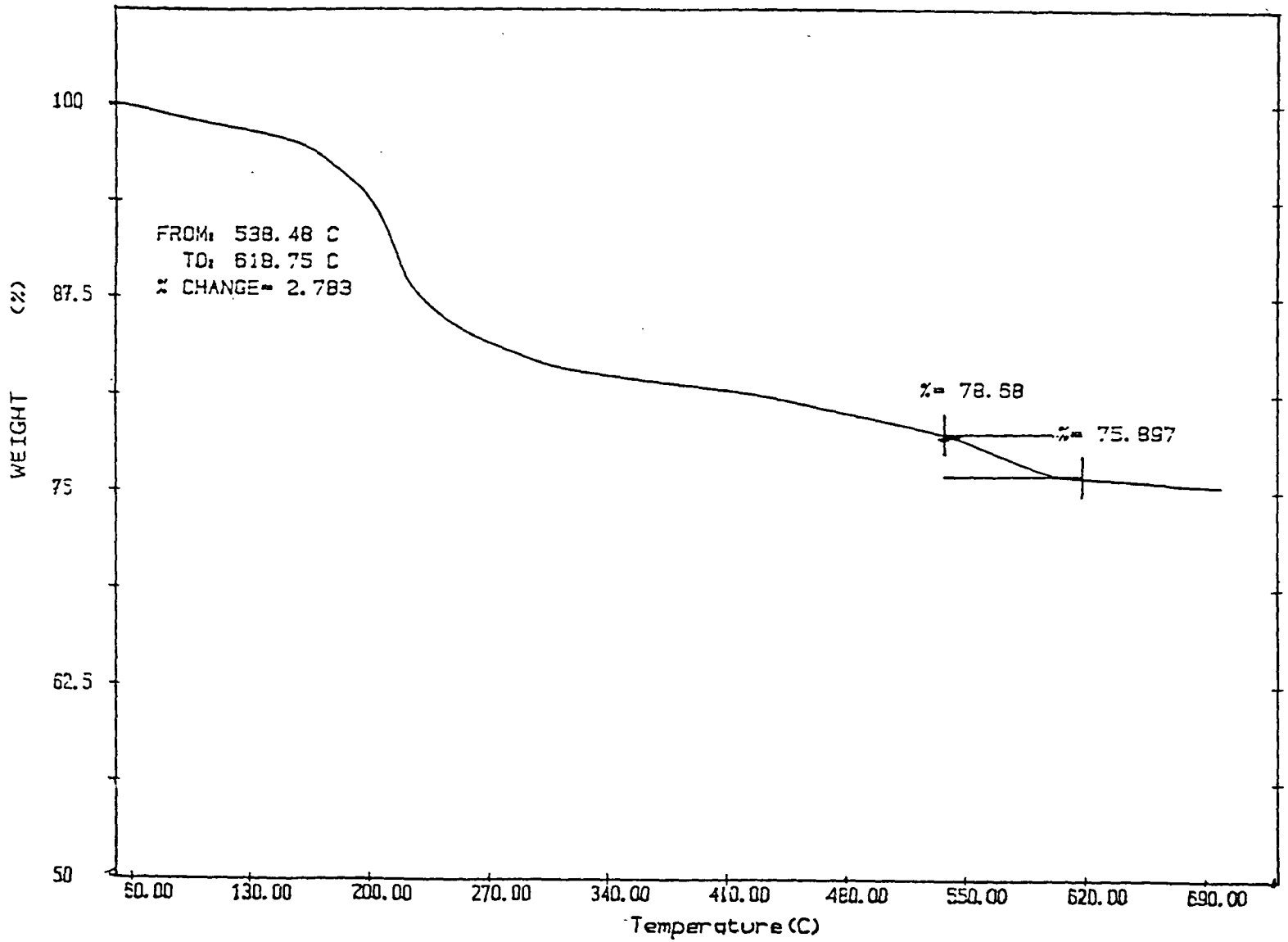
$Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$	893s	ν(U=O)[transO=U=O]
	800m	ν(O–O)
	3421s	ν(O–H)
	1626w	δ(H–O–H)
	720w	$(\rho_r)(H_2O)$



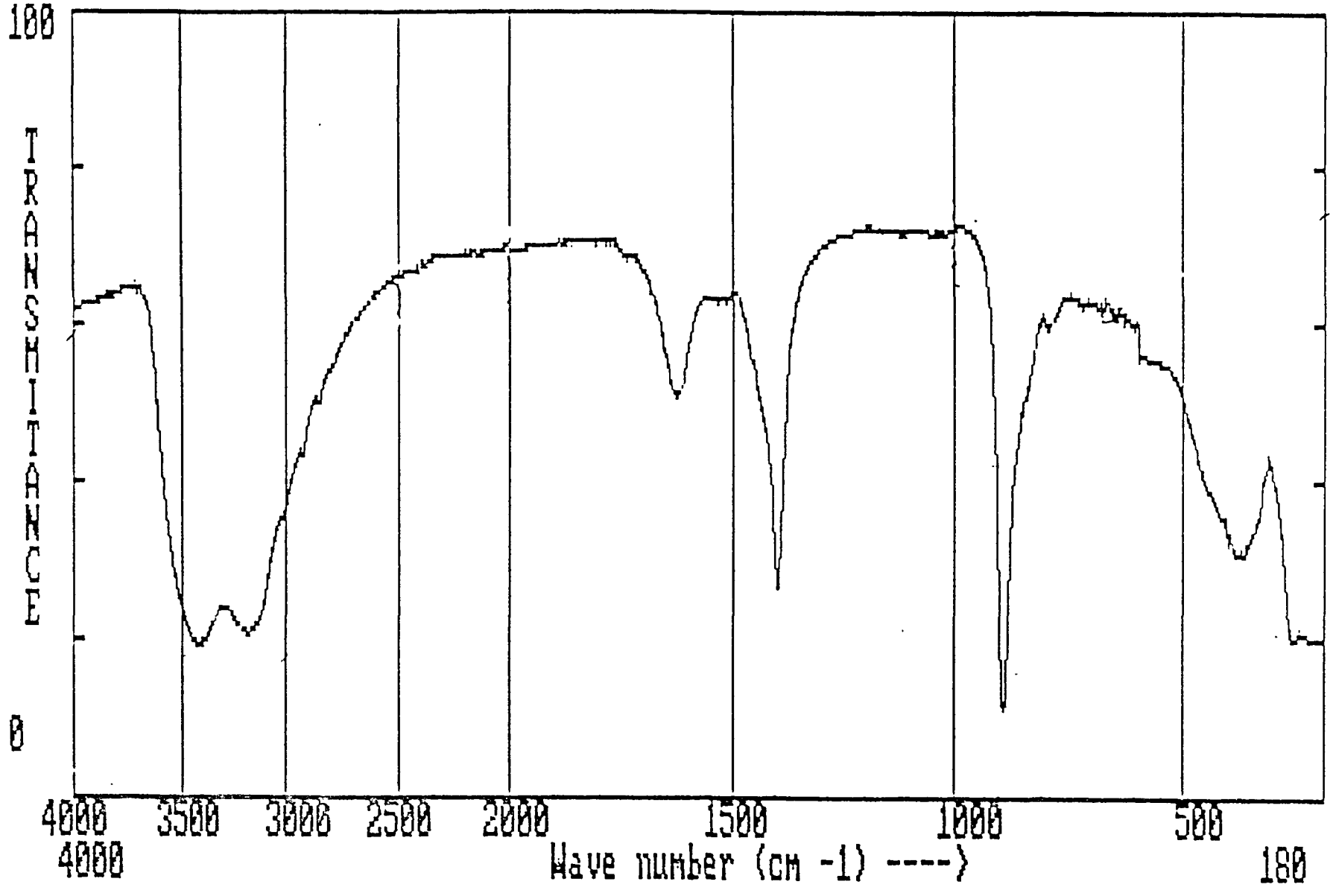
4.1 Infrared Spectrum of $(NH_4)_2[UO_2(O_2)F_2].H_2O$



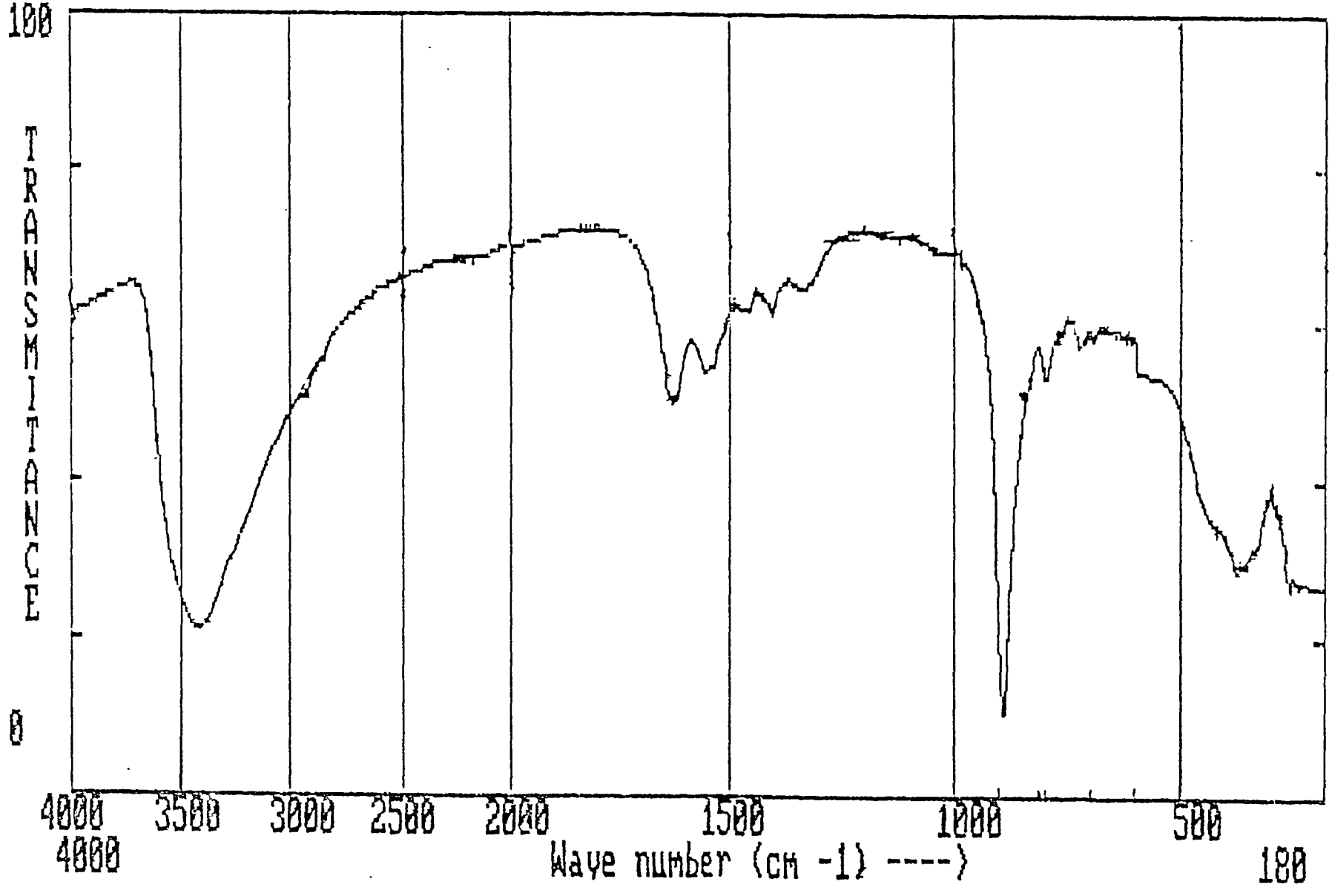
4.2. Infrared Spectrum of $K_2[UO_2(O_2)F_2(H_2O)]$



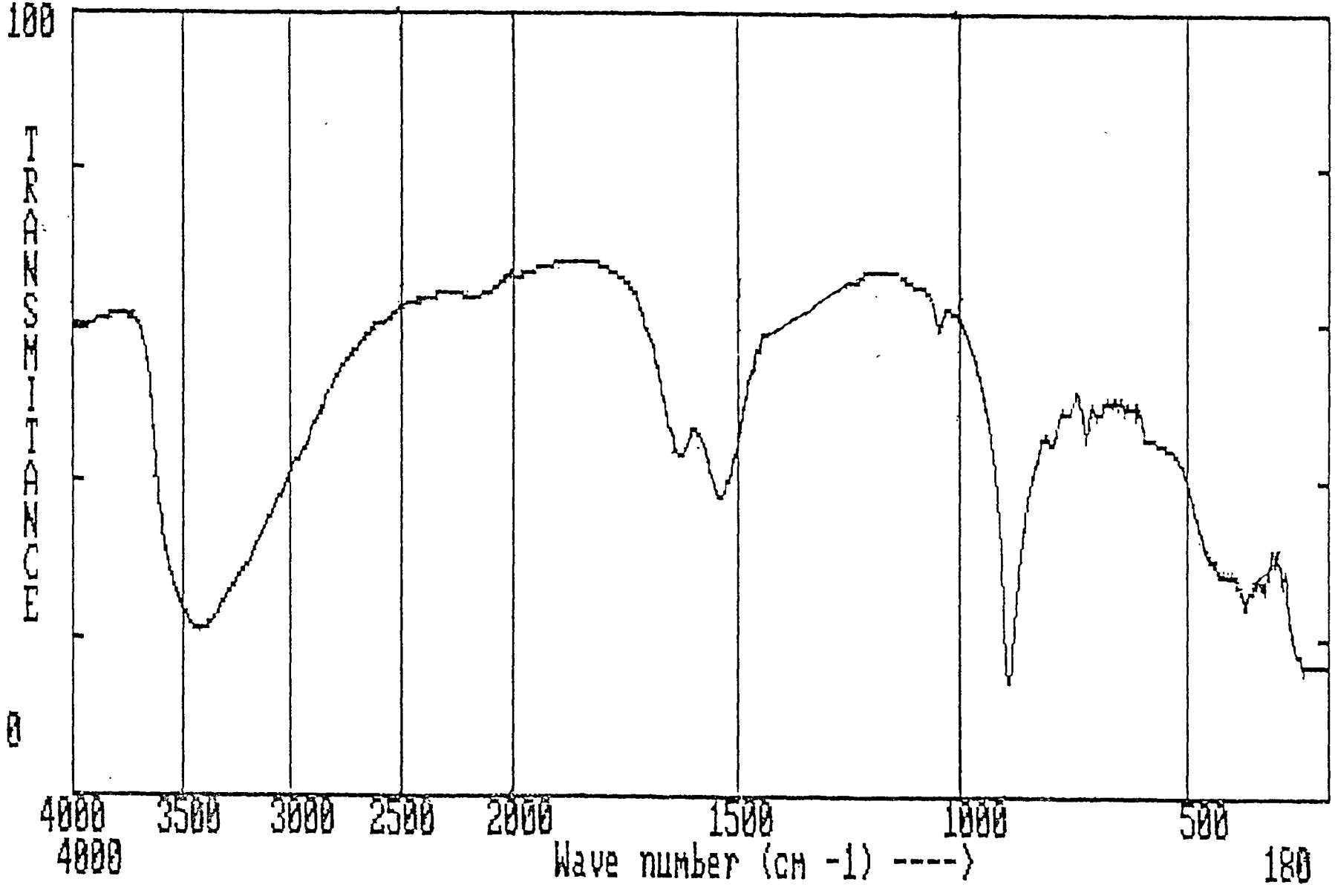
4.3 Thermogram of $(NH_4)_2[UO_2(O_2)F_2].H_2O$



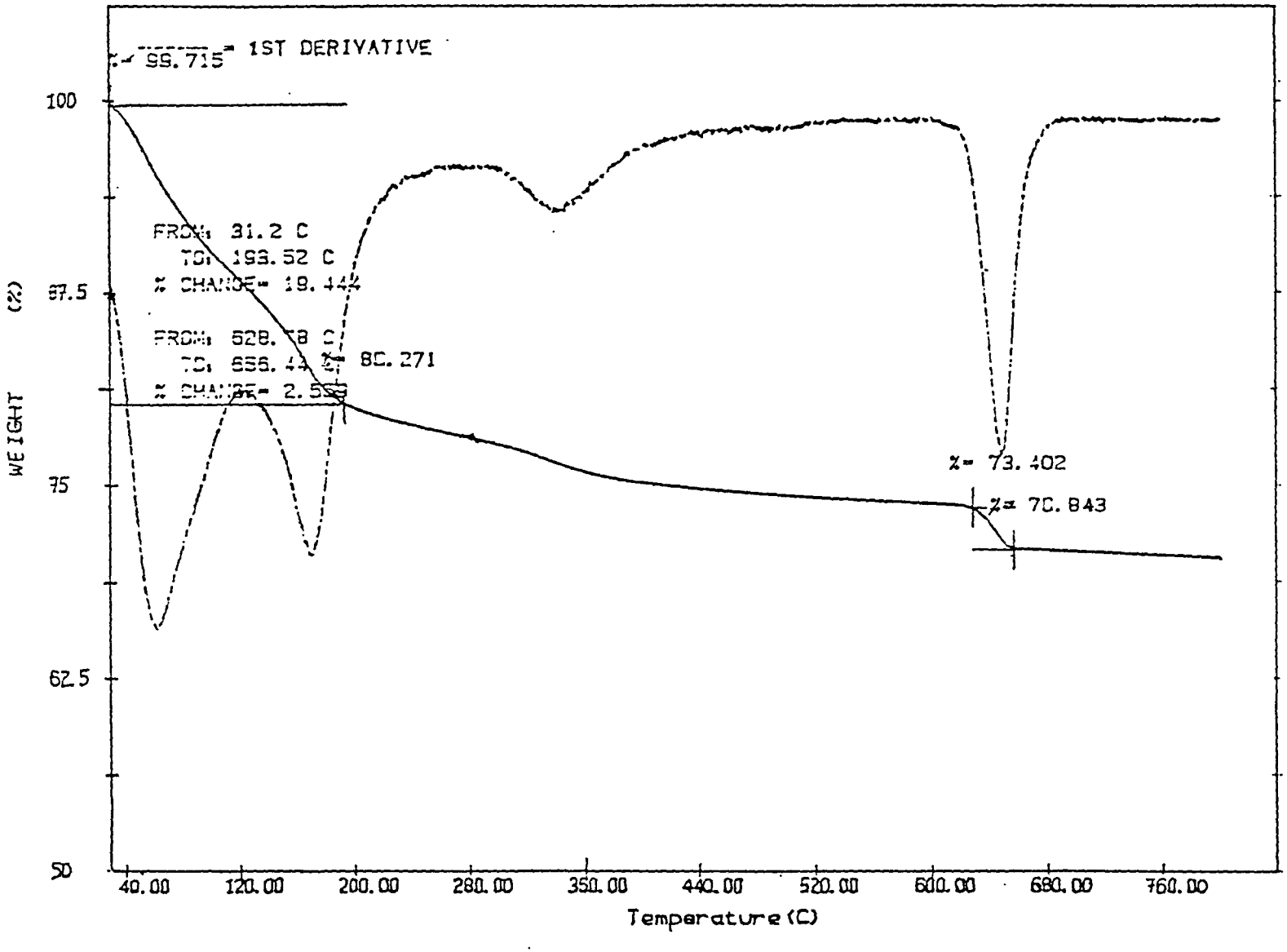
4.4. Infrared Spectrum of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$



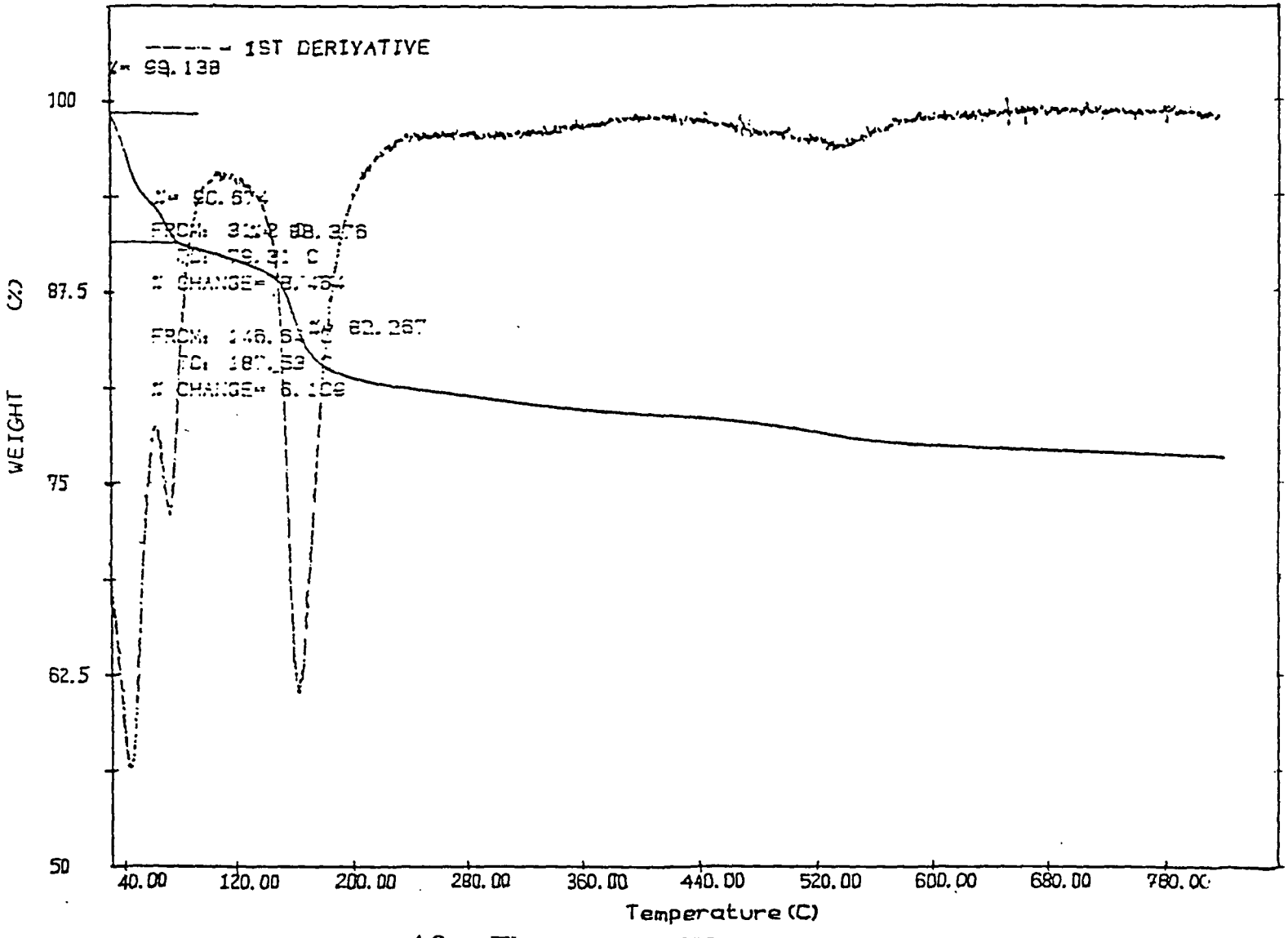
4.5 Infrared Spectrum of $K_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$



4.6. Infrared Spectrum of $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$



4.7. Thermogram of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$



4.8. Thermogram of $Na_2[U_2O_4(O_2)_3(H_2O)_4].4H_2O$

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CHAPTER V

CHAPTER V

Peroxo-metal Mediated Synthesis of Organic Ammonium Tribromide (OATB). An Environmentally Benign Route to Br_3^-, and Bromination of Selected Substrates by Tetrabutyl-Ammonium Tribromide(TBATB)

The isolation of vanadium bromoperoxidase (V-BrPO), from several marine algae, fungi, and a lichen [1-4] which plays a catalytic role in the biosynthesis of several halogenated marine natural products[4] and several compounds with potential medicinal uses[4] has provided a tremendous impetus to studies addressed to biomimics of this enzymatic activity.[5-8]

Vanadium is an essential cofactor in V-BrPO and its role lies primarily in co-ordination of H_2O_2 causing its activation towards oxidation of halide (scheme 1).[9] The

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This work has been published : Tetrahedron Letter 1998, 39, 8163.

mechanism involved in halide oxidation is proposed[10] (Fig.5.1) to occur via nucleophilic attack on bound peroxide without binding of halide directly to vanadium. Unlike Fe heme-BrPO[4,11] the metal centre does not undergo redox cycling[4,12] as no EPR signal was observed during turnover conditions.[4]

From the proposed catalytic cycle (Fig 5.1) for the vanadium haloperoxidase, it is inferred that the vanadium(V) ion first binds 1 or 2 equivalent of peroxide and this peroxovanadium(V) complex then reacts with halide to generate an oxidised halogen

$$H_2O_2 + Br^- \xrightarrow{\text{V-BrPO}} \text{"intermediate" (formally } Br^+\text{)}$$

(eg., $HOBr=Br_2 = Br_3^- =$ Enz-OBr , Enz-Br)

Scheme 1

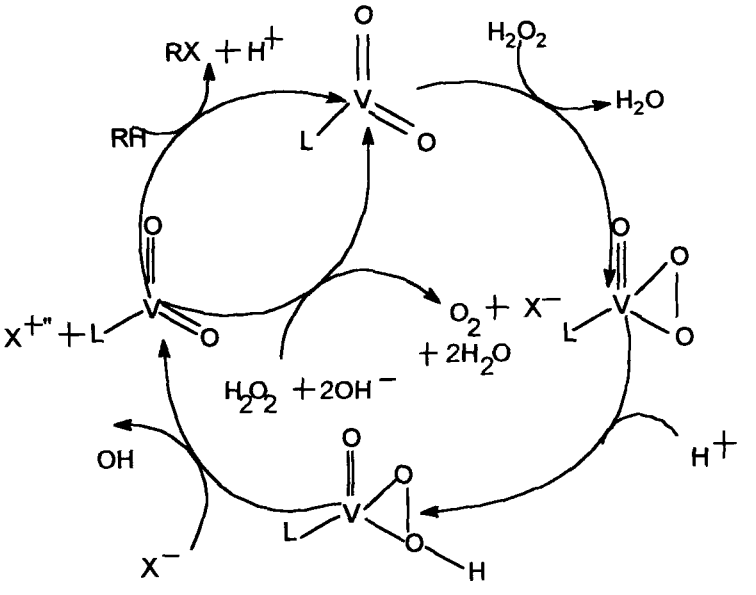
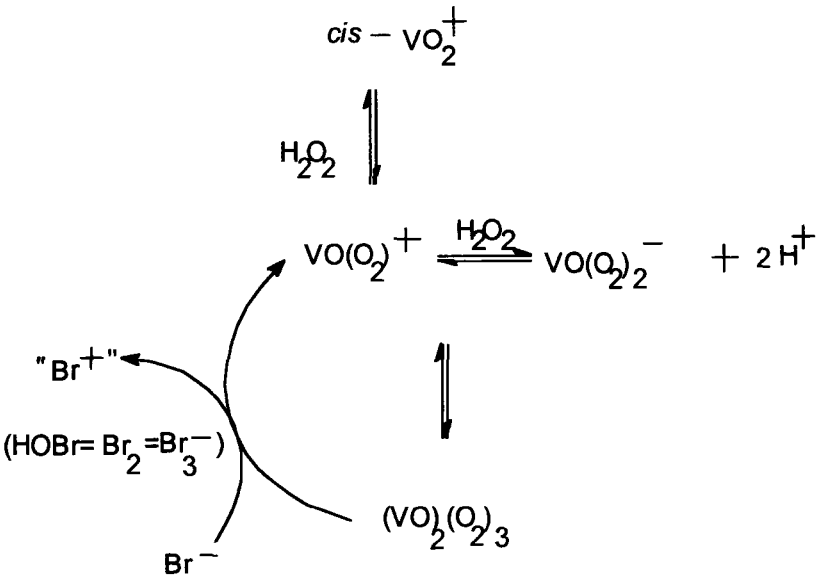


Fig 5.1. Proposed catalytic cycle for the vanadium haloperoxidase

species, which then may halogenate an organic substrate or in the absence of substrates under basic conditions, react with additional hydrogen peroxide to form singlet oxygen.[13-15]

It was also shown by Butler et al.[5] that bromide oxidation by hydrogen peroxide was catalysed by *cis*-dioxovanadium(V) in acidic, aqueous and aqueous/ethanolic solution. Co-ordination of hydrogen peroxide by vanadium(V) gave rise to an equilibrium mixture of oxomonoperoxo-and oxodiperoxovanadium(V), and the composition was dependent on the concentrations of acid and hydrogen peroxide. By kinetic and spectroscopic[5] analyses it was suggested that catalysis occurs by dimerisation of oxomonoperoxo and oxodiperoxovanadium(V) to form a binuclear, triperoxovanadium(V) complex followed by oxidation of bromide (Scheme-2).



Scheme-2

The involvement of an oxidised bromine equivalent intermediate is common in all reaction mechanisms proposed for V-BrPO biomimetic reactions with bromide. However,

no isolation and structural characterisation of such an intermediate were reported previously. Instability of Br_3^- in aqueous solution was probably an impediment. However, in a biochemically related study, the generation and trapping of tribromide(Br_3^-), and the crystal structure of Bu_4NBr_3(TBATB) were described in an earlier thesis from our laboratory.[16] In this chapter, we present the preparation of tetrabutylammonium tribromide(TBATB), by peroxovanadium(V)-mediated oxidation of bromide following the general procedure reported by Mandal,[16] and emphasise on its reactivity towards a variety of organic substrates.

EXPERIMENTAL

The chemicals and solvents used were of reagent grade or better quality products. The details of the instruments/equipment used for characterisation of the products are given in chapter II.

Synthesis of tetrabutylammonium tribromide : A quantity of 1.0g (5.49mmol) of vanadium pentaoxide, V_2O_5, was dissolved in $10cm^3$(88.20mmol) 30% H_2O_2 in an ice-cold condition (0–5°C). The pH of the solution was measured to be 1. This was then treated with a solution of 7.1g (22.02mmol) of tetrabutylammonium bromide, Bu_4NBr, in $30cm^3$ water. Immediately, the solution turned yellow which on standing for 5min produced a yellow compound. The reaction mixture was left at room temperature for 15–20min for complete precipitation. The product was isolated by filtration washed two or three times with water and dried in air or by pressing between the folds of a filter paper. The yield of NBu_4Br_3 was 2.4g (68%). M.P=75°C (lit [4] 76°C). The compound on recrystallisation from acetonitrile produced orange yellow crystals.

Bromination Reaction

Bromination of Anthracene

(a) To the gently refluxing solution of 0.369g(2.07mmol) anthracene in $10cm^3$ acetic acid, 1g(2.08mmol) NBu_4Br_3 (TBATB) was added over a period of 10min. The mixture was stirred at reflux for 15min until no more HBr was evolved. The cold reaction mixture was diluted with water and extracted with ether. The organic layer was separated, washed with water and aqueous $NaHCO_3$, dried and evaporated under reduced pressure. [Yield=0.35g(68%)]; M.P=96°C (Lit [17] 96-98°).

(b) To the gently refluxing solution of 1.78g(10mmol) anthracene in $10cm^3$ acetic acid, 9.64g(20mmol) NBu_4Br_3(TBATB) was added over a period of 10min maintaining the molar ratio of anthracene and TBATB as 1:2. The mixture was stirred at reflux for 15min until no more HBr was evolved. The cold reaction solution was diluted with water and extracted with ether. The organic layer was separated, washed with water and aqueous $NaHCO_3$ dried and evaporated under reduced pressure. [Yield=0.5g (72%)]; M.P=220°C(lit [18] 223-224°C).

Bromination of Aniline

TBATB (14.46g, 30mmol) was added to a vigorously stirred solution of aniline (0.93g, 10mmol) in 50% aqueous DMF ($25cm^3$) over a period of 10min maintaining the molar ratio between TBATB and aniline at 3:1. The mixture was stirred at room temperature for 15min and then diluted with water (100mL). After complete precipitation of the product the aqueous solution was extracted with ether, separated , washed with

water, dried and evaporated under reduced pressure. [Yield =2.1g (65%)]; M.P=119°C(lit [19] 120-122°C).

Bromination of Benzene

A mixture of benzene (0.8g, 10mmol), Ag_2SO_4 (4.7g, 15mmol), and conc. H_2SO_4 ($25cm^3$) was stirred vigorously at room temperature, for *ca.* 10min followed by the addition of TBATB (5.8g, 12mmol). The reaction mixture was stirred for 30min and then poured into 150g of crushed ice. The precipitated AgBr was separated by suction filtration. The filtrate and the precipitate were extracted with ether, and the combined extracts were washed several times with water to remove any remaining acid and evaporated under reduced pressure. [Yield=0.38g(40%)].

Bromination of Phenol

A mixture of phenol (10mmol), TBATB (30mmol), and $CaCO_3$ (2g, 20mmol) in $25cm^3$ of CH_2Cl_2 and CH_3OH (1:1) mixture was vigorously stirred for 60min. The reaction mixture was filtered *in vacuo*, the filtrate was diluted with 100-$120cm^3$ of water to completely precipitate the product. The product was then filtered and washed with water and dried *in vacuo* over conc. H_2SO_4. [Yield=1.98g (60%)];M.P=94°C(lit [20] 95°C).

Bromination of Imidazole

A mixture of imidazole (0.68g, 10mmol), TBATB (14.66g, 30mmol), and $CaCO_3$ (2g ,20mmol) in $25cm^3$ of CH_2Cl_2 and CH_3OH (1:1) mixture was stirred vigorously for 60min. The reaction mixture was filtered *in vacuo*, the filtrate was diluted with 100-$120cm^3$ of water to completely precipitate the product. The product was then filtered *in vacuo* and washed with water , dried over anhydrous Na_2SO_4 and finally evaporated under

reduced pressure to give 2,4,5-Tribromoimidazole. [Yield= 68%]; M.P=219°C (lit [21] 221-222°C).

Bromination of Phenanthrene

To the gently refluxing solution of (1.78g,10mmol) phenanthrene in 10cm^3 acetic acid, (4.82g,10mmol) TBATB was added over a period of 10min. The mixture was stirred at reflux for 15 min until no more HBr was evolved. The cold reaction mixture was diluted with water and extracted with ether. The organic layer was separated, washed with water and aqueous $NaHCO_3$, dried and evaporated under reduced pressure. [Yield=1.18g(46%)]; M.P=65°C(lit [22] 65°C).

Results and Discussion

From the recent literature on the reactivity of functional mimics of V-BrPO[5,7,10,23-25] as well as our experience in the field of peroxo-metal chemistry,[26-28] it was conjectured that the peroxo-metal mediated oxidation of a suitably chosen salt of bromide might eventually lead to the formation of Br_3^- in aqueous solution. One of the objectives of the present work was to reinvestigate the nature of oxidised form of bromide generated in a peroxo-metal mediated oxidation of bromide and then to study in detail some bromination reactions of organic substrates. Accordingly, we planned a strategy, where the reactants namely, vanadium(V), hydrogen peroxide and bromide were added in succession. The rationale was that a peroxo-vanadium(V) intermediate would first form, which would then activate peroxide to oxidise Br^-. Importantly, when the reaction of vanadium or hydrogen peroxide alone was conducted with Br^-, oxidation of the halide did not take place.

Apart from what has been discussed above, it is significant to note that organic ammonium tribromides(OATB) including pyridine hydrobromide perbromide ($PyHBr_3$) are excellent brominating agents for organic substrates with several advantages over elemental bromine.[29] The principal advantages of OATB are that they are crystalline, stable, and easy to handle. With OATBs, however, it is rather easy to maintain the desired stoichiometry in a chemical reaction. Several tribromides e.g., tetramethylammonium tribromide (TMATB)[30], phenyltrimethylammonium tribromide (PTATB)[31], cetyltrimethylammonium tribromide(cetTMATB), tetrabutylammoniumtribromide(TBATB)[32],1,8-diazabicyclo[5,4,0] tetrabutylammoniumtribromide($DBuHBr_3$)[33] and pyridine hydrobromide perbromide ($PyHBr_3$)[34] have been reported in literature However, their preparation invariably involves elemental bromine and in some cases HBr as well. This certainly causes environmental concern. On the other hand, there is an obvious demand for brominated organic substrates due to their use both as synthetic intermediates and as potent antitumor, antifungal, antibacterial, antineoplastic and antiviral compounds.[4] Therefore, it would be extremely useful to develop an environmentally benign alternative synthetic protocol for the synthesis of OATB. Hence, a synthesis of OATB has been developed and the preparation of tetrabutylammonium tribromide (TBATB) as a typical example is described.

TBATB is yellow to orange yellow in colour and stable in air for a prolong period. It is soluble in a variety of organic solvents. Bromide was estimated by Volhard's method as

described in chapter II. The solution electrical conductance measurement of TBATB in acetonitrile gave a value (Table 5.1) indicating it to be a 1:1 type of elecrolyte.[35] Analytical data are listed in Table 5.1. The crystal structure of TBATB was described in an earlier thesis from our laboratory.[16]

For linear triatomic molecules, bands due to three normal modes of vibrations, *viz.*, two stretching ν_1 and ν_3, and a bending mode, ν_2,[36] are expected. The IR spectrum (Fig 5.1) of TBATB shows two bands at 171 and 191cm^{-1} due to ν_1 and ν_3 respectively .[37] The ν_2 mode is expected to occur (at 53cm^{-1}) well below the region scanned in the present studies.

The electronic absorption spectrum of TBATB matched vary well with those of the other reported [38] Br_3^- complexes in so far as the characteristics of Br_3^- absorption are concerned. The spectra was recorded in dry acetonitrile . A strong absorption at 267 nm (ε=14,721 $dm^3mol^{-1}cm^{-1}$) with a shoulder at 400nm (ε=612 $dm^3mol^{-1}cm^{-1}$) typical of Br_3^- [8,38] was observed.

The present investigation provides an environmentally favourable procedure for peroxovanadium(V)-mediated biomimetic oxidation of bromide leading to the synthesis of tetrabutylammonium tribromide(TBATB), without the use of Br_2 and HBr. The reagent TBATB synthesised in this way has been shown to be a very efficient brominating agent for a variety of organic substrates under mild conditions. The bromination reactions disclosed in this chapter are clean and non hazardous. It is expected that TBATB might as well be the reagent of choice for the synthesis of bromorganics.

Table 5.1 : Analytical Data and Solution Electrical Conductance of TBATB

Compound	Conductance ($\Omega^{-1}cm^2mol^{-1}$)	Element	Found (%)	Calc.(%)
$C_{16}H_{36}NBr_3$ (TBATB)	150	C	39.82	39.85
		H	7.48	7.47
		N	3.11	2.90
		Br	49.78	49.71

Table 5.2 : Structurally Significant IR Bands of $C_{16}H_{36}NBr_3$ in the range 200cm^{-1} to 150cm^{-1}

Compound	IR Bands(cm^{-1})	Assignment
$C_{16}H_{36}NBr_3$	191	ν_3
	171	ν_1

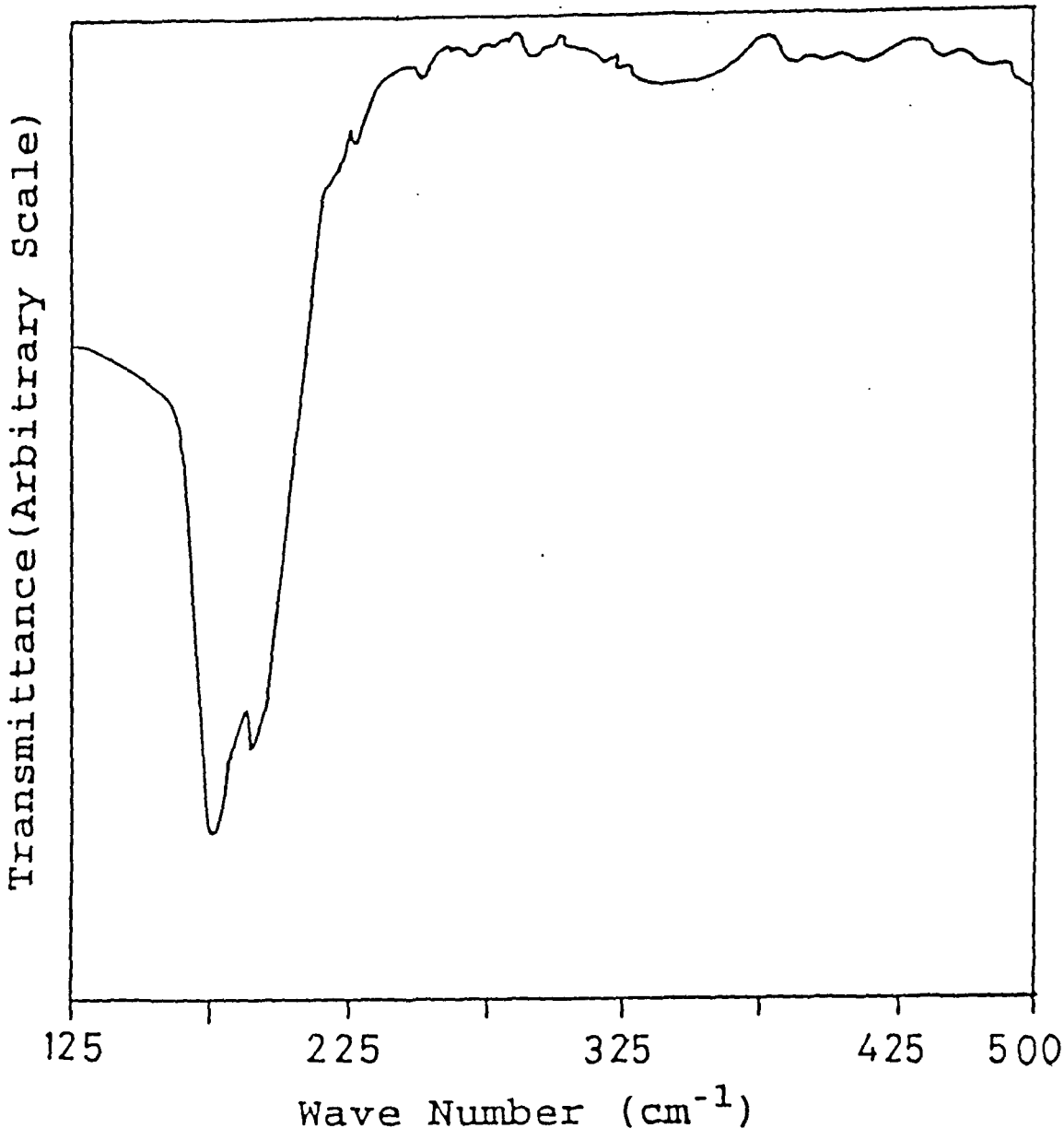
Table 5.3 : Electronic Spectral Data of Br_3^-

Compound	Wavelength (nm)	Wavenumber (cm^{-1})	ε ($d^3mol^{-1}cm^{-1}$)	Assignment
Br_3^-	267	37,453	14,721	σ–σ^*
	400	25,000	612	π–π^*

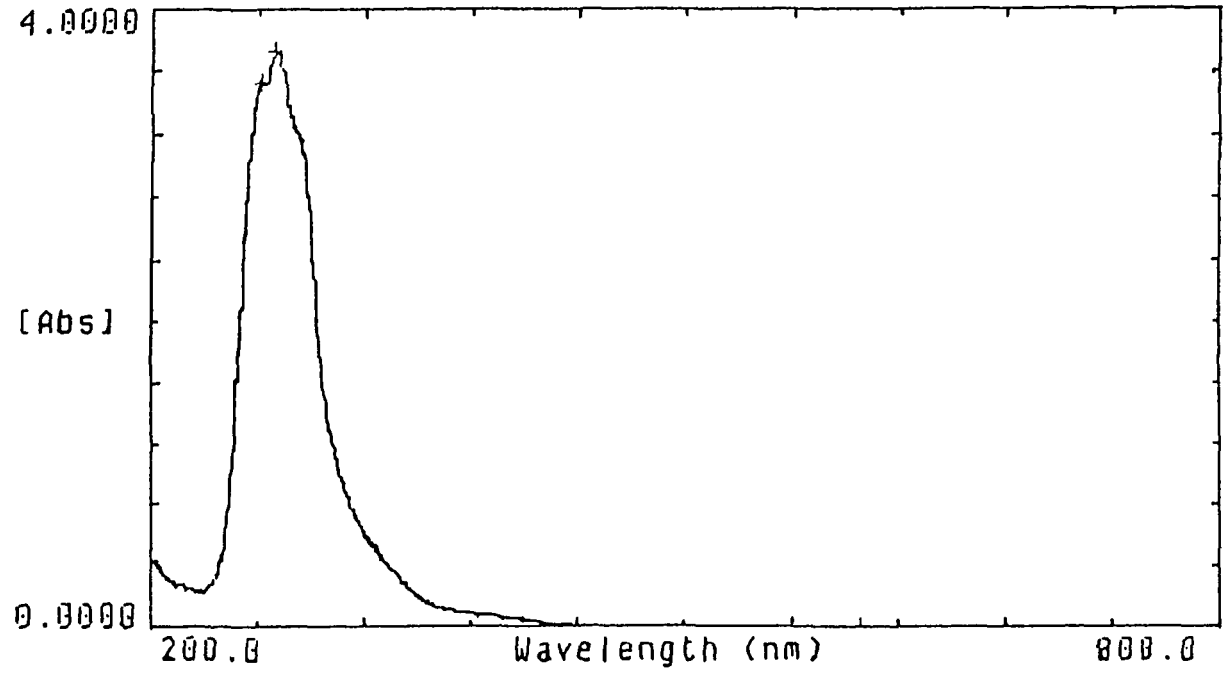
Table 5.4 : Bromination of Some Organic Substrates with TBATB

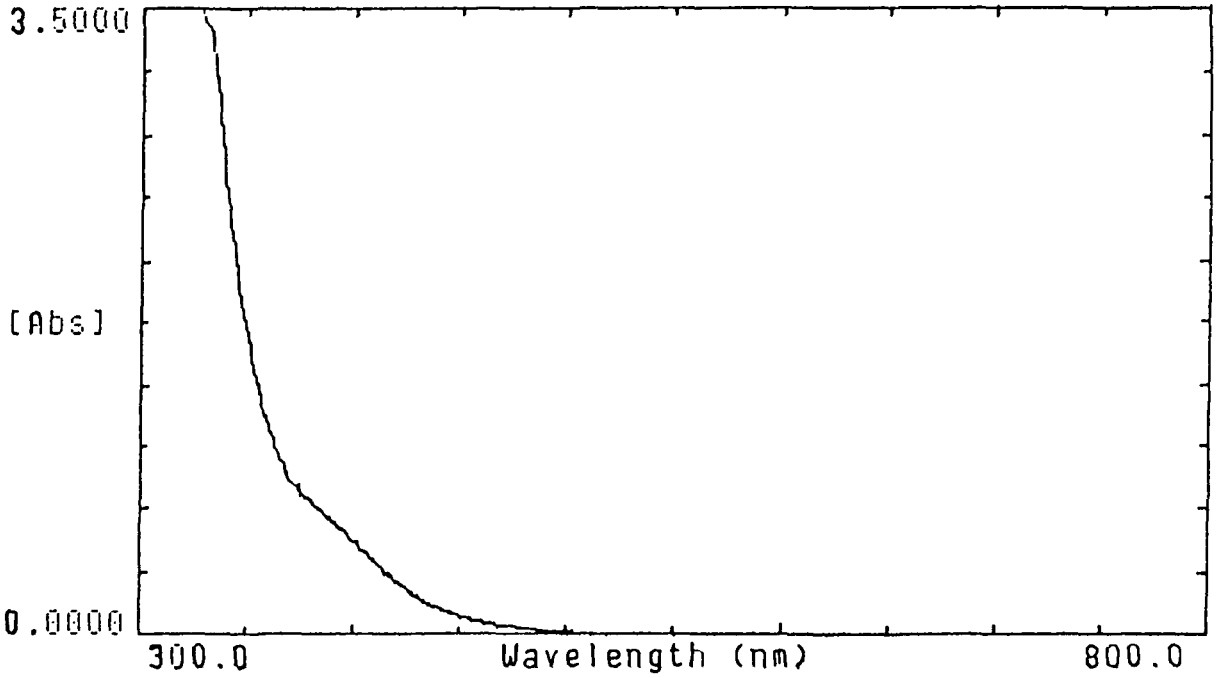
Substrate	Solvent/Time in min.[a]	Substrate: TBATB	Product(s)[b]	%yield[c]
Anthracene	Acetic acid/30	1 1	9-bromoanthracene	68
Anthracene	Acetic acid/30	1 2	9,10-dibromoanthracene	72
Aniline	50%AqDMF/15	1·3	2,4,6-tribromoaniline	65
Benzene	Conc.H_2SO_4,Ag_2SO_4/30	1.3	bromobenzene	40
Phenol	CH_2Cl_2/MeOH(1·1),$CaCO_3$/60	1·3	2,4,6-tribromophenol	60
Imidazole	CH_2Cl_2/MeOH(1.1),$CaCO_3$/60	1:1	2,4,5-tribromoimidazole	68
Phenanthrene	Acetic acid/30	1:1	9-bromophenanthrene	46

[a]Reactions were monitored by TLC, GC. [b] Products were characterised by comparision with authentic pure samples. [c] Isolated yields are reported.



5.2 Infrared Spectrum of Br_3^-





5.3 Electronic Spectra of Br_3^-

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CHAPTER VI

Chapter VI

Synthesis, Characterisation and Structural Evaluation of some mixed-Ligand Molecular Complexes of Manganese, nickel, cobalt, uranium and Vanadium and an Easy Access to Pyridinium Fluorochromate(VI) (PFC), $C_5H_5NH[CrO_3F]$

Metat-acetylacetone complexes are known for a long time[1] so is their synthesis[2]. The role of metal-acetylacetonates as catalysts in important organic reactions,[2] their applications in various industrial processes [2-12] and ability to function as probes in NMR spectroscopic studies[13] are well recognised. Besides these, the synthetic potentiality of metal-acetylacetonates as precursors for organometallic synthesis is well documented[2,14,15] in the literature.

Apart from metal-acetylacetonates, complex inorganic compounds suitable for oxidation of organic substrates are always sought after. The search for mild,[16,17] versatile and selective reagents for the operationally simple oxidation of alcohols to carbonyl

compounds has long been the objective of many research laboratories. In the process a number of higher valent transition metal oxo derivative have been successfully used for alcohol oxidation.[16,17] Of all such reagents chromium(VI) oxidants seem to have been most widely used and studied. Efforts on the development of new reagents and methodologies led to the introduction of pyridinium fluorochromate (PFC) from our laboratory more then one and half decades ago.[18] Subsequently its efficacy was ascertained and advantages highlighted. Because of its selectivity and controlled acidity, PFC has emerged as the most effective among the known chromium(VI) oxidants.

In this chapter, we first describe the application of metal-acetylacetonates as synthetic precursors for the synthesis of some chosen inorganic compounds which might otherwise be difficult to get an access to. This is followed by an easy synthesis of pyridinium fluorochromate (PFC), $C_5H_5NH[CrO_3F]$, without the use of hydrofluoric acid.

EXPERIMENTAL

All the chemicals and solvents were of reagent grade. $Mn(acac)_2.2H_2O$, $Ni(acac)_2.2H_2O$, $Co(acac)_2.2H_2O$ and $UO_2(acac)_2\ .2H_2O$ were prepared as described in chapter II. The details of the instruments/equipment used for the characterisation of the products are also given in chapter II.

Synthesis of $[Mn(acac)_2(dmpz)_2]$

$Mn(acac)_2.2H_2O$ (1.0g, 3.46mmol) was dissolved in $35cm^3$ of acetone and treated with (0.7g, 7.28mmol) of 3,5-dimethylpyrazole(dmpz). The solution was refluxed for 30min to get a dark brown solution. The solution was left at room temperature for 1h, during this period a yellow crystalline product precipitated out. This was isolated by

vaccum filtration and dried *in vacuo* over conc. H_2SO_4. The yield of $[Mn(acac)_2(dmpz)_2]$ was 1.4g (86%).

Synthesis of $[Ni(acac)_2(dmpz)_2]$

To a solution of 1.0g (3.41mmol) $Ni(acac)_2.2H_2O$ in $35cm^3$ acetone, 0.65g (6.76mmol) of 3,5-dimethylpyrazole(dmpz) was added. The solution was refluxed on a steam-bath for 30min. This resulted to clear green solution which on cooling to room temperature afforded a blue micro crystalline product. The product was filtered, washed with acetone and air-dried. The yield of $[Ni(acac)_2(dmpz)_2]$ was 1.3g(85%).

Synthesis of $[Co(acac)_2(dmpz)_2]$

A quantity of 1.0g (3.41mmol) $Co(acac)_2.2H_2O$ was dissolved in $35cm^3$ of acetone followed by the addition of 0.66g (6.87mmol) of 3,5-dimethylpyrazole(dmpz). The solution was refluxed for 30min to give a clear violet solution which on cooling to room temperature afforded a pink microcrystalline product. The compound was filtered, washed with acetone three or four times and air-dried. The yield of $[Co(acac)_2(dmpz)_2]$ was 1.3g(85%).

Synthesis of $[UO_2(acac)_2(dmpz)_4]$

A quantity of 0.25g(4.96mmol) of $UO_2(acac)_2.2H_2O$ was dissolved in $15cm^3$ of $CHCl_3$. To this 0.14g(1.45mmol) of 3,5-dimethylpyrazole(dmpz) was added and the solution refluxed for 45min. The solution was left at room temperature for 2h whereupon an orange coloured compound precipitated out. This was separated by filtration and dried *in vacuo* over conc. H_2SO_4. The yield of $[UO_2(acac)_2(dmpz)_4]$ was 0.34g(80%).

Synthesis of $[VO(acac)_2(dmpz)]$

To an aqueous solution of 0.5g(2.76mmol) of $VOSO_4.H_2O$, 0.8g(8.33mmol) 3,5-dimethylpyrazole(dmpz) in $15cm^3$ of ethanol was added and then filtered to remove any undissolved residue. To the solution thus obtained was added 1.23g(11.04mmol) of acetylacetone and stirred for 15min. The resulting green solution was concentrated and left at room temperature for *ca* 12h. A green compound precipitated out. The product was separated by filtration and washed with water. The compound was recrystallised from acetonitrile. The yield of $[VO(acac)_2(dmpz)]$ was 0.6g(60%).

Synthesis of Pyridinium Fluorochromate, $C_5H_5NH[CrO_3F]$

A 1.0g(17.52mmol) of NH_4HF_2 was dissolved in $7cm^3$ water in a polyethylene beaker followed by the addition of 1.0g(10mmol) of CrO_3. To the resulting orange solution $2cm^3$ (24.40mmol) of pyridine was added with stirring. The reaction solution was then heated on a steam-bath for *ca* 15min. On cooling to room temperature this produced a solid orange product which on recrystallisation from acetone afforded a crystalline orange-yellow pyridinium fluorochromate (PFC),$[C_5H_5NH(CrO_3F)]$. The yield of $[C_5H_5NH(CrO_3F)]$ was 0.9g(45%).

Results and Discussion

The synthetic potentiality of metal-acetylacetonato compounds, $M(acac)_2.2H_2O$, as precursor in organometallic synthesis is well documented[14,15] in the literature. Having achieved an easy access to such compounds, we got interested in exploring a newer facet

of application of metal-acetylacetonates as a synthetic precursor for the synthesis of inorganic compounds that are otherwise rather difficult to obtain.

From the composition [e.g. $M(acac)_2.2H_2O$] of these complexes it is evident that two co-ordinating sites of the metals are occupied by labile aquo ligands. It was expected that the water molecules could be replaced by other ligands of choice with a relatively stronger co-ordinating ability, for instance, a N-donor ligand like 3,5-dimethylpyrazole(dmpz). Accordingly, an acetone solution of $M(acac)_2.2H_2O$ (M=Mn, Ni or Co) was refluxed with two equivalents of 3,5-dimethylpyrazole(dmpz) for 30min. It may be relevant to mention that earlier (in 1976), Garnovskii et al.[19] had reported the synthesis of $M(acac)_2(dmpz)_2$ (M=Mn, Ni or Co) but the method was complicated and chances of contamination of the end product owing to the use of ammonia for precipitating the product cannot be ruled out. The present method of synthesis is apparently a clean one producing pure products.

While $Mn(acac)_2(dmpz)_2$ is a yellow crystalline product, $Ni(acac)_2(dmpz)_2$ and $Co(acac)_2(dmpz)_2$ are blue and pink, respectively. The compounds are stable and can be stored for a prolong period. The compounds analysed very well (Table 6.1). The molar conductances of 10^{-3}M methanolic solutions of the compounds are in agreement with their non-electrolytic nature (Table 6.1).

The infrared absorption patterns of $M(acac)_2(dmpz)_2$ (M=Mn, Ni or Co) (Figure 6.1, 6.2 and 6.3) indicate the presence of both $acac^-$ and dmpz ligands. A few bands due to $acac^-$ and dmpz have overlapped as expected. The strong bands (Table 6.2) at *ca.*1605s, .*ca.*1513s, *ca.*1462s and *ca.*1398s cm^{-1} owe their origin to acac.[20] The evidence of acac

co-ordination comes also from the presence of two medium intensity bands at *ca.*418m and *ca.*285m cm^{-1} arising from $\nu(M-O)+\nu(C-CH_3)$ and $\nu(M-O)$ vibrational modes, respectively.[20] A strong band at *ca.*1371s cm^{-1} due to $\nu(C-N)+\nu(C-C)$ mode indicates the presence of dmpz.[21a] In all the three complexes, the band at 1590 cm^{-1} for dmpz[21b] appears to be obscured by the strong and broad band at *ca.*1605s cm^{-1} arising from $acac^-$. The co-ordination of dmpz has been further supported by the appearance of a medium intensity band at *ca.*350m cm^{-1} assignable to $\nu(M-N)$ mode.[22,23] The appearance of a strong band at *ca.*3310s cm^{-1} may be due to $\nu(N-H)$ mode of vibration.[21b,21c] From the above results it may be inferred that pyridine N atom of dmpz is involved in the co-ordination with metal. The other properties of the compounds compare well with those reported in the literature. [19]

The electronic absorption spectrum of $Mn(acac)_2(dmpz)_2$ (Figure 6.4) in dry acetonitrile shows three intense absorptions (Table 6.3) having charge-transfer origin as evident from their high extinction coefficient values. Band at 213 nm(46,948 cm^{-1} ,ε=37,006 $dm^3mol^{-1}cm^{-1}$) owes its origin to combined $\pi(dmpz)\rightarrow\pi^*$ and $n(dmpz)\rightarrow Mn(II)$ LMCT bands.[24] Absorption at 383 nm (26,109 cm^{-1} , ε=11,215 dm^3 $mol^{-1}cm^{-1}$) is due to $\pi(dmpz)\rightarrow Mn(II)$ LMCT transition.[24] Taking reference to the position of acac to manganese charge-transfer transitions in $Mn(acac)_2.2H_2O$, the band at 272 nm (36,764 cm^{-1} ,ε=17,295 $dm^3mol^{-1}cm^{-1}$) for $Mn(acac)_2(dmpz)_2$ may be assigned to $acac^-$ to manganese charge-transfer transition .

The electronic spectrum of $Ni(acac)_2(dmpz)_2$ (Fig 6.5) in methanol solution displays three intense bands at 218 nm (45,871 cm^{-1}, ε=10,942 $dm^3mol^{-1}cm^{-1}$), 289 nm (34,602 cm^{-1},ε=19,664 $dm^3mol^{-1}cm^{-1}$) and 300 nm (33,333 cm^{-1}, ε=19,030 $dm^3mol^{-1}cm^{-1}$), a maximum at 630 nm (15,873 cm^{-1}, ε=5.6 $dm^3mol^{-1}cm^{-1}$) and a shoulder at 740 nm (13,513 cm^{-1}) due to d–d transition. The broad unresolved band at 218 nm is expected to be due to the overlap of π(dmpz)→π^* absorption with n(dmpz)→Ni(II) LMCT band.[24] The band at 289 nm might have originated from $acac^-$ to Ni(II) LMCT transition. The combined ($\pi_1+\pi_2$)(dmpz) →Ni(II) LMCT transitions appear as a weak spectral feature at 300 nm. Two spin allowed d–d transitions are observed at 630 nm due to $^3A_{2g}\rightarrow{}^3T_{1g}$ and a shoulder at 740 nm due to $^3A_{2g}\rightarrow{}^3T_{2g}$ transition respectively.[25a]

Electronic absorption spectrum of $Co(acac)_2(dmpz)_2$ (Fig 6.6) in methanol solution consists of three maxima at 219 nm (45,662 cm^{-1} , ε=5747 $dm^3mol^{-1}cm^{-1}$), 283 nm (35,335 cm^{-1}, ε=18,519 $dm^3mol^{-1}cm^{-1}$) and 289 nm (34,602 cm^{-1}, ε=16,923 $dm^3mol^{-1}cm^{-1}$) and a multiple band centred at 511 nm (19,569 cm^{-1}, ε=19 $dm^3mol^{-1}cm^{-1}$). The broad band at 219 nm owes its origin to the combined π(dmpz)→π^*(dmpz) and n(dmpz)→Co(II) transitions similar to those observed in the cases of Mn(II) and Ni(II) complexes. The band at 289 nm is due to the combined ($\pi_1+\pi_2$)(dmpz)→Co(II)LMCT transition.[24] $Acac^-$ to Co(II) LMCT transition is observed at 283nm. The multicentre band at 511 nm has been assigned to $^4T_{1g}\rightarrow{}^4T_{1g}(P)$ transition.[25b]

In order to understand the thermal stability and the decomposition pattern, thermoanalytical (TG and DSC) studies of the complexes $[Mn(acac)_2(dmpz)_2]$,

$[Ni(acac)_2(dmpz)_2]$ and $[Co(acac)_2(dmpz)_2]$ were conducted. The compounds were expected to be suitable probes for thermal studies because of the presence of volatile ligands. Thermogravimetric(TG) experiment on $[Mn(acac)_2(dmpz)_2]$ was performed in the range of temperature 31–430°C and DSC at 31–525°C under a constant flow of nitrogen. The thermogram of $Mn(acac)_2(dmpz)_2$ (Figure 6.7) reveals that the compound is stable upto 124.27°C. The first weight change starts at 124.27°C and continues upto 187.38°C with the loss of weight corresponding to the expulsion of one dmpz, two C_2H_2 and N_2 (calc. 39.56, obs.38.28%). The thermogram exhibits a slow rate of weight loss from 187.38°C to 209.98°C followed by a sharp loss between 209.98°C and 301.66°C. The weight loss at the temperature range 187.38°C to 209.98°C gets along well with the loss of CH_3 (calc.3.37, obs.3.03%). The rest, i.e., $C_5H_7O_2$, $2C_2H_2$ and CH_4, is lost (calc.37.54 ,obs.37.76%) between 209.98°C and 301.66°C resulting to the formation of MnO_2. The corresponding DSC pattern shows a sharp endotherm at 166°C. This seems to correspond to the TG event of a dmpz ligand expulsion from the compound. In addition, an exotherm is observed at 262°C that could be connected to the loss of one acac ligand.

The thermogram of $[Ni(acac)_2(dmpz)_2]$ (Figure 6.8) recorded under similar conditions indicates that it is stable upto 127.92°C. The first weight loss starts at 127.92°C and continues upto 206.95°C as evident from the thermogram. The percentage weight loss at this stage matches well with the expulsion of two dmpz ligands (calc.42.80%, obs.43.1%). The thermogram also shows weight loss initiating at 256.48°C and ending at 356°C with the expulsion of one acac, CH_3 and two C_2H_2 molecule (calc.37, obs.36.65%) leading to the formation of NiO_2. It is indeed interesting to note the similarity

between $[Mn(acac)_2(dmpz)_2]$ and $[Ni(acac)_2(dmpz)_2]$ in terms of their thermal behaviour. The formation of "NiO_2" also requires comments in that it is a rather unusual species formed under a rather stringent condition. But the product might not be stable in air. Further experimentations are necessary to establish the possibilities of obtaining "NiO_2" in a scaled -up quantity. Unlike the DSC pattern of $Mn(acac)_2(dmpz)_2$ showing two peaks, that of $Ni(acac)_2(dmpz)_2$ displays only one endotherm at 182°C corresponding to the loss of dmpz.

As a continuation to our thermoanalytical studies, $[Co(acac)_2(dmpz)_2]$ was also subjected to thermogravimetric analysis. The temperature range covered for TG experiment was 82 to 435°C and that for DSC was 31 to 490°C. The TG curve (Fig 6.9) showed three successive weight losses at 100 to 156°C, 207 to 257°C and 321 to 421°C. The first weight loss was consistent with the loss of two dmpz ligands (calc.42.76, obs.43.47%) indicating the formation of $Co(acac)_2$. The second weight loss corresponds to expulsion of C_2H_2, CH_3 and $1/2O_2$ (calc.12.70, obs.16.48%). Finally, the sample showed the loss of C_2H_2 and acac (calc.27.85, obs.27.70%) to produce CoO. The DSC pattern of $Co(acac)_2(dmpz)_2$ shows three peaks. The first peak is endothermic, while the second and the third peaks are exothermic in nature.

From the perusal of the thermal behaviour of all the three compounds it may be inferred that they can be used as a good starting material for MOCVD studies.

Chemistry of both uranium and vanadium compounds containing acac as a ligand are gaining attention. One of the reasons could be the high volatility imparted to the resulting compounds by the ligand rendering them good probes for MCVD/CVD. Also

metal acetylacetonates are good synthons for organometallic as well as inorganic compounds. Our aim was to use $UO_2(acac)_2.2H_2O$ and $VO(acac)_2$ for synthesising new compounds of the type $UO_2(dmpz)_n$ and $VO(dmpz)_n$ but so far the targeted compounds could not be obtained, instead we have landed up with mixed-ligand complexes of the type $[UO_2(acac)_2(dmpz)_4]$ and $[VO(acac)_2(dmpz)]$ containing both acac and dmpz ligands. $[UO_2(acac)_2(dmpz)_4]$ was obtained by refluxing a solution of $UO_2(acac)_2.2H_2O$ with dmpz in chloroform while the reaction of $VOSO_4.H_2O$ with dmpz and acac in ethanolic solution afforded $[VO(acac)_2(dmpz)]$.

While $[UO_2(acac)_2(dmpz)_4]$ is orange and $[VO(acac)_2(dmpz)]$ is green in colour. Both the compounds are soluble in common organic solvents. The compounds analysed satisfactorily (Table 6.1). The X-band EPR spectrum of $[VO(acac)_2(dmpz)]$ at room temperature in acetonitrile solution give an eight-line spectrum typical of vanadium(IV)[26] with the g value being 2.0133.

The infrared spectra of $[UO_2(acac)_2(dmpz)_4]$ and $[VO(acac)_2(dmpz)]$, reproduced in Figure 6.10 and 6.11 exhibit characteristic bands for co-ordinated acetylacetonato and 3,5-dimethylpyrazole ligands. The characteristic bands of acetylacetonate[20] ligand were observed at *ca.* 1577 cm^{-1}, *ca.* 1517 cm^{-1} and 1419 cm^{-1}. Both the compounds exhibit a strong band at *ca.* 1365 cm^{-1} due to $\nu(C-N)+\nu(C-C)$[21a,21b] indicating the presence of dmpz. The band at *ca.* 1590 cm^{-1} for dmpz appears to be obscured by the strong band at that region due to acetylacetonate. The appearance of a medium intensity band at *ca.* 3318 cm^{-1} due to N–H [21b,21c] stretching frequency provides an evidence for this nitrogen not getting involved in co-ordination and suggesting in turn that it is the tertiary nitrogen atom

of dmpz that co-ordinates with the metal centre. The band due to ν(UFO)(trains linked O=U=O) is observed at 921s cm^{-1}. The band at this position is well documented in the literature. [22] The V=O stretching frequency of $[VO(acac)_2(dmpz)]$ at 947 cm^{-1} is compatible with six-co-ordination. [23] Further a medium intensity band observed for both the compounds at *ca.* 344 cm^{-1} has been assigned to ν(M–N). [22,23]

The electronic spectrum of $[VO(acac)_2(dmpz)]$ in acetonitrile is shown in Figure 6.12. The UV-visible spectrum contains six well defined absorption bands. The combined $\pi(dmpz)\rightarrow\pi^*$ absorption and $n(dmpz)\rightarrow VO^{2+}$ LMCT due to dmpz appears as a broad band at 206 nm (48,543 cm^{-1}, ε=7051 $dm^3mol^{-1}cm^{-1}$). A high intensity band at 301 nm(33,222 cm^{-1}, ε=11,980 $dm^3mol^{-1}cm^{-1}$)with a shoulder at 254 nm (39,371 cm^{-1}) are observed due to $\pi(V-O)\rightarrow d_{X^2-Y^2}$ and $\pi(V-O)\rightarrow d_{XZ}$, d_{YZ} electronic excitation respectively .[27] These assignments are in agreement with the earlier results found for $VO(H_2O)_5^{2+}$ ion ,[28] which indicated analogous electronic excitations in the near UV region. Three ligand -field absorption bands are observed at 391 nm (25,575 cm^{-1}), 593 nm(16,863 cm^{-1}) and 707 nm(14,144 cm^{-1}). These transitions can be assigned (from highest to lowest energy) as the $b_2\rightarrow a_1^*(d_{XY}\rightarrow d_{Z^2})$, $b_2\rightarrow b_1^*(d_{XY}\rightarrow d_{X^2-Y^2})$ and $b_2\rightarrow e_\pi^*(d_{XY}\rightarrow d_{XZ},d_{YZ})$ transition, respectively.[28]

In order to understand the thermal decomposition patterns of the compounds, $[UO_2(acac)_2(dmpz)_4]$ and $[VO(acac)_2(dmpz)]$ were separately subjected to thermogravimetric (TG) experiments. The temperature range covered in the TG experiment for $[UO_2(acac)_2(dmpz)_4]$ (Fig 6.13) was 31 to 740°C. The loss of weight

started at 75°C and continued upto 135.72°C as evident from the thermogram. The percentage weight loss at this stage matches well with the expulsion of three dmpz ligands (calc. 33.80, obs. 30.85%). The second weight loss initiated at 166°C and continued upto 189°C . The weight loss at this range gets along well with the loss of two C_2H_2 (calc. 6.10, obs. 6.79%). Finally, there was a weight loss corresponding to the expulsion of one acac, CH_4, N_2,1/2O_2, CH_3 and $2C_2H_2$ in the temperature range 216.85°C to 460°C (calc. 26.52, obs. 23.45%) leading to the formation of UO_3. Derivative thermogravimetric (DTG) curve showed three peaks at 113, 183 and 237°C matching very well with the weight loss in TG experiment.

Similarly, $[VO(acac)_2(dmpz)]$ was also subjected to TG experiment. The temperature range covered in this experiment was from 31 to 370°C. The thermogram (Fig 6.14) showed that the compound was stable upto 62.58°C. The weight loss initiated at 62.58°C and continued upto 148.94°C. The loss of weight at this step corresponds to the expulsion of one dmpz molecule (calc.26.59, obs. 28.93%). The intermediate at this stage was expected to be $VO(acac)_2$. The second weight loss initiates at 188°C and continues upto 259.39°C, this corresponds to the loss of two acac molecules resulting to the formation of VO_2 (calc. 54.85, obs. 55.183%). The first derivative of the TG curve showed two sharp peaks one at 119.5°C and the second one at 238°C. While the first peak corresponds to the loss of one dmpz and the second peak is due to the loss of two acac ligands.

An easy synthesis of pyridinium fluorochromate(PFC), was achieved by the reaction of CrO_3 with ammonium hydrogen fluoride, NH_4HF_2, in an aqueous medium

followed by the precipitation of [CrO_3], formed in solution by the addition of pyridine. The melting point, elemental analyses (Table 6.1) and spectral features match very well with the reported data.[29,30] The X-ray crystal structure of PFC was reported earlier from this laboratory.[31] The redundancy of hydrofluoric acid is one of the main advantages of the new method of synthesis of PFC.

Table 6.1: Analytical Data and Solution Electrical Conductance of $[M(acac)_2(dmpz)_2]$ (M=Mn, Ni or Co),$[UO_2(acac)_2(dmpz)_4]$ and $[VO(acac)_2(dmpz)]$

Compound	Molar conductance ($\Omega^{-1}cm^2mol^{-1}$)	Elements	Found(%)	Calc.(%)
$[Mn(acac)_2(dmpz)_2]$	29	C	53.21	53.96
		H	6.60	6.74
		N	11.60	12.58
		Mn	12.33	12.33
$[Ni(acac)_2(dmpz)_2]$	8	C	53.78	53.51
		H	6.65	6.68
		N	12.97	12.47
		Ni	12.71	13.07
$[Co(acac)_2(dmpz)_2]$	16	C	53.96	53.48
		H	6.67	6.68
		N	13.14	12.46
		Co	12.33	13.12
$[UO_2(acac)_2(dmpz)_4]$	_	C	41.92	42.27
		H	5.34	5.39
		N	12.51	13.14
		U	27.57	27.90
$[VO(acac)_2(dmpz)]$	_	C	47.62	49.89
		H	6.45	6.09

		N	7.94	7.75
		V	16.16	14.10
$C_5H_5NH(CrO_3F)$	128	**C**	30.2	30.16
		H	3.06	3.04
		N	7.1	7.04
		Cr	26.25	26.12
		F	9.6	9.54

Table 6.2 : Structurally Significant IR Band of $[M(acac)_2(dmpz)_2]$ (M=Mn, Ni or Co), $[UO_2(acac)_2(dmpz)_4]$ and $[VO(acac)_2(dmpz)]$

Compound	Band Position (cm^{-1})	Assignment
$[Mn(acac)_2(dmpz)_2]$	3307m	ν(N–H)
	2922	$\nu(CH_3)$
	1605s	ν(C--C)+ν(C--O)
	1507s	ν(C--O)+ν(C--C)
	1447s	δ(CH)+ν(C--C)
	1394s	$\delta_d(CH_3)$
	1372	ν(C--N)+ν(C--C)
	1248	$\nu(C–CH_3)$+ν(C--C)
	423m	$\nu(Mn–O)+\nu(C–CH_3)$

	353m	ν(Mn–N)
	283m	ν(Mn–O)
[Ni(acac)$_2$(dmpz)$_2$]	3313m	ν(N–H)
	2922	ν(CH_3)
	1605s	ν(C--C)+ν(C--O)
	1520s	ν(C--O)+ν(C--C)
	1471s	δ(CH)+ν(C--C)
	1471s	δ(CH)+ν(C--C)
	1409s	$\delta_d(CH_3)$
	1371	ν(C--N)+ν(C--C)
	1255	ν(C–CH_3)+ν(C--C)
	419m	ν(Ni–O)+ν(C–CH_3)
	353m	ν(Ni–N)
	286m	ν(Ni–O)
[Co(acac)$_2$(dmpz)$_2$]	3312	ν(N–H)
	2921	ν(CH_3)
	1605s	ν(C--C)+ν(C--O)
	1513s	ν(C--O)+ν(C--C)
	1470s	δ(CH)+ν(C--C)
	1409s	$\delta_d(CH_3)$
	1370	ν(C--N)+ν(C--C)

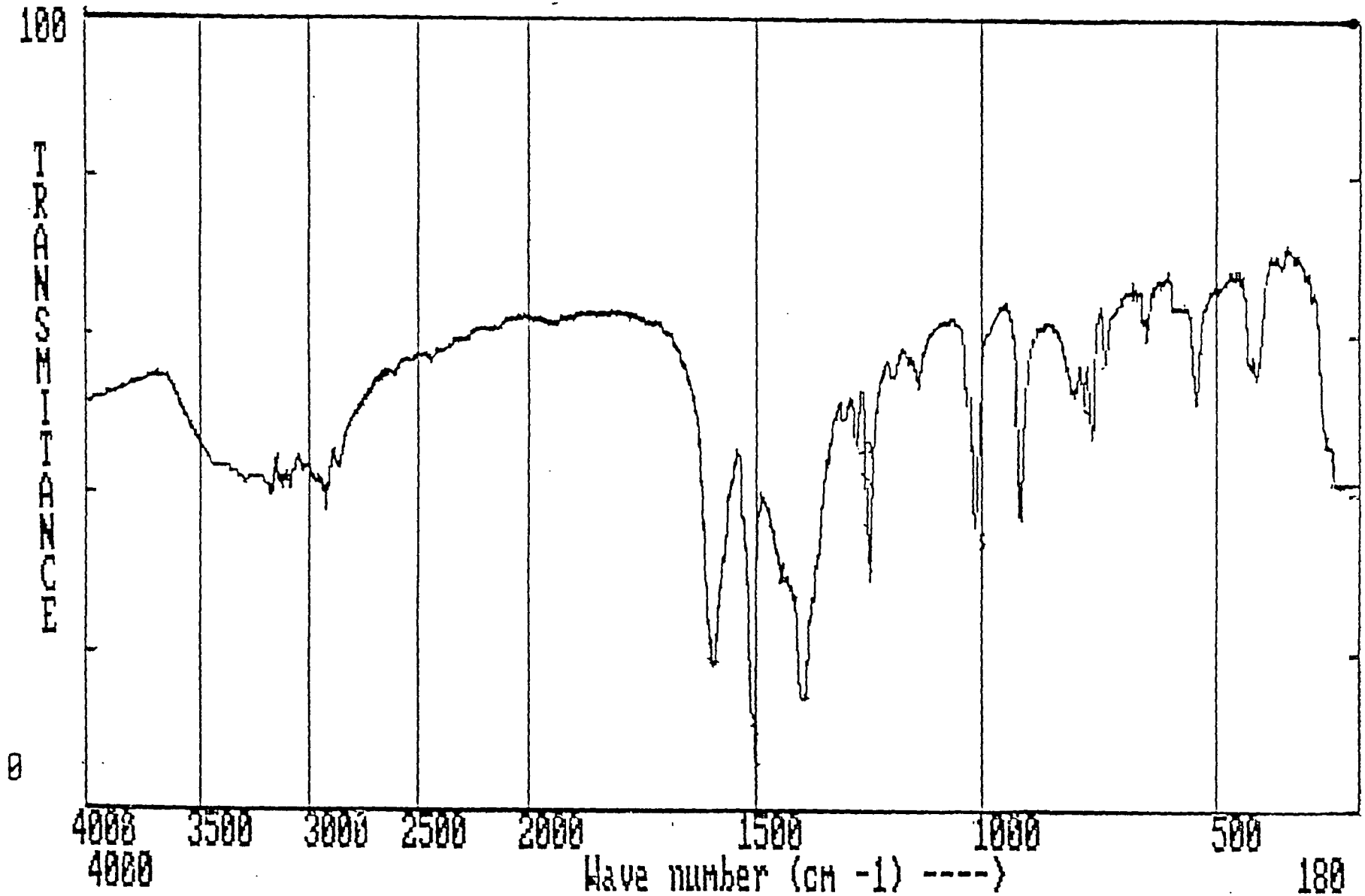
	1252	$\nu(C–CH_3)+\nu(C--C)$
	413m	$\nu(Co–O)+\nu(C–CH_3)$
	346	$\nu(Co–N)$
	286m	$\nu(Co–O)$
$[UO_2(acac)_2(dmpz)_4]$	3328	$\nu(N–H)$
	2920	$\nu(CH_3)$
	1567	$\nu(C--C)+\nu(C--O)$
	1513	$\nu(C--O)+\nu(C--C)$
	1480	$\delta(CH)+\nu(C--C)$
	1418	$\delta_d(CH_3)$
	1364	$\nu(C--N)+\nu(C--C)$
	1270	$\nu(C–CH_3)+\nu(C--C)$
	399	$\nu(U–O)+\nu(C–CH_3)$
	283	$\nu(U–N)$
	921	$\nu(U=O)$
$[VO(acac)_2(dmpz)]$	3308	$\nu(N–H)$
	2894	$\nu(CH_3)$
	1586	$\nu(C--C)+\nu(C--O)$
	1520	$\nu(C--O)+\nu(C--C)$
	1420	$\delta(CH)+\nu(C--C)$
	1393	$\delta_d(CH_3)$

	1366	ν(C--N)+ν(C--C)
	1273	ν(C–CH_3)+ν(C--C)
	340	ν(V–N)
	947	ν(V=O)

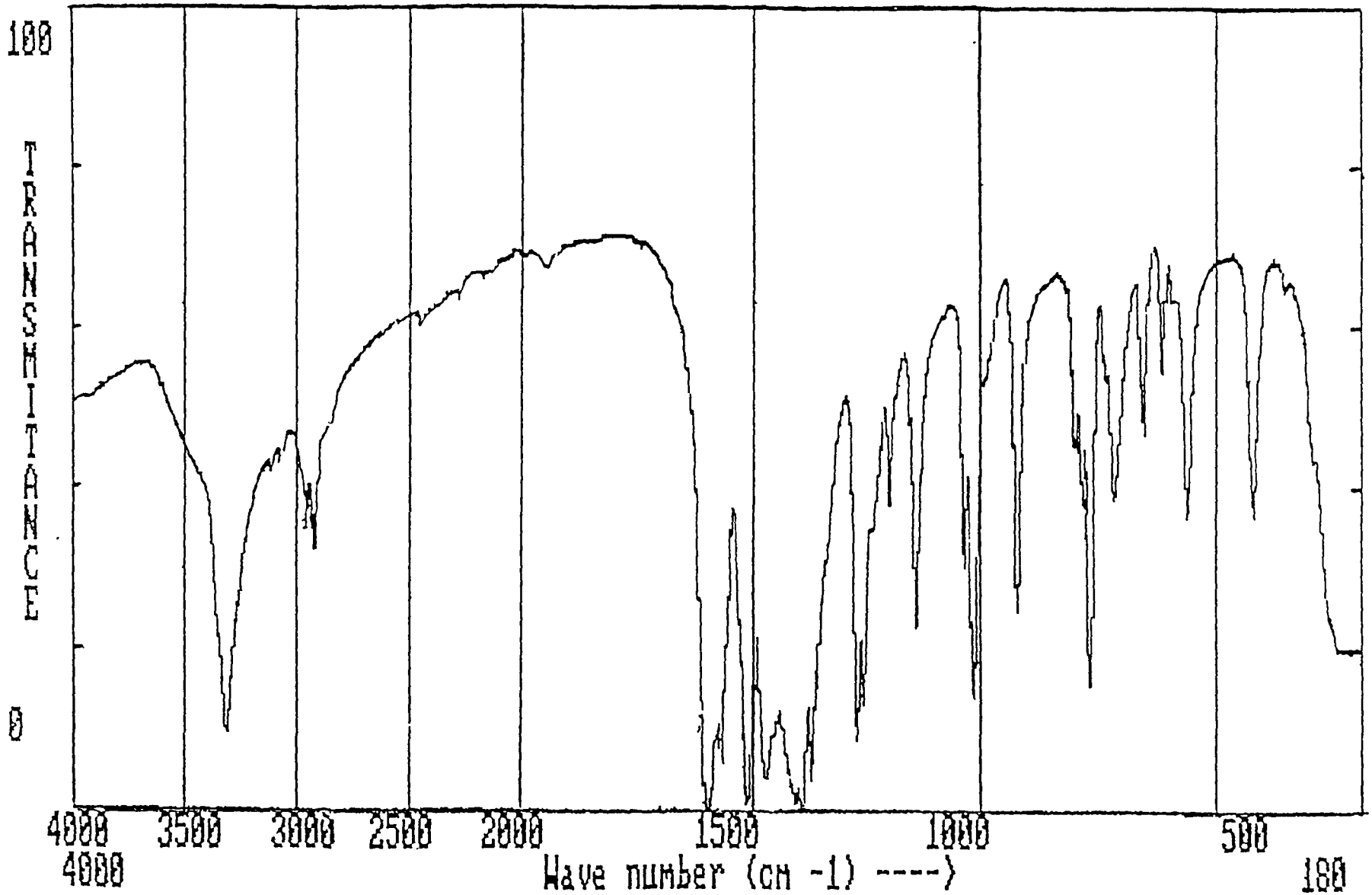
Table 6.3 : Electronic Spectral Data of $[M(acac)_2(dmpz)_2]$ (M=Mn,Ni or Co) and $[VO(acac)_2(dmpz)]$

Compound	Wavelength (nm)	Wavenumber (cm^{-1})	ε(dm^3mol^{-1} cm^{-1})	Assignment
$Mn(acac)_2(dmpz)_2$	213	46,948	37,006	π(dmpz)→π* + n(dmpz)→Mn(II)
	272	36,764	17,295	π(acac)→Mn(II)
	383	26,109	11,215	π(dmpz)→Mn(II)
$Ni(acac)_2(dmpz)_2$	218	45,871	10,942	π(dmpz)→π* + n(dmpz)→Ni(II)
	289	34,602	19,664	π(acac)→Ni(II)
	300	33,333	19,030	π(dmpz)→Ni(II)
	630	15,873	5.6	$^3A_{2g}\rightarrow{}^3T_{1g}$

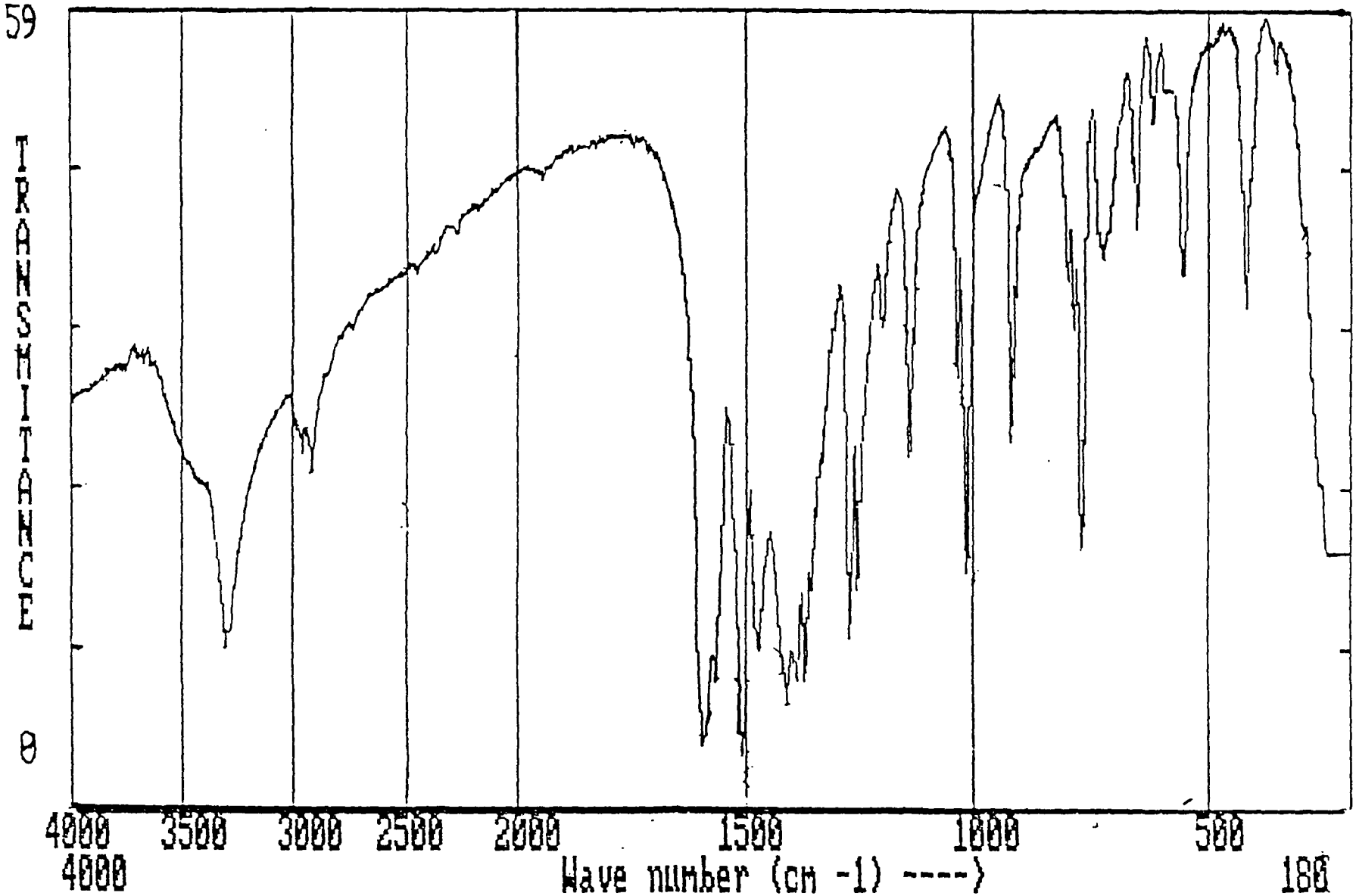
	740	13,513	2.7	$^3A_{2g} \rightarrow {}^3T_{2g}$
$Co(acac)_2(dmpz)_2$	219	45,662	5747	$\pi(dmpz) \rightarrow \pi^*$ + $n(dmpz) \rightarrow Co(II)$
	283	35,335	18,519	$\pi(acac) \rightarrow Co(II)$
	289	34,602	923	$\pi(dmpz) \rightarrow Co(II)$
	511	19,569	19	$^4T_{1g} \rightarrow {}^4T_{1g}(P)$
$VO(acac)_2(dmpz)$	206	48,543	7051	$\pi(dmpz) \rightarrow \pi^*$ + $n(dmpz) \rightarrow VO^{2+}(II)$
	254	39,371	11,980	$\pi(V-O) \rightarrow d_{XZ}, d_{YZ}$
	301	33,222		$\pi(V-O) \rightarrow d_{X^2-Y^2}$
	391	25,575		$b_2 \rightarrow a_1^*(d_{XY} \rightarrow d_{Z^2})$
	593	16,863		$b_2 \rightarrow b_1^*(d_{XY} \rightarrow d_{X^2-Y^2})$
	707	14,144		$b_2 \rightarrow e_\pi^*(d_{XY} \rightarrow d_{XZ}, d_{YZ})$



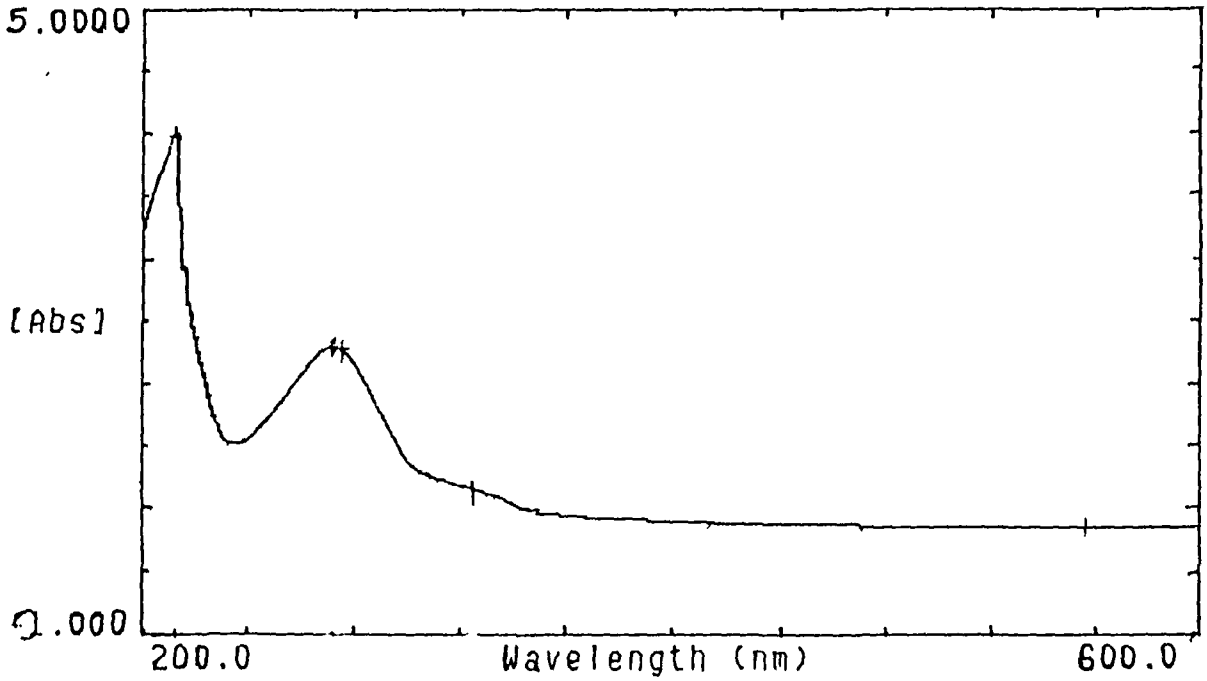
6.1 Infrared spectrum of $[Mn(acac)_2(dmpz)_2]$



6.2 Infrared Spectrum of $[Ni(acac)_2(dmpz)_2]$



6.3 Infrared Spectrum of $[Co(acac)_2(dmpz)_2]$



6.4 Electronic Spectrum of $[Mn(acac)_2(dmpz)_2]$

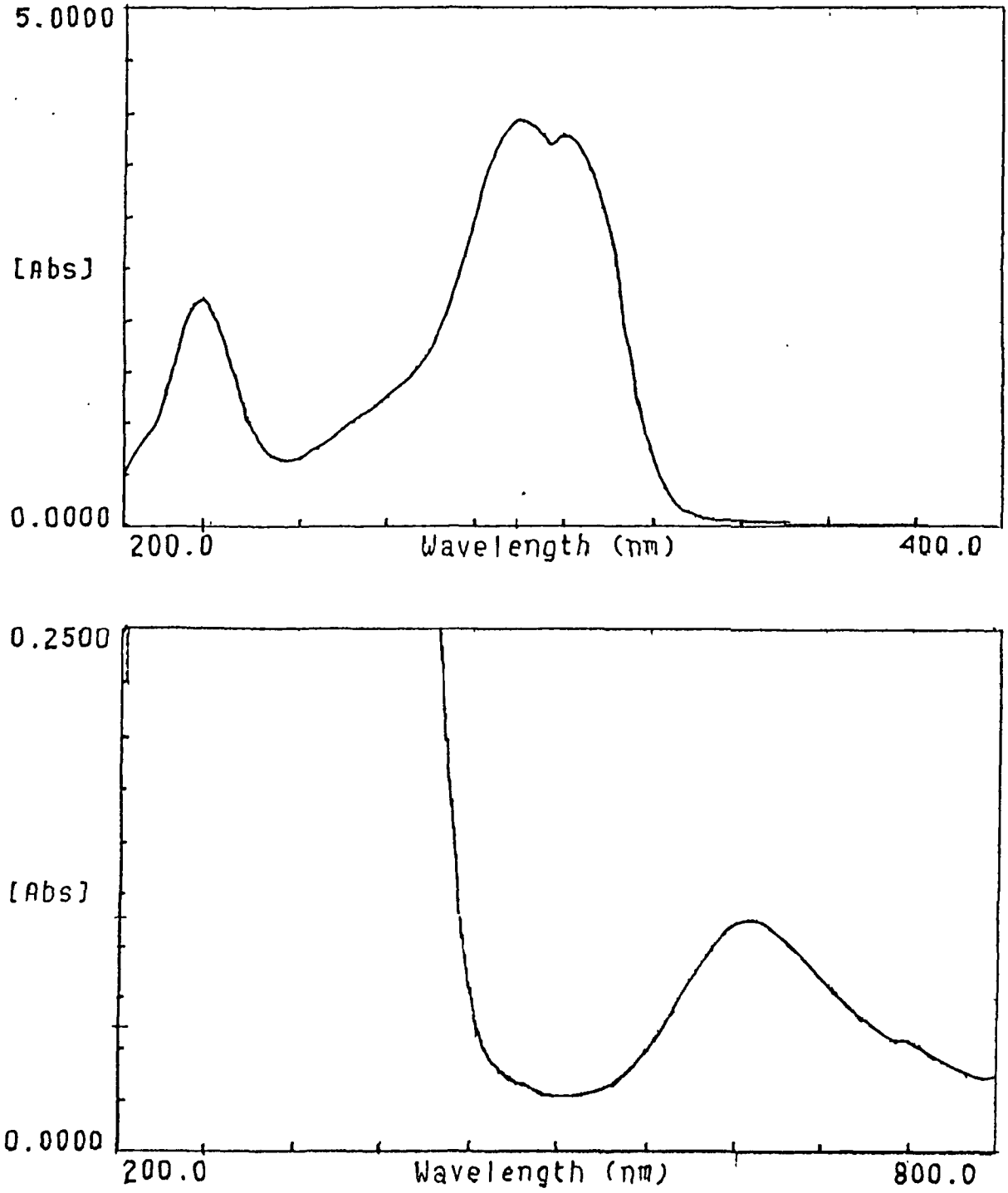
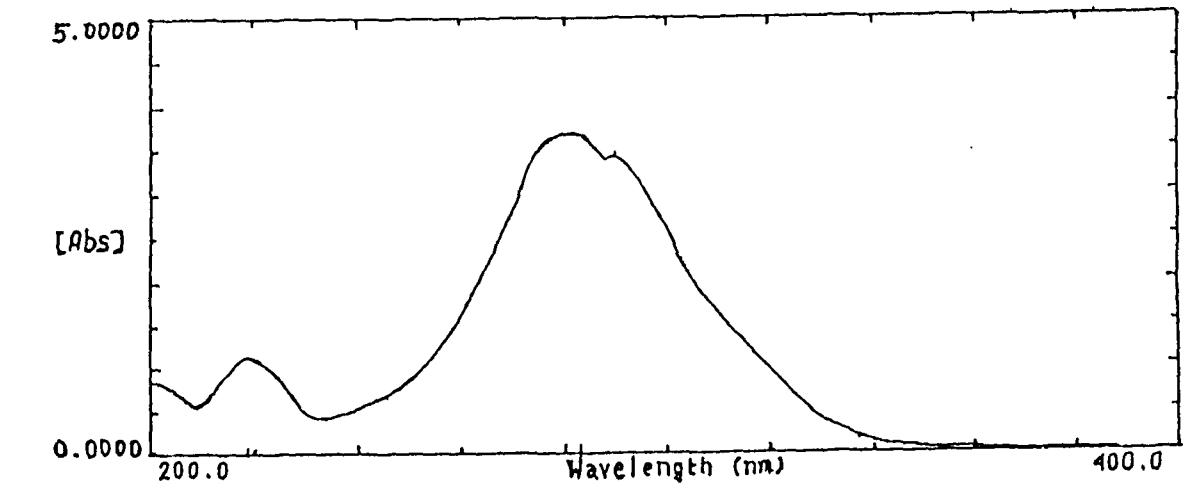


Figure 6.5 Electronic Spectra of $[Ni(acac)_2(dmpz)_2]$



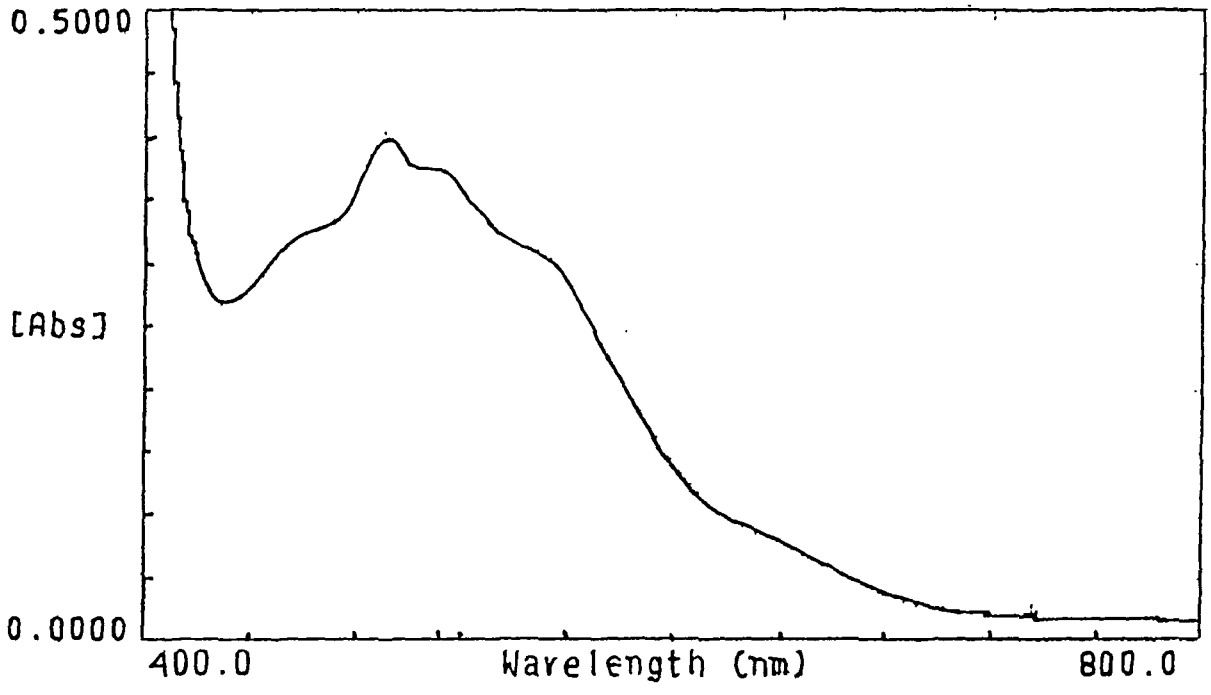
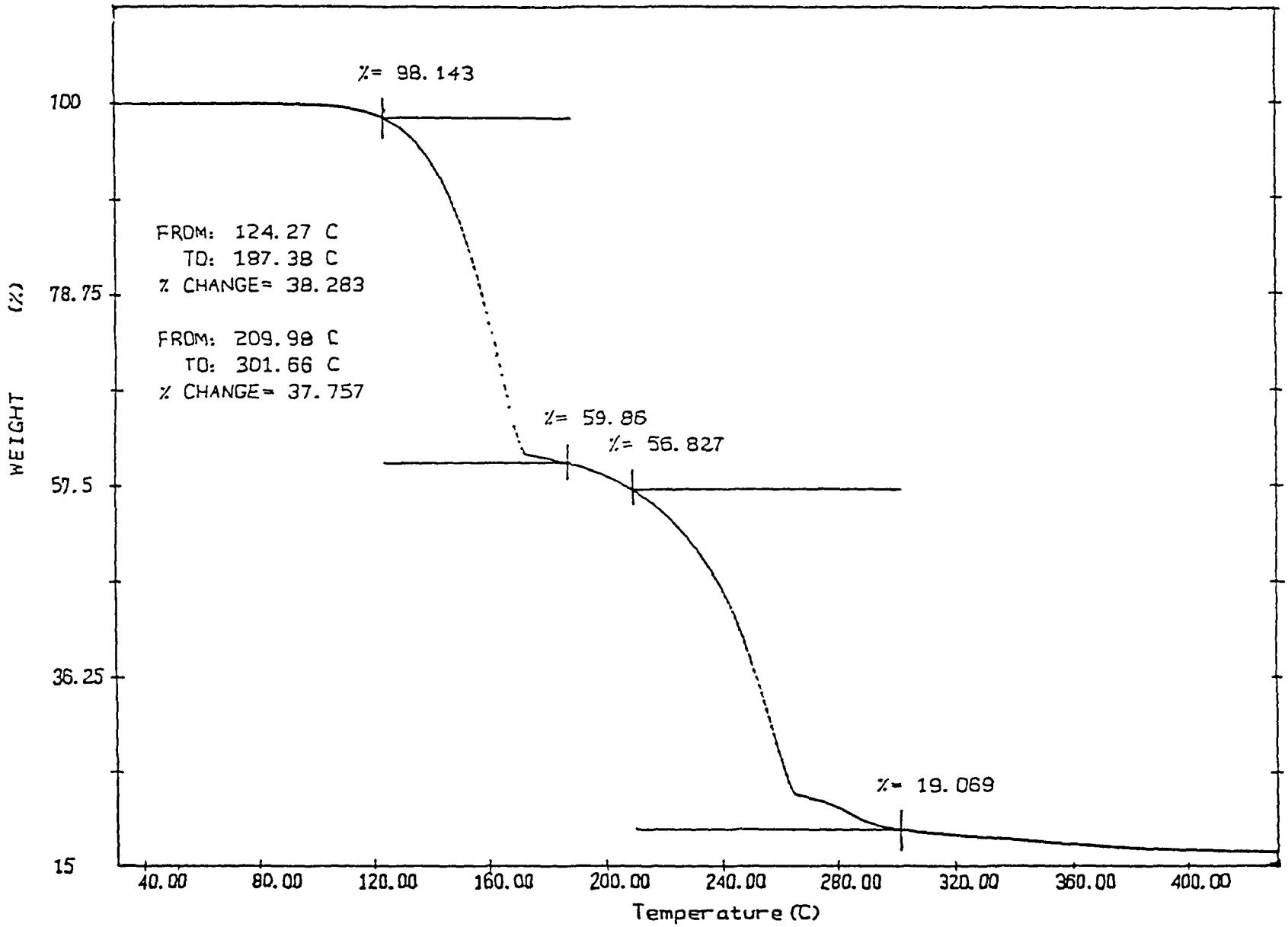
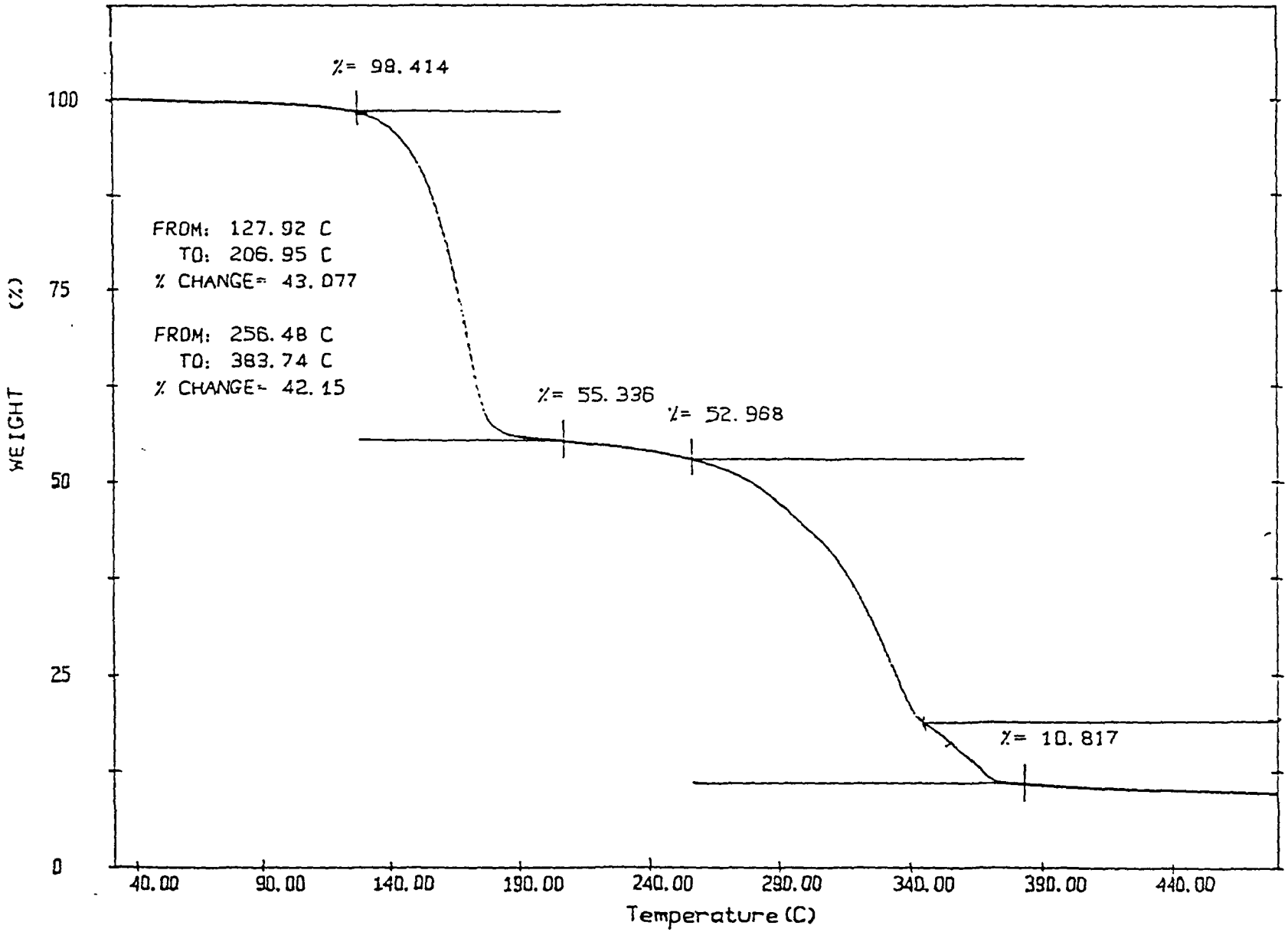


Figure 6.6 Electronic Spectra of $[Co(acac)_2(dmpz)_2]$



6.7 Thermogram of $[Mn(acac)_2(dmpz)_2]$



6.8 Thermogram of $[Ni(acac)_2(dmpz)_2]$

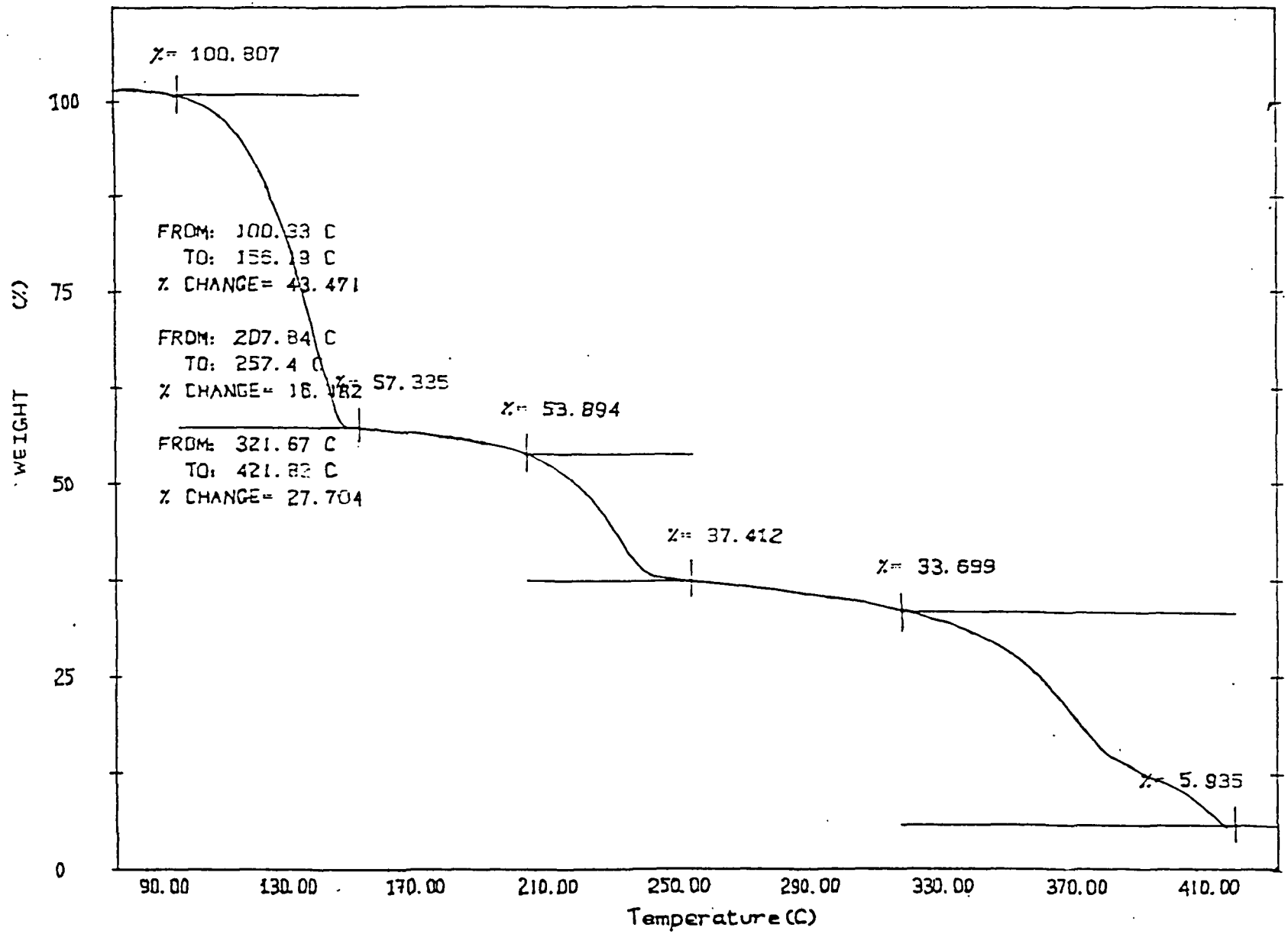
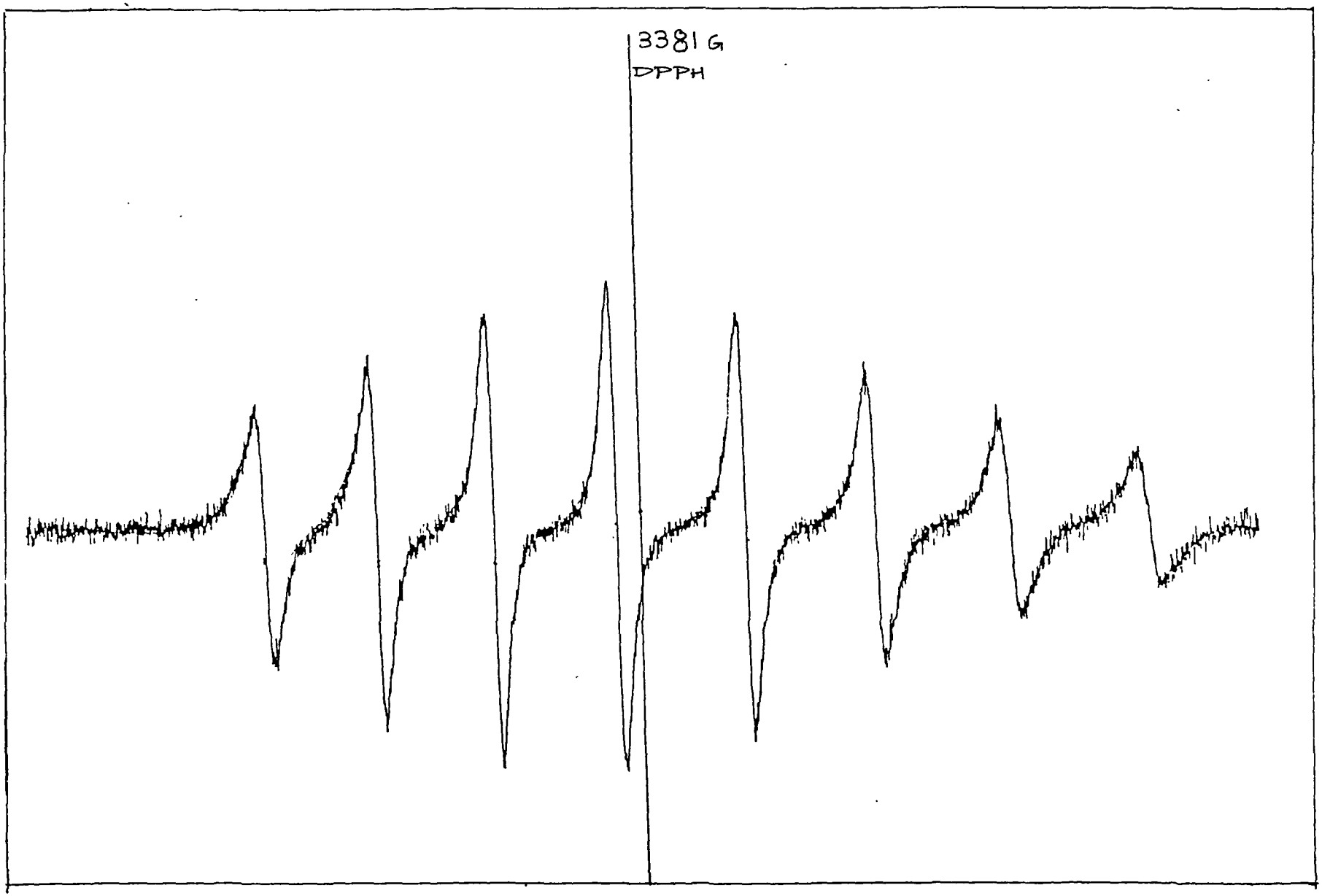
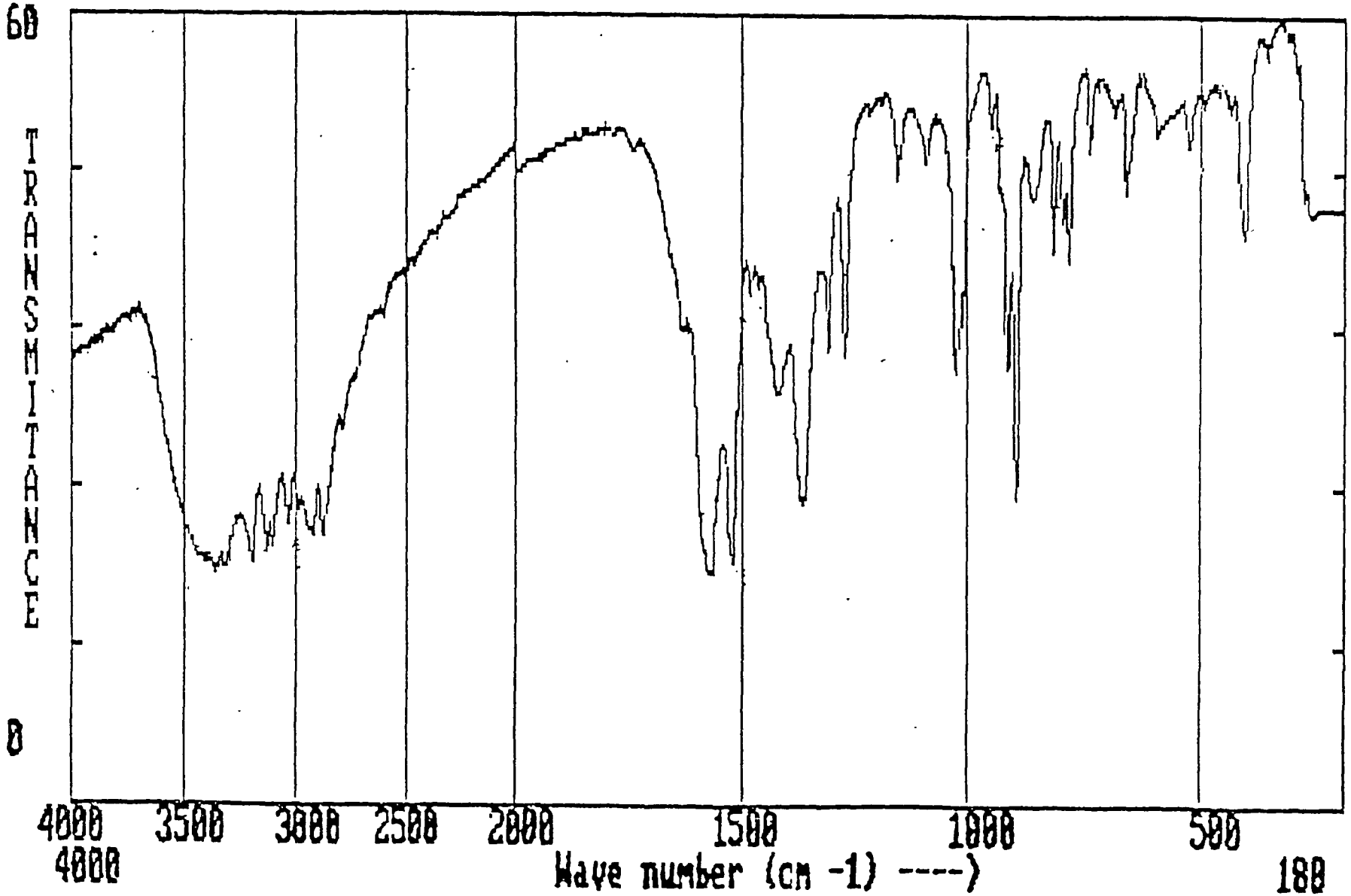


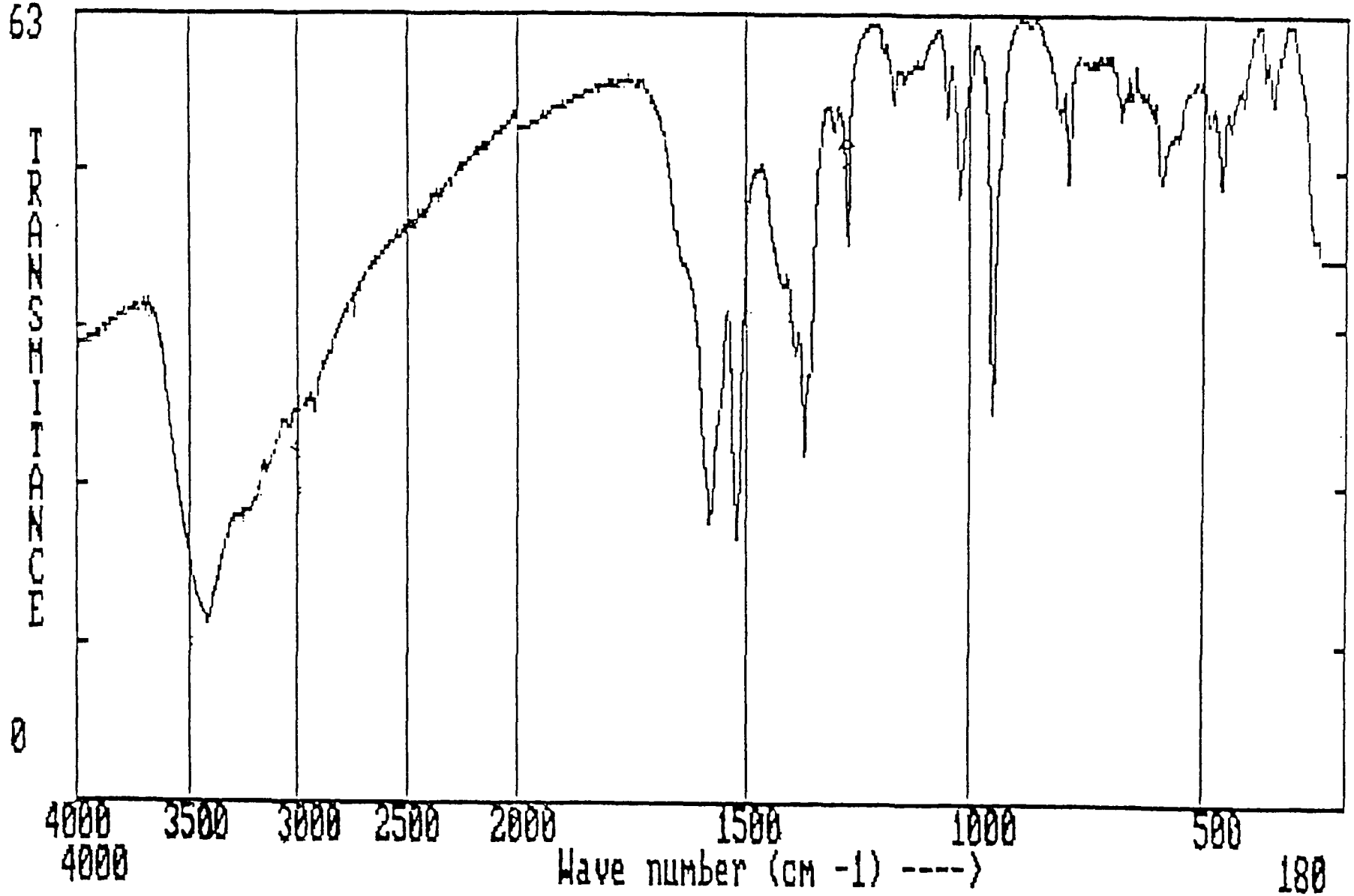
Figure 6.9 Thermogram of $[Co(acac)_2(dmpz)_2]$



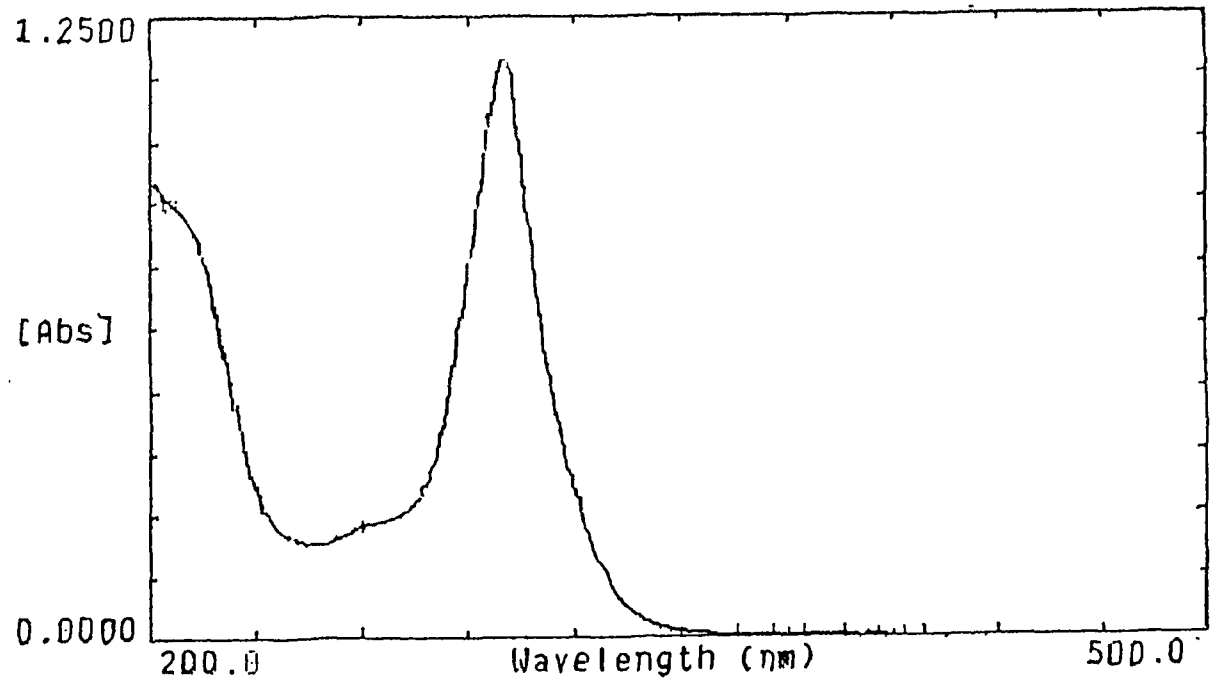
6.10 ESR spectrum of $[VO(acac)_2(dmpz)]$

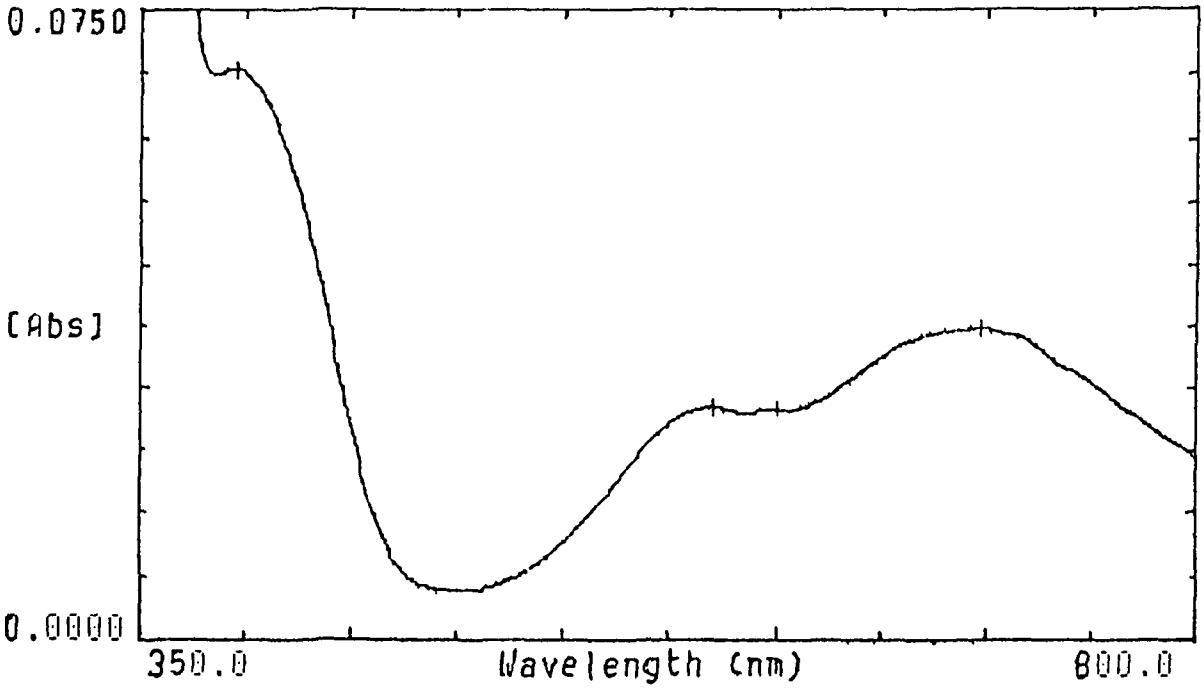


6.11 Infrared Spectrum of $[UO_2(acac)_2(dmpz)_4]$

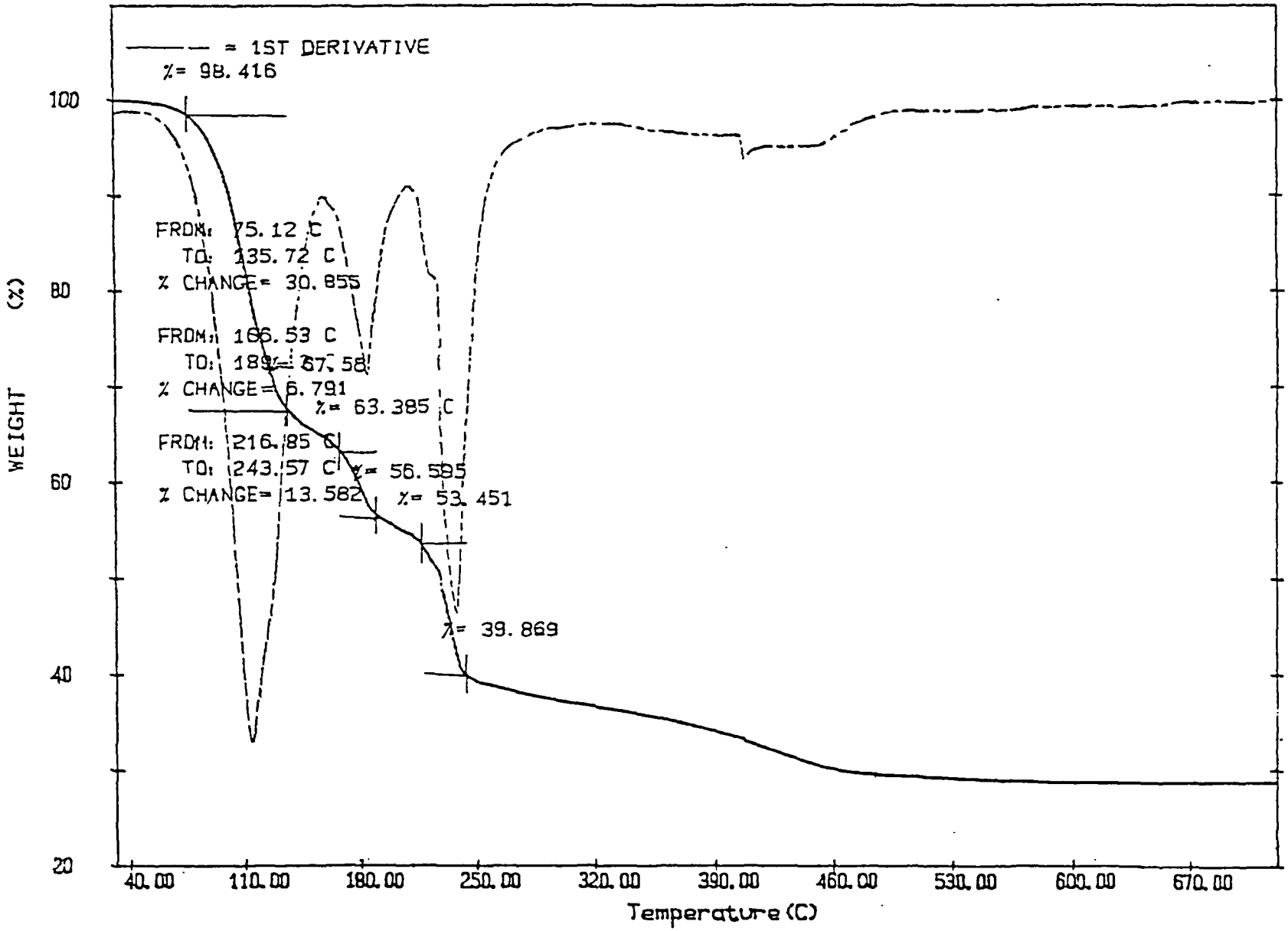


6.12 Infrared Spectrum of $[VO(acac)_2(dmpz)]$

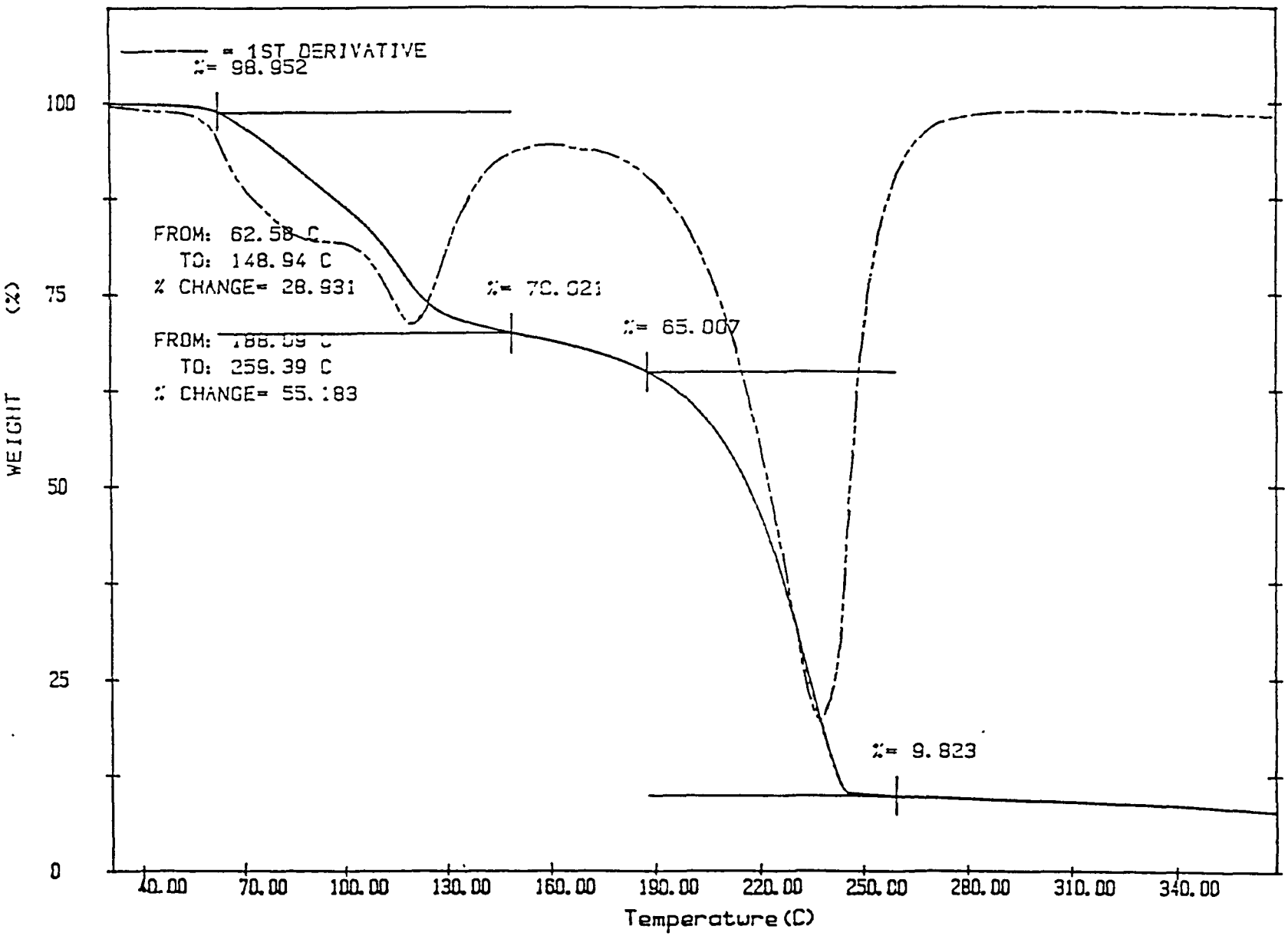




6.13 Electronic Spectrum of $[VO(acac)_2(dmpz)]$



6.14 Thermogram of $[UO_2(acac)_2(dmpz)_4]$



6.15 Thermogram of $[VO(acac)_2(dmpz)]$

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List of Publications:-

[1] Easy Synthesis Of Pyridinium Fluorochromate, $C_5H_5NH[CrO_3F]$, And Its Crystal Structure.

M.K.Chaudhuri, S.K.Chettri, **Deepa Dey**, Gagan C.Mandal, Pradip C. Paul, Wancydora Kharmawphlang

Journal of Fluorine Chemistry, 1997, **81**, 211.

[2] An Environmentally Benign Synthesis Of Organic Ammonium Tribromide(OATB) And Bromination Of Selected Organic Substrates By Tetrabutylammonium Tribromide(TBATB)

M.K.Chaudhuri, A.T.Khan, B.K.Patel, **D.Dey**, G.C.Mandal, T.R.Lakshmiphrabha and W.Kharmawphlang

Tetrahedron Letter, 1998, **39**,8163.

JOURNAL OF FLUORINE CHEMISTRY

Journal of Fluorine Chemistry 81 (1997) 211–213

Easy synthesis of pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$, and its crystal structure

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Received 23 April 1996; accepted 16 July 1996

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JOURNAL OF FLUORINE CHEMISTRY

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Abstract

An easy synthesis of pyridinium fluorochromate (PFC), $C_5H_5NH[CrO_3F]$, was developed by reacting CrO_3 with NH_4HF_2 in the presence of pyridine. The structure of PFC was determined by X-ray diffraction. The crystals are orthorhombic, space group $Cmc2_1$, with $a = 8.360(3)$ Å, $b = 7.312(4)$ Å, $c = 12.160(5)$ Å, $V = 743.4(6)$ Å^3, and $Z = 4$; $R = 0.0347$ for 409 reflections with $I > 2\sigma I$. The structure consists of discrete pyridinium, $C_5H_5NH^+$, cations and fluorochromate, $[CrO_3F]^-$, anions with a crystallographic mirror plane passing through the chromium, one oxygen and a fluorine atom.

Keywords: Pyridinium fluorochromate; Synthesis; Crystal structure

1. Introduction

One of the main thrusts of research in chromium(VI) chemistry is the synthesis of halochromate(VI) compounds suitable for the effective and selective oxidation of organic substrates, particularly alcohols, under mild conditions. Two such species, i.e. pyridinium chlorochromate (PCC), $C_5H_5NH[CrO_3Cl]$, [1] and pyridinium fluorochromate (PFC), $C_5H_5NH[CrO_3F]$, [2] have emerged as very useful newer reagents for the oxidation of organic substrates. Both the reagents are very effective, with the latter having some specific advantages [2,3]. PFC, synthesized [2,4] from the reaction of CrO_3 with 40% hydrofluoric acid and pyridine, was first developed as an efficient oxidizing agent in this laboratory [2] in 1982 and since then it has been used extensively in preparative oxidations as well as in the kinetic and mechanistic studies of oxidation reactions [5,6]. Considering its usefulness it was decided to improvise an easier alternative synthesis of the reagent.

From our experience in the field of fluorometal chemistry [7], we thought that it should be possible to prepare this reagent without using hydrofluoric acid and to ascertain the structure of pyridinium fluorochromate (PFC) by X-ray crystallography. To our knowledge this has not been characterized crystallographically previously.

Reported herein are an easy synthesis of PFC, $C_5H_5NH[CrO_3F]$, and the crystal structure of the compound.

2. Experimental details

Reagent grade chemicals were used throughout. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. The electrical conductance of the solution was measured using a Wayne Kerr automatic precision bridge B905 conductometer.

2.1. Synthesis of pyridinium fluorochromate, $C_5H_5NH[CrO_3F]$

1 g (17.52 mmol) NH_4HF_2 was dissolved in 7 cm^3 water in a polyethylene beaker followed by the addition of 1 g (10 mmol) CrO_3. To the resulting orange solution 2 cm^3 (24.40 mmol) pyridine was added with stirring. The reaction solution was then heated on a steam-bath for ca. 15 min. On cooling to room temperature this produced a solid orange product which on recrystallization from acetone afforded crystalline orange–yellow pyridinium fluorochromate (PFC), $C_5H_5NH[CrO_3F]$: yield 0.9 g (45%), MP 106–108 °C (literature [2,4] MP 106–108 °C). Analysis calculated for $C_5H_5NH[Cr_3F]$: C, 30.16; H, 3.04; N, 7.04; F, 9.54; Cr, 26.12%. Found: C, 30.2; H, 3.06; N, 7.1; F, 9.6; Cr, 26.25%.

The chromium content of PFC, $C_5H_5NH[CrO_3F]$, was determined by iodometry; the fluoride content was estimated

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PII S0022-1139(96)03527-0

Table 1
Data collection and structure refinement parameters for PFC

Molecular formula	$C_5H_6CrFNO_3$
Molecular weight	199.12
Crystal size (mm)	0.5×0.5×0.6
Space group	$Cmc2_1$
Z	4
a (Å)	8.360(3)
b (Å)	7.312(4)
c (Å)	12.160(5)
V (Å^3)	743.4(6)
d calculated (g cm^{-3})	1.779
Temperature (°C)	20
Radiation	Mo Kα (λ=0.71073 Å)
Scan type	ω
2Θ range (deg)	3.0–60.0
Range of h	$0 \le h \le 11$
Range of k	$0 \le k \le 7$
Range of l	$-16 \le l \le 0$
Reflections collected	507
Observed reflections ($I > 2\sigma I$)	409
Number of parameters refined	64
Weighing scheme	$W^{-1} = \sigma^2(F) + 0.0001F^2$
R	0.0347
R_w	0.0397
Goodness-of-fit	2.13
Largest difference peak (e Å^{-3})	0.34
Largest difference hole (e Å^{-3})	−0.21

by first precipitation as PbClF followed by estimation of the chloride content by Volhard's method [8]. Carbon, hydrogen and nitrogen contents were determined by the Microanalytical Laboratory, Central Drug Research Institute (CDRI), Lucknow.

2.2. Crystallization of PFC

A quantity of 0.5 g PFC was dissolved in ca. 8 cm^3 acetone and filtered. The orange–yellow solution was set aside at ca. 20 °C for 2 days by which time shiny bright orange crystals of PFC, suitable for X-ray crystallography, were formed. The crystals were isolated by filtration and dried in vacuo.

2.3. X-ray crystallography

Data collection was performed on a Siemens P_4 automatic diffractometer using graphite monochromated Mo Kα radiation (λ=0.71073 Å). Significant crystal data, data collection and structure refinement parameters are compiled in Table 1. Calculations for solution of the structure were done with the Siemens SHELXTL PLUS (PC version) programs. Three check reflections were measured after every 97 reflections during the period of data collection to monitor the stability of the crystal. The space group $Cmc2_1$ was identified uniquely from systematic absences observed during the collection of data. The structure was solved by the direct method (all non-hydrogen atoms were refined anisotropically). Hydrogen atoms were affixed at their idealized positions and refined isotropically with fixed thermal parameters.

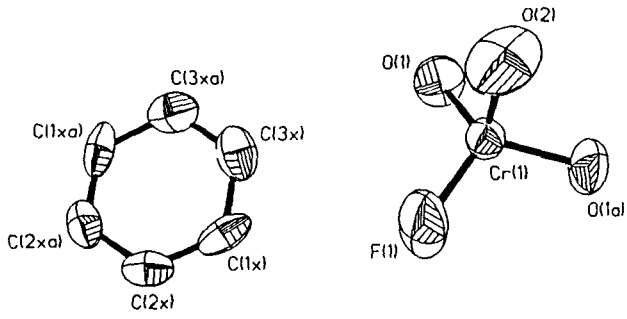

Fig. 1 ORTEP diagram of PFC showing the atom numbering scheme. The 50% probability thermal ellipsoids are shown. The crystallographic mirror plane passes through Cr(1) with O(2) and F(1) lying on it.

3. Results and discussion

3.1. Synthesis

The reaction of CrO_3 with ammonium hydrogen fluoride, NH_4HF_2, in an aqueous medium followed by precipitation of $[CrO_3F]^-$, formed in solution, by the addition of pyridine has now provided an easy synthesis of PFC. No use of hydrofluoric acid is the main advantage of the new synthesis. The melting point, analysis and spectral features match very well with the reported data [2,4].

3.2. Structure of PFC

The structure of the compound (Fig. 1) consists of discrete pyridinium, $C_5H_5NH^+$, cations and fluorochromate, $[CrO_3F]^-$, anions with no significant hydrogen bonding. This results in total disorder of the $C_5H_5NH^+$ cation. Because

Table 2
Refined atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$)

Atom	x	y	z	U_{eq} [a]
Cr	0	1450(1)	859	50(1)
F(1)	0	57(12)	1859(9)	153(1)
O(1)	1601(4)	2699(5)	802(10)	84(1)
O(2)	0	423(14)	−313(8)	128(12)
C(1X)	3413(5)	−29(16)	3453(9)	66(1)
C(2X)	4189(12)	−1074(12)	4143(7)	59(1)
C(3X)	4198(13)	9661(13)	2681(8)	72(1)

[a] U_{eq} indicates one-third of the trace of the orthogonalized U_{ij} tensor

Table 3
Anisotropic displacement coefficients ($Å^2 \times 10^1$)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	45(1)	50(1)	56(1)	0	0	10(1)
F(1)	77(2)	153(2)	230(2)	0	0	137(2)
O(1)	63(1)	82(2)	106(2)	−28(1)	1(3)	27(3)
O(2)	113(3)	172(3)	98(3)	0	0	−87(2)
C(1X)	43(2)	67(2)	88(2)	−21(3)	26(2)	−25(2)
C(2X)	73(2)	54(2)	51(2)	−18(2)	17(2)	−6(2)
C(3X)	84(2)	53(2)	78(3)	8(2)	−23(2)	−6(2)

Table 4
Bond lengths (Å) and bond angles (deg) for PFC

Cr–F(1)	1 586(10)	Cr–O(1)	1 622(3)
Cr–O(2)	1 611(10)	Cr–O(1A)	1 622(3)
C(1X)–C(2X)	1 308(13)	Cr(1X)–C(3X)	1 357(14)
C(2X)–C(2XA)	1 356(20)	C(3X)–C(3XA)	1 340(22)
F(1)–Cr–O(1)	113 2(4)	F(1)–Cr–O(2)	112 3(5)
O(1)–Cr–O(2)	103 0(4)	F(1)–Cr–O(1A)	113 2(4)
O(1)–Cr–O(1A)	111 2(2)	O(2)–Cr–O(1A)	103 0(4)
C(2X)–C(1X)–C(3X)	121 1(7)	C(1X)–C(2X)–C(2XA)	119 8(5)
C(1X)–C(3X)–C(3XA)	119 0(5)		

nitrogen is disordered on all six positions, the non-hydrogen atoms of the cation were refined as carbon atoms (labeled as C(X)) with every ring position being 5/6th carbon and 1/6th nitrogen. The hydrogen atoms are in calculated positions and included in the refinement. The chromium atom environment in the CrO_3F^- ion is nearly tetrahedral with the crystallographic mirror plane passing through the chromium atom and perpendicular to the crystallographic *a* axis. The two atoms lying on the mirror plane are an oxygen and a fluorine atom, both being disordered on the two positions. A similar disorder was observed in the case of $Rb[CrO_3F]$ [9]. The three metal–oxygen bond distances (Fig 1, Table 4), Cr–O(1), Cr–O(1A) and Cr–O(2), are 1.622(3), 1.622(3) and 1.611(10) Å respectively. As the fluorochromate unit is quite ordered, the Cr–O(1) and Cr–O(2) distances must be comparable, as observed. The Cr–F distance is 1.586(10) Å. It may be mentioned that the temperature factor for O(2) is lower compared with the lighter F(1). If one switches O(2) for F(1), the thermal parameters become unrealistic. The bond distances compare well with those [9] of $NH_4[CrO_3F]$ and $Rb[CrO_3F]$. Final atomic coordinates and isotropic displacement coefficients are given in Table 2 while anisotropic displacement coefficients are set out in Table 3. The bond distances and bond angles are summarized in Table 4.

3.3. Supplementary materials

The packing diagrams (Figs. S_1–S_3), tables for fractional atomic coordinates, equivalent thermal parameters and hydrogen atom coordinates (SI–SIII) and tables of observed and calculated structure factors (two pages) are contained in supplementary material.

Acknowledgements

We thank the University Grants Commission, New Delhi, for financial assistance to this Department under the Special Assistance Programme and research fellowship to G.C.M We are grateful to Professor K. Wieghardt and Dr. T. Weyhermüller for help in structure determination done in Ruhr Universität Bochum.

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Pergamon

Tetrahedron Letters 39 (1998) 8163–8166

TETRAHEDRON LETTERS

An Environmentally Benign Synthesis of Organic Ammonium Tribromides (OATB) and Bromination of Selected Organic Substrates by Tetrabutylammonium Tribromide (TBATB)

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Received 16 June 1998; accepted 28 August 1998

Abstract: Stable crystalline organic ammonium tribromides (OATB), like Me_4NBr_3, Et_4NBr_3, Bu_4NBr_3, cetyltrimethylammonium tribromide, $PyHBr_3$, can be readily synthesised from the reaction of the corresponding bromides with V_2O_5 and aqueous H_2O_2 Typically, TBATB, Bu_4NBr_3, brominates a variety of organic substrates rather easily under mild conditions An activated aromatic ring is selectively brominated in the presence of an olefinic double bond

Key words: Brominating reagents, Halogenation, Biologically active compounds

Bromination, especially of aromatic substrates, is usually carried out by elemental bromine,[1] but organic ammonium tribromides (OATB) including pyridine hydrobromide perbromide ($PyHBr_3$) are preferable owing to hazards associated with bromine The other advantages of OATB are that they are crystalline, easy to handle and maintain the desired stoichiometry Several tribromides have been reported i e, tetramethylammonium tribromide (TMATB),[2] phenyltrimethylammonium tribromide (PTATB),[3] cetyltrimethylammonium tribromide (CetTMATB), tetrabutylammonium tribromide (TBATB),[4] 1,8-diazabicyclo[5,4,0]-tetrabutylammonium tribromide ($DBUHBr_3$)[5] and pyridine hydrobromide perbromide ($PyHBr_3$)[6] However, their preparations invariably involve elemental bromine and in some cases HBr as well This again causes an environmental concern On the other hand, there is an obvious demand for brominated organic substrates due to their importance both as synthetic intermediates and as potent antitumor, antifungal, antibacterial, antineoplastic and antiviral compounds [7] It would be extremely useful to develop an environmentally benign alternative synthetic protocol for the synthesis of OATB A new synthesis of OATB is reported in this communication with TBATB as a typical example In the course of our investigation of the reactivity of peroxovanadium systems,[8] the

0040-4039/98/$ - see front matter
PII S0040-4039(98)01818-8

oxidation of bromide leading to tribromide was noticed Vanadium bromoperoxidase (VBrPO) related biomimetic oxidations of bromide have also been studied in solution by others [9] Consequently, it has become clear that a peroxovanadium(V) intermediate is capable of the catalytic oxidation of bromide Based on this, our strategy was to isolate the ultimate oxidation product of bromide employing organic quaternary ammonium cations so that the organic ammonium tribromides (OATB) could be synthesised in an environmentally acceptable way Thus, in a typical reaction 2 75 mmol of V_2O_5 was dissolved in 44 1 mmol of 30% H_2O_2, with stirring at *ca* 5°C To the clear red solution 11 mmol of tetrabutyl ammonium bromide, dissolved in 7 mL of water, was added and the reaction was stirred at ambient temperature The reaction took place readily and the solution became yellow with concurrent precipitation of yellow or orange yellow tetrabutylammonium tribromide (TBATB), Bu_4NBr_3 The product was isolated after 15-20 min, washed with water 2 or 3 times and dried in air or by pressing between the folds of a filter paper The isolated yield[10] was 68%, m p 75°C (Lit[4] 76°C) TBATB can be recrystallised from acetonitrile The compound showed an intense electronic absorption at 267 nm typical of tribromide (Br_3^-) [11] Importantly, the same methodology worked very well for TMATB, tetraethylammonium tribromide (TEATB), PTATB, CetTMATB and $PyHBr_3$ which were synthesised in very high isolated yields from the corresponding organic ammonium bromides and pyridinium hydrobromide, respectively The involvement of peroxovanadate(V) as the active oxidant has been ascertained from the observance of the peroxovanadium charge-transfer (CT) band at 430 nm (ε=300) in aqueous V_2O_5-H_2O_2 solution

$$Bu_4NBr \xrightarrow{V_2O_5,\ H_2O_2} Bu_4NBr_3\ (TBATB)$$

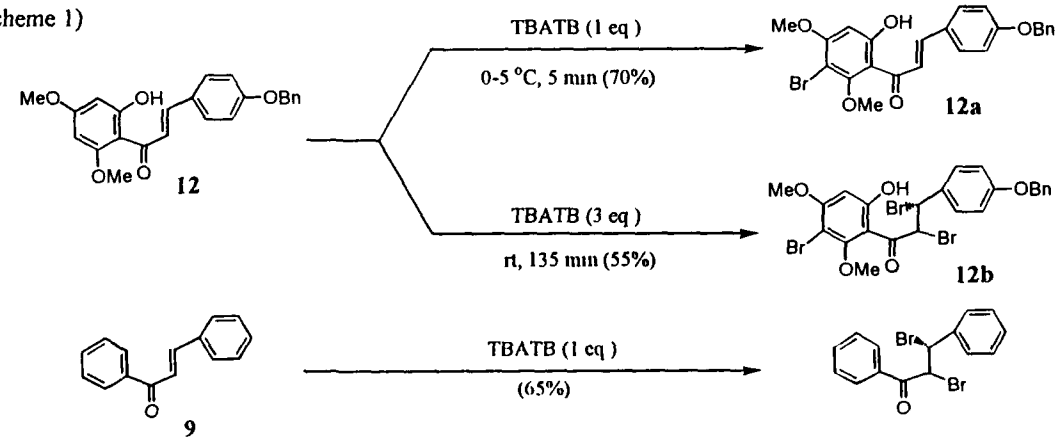
As a typical example, the efficacy of TBATB obtained by the new protocol was ascertained The results of room temperature bromination of aromatics including polycyclic hydrocarbons **1-5**, sensitive substrates such as imidazole **6**, allyl alcohol **7**, alkenes **8-10** and ketone **11** are summarised in Table 1 Thus, TBATB brominates activated aromatics such as aniline **1** very smoothly to give bromoaniline in H_2O-DMF Both p-bromo- and 2,4,6-tribromo aniline may be selectively synthesised depending on the molar ratio of the reagent that is used Polycyclic aromatics such as anthracene **3** and phenanthrene **4** can be brominated in acetic acid Here again, 9-bromo and 9,10-dibromo anthracene can be prepared selectively by setting the molar ratio between the substrate TBATB at (1 1) or (1 2), respectively Unreactive rings like benzene **5** were brominated to afford the corresponding bromide in good yield by treating the substrate with Ag_2SO_4 in H_2SO_4 [12] TBATB is also capable of brominating heteroaromatics sensitive to usual bromination, for instance, imidazole **6** in CH_2Cl_2 MeOH (1 1) mixture was brominated to 2,4,5-tribromoimidazole in a high yield (68%) Treatment of allyl alcohol **7** with the reagent in CH_2Cl_2 afforded 2,3-dibromopropanol in 72% yield Also TBATB allows easy double bond bromination **8-10** under mild reaction conditions The reaction of acetophenone **11** with the reagent produced bromomethyl phenyl ketone

Table 1. Bromination of Aromatic and Some Other Substrates with TBATB

Substrate(Entry)	Solvent/Time in min.[a]	Substrate :TBATB	Product(s)[b]	% yield[c]
Aniline (1)	50% Aq DMF/ 15	1·1	p-bromoaniline	60
Aniline (1)	50% Aq DMF/ 15	1 3	2,4,6-tribromoaniline	65
Phenol (2)	CH_2Cl_2/MeOH(1 1),$CaCO_3$/ 60	1.3	2,4,6-tribromophenol	60
Anthracene (3)	Acetic acid/ 30	1 1	9-bromoanthracene	70
Anthracene (3)	Acetic acid/ 30	1.2	9,10-dibromoanthracene	55
Phenanthrene (4)	Acetic acid/ 30	1 1	9-bromophenanthrene	46
Benzene (5)	conc H_2SO_4, Ag_2SO_4/ 30	1 1	bromobenzene	40
Imidazole (6)	CH_2Cl_2/MeOH(1 1),$CaCO_3$/ 60	1 3	2,4,5-tribromoimidazole	68
Allyl alcohol (7)	CH_2Cl_2/ 60	1 2	2,3-dibromopropanol	72
Styrene (8)	CH_2Cl_2/ 60	1 2	*vic*-dibromostyrene	62
Chalcone (9)	$CHCl_3$/ 180	1.2	Threo-dibromochalcone	65
Cinnamic acid (10)	$CHCl_3$/ 120	1 2	2,3-dibromo-3-phenyl propanoic acid	60
Acetophenone (11)	50% Aq DMF/ 30	1 1	bromomethyl phenyl ketone	46

[a] Reactions were monitored by TLC, GC [b] Products were characterised by comparision with authentic pure samples [c] Isolated yields are reported

Heretofore unprecedented is the selective bromination of an activated aromatic ring in the presence of an olefinic double bond by TBATB For example substrate **12**, an important synthetic precursor for naturally occuring flavonoids (*c.f.* Vitexin),[13] on being reacted with an equimolar amount of TBATB gave **12a**[14] as the exclusive product, while a similar reaction when conducted with **12**.TBATB at a molar ratio of 1 3 yielded **12b**[14] (Scheme 1)



Scheme-1

Bromination of organic substrates The substrate (10 mmol) and TBATB (10, 20 or 30 mmol as indicated in Table 1) in 25 mL of the specified organic solvents, and 20 mmol of $CaCO_3$ for phenol and imidazole, were vigorously stirred for the specified period of time The reaction mixture was filtered *in vacuo*, the filtrate was

diluted with 100-120 mL of water to completely precipitate the product The product was then filtered *in vacuo* and washed with water For the liquid product the aqueous layer was extracted with ether and the separated ether layer was washed with water, dried over anhydrous Na_2SO_4 and finally evaporated under reduced pressure

For benzene, a mixture of the substrate (10 mmol), Ag_2SO_4 (15 mmol) and 25 mL of conc H_2SO_4 was stirred at room temperature for *ca.*10 min followed by the addition of TBATB (12 mmol) The reaction mixture was stirred for 30 min and then poured into 150 g of crushed ice The precipitated AgBr was separated by suction filtration The filtrate and the precipitate were separately extracted with ether and washed several times with water until they were free from acid The combined ether extract was evaporated under reduced pressure

In conclusion, we have found an environmentally favourable procedure for peroxovanadium(V)-mediated biomimetic oxidation of bromide leading to the synthesis of organic ammonium tribromides (OATB) Synthesised in this way the crystalline tribromides are stable, and no Br_2 and HBr was used Using OATB bromination proceeded smoothly with a variety of substrates which afforded the corresponding bromoorganics in good yields Furthermore, selective bromination of an activated aromatic ring in the presence of an olefinic double bond is possible with such a reagent

Acknowledgements: The authors thanks CSIR, New Delhi for award of research fellowships to D D and G C M.

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[10] The compound analysed correctly $C_{16}H_{16}NBr_3$ Calc C, 39 85, H, 7 54, N, 2 91, Br, 49 71 Found C, 39 82, H,7 48, N, 3 11, Br, 49 78

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[14] Products **12a** and **12b** gave satisfactory analytical and spectral data **12a** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3 98 (s, 6H), 5 11 (s, 2H), 6 04 (s, 1H), 6 98 (d, 1H), 7 36-7 56 (m, 9H), 7 77 (d, 1H), 14 97 (s, 1H) **12b** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3 96 (s, 3H), 3 99 (s, 3H), 4 79 (d, 1H), 5 08 (s, 2H), 5 58 (d, 1H), 6 06 (s, 1H), 7 00-7 56 (m, 9H), 14 09 (s, 1H)