SOME ASPECTS OF MIXED-LIGAND COMPLEXES OF MANGANESE, PEROXO COMPOUNDS OF MOLYBDENUM AND BIOMIMETIC CHEMISTRY OF VANADIUM BROMOPEROXIDASE

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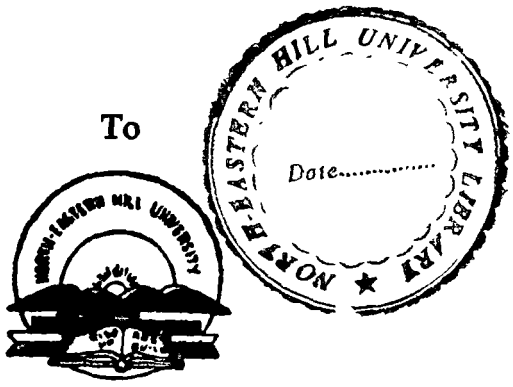
A THESIS SUBMITTED
IN FULFILMENT OF THE REQUIREMENT
FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

To



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I certify that the thesis entitled ***"Some Aspects of Mixed-Ligand Complexes of Manganese, Peroxo Compounds of Molybdenum and Biomimetic Chemistry of Vanadium Bromoperoxidase"*** *submitted by Mr. Gagan C. Mandal for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the Ph.D. Degree. This work has not been submitted for any Degree of any other University.*

Signature of the Supervisor

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ACKNOWLEDGEMENTS

It is with the feelings of pleasure that I would like to place the acknowledgements. My heartfelt thanks are due to Prof. Mihir K. Chaudhuri for his guidance, constant encouragement and affection throughout my Ph.D. research.

I feel very happy to acknowledge the help, inspiration and good wishes of all those who bestowed on me during the period of my Ph.D. work. However, it is a formidable task to name them all. I should like to thank all my laboratory colleagues, friends, seniors as well as the Faculty Members of the Department of Chemistry, NEHU.

I am grateful to Dr. Manish Bhattacharjee for magnetic measurements, Prof. K. Wieghardt, Dr. Weyhermüller, Prof. A. Chakravorty, Dr. S. Chattopadhyay and Prof. P. K. Bharadwaj for X-ray structure determination of our compounds.

Thanks are due to the Dean, School of Physical Sciences, NEHU, Head, RSIC, NEHU, and the University authorities in general for permitting me to use all the research facilities. I also wish to thank all the non-teaching staff members of the Department of Chemistry as well as the technical staff of RSIC, NEHU, for their help. Research Fellowships(NET) received from the University Grants Commission, New Delhi, is gratefully acknowledged.

It will remain incomplete if I do not place on record the gratitude to my beloved parents for their blessings, encouragement and support. My profound thanks are also due to all other members of our family which they rightly deserve.

G. C. Mandal

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Date: 8.4.96

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Some Aspects of Mixed-Ligand Complexes of Manganese, Peroxo Compounds of Molybdenum And Biomimetic Chemistry of Vanadium Bromoperoxidase

Abstract

The thesis, consisting of six chapters, deals with the results of investigation on some chosen aspects of the chemistry of manganese, peroxo and heteroligand peroxo complexes of molybdenum, and the oxidation of bromide to tribromide by titanium, vanadium, molybdenum, and uranium peroxo intermediates. The relevance of oxidation of bromide by transition-metal peroxides to the vanadium bromoperoxidase activity has been highlighted.

Chapter I gives a brief background information related to the types of problems selected for the present Ph.D. research. The importance of and interest in the coordination chemistry of manganese, peroxo complexes of molybdenum and the chemistry related to the vanadium bromoperoxidase activity has been underscored in this chapter.

Chapter II presents details of the methods adopted for the preparation of some starting materials, sources of ready-made

reagents and elemental analyzes as well as the particulars of instruments/equipment used for the characterization and structural assessment of the compounds.

Chapter III provides an improved methodology for $K_2[MnF_3(SO_4)]$ based on redox reaction between $KMnO_4$ and $SO_2(g)$ in the presence of KHF_2. The compound bears an acknowledged importance because of its unusual structural and magnetic properties.

Also incorporated in this chapter is the study of some newer reactions of $Mn(acac)_3$ by the way of product isolation. Reactions of $Mn(acac)_3$ with H_2O_2 in the presence of 2,2'-bipyridine(bpy) or 1,10-phenanthroline(phen) have been performed. This has led to the generation of $[Mn(acac)_2(bpy)]$ **1** or $[Mn(acac)_2(phen)]$ **2**, respectively. The reaction provides a rarely encountered example of the reduction of Mn(III) by H_2O_2. Further the treatment of $Mn(acac)_3$ with H_2O_2 in the presence of bpy or phen followed by the interaction of $Cl_2(g)$ has led to the oxidation of Mn(II) compounds formed *in situ* to $[MnCl_3(bpy)]$ **3** and $[MnCl_3(phen)]$ **4**, respectively. Similar reaction sequence has been observed by using $KF.H_2O_2$ in place of H_2O_2. In separate reaction runs the interaction of $Cl_2(g)$ with **1** and **2** has brought about their oxidation respectively to **3** and **4**. The compounds produced in the reactions have been isolated in good yields and characterized by analysis, IR, UV-Vis and EPR spectroscopies, magnetic susceptibility measurements, TG, DSC and cyclic

voltammetry. The single crystal X-ray structure of $[Mn(acac)_2(phen)]$ **2** has been determined. The compound has a distorted octahedral geometry and crystallizes in orthorhombic space group Pbcn.

Chapter IV is devoted to the stabilization of a combination of Mn(III) and chloride, bromide or iodide with salicylic acid, a biologically relevant coligand. Described in this chapter is the synthesis of $A_2[Mn_2X_2(salH)_4(sal)].nH_2O$ (A = NH_4, Na or K; X = Cl, n = 4; X = Br, n = 6) and $K[Mn_2I(sal)_3(H_2O)_4].2H_2O$. The syntheses have been achieved from the reaction of manganese oxide hydroxide, MnO(OH), with salicylic acid in the presence of corresponding halide salts at the molar ratio 1:1.25:14.1. Characterization of the compounds has been made by analysis, IR, laser Raman, UV-Vis spectroscopies, magnetic measurements, TG, DSC experiments, and cyclic voltammetry.

Chapter V reports the effect of fluoride on dimeric peroxomolybdates as well as the synthesis of newer heteroligand peroxomolybdenum compounds. The dimeric peroxomolybdates, $A(NH_4)[MoO_2O_3(O_2)_4(H_2O)_2].2H_2O$ (A = Na(1) or K(2)), have been synthesized by reacting $(NH_4)_2[MoO_4]$ with H_2O_2 at pH 6. The action of fluoride on the dimeric complexes has been investigated by product isolation. Similar reaction on being conducted in the presence of fluoride afforded monomeric fluoroperoxomolybdates, $A(NH_4)[MoO(O_2)_2F_2].3H_2O$ **4** and $K(NH_4)[MoO(O_2)_2F_2].H_2O$ **5**. The reaction of NH_4HF_2 with **1** and **2** produced in each case

$(NH_4)_2[MoO(O_2)_2F_2].H_2O$ 3. New quaternary fluoroperoxomolybdenum complexes of the type $(NH_4)[MoO(O_2)_2F(L)]$ where L = glycine (6), alanine (7), valine (8) and leucine (9) have been synthesized from the reaction of $H_2MoO_4.H_2O$ with H_2O_2, aqueous HF and the corresponding organic heteroligands at pH 6. The corresponding reaction with L being oxinate, however, afforded $(NH_4)[MoO(O_2)_2(oxinate)]$ 10. Compounds are all diamagnetic and have been characterized by analysis, IR, laser Raman and electronic spectroscopies. In all cases peroxide is bonded in a side-on(C_{2v}) fashion. Vibrational spectra of compounds 6-9 showed the presence of amino acids in zwitterionic form and their coordination through carboxylate oxygen to the metal centre. In 10 oxine is ligated in a bidentate manner, through its -O and -N atoms to molybdenum. Two well resolved LMCT (O_2^{2-} ----> Mo) bands in the electronic spectra of these compounds have been observed. Transformation of a few chosen substrates involving some of these peroxo complexes have been accomplished.

Chapter VI, indeed the concluding chapter of the thesis, evidences the peroxo-metal mediated generation and trapping of tribromide, Br_3^-. This is important in understanding the nature of intermediate in the reactions catalyzed by vanadium bromoperoxidase (V-BrPO). Bromide has been oxidized by Ti-, V-, Mo- and U- peroxo complexes generated *in situ*. To trap the oxidized bromine species in aqueous solution NBu_4^+ was used as a heavy organic cation. That bromide is oxidized also by the other

transition-metal intermediates, than that of vanadium alone, indicates that the V-BrPO activity may not be restricted to only vanadium, rather it is specific to such metals that are capable of forming peroxo compounds. Trapping of the tribromide has also been accomplished by precipitating with NEt_4^+ or $NCetMe_3^+$ (Cet = Cetyl group, $CH_3(CH_2)_{15}-$) from the titanium peroxomediated oxidation of bromide. The products have been isolated in good yields. This work provides an evidence that Br_3^- is one of the intermediates in V-BrPO catalyzed biomimetic reactions. The products have been characterized by analysis, UV-Vis, IR, laser Raman spectroscopies and solution electrical conductance measurements. NBu_4Br_3 has been characterized by X-ray crystallography. Bromination of some selected organic substrates has been carried out with NBu_4Br_3 to ascertain its efficacy as a brominating agent. It is anticipated that the present methodology for the generation of tribromide will have a tremendous potential in replacing the existing methods. The major advantages of the new protocol include ease of synthesis of the reagent and redundancy of use of the hazardous chemicals Br_2 and HBr.

CHAPTER I

Introduction

[Background and Scope of Work]

The entire thesis is based on the experiments conducted on some chosen aspects of the chemistry of manganese, molybdenum and vanadium, collection and interpretation of data and the inference drawn thereof. While presenting the introduction attempts will be made to give a brief background information relating to the topics selected for the present Ph. D. programme. Manganese has been a metal much neglected by chemists before 1970. In recent years it has occupied the central place of interest of both coordination and biochemists after understanding its biological significance. Interestingly, the metal exhibits a wide spectrum of accessible oxidation states ranging from -III to +VII. The chemistry of lower oxidation states (-III to +I) is largely

represented by the compounds containing Π- and Π-acid ligands such as arenes, phthalocyanine, NO^+, CO and PR_3. The chemistry of +II to +IV oxidation states is principally that of classical coordination compounds mainly with the ligands having nitrogen, oxygen, sulfur donor atoms and the halides. The +V to +VII oxidation states of manganese are essentially confined to its coordination chemistry involving oxo ligands. Because the metal ions of very high oxidation states preferably require for their stabilization the presence of ligands that are not only good σ-donors but also good Π-donors so that, sufficient charge density can be placed on the metal to satisfy Pauling Electroneutrality Principle.[1] This needs ligands with filled p orbitals that are not otherwise engaged in bonding with other atoms. Ligands of this kind includes O^{2-}, S^{2-}, Se^{2-} and in certain cases O_2^{2-}, S_2^{2-} (persulfido), NR^{2-}, N^{3-}, RC^{3-}, R_2NN^{2-} and R_2NO^- which can form complexes with strict analogues in oxo chemistry.[2] Although it is by and large true that the oxidation states dictate the kinds of compounds expected to form, there have been many exceptions.[3a]

A number of coordination compounds of manganese in its higher-valent states are useful in bringing about desired organic transformations.[3b,4-6a,7,8] Importantly, MnF_3, the only binary manganese(III) halide exists at ordinary temperature, is an acknowledged fluorinating agent in organic chemistry both on a laboratory and an industrial scale.[9] Besides the intrinsic importance, the profound recent interest in the coordination chemistry of manganese stems from the recognition of its role on

a number of biochemical redox processes associated with the metabolism of oxygen and its reduced derivatives (O_2^{n-}, n = 1,2). Recognition of manganese metalloenzymes began in 1970 with the discovery of manganese superoxide dismutase (SOD),[10] which decomposes O_2^- radicals, $2O_2^- + 2H^+ \longrightarrow H_2O_2 + O_2$. The occurrence of manganese enzymes in biosystems with varying nuclearities are being increasingly identified such as the oxygen evolving complex (OEC) in photosystem II (PS II),[11a] some bacterial catalase,[11] manganese ribonucleotide reductase,[11a] and purple acid phosphatase,[11a,12-14] and manganese peroxidase.[15] So far in metalloenzymes, manganese has been found to occur with the oxidation states ranging from +II to +IV with varying nuclearities.[16-21] The work related to the active sites in manganese containing metalloproteins has been excellently reviewed by Wieghardt.[11a] Many research groups are thoroughly engrossed in developing manganese coordination chemistry aiming at understanding the structure and function of manganese containing enzymes. Some groups have made considerable success in synthesizing model compounds[22-34] which significantly mimic the properties of active sites of a number of manganese enzymes. As part of our ongoing programme on dealing with some chosen aspects of manganese(III) chemistry our research group has made some success.[35-37] One of the significant contributions has been the stabilization of manganese(III) both in aqueous solution as well as in the solid state.[36] In this endeavour the group has come out

with a very convenient synthesis of $Mn(acac)_3$ involving a direct redox reaction between $KMnO_4$ and acetylacetone.[37]

The preparation of higher-valent manganese compounds in aqueous solution is often complicated by their pronounced tendency to form intractable brown precipitates (MnO_2?).[3c] Incidentally, $Mn(acac)_3$ is an important precursor, with desired solubility properties, for the preparation of a variety of compounds. The compound has been also known as highly useful catalyst[3d] as well as a one electron oxidant.[38] It is now evident that in biomolecules manganese ions are bound to N and/or O donor atom functionalities from within the protein. Functional groups from different amino acid side chains include, for example, carboxylato (from aspartate and glutamate), phenoxy- (from tyrosine), the N atom from imidazole ring of histidine and alkoxy.[11a] As mentioned above that the biological connection of manganese is associated with the metabolism of oxygen and its reduced forms the study of the interaction of dioxygen with manganese is of much significance. $Mn(acac)_3$ being a useful compound we felt it necessary to investigate the interaction of H_2O_2 with it, in the presence of biologically relevant ligands[3d,39,40] such as 2,2'-bipyridine and 1,10-phenanthroline through product isolation. In addition, our aim has been to study the reaction of $Mn(acac)_3$ leading to the generation of higher valent manganese compounds containing halides, with an anticipation of their potential oxidative halogenating properties for organics.

Keeping in view the chloride ion requirement[11a] for the optimal activity of PS II it was also of our concern to synthesize mixed-ligand chloro manganates comprising biologically relevant ligand. Coordination of carboxylate functionalities is prevalent in manganese biochemistry and the phenoxide coordination although less common but not unprecedented.[11a] Interestingly, both phenoxide and carboxylate coordinations can be provided by a single ligand, viz. salicylic acid (2-hydroxy benzoic acid). Pertinent to mention here that salicylic acid has been suggested[41] as a convenient ligand substitute for the biochemically relevant tyrosine phenoxide and aspartic or glutamic carboxylate functionalities. In addition, salicylic acid itself is well known for its medicinal utility[42] as antipyretic and in the treatment of certain kinds of rheumatism. It is believed that its action[43] is dependent on its ability to form complexes with metal ions present in biosystems. Notably salicylate ions exhibit interesting bonding patterns[44] with the transition metals which may be useful to elucidate the interaction of metals with humic materials in nature.[44] Considering the importance of salicylic acid and mixed-ligand chloro complexes of manganese it can be stated that the above mentioned overview may result in a search for mixed-ligand complexes of manganese containing chloride and salicylate. From the view point of synthetic inorganic chemistry it is worthwhile to extend the study to include other halides viz., bromide and

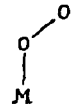
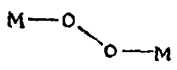
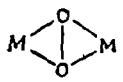
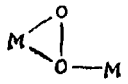
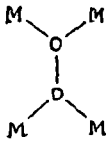
iodide, while some work on mixed-fluoro manganate(III) have already been carried out by one of my predecessors.

Like the current enormous interest in manganese coordination chemistry the transition-metal dioxygen chemistry in general has been in the focus of attention over the past half century.[45-55] This is in a large part from the importance of metal-dioxygen complexes in industry,[56] biology[46,57,58] and academics.[59-61] Pertinent in this context is to give an idea about the terminology used in dioxygen chemistry. While the term oxygen refers to only uncoordinated O_2 molecule; as a generic designation dioxygen implies either coordinated or free O_2 entity in any of its oxidation states[62] viz., O_2^{2+}, O_2, O_2^- and O_2^{2-}. Another convension is the classification of dioxygen complexes into simple and heteroligand ones. Simple dioxygen compounds are comprised of either only dioxygen ligands or in some cases they contain water molecules also. Whereas heteroligand dioxygen compounds contain dioxygen in combination with one or more monodentate or polydentate ligands.

Vibrational spectroscopy is a very useful technique to identify different kinds of dioxygen complexes. The characteristic IR bands[55] for O_2^+, O_2, O_2^-, and O_2^{2-} appear at *ca.* 1905 [6b], *ca.* 1508 [6b], *ca.* 1145 [63], and *ca.* 842 cm^{-1} [64], respectively. IR and Raman spectroscopies have been very extensively used as diagnostic techniques.

The nature of bonding of dioxygen with the metal is of much importance both in catalysis and biology. It is interesting to

note that the dioxygen ligands exhibit a variety of coordination modes[48,59,62] in their complexes with transition metals. Though most of the complexes fall under Vaska's classifications, a few examples of new structural types have been recently reported.[48] **Figure 1** summarizes the different kinds of coordination modes of dioxygen with transition metals.

Structural Type	Structural Designation (Vaska's Classification)	Example	*Ref.*
	η^2 (superoxo)	$[Co(CN)_5(O_2)]^{3-}$	65
	η^2 (peroxo)	$[V(O_2)_4]^{3-}$	66
	η^2 (superoxo)	$[Cu(O_2)(HB(3\text{-}^tBu\text{-}5\text{-}^iPrpz)_3)]$	67
	η^1: η^1 (both peroxo and superoxo)	$[[Cu(TMPA)]_2(O_2)]^{2+}$	68,69
	η^2: η^2 (peroxo)	$[Cu(HB(3,5\text{-}^iPr_2pz)_3]_2(O_2)$	70
	η^1: η^2 (peroxo)	$[(PO_4)W_4O_4(O_2)_8]^{3-}$	71
		$[Mo_4O_{12}(O_2)_2]^{4-}$	71
		$[Ir_2I_2(CO)_2(\mu\text{-}O_2)(Ph_2PCH_2PPh_2)]$	48

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

Figure 1: Structural Classification of Dioxygen Complexes

Importantly, the electronic spectroscopy is expected to provide a direct and sensitive probe to understanding the nature of electronic interactions of O_2 with the metal ions in catalysis and biosystems.[61] The coordination mode of peroxide may as well be ascertained from electronic spectroscopy considering the number, energies and intensities of the bands.[59,61] A qualitative and simplified molecular orbital energy level diagram[59] for a μ_2-superoxometal complex is shown in Figure 2. If Z-axis is

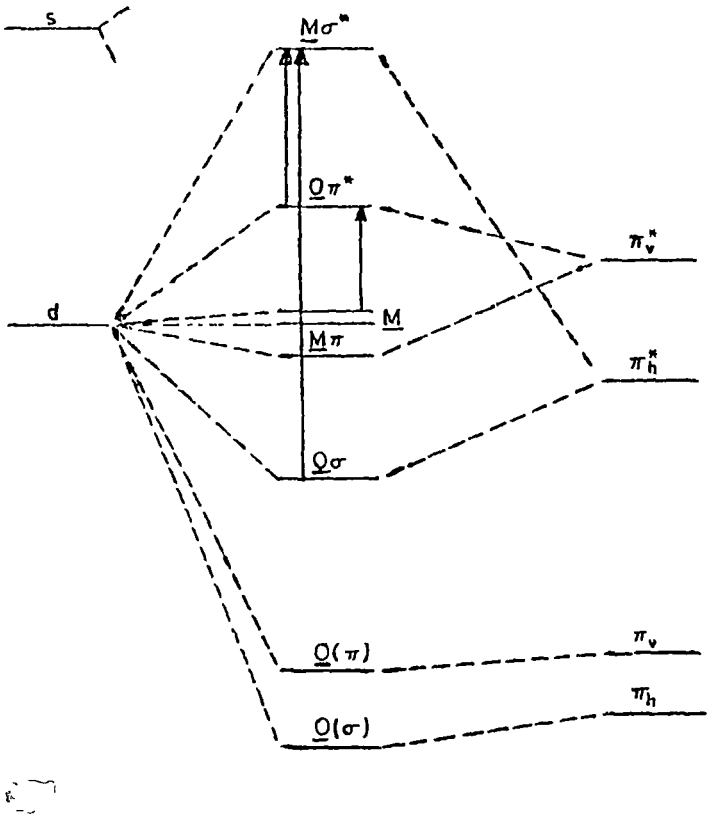


Figure 2: Simplified molecular orbital energy level diagram of μ_2- superoxometal complex

assumed to be the molecular axis then d_σ^* is derived from d_z2

metal orbital. This diagram is also applicable to bridging superoxo complexes after considering the d_{σ}^{*} levels as appropriate combinations of orbitals on each metal atom.[59,72] The MO diagram of peroxometal complexes should not perceptively differ from that has been shown in Figure 2 because the addition of one electron to the Π_{v}^{*} level of superoxide does not seriously perturb the energy levels although electron-electron repulsion increases to some extent.[59] The significant difference in the electronic transition between superoxo and the peroxo complexes lies in the fact that metal to ligand charge transfer (LMCT) transition is not observed in the latter case. This is because of the filled nature of Π_{v}^{*} orbital of peroxide whereas in case of superoxide it is half filled.

Transition-metal peroxo complexes are found to be an important class of reactive intermediates in catalytic oxidations[54] and potential oxygen donors in oxygen transfer reactions to organic substrates including hydrocarbons.[52] Sharpless asymmetric epoxidation[73] of olefins using $(CH_3)_3C\text{-}OOH$ catalyzed by $Ti(O^{i}Pr)_4$ is a remarkable example to mention at this juncture. Molybdenum peroxides, in particular, has received a considerable attention as reagents for organic transformations.[47,50,51] Specifically notable is the molybdenum catalyzed epoxidation of propylene by organic hydroperoxide in Halcon process[56] in which a molybdenum hydroperoxide intermediate is believed to be the active species. Recently, heteroligand oxodiperoxomolybdates containing HMPA such as

$[MoO(O_2)_2(HMPA)(H_2O)]$ and $[MoO(O_2)_2(HMPA)(py)]$ (HMPA = hexamethyl phosphoric triamide) have been used as stoichiometric reagents for a number of organic transformations. A few important examples are the stereospecific conversion of olefins to epoxides,[74-76a] hydroxylation of cyanide to cyanohydrin[77] (>CH-CN ----> >C(OH)-CN, enolates to acyloin[76b] (-C(=O)-CH< ----> -C(=O)-C(OH)<), and naphthalene to naphthol,[78] oxidation of amides to hydroxamic acids[79] (R-C(=O)-N< ----> R-C(=O)-N(OH)-) and autoxidation of cyclohexene.[80]

Preparation of desired peroxo compounds is an important prerequisite for these studies. Incidentally, the preparation of transition-metal peroxides often requires delicate reaction conditions and precise pH adjustment. The synthesis of peroxo compounds generally becomes difficult by the formation of more than one products even within a narrow range of pH. The composition of various peroxo-vanadates[66,81-83] and molybdates[84,85] form at different pH has been rationalized in some recent reports.

Many simple peroxo compounds undergo spontaneous explosion, decomposition above 0°C, some are sensitive to shock, while several do not even exist as stoichiometric compounds. On the other hand, selective heteroligand combinations generally enhance the stability of peroxo-metal systems. What is important is the choice of appropriate coligand and evaluation of suitable experimental conditions. The enhanced stability can be explained[86] on the basis of electrostatic interaction, steric effect and back donation.

The interaction of dioxygen with Mo in enzyme has not been evidenced in physiological processes.[2b] However, keeping in view the ubiquitous presence of molybdenum enzymes in plants and animals the interaction of molybdenum with dioxygen may be speculated.

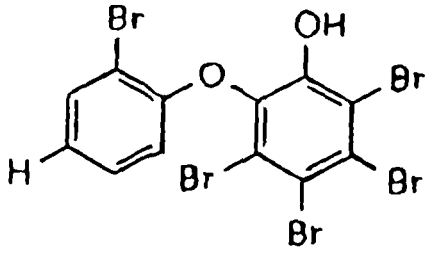
Whereas chloride is known to be essential for appropriate function of a metalloenzyme, OEC of PS II[11a] for instance, fluoride plays a role of effective inhibitor of enzyme activity e.g.,the activity of OEC of PS II[11a] and cytochrome C peroxidase.[87] Coordination of fluoride to the iron centre[87] of fluoride-inhibited cytochrome C peroxidase has been evidenced by x-ray crystallography. The coordinated fluoride then form hydrogen bond with N-H hydrogen of neighbouring histidine or arginine groups, thereby disabling the enzyme. Therefore it is quite relevant to investigate the effect of fluoride on simple peroxo compounds. Also important is the synthesis and spectroscopic evaluation of the structural motifs of heteroligand peroxomolybdates containing fluoride and/or biologically relevant ligands such as amino acids. Equally important is the studies of their reaction profiles with a selection of substrates.

Apart from the topical importance of and interest in the chosen aspects of manganese and molybdenum chemistry as highlighted above, this group has been engaged in the investigation of different aspects of vanadium chemistry[88-91] for last fifteen years or so. Incidentally, the chemistry of molybdenum and vanadium in aqueous solution are quite similar,[6c]

indeed both the metal exist as oxo species in aqueous solution. Among the various facets of vanadium chemistry, different aspects of peroxovanadates have drawn the attention of a number of researchers world over.[66,81,88-92] The main reasons for this are their importance as catalytic intermediates and biochemical relevance of metal-peroxide interactions. The monoperoxovanadate entity "$[VO(O_2)]^+$" has been implicated to be one of the most reactive intermediates[81] of the metal. Some heteroligand peroxovanadates of the type $A_n[VO(O_2)_xL\text{-}L'].yH_2O$ where $A = NH_4^+$ or K^+, n is 0-3, x is 1 or 2, and L-L' is generally a bidentate ligand[92] have been found to be insulin mimetic for the treatment of diabetes of rats. The "$VO(O_2)_2^-$" core is implicated to be the active species responsible for the increase in life-span of mice with murine leukemia.[93] Of the few compounds so far tested positive as potential insulin mimics some were also synthesized in this laboratory[94] a few years ago. Notably the metal constitutes the active sites of many enzymes such as amavadine[95] and vanadium bromoperoxidase[96] (V-BrPO).

The interest in peroxo vanadium chemistry has been further triggered by the isolation of V-BrPO from marine algae in 1983.[96] The enzyme catalyzes the oxidation of halides by H_2O_2. The oxidized halogen species in turn halogenates organic compounds, which is the presumed biogenesis of halogenated marine natural products.[57] Many of these compounds have pharmaceutical significance, which include antifungal, antibacterial, antiviral (e.g., anti HIV), antiinflamatory, and other properties thereby

providing chemical defence to marine organisms.[57] One such antimicrobial halogenated organic[57] is 2-(2'-bromophenoxy)-3,4,5,6-tetrabromophenol(1).



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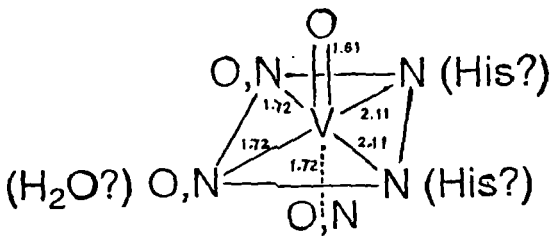
In the absence of substrates the oxidized halogen intermediate disproportionates the second equivalent of H_2O_2 producing oxygen.[57]

Molecular weight of V-BrPO subunit is 65,000 D and four molecules are present per asymmetric subunit.[57] Based on EXAFS studies the coordination environment[57] of V-BrPO has been suggested to be:



There are conflicting evidences about the nature of the unknown oxygen donors. The oxygen coordination has been speculated to be provided by phenolate group of tyrosine, carboxylate group of glutamic or aspartic acid, or deprotonated alcohol of serine or thrionine. Absence of characteristic LMCT bands seems to preclude a tyrosine phenol. Carboxylate from glutamic acid or aspartic acid seem unlikely to give a V-O bond as short as 1.72 Å. This suggests the deprotonated alcohols of serine or thrionine remains to be the only candidate ligand.[97] Several groups[98,99] suggested that the oxygen donors represent protonated oxo group on the vanadium centre. Detailed mechanistic studies suggest a peroxovanadium intermediate[100] in the catalytic reaction of V-BrPO and the oxidized bromine intermediate is believed to remain in an equilibrium mixture[100] of Br_2, HOBr and Br_3^-. However, the exact identity of active brominating intermediate is not yet clearly known.[101, 102] The foregoing facts appears to be warranting investigation of the oxidation of bromide by vanadium peroxide as well as with other transition metals in order to concritize the results.

In cognizance to the aforementioned background we decided to address to the following problems:

(i) Investigation on the reaction of $Mn(acac)_3$ with H_2O_2 separately in the presence of 2,2'-bipyridine and 1,10-phenanthroline and rationalize the reaction profile in terms of isolation of products. Chlorine oxidation of the compounds formed by the interaction of $Mn(acac)_3$ with H_2O_2 in the presence of bpy

or phen. The comprehension of this investigation is presented in **Chapter III** of the thesis.

(ii) The essential requirements for a model compound of metalloenzyme are the mimicing of active site coordination environment, structure and function. Even though chloride has been recognized as an essential component of PS II, as already highlighted, not much studies have been accomplished on the mixed ligand halomanganates. To the best of our knowledge no manganese salicylate containing halide ligand has reported existence. Studies on manganese fluoro-salicylate has already been carried out by one of my senior colleagues. Therefore, we concerned ourselves to explore the chemistry of salicylate compounds of manganese bearing Cl^-, Br^- or I^- as coligands. The endeavour has led to the generation of a number of newer compounds of manganese(III). The outcome of these studies has been incorporated in **Chapter IV.**

(iii) The subject matter of **Chapter V** consists of the following bits of work: A newer access to $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ followed by the studies of the influence of fluoride on it by way of product isolation. Synthesis of heteroligand peroxomolybdates containing amino acids and fluoride as coligands, their characterization and spectroscopic evaluation of structural motifs. Exploration of the reaction profiles of some suitably chosen peroxomolybdates with a selection of substrates.

(iv) **Chapter VI**, indeed the concluding chapter of the thesis, is devoted to the peroxo-metal (Ti, V, Mo and U)

mediated, generation and trapping of tetra-n-butyl ammonium tribromide, NBu_4Br_3. Characterization including x-ray crystal structure of the tribromide (*cf.* active brominating intermediate of V-BrPO) is at the heart of this investigation.

The chapter in hand gives a brief background information pertinent to the topics chalked out for the present Ph.D. research and identifies some problems considered imperative to investigate. **Chapter II** mentions the sources of ready-made materials and describes the details of the procedures used for the preparation of some of the starting materials, the methods of elemental analyzes and relevant particulars of instruments/equipment used for physico-chemical studies and structural characterization. **Chapter III to VI** incorporate the results of studies on the identified problems. In order to make the chapters independent,each has been provided with appropriate sections followed by citation of the relevant references. Adoptation of this format of presentation rendering the chapters self contained leads to some unavoidable repetitions. Sincere attempts have been made to keep this to a minimum. A part of the work has been already published while the rest are under communication.

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CHAPTER II

Materials, Elemental Analyzes and Physical Measurements

Detailed procedures adopted for the preparation of different starting materials as well as for quantitative estimation of various constituents and the relevant particulars of the instruments/equipment made use of for physico-chemical and structural characterization of the compounds are presented in this Chapter.

Preparation of Starting Materials

$Mn(acac)_3$ [1].——— A quantity of 2.0 g $KMnO_4$ was dissolved in 20 cm^3 water by slight warming on a steam-bath. The solution was filtered to remove any undissolved matter. To this solution 10 cm^3 acetylacetone was added dropwise over 10 min. An exothermic reaction took place and the solution became dark-brown. The solution was heated on a steam-bath for 10 min whereupon a shiny black crystalline product formed. The whole

was allowed to stay for 10 min at room temperature and the product was isolated by vacuum filtration, washed two or three times with petroleum ether and dried in a vacuum desiccator over conc. H_2SO_4. The compound has an innate tendency to decompose in air, but remains unchanged for months in sealed container.

MnO(OH).——— A 10 g of $MnSO_4.H_2O$ was dissolved in 250 cm^3 water. To this solution 15 cm^3 25% ammonia was added with stirring. A white precipitate formed. The precipitate was washed three times with 400 cm^3 water by decantation. At this stage the suspension should remain slightly ammoniacal. Through the suspension air was bubbled for 4h whereupon a dark-brown compound was obtained. The product was washed with water by decantation until it became free from ammonia. The volume of the suspension of MnO(OH) in water was measured and stored in a closed vessel. Subsequently the requisite amount was transferred and used for reactions.

$KF.H_2O_2$.——— This compound was prepared by recrystallization of KF from 30% H_2O_2.

***Alkali hydrogen fluorides*, AHF_2 (A = NH_4, Na or K).**——— An amount of 36 mmol of alkali carbonate A_2CO_3 was dissolved in 7.2 cm^3 (144 mmol) 40% hydrofluoric acid. A clear solution was obtained. Pyridine was slowly added to the solution with constant stirring until the precipitation was complete. The white crystalline compound was isolated by vacuum filtration, washed with acetone and finally dried in a vacuum desiccator.

Tetraalkylammonium perchlorate (R_4NClO_4).——— This was prepared by a slightly modified procedure published earlier.[3] To a solution of 155.28 mmol tetraalklammonium bromide in 200 cm^3 water 15 cm^3 70% $HClO_4$ was dropwise added with vigorous stirring. A white compound thus formed was isolated by vacuum filtration, washed several times with water and dried in vacuum over conc. H_2SO_4. The product was twice recrystallized from ethanol and finally dried in vacuum over conc. H_2SO_4.

All other chemicals and organic solvents were of reagent grade or better quality commercial materials (E. Merck, Glaxo, SD-Fine Chemicals, CDH, Aldrich and Sigma) and used without further purification.

Elemental Analyzes

Manganese

(a) ***Iodometry***

In a conical flask *ca.* 100 cm^3 water was taken and acidified with 25 cm^3 3.5M H_2SO_4 followed by the addition of two portions of *ca.* 5 g pure $NaHCO_3$. To this 5-6 g of iodate-free potassium iodide was added. Immediately after this an accurately weighed amount of *ca.* 0.1 g manganese(III) compound was added and shaken well. The mouth of the conical flask was covered with a clock-glass and kept in the dark for 10 min. The under side of the clock-glass and the side of the conical flask was rinsed with water and the washings were collected. The liberated iodine was

titrated against standard sodium thiosulfate solution using starch as indicator.

$$1\ cm^3\ 1M\ Na_2S_2O_3 \equiv 0.05494\ g\ Mn(III)$$

(b) *Gravimetry* [4]

To an accurately weighed amount (*ca.* 0.1 g) of manganese compound was added 100 cm^3 5% NaOH solution and the mixture was boiled for 1h to decompose the compound. Hydrated manganese oxide thus formed was filtered out, washed thoroughly with water and dissolved in *ca.* 10 cm^3 concentrated HCl. The dark-brown solution so obtained was boiled to get a clear colorless solution. Then it was diluted to 150 cm^3 with water followed by the addition of 15 g NH_4Cl and 2 g diammonium hydrogen phosphate, $(NH_4)_2HPO_4$. The solution was heated to boiling (90-95°C) and dilute (1:1) ammonia was dropwise added with constant stirring until a precipitate of silky appearance formed. After this *ca.* 0.8cm^3 (1:1) ammonia was added dropwise with stirring to complete the precipitation. Much 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 10 min until the precipitate became crystalline. At this stage 1 or 2 drops of ammonia was added and the precipitate was allowed to settle for 2h at room temperature. The precipitate was then filtered through a sintered glass (G-4) crucible of known weight, washed thoroughly with 1% NH_4NO_3 until free from chloride and dried at

100-105°C to constant weight. Finally the precipitate was weighed as $MnNH_4PO_4.H_2O$.

Molybdenum [5]

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

The oxine solution was prepared by dissolving 4.0 g reagent grade oxine in 8.5 cm^3 warm glacial acetic acid, pouring into 80 cm^3 water and diluting to 100 cm^3.

Fluoride

An accurately weighed amount of $K_2[MnF_3(SO_4)]$ (*ca.* 0.1 g) was treated with 20 cm^3 20% NaOH and the mixture was boiled for 30 min to decompose it completely. The hydrated manganese oxide thus formed was separated by filtration and thoroughly washed with water. To the combined washing and filtrate *ca.* 10 g NaOH was added followed by the addition of 3 cm^3 10% NaCl solution and a pinch of bromophenol blue indicator. Dilute (1:1) HNO_3 was added dropwise until the blue colour of the solution turned yellow. Then a few drops of dilute NaOH solution was added such that the colour just changed to blue. The solution was heated to *ca.* 65-70°C and to the hot solution 2 cm^3 6M HCl was added. The colour changed to yellow. Immediately after this 0.5 g $Pb(NO_3)_2$ was added and the solution was vigorously stirred until all $Pb(NO_3)_2$ dissolved completely followed by the addition of 5 g solid sodium acetate without delay. A white precipitate of PbClF formed. The mixture was digested on a steam-bath for 1h with occasional stirring and allowed to stand overnight. The precipitate was filtered through a Whatman 542 filter paper, washed 5-6 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 $AgNO_3$ solution was added and the suspension of AgCl was heated almost to boiling and then stirred vigorously. The beaker and the content was kept in the dark for 1h. The precipitated AgCl was filtered out, 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 then calculated from the volume of $AgNO_3$ solution consumed.

$$1\ cm^3\ \ 1M\ \ AgNO_3 \equiv 0.019\ g\ F$$

Fluoride contents of complex fluoroperoxomolybdates were determined by adopting the procedure described by Chakravorti and Pandit.

Chloride [7]

Chloride was estimated volumetrically following Volhardt's method.

An accurately weighed amount of about 0.1 g of a manganese compound containing chloride was decomposed with 100 cm^3 2% NaOH solution. The mixture was heated on a hot plate for 30 min to ensure complete decomposition. The hydrated manganese oxide thus formed was separated by filtration and washed several times with water. The filtrate and the washings were collected for chloride estimation. The alkali chloride solution was neutralized with dilute(1:1) HNO_3 and acidified by adding 20 cm^3 excess acid. The acidified chloride solution was then treated with an excess of standard silver nitrate ($AgNO_3$) solution. The suspension was heated to almost boiling and then stirred vigorously. The container alongwith the

suspension was kept in the dark for 30 min. The precipitated AgCl 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^{3+} as indicator. The end point was marked with the appearance of faint red brown color. 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.

$$1\ cm^3\ 1M\ AgNO_3 \equiv 0.03545\ g\ Cl$$

Bromide [8]

Bromide was estimated in a similar way as described for chloride. For the decomposition of tetrabutylammonium tribromide, NBu_4Br_3, an accurately weighed amount of the sample (*ca.* 0.1 g) was dissolved in 20 cm^3 acetonitrile. Then the solution was treated with 20 cm^3 20% NaOH solution followed by the addition of 100 cm^3 water. The solution was boiled for 1h, acidified with HNO_3 and bromide was estimated by following Volhardt's method.

$$1\ cm^3\ 1M\ AgNO_3 \equiv 0.07990\ g\ Br$$

Iodide [8]

For the determination of iodide content of $K[Mn_2I(Sal)_3(H_2O)_2].2H_2O$, a procedure similar to that of Cl^- was adopted.

$$1\ cm^3\ 1M\ AgNO_3 \equiv 0.12690\ g\ I$$

Peroxide [9]

Nearly 1 g boric acid was dissolved in 100 cm^3 water in a conical flask. This was acidified with 20 cm^3 2.5 M H_2SO_4. To this was added an accurately weighed amount (*ca.* 0.1g) peroxomolybdate 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.

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

Sulfate [10]

An accurately weighed amount of *ca. 0.1 g* sulfato compound was dissolved in 150 cm^3 water and 20 cm^3 20% NaOH solution was added to it. The mixture was boiled for 1h to decompose the compound. The solution was allowed to cool and filtered to remove undissolved materials, if any, and washed with water. The filtrate and the washings were collected and acidified with dilute(1:1) HCl such that the acid strength of the solution remained within 0.05-0.1M. The volume of the solution at this stage should be 125-150 cm^3. The solution was boiled and a 10 cm^3 warm solution of 5% barium chloride was dropwise added to it with constant stirring. A white precipitate formed which was allowed to settle for *ca.* 10 min. Then the supernatant liquid was tested for complete precipitation by adding a few drops of barium chloride solution. The mixture was warmed on a steam-bath to achieve complete precipitation of $BaSO_4$. The precipitate was filtered through a preweighed G-4 sintered glass crucible, washed

with cold water until free from chloride and dried at *ca.* 110°C to a constant weight. The precipitate was weighed as $BaSO_4$.

Carbon, Hydrogen and Nitrogen

The carbon, hydrogen and nitrogen contents were estimated by micro-analytical methods by the Micro-Analytical Laboratories of Central Drug Research Institute, Lucknow and also of Indian Association for the Cultivation of Science, Calcutta.

Determination of Elements by Atomic Absorption Spectroscopy

The Perkin-Elmer Model 2380 Atomic Absorption Spectrophotometer(AAS) was used for the quantitative determination of sodium, potassium and manganese. In each case, a solution of known amount of compound containing the element under determination was used for the AAS experiment.

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

For the solution electrical conductance measurements a Systronics Type 304 digital direct reading conductivity meter and also a Wayne Kerr automatic Precision Bridge B905 conductometer were made use of.

Magnetic Measurements

Magnetic susceptibility measurements were performed by Gouy Method using $Hg[Co(NCS)_4]$ as the the calibrant. The X-band EPR spectra were recorded on a Varian E 102 spectrometer with 100 KHz field modulator.

Infrared Spectra

Infrared spectra were recorded for KBr pellets on Perkin-Elmer models 297 and 983 as well as with a Bomem DA8 FT-IR spectrophotometers. For recording the spectra below 400 cm^{-1} region polyethylene powder was used as the medium.

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

To record the electronic spectra a Hitachi 330 UV-Vis-NIR, a JASCO UVDEC-610/UV-Vis, or a Shimadzu UV-160A spectrophotometer was made use of.

Reflectance Spectra

Reflectance spectra were recorded against MgO using a Zeiss Tena VSU 2-P instrument.

X-ray Crystallography

X-ray diffraction data were collected either on a Siemens P4 automatic diffractometer or on a Simens Nicolet R3m/V diffractometer with graphite monochromated Mo-Kα radiation (λ = 71073A) applying ω scan technique. The structure was solved by heavy atom patterson method and refined by full matrix least square technique using the programmes of Siemens SHELXTL PLUS (PC Version).

Thermal Studies

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

Cyclic Voltammetry

For the cyclic voltammetric experiments the PAR Model 370-4 electrochemistry system, equipped with 174A polarographic analyzer, 175 Universal programmer and RE 0089 X-Y recorder, was used. A standard three electrode cell comprised of a platinum disc working electrode, a platinum wire auxiliary electrode, and a saturated colomel reference electrode (SCE) was used for recording the voltammograms. The electrochemical experiments were carried out under a dry and purified nitrogen atmosphere. The reported potentials are uncorrected for junction contributions.

NMR Spectra

Nuclear Magnetic Resonance spectra were recorded on a 90 MHz Varian EM 390 CW and a 300 MHz Bruker AC-F 300 FT NMR spectrometers. Appropriate deuterated solvents and TMS as the internal standard were used for recording the spectra.

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CHAPTER III

Improved Synthesis of $K_2[MnF_3(SO_4)]$ and Newer Reactions of $Mn(acac)_3$ Leading to the Direct Access to $Mn(acac)_2(bpy)$, $Mn(acac)_2(phen)$, $MnCl_3(bpy)$, and $MnCl_3(phen)$ and X-ray Structure of $Mn(acac)_2(phen)$*

The chemistry of trivalent manganese has drawn our interest since 1981[1-5] with one of the major concerns being gaining an easy access to manganese(III) compounds. Incidentally, tripositive manganese (high spin d^4) is amneable to Jahn-Teller distortion. Important in this context is the complex trifluorosulfatomanganate(III), $[MnF_3(SO_4)]^{2-}$, exhibiting an

*A part of this work has been published: *J.Chem.Soc.,Dalton Trans.*, 1993, 3497; *Proc.Ind.Acad.Sci.,(Chem. Sci.)* 1995, 107, 305

opposite kind of distortion,[6] i.e., 4-long-2-short. This kind of distortion is not commonly encountered. A method for the synthesis of this complex was achieved first in 1984 in this laboratory.[3] Subsequently it was observed that if the experimental conditions are not maintained appropriately it ends up with a non-sulfato product. A direct method was conceived involving a reaction between $KMnO_4$ and SO_2 in the presence of F^-.

Tris(acetylacetonato)manganese(III), $Mn(acac)_3$, is one of the very important compounds of trivalent manganese with its most important use being an oxidant for organic compounds. This can be readily synthesized[2] from the reaction of 2,4-pentanedione (acetylacetone, acacH) with concentrated solution of $KMnO_4$. The reaction chemistry of $Mn(acac)_3$ complex leading to easy access to a variety of inorganic compounds is relatively unexplored even though the potentially interesting synthetic chemistry may be anticipated for such systems. $Mn(acac)_3$ is amenable to electrochemical oxidation leading to $Mn(acac)_3^+$ which in turn readily oxidizes H_2O_2.[6] From our experience in Mn(III) chemistry[1-5] it was anticipated that $Mn(acac)_3$ might as well be reduced by H_2O_2. By conducting such redox reactions in the presence of chosen ligands one might be able to develop newer synthetic routes to desired complexes.

In this context our attention was drawn to complexes of the type[7,8] $[Mn(acac)_2L]$ (L is bipyridine(bpy) or 1,10-phenanthroline(phen)) because of their importance as viable synthetic precursors with desired solubility properties. Though

the compounds are reported[8] their preparation requires $[Mn(acac)_2(H_2O)_2]$ which has an innate tendency to get oxidised. Neither of them was structurally characterised. In a quest we have synthesised $[Mn(acac)_2(bpy)]$ 1 and $[Mn(acac)_2(phen)]$ 2 by the reduction of $Mn(acac)_3$ by H_2O_2 in the presence of bpy and phen, respectively. The reduction of Mn(III) by H_2O_2 is a rarely encountered[9] reaction in the coordination chemistry of the metal. H_2O_2 is generally used to obtain higher valent manganese compounds from a lower valent one.[10]

It may be noted that in an earlier paper the synthesis of $[MnF_3(H_2O)L]$ (L is bpy or phen) was reported from this laboratory[4] but adaptation of a similar reaction strategy involving MnO(OH), aqueous HCl and L did not produce the corresponding chloro derivative. Indeed the metal was reduced to its +II state. Our interest in compounds of the type $[MnCl_3L]$, however, persisted because of their anticipated potential as oxidative chlorinating agents. To this end we have now shown that starting from $Mn(acac)_3$, the mixed-ligand chloro complexes can be synthesised through the *in situ* generation of 1 or 2 followed by oxidation with Cl_2. It is relevant to mention that the literature method[11] for $[MnCl_3(bpy)]$ 3 and $[MnCl_3(phen)]$ 4 is very cumbersome requiring stringent reaction conditions.

This Chapter pesents an improved synthesis of $K_2[MnF_3(SO_4)]$ as well as the synthetic reactions of $Mn(acac)_3$ affording 1-4, the results of EPR, cyclic voltammeric, thermoanalytical studies of 1 and 2 and molecular structure of 2.

Experimental

$Mn(acac)_3$, $KF.H_2O_2$ and tetrabutylammonium perchlorate were prepared as described in Chapter II. All other chemicals and organic solvents were of reagent or better quality commercially available products and used as received. The details of the instruments/equipment used for the characterization of the products are given in Chapter II.

(a)Synthesis of $K_2[MnF_3(SO_4)]$.——— Potassium permanganate (1.0g, 6.33 mmol) was thoroughly mixed with KHF_2 (0.98 g, 12.55 mmol), to give a Mn:F ratio of 1:4. The mixture was then dissolved in 30 cm^3 water and SO_2 gas was bubbled through the solution with constant stirring until a brown solid precipitated. The flow of SO_2 was continued whereupon the solid redissolved to give a clear solution. On further bubbling of SO_2 a crystalline pink solid precipitated. At this stage the pH of the reaction solution was found to be in the range of 2-2.5 and the flow of SO_2 was stopped. The product obtained as above was filtered, washed two or three times wtih ethanol and finally dried in a vacuum desiccator over conc. H_2SO_4. Yield 1.2 g (66 %). Anal. Calc.(Found) for $K_2F_3SO_4Mn$: K, 27.30(27.55); F, 19.92(20.30); SO_4, 33.56(33.65); Mn, 19.20(19.30%). IR (KBr, cm^{-1}) 1230s, 1145s and 1030s [ν_3(S-O)], 975s [ν_1(S-O)], 680s, 635s and 605s [ν_4(S-O)], 525s [ν(Mn-F)].

(b) Reactions of Mn(acac)$_3$ *with* H_2O_2 *in the Presence of bpy or phen. Synthesis of* [Mn(acac)$_2$L] (L=*bpy* 1, *phen* 2).——— To a solution of 1.0g (2.84 mmol) of Mn(acac)$_3$ in 20 cm^3 acetonitrile was added a solution of bpy (0.89g, 5.70 mmol in 10cm^3 acetonitrile) or 1,10-phenanthroline monohydrate (1.13g, 5.70 mmol in 15cm^3 acetonitrile). Then 30% H_2O_2 (1.2cm^3, 11.75 mmol) was added dropwise with stirring. The colour of the solution changed from dark-brown to yellow and a yellow microcrystalline compound was precipitated out. The reaction mixture was allowed to stand for 15 min. The product was isolated by vacuum filtration, washed three times with acetonitrile and dried in air, m.p. 252°C (dec.) 1, 261°C (dec.) 2. Yields of [Mn(acac)$_2$(bpy)] 0.4 (34) and [Mn(acac)$_2$(phen)] 0.5g (41%). Complex 1 Anal. Calc.(Found) for $C_{20}H_{22}N_2O_4Mn$: C, 58.67(58.56); H, 5.43(5.40); N, 6.84(6.81); Mn, 13.42(13.36%). Complex 2 Calc.(Found) for $C_{22}H_{22}N_2O_4Mn$: C, 60.96(60.84); H, 5.13(5.12); N, 6.47(6.49); Mn, 12.68(12.64%). IR(KBr, cm^{-1}) 1 1578 vs, 1516s, 1459s, 1421s, 1010s, 771s, 534w; 2 1585 vs, 1505s, 1447 s, 1396 vs, 1012m, 727m, 538w.

(c) Reaction of Mn(acac)$_3$ *with phen,* H_2O_2 *and* Cl_2. *Synthesis of* [MnCl$_3$(phen)] 4.——— A solution of 1.13g (5.70 mmol) phen in 20 cm^3 acetonitrile was added to the solution of 1.0g (2.84 mmol) Mn(acac)$_3$ in 75 cm^3 acetonitrile. This was followed by the dropwise addition of 30% H_2O_2 (1.2cm^3, 11.75 mmol) while stirring to get a yellow solution. Then a slow stream of Cl_2(g) was passed through this. After 1 or 2 min a light-yellow compound

separated out with the colour of the solution being light-yellow. Chlorine was continued to pass for 1h when a mixture of dark-brown and white compound settled at the bottom of the container. The colour of the supernatent liquid at this stage was green. The reaction vessel was kept closed overnight by which time the solid was converted to dark-brown. This was separated by filtration, washed thoroughly with acetonitrile and dried in vacuum. Yield 0.8g (82%). Anal. Calc.(Found) for $C_{12}H_8N_2Cl_3Mn$: C, 42.20(42.12); H, 2.37(2.40); N, 8.20(8.20); Mn, 16.09(16.50); Cl, 31.14(30.50%). IR (KBr, cm^{-1}) 1621 m, 1603s, 1575m, 1515s, 1420s, 718s, 368s, 296m.

(d) Reaction of $[Mn(acac)_2(phen)]$ 2 *and* Cl_2. *Synthesis of* $[MnCl_3(phen)]$ 4.——— Through a solution of $[Mn(acac)_2(phen)]$ (0.5g, 1.15 mmol) in 125 cm^3 of acetonitrile was passed a slow stream of $Cl_2(g)$. A light-yellow compound was separated out after 1 or 2 min. The $Cl_2(g)$ bubbling was continued for 1h. In this process the light-yellow compound was slowly dissolving with the generation of a dark-brown complex. The colour of the supernatent liquid became green at this stage. The reaction mixture was kept overnight in a closed container. The microcrystalline dark-brown product was isolated by filtration, washed thrice with acetonitrile and dried in vacuum. Yield 0.3g (76%).

(e) Reaction of $Mn(acac)_3$ *with bpy,* H_2O_2 *and* Cl_2. *Synthesis of* $[MnCl_3(bpy)]$ 3.——— The reaction was done in much the same way as described in (b) above. The difference being that bpy was

used instead of phen and the reaction was comperatively slower. After passing Cl_2(g) for 45 min the reaction solution was slightly warmed and the flow of gas, through the warm solution, was continued for 15 min. Yield: 55%. Anal. Calc.(Found) for $C_{10}H_8N_2Cl_3Mn$: C, 37.83(37.81); H, 2.54(2.53); N, 8.83(8.80); Mn, 17.30(17.05); Cl, 33.50(32.64%). IR(KBr, cm^{-1}) 1628m, 1596s, 1559m, 1470m, 1436s, 1016m, 772vs, 368s, 282m.

(f) Reaction of **[Mn(acac)$_2$(bpy)] 1** *with* **Cl_2**. ***Synthesis of* [$MnCl_3$(bpy)] 3.**——— The reaction was carried out in a similar fashion as described under (c) except that the reaction solution was warmed *ca.* 15 min before completion of the reaction. Yield: 61% .

(g) Reaction of **Mn(acac)$_3$** *with* **KF.H_2O_2** *in the presence of bpy or phen leading to***1** *and* **2**, *respectively.*——— The reaction was conducted in a similar fashion as described in (a) with the difference that an aqueous solution of KF.H_2O_2 was used in the molar ratio of Mn: KF.H_2O_2 at 1:4 as a substitute for H_2O_2. Yields of 1 and 2 were similar and they analysed well.

X-ray Crystallography.——— Single crystals of 2 was obtained by recrystallisation of it from acetonitrile at 5°C. X-ray diffraction data were collected at 293K on a Siemens P_4 automatic diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å) applying ω scan technique. The intensities of three standard reflections measured after each 97 reflections showed negligible variation. The significant crystal

data, the experminetal details of the data collection and structure refinements are compiled in Table 1. The structure was solved by heavy-atom patterson method and refined by full matrix least square technique using the programs of Siemens SHELXTL PLUS (PC Version). The non-hydrogen atoms were refined anisotropically. H atom were located in the difference map and refined using riding model with fixed isotropic thermal parameters.

Elemental Analyzes. Manganese was estimated by gravimetry as $MnNH_4PO_4.H_2O$. Also in $K_2[MnF_3(SO_4)]$, 3 and 4 manganese contents were verified by iodometry. Quantitative determination of chloride, fluoride, sulfate, carbon, hydrogen and nitrogen were performed as described in Chapter II.

Chemical Determination of the Oxidation State of Manganese. For this the manganese content of the compound was first determined independently by the method described in Chapter II. The oxidation state of manganese was then determined iodometrically by treating a freshly prepared potassium iodide solution, acidified with dilute sulfuric acid, with the compound followed by the titration of the liberated iodine against standard sodium thiosulfate solution.

Results and Discussion

Synthesis and Characterization of $K_2[MnF_3(SO_4)]$.——— $K_2[MnF_3(SO_4)]$ is an interesting compound of manganese(III) from the view point of its magnetic properties and structure. A dedicated method for its synthesis has now been improvized by the $[MnO_4]^-/SO_2$ redox reaction in the presence of fluoride. The underlying principle of this method is the generation of SO_4^{2-} *in situ* by the oxidation of SO_2 with $KMnO_4$. In this process manganese was reduced by SO_2 to produce a coordinatively unsaturated Mn(III) species that was trapped by the coordination of sulfate and fluoride. The product analyzed well.

Figure 3.1 presents the IR spectrum of $K_2[MnF_3(SO_4)]$. The most important features of the spectrum include the splitting of ν_3(S-O) and ν_4(S-O) modes into three bands each at 1230s, 1145s, 1030s and 680s, 635s, 605s cm^{-1}, respectively and the observance of ν_1(S-O) at 975s cm^{-1}. The observed spectral pattern is typical of chelated sulfate.[12] A strong band at 525 cm^{-1} has been assigned to ν(Mn-F) vibration.[12b,13] It is interesting to note that while the room temperature magnetic moment of $K_2[MnF_5]$ occurs at 3.2 B.M (strong antiferromagnetic coupling)[1,14] and those of sulfato compounds of manganese(III) at *ca.* 4.8 B.M as expected for normal manganese(III),[15,16] the magnetic moment of $K_2[MnF_3(SO_4)]$ is found to be 4.1 B.M. It is evident that the degree of antiferromagnetic exchange interaction can be controlled by the replacement of two F^- ligands by an SO_4^{2-} ligand in going from $[MnF_5]^{2-}$ to $[MnF_3(SO_4)]^{2-}$. This

property is expected to be of importance for magnetochemical engineering.

Owing to the insolubility of $K_2[MnF_3(SO_4)]$ it was subjected to diffuse reflectance spectral studies. The spectrum shown in Figure 3.2 is characteristic of Mn(III).[4,17] Three bands at 730, 350 and 462 nm have been attrributed to $^5B_{1g}$ ----> $^5A_{1g}$, $^5B_{1g}$ ----> $^5B_{2g}$ and $^5B_{1g}$ ----> ^5E_g transitions, respectively.

Reactions of **Mn(acac)$_3$** ***with*** **H_2O_2** ***and*** **L (L = *bpy or phen*).** ***Isolation of*** **1** ***and*** **2.**——— An acetonitrile solution of freshly prepared Mn(acac)$_3$ was interacted with H_2O_2 in the presence of L (L is bpy or phen). The strategy was that Mn(acac)$_3$ would undergo a reductive elimination reaction to produce coordinatively unsaturated [Mn(acac)$_2$] which in the presence of a bidentate ligand L would form [Mn(acac)$_2$L]. The strategy worked as evident from an immediate change of the solution colour from deep brown to yellow ultimately affording 1 and 2 in reasonably good yields. The reactions were clean producing pure products. The relatively low yields of 1 and 2 are due to their solubility in acetonitrile.

Reactions of **Mn(acac)$_3$** ***with*** **H_2O_2, L (L = *bpy or phen) and*** **Cl_2(g).** ***Isolation of*** **[$MnCl_3$(bpy)] 3** ***and*** **[$MnCl_3$(phen)] 4.**——— Reactions similar to those of the above were conducted till the yellow solutions were obtained. Bubbling of chlorine gas through these solutions first led to the appearance of a light-yellow suspension which dissolved to produce a clear green solution.

Further passing of chlorine gas afforded dark-brown 3 and 4 in very high yields in the respective cases. It may be mentioned that while the reaction leading to 4 was quite facile, the corresponding synthetic reaction for 3 was somewhat sluggish (vide Experimental).

Reactions of** 1 **and** 2 **with chlorine gas leading to** 3 **and** 4, **respectively. ——— In separate reaction runs $Cl_2(g)$ was bubbled through the acetonitrile solutions of 1 and 2. The yellow coloured solutions of 1 and 2 first turned green and then afforded microcrystalline products 3 and 4, respectively, in high yields.

In this way newer routes to 1, 2, 3 and 4 have been now developed exploiting the reaction chemistry of $Mn(acac)_3$. The main advantages of the new methodologies[8,11] are that for 1 and 2 the use of unstable $[Mn(acac)_2(H_2O)_2]$ is not required and that for 3 and 4 the use of dry HCl(g) and stringent experimental conditions are averted.

Reaction of** $Mn(acac)_3$ **with** $KF.H_2O_2$ **and** L (L=**bpy or phen**).* ***Isolation of** 1 **and** 2. ——— An acetonitrile solution of freshly prepared $Mn(acac)_3$ was caused to react with an aqueous solution of $KF.H_2O_2$ in presence of bpy or phen. The advantage of using $KF.H_2O_2$ over that of H_2O_2 is that this can be used in requisite stoichiometry. The other objective was to investigate the effect of fluoride on the reaction of $Mn(acac)_3$ with peroxide and L. The products isolated from these reactions were found to be

similar to those obtained with aqueous H_2O_2. Therefore it is evident that fluoride has no influence on the reaction.

Compounds 3 and 4 are partly soluble in acetonitrile giving green solutions whereas in DMF and DMSO they are completely soluble producing brown solutions which, however, decompose slowly to give colourless solutions. It is interesting to note that the manganese(III) compounds 3 and 4 are highly soluble in water. In separate reaction runs the light-yellow product formed at the initial stage of the reaction between Cl_2(g) and the yellow solutions of 1 and 2 were isolated and characterised to be Mn(II) products as evident from its six-line EPR spectrum in aqueous solution. IR spectra suggested the absence of acac while absorbtions for bpy or phen were present. The presence of chloride was confirmed by chemical test. Unfortunately, these products did not conform to any definite formula. After isolation of the dark-brown compounds 3 and 4 a lemon yellow product was precipitated out of the green mother liquor by the addition of NBu_4ClO_4. Here again no definite formula could be assigned because of anomalous chemical analyses. IR spectra showed the absence of both acac and bpy or phen, however, chemical tests indicated the presence of chloride. The oxidation state of manganese was determined to be +3 which was further confirmed by EPR spectroscopy. No resonance was observed in the EPR spectrum as expected for Mn(III) in high spin state. Therefore, it may be stated that the green mother liquor consists of mainly chloro complex of Mn(III) with varying compositions.

Molecular Structure of Complex 2.——— A perspective view of the molecular structure of 2 has been depicted in Figure 3.3. Table 3.1 summarizes the crystal data and details of structure solution and refinement for [Mn(acac)$_2$ (phen)]. The compound crystallises in the orthorhombic space group Pbcn. The molecule has a distorted octahedral geometry with its six coordination being satisfied by two nitrogen atoms from one phen and four oxygen atoms from two acac ligands. A two-fold axis passes through Mn atom and the midpoints of C_{10}-C_{10A} and C_{11}-C_{11A} bonds of phen. Half of the molecule including manganese(II) is unique, the rest are symmetry generated. The Mn-O(2) distance is slightly longer than Mn-O(1). Atomic coordinates of non-hydrogen atoms, selected bond distances and angles are listed in Tables 2 and 3, respectively. The Mn-O and Mn-N bond lengths are within the range expected for such systems.

Magnetism.——— The bulk susceptibility measurements of the powdered samples at 301K give μ_{eff} values of 5.80, 5.91, 4.6, and 4.4 B.M for complexes 1, 2, 3 and 4, respectively. For 1 and 2 the μ_{eff} values correspond to high spin d^5 configuration of Mn(II). However, the values for complexes 3 and 4 are considerably lower than expected for high spin(d^4) arrangement of Mn(III). The lower magnetic moments of 3 and 4 may be due to dimeric nature of the complexes involving chloride bridge[8] in the solid state. At room temperature the X-band EPR spectrum of 1 in the polycrystalline state consists of a single resonance centred at 3395 G, g = 2.00 whereas the spectrum of 2 shows three

resonances at 3014, 3324 and 3500 G, g = 2.02. The occurrence of three resonances for 2 may presumably be due to its rhombic distortion while the symmetric one signal spectrum for 1 indicates its axial distortion. Incidentally, our results are different from the earlier findings[8] of one signal for [Mn(acac)$_2$(phen)] and three signals for [Mn(acac)$_2$(bpy)]. The solid state EPR spectra of 1 and 2 are shown in **Figure 3.4.** Acetonitrile solution of both 1 and 2 at room temperature exhibit six-line hyperfine splitting pattern arising from ^{55}Mn (I=5/2) in their EPR spectra (**Figure 3.5**) at g values 2.01 with A_{av} = 90.5 G and 2.00 with A_{av} = 91.1 G, respectively. These hyperfine coupling constants are slightly lower than the reported 96.0 G for $[Mn(H_2O)_6]^{2+}$.[18] In our experimental conditions A^{Mn} = 95.2 G was observed for $MnCl_2.4H_2O$ in aqueous solution. A slightly lower value of A for the complexes is indicative of electron delocalisation of Mn(II) onto the ligand orbitals. As expected[19] for high spin d^4 systems, complexes 3 and 4 are insensitive to EPR. This is because of the non-degenerate spin state of the ground state of Mn(III) and the energy difference between the ground and the first excited state is so high that no transition is possible in the microwave region.

IR Spectra.——— The IR spectra of 1 and 2, displayed in **Figure 3.6,** exhibit the characteristic bands of acetylacetonato ligand at *ca.* 1581vs, Ca. 1511s and *ca.* 1408s cm^{-1}. A strong band at 1459 cm^{-1} indicate the presence of bpy in complex 1 while the corresponding absorption due to phen in complex 2 is observed at

1447s cm^{-1}. In both 1 and 2 the band at *ca.* 1595 cm^{-1} for bpy and phen appears to be obscured by the strong and broad band at *ca.* 1581 cm^{-1} due to acetylacetonate. In complex 3 the significant bands arising from bpy are observed at 1628m, 1596s, 1559m and 1436s cm^{-1}, whereas the characteristic absorptions for phen in complex 4 appear at 1621m, 1603s, 1575m, 1515s and 1420s cm^{-1}. A strong band at 368 cm^{-1} in 3 and 4 has been assigned to ν(Mn-Cl) mode of coordinated chloride.[20] The coordination of bpy and phen has been further confirmed by the presence of medium intensity ν (Mn-N) bands at 282 and 296 cm^{-1} in complexes 3 and 4, respectively.[21]. The IR spectra of 3 and 4 are shown in Figure 3.7.

Electronic Spctra.——— The electronic spectra of 3 and 4, presented in Figure 3.8, recorded in aqueous solution exhibit three intense bands each at *ca.* 212, *ca.* 226 and *ca.* 257 nm and two shoulders at *ca.* 426 and *ca.* 531 nm . Three intense bands have been assigned to ligand (bpy or phen)-to-metal charge transfer (l.m.c.t.) transitions and the shoulders at *ca.* 426 and *ca.* 531 nm to $^5B_{1g}$ ----> ^5E_g and $^5B_{1g}$ ----> $^5B_{2g}$ transitions[17,22], respectively. The other expected transition for Mn(III) in distorted octahedral geometry ($^5B_{1g}$ ----> $^5A_{1g}$) is missing in these cases. This may be because of its very low intensity. Manganese(II) complexes 1 and 2 display four-band electronic spectra in acetonitrile solutions as depicted in Figure 3.9. Considering their intensities all bands have been attributed to l.m.c.t. transitions. Comparing the band positions

in 3 and 4 for bpy or phen to metal charge transfer transitions the bands for 1 and 2 at *ca.* 229 and *ca.* 255 nm have been assigned to bpy or phen to Mn(II) charge transfer transitions, another intense band at *ca.* 286 nm and a shoulder at 310 nm may be assumed to have acac to manganese(II) charge transfer origin. In these cases no bands due to d-d transition occur because of the highly forbidden nature of this type of transitions. The electronic spectral and magnetic moment data of 1-4 are listed in Table 3.4.

Cyclic Voltammetry.——— The cyclic voltammetric experiments on 1 and 2 were conducted in acetonitrile at room temperature using NBu_4ClO_4 as supporting electrolyte and a platinum disc working electrode. Cyclic voltamonogram of 1 (Figure 3.10) in acetonitrile reveals two irreversible oxidation waves at 0.54V and 1.1V versus SCE which may be assigned as Mn(II) to Mn(III) and Mn(III) to Mn(IV) oxidations, respectively. Whereas 2 (Figure 3.10) gives only one irreversible oxidation response at 0.8V versus SCE attributable to Mn(II) ----> Mn(III) process.

Thermal Studies.——— In order to throw light on the thermal stability and the decomposition pattern, and also to demonstrate whether acac or bpy or phen suffers preferential loss on application of heat, thermoanalytical (TG and DSC) study of complexes 1 and 2 was undertaken. The suitability of 1 and 2 for thermal studies was envisaged because of the presence of volatile

ligands. The thermogravimetric experiment was performed in the range 25-700°C and DSC 25-500°C under a constant flow of nitrogen. The thermogram of 1 (Figure 3.11) reveals that the compound is stable up to 128°C. The weight loss begins at 128.3°C and continues up to 278°C with the loss of weight corresponding to the loss of bpy and one acac unit (calc. 62.37, obs. 62%). Immediately followed by this has been a continuous loss of weight corresponding to the loss of $CH_3COCHCCH_3$ leading to the formation of MnO. The observed loss for this event is 21 as compered with the expected loss of 20.3%. The corresponding DSC shows a sharp endotherm at 250°C attributable to the loss of bpy as observed in TG. In addition, two broad and weak endotherms appear at 288 and 320°C which have been ascribed to phase transitions.

The thermogram of 2 (Figure 3.11) recorded under similar conditions indicates its stability up to 152°C, unlike 1. The loss of weight starts at 152.5°C and continues up to 308°C as evident from the thermogram. The percentage of weight loss at this stage matches well with the expulsion of phen (calc. 42, obs. 45%). After the inflection at 308°C the thermogram exhibits a slow rate of weight loss up to 378°C followed by a sharp loss between 378 and 492°C. The weight loss from 308-378°C gets along well with the loss of CH_2CO (calc. 9.7, obs. 9%). The rest (CH_2COCH_3 and $CH_3COCHCCH_3$) is lost (calc. 32.35, obs. 31%) between 378 and 492°C resulting into the formation of MnO. In both the cases oxygen for MnO formation is believed to originate

from acac only as the experiments were conducted in nitrogen atmosphere. Unlike the DSC pattern of 1 showing three endotherms, that of 2 displays only one exotherm at 288°C corresponding to the loss of phen. It is of interest to note that the phase transitions in 1 are endothermic whereas in 2 the transition is exothermic.

A perusal of the thermal behaviour of both the compounds causes us to state that the complexes 1 and 2 might serve as suitable precursors for the preparation of MnO through a significantly softer route, as against the literature method.[23]

Concluding Remarks

SO_2(g) reduction of MnO_4^- in the presence of HF_2^- appears to be a better route to $[MnF_3(SO_4)]^{2-}$. $Mn(acac)_3$ is reduced to Mn(II) by H_2O_2 producing a coordinatively unsaturated species, presumably "$[Mn(acac)_2]$", which in the presence of neutral ligand L affords $[Mn(acac)_2L]$ (L = bpy or phen). Chlorine oxidizes $[Mn(acac)_2L]$ to afford $MnCl_3L$. Further work is indeed needed to explore the nature of interaction of H_2O_2 with other metal acetylacetonates.

Table 3.1: Crystal data and details of the structure solution and refinement for $[Mn(acac)_2(phen)]$ 2

Empirical formula	$C_{22}H_{22}MnN_2O_4$
M	433.4
Crystal size/mm	0.41 x 0.22 x 0.20
Crystal system	Orthorhombic
Space group	Pbcn
a/Å	15.865(5)
b/Å	10.245(3)
c/Å	12.769(5)
$U/Å^3$	2075.3(11)
Z	4
$D_c/g\ cm^{-3}$	1.464
$\mu(Mo\text{-}K_\alpha)/cm^{-1}$	6.71
F(000)	948
T/K	293
2Θ range/°	3.0 to 50.0
Scan type	ω
h,k,l	0-18, 0-12, 0-15
Reflections collected	1843
Observed reflections ($I>2\sigma(I)$)	1138
Weighing scheme	$W^{-1} = \sigma^2(F)+0.0004F^2$
Number of parameters refined	172
R	0.0404
R_w	0.0408
Goodness of fit	1.14
Largest difference peak/$eÅ^{-3}$	0.23
Largest difference hole/$eÅ^{-3}$	-0.26

Table 3.2: Non-hydrogen atomic coordinates ($X10^4$) for $[Mn(acac)_2(phen)]$ 2 with estimated standard deviations (e.s.d.s) in parentheses

Atom	X	Y	Z
Mn(1)	0	288(1)	2500
O(1)	610(2)	1578(3)	1458(2)
O(2)	1213(2)	216(3)	3255(2)
N(1)	-345(2)	-1523(3)	3476(2)
C(1)	1621(5)	2465(7)	324(6)
C(2)	1388(3)	1702(4)	1291(3)
C(3)	2026(3)	1188(5)	1921(4)
C(4)	1911(3)	487(4)	2841(3)
C(5)	2682(3)	-16(7)	3405(5)
C(6)	-676(3)	-1519(4)	4428(3)
C(7)	-884(3)	-2653(5)	4968(3)
C(8)	-738(3)	-3834(4)	4514(3)
C(9)	-370(2)	-3885(4)	3509(3)
C(10)	-191(2)	-2693(3)	3019(3)
C(11)	-178(2)	-5080(4)	2980(3)

Table 3.3: Selected bond lenths(Å) and angles(°) for [Mn(acac)$_2$(phen)] 2 with the e.s.d.s in parentheses

Mn(1)-O(1)	2.111(3)	Mn(1)-O(2)	2.154(3)
Mn(1)-N(1)	2.301(3)	Mn(1)-O(1A)	2.111(3)
Mn(1)-O(2A)	2.154(3)	Mn(1)-N(1A)	2.301(3)
O(1)-Mn(1)-O(2)	83.9(1)	O(1)-Mn(1)-N(1)	162.8(1)
O(2)-Mn(1)-N(1)	86.7(1)	O(1)-Mn(1)-O(1A)	102.4(2)
O(2)-Mn(1)-O(1A)	98.6(1)	N(1)-Mn(1)-O(1A)	93.1(1)
O(1)-Mn(1)-O(2A)	98.6(1)	O(2)-Mn(1)-O(2A)	176.1(2)
N(1)-Mn(1)-O(2A)	90.1(1)	O(1A)-Mn(1)-O(2A)	83.9(1)
O(1)-Mn(1)-N(1A)	93.1(1)	O(2)-Mn(1)-N(1A)	90.1(1)
N(1)-Mn(1)-N(1A)	72.5(1)	O(1A)-Mn(1)-N(1A)	162.8(1)
O(2)-Mn(1)-N(1A)	86.7(1)	Mn(1)-O(1)-C(2)	128.3(3)
Mn(1)-O(2)-C(4)	126.2(2)	Mn(1)-N(1)-C(6)	126.0(2)
Mn(1)-N(1)-C(10)	115.9(2)		

Table 3.4: Electronic spectral and magnetic moment data of 1 - 4

Compounds	λ_{max}/nm(ε,$M^{-1}cm^{-1}$)	Assignments	μ_{eff}(B.M)
$[Mn(acac)_2(bpy)]$	234(17642)	$L_{(\Pi)}$ ----> $Mn(d_\Pi)$	5.80
	244(17092)	$L_{(\Pi)}$ ----> $Mn(d_\Pi)$	
	283(27958)	$L^1_{(\Pi)}$ ----> $Mn(d_\Pi)$	
	310sh(7325)	$L^1_{(\Pi)}$ ----> $Mn(d_\Pi)$	
$[Mn(acac)_2(phen)]$	224(49598)	$L^2_{(\Pi)}$ ----> $Mn(d_\Pi)$	5.91
	266(40387)	$L^2_{(\Pi)}$ ----> $Mn(d_\Pi)$	
	289(22673)	$L^1_{(\Pi)}$ ----> $Mn(d_\Pi)$	
	310sh(7085)	$L^1_{(\Pi)}$ ----> $Mn(d_\Pi)$	
$[MnCl_3(bpy)]$	215(11268)	$L_{(\Pi)}$ ----> $Mn(d_\Pi)$	4.6
	230(11254)	$L_{(\Pi)}$ ----> $Mn(d_\Pi)$	
	245(9254)	$L_{(\Pi)}$ ----> $Mn(d_\Pi)$	
	424sh(910)	$^5B_{1g}$ ----> ^5E_g	
	532sh(264)	$^5B_{1g}$ ----> $^5B_{2g}$	
$[MnCl_3(phen)]$	210(31541)	$L^2_{(\Pi)}$ ----> $Mn(d_\Pi)$	4.4
	222(31594)	$L^2_{(\Pi)}$ ----> $Mn(d_\Pi)$	
	269(24951)	$L^2_{(\Pi)}$ ----> $Mn(d_\Pi)$	
	428sh(947)	$^5B_{1g}$ ----> ^5E_g	
	531sh(241)	$^5B_{1g}$ ----> $^5B_{2g}$	

L = bpy, L^1 = acac, L^2 = phen, sh = shoulder

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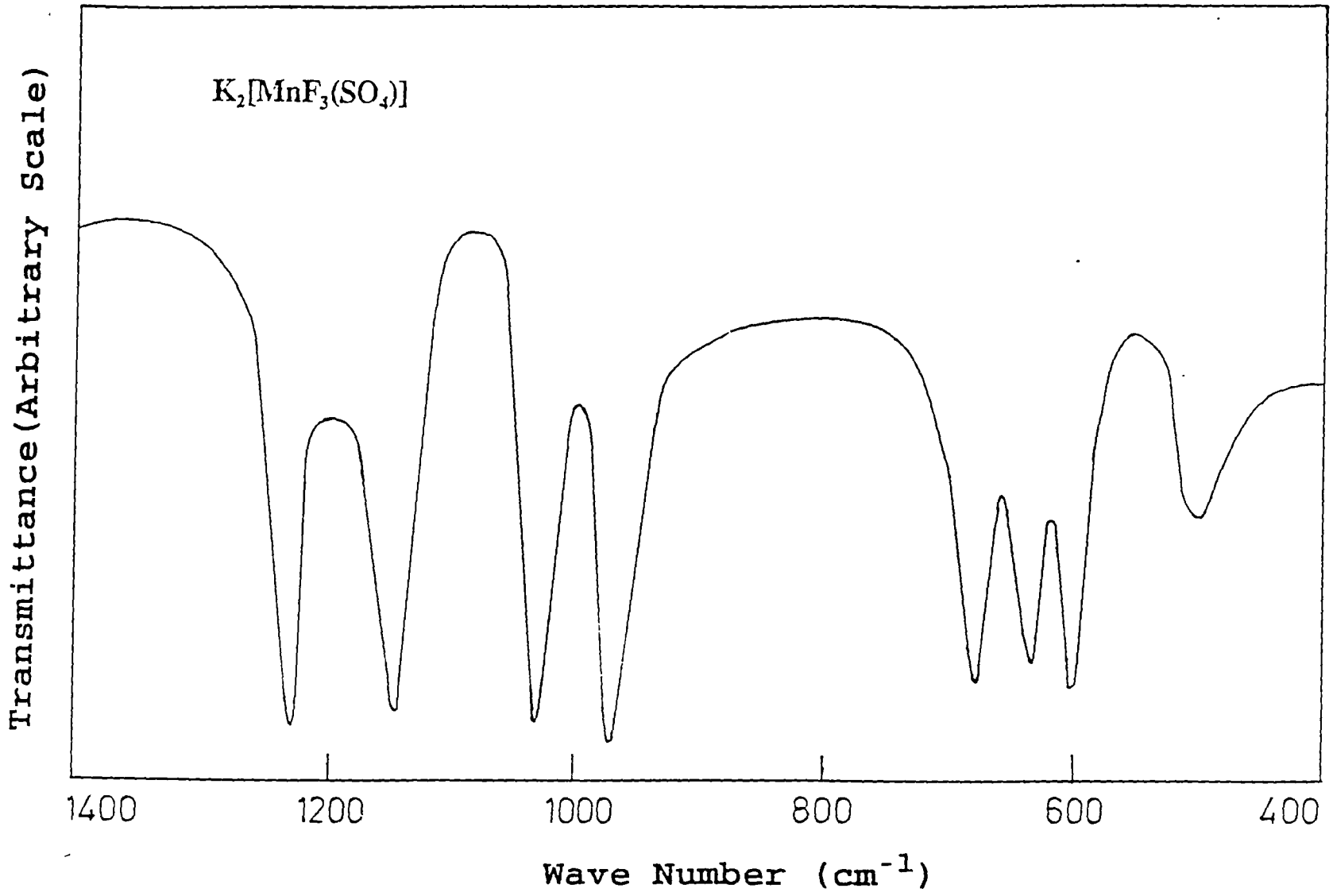

Figure 3.1: IR Spectrum

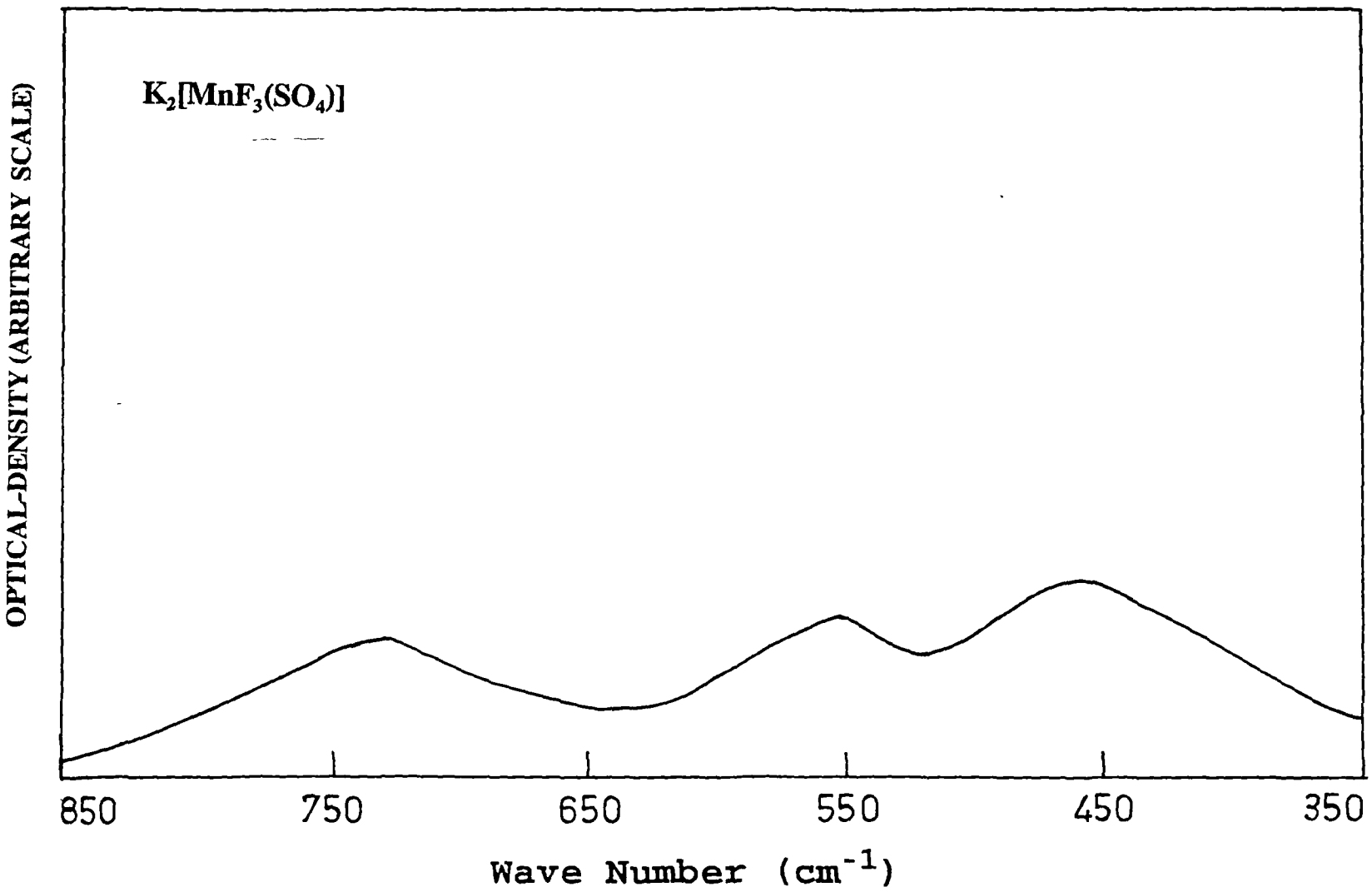

Figure 3.2: Diffuse-Reflectance Spectrum

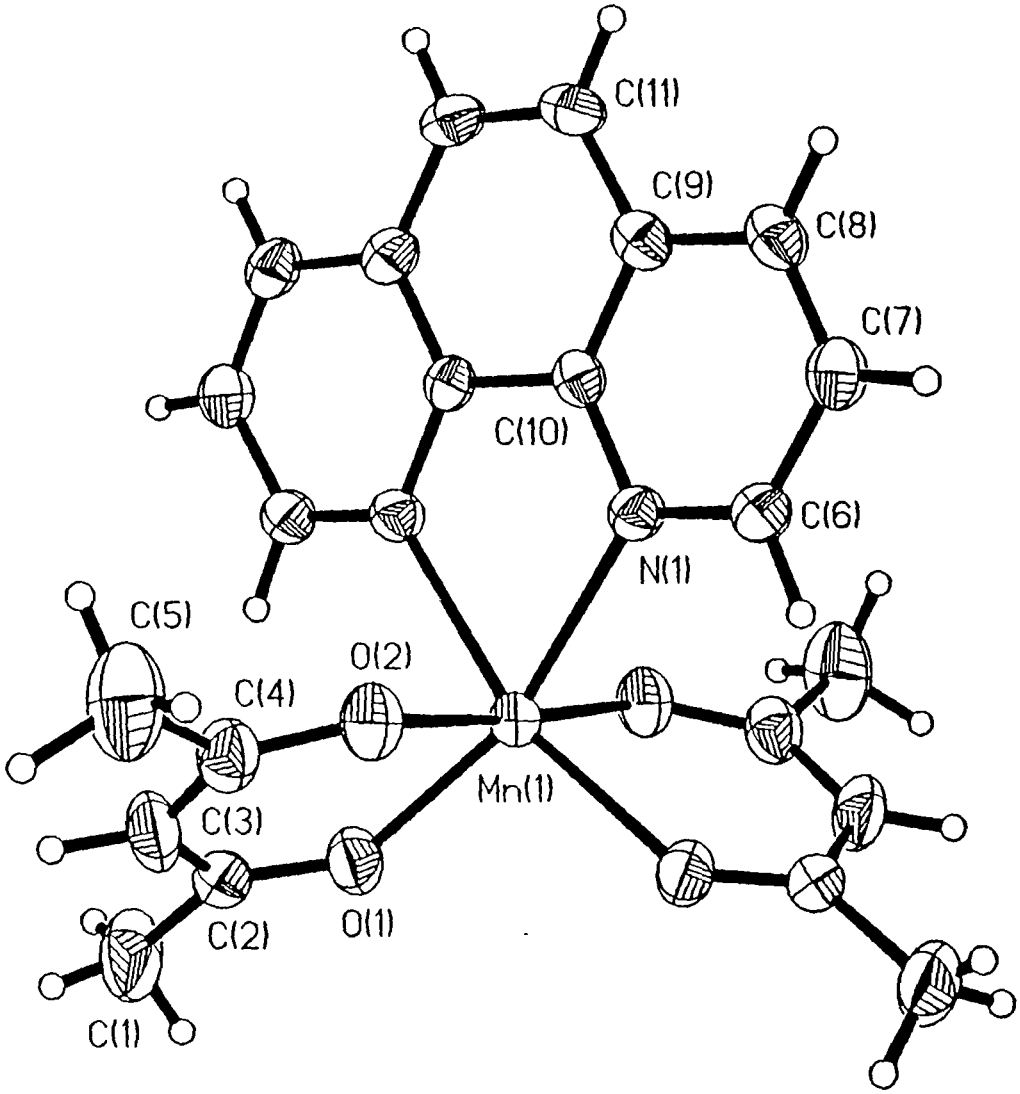

Figure 3.3: Perspective View of

$Mn(acac)_2(phen)$

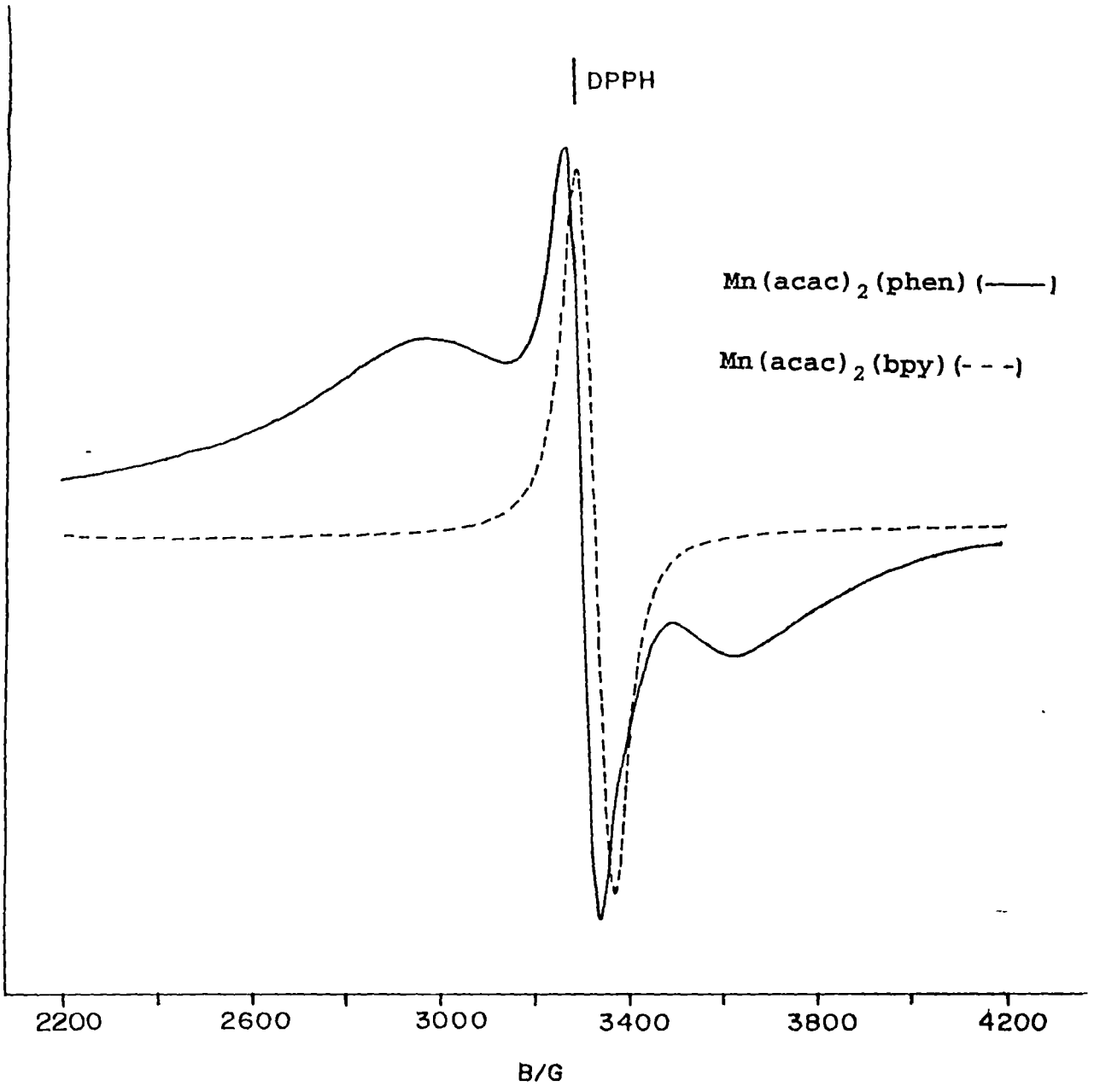

Figure 3.4: X-Band EPR Spectra of Polycrystalline Samples

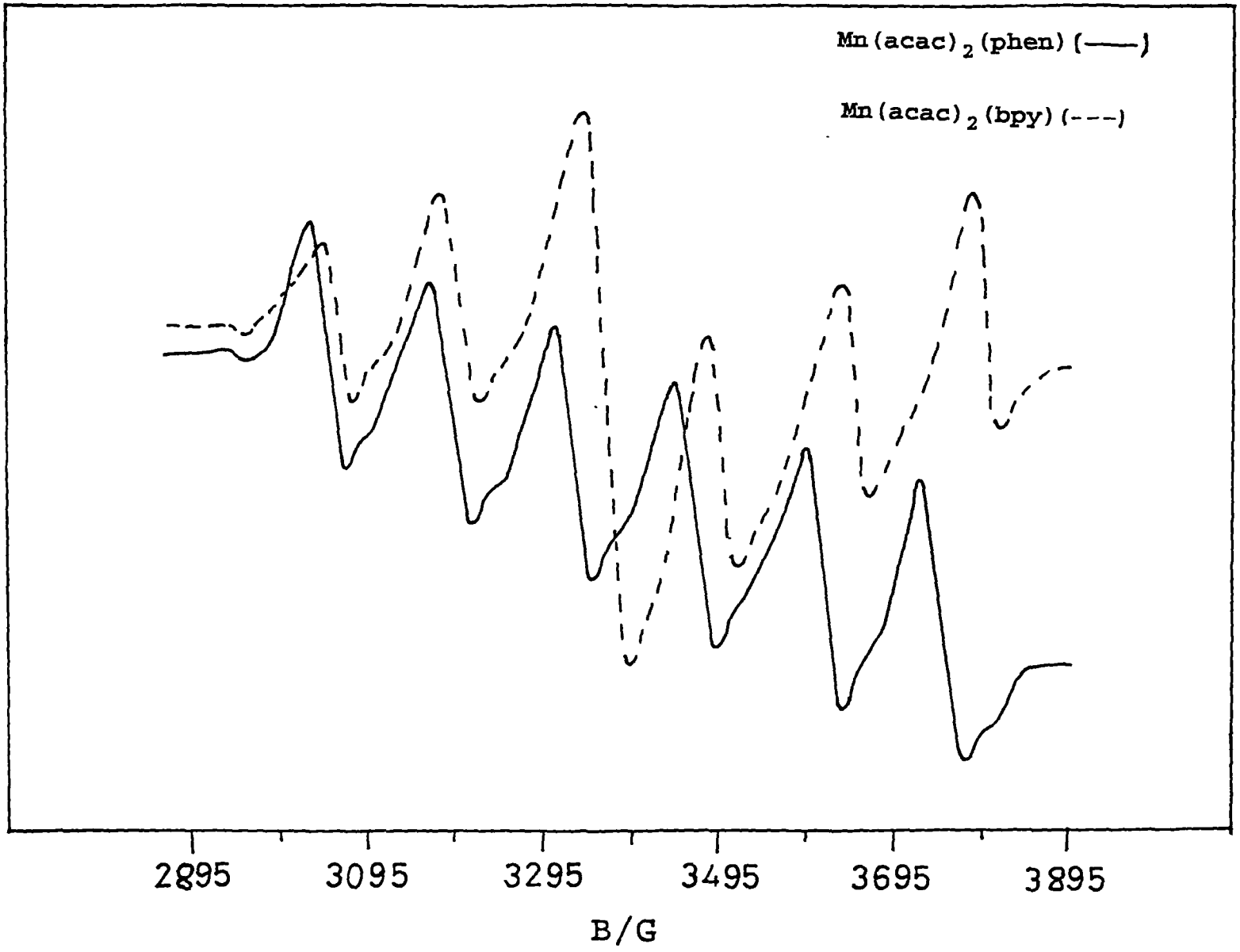

Figure 3.5: X-Band EPR Spectra in Acetonitrile

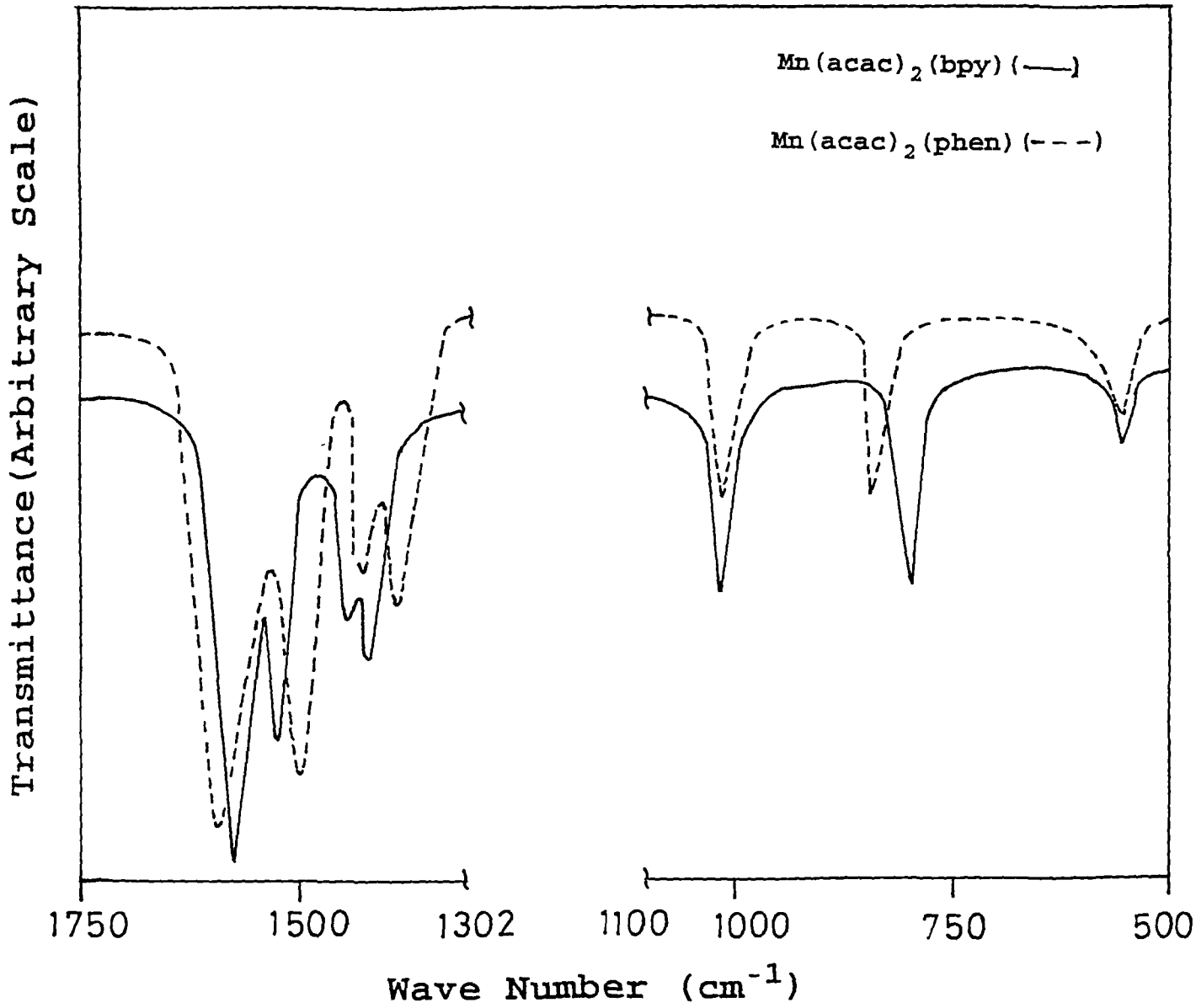

Figure 3.6: IR Spectra

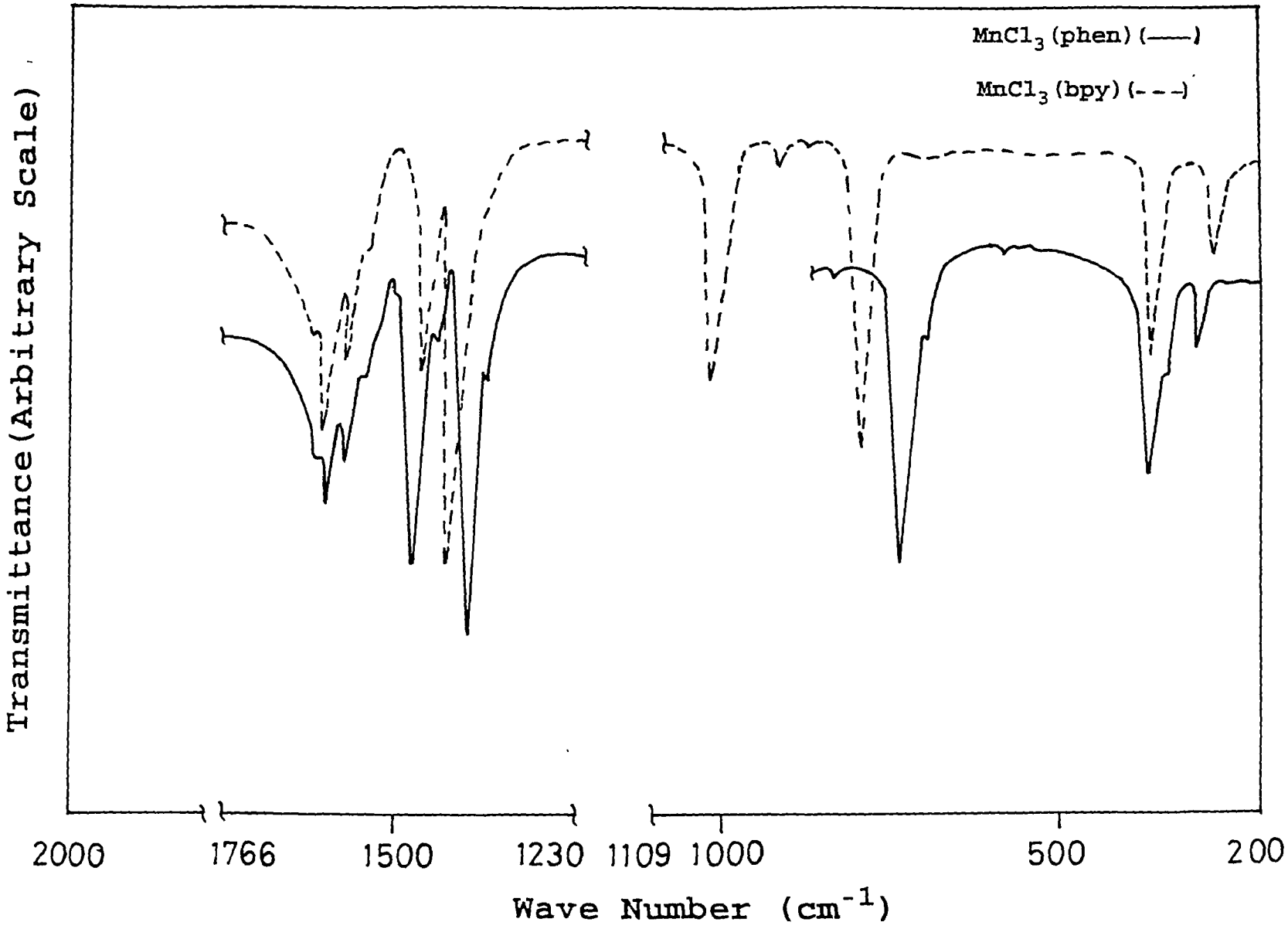

Figure 3.7: IR Spectra

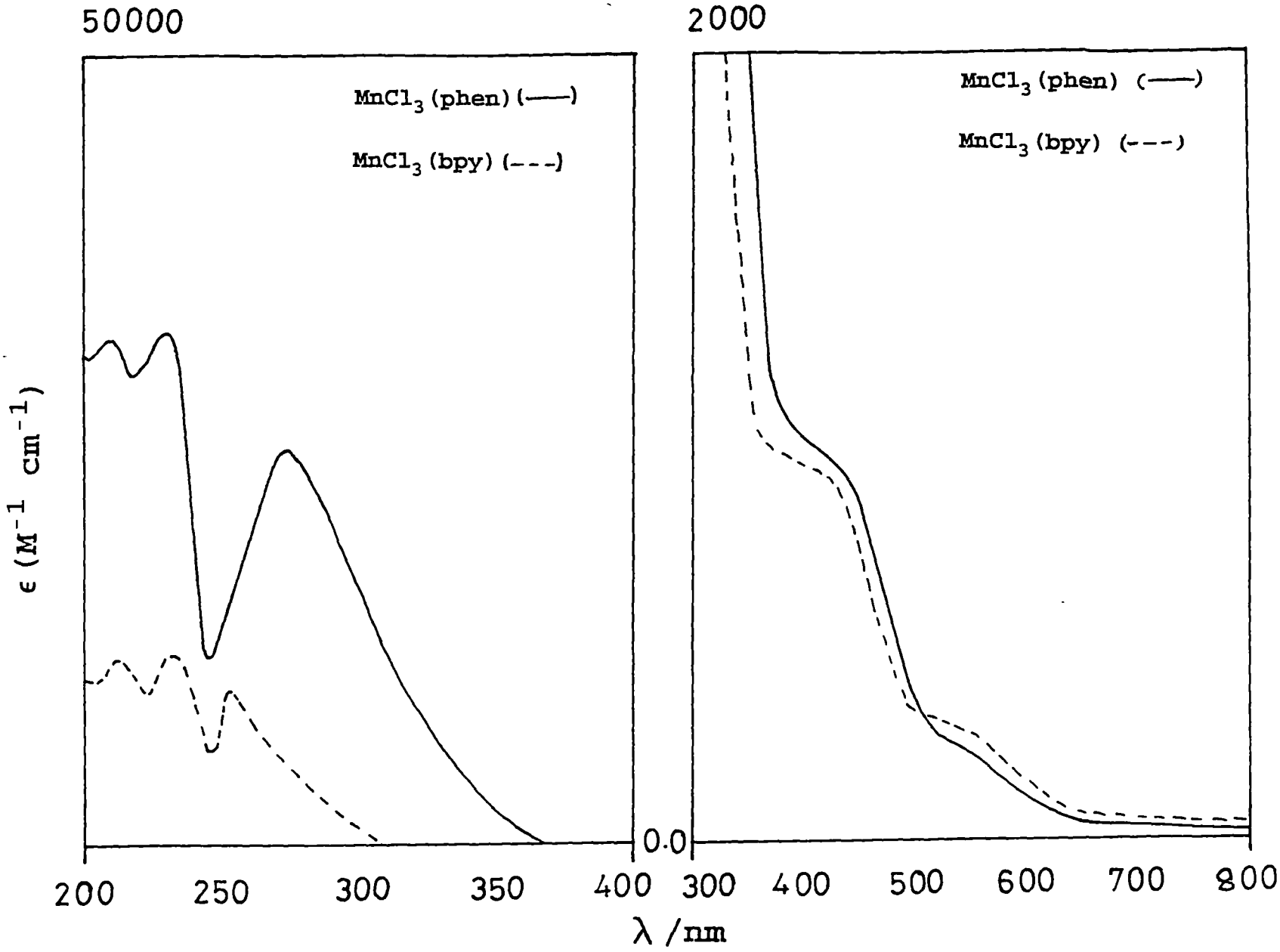

Figure 3.8: Electronic Spectra

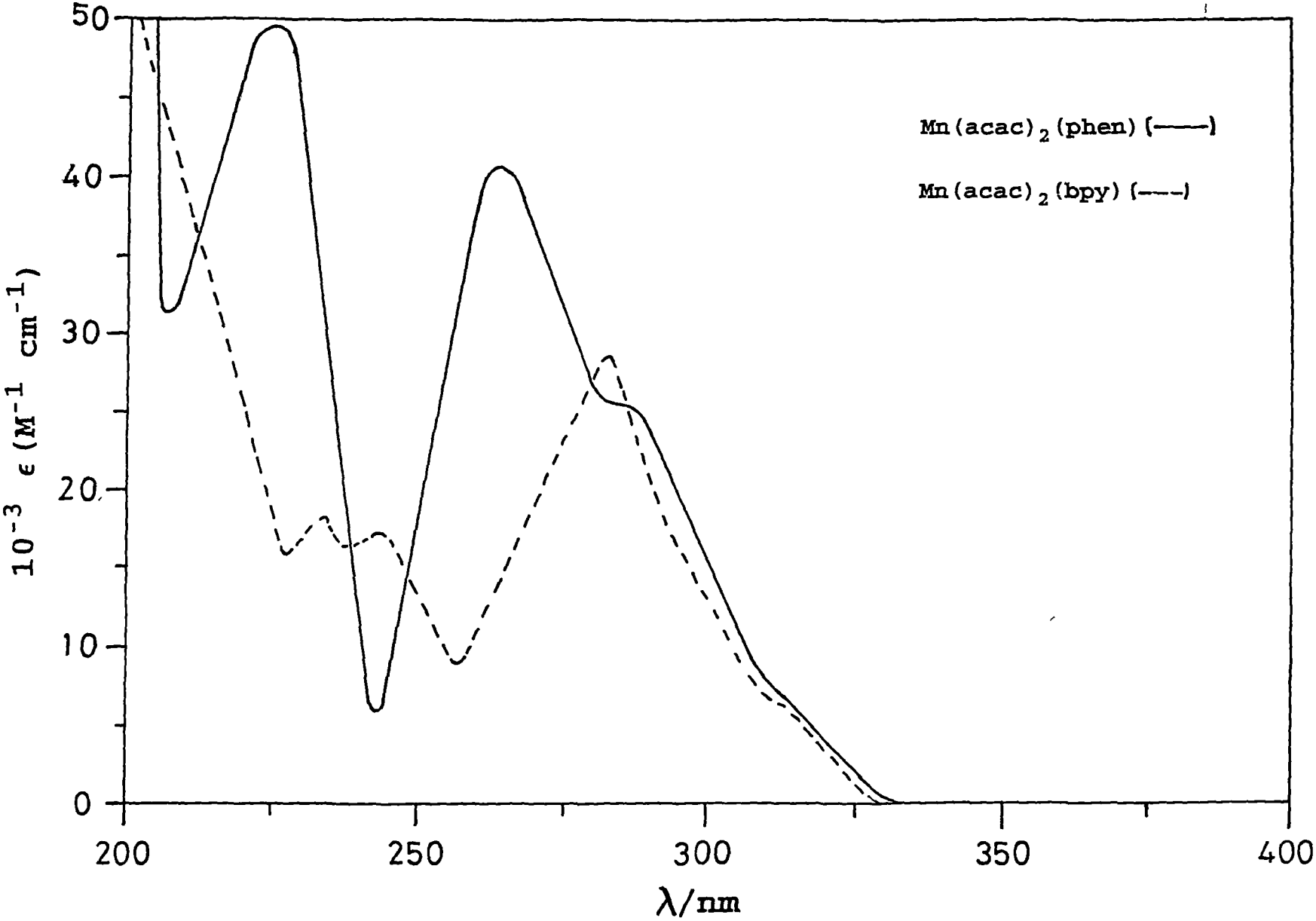

Figure 3.9: Electronic Spectra

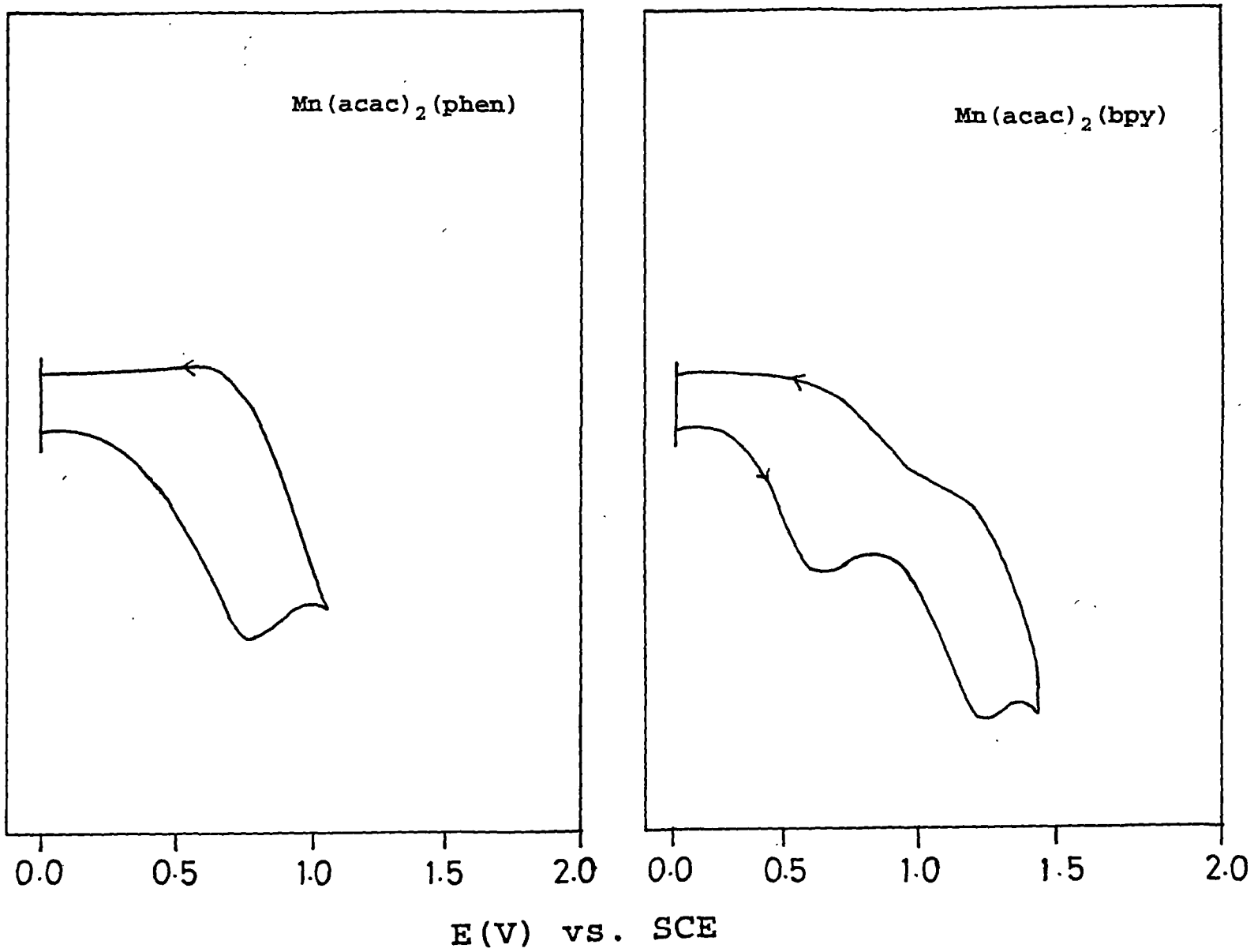

Figure 3.10: Cyclic Voltammograms

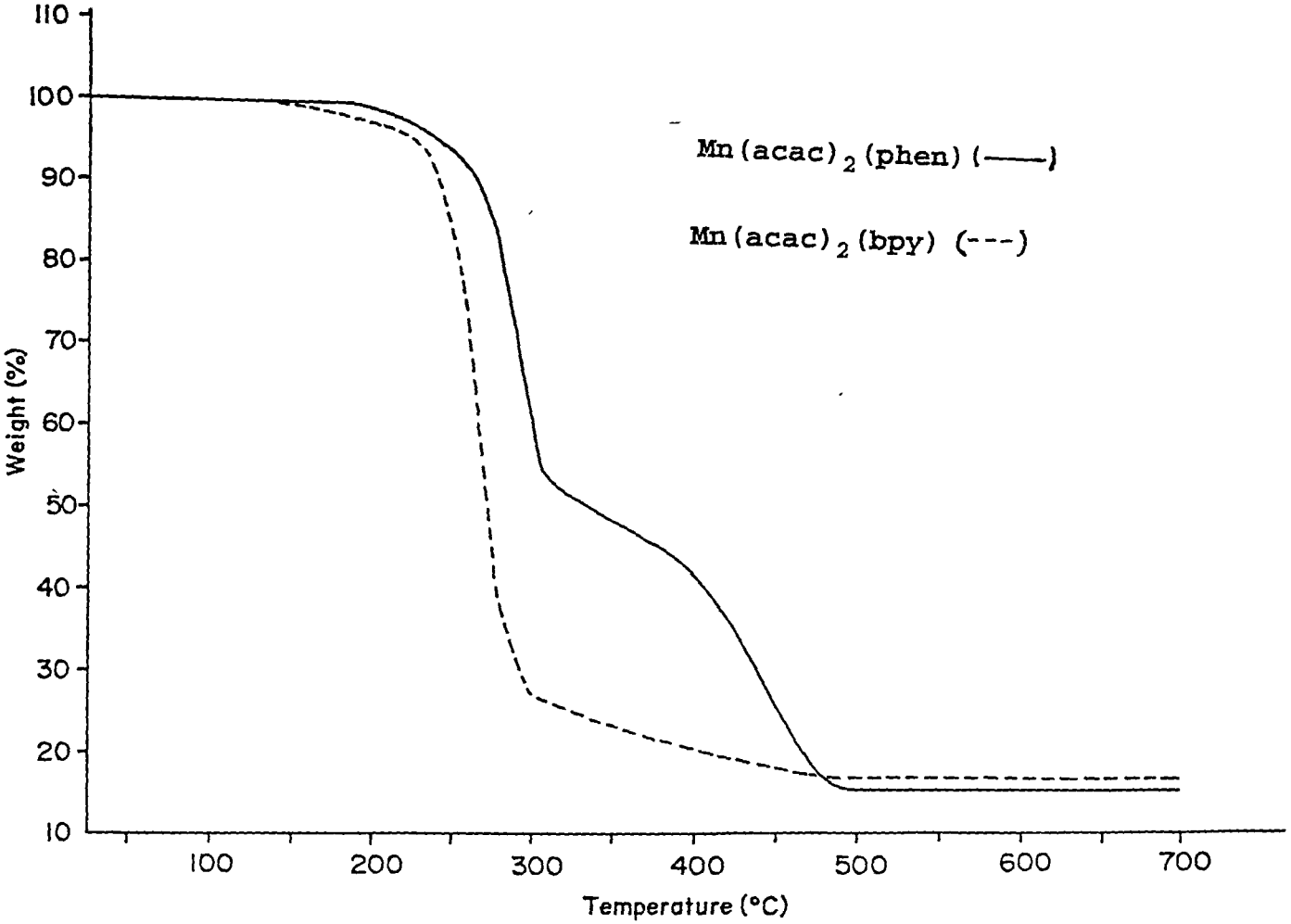

Figure 3.11: Thermograms

CHAPTER IV

Mixed-Ligand Manganese(III) Salicylates of the Types $[Mn_2X_2(salH)_4(sal)]^{2-}$ ($salH_2$ = Salicylic Acid). Synthesis and Structural Assessment

Further to the interest on the chemistry of manganese as highlighted in Chapters I and III our attention was drawn to Mn(III) systems comprising halides (Cl, Br or I) and salicylic acid. Salicylic acid is a very important biologically relevant ligand.[1,2] And in appreciation of this in recent years a number of reports on manganese complexes involving salicylate have appeared.[1-5] However, none of these contain any halide. Our interest in mixed-halo manganese complexes are owing to the following reasons. As already mentioned in Chapter I, the effect of fluoride on metalloproteins is totally different from that of its congener, chloride.[4] From the perspectives of inorganic chemistry also the nature of fluoride is significantly, different

from other halides (Cl, Br or I). For instance fluoride stabilizes the tripositive state of manganese[6] whereas Cl^-, Br^- or I^- bears an antagonistic relationship with manganese(III) in that they are not redox innocuous. The redox factor makes the synthesis of chloro, bromo and iodo-manganates(III) rather difficult. For instance, MnF_3 is the only binary halide[7a] of manganese(III) that exists at room temperature and a very few[7b,8] iodo manganese(III) compounds have reported existence. .pn2 Studies on fluoro salicylato complexes of manganese(III) was carried out earlier in our laboratory.[9] As a logical extension we have embarked on the studies of similar complexes with other halides (Cl, Br and I). Incorporated in this chapter are the synthesis and physico-chemical characterization of complexes of the types $[Mn_2X_2(salH)_4(sal)]^{2-}$ (X = Cl or Br) and $[Mn_2I(sal)_3(H_2O)_4]^-$.

Experimental

All the chemicals used were of reagent grade commercial materials. Preparation of MnO(OH) and NEt_4ClO_4 as well as the details of the instruments/equipment used for the characterization of the products are given in Chapter II.

Synthesis

$A_2[Mn_2Cl_2(salH)_4(sal)].4H_2O$, (A = NH_4, (*1*); Na, (*2*), or K (*3*)).——— To a suspension of 0.52 g (5.91 mmol) MnO(OH) in 10 cm^3 water a solution of 83.33 mmol ACl in 20-25 cm^3 water was added. Then a solution of 1.02 g. (7.38 mmol) salicylic acid in

8 cm^3 ethanol was added while the mixture being stirred magnetically. The stirring was continued for 45 min to 1 h. A green compound formed with a dark brown-black supernatent. At this stage the pH of the solution was measured to be 5-5.5. The product was isolated by vacuum filtration, dried by pressing between the folds of filter paper and finally in a vacuum desiccator using conc. H_2SO_4 as the desiccant. Yields of 1, 2 and 3 were 1.2 g (42%), 1.4 g (48%), and 1.4 g (47%), respectively. Anal. Calc.(Found) for $C_{35}H_{40}N_2O_{19}Cl_2Mn_2$), 1: C, 43.18(42.58); H, 4.15(4.20); N, 2.88(3.10); Cl, 7.28(7.12); Mn, 11.29(10.92%). Calc.(Found) for $C_{35}H_{32}O_{19}Na_2Cl_2Mn_2$, 2: C, 42.74(41.96); H, 3.29(3.57); Cl, 7.21(7.11); Mn, 11.17(11.12); Na, 4.67(4.70). Calc.(Found) for $C_{35}H_{32}O_{19}K_2Cl_2Mn_2$, 3: C, 41.39(40.64); H, 3.18(3.25); Cl, 6.98(6.52); Mn, 10.82(10.48); K, 7.70(7.80).

$A_2[Mn_2Br_2(salH)_4(sal)].6H_2O$ (A = NH_4, (*4*); Na, (*5*) or K (*6*)).——— These compounds were prepared in a similar fashion as described for 1, 2 or 3. The only difference was that ABr was used instead of ACl. Starting from 0.52 g MnO(OH) the yields of 4, 5, and 6 were 1.4 g (43%), 1.6 (49%), and 1.6 g (47%), respectively. Anal. Calc.(Found) for $C_{35}H_{44}N_2O_{21}Br_2Mn_2$, 4: C, 38.27(38.81); H, 4.05(4.12); N, 2.55(2.66); Br, 14.55(14.10); Mn, 10.00(10.20%). Calc.(Found) for $C_{35}H_{36}O_{21}Na_2Br_2Mn_2$, 5: C, 37.92(37.64); H, 3.28(3.40); Br, 14.42(14.18); Mn, 9.91(9.94); Na, 4.15(4.21%). Calc.(Found) for $C_{35}H_{36}O_{21}K_2Br_2Mn_2$, 6: C,

36.85(36.68); H, 3.19(3.12); Br, 14.01(13.92); Mn, 9.63(9.72); K, 6.86(6.96).

$K[Mn_2I(sal)_3(H_2O)_4].2H_2O$, 7.——— A solution of 13.75 g (82.83 mmol) potassium iodide in 20 cm^3 water was added to a suspension of 0.52 g (5.91 mmol) MnO(OH) in 10 cm^3 water. Then a solution of 1.02 g (7.38 mmol) salicylic acid in 8 cm^3 ethanol was added to it while stirring magnetically. After 5 min of stirring a clear red-brown solution resulted. At this stage the pH of the reaction solution was recorded to be 6. The stirring was continued for a further period of 20 min and the solution was kept at room temperature for 24h whereupon a brown product precipitated which was separated by filtration. The red-brown filtrate on keeping in the refreezeratorfor for 24h resulted in the formation of dark-brown crystals of 7. The crystals were isolated by filtration and dried in a vacuum. Yield 0.6 g (26%), Anal. Calc.(Found) for $C_{21}H_{24}O_{15}KIMn_2$: C, 31.83(30.21); H, 3.06(3.10); I, 16.02(16.51); Mn, 13.87(13.40); K, 4.93(4.96%).

Elemental Analyzes.——— Quantitative determination of manganese was done both by gravimetry as well as by iodometry. Carbon, hydrogen, nitrogen, sodium, potassium, chloride, bromide and iodide were determined by the methods described in Chapter II.

Chemical Determination of the Oxidation State of Manganese.——— For this experiment a procedure described in Chapter III was adopted.

Results and Discussion

Synthesis and general considerations.——— The reaction of MnO(OH) with salicylic acid and an excess of halides leads to the formation of 1-7 in good yields. The strategy was that MnO(OH) being basic in nature would react with salicylic acid producing a coordinatively unsaturated species which in the presence of halide ions would lead to the generation of mixed-halo salicylates of manganese. The strategy worked well affording air-stable products. After the reaction is complete the pH of the reaction solutions were measured to be 5.5-6.

The complexes **1-6** are green and dissolve in common organic solvents, however, the dissolution is accompanied by decomposition. A methanolic solution is moderately stable. In contrast compound **7** is dark-brown in colour and dissolves in common organic solvents without significant decomposition.

Vibrational Spectra.——— The IR spectra of chloro-(**1**, **2** and **3**), bromo-(**4**, **5** and **6**) and iodo-(**7**) salicylates of manganese(III) are shown in **Figures 4.1**, **4.2** and **4.3**, respectively. Significant vibrational spectroscopic data of compounds **1-7** are compiled in **Table 4.1** The IR spectra of complexes exhibit a pattern typical of coordinated salicylate and the halides. The $\nu_{as}(COO^-)$ and the $\nu_{s}(COO^-)$ of free salicylic acid appear respectively at 1651s and 1294s cm^{-1} are known to shift[10a] to different frequencies on coordination. Characteristically, the difference of frequencies ($\Delta\nu$) of as

$\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ is considered to be, the most important criterion[10a] to differenciate uni- and bi-dentate modes of coordination. Generally, $\Delta\nu > 200$ cm^{-1} indicates a unidentate fashion of coordination while $\Delta\nu = 50$ cm^{-1} is indicative of the presence of bidentate chelated carboxylate. In the present case $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ frequencies for compounds 1-7 have been observed at 1600s and *ca.* 1378s cm^{-1} with the difference between them being 222 cm^{-1}. Therefore, it is rational to assume that the carboxylate group of the salicylate ligand in 1-7 is coordinated in unidentate manner.

In order to ascertain the coordination mode of hydroxyl group of salicylate the most important bands to locate in the IR spectra are those originate from ν(O-H) and δ(O-H) vibrations.[11] For compounds 1-6 the ν(O-H) and δ(O-H) modes of salicylate hydroxyl group have been observed at *ca.* 3246s and *ca.* 1213m cm^{-1}, respectively. These frequencies are somewhat lower than those observed for uncoordinated hydroxyl group (ν(O-H) = 3414s and δ(O-H) = 1248m cm^{-1}). This coordination mode is further supported by the appearance of a band at *ca.* 373w cm^{-1} attributable to the Mn-O stretching mode[12] of O-bonded OH group. Thus the presence of $salH^-$ ligand in complexes 1-6 is apparent from their IR spectral pattern. The appearance of a medium intensity band at *ca.* 368 cm^{-1} for compounds 1-3 evidences the presence of coordinated chloride.[10b,13] The band at *ca.* 265 cm^{-1} in the IR spectra of compounds 4-6 has been assigned to Mn-Br stretching mode.[10b,13] The IR spectral pattern of 7 is somewhat

different from that of 1-6. The bands for ν(O-H) (*ca.* 3250 cm^{-1}) and δ(O-H) (*ca.* 1230 cm^{-1}) of the salicylate hydroxyl group are absent while that due to ν(Mn-O) has been observed at 349w cm^{-1}.[12] This suggests the presence of phenoxide coordination in the compound. The occurrence of a weak band at 190 cm^{-1} points to the coordination of iodide[8] to the metal centre.

In an attempt to complement the IR spectral evidences, laser Raman (LR) spectroscopic experiments have been conducted. The Raman spectra of complexes 1 and 4 as representatives have been presented in **Figures 4.4.** The prominant features of LR-spectra of 1-6 are the appearance of signals at *ca* 1609, *ca.* 1329, and *ca.* 1242 cm^{-1} which owe their origin to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$, and δ(O-H) modes of vibration, respectively. This provides further support to the presence of salicylate as $salH^-$ in the complexes. No sensible LR-spectrum could be recorded for 7 presumably because of an intense colour of the sample.

Magnetism and Electronic Spectra. The bulk susceptibility measurements has been performed at 308 K on polycrystalline samples of 1-7. The μ_{eff} values are collected in **Table 4.2** The magnetic moment values for 1-6 correspond to high spin d^4 configuration[14,15] of manganese which indicates the absence of any significant magnetic interaction between the metal centres in these complexes. Whereas the μ_{eff} value for 7 is far less than expected for normal manganese(III) complexes. The lower value may be explained on the basis of the antiferromagnetic interaction[16,17] between two manganese centres

operative through bridging iodide. The EPR silence of 1-7 at room temperature gets along with the presence of manganese(III) in the compounds. Indeed this is what is expected for high spin d^4 systems,[18] because of the occurrence of non-Kramers spin states within which no transitions are feasible because of either large zero-field splitting or very fast spin-relaxation process.

The electronic spectra of compounds 1-6 recorded in methanolic solution present a unique feature exhibiting a shoulder at *ca.* 565 nm and two intense bands at *ca.* 290 and *ca.* 211 nm. The spectra for chloro-(1, 2 and 3) and bromo-(4, 5 and 6) complexes have been displayed in **Figures 4.5 and 4.6**, respectively. The shoulder of lower intensity has been assigned as due to d-d transition while the more intense bands are attributable to ligand-to-metal charge transfer(LMCT) transitions.[1] The spectrum for 7 (**Figure 4.7**) recorded in (LMCT) acetonitrile is found to be practically similar to what has been observed for the others. The only notable difference is the comparable intensity of the latter two bands unlike their different intensities for the corresponding absorptions for 1-6. This is demonstrated in **Figures 4.5 to 4.7**. The assignment of the bands remains to be similar as those of 1-6. The electronic spectral data of 1-7 are summarized in **Table 4.2**.

Cyclic Voltammetry.——— The cyclic voltammetric experiment on complex 7 has been carried out at room temperature in acetonitrile solution using NEt_4ClO_4 as supporting electrolyte. The voltammogram, shown in **Figure 4.8**, displays a

quasi-reversible oxidation wave with $E_{½}$ at 0.56 V (E_{pa} = 0.63, E_{pc} = 0.5 V) vs. saturated colomel electrode (SCE) that corresponds to Mn^{III}/Mn^{IV} couple. It may be noted that no signal is observed in the cathodic range implying the absence of reduction. Unfortunately, no cyclic voltammetric experiment could be conducted for 1-6 owing to their instability in solution.

Thermal Studies.——— With a goal to understand the thermal stability and the decomposition pattern, thermogravimetric (TG) and differential scanning calorimetric (DSC) experiments were performed on compound 1. The temperature range covered for TG was 25-700°C whereas DSC measurement was conducted over the temperature range of 25-500°C. The thermogram of 1 (**Figure 4.9**) shows that the compound is stable up to 101°C. The weight loss initiates at 102°C and continues up to 225°C. The loss of weight at this step corresponds to the expulsion of four water molecules, two ammonia molecules, one molecule of salicylic acid, two salH units and two molecules of carbon dioxide (*calc. 62.30%, obs. 60%*). The intermediate at this stage has been suggested to be a phenoxide bridged compound, $Mn_2Cl_2(oph)_2$. Immediately after this the thermogram shows another loss of weight by 8% in the temperature range of 225-300°C corresponding to the loss of one chlorine molecule (*calc. 7.28%*) leading probably to the formation of a volatile phenoxide bridged compound, $Mn_2(oph)_2$. After this, the thermogram shows a slow weight loss that continues until it touches the base line at 530°C. The observed thermal events

cause us to state that the compounds though decomposes in stages but finally leaves no residue.

The corresponding DSC exhibits three broad endotherms at 239, 304 and 445°C indicating three phase transitions. The temperatures at which the peaks have been observed in DSC are by and large coincident with the temperature ranges where the compound incurred losses of weights under thermogravimetric conditions.

Concluding Remarks

Although the binary complexes of the type MnX_3 (X = Cl, Br or I) do not exist at ambient temperature because of internal electron transfer between Mn(III) and X their association is possible in combination with suitable heteroligands, for instance, salicylic acid (present work), PMe_3[8] and salen[7b]. X-ray crystal structure of such compounds is expected to provide a clear delineation of their structural motifs.

Table 4.1: Vibrational Spectroscopic Data

Compounds	IR (cm^{-1})	LR (cm^{-1})	Assignments
$(NH_4)_2[Mn_2Cl_2(salH)_4(sal)].4H_2O$ (1)	1600s	1612	$\nu_{as}(COO^-)$
	1380s	1330	$\nu_s(COO^-)$
	1231m	1241	δ(O-H)
	3250s		ν(O-H)
	1648m		δ(H-O-H)
	1398s		ν(N-H) ν_4
	371w		ν(Mn-O)
	368m		ν(M-Cl)
$Na_2[Mn_2Cl_2(salH)_4(sal)].4H_2O$ (2)	1600s	1608	$\nu_{as}(COO^-)$
	1379s	1329	$\nu_s(COO^-)$
	1230m	1244	δ(O-H)
	3238s		ν(O-H)
	1649m		δ(H-O-H)
	373w		ν(Mn-O)
	369m		ν(Mn-Cl)
$K_2[Mn_2Cl_2(salH)_4(sal)].4H_2O$ (3)	1600s	1610	$\nu_{as}(COO^-)$
	1376s	1330	$\nu_s(COO^-)$
	1231m	1242	ν(O-H)
	3241s		ν(O-H)
	1650m		δ(H-O-H)
	373w		ν(Mn-O)
	366m		ν(Mn-Cl)

Table 4.1: Contd.

$(NH_2[Mn_2Br_2(salH)_4(sal)].6H_2O$ (4)	1600s	1608	$\nu_{as}(COO^-)$
	1380s	1330	$\nu_s(COO^-)$
	1231m	1244	δ(O-H)
	3250s		ν(O-H)
	1650s		δ(H-O-H)
	1400s		$\nu_{(N-H)}$ ν_4
	373m		ν(Mn-O)
	268m		ν(Mn-Br)
$Na_2[Mn_2Br_2(salH)_4(sal)].6H_2O$ (5)	1600s	1610	$\nu_{as}(COO^-)$
	1381s	1329	$\nu_s(COO^-)$
	1231s	1240	δ(O-H)
	3250s		ν(O-H)
	1651m		δ(H-O-H)
	374w		ν(Mn-O)
	264m		ν(Mn-Br)
$K_2[Mn_2Br_2(salH)_4(sal)].6H_2O$ (6)	1600s	1608	$\nu_{as}(COO^-)$
	1374s	1328	$\nu_s(COO^-)$
	1231m	1240	δ(O-H)
	3250s		ν(O-H)
	1646m		δ(H-O-H)
	376w		ν(Mn-O)
	264m		ν(Mn-Br)
$K[Mn_2I(sal)_3(H_2O)_4].2H_2O$ (7)	1600s		$\nu_{as}(COO^-)$
	1378s		$\nu_s(COO^-)$
	1640m		δ(H-O-H)
	349w		ν(Mn-O)

Table 4.2: Magnetic Moment and Electron Spectroscopic Data

Compounds	λ_{max}(nm) ($\varepsilon(M^{-1}cm^{-1})$)	Assignments	μ_{eff}(BM)
$(NH_4)_2[Mn_2Cl_2(salH)_4(sal)].4H_2O$ (1)	560sh(351)	d-d trans.	4.93
	290 (24216)	LMCT	
	215 (81000)	LMCT	
$Na_2[Mn_2Cl_2(salH)_4(sal)].4H_2O$ (2)	560sg(385)	d-d trans.	5.16
	288 (26431)	LMCT	
	216 (71124)	LMCT	
$K_2[Mn_2Cl_2(salH)_4(sal)].4H_2O$ (3)	560sh(436)	d-d trans.	4.48 (4.94)
	292 (20893)	LMCT	
	215 (36446)	LMCT	
$(NH_4)_2[Mn_2Br_2(salH)_4(sal)].6H_2O$ (4)	569sh(397)	d-d trans.	4.88
	291 (5216)	LMCT	
	207 (19874)	LMCT	
$Na_2[Mn_2Br_2(salH)_4(sal)].6H_2O$ (5)	569sh(334)	d-d trans.	5.15
	289 (4197)	LMCT	
	206 (17403)	LMCT	
$K_2[Mn_2Br_2(salH)_4(sal)].6H_2O$ (6)	569sh(437)	d-d trans.	5.52
	289(4921)	LMCT	
	206 (19608)	LMCT	
$K[Mn_2I(sal)_3(H_2O)_4].2H_2O$ (7)	584sh(250)	d-d trans.	3.12
	294 (3120)	LMCT	
	243 (3675)	LMCT	

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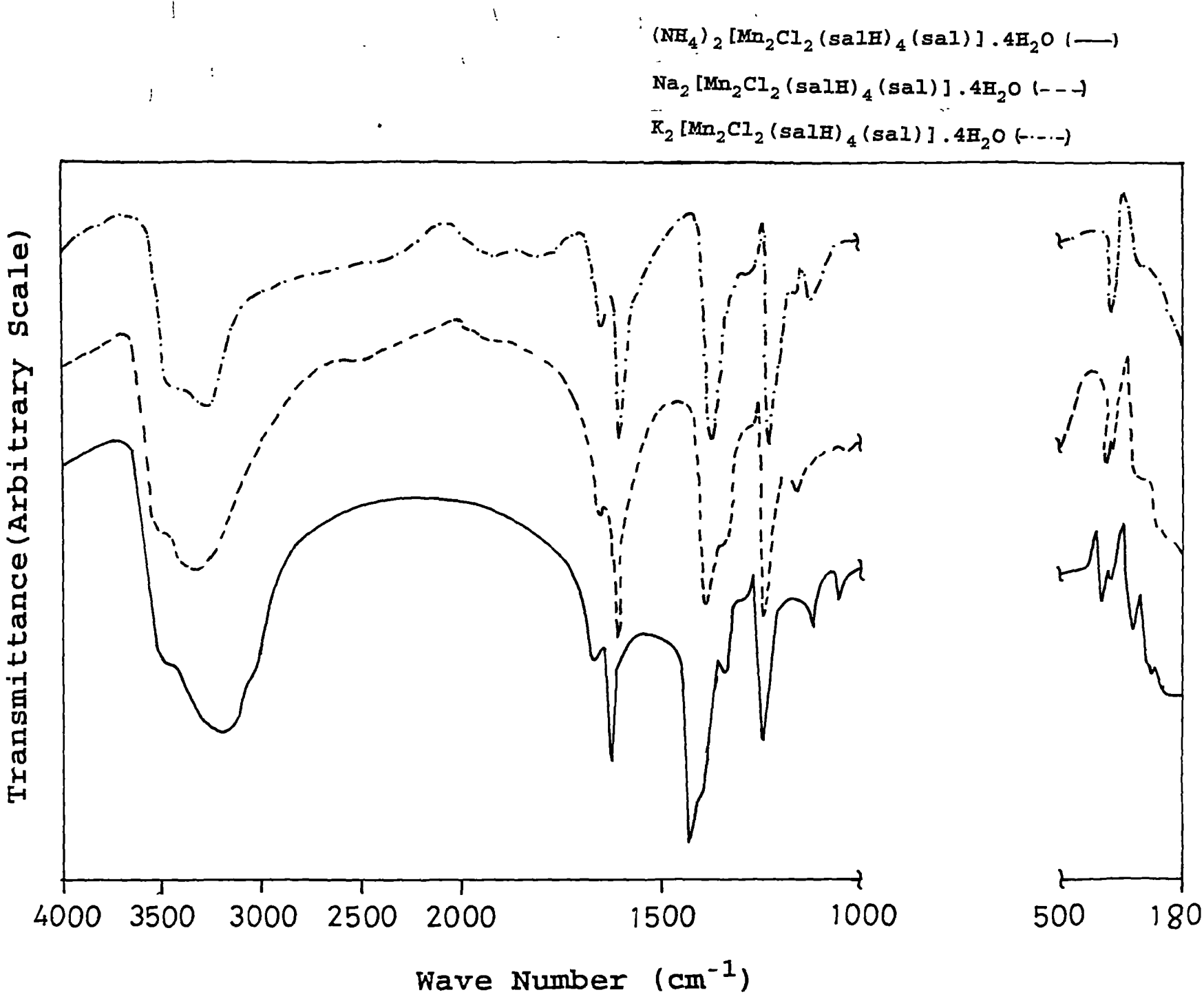

Figure 4.1: IR Spectra

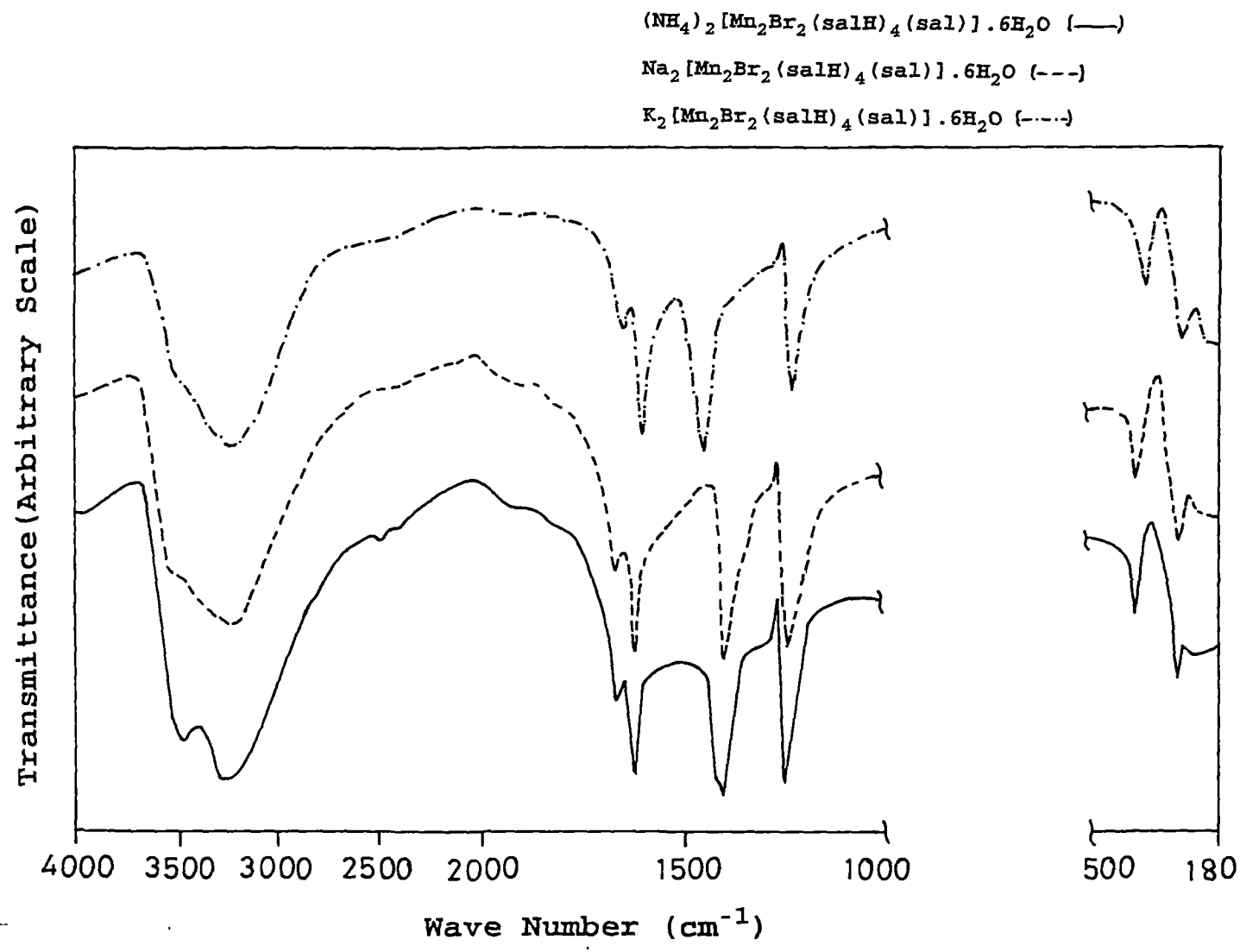

Figure 4.2: IR Spectra

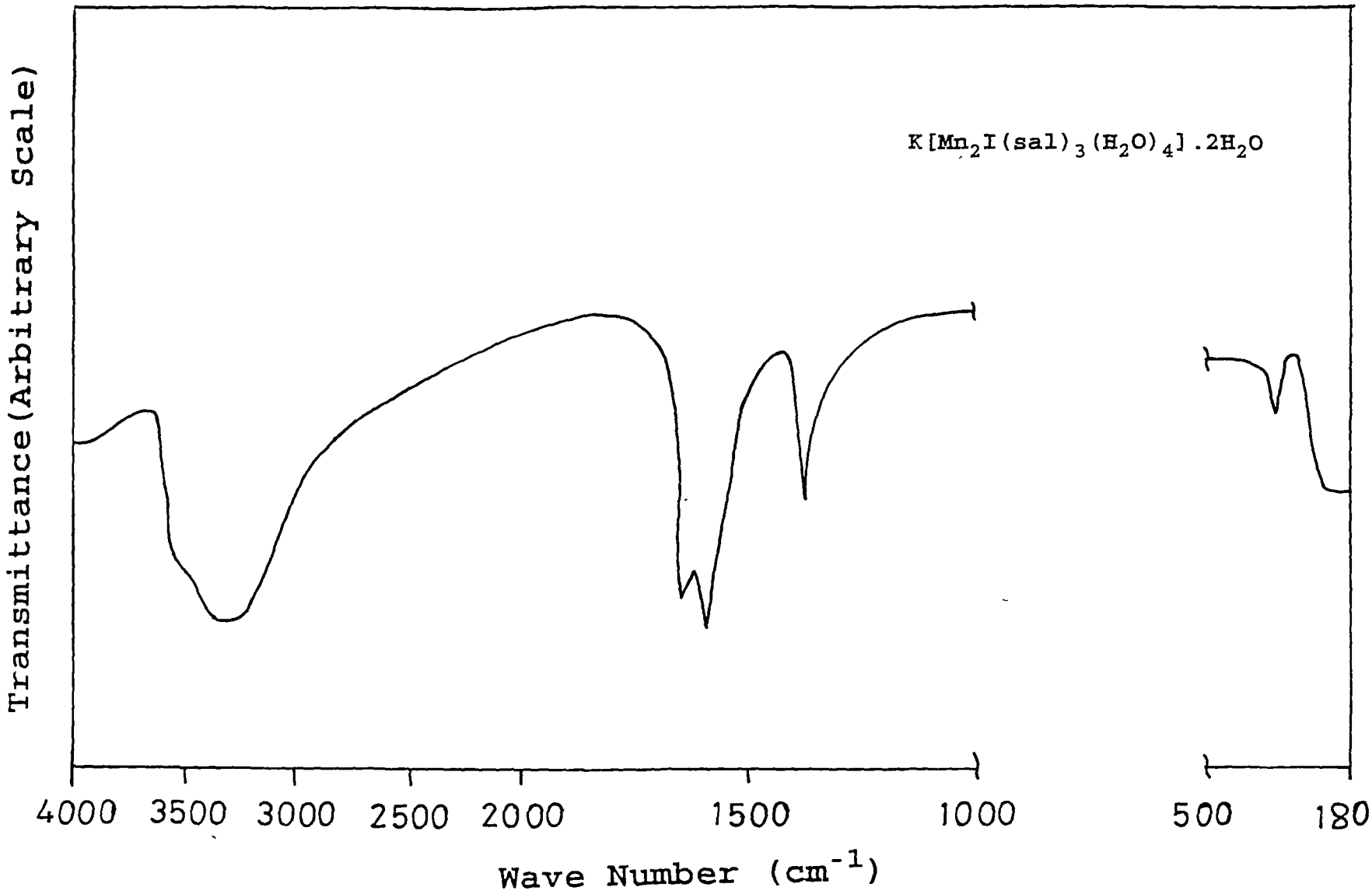

Figure 4.3: IR Spectrum

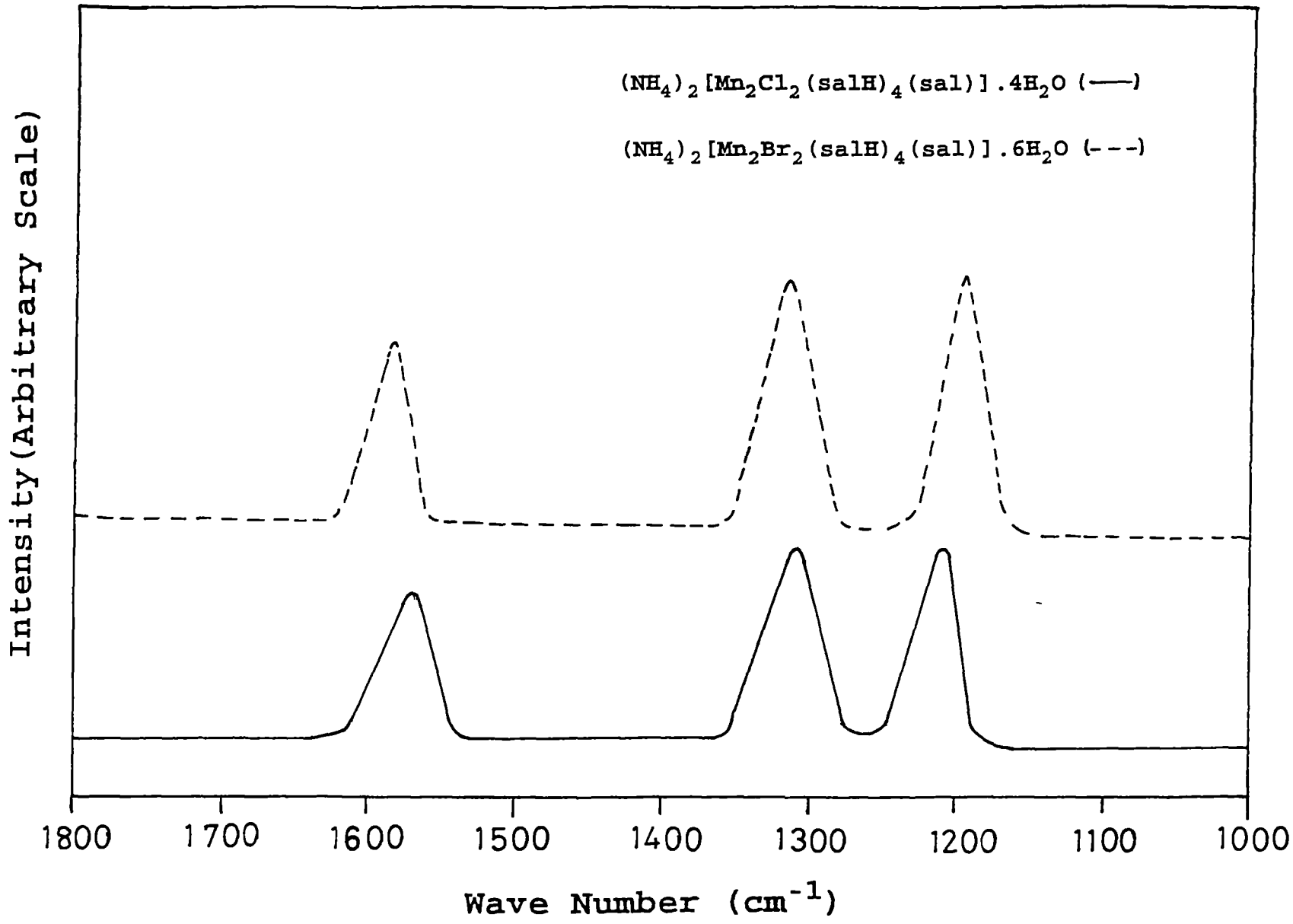

Figure 4.4: Raman Spectra

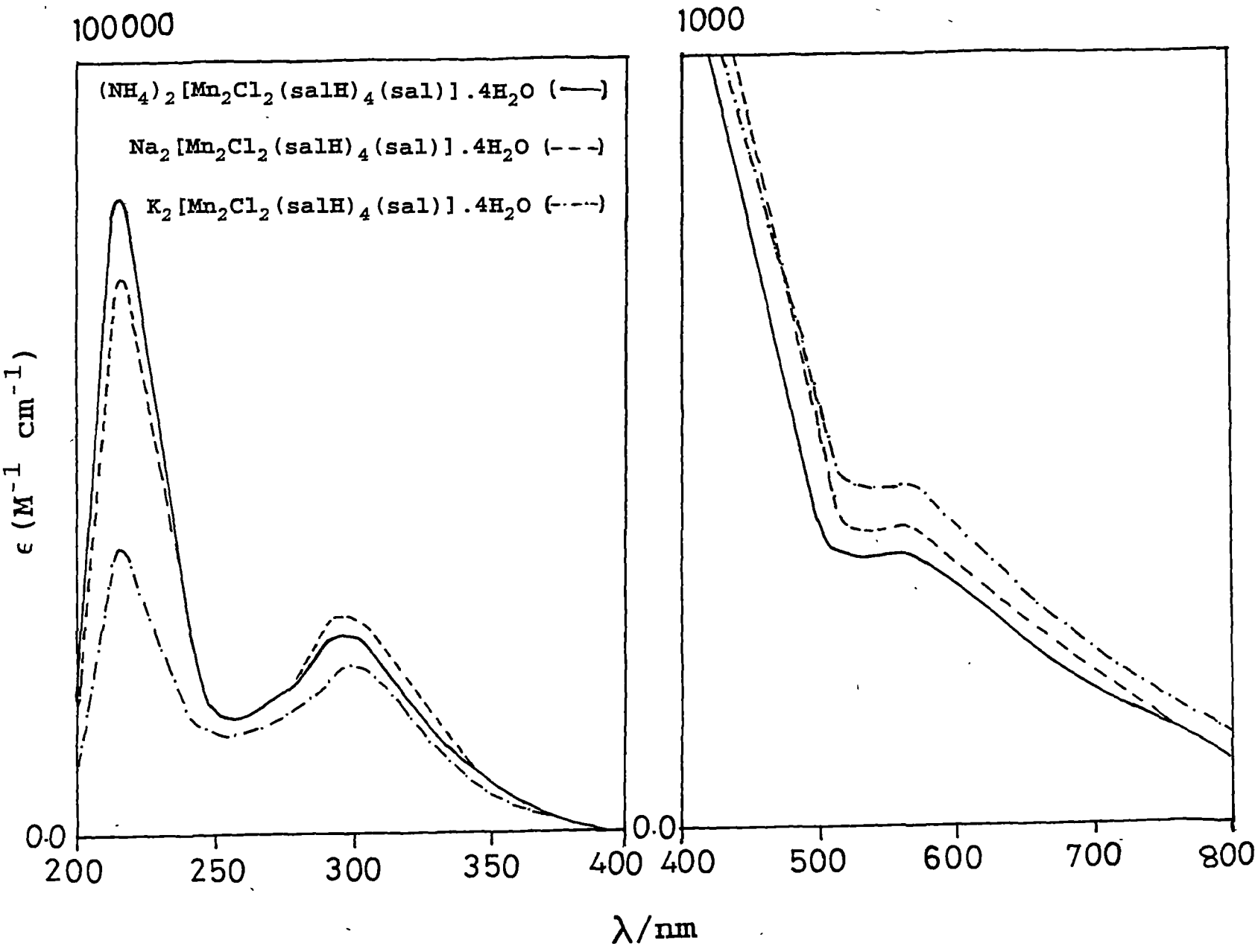

Figure 4.5: Electronic Spectra

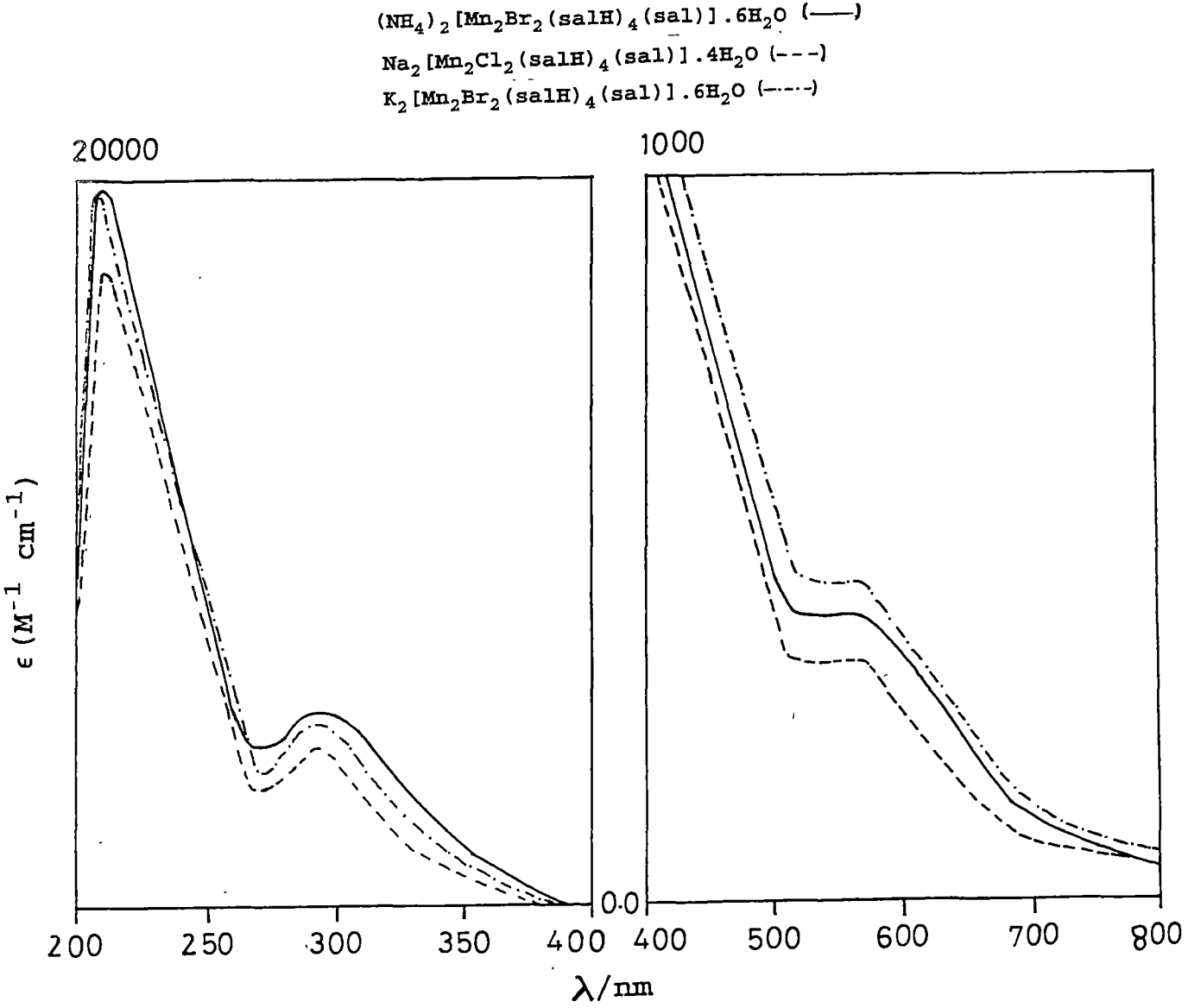

Figure 4.6: Electronic Spectra

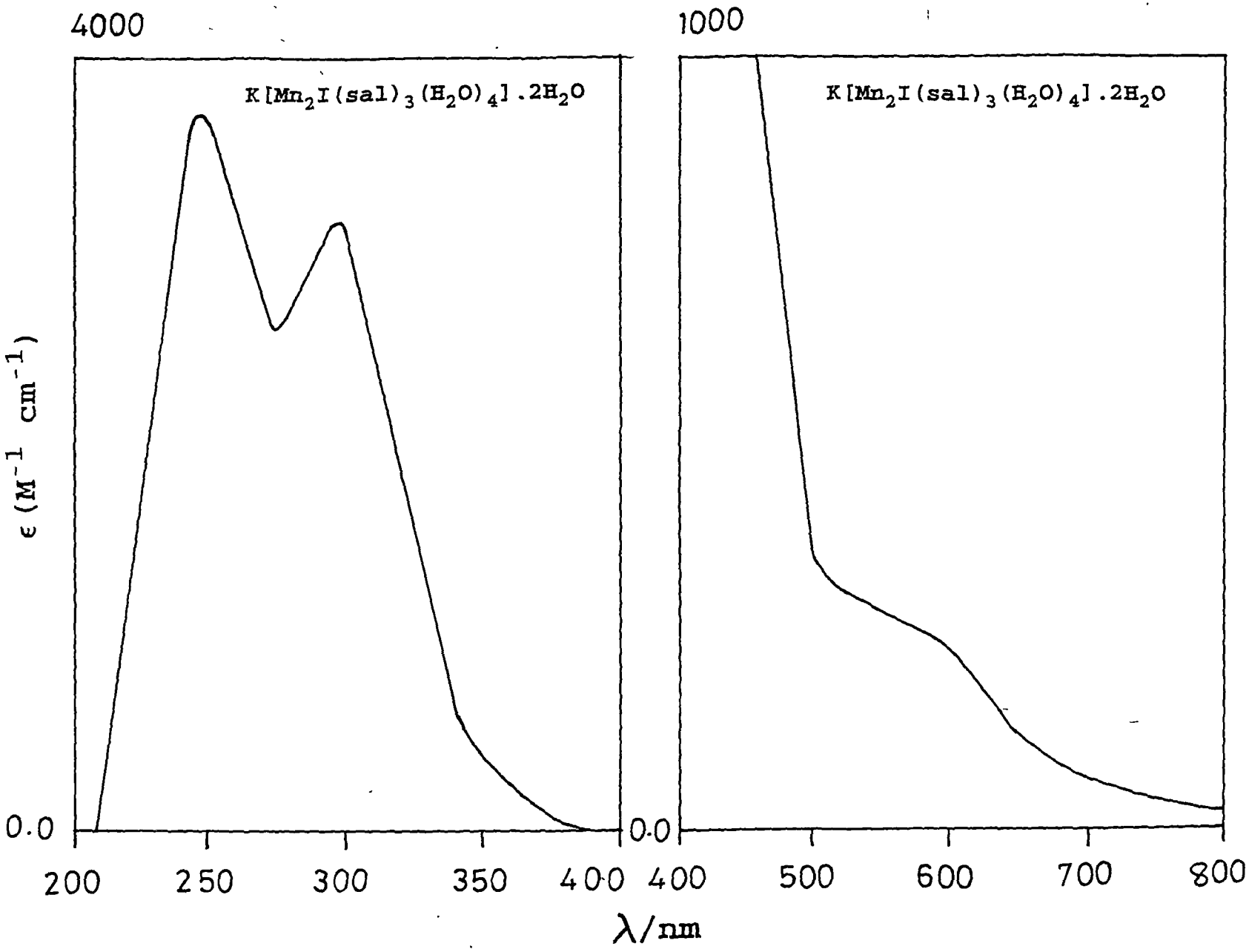

Figure 4.7: Electronic Spectrum

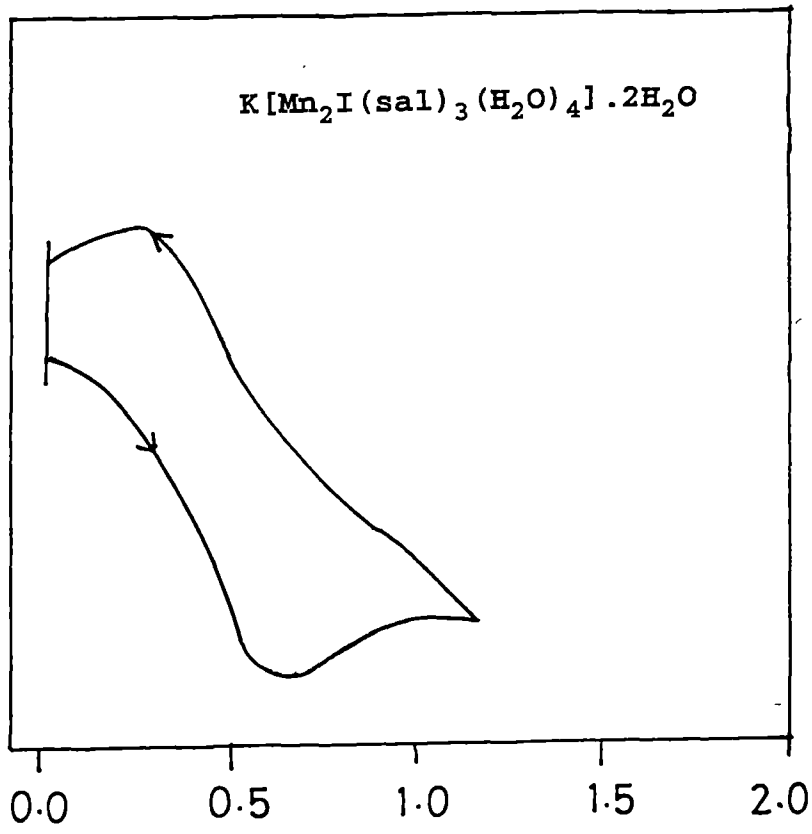

Figure 4.8: Cyclic Voltammogram

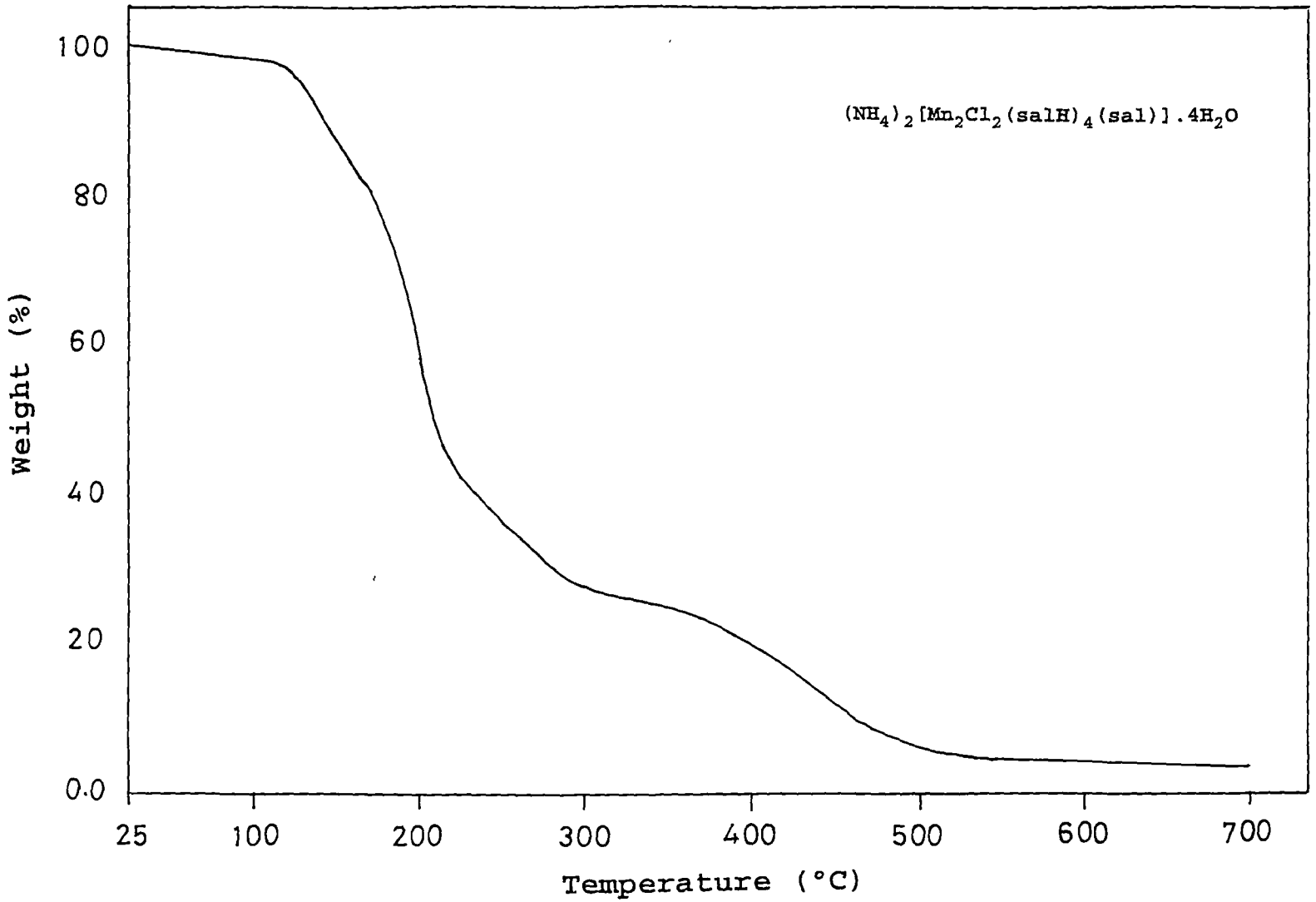

Figure 4.9: Thermogram

CHAPTER V

Interaction of Fluoride with $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ Leading to $[MoO(O_2)_2F_2]^{2-}$ and Synthesis and Spectroscopic Characterization of New Complex Peroxomolybdates $(NH_4)[MoO(O_2)_2F(L)]$ (L = Glycine, Alanine, Valine and Leucine) and $(NH_4)[MoO(O_2)_2(oxinate)]$

There has been a great deal of interest in the studies of peroxomolybdates.[1] In addition to identifying the nature of such complexes formed in aqueous solution[2,3] at different pH, catalytic oxidations of a variety of organic substrates[4] including alcohols[5] by peroxomolybdenum(VI) systems have drawn a considerable attention. The other interest is of biochemical relevance.[6] Incidentally, the reaction of molybdate, $[MoO_4]^{2-}$, with H_2O_2 is very complicated owing to the formation of a variety of peroxo species with varying pH of the reaction solution.[2,3] It is apparent[2,3] that at a pH value of *ca.* 6 the dimeric complex $[Mo_2O_3(O_2)_2(H_2O)_2]$ is

the major species.[2,3]

We became interested in this complex particularly because of the following reasons. The complex $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ ion is stable at an appreciable range of pH and appears to be an effective oxidant as well.[2] One of our major concerns was to investigate the effect of fluoride(F^-) on the dimeric complex. To this end we conducted reaction runs between $(NH_4)_2[MoO_4]$ and H_2O_2 at pH 6, attained by adding separately NaOH and KOH solutions leading to mixed cationic salts, $Na(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$, 1, and $K(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$, 2. We further sought to examine the reaction of 1 and 2 with NH_4HF_2 and identify the product. This afforded $(NH_4)_2[MoO(O_2)_2F_2].H_2O$, 3. In addition, when the reactions otherwise leading to 1 and 2 were conducted in the presence of NH_4HF_2, $NaHF_2$ and KHF_2 afforded 3, $Na(NH_4)[MoO(O_2)_2F_2].3H_2O$, 4, and $K(NH_4)[MoO(O_2)_2F_2].H_2O$, 5, respectively.

One of our major interests was to generate newer compounds containing both fluoride and amino acids. This is expected to through light on the nature of the compounds formed among molybdenum, peroxide and amino acids. in the presence of fluoride, an acknowledged enzyme inhibitor.[7,8]

In our earlier studies[9] attention was focused mainly on vibrational spectroscopic characterization. Importantly, the electronic spectroscopy is expected to provide an insight into the nature of electronic interactions of O_2 with the metal ions[10]. The coordination mode of peroxide may also be

ascertained from electronic absorption spectroscopy on the basis of the number, energies and intensities of the bands.[10,11] Incidentally, most of the side-on bonded peroxo complexes of metals with high oxidation states[11] do not seem to exhibit well resolved LMCT (π_v^* ----> d_σ^* and π_h^* ----> d_σ^*) bands.[11] Our concern in this context was to investigate the electronic spectral profiles of this compounds.

This paper reports the effect of fluoride on the dimeric peroxomolybdates, $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$, leading to a softer route to fluoroperoxomolybdate complex $[MoO(O_2)_2F_2]^{2-}$, the synthesis and spectroscopic characterization of new complex fluoroperoxomolybdates of the type $(NH_4)[MoO(O_2)_2F(L)]$ (L = glycine, alanine, valine and leucine), and $(NH_4)[MoO(O_2)_2(oxinate)]$, electronic spectral results of the compounds, and the results of reactions of some of the newly synthesized compounds with a few selected substrates.

Experimental

The hydrogen fluoride salts NH_4HF_2, $NaHF_2$ and KHF_2 were prepared following the method developed earlier.[12] All other chemicals were of reagent grade quality. Water used for reactivity studies was deoxygenated as described previously.[9b] The IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer and laser Raman spectra on a SPEX Ramalog Model 1403 spectrometer using 4880Å argon laser line.

Electronic spectral measurements were made on a JASCO UVDEC-610/UV-Vis spectrophotometer. The pH values of the reaction solutions were recorded with a Systronics Type 335 digital pH meter. For the determination of sodium and potassium contents a Perkin-Elmer 2380 spectrometer was used.

Synthesis

$A(NH_4)[Mo_2O_3(O_4)_4(H_2O)_2].2H_2O$ (A = Na(1), K(2)).——— A 1.0g (5.1 mmol) ammonium molybdate was dissolved in $4cm^3$ (39.15 mmol) 30% H_2O_2 under ice-cold condition. The pH of the solution at this stage was recorded to be 5. Dilute solutions (5-6%) of AOH (A = Na or K) was added dropwise with stirring to raise the pH to 6 with the reaction solution colour turning red. To the resulting solution $20cm^3$ precooled ethanol was added with continuous stirring whereupon a yellow microcrystalline product was formed. The product was allowed to settle for 5min, separated by vacuum filtration, washed thrice with ethanol and dried in air. Yields of $A(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$ 1(81)(A = Na) and 1g(79%)(K).

Reaction of NH_4HF_2 *with* 1 *and* 2 *and isolation of* $(NH_4)_2[MoO(O_2)_2F_2].H_2O$(3).——— To a suspension of 0.4 mmol compound 1 or 2 in $10cm^3$ of water 8.77 mmol ?solid NH_4HF_2 was added .The reaction mixture was stirred for 30min to get a clear yellow solution. To this solution about $40cm^3$ ethanol was added and the whole was kept at 0°C for 24h whereupon a yellow precipitate was formed. The product was isolated by filtration,

washed thrice with ethanol and dried in air. In both the cases the product was identified as $(NH_4)_2[MoO(O_2)_2F_2].H_2O$(3) in 60% yield.

Reaction of $(NH_4)_2[MoO_4]$ ***and*** H_2O_2 ***in the presence of*** AHF_2 **(A = Na or K)** ***as a softer route to*** $A(NH_4)[MoO(O_2)_2F_2].nH_2O$ **(A = Na, n = 3 (4); K, n = 1 (5)).**——— A mixture of 1.0g (5.1 mmol) ammonium molybdate and 10.2 mmol of AHF_2 was dissolved in $4cm^3$(39.15 mmol) 30% H_2O_2 under ice-cold condition. From this stage till isolation of the compounds the procedure was similar to that adopted for the synthesis of 1 and 2. Yields of $A(NH_4)[MoO(O_2)_2F_2].nH_2O$ 1.2 (76)(A = Na, n = 3) and 1.1g(75%)(K, n = 1).

$(NH_4)_2[MoO(O_2)_2F_2].H_2O$(3).——— For the synthesis of this a recipe similar to that for 4 and 5 was followed with the difference that NH_4HF_2 was used instead of AHF_2 and dilute (1:1) aqueous ammonia was used to raise the pH. Yield 0.9g(66%).

$(NH_4)[MoO(O_2)_2F(L)]$ **(L =** ***glycine*****(6) or** ***alanine*****(7)).**——— To 1.0g(5.56 mmol) $H_2MoO_4.H_2O$ was added a solution of 8.34 mmol glycine or alanine in $4cm^3$(39.15 mmol) of 30% H_2O_2 maintaining the ratio of Mo:L at 1:1.5. This was followed by the addition of $0.2cm^3$(4.80 mmol) 48% HF. The reaction mixture was left at room temperature for 1h with occasional stirring. The resultant clear yellow solution was cooled to ice-bath temperature and the pH of the reaction solution was raised to 6 by the addition of

1:1 aqueous ammonia. At this stage the solution turned red. On addition of $20cm^3$ ethanol under stirring to the red solution afforded a yellow microcrystalline compound. The product was isolated by filtration and air dried. Yield of $(NH_4)[MoO(O_2)_2F(glyH)]$(6) is 1g(62%) and $(NH_4)[MoO(O_2)_2F(alaH)]$(7) is 0.9g(54%).

$[(NH_4)[MoO(O_2)_2F(L)]$ (L = *valine*(8) *or leucine*(9)).——— To 1.0g(5.56 mmol) $H_2MoO_4.H_2O$ was added a solution of 6.95 mmol of valine or leucine in $8cm^3$(78.31 mmol) 30% H_2O_2 maintaining the concentration ratio of Mo:L at 1:1.25 followed by the addition of $0.2cm^3$(4.80 mmol) 48% HF. The reaction mixture was left at room temperature for 1h with occasional stirring. The yellow solution thus obtained was cooled in an ice bath and the pH raised to 6 by the addition of 1:1 ammonia solution. This resulted into a red colouration of the reaction solution. From this an orange microcrystalline compound was precipitated by adding $25cm^3$ ethanol. The product was isolated by filtration and dried in a vacuum desiccator. While drying up the colour of the compound changed to yellow. Yields of $(NH_4)[MoO(O_2)_2F(valH)]$(8) and $(NH_4)[MoO(O_2)_2F(leuH)]$(9) are 1.4(76) and 1.4g(73%), respectively.

$(NH_4)[MoO(O_2)_2$(oxinate)](10).——— To 1.0 g (5.56 mmol) $H_2MoO_4.H_2O$ $4cm^3$ (39.15 mmol) 30% H_2O_2 was adeded followed by the addition of $0.2cm^3$(4.80 mmol) 48% HF. The reaction mixture was left at room temperature for 30min with occasional stirring

so as to obtain a clear yellow solution. To this a solution of 0.9g(6.20 mmol) 8-hydroxyquinoline in $6cm^3$ acetonitrile was added under stirring. The reaction solution was allowed to stand at room temperature for 1h by which time a yellow microcrystalline compound was formed. The product was filtered out and dried in air. Yield 0.9g(48%).

Oxidation of sulfur dioxide.——— Through a solution of 1.0g of 1 in $20cm^3$ deoxygenated water a slow stream of SO_2(g) was passed for *ca.* 5min. The resulting light-blue solution was concentrated on a steam-bath, in a fume hood. The solution was allowed to cool to room temperature followed by the addition of ethanol to obtain a white precipitate containing sulfate while the supernatent liquid was blue. The product was filtered off, washed with ethanol and air dried. Similar observations were made by conducting the reactions involving 2-9.

Oxidation of PPh_3.——— In separate reaction runs to a solution of 1.0g(3.81 mmol) PPh_3 in $50cm^3$ degased DMF 1.9 mmol of each of the compounds 1 and 2 or 3.81 mmol of each of 3-5 was added while N_2 gas was passed through the solution. The reaction mixture was then refluxed for 30min under N_2 atmosphere and subsequently allowed to cool to room temperature. Addition of $200cm^3$ of water to this caused a white product to appear as a suspension. This was allowed to settle for 2h and the compound was isolated by

centrifugation. The off-white product thus obtained was recrystallised from chloroform, m.p. 154-155°C (lit. 156-158°C). Yield 55-65%.

From the complexes containing organic ligands, $(NH_4)[MoO(O_2)_2(oxinate)]$, **10**, was chosen for the oxidation of PPh_3. The reaction was conducted in a similar way as above except that after the reflux was over the solution was concentrated on a steam-bath and the product was isolated by column chromatography using ethyl acetate and hexane mixture (1:4) as eluent. The fraction collected for PPh_3=O was evaporated to dryness on a steam-bath to get a white compound. The product was recrystallized from chloroform, m.p. 154-155°C. Yield 50%.

Transformation of C_6H_5CN **to** $C_6H_5CONH_2$.——— To the solution of 2.42 mmol of each of the compounds **1** and **2** or 4.85 mmol of each of **3**-**5** in $40cm^3$ deoxygenated water was added a solution of 0.5g(4.85 mmol) benzonitrile in $10cm^3$ acetonitrile. The reaction mixture was stirred at *ca.* 50°C for 4h. From the resulting yellow solution the product was extracted in $CHCl_3$. The combined organic layer was dried over anhydrous Na_2SO_4 and evaporated to dryness to obtain an orange product. The crude product on recrystallisation from $CHCl_3$ yielded a white compound, m.p. 128°C (lit. 128-129°C). Yield 20-25%.

Oxidation of $C_6H_5CH_2OH$.——— A solution of 0.5g(4.62 mmol) benzyl alcohol in $10cm^3$ acetonitrile was added separately to the solution of (2.31 mmol) each of the compounds **1** and **2** or 4.62

mmol of each of 3-5 in $45cm^3$ deoxygenated water. The mixture was refluxed for 30min in N_2 atmosphere to get a yellow solution. The product was extracted in $CHCl_3$ and it was dried over anhydrous Na_2SO_4. The $CHCl_3$ extract on concentration over steam-bath to *ca.* $5cm^3$ followed by the addition of a solution of 0.9g 2,4-dinitrophenylhydrazine in $10cm^3$ of acetonitrile afforded a red colour precipitate of the hydrazone of benzaldehyde. The product was isolated by filtration and recrystallised from acetonitrile and dried *in vacuo* over concentrated H_2SO_4, m.p. 240°C(dec.) (lit. 237°C). Yield 40-45%.

Oxidation of methyl-1,4-hydroquinone by **$(NH_4)[MoO(O_2)_2(oxinate)]$(10).**——— To a solution of 0.5g(4.03 mmol) methyl-1,4-hydroquinone in $100cm^3$ methanol 2.7g(7.98 mmol) **10** was added in portions. Then it was refluxed for 2h and cooled. The solution was filtered and the residue washed with methanol. The combined filtrate and the washing was concentrated on a steam-bath and the product was isolated by column chromatography using ethyl acetate and hexane mixture(1:4) as eluent. The fraction collected for methyl-1,4-benzoquinone was concentrated on a steam-bath to get a very bright yellow compound, m.p. 67-68°C (lit. 67-70°C). Yield 0.2g (41%). NMR(CD_3CN): ^1H(300 MHz), d 2.1 (s, CH_3), 6.7(s, 1H, aryl H) and 6.8 (d, 2H, aryl H).

Elemental Analyzes

Molybdenum contents were determined gravimetrically

as molybdenum oxinate,[13] $MoO_2(C_9H_6ON)_2$. The peroxide contents were determined by redox titration with standard $KMnO_4$ solution. Determination of the peroxide contents of compounds **6-10** was done by iodometry. To prevent the loss of active oxygen the redox titrations were conducted in presence of boric acid. Sodium and potassium contents were determined by AAS. Fluoride was estimated by adopting the procedure described by Chakravorti and Pandit.[14] Sulfate was estimated by gravimetry as $BaSO_4$. Carbon, hydrogen and nitrogen contents were determined by the Microanalytical Laboratory of CDRI, Lucknow.

Results and Discussion

Although the dimeric complex $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ exists in solution[2,3] at a wide range of pH, the synthesis of $Na(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$, **1**, and $K(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$, **2**, was accomplished at pH 6. Dilute solutions of NaOH and KOH were separately added, to adjust the pH. Use of ammonium molybdate has been responsible for the fomation of mixed cationic salts. A pH value higher than 6 was not conducive to the desired synthesis because at a higher pH (*cf.* $\gg$ 7) some other peroxo species also exist in addition to the dimer.[3] The most important IR bands of **1** and **2** are ν(Mo=O), ν(O-O), ν_2(Mo-O_2), ν_3(Mo-O_2), ν_s(Mo_2O), ν_{as}(Mo_2O), and ν(Mo-OH_2) occurring at *ca.* 936s, *ca.* 858s, *ca.* 570m, *ca.* 623m, *ca.* 474w, *ca.* 713s, and *ca.* 353w

cm^{-1}, respectively.[2] The complementary Raman signals due to $\nu(Mo=O)$, $\nu(O-O)$, $\nu_2(Mo-O_2)$, $\nu_3(Mo-O_2)$, $\nu_s(Mo_2O)$, $\nu_{as}(Mo_2O)$, and $\nu(Mo-OH_2)$ have been observed at *ca.* 959, *ca.* 862, *ca.* 557, *ca.* 591, *ca.* 458, *ca.* 722, and *ca.* 347 cm^{-1}, respectively. The IR and Raman spectra support the identity of the complexes. Pyrolysis of 1 and 2 at *ca.* 110°C for *ca.* 2h suffered loses of weights corresponding to two molecules of water per formula weight. The IR spectra of pyrolyzed products were essentially similar to those of 1 and 2 including the presence of $\rho_r(H_2O)$ and $\nu(Mo-OH_2)$. Taking into account the weight loses and IR spectral features, it is inferred that 1 and 2 contain both lattice and coordinated water and what was lost in pyrolysis was the two lattice water molecules.

Effect of Fluoride on the Dimeric Peroxomolybdates .——— One of our major concerns was to study the effect of fluoride on the reactions leading to 1 and 2. Similar reactions on being conducted in the presence of fluoride, with the Mo:F concentration being maintained at 1:2, afforded $Na(NH_4)[MoO(O_2)_2F_2].3H_2O$, 4, and $K(NH_4)[MoO(O_2)_2F_2].H_2O$, 5. $NaHF_2$ and KHF_2 were the source of fluoride for 4 and 5, respectively. When a similar reaction was conducted in the presence of NH_4HF_2, the corresponding $(NH_4)_2[MoO(O_2)_2F_2].H_2O$, 3, was obtained. An increase of fluoride ion concentration upto a level of Mo:F at 1:6 did not alter the results.

Thus it is now evident that fluoride has an antagonistic effect on the synthesis of the dimeric complex, at least under

the present experimental conditions. Importantly this has provided a direct access to peroxofluoromolybdates(VI) which are otherwise synthesized by peroxygenation of fluoromolybdate precursor complexes.[15] An additional advantantage is the redundancy of use of hydrofluoric acid. Being intrigued by the afore-mentioned results it became necessary to study independent reactions between 1 or 2 and NH_4HF_2 to understand the effect of fluoride on a preformed dimer. The reaction was conducted in molar ratio of 1 or 2:NH_4HF_2 at 1:22, which directly afforded $(NH_4)_2[MoO(O_2)_2F_2].H_2O$, 5. This implies that in a weakly acidic solution fluoride does not permit the dimeric complex to exist but leads to the formation of fluoroperoxomolybdate(VI) as obtained.

The significant difference of vibrational spectra of the fluoroperoxo complexes 3-5 to those of 1 and 2 are the absence of absorptions due to Mo_2O and $Mo-OH_2$ and the appearance of bands for Mo-F[16] at *ca.* 512 cm^{-1}. The IR spectra of 2 and 3 have been shown in Figures 5.1 and 5.2, respectively. To provide further support to the structure, Raman spectrum of 3, (Figure 5.3) as a representative, was recorded. The bands at 957cm^{-1} with a shoulder at 933cm^{-1} has its origin to ν(Mo=O), while the absorptions due to ν(O-O), ν_2(Mo-O_2), ν_3(Mo-O_2), and ν(Mo-F) occurred at 906, 589, 636, and 453cm^{-1}, respectively. In addition, two IR bands at *ca.* 1594 and *ca.* 3477cm^{-1}, observed for 1-5, have been assigned respectively to

δ(H-O-H) and ν(O-H) modes, [17a, 18] of lattice water.

Synthesis and Characterisation of New Mixed-Ligand Complex Peroxomolybdates. ——— In order to synthesise the newer complex peroxomolybdates containing both fluoride and amino acid as the heteroligands the reaction of $H_2MoO_4.H_2O$, H_2O_2 with amino acids and HF were conducted (vide Experimental] affording $(NH_4)[MoO(O_2)_2F(L)]$ (L = glycine(6), alanine(7), valine(8) or leucine(9))in very good yields. An attempt to prepare the corresponding 8-hydroxyquinoline(oxine) complex resulted to a nonfluoro specise, $(NH_4)[MoO(O_2)_2$(oxinate)], (10) probably owing to the chelate effect of oxinate.

In view of a pronounced tendency of F^- to form stable complex with MoO^{4+} the fluoride ion concentration was maintained at a relatively lower level than the organic co-ligands such that both the ligands could coordinate. The reaction pH was adjusted to 6 by the addition of 1:1 ammonia. Ammonia solution was added at ice-bath temperature in order to reduce the catalytic decomposition of peroxide by MoO_4^{2-}. Ethanol was added to bring about the precipitation of the product. It may be noted that in the case of **10** neither the adjustment of pH nor the addition of ethanol was necessary. The compound was spontaneously precipitated on addition of oxine to the reaction solution.

The compounds **1-9** are all yellow, while **10** is orange. The products were all microcrystalline and indefinitely stable. In water the solubility of **3-9** are

comperatively higher than that of 1 and 2, whereas 10 is sparingly soluble though it dissolves in acetonitrile, dimethylformamide and dimethylsulfoxide. The active oxygen oxygen contents of 1-5 were determined by redox titration with standard $KMnO_4$ solution, while those of 6 to 10 were estimated iodometrically to avoid any interference from organic heteroligands. The analytical results are in full agreement with the formulation of the compounds. The compounds are all diamagnetic. Analytical data of compounds 1-10 are listed in Table 5.1.

Important features of the IR spectra of compounds 6-10 are the appearance of two strong bands in close proximity in the region 945-975cm^{-1} owing to Mo=O stretching and the absorptions at *ca.*858s, *ca.* 575m, and *ca.* 653m are due to $\nu(O-O)$, $\nu_2(Mo-O_2)$, and $\nu_3(Mo-O_2)$, respectively.[16] Other significant IR bands for 6-9 are at *ca.* 1594s, *ca.* 1400s, *ca.* 1505s, *ca.* 1160m, and *ca.* 460m cm^{-1} assignable to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$, $\delta_s(NH_3^+)$, $\rho_r(NH_3^+)$, and $\nu(Mo-O)$ respectively.[19,20] The increase of $\nu_{as}(COO^-)$ and decrease of $\nu_s(COO^-)$ frequencies compared to the corresponding free amino acids, and the appearance of $\delta(NH_3^+)$, $\rho_r(NH_3^+)$ and $\nu(Mo-O)$ indicate the presence of glycine, alanine, valine and leucine in zwitterionic form being coordinated through the carboxylate oxygen.[17b,19,20] The bands due to $\nu(Mo-F)$ and $\nu(N-H)$ ν_4 mode of ammonium cation have been obscured by the strong absorptions arising from amino acids. The IR spectra of 6-

10 have been displayed in Figures 5.4 - 5.8, respectively. In order to complement the IR spectral evidence Raman spectra of compounds 6-9 were recorded. The signals at *ca.* 952 and *ca.* 937cm^{-1} due to ν(Mo=O) as well as the appearance of three bands due to ν(O-O), ν_2(Mo-O_2), and ν_3(Mo-O_2), respectively, at *ca.* 893 *ca.* 554, and *ca.* 634cm^{-1} indicate the presence of chelated peroxo group.[16] The Raman spectrum of 6 has been depicted in Figure 5.3.

In 10 the absence of ν(O-H) of the hydroxyl and the decrease of ν(C=N) frequency(1595cm^{-1}) compared to that in free oxine(1613cm^{-1}) indicate that the coordination of oxine through its -O and -N atoms.[21] The appearance of medium intensity bands at 368 and 296cm^{-1} attributable to ν(Mo-O) and ν(Mo-N) modes, respectively, support the above coordination pattern. The occurrence of a strong band at 1420cm^{-1} has been assigned to ν(N-H) ν_4 mode of ammonium cation. The structurally significant vibrational spectroscopic data of compounds 1-10 are compiled in Table 5.2.

Electronic spectra

The electronic spectroscopy of transition metal dioxygen complexes is rather complicated as described by Lever and Gray.[11] It is relevant to note that the side-on peroxometallates containing UV-transparent co-ligands are expected to give two absorption bands (LMCT) due to Π_v^* ----> d_σ^* and Π_h^* ----> d_σ^* transitions.[11] The latter transition involving

a comperatively higher energy than the former is rarely observed.[10,11] Incidentally, compounds **1-10**, all showed clearly distinguishable electronic spectral features exhibiting the two predicted LMCT bands. Typically the spectra of compounds **2**, **3** and **6** are shown in **Figure 5.9**. The lower energy, lower intensity band at *ca.* 308nm and the higher energy, higher intensity band at *ca.* 229nm have been assigned to Π_v^* ----> d_σ^* and Π_h^* ----> d_σ^* transitions, respectively. The electronic spectral data are listed in **Table 5.3**. Based on these results, it is hoped that the compounds might serve as ideal probes for studying the detailed electronic interactions involved in metal-dioxygen systems.

Reactivity

Peroxometallates are, in general, anticipated to be potential oxygen donors to a variety of substrates.[4] In order to investigate the reactivity profile of the compounds described herein, reactions involving some selected organic substrates and SO_2 were separately carried out. The results (Vide Experimental) indicate clearly that the peroxomolybdates reacted to bring about oxidations or transformations depending on the nature of the substrates. Thus, PPh_3, C_6H_5CN, $C_6H_5CH_2OH$, and methyl-1,4-hydroquinone were converted to PPh_3=O, $C_6H_5CONH_2$, C_6H_5CHO, and methyl-1,4-benzoquinone, respectively, in moderate to good yields while SO_2 was oxidized to SO_4^{2-}. The products have been characterised by melting point determination, IR and

NMR spectroscopies. The characterization data of the organic products match well with the literature values, while sulfate was characterized by chemical analysis and IR spectroscopy. Among the peroxomolybdates, **10** appears to have a relatively better solubility in organic solvents.

Concluding remarks

The salient features of the present investigation are: (i) in solution fluoride inhibits the existance of dimeric complex, $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$, by cleaving the Mo-O-Mo dimeric link finally leading to the formation of fluoroperoxomolybdate, $[MoO(O_2)_2F_2]^{2-}$, thereby providing a direct route to these complexes, (ii) an interaction of molybdate with H_2O_2 in the presence of fluoride and biochemically relevant ligand, L, (L = glycine, alanine, valine or leucine) affords newer quaternary complex of the type $[MoO(O_2)_2F(L)]^-$, while a similar reaction with L being oxine gives a non-fluoro complex, $[MoO(O_2)_2(oxinate)]^-$, probably because of a pronounced chelate effect of oxinate. The complexes all exihibit two well resolved LMCT transitions (Π_v^* ----> d_σ^* and Π_h^* ----> d_σ^*). The latter transition is rarely observed. From the limited studies so far made on their spectral behaviour and reactivity properties it is evident that the compounds offer definite possibilities for further investigations related especially to newer reactions and detailed electronic interactions in such complexes.

Table 5.1: Analytical data[a]

Compounds	Mo	O_2^{2-}	F	C	H	N
$Na(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$	41.09	26.10		4.80	2.60	2.89
(1)	(39.89)	(26.61)		(4.78)	(2.52)	(2.91)
$K(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$	39.70	25.70		7.90	2.50	2.80
(2)	(38.60)	(25.75)		(7.86)	(2.44)	(2.82)
$(NH_4)_2[MoO(O_2)_2F_2].H_2O$	36.50	24.02	13.89		3.80	10.42
(3)	(35.97)	(23.87)	(14.17)		(3.77)	(10.45)
$Na(NH_4)[MoO(O_2)_2F_2].3H_2O$	30.64	20.78	12.06	7.60	3.28	4.50
(4)	(31.04)	(20.71)	(12.30)	(7.44)	(3.27)	(4.53)
$K(NH_4)[MoO(O_2)_2F_2].H_2O$	33.79	22.62	13.20	13.77	2.12	4.84
(5)	(33.18)	(22.14)	(13.14)	(13.52)	(2.10)	(4.85)
$(NH_4)[MoO(O_2)_2F(glyH)]$	32.86	21.09	6.60	8.84	3.45	9.61
(6)	(33.30)	(22.22)	(6.59)	(8.34)	(3.14)	(9.73)
$(NH_4)[MoO(O_2)_2F(alaH)]$	31.93	21.36	6.19	11.29	3.58	9.35
(7)	(31.76)	(21.18)	(6.29)	(11.93)	(3.68)	(9.27)
$(NH_4)[MoO(O_2)_2F(valH)]$	29.69	19.26	5.85	17.95	4.99	8.87
(8)	(29.06)	(19.38)	(5.75)	(18.19)	(4.59)	(8.49)
$(NH_4)[MoO(O_2)_2F(leuH)]$	27.76	18.22	5.68	20.75	5.26	8.39
(9)	(27.87)	(18.59)	(5.52)	(20.94)	(4.99)	(8.14)
$(NH_4)[MoO(O_2)_2(oxinate)]$	28.89	18.26		32.61	3.06	8.42
(10)	(28.37)	(18.93)		(31.96)	(2.99)	(8.29

[a]Calculated values are in parentheses [b]Sodium [c]Potassium

Table 5.2: Structurally significant vibrational spectroscopic data

Compounds	IR	Laser Raman	Assignment
$Na(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$ (1)	910vs	958	ν(Mo=O)
	862vs	867	ν(O-O) ν_1
	559m	558	ν(Mo-O_2) ν_2
	620m	591	ν(Mo-O_2) ν_3
	705s	721	ν_{as}(Mo_2O)
	480w	460	ν_s(Mo_2O)
	355m	348	ν(Mo-OH_2)
	740w		ρ_r(H_2O)
	1640m,br		δ(H-O-H)
	1410vs,br		ν(N-H) ν_4
	3470m,br		ν(O-H)
$K(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$ (2)	961vs	960	ν(Mo=O)
	854vs	856	ν(O-O) ν_1
	580m	556	ν(Mo-O_2) ν_2
	625m	590	ν(Mo-O_2) ν_3
	720s	722	ν_{as}(Mo_2O)
	468w	456	ν_s(Mo_2O)
	350m	345	ν(Mo-OH_2)
	738w		ν(H-O)
	1606m		δ(H-O-H)
	1451s		ν(N-H) ν_4
	3425s		ν(O-H)

Table 5.2: Contd.

$(NH_4)_2[MoO(O_2)_2F_2].H_2O$ (3)	957vs	933sh	ν(Mo=O)
	978vs	957	
	857vs	906	ν(O-O) ν_1
	580s	589	ν(Mo-O_2) ν_2
	657s	636	ν(Mo-O_2) ν_3
	516m	453	ν(Mo-F)
	1402s		ν(N-H) ν_4
	1449m		δ(H-O-H)
	3523m,br		ν(O-H
$Na(NH_4)[MoO(O_2)_2F_2].3H_2O$ (4)	958s		ν(Mo=O)
	969s		
	860s		ν(O-O) ν_1
	578s		ν(Mo-O_2) ν_2
	614s		ν(Mo-O_2) ν_3
	507m		ν(Mo-F)
	1406vs		ν(N-H) ν_4
	1629s		δ(H-O-H)
	3458m,br		ν(O-H)
$K(NH_4)[MoO(O_2)_2F_2].H_2O$ (5)	961s		ν(Mo=O)
	977s		
	863vs		ν(O-O) ν_1
	577s		ν(Mo-O_2) ν_2
	638vs		ν(Mo-O_2) ν_3
	514s		ν(Mo-F)

Table 5.2: Contd.

	1415s		ν(N-H) ν_4
	1645m		δ(H-O-H)
	3508m,br		ν(O-H)
$(NH_4)[MoO(O_2)_2F(glyH)]$ (6)	972s	954	$\nu_{(Mo=O)}$
	953s	936	
	851s	905	$\nu_{(O-O)}$ ν_1
	570s	546	$\nu_{(Mo-O_2)}$ ν_2
	643s	610	$\nu_{(Mo-O_2)}$ ν_3
	1608s		$\nu_{as}(COO^-)$
	1402s		$\nu_s(COO^-)$
	1489s		$\delta_s(NH_3^+)$
	1123m		$\rho_r(NH_3^+)$
	1320s		$\delta(CH_2)$
	456m		ν(Mo-O)
$(NH_4)[MoO(O_2)_2F(alaH)]$ (7)	970s	950	ν(Mo=O)
	949s	938	
	861s	860	ν(O-O) ν_1
	577m	556	$\nu_{(Mo-O_2)}$ ν_2
	667m	665	$\nu_{(Mo-O_2)}$ ν_3
	1611s		$\nu_{as}(COO^-)$
	1400s		$\nu_s(COO^-)$
	1521m		$\delta_s(NH_3^+)$
	1235m		$\rho_r(NH_3^+)$
	463m		ν(Mo-O)

Table 5.2: Contd.

$(NH_4)[MoO(O_2)_2F(valH)]$ (8)	955s	950	ν(Mo=O)
	933		
	861s	906	ν(O-O) ν_1
	573m	555	ν(Mo-O_2) ν_2
	660s	634	ν(Mo-O_2) ν_3
	1581s		$\nu_{as}(COO^-)$
	1394s		$\nu_s(COO^-)$
	1503s		$\delta_s(NH_3^+)$
	1137m		$\rho_r(NH_3^+)$
	458m		ν(Mo-O)
$(NH_4)[MoO(O_2)_2F(leuH)]$ (9)	973s	952	ν(Mo=O)
	950s	940	
	863s	901	ν(O-O) ν_1
	583m	560	ν(Mo-O_2) ν_2
	657s	626	ν(Mo-O_2) ν_3
	1577s		$\nu_{as}(COO^-)$
	1405s		$\nu_s(COO^-)$
	1508s		$\delta_s(NH_3^+)$
	1144m		$\rho_r(NH_3^+)$
	461w		ν(Mo-O)

Table 5.2: Contd.

$(NH_4)[MoO(O_2)_2(oxinate)]$ (10)	950s	ν(Mo=O)
	852s	ν(O-O) ν_1
	573m	ν(Mo-O_2) ν_2
	636m	ν(Mo-O_2) ν_3
	1595m	ν(C=N)
	368m	ν(Mo-O)
	296m	ν(Mo-N)
	1420s	ν(N-H) ν_4

Table 5.3: Electronic spectroscopic data

Compounds	λ_{max} (nm) (ε (dm^3 mol^{-1} cm^{-1}))	
	Π_v^* ----> d_σ^*	Π_h^* ----> d_σ^*
$Na(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$ (1)	308 (491)	227 (11471)
$K(NH_4)[Mo_2O_3(O_2)_4(H_2O)_2].2H_2O$ (2)	303 (1060)	228 (8421)
$(NH_4)_2[MoO(O_2)_2F_2].H_2O$ (3)	309 (1284)	230 (2150)
$Na(NH_4)[MoO(O_2)_2F_2].3H_2O$ (4)	308 (1047)	233 (2586)
$K(NH_4)[MoO(O_2)_2F_2].H_2O$ (5)	310 (801)	232 (2054)
$(NH_4)[MoO(O_2)_2F(glyH)]$ (6)	330 (720)	250 (1782)
$(NH_4)[MoO(O_2)_2F(alaH)]$ (7)	330 (1013)	254 (1796)
$(NH_4)[MoO(O_2)_2F(valH)]$ (8)	310 (631)	228 (1638)
$(NH_4)[MoO(O_2)_2F(leuH)]$ (9)	310 (702)	230 (1833)
$(NH_4)[MoO(O_2)_2(oxinate)]$ (10)	310 (194)	245 (1730)

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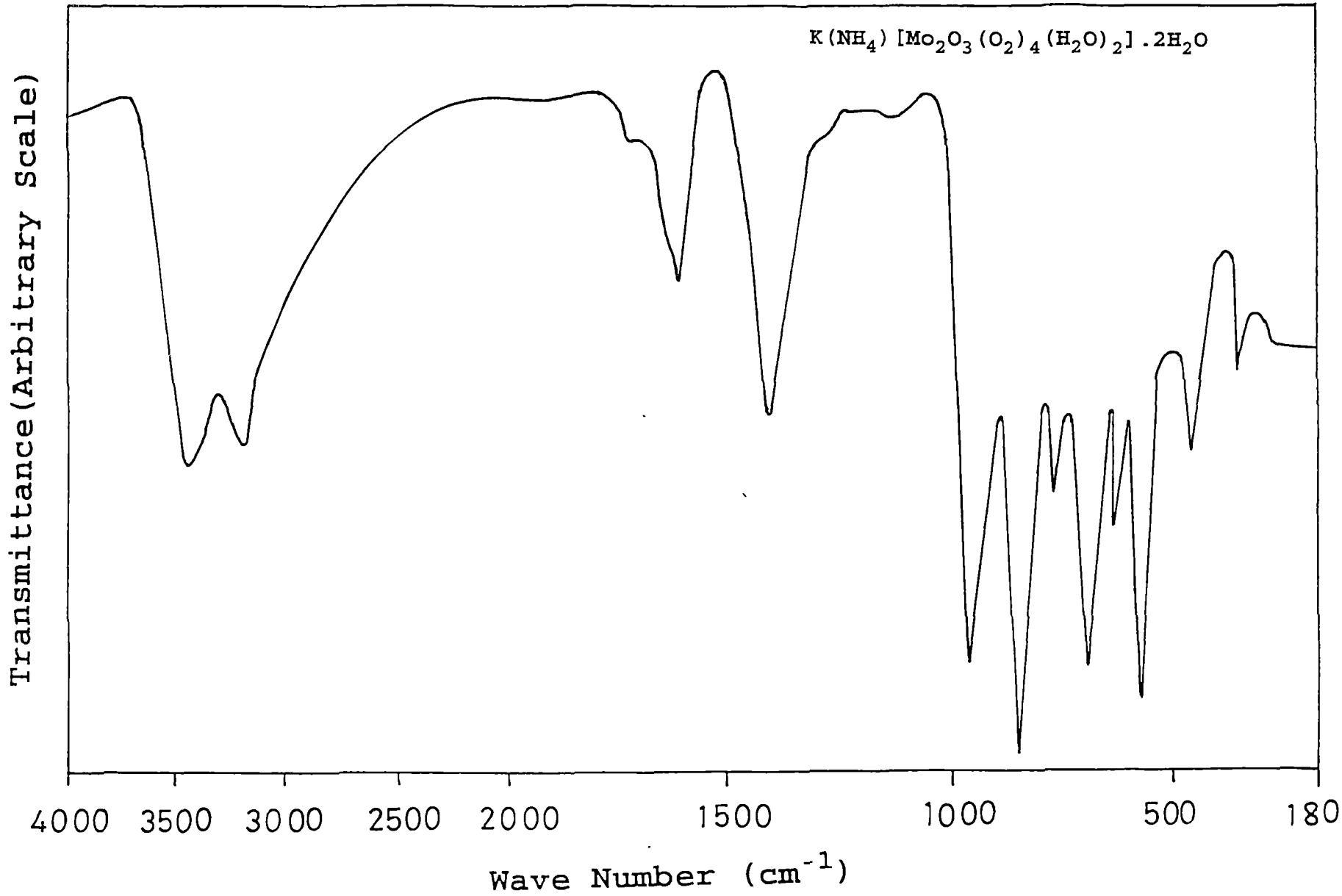


Figure 5.1: IR Spectrum

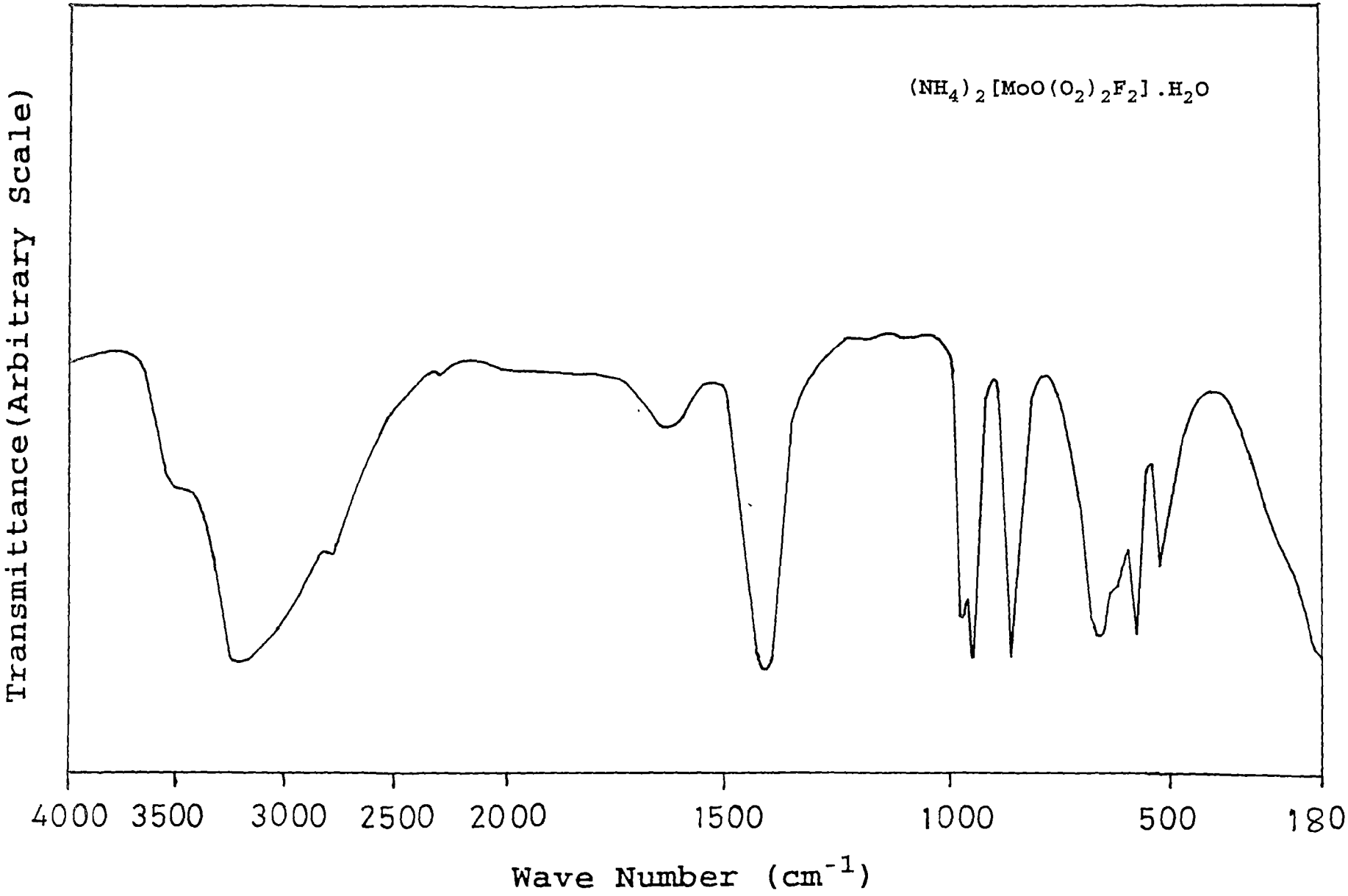


Figure 5.2: IR Spectrum

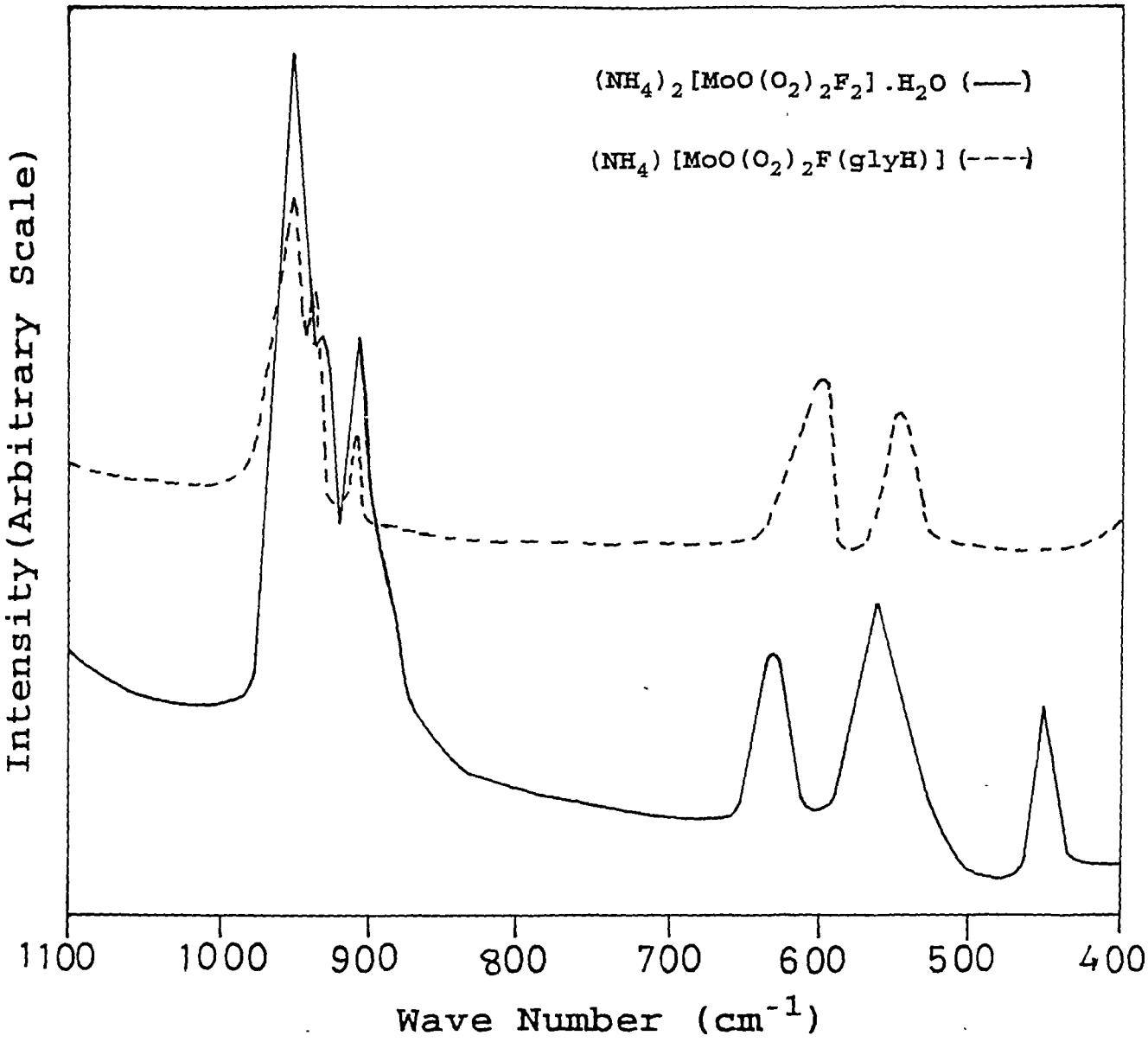


Figure 5.3: Raman Spectra

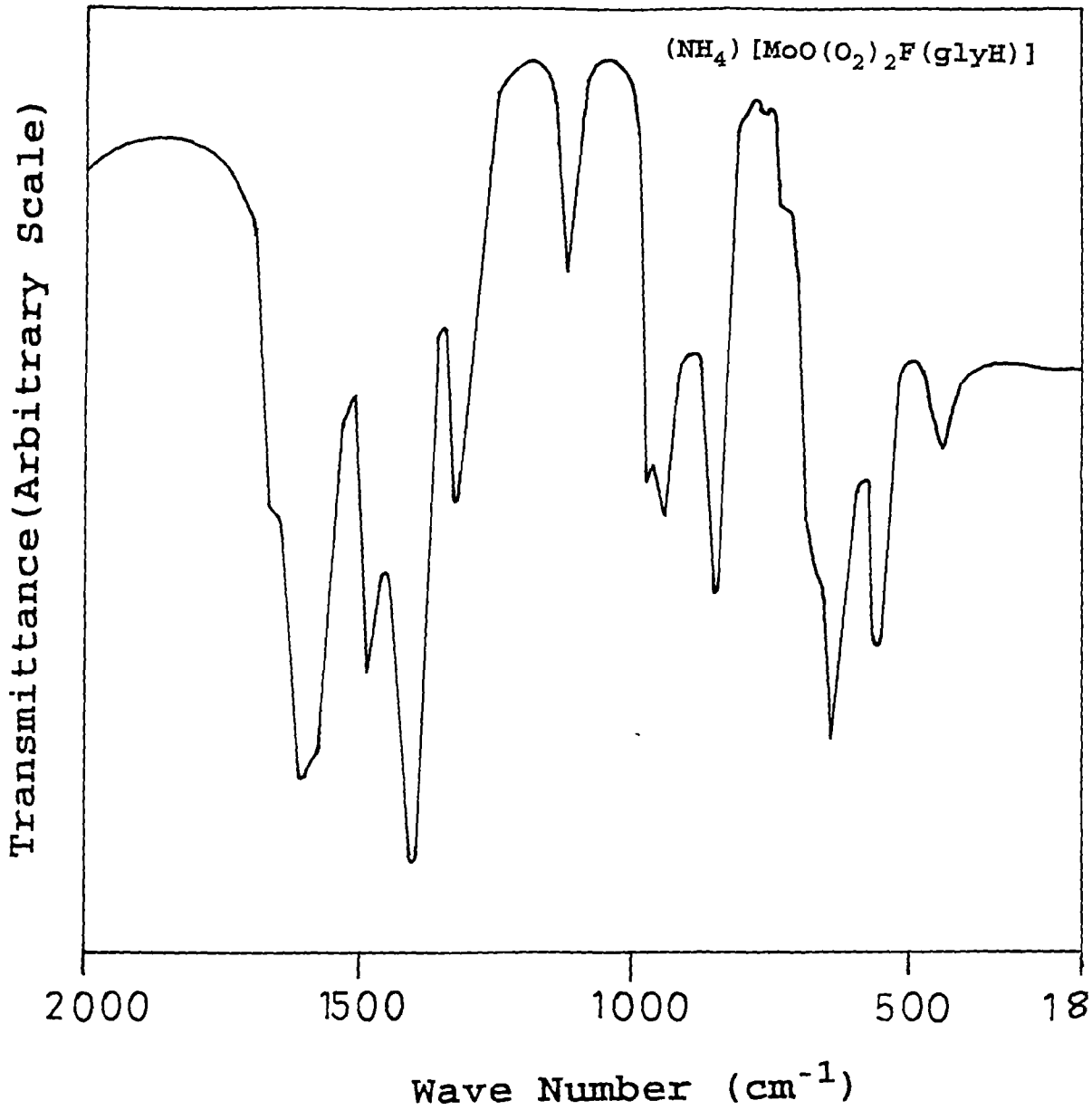


Figure 5.4: IR Spectrum

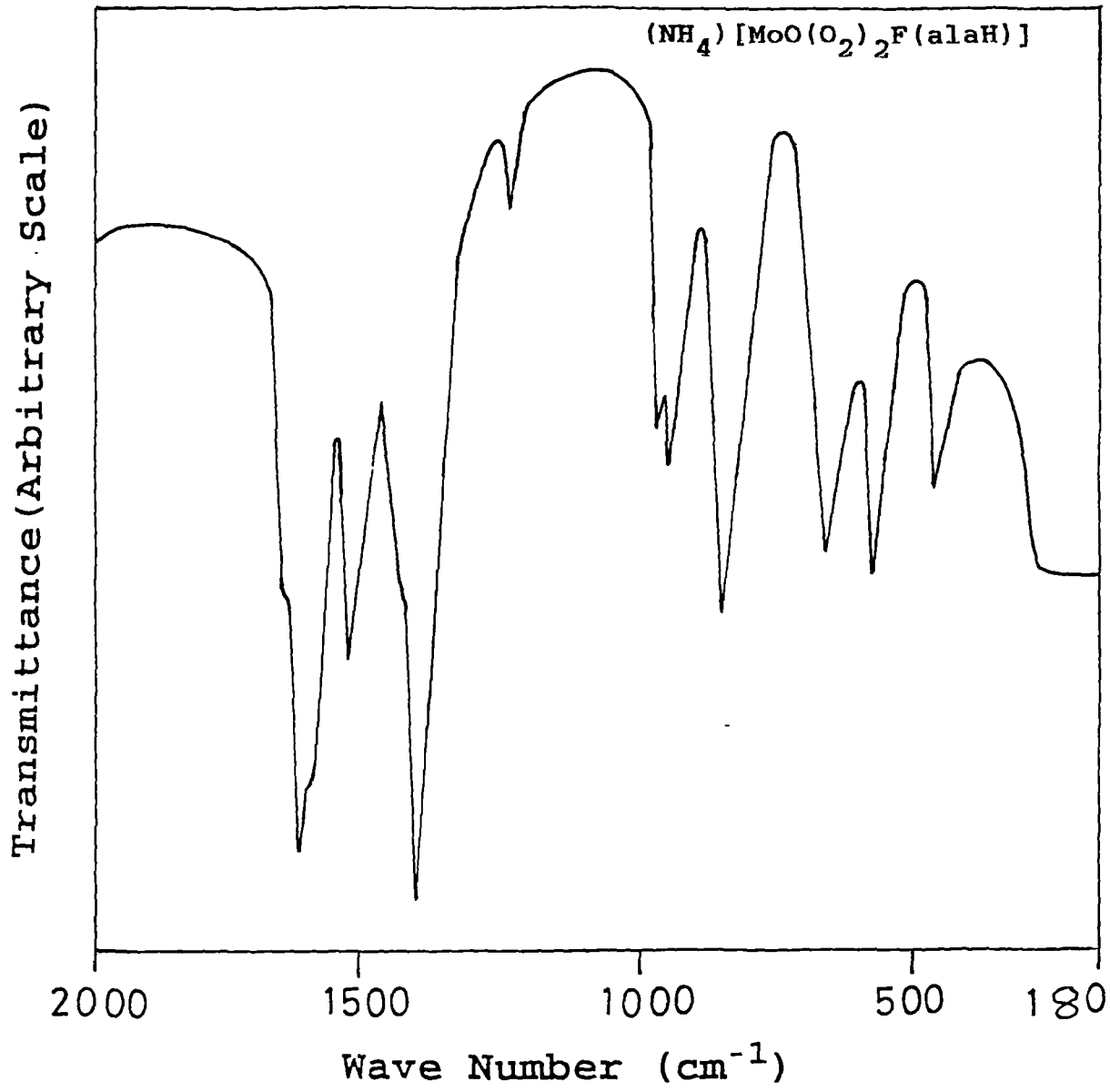


Figure 5.5: IR Spectrum

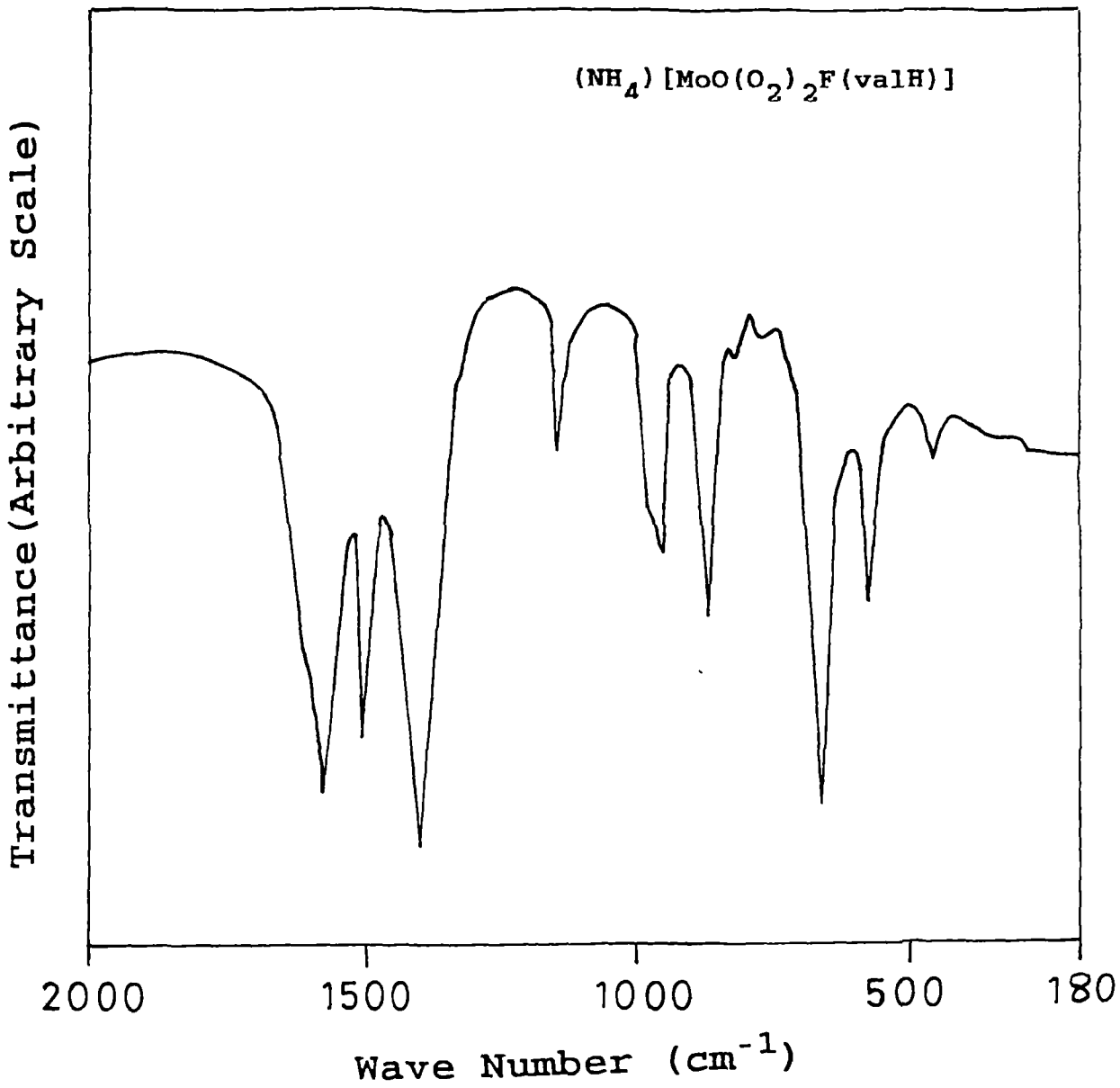


Figure 5.6: IR Spectrum

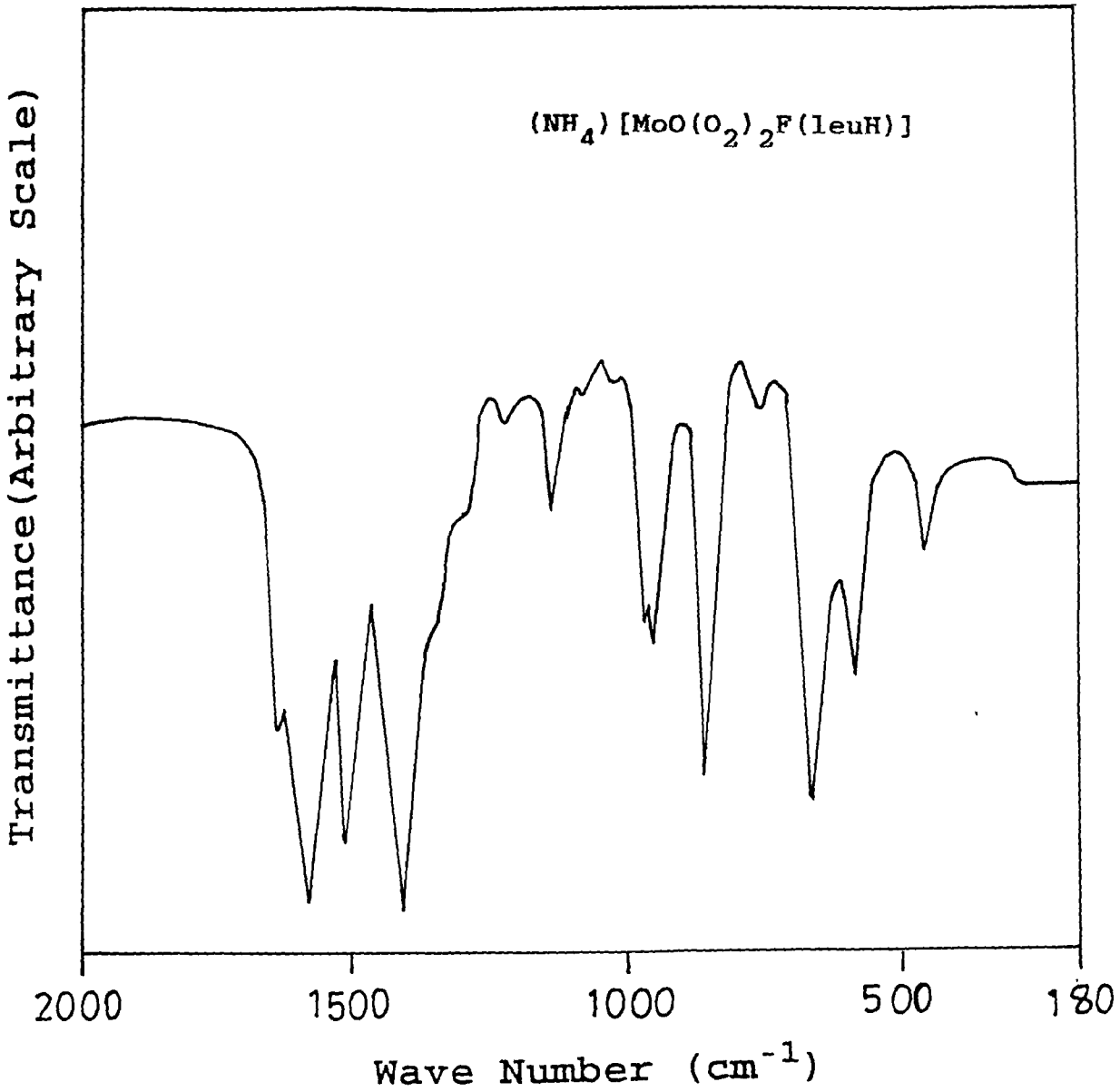


Figure 5.7: IR Spectrum

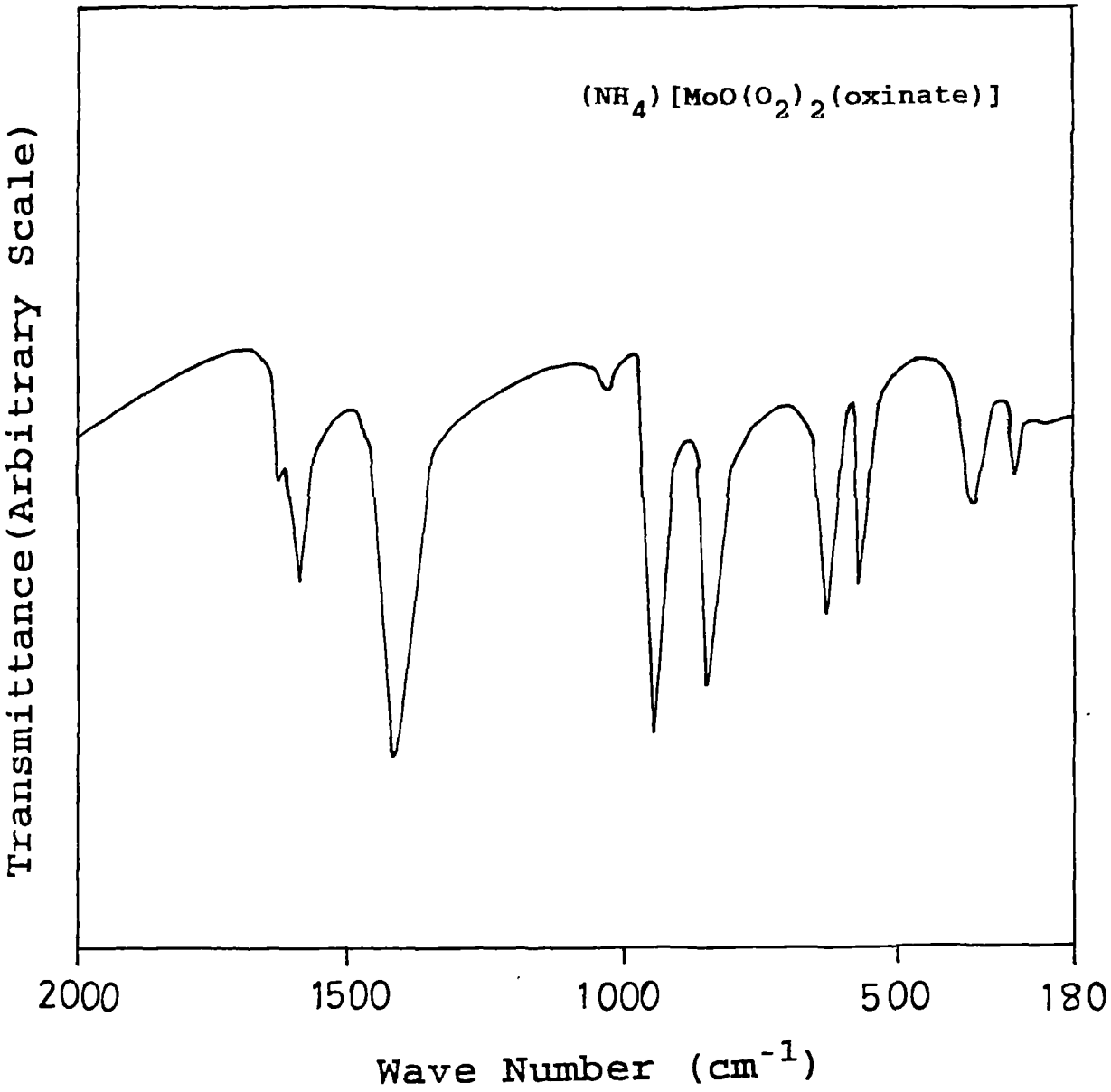


Figure 5.8: IR Spectrum

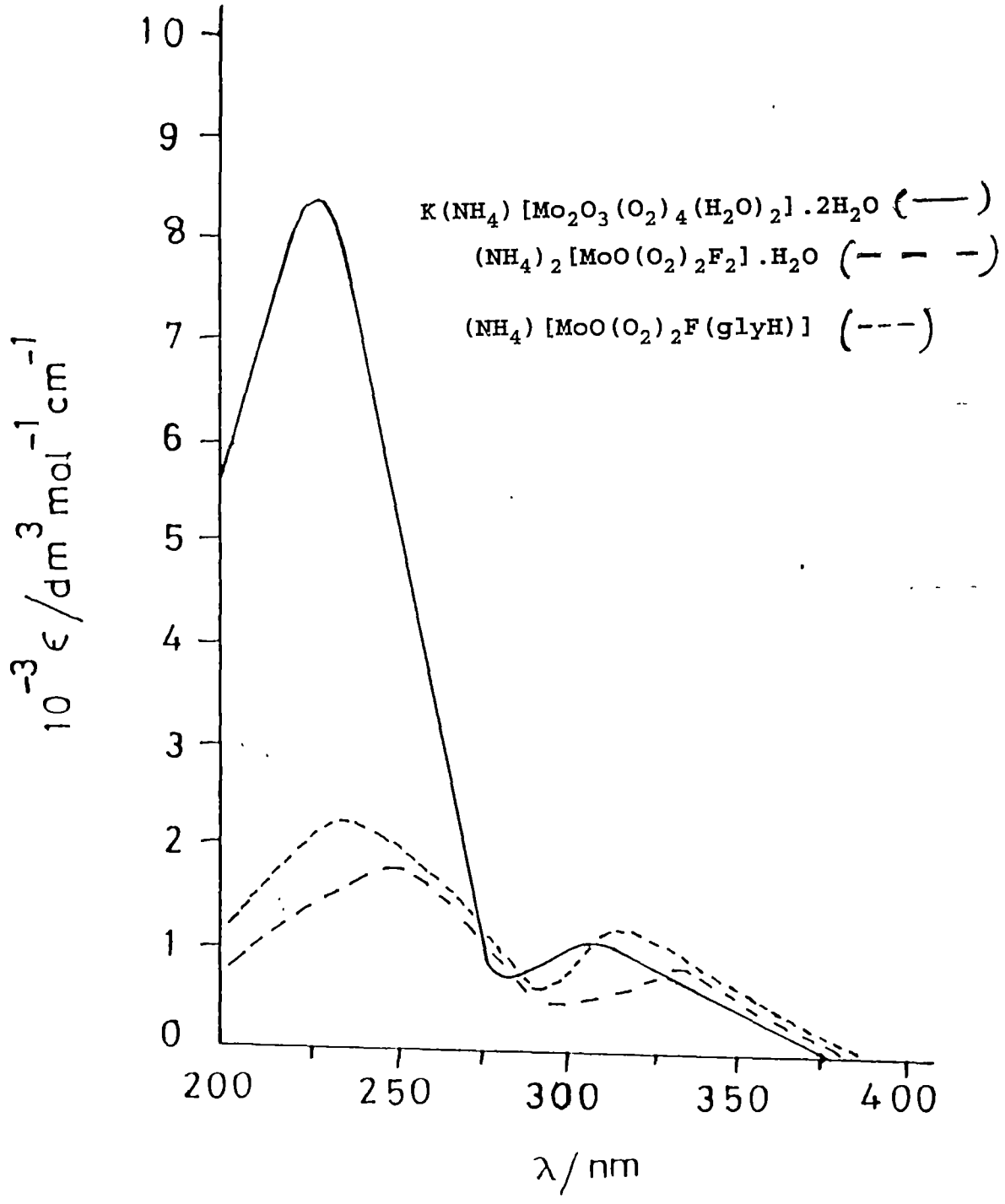


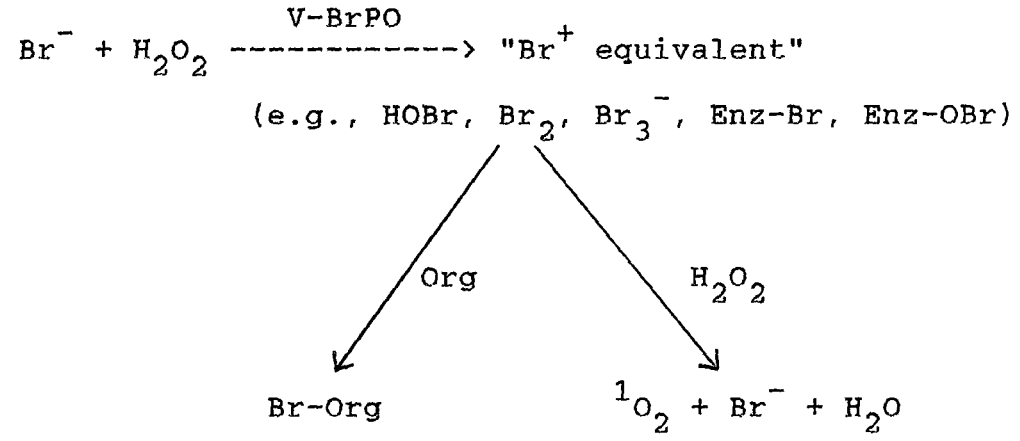
Figure 5.9: Electronic Spectra

CHAPTER VI

Peroxo-Metal Mediated Generation and Trapping of Tribromide (Br_3^-), an Active Brominating Intermediate of Vanadium Bromoperoxidase (V-BrPO) Catalyzed Reaction

The isolation of vanadium bromoperoxidase (V-BrPO), from marine algae,[1-5] which plays a catalytic role in the biosynthesis of a large variety of halogenated marine natural products,[2] has provided a tremendous impetus to studies addressed to biomimics of this enzymatic activity.[6-9] An overall understanding as of now is that V-BrPO catalyzes the oxidation of halides by H_2O_2 producing a two-electron oxidized halogen intermediate species which in turn either halogenates appropriate organic substrates or in the absence of organic substrates reacts with the second equivalent of H_2O_2 generating dioxygen as shown in Scheme I for bromide.[10,11]

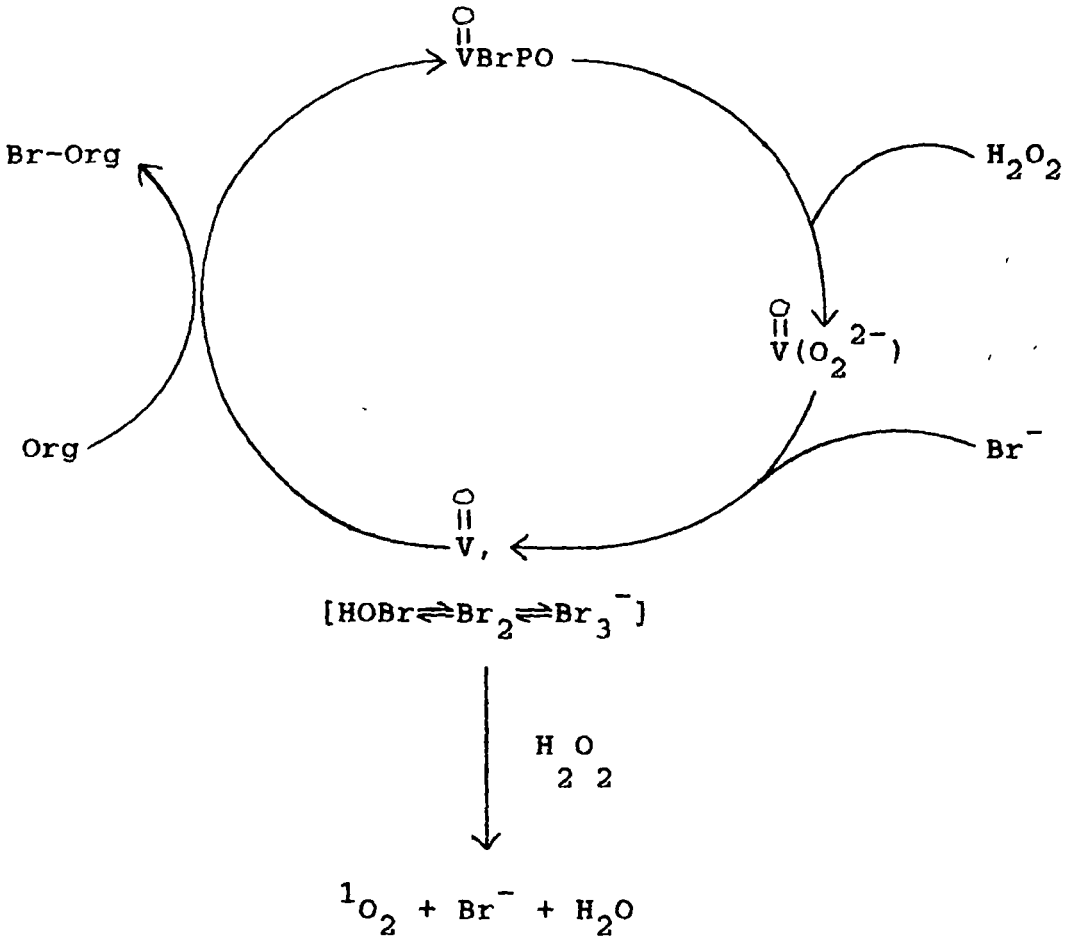
Scheme I: Summary of the General Reactivity of V-BrPO with Bromide



In case of bromide, the oxygen evolved has been identified to be in the singlet spin state.[12] The exact chemical composition of the active oxidant and the active brominating intermediate are not clearly known[6,8] probably because of the rapid formation of an equilibrium mixture of HOBr, Br_2 and Br_3^-.[9]

Vanadium is an essential cofactor in V-BrPO and its role lies primarily in coordination of H_2O_2 causing its activation toward oxidation of halide.[13] A vanadium peroxo intermediate is believed to be responsible for the oxidation of halides.[6,9] It is worthwhile to note that unlike Feheme-BrPO [2,14] the metal centre does not undergo redox cycling[2,15] (**Scheme II**) as no EPR signal is observed during turnove conditions.[2]

Scheme II Catalytic Cycle for V-BrPO with Bromide



The involvement of an oxidized bromine equivalent intermediate is common to all reaction mechanisms proposed for V-BrPO biomimetic reactions with bromide. However, no isolation and structural characterization of such an intermediate have been reported so far. Instability of Br_3^- in aqueous solution[6,16] presumably is a hurdel. In this chapter, we describe the isolation of tribromide, Br_3^-, from aqueous solution obtained as

tetraalkylammonium salts, by peroxo-metal mediated oxidation of bromide in acidic medium. The products have been characterized unambiguously by various techniques including X-ray crystallography, for NBu_4Br_3.

Experimental

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

Generation of Br_3^- and Trapping as NBu_4Br_3

Method I.——— A quantity of 1.0 g (5.5. mmol) of vanadium pentoxide, V_2O_5, was dissolved in 10 cm^3 (97.88 mmol) 30% H_2O_2 under ice-cold conditions. The pH of the solution was measured to be 1. This was then treated with a solution of 7.1 g (22.02 mmol) of tetrabutylammonium bromide, NBu_4Br, in 30 cm^3 water. Immediately the solution turned yellow which on standing for 5 min produced a yellow compound. The reaction mixture was left at room temperature for 1h for complete precipitation. The product was isolated by filtration, washed two or three times with water and dried *in vacuo* over conc. H_2SO_4. Yield 2 g (56%), m.p. 72-75°C. Anal. Calc.(Found) for $C_{16}H_{36}NBr_3$: C, 39.85(39.82); H, 7.54(7.60); N, 2.90(2.91); Br, 49.71 (49.50%). The compound on recrystallization from acetonitrile produced orange-yellow X-ray quality crystals.

Method II.——— In a polyethylene beaker 1.0 g (12.52 mmol) TiO_2 was dissolved in 6.0 cm^3 (143.93 mmol) 48% HF by warming on a steam-bath. The solution was filtered to remove traces of undissolved impurity. To the filtrate was added a 10 cm^3 (97.88 mmol) 30% H_2O_2 followed by the addition of 16.1 g (49.93 mmol) tetrabutylammonium bromide, NBu_4Br, dissolved in 60 cm^3 water, with stirring. Immediately the solution turned yellow and a yellow product began to appear. The reaction mixture was kept at room temperature for 1h for the precipitation to complete. The compound was isolated by vacuum filtration, washed with water and dried *in vacuo* over conc. H_2SO_4. Yield 5.2 g (65%). The compound melted at 72-75°C. anal. Calc.(Found) for $C_{16}H_{36}NBr_3$: C, 39.85(39.86); H, 7.54(7.58); N, 2.90(2.88); Br, 49.71(50%).

Method III.——— To a solution of 1.0 g (5.56 mmol), $H_2MoO_4.H_2O$ in 20 cm^3 (195.77 mmol) 30% H_2O_2 (pH = 1.2) an aqueous solution (30 cm^3) of 7.15 g (22.17 mmol) NBu_4Br was added with stirring. A light-yellow product immediately separated out. The product was isolated by vacuum filtration, washed two times with water and dried *in vacuo* over con. H_2SO_4. This was recrystallized from acetonitrile to afford orange-yellow crystals of NBu_4Br_3. Yield 0.9 g (25.25%). Anal. Calc.(Found) for $C_{16}H_{36}NBr_3$: C, 39.85(39.90); H, 7.54(7.56); N, 2.90(2.91); Br, 49.71(49.50%).

Method IV.——— A quantity of 0.5 g (0.99 mmol) $UO_2(NO_3)_2.6H_2O$ was dissolved in 10 cm^3 water and 0.8 cm^3 (19.19 mmol) 48% HF was added to it followed by the addition of 5 cm^3 (48.94 mmol) 30% H_2O_2. The pH of the reaction was found to be <2. To the resulting yellow solution a 1.3 g (4.03 mmol) NBu_4Br dissolved in 5 cm^3 water was added with stirring. The rest of the methodology was similar to that described under method II. Yield 0.3g (46%); m.p. 72-75°C. Anal. Calc. (Found) for $C_{16}H_{36}NBr_3$: C, 39.85(39.76); H, 7.54(7.54); N, 2.90(2.89); Br, 49.71(49.84%). The possibility of isolating Br_3^- from aqueous solution using tetraethylammonium bromide, NEt_4Br, and cetyltrimethylammonium bromide, $CH_3(CH_2)_{15}N(CH_3)_3Br$, was also explored. So far we have succeeded in obtaining NEt_4Br_3 and $(CH_3)(CH_2)_{15}N(CH_3)_3Br_3$ by method II.

Bromination Reactions with NBu_4Br_3

Bromination of Phenol.——— To a solution of 0.5 g (5.31 mmol) phenol in 15 cm^3 CH_2Cl_2 was added a solution of 5.2 g (10.78 mmol) NBu_4Br_3 in 50 cm^3 CH_2Cl_2. To this 2.5 g (24.98 mmol) $CaCO_3$ was added and the reaction mixture was stirred for 10 min at room temperature. The orange-yellow colour of tribromide disappeared.The solution was filtered and the filtrate concentrated on a steam-bath followed by the addition of *ca.* 100 cm^3 water. An off-white compound precipitated immediately which was isolated by filtration and dried in a vacuum desiccator over conc. H_2SO_4. The product on recrystallization from ethanol

produced a white crystalline compound, m.p. 94°C (lit. 95°C). Yield 0.9 g (51%). NMR data: δ = 5.4, 7.6

Bromination of Benzene. ——— A mixture of 0.25 g (3.20 mmol) benzene, 0.98 g Ag_2SO_4 (3.14 mmol) and 10 cm^3 conc. H_2SO_4 was stirred at room temperature for 10 min followed by the addition of 1.55 g (3.21 mmol) NBu_4Br_3. The reaction mixture was stirred for a further period of 20 min whereupon the solution became colourless. The reaction mixture was then poured into *ca.* 100 g crushed ice and the resulting AgBr was filtered off. The product was extracted with ether and the ether extract was washed several times with water to remove any remaining acid. This was evaporated on a steam-bath to get 1,4-dibromobenzene, m.p. 86-88°C (lit. 87-89°C). NMR data: δ = 7.4. Bromination of phenol red to bromophenol blue has been conducted in solution (1:1 $CH_3CN:H_2O$) and the reaction was followed by electronic absorption spectroscopy.

Elemental Analyzes. ——— Quantitative determination of carbon, hydrogen, nitrogen and bromide was performed as described in Chapter II.

Results and Discussion

Generation and Trapping of Oxidized Bromine Intermediate and General Considerations. The major aim of the present study was to investigate the nature of the oxidized form of bromine generated in a peroxo-metal mediated oxidation of bromide. The peroxo-metal mediated reaction was chosen to establish a probable link between the results of such reactions and V-BrPO enzyme catalyzed process. Strategically the reactants, vanadium(V), hydrogenperoxide and bromide were added in succession. The rationale for this strategy was that a peroxo-vanadium(V) intermediate would first form, thereby activating the peroxide, which would in turn oxidize Br^-. The oxidation of bromide by either vanadium(V) or hydrogenperoxide alone is not considered to be a feasible proposition.

With the above-mentioned background, a reaction of V_2O_5 with H_2O_2 and NBu_4Br was carried out in aqueous medium. The reason for selecting tetrabutyammonium as the counter cation was to bring about an immediate precipitation of the oxidized bromine species on its formation. This was essential as the oxidized bromine was apprehended to be unstable in aqueous solution.

Following the reaction protocol given above, crystalline NBu_4Br_3 was isolated as the product. Obviously, Br_3^- must have been an oxidized bromine species generated in the reaction. The orange-yellow NBu_4Br_3 is stable in air for a prolong period and soluble in a variety of organic solvents.

Interestingly, similar reactions on being conducted involving metals like Ti, Mo and U afforded in each case NBu_4Br_3 as the product (vide Experimental). This implies that the oxidation of bromide to tribromide may not be only vanadium specific but possibly specific to a metal capable of forming a peroxo intermediate. Further notable point in this context is the isolation of tribromide salts with tetraethylammonium(NEt_4^+) and cetyltrimethylammonium ($NCetMe_3^+$) being the cations from analogous reactions of the corresponding bromides. This indicates the importance of a heavy cation in trapping the oxidized bromine in an aqueous medium. All the tribromides obtained by the newer methodology analyzed well.

In addition to all that has been discussed above, it is significant to note that the quaternary ammonium tribromides are excellent brominating agents for organic substrates. Indeed they are preferred over the conventional reagent, bromine, particularly because of the ease of operation and handling, maintenance of reagent stoichiometry and stability. The existing methods for the preparation of tribromides require stringent conditions because of the involvement of Br_2 and/or HBr. Incidentally, the present methodology not only provides a very simple route to such reagents but also does not make use of any hazardous reagents. It is anticipated that the present procedure will be a method of choice for the synthesis of tribromide reagents useful in synthetic organic chemistry.

Electronic Spectra. The tribromide is easily characterized by its typical electron absorption spectrum recorded on a freshly prepared solution in dry acetonitrile. The strong absorption at 267 nm (ε = 52000 M^{-1} cm^{-1}) with a shoulder at 400 nm (ε = 145 M^{-1} cm^{-1}) is typical of Br_3^- [9,21] (Figure 6.1).

IR and laser Raman Spectroscopies. For linear triatomic molecules bands due to three normal modes of vibrations, viz., two stretching ν_1 , and ν_3, and a bending mode, $_2$,[22a] are expected. Typically in the IR spectrum (Figure 6.2) of NBu_4Br_3 the bands at 171 and 191 cm^{-1} have been assigned respectively to ν_1 and ν_3 modes of vibrations.[22b] The ν_2 mode is expected to occur (*ca.* 50 cm^{-1}) below the region scanned in the present studies. The occurrence of bands at 146 and 164 cm^{-1}, owing to ν_1 and ν_3 modes respectively, in the Raman spectrum (Figure 6.3) of the compound further supports our view regarding linearity of the tribromide.

X-ray Crystallography. The molecular structure of NBu_4Br_3 has been shown in Figure 6.4. Table 6.1 summarizes the crystal data and details of structure solution and refinement for NBu_4Br_3. The compound crystallizes in the monoclinic space group C2/c. As evident the tetrabutylammonium cation and the tribromide anion are present in the molecule. The nitrogen atom of the cation (NBu_4^+) resides on a crystallographic twofold axis. Importantly, the central Br atom of the tribromide ion lies on

centre of symmetry. Half of the remaining atoms are unique. The Br-Br-Br unit is totally symmetrical with the Br2a-Br1-Br2 angle being 180°. The two Br-Br distances are identical (2.533(3)°). Bond angles and bond distances have been listed in **Table 6.2** and 6.3, respectively. To the best of our knowledge this is the second example of a compound containing completely symmetrical tribromide ion having perfectly linear Br_3^- unit with identical Br-Br distances, the first example being $[VBr_2(CH_3CN)_4]Br_3$.[23]

Conductance Measurements.——— The solution (10^{-3}M) electrical conductance measurements of tribromide salts in dry acetonitrile gave values in the range 150-160 mho cm^2 mol^{-1}. This is in full agreement with their 1:1 electrolytic nature.[24]

Bromination Reactions.——— In an attempt to ascertain the efficacy of tribromide compound generated by our method we have performed some typical bromination reaction runs of phenol, benzene and phenol red with NBu_4Br_3. The bromination of phenol and benzene to 2,4,6-tribromophenol and 1,4-dibromobenzene, respectively is satisfactory both in terms of reaction time and yield. In a stoichiometric reaction, phenol red (sodium salt) in aqueous acetonitrile has been readily converted to bromophenol blue by NBu_4Br_3. The reaction was monitored by UV-Vis spectroscopy. The maximum at 420 nm typical of phenol red disappeared in favour of 588 nm characteristic of bromophenol blue with the establishment of an isosbestic point at 485 nm under conditions indicated in **Figure 6.5.** It may be mentioned in

passing that this reaction is used to assay activity of haloperoxidase enzymes by electron absorption spectroscopy.[8,25]

Concluding Remarks

The present investigation provides a solid evidence that tribromide (Br_3^-) is formed in the peroxo-metal mediated oxidation of bromide and that the tribromide permits isolation from an aqueous solution under the present experimental conditions. In other words Br_3^- is evidently an intermediate involved in the V-BrPO catalyzed biomimetic reaction. The reactivity obtained here bears relevance to vanadium bromoperoxidase enzyme reactions. Further studies addressed to the synthesis of some other salts of Br_3^- and comparative studies in terms of bromination of a variety of organic substrates are now underway in our laboratory. The results of these studies will be reported elsewhere.

Table 6.1: Crystal data and details of the structure solution and refinement for NBu_4Br_3

Empirical formula	$C_{16}H_{36}Br_3N$
M	482.23
Crystal size/mm	0.42 x 0.46 x 0.38
Crystal system	Monoclinic
Space group	C2/c
a/Å	12.975(7)
b/Å	10.371(6)
c/Å	16.220(9)
β°	93.99(4)
$U/Å^3$	2177(2)
Z	4
$D_c/g\ cm^{-3}$	1.471
μ(Mo-Kα)/mm^{-1}	5.553
F(000)	976
T/K	295
2θ range/°	30.0 to 45.0
Scan type	ω
h, k, l	$-12<h<12$, $0<k<10$, $0<l<16$
Reflections collected	1570
Observed reflections ($F>6.0\sigma(F)$)	483
Weighing scheme	$W^{-1} = \sigma^2(F) + 0.0005F^2$
Number of parameters refined	73
R	0.0580
R_w	0.0580
Goodness of fit	1.97
Largest difference peak/e $Å^{-3}$	0.53
Largest difference hole/e $Å^{-3}$	-0.64

Table 6.2: bond angles (°)

Br(2)-Br(1)-Br(2A)	180.0(1)	C(1)-N(1)-C(5)	110.8(9)
C(1)-N(1)-C(1A)	105.2(17)	C(5)-N(1)-C(1A)	112.0(9)
C(1)-N(1)-C(5A)	112.0(9)	C(5)-N(1)-C(5A)	106.2(18)
C(1A)-N(1)-C(5A)	110.8(9)	N(1)-C(1)-C(2)	116.3(15)
C(1)-C(2)-C(3)	110.4(15)	C(2)-C(3)-C(4)	111.6(16)
N(1)-C(5)-C(6)	115.4(14)	C(5)-C(6)-C(7)	111.5(15)
C(6)-C(7)-C(8)	113.6(16)		

Table 6.3: Bond angles (A)

Br(1)-Br(2)	2.533(3)	Br(1)-Br(2A)	2.533(3)
N(1)-C(1)	1.519(20)	N(1)-C(5)	1.513(20)
N(1)-C(1A)	1.519(20)	N(1)-C(5A)	1.513(20)
C(1)-C(2)	1.536(23)	C(2)-C(3)	1.510(26)
C(3)-C(4)	1.559(24)	C(5)-C(6)	1.530(24)
C(6)-C(7)	1.494(25)	C(7)-C(8)	1.497(27)

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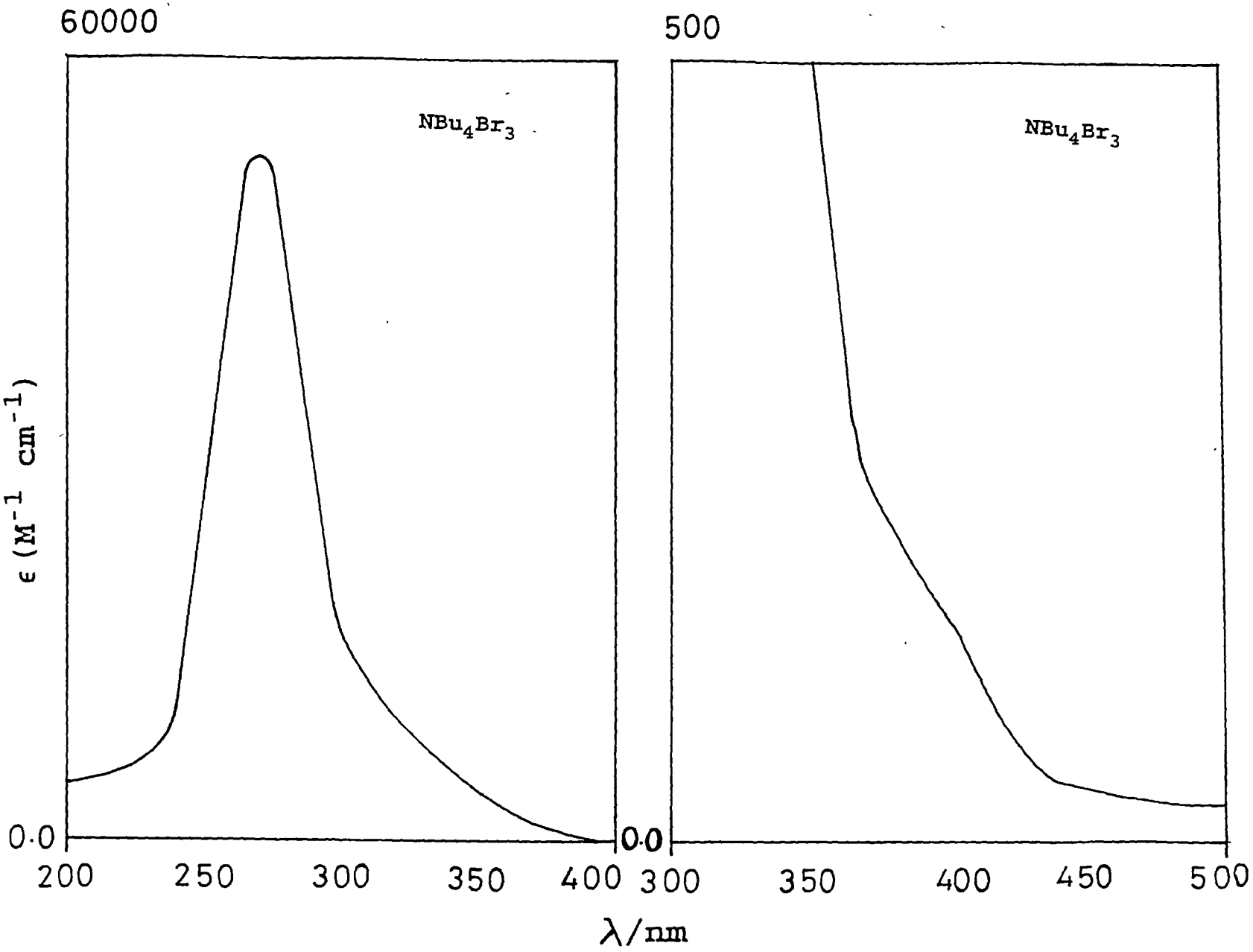

Figure 6.1: Electronic Spectrum

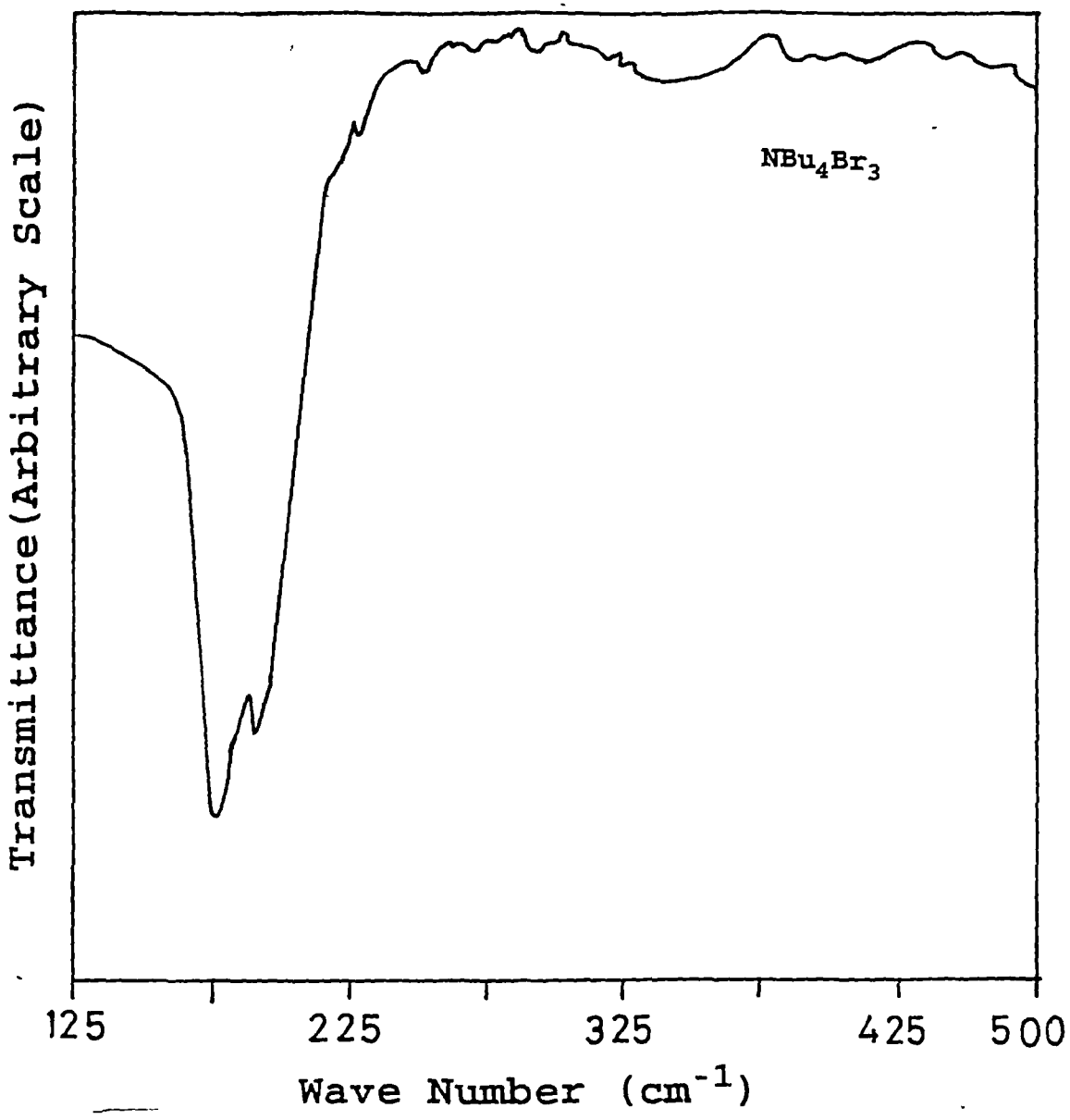

Figure 6.2: IR Spectrum

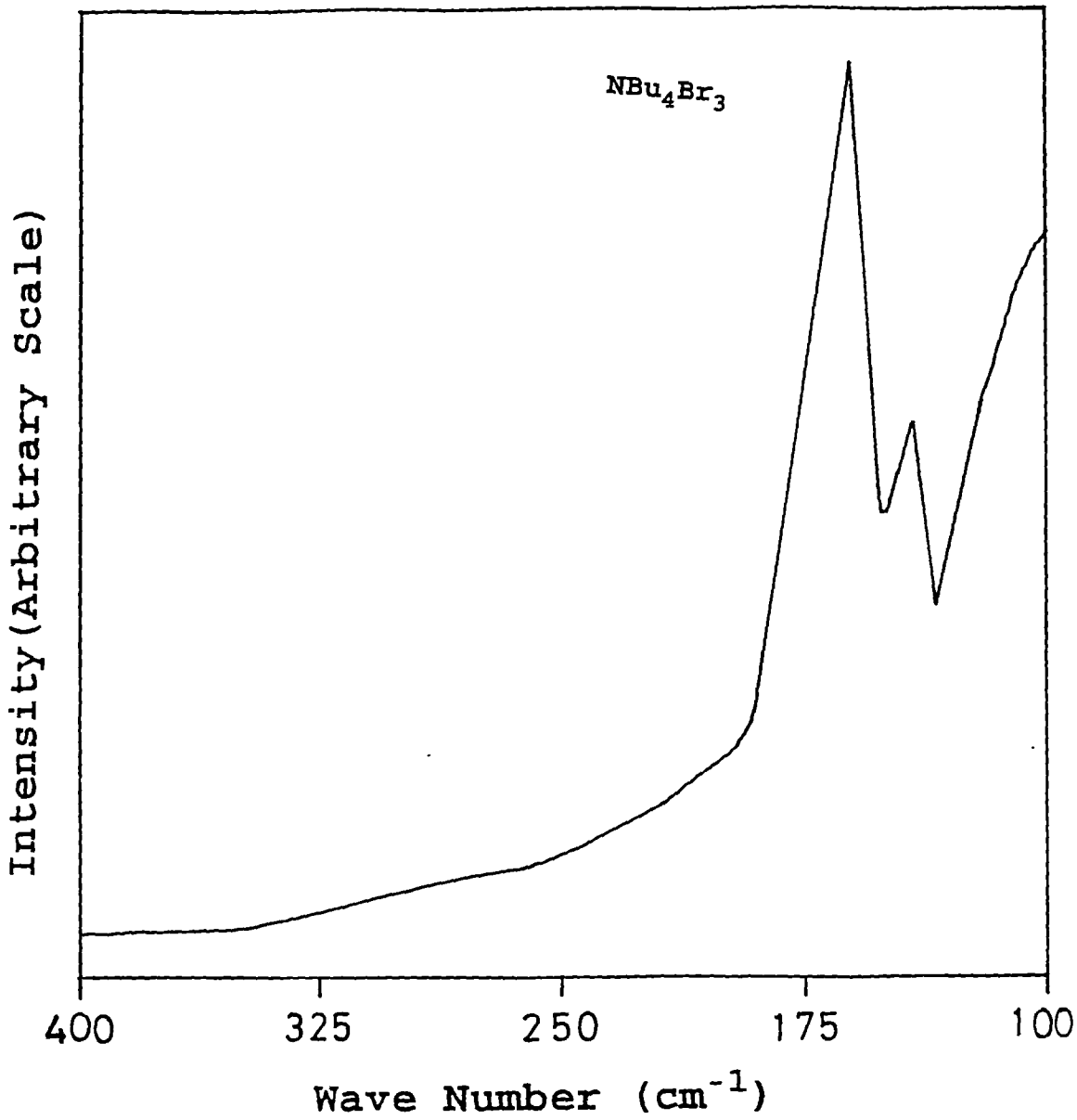

Figure 6.3: Raman Spectrum

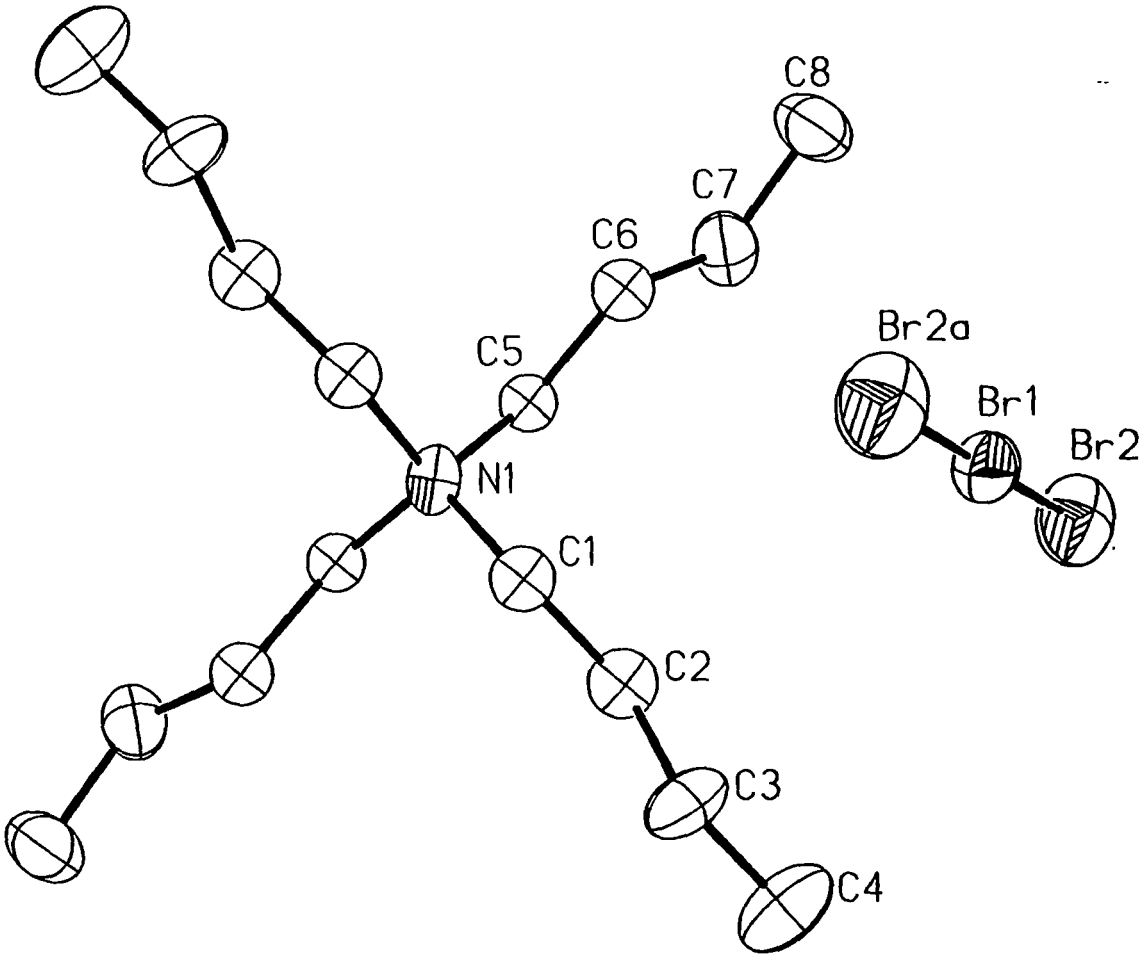

Figure 6.4: ORTEP Diagram of NBu_4Br_3

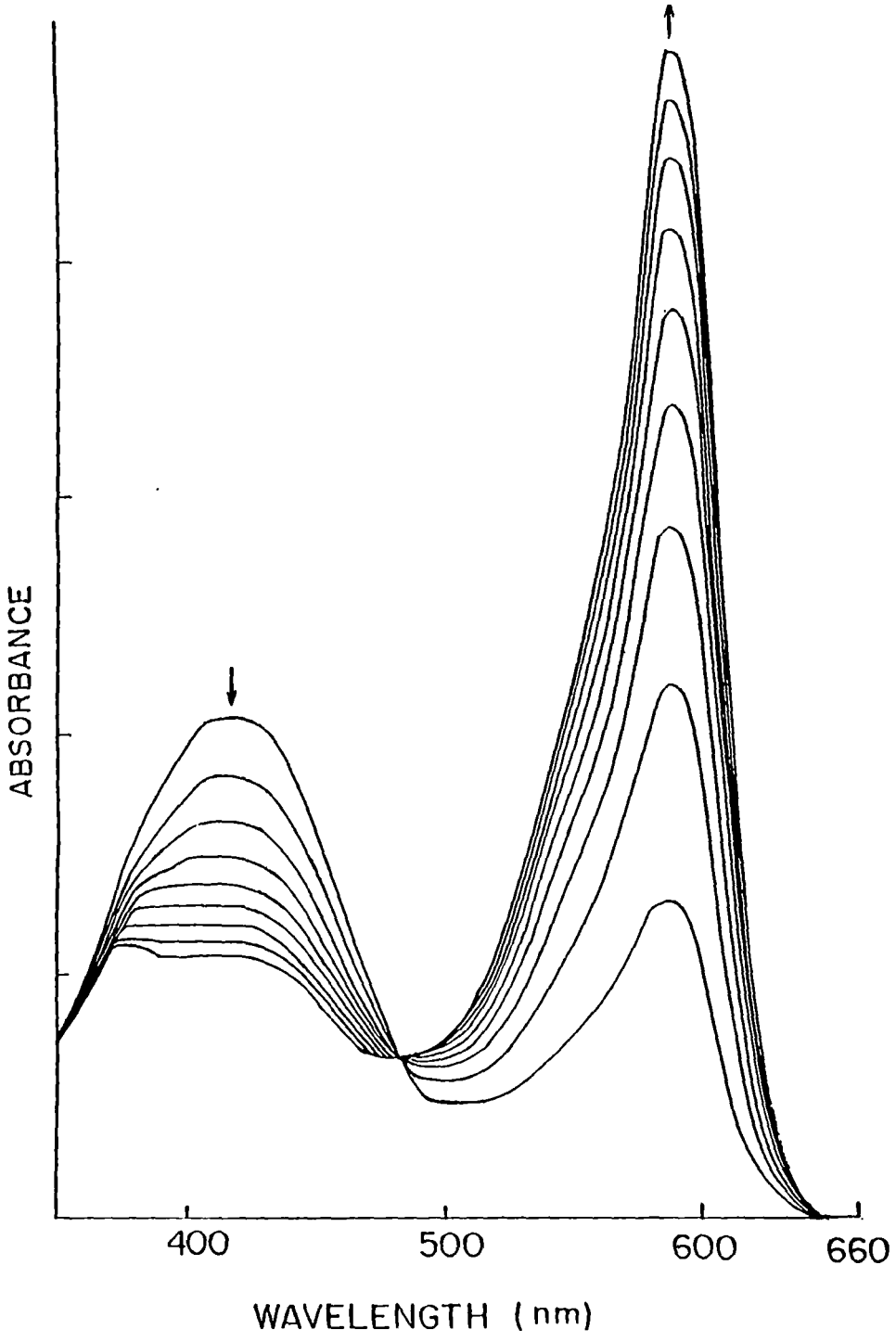

Figure 6.5: Spectral Changes at 2min Intervals for the Bromination of Phenol Red (λ_{max} 420nm) to Bromophenol Blue (λ_{max} 588 nm)

APPENDIX

LIST OF PUBLICATIONS

1. Occurrence of Manganese(III) Intermediate in the $[MnO_4]^-$-SO_2 Redox Reactions

   C. Bhattacharjee, M.K. Chaudhuri, G.C. Mandal, P.C. Paul and P. Srinivas

   J. Chem. Soc., Dalton Trans., 1993, 3497.

2. Direct Synthesis of Anhydrous Alkali-Metal Tetrafluorodioxouranates(VI), $A_2[UO_2F_4]$, and the First Synthesis of Alkali-Metal Diaquatetrafluorodioxouranate(VI) Monohydrates, $A_2[UO_2F_4(H_2O)_2].H_2O$ (A = Na, K or NH_4)

   M. Bhattacharjee, M.K. Chaudhuri, G.C. Mandal and P. Srinivas

   J. Chem. Soc., Dalton Trans., 1994, 2693.

3. Nonaqueous Synthesis and Thermogravimetric Studies of Tris(acetylacetonato)metals, $M(acac)_3$ [M = Cr, Mn or Ru]

   M.K. Chaudhuri, G.C. Mandal, P.C. Paul, A. Rumnong and P. Srinivas

   Chem. Mater. : In Press.

4. Reactivity Investigations of Some Chosen Peroxo-vanadium(V), Manganese(III) and Chromium(VI) Compounds

   M.K. Chaudhuri, S.K. Chettri, G.C. Mandal, P.C. Paul, S.B. Paul and P. Srinivas

   Proc. Ind. Acad. Sci., 1995, **107**, 305.