SYNTHESIS AND STRUCTURAL ASSESSMENT OF HETERO-LIGAND—PEROXO, ACETATO, AND ACETYLACETONATO COMPLEXES OF URANIUM(VI) AND OXALATO AND MIXED-LIGAND—FLUORO COMPLEXES OF MANGANESE(III)

ABSTRACT

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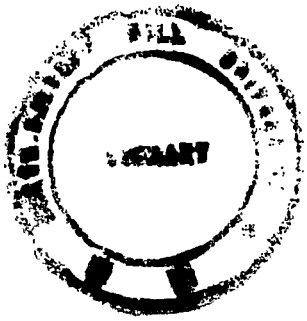

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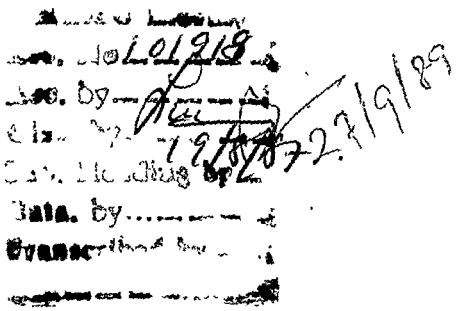
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ABSTRACT

Synthesis and Structural Assessment of Hetero-Ligand-Peroxo, Acetato, and Acetylacetonato Complexes of Uranium(VI) and Oxalato and Mixed-Ligand-Fluoro Complexes of Manganese(III)

Abstract

The present thesis deals with the results of studies involving the syntheses and assessment of structures of some hetero-ligand-peroxo, acetato and acetylacetonato complexes of uranium(VI), and the synthesis and physico-chemical studies of oxalato and mixed-ligand-fluoro complexes of manganese(III). The thesis comprises of a total of eight Chapters. The results described in Chapters 3-8 have been grouped into two, namely, Part A and Part B. While Part A, consisting of Chapters 3-5, deals with the studies on the above-mentioned aspects of uranium chemistry, Part B, which includes Chapters 6-8, contains the results of studies on manganese(III) chemistry.

Chapter 1 presents a brief introduction pertaining to the work embodied in the thesis. The importance of and the interest in the studies of peroxo-metal chemistry in general, and heteroligand peroxouranate(VI) compounds in particular, and the problems associated with the reported methods of syntheses

of acetato, and acetylacetonato complexes of uranium are highlighted in this Chapter. Another piece of a problem, as emphasized in this Chapter, is the lack of evidence regarding the mass spectrometric studies of bis(acetylacetonato)dioxo-uranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$. Apart from uranium, the difficulties encountered in stabilizing manganese(III) in an aqueous medium, and the importance of F^- ligand in stabilizing this particular oxidation state of the metal both in solution as well as in solid state have been accentuated in this Chapter. Peculiarities encountered with structural and magnetic properties of some fluoro and mixed-fluoro complexes of manganese(III) are highlighted. This Chapter also projects the scope of work on the chosen aspects of uranium and manganese chemistry.

Chapter 2 describes the details of the methods of elemental analyses, and the instruments/equipment used for characterization and structural assessment of the newly synthesised compounds.

PART A

Synthesis and structural assessment of alkali-metal and ammonium difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ ($A = NH_4$ or Cs) and alkali-metal difluorodioxoperoxo-uranate(VI) monohydrates, $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb), constitute the subject matter of Chapter 3.

The synthesis of $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb), were achieved from the reaction of the product obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with NH_4OH or KOH, with AF (A = NH_4, Rb or Cs) or KF, 30% H_2O_2, and a very small amount of 40% HF in the mol ratio of $UO_2(NO_3)_2.6H_2O$: AF : H_2O_2 at 1 : 4 : 110.8 at pH 6.5-7. The compounds have been characterized by chemical analyses, magnetic susceptibility measurements, and IR spectroscopic studies. The IR spectra provide evidence for the occurrence of translinked O=U=O, coordinated peroxide, and coordinated fluoride. Further the spectra suggest that the peroxo group is bonded to the UO_2^{2+} center in a triangular bidentate (C_{2v}) manner. The complex $[UO_2(O_2)F_2]^{2-}$ may have a polymeric structure through -U-F-U-F-U- chains.

Chapter 4 of the thesis provides an account of synthesis and physico-chemical studies of alkali-metal dioxoperoxo(carbonato)uranate(VI) monohydrates, $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K), alkali-metal and ammonium dioxoperoxo(sulphato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4), and molecular complex peroxouranates $[UO_2(O_2)L\text{-}L]$ (L-L = ethylenediamine (en), 2,2'-bipyridine (bipy), 1,10-phenanthroline (o-phen), and $[UO_2(O_2)glyH]$ (glyH = glycine). The complexes $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K) have been synthesised

from the reaction of the product obtained by treating $UO_2(NO_3)_2.6H_2O$ with AOH and $AHCO_3$ (ratio $U:CO_3^{2-}$ = 1:4) with an excess of 30% H_2O_2 at pH 7-8. The presence of trans O=U=O, triangular bidentate O_2^{2-} and chelated CO_3^{2-} groups in $[UO_2(O_2)(CO_3)]^{2-}$ has been ascertained from the results of IR and laser 'Raman (lR) spectroscopic studies. The complex $A_2[UO_2(O_2)(CO_3)].H_2O$ can be dehydrated at ca 100 °C.

The syntheses of yellow microcrystalline alkali-metal and ammonium dioxoperoxo(sulphato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4 or Na) have been achieved from the reaction of the product obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with alkali-metal or ammonium hydroxide, AOH, with 30% H_2O_2 and aqueous sulphuric acid, in mol ratio $UO_2(NO_3)_2.6H_2O:H_2O_2:SO_4^{2-}$ of 1:111:5, at pH 6 maintained by the addition of the corresponding alkali-metal or ammonium hydroxide. Precipitation of the compound was completed by the addition of ethanol. IR and lR spectra suggest that peroxide (O_2^{2-}) and SO_4^{2-} ions in $[UO_2(O_2)SO_4(H_2O)]^{2-}$ are bonded to the UO_2^{2+} center in a bridging and in a monodentate manner, respectively. The H_2O molecule is also coordinated to the uranyl center. The complex peroxo(sulphato)uranates are diamagnetic in nature and are practically insoluble in water. They are stable upto 110 °C. The complex species $[UO_2(O_2)SO_4(H_2O)]^{2-}$ very likely has a hexacoordinated polymeric structure through a -U-O-O-U-O-O-U- chain containing peroxide bridges.

The synthesis of molecular peroxouranates $\lceil UO_2(O_2)L\text{-}L\rfloor$ (L-L = o-phen or bipy) was accomplished from the reaction of an aqueous solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$, with an ethanolic solution of o-phen or bipy, and an excess of H_2O_2, with the ratio of U:o-phen or bipy being maintained at 1:1, at pH 3.5-4. The infrared spectra provide evidence for the presence of triangular bidentate O_2^{2-} and chelated bidentate o-phen or bipy ligands in the compounds. The compounds are insoluble in water and practically insoluble in organic solvents at room temperature. The compounds $\lceil UO_2(O_2)en\rfloor$ and $\lceil UO_2(O_2)glyH\rfloor$ were synthesised from the reaction of the product, obtained by treating an aqueous solution of $UO_2(NO_3)_2 \cdot 6H_2O$ with aqueous ammonia, with a small amount of aqueous sulphuric acid, ethylenediamine(en) and glycine (glyH), respectively, and an excess of 30% H_2O_2. The suitable pH for the synthesis of $\lceil UO_2(O_2)glyH\rfloor$ was found to be ca 6.5, while that for $\lceil UO_2(O_2)en\rfloor$ was ascertained to be ca 9. The IR spectra of $\lceil UO_2(O_2)en\rfloor$ and $\lceil UO_2(O_2)glyH\rfloor$ exhibit bands characteristic of $\nu(U{=}O)$ (translinked O=U=O), $\nu(O\text{-}O)$, and $\nu(U\text{-}O_2)$ in addition to the absorptions originating from the presence of coordinated en and glyH in the respective cases. While en in the former is bonded to the UO_2^{2+} center in a chelated fashion, glyH in the latter occurs in its Zwitterionic form and coordinates with the metal center through its carboxylic oxygen atom. The spectra also provide strong

evidence for the presence of a triangularly bonded (C_{2v}) peroxide (O_2^{2-}) in each of the complexes. The compounds are all diamagnetic in nature in accord with the presence of hexavalent uranium.

Reported in Chapter 5 are new method of syntheses of alkali-metal and ammonium triacetatodioxouranates(VI), A$[UO_2(CH_3COO)_3]$ (A = Na, K, or NH_4), diacetatodioxouranate(VI) dihydrate $[UO_2(CH_3COO)_2].2H_2O$, and bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$. Also reported in this Chapter is an interpretative account of the results of electron ionization mass spectrometric studies of $UO_2(C_5H_7O_2)_2$.

The A$[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4) compounds have been synthesised from the reaction of the product, obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with NaOH or KOH or aqueous ammonia, with ACH_3COO (A = Na, K or NH_4) and a small amount of 10% acetic acid in the mol ratio of $UO_2(NO_3)_2.6H_2O$:ACH_3COO as 1:3. The synthetic reactions were conducted at pH 5. The synthesis of $[UO_2(CH_3COO)_2].2H_2O$ has been achieved from the reaction of the product, obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with aqueous ammonia, with an excess of glacial acetic acid. Characterization of the compounds were made by elemental analyses and IR spectroscopic studies.

A direct method for the synthesis of bis(acetylacetonato)-dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$, has been developed. The new method does not require any buffer. The electron ionization (EI) mass spectra of $UO_2(C_5H_7O_2)_2$ showed a molecular ion signal at m/z 468 without indication of any association in the gaseous state. The molecular ion $[UO_2(C_5H_7O_2)_2]^{+\bullet}$ loses either $CH_3^\bullet$ and $C_4H_4O_2$, or $OCCH_2$ and undergoes internal reduction to give $[UO_2(C_5H_7O_2)]^{+\bullet}$. The radical ion $[UO_2(C_5H_7O_2)]^{+\bullet}$ suffers a sequential loss of $CH_3^\bullet$ and $C_4H_4O_2$ to produce ultimately the bare species $[UO_2]^+$.

PART B

Chapter 6 of the thesis deals with a direct synthesis of potassium tris(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$. The new method of synthesis involves a reaction among MnO(OH), $H_2C_2O_4$, and $K_2C_2O_4$, in the ratio of 1:1.5:1.5, at ca 0°C directly giving $K_3[Mn(C_2O_4)_3].3H_2O$ in a high yield. The identity of the compound has been ascertained on the basis of the results of elemental analyses, magnetic susceptibility measurements, electronic and IR spectroscopic studies. Evidence for the existence of the complex $[Mn(C_2O_4)_3]^{3-}$ ion in solutions in the presence of countercations like Na^+, Rb^+, Cs^+ or NH_4^+ has also been provided in this Chapter. Isolation of the corresponding salts in the solid state was not possible owing to their instability.

Synthesis and assessment of structures of a number of new mixed ligand fluoro complexes of manganese(III) of the types $A_3[MnF_2L_2].3H_2O$ ($L = C_2O_4^{2-}$, A = K; $L = HPO_4^{2-}$, A = Na, K or NH_4), and $A[MnF_4L_n].3H_2O$ (L = EDTA, n = 1, A = K; L = glyH, n = 2, A = Na, K or NH_4), form the subject matter of Chapter 7.

Synthesis of the compounds were accomplished by the following methods:

(i) $K_3[Mn(C_2O_4)_2F_2].3H_2O$ was obtained from the reaction of $KMnO_4$ with $H_2C_2O_4$, and KF in the ratio of 1:4:2 at ca 0°C in the absence of light;

(ii) $A_3[Mn(HPO_4)_2F_2].3H_2O$ (A = Na, K or NH_4) was prepared from the reaction of MnO(OH) with H_3PO_4 and AF;

(iii) $K[Mn(EDTA)F_4].3H_2O$ was synthesised from the reaction of MnO(OH), 48% HF, KF, and ethylenediaminetetra-acetic acid (EDTA); and

(iv) $A[Mn(glyH)_2F_4].3H_2O$ (A = Na, K or NH_4) was obtained from the reaction of MnO(OH), 40% HF, glycine (glyH), and A_2CO_3.

The compounds are cherry-red to pink-brown in colour. While $K_3[Mn(C_2O_4)_2F_2].3H_2O$ is unstable, the other compounds are generally stable. The compounds have been characterized by chemical analysis, chemical determination of oxidation

state of manganese, magnetic susceptibility measurements, and IR and electronic spectroscopic studies. The results suggest that complex species in each case has a distorted octahedral structure. The compounds have normal magnetic moments in conformity with the occurrence of a high spin d^4 manganese(III) in each of them.

Chapter 8 indeed the last Chapter of the thesis describes synthesis and physico-chemical studies of molecular mixed-ligand fluoro complexes of manganese(III), viz., $[Mn(o\text{-phen})F_3(H_2O)]\cdot 2H_2O$, $[Mn(bipy)F_3(H_2O)]\cdot 2H_2O$, and $[Mn(urea)_2F_3]\cdot 3H_2O$. The compounds were synthesised from the reaction of a solution of MnO(OH) in 48% HF with an ethanolic solution of 1,10-phenanthroline (o-phen), an ethanolic solution of 2,2'-bipyridine (bipy), and solid urea, respectively. They are stable in the solid state. Characterization of the compounds were made from the results of elemental analyses, chemical determination of oxidation state of the metal, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. While o-phen and bipy occur as bidentate ligands in the respective compounds, urea in $[Mn(urea)_2F_3]\cdot 3H_2O$ acts as a monodentate ligand. The compounds $[Mn(o\text{-phen})F_3(H_2O)]\cdot 2H_2O$ and $[Mn(bipy)F_3(H_2O)]\cdot 2H_2O$ exhibit normal magnetic moments (ca $5\ \mu_B$) at room temperature, whereas $[Mn(urea)_2F_3]\cdot 3H_2O$

has a magnetic moment of 4.3 μ_B. The complexes have distorted octahedral structures.

The results of studies described in Chapters 3,4,5 and 6 have been published, and those described in Chapters 7 and 8 are under communication.

Chapter 3

J. Chem. Soc., Dalton Trans., 1985, 409.

Chapter 4

J. Chem. Soc., Dalton Trans., 1986, 709; Inorg. Chem., 1986, 25, 2354.

Chapter 5

Ind. J. Chem., 1986, 25A, 1048;

Int. J. Mass Spectrom. Ion Processes, 1986, 71, 109.

Chapter 6

Inorg. Chem., 1985, 24, 447.

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INDIA

MARCH, 1987

Dedicated
To
my Mother
And
To the Revered Memory
of my Father

Phone:
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Dr. Mihir K. Chaudhuri
Professor of Chemistry

I certify that the thesis entitled "SYNTHESIS AND STRUCTURAL ASSESSMENT OF HETERO-LIGAND-PEROXO, ACETATO, AND ACETYL-ACETONATO COMPLEXES OF URANIUM (VI) AND OXALATO AND MIXED-LIGAND-FLUORO COMPLEXES OF MANGANESE (III)", submitted by Mr. Ranendra N. Dutta Purkayastha for the Degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong, embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the award of the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Date : March 31, 1987
Place : Shillong

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March 16, 1987

This is to certify that Sri Ranendra N. Dutta Purkayastha has satisfactorily completed the following Pre-Ph.D. Courses, as prescribed by the university:

1.	Bioinorganic Chemistry	Chem 608
2.	Electrochemistry	Chem 668
3.	French Language	SPS 601
4.	Experimental Techniques	SPS 630

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C O N T E N T S

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R.N. Dutta Purkayastha

CHAPTER 1

Chapter 1.

INTRODUCTION

Uranium is the fourth element in the actinide series having ground state electronic configuration $[Rn]5f^3 6d^1 7s^2$. It is the heaviest element to occur in nature, in recoverable amounts, and its isotopes are all α-emitters, occurring in the proportions ^{238}U 99.28%, ^{235}U 0.71% and ^{234}U 0.005%.[1] The chemistry of the element shows considerable difference with the earlier actinides. Stable oxidation states of the metal range progressively from +3 to +6, with the corresponding f^n configuration ranging from f^3 to f^0. The most stable oxidation state of uranium is its hexavalent state, and the ligands which stabilizes this particular oxidation state of the metal include halides, nitrate, carboxylates, sulphate, β-diketonates and the peroxide etc. In simple compounds the hexavalent state occurs only in hexafluoride UF_6 and hexachloride UCl_6,[2] and the principal chemistry of the +6 state in solid as well as in solution is that of dioxo cation UO_2^{2+}, which forms stable complexes with neutral or anionic molecules. The +5 oxidation state of the metal, is stable only in dilute acidic solution and in the presence of organic complexing agent. The oxo cation UO_2^+ as such is normally not stable in an aqueous solution, as it undergoes

rapid disproportionation. In tetravalent state, U^{+4} ion is stable only in absence of air or any other oxidising agents, whereas the trivalent state, U^{+3} ion is produced in solutions by the action of powerful reducing agents, but is very susceptable to oxidation.[1] The oxo ions are evidently linear in crystalline compounds as well as in solutions. The uranyl ion, UO_2^{2+} characteristic of its +6 state, form a great variety of complexes with anionic ligands and neutral molecules. Some of these complexes of uranyl ion are important from the point of view that, they may have possible application in solar energy conversion system, due to their inherent spectral properties, and may be of potential use in photo-generation of oxygen, which is of great importance for the photo cleavage of water.[3,4] Structural information of the uranyl complexes based on crystallographic data show that four, five or six atoms can lie in the equitorial plane of the O-U-O group, the ligand atoms may or may not be entirely coplanar depending on the circumstances. Planar 5 and 6 coordination in the equitorial plane are most common and appear to give geometry more stable than the puckered hexagonal configuration. Planar 5-coordination best allows rationalization of a number of hydroxides and other structures, as well as the behaviour of polynuclear uranyl ion in hydrolysed solutions,[5] and the complex ion $\left[UO_2(CH_3COO)_3\right]^-$ represents a typical example of the planar 6-coordination, in the equitorial plane of the O-U-O ion.[6]

In an aqueous solution, uranyl salts give an acid reaction due to hydrolysis, and the main hydrolysed species of UO_2^{2+} ion at ca 25 °C are $[UO_2OH]^+$, $[(UO_2)_2(OH)_2]^{2+}$ and $[(UO_2)_3(OH)_5]^+$, but the system is a complicated one, with the monomer being a predominant species at higher temperatures. The solubility of large amounts of UO_3, in UO_2^{2+} solutions is also attributed to the formation of UO_2OH^+ and polymerized hydroxo bridged species.[5]

Thus it is evident from the foregoing discussion, that the chemistry of hexavalent uranium is mainly that of the uranyl ion. As mentioned earlier, peroxide (O_2^{2-}) acts as a stabilising ligand for uranium and the metal is known to form peroxo compounds in its highest oxidation state. Peroxo derivatives of metals, besides having an intrinsic interest of their own, are of considerable and growing importance in relation to the catalysis of oxidation[7] involving hydrogen peroxide[8] or oxygen gas, the catalytic decomposition of H_2O_2 itself, and the storage and transport of oxygen in biological systems.[9,10] Some transition and actinide metal peroxides have found application as reagents for epoxidation of olefins, and hydroxylation of alkenes and aromatic hydrocarbons.[8,11,12]

Although the term molecular oxygen refers only to the free uncoordinated O_2 molecule with the ground state configuration $^3\Sigma_g^-$, the term dioxygen has been used as a generic

designation for O_2 moiety in any of its several forms and can be referred to O_2 in either a free or combined state.[13] For use of this term it is essential that a covalent bond has to exist between the oxygen atoms. Thus a metal dioxygen complex refers to a metal containing O_2 group coordinated to the metal center, and no distinction is made between neutral dioxygen or dioxygen in any of its reduced forms. According to the rationalization made by Vaska,[13] transition and actinide metal peroxides involve covalently bound dioxygen resembling O_2^{2-} in the peroxo configuration. A common characteristic of these complexes is the O-O distance, which occurs between 1.4 and 1.52 Å (1.49 for O_2^{2-}), and the corresponding infrared frequency ν(O-O) which lies between 800 and 950 cm^{-1} (802 cm^{-1} for O_2^{2-}). Simple peroxo compounds of transition metals are the ones which contain peroxides, hydroperoxides and water molecules. Whereas heteroligand peroxo complexes are mixed-ligand metal complexes containing one to three coordinated peroxo groups and one or more monodentate or polydentate ligands. Heteroligands may range from monodentate ions to bulky porphyrins[10] (F^-, Cl^-, NH_3, $C_2O_4^{2-}$, SO_4^{2-}, CO_3^{2-}, NTA, EDTA, bipy, o-phen, oxine, porphyrins, pyridine-2,6-dicarboxylic acid etc). The stability of peroxo complexes is generally enhanced by specific heteroligand combinations. Many simple metal peroxides often explode spontaneously, some are sensitive to shock or decompose above

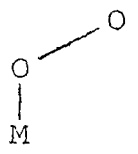
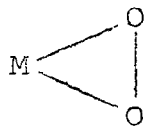
0°C, and several donot exist at all as stoichiometric compounds,[14] but many heteroligand peroxo complexes, on the other hand, survive recrystallization from boiling aqueous solutions, heating in vacuo, and remain unchanged for prolong periods in closed containers.[15] The biochemical significance of peroxo metal complexes has been emphasized recently in the literature.[9,10,16-21] The reactivity of peroxides,[22-24] and the lability of metal-oxygen bonds in special heteroligand environments in solutions are of particular interest to biochemistry although not easy to measure directly.

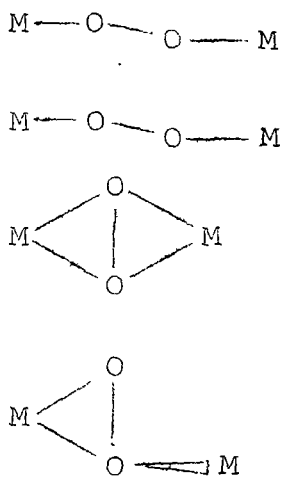
A comparison between the peroxo and unreduced dioxygen heteroligand complexes reflects that the chemistry of the two is very different owing to the presence of two extra electrons in the antibonding O-P π^* orbitals of the peroxide ion.[10] The electron rich O_2^{2-} ion therefore preferably forms complexes with metal ion of low d^n including d^o, and also of f^o electronic configurations, while the neutral dioxygen molecule favours higher d^n metal acceptors. However, there are atleast two things that these two oxygen species have in common, viz., both are stabilised by specific heteroligand spheres, both are of importance in biochemistry. The importance of neutral dioxygen complexes in biochemistry is well known,[9] but the biochemical connection of the metal peroxo complexes with biological processes is not very well understood.

Molecular oxygen is a paramagnetic molecule having a triplet $^3\Sigma_g^-$ ground state, a molecular orbital description of $^3\Sigma_g^-$ level is

$$O_2\ KK\ (2s\sigma g)^2\ (2\sigma u^*)^2\ (2P\sigma g)^2\ (2P\pi_u)^4\ (2P\pi_g^*)^1\ (2P\pi_g^*)^1$$

where the KK term indicates that the K shells of the two oxygen atoms are filled. Two unpaired electrons in the $^3\Sigma_g^-$ ground state are found in the two degenerate antibonding $2P\pi_g^*$ orbitals leaving O_2 with a formal bond order of two. The addition of one or two electrons to a neutral O_2 results in the formation of the superoxide (O_2^-) and peroxide (O_2^{2-}) species, respectively, leaving O_2^- with a bond order of 1.5 and the peroxide O–O link with a bond order of one. The way in which a peroxo group is expected to coordinate to metals can range from symmetrical bidentate to a terminal monodentate position, including all the possible angles in between them. The structural classification of dioxygen complexes, rationalized by Vaska[13] can be represented as follows.

Structural type	Structural designation	Vaska classification
	η^1 dioxygen	Type a (superoxo)
	η^2 dioxygen	Type IIa (peroxo)



η^1 : η^1 dioxygen	Type Ib (superoxo)	
η^1 : η^1 dioxygen	Type IIb (peroxo)	
η^2 : η^2 dioxygen	-	
η^1 : η^2 dioxygen	-	

The bridging μ-peroxo could vary from cisplanar and transplanar to trans nonplanar configurations. An unusual symmetrical double bridging was also found,[25,26,40] however, such examples are very rare. Deviations from the ideal symmetry are common. In the cases of heteroligand fields they are due to the inherent symmetry of different donor atoms. Additional $P\pi^*$ electron delocalization to the metal ion is anticipated, which would therefore favour d^o/f^o or low d^n metal ion configuration. The stereochemical polyhedra in heteroligand peroxo complexes are often fairly predictable. In oxoperoxo heteroligand surroundings, the pentagonal bipyramidal arrangement is most common for transition metal complexes, usually with two coordinated peroxo groups in cis position and oxo group in the axial position. Although less structural information is available, the situation would be different for heteroligand peroxo complexes of UO_2^{2+}.

Infrared spectra are essential for the characterization of complexes containing peroxo groups. For, a bidentate peroxide, regarded as C_{2v} unit, three IR active modes are expected,[27] the peroxo stretching (A_1) and symmetric and asymmetric M-O_2 stretching A_1 and B_2. The ν(O-O) band is the most sensitive and intense one and characteristically occurs between 800-950 cm^{-1}. The frequency of this band remains fairly independent of the heteroligand environment but is affected by the mass of the metal ion, indicating some degree of coupling of the ν(O-O) with M-O_2 vibrations. The most familiar way of bonding of O_2^{2-} groups, in a triangular bidentate manner is similar to the one proposed by Griffith[28] for the bonding of O_2 in oxyhaemoglobin, and the ν(O-O) values, which are similar to those observed for O_2^{2-} ions. While the importance of infrared spectroscopy in this field has been highlighted, the usefulness of Raman spectroscopy cannot be underestimated. All the three IR active modes as mentioned above are also Raman active. Thus the results of Raman spectral studies augment the IR results. Moreover, Raman spectroscopy can also be easily applied to solutions, and the results of which provide further information concerning identity and structure of a complex species in solutions.

As mentioned earlier in this section, uranium is also known to form peroxo complexes in its highest oxidation state. The complexity involved in peroxouranate chemistry is an

acknowledged problem[1,29] and the system is exceedingly complicated,[30] owing to the formation of a host of different peroxouranate(VI) species with a slight variation of pH of the reaction medium. Peroxouranates containing O_2^{2-}:U as 1:1, 1:2, 2:1, 3:1, 3:2 and 5:2 have been described in the literature,[29,31] in addition to a few more which were rationalized only on the basis of peroxide to uranium ratio.[32,33] Among these peroxouranates, however, $UO_2(O_2).nH_2O$ (n = 2 or 4) appears to be the best characterized one. This species has been known since 1876,[34] and was also a subject of extensive investigations.[35,36] Nevertheless its constitution was not well established for a long period, since different groups described it in different manners, eg. true peroxide hydrate or a peroxide having the composition U_2O_7, a peroxy acid or an addition compound of uranium oxide, $UO_3.H_2O_2.H_2O$.[36,37] Finally Gordon and Taube[38] showed it to be a true peroxide hydrate on the basis of their isotopic tracer studies on thermal decomposition of uranium-peroxide system.

Albeit formation of simple peroxides[1,29] of uranium is evident from the above discussion but its heteroligand peroxo chemistry seems to be rather poorly investigated.[1,29] Despite a long history of peroxo-uranium chemistry earlier reports on heteroligand peroxouranates are rather scanty, except for some carbonato and oxalato peroxouranates,[29] and the only fluoroperoxouranate[29] Na $[UO_2(O_2)F(OH_2)].4H_2O$.

Relatively recent reports on heteroligand peroxouranates include a few nonelectrolytic peroxouranates[39] of the type $[UO_2(O_2)L_2]$ (L = Ph_3PO, Ph_3ASO, Py-N oxide and Quinoline N-oxide), and a unique μ_2-peroxo bridged complex benzyltrimethylammonium μ_2-peroxo bis [trichlorodioxouranate (VI)].[40] The above-mentioned chloro-peroxo complex is one of the rare examples of a complex containing a dioxygen molecule being bonded as a μ_2-peroxo group. In addition, subsequently in 1981 a few more novel mono and diperoxo complexes of uranate(VI) containing organic ligands have been reported.[41]

In view of the above non-exhaustive discussion, and also taking note of some of the recent results on heteroligand peroxo complexes of other metals,[42-46] it appeared that suitably chosen heteroligands could impart stability to peroxo metal systems also permitting their isolation in the solid state. A systematic study involving synthesis and structural assessment of heteroligand dioxoperoxouranates(VI), a field in which very little work was done earlier, was considered to be a rewarding aspect of research.

Accordingly, such studies were undertaken as a part of the present research programme. Synthetic strategies were planned, and several new heteroligand peroxo complexes of uranium have been synthesised and their structural assessment made. Heteroligands have been drawn from F^-, CO_3^{2-}, SO_4^{2-},

ethylenediamine (en), glycine (glyH), 2,2'-bipyridine (bipy), 1,10-phenanthroline (o-phen). Some attempts have been also made to explore the reactivity of coordinated peroxide selecting one peroxo-uranium complex from amongst the newly synthesised compounds. The results of these studies have been described in Chapters 3 and 4.

Apart from peroxide, β-diketonates and acetate are also known as important stabilizing ligands for UO_2^{2+} ion. Most of the actinide elements are known to form stable carboxylate derivatives.[47] Carboxylic acids are potential bidentate ligands, with a very short O•••O distance, and the large actinide cations very easily form complexes, sometimes with high coordination number. Though acetate forms stable compounds with UO_2^{2+}, the acetato-uranate(VI) chemistry is believed to be rather complicated, due to the formation of a great variety of compounds between acetic acid and uranyl ion.[48] The nature of the compounds formed depend highly on the reaction conditions and the proportions of acetic acid and UO_2^{2+} ion maintained in the reaction medium. Both diacetato and triacetato complexes of UO_2^{2+} are known for quite sometime,[48-50] while the $UO_2(CH_3COO)_2 \cdot 2H_2O$ can be obtained either from the reaction of $UO_2(NO_3)_2 \cdot 6H_2O$, or UO_3, which involves an extra preparation steps, with acetic acid,[51-54] the synthesis of triacetato complexes of UO_2^{2+} requires in addition, an excess of alkali nitrate or alkali acetate[49] for

adjusting pH of the reaction medium. The chances of contamination of the end products in the latter owing to the use of an excess of nitrate or acetate cannot be ruled out.

Besides acetato complexes of dioxouranate(VI), β-diketonato compounds of UO_2^{2+} are also very important because of their being moderately volatile. Acetylacetone, the simplest of β-diketones, forms compounds with many metals of the periodic table,[55] and the interests in their syntheses, and chemical and physico-chemical studies seem to be never diminishing.[56-70] Bis(acetylacetonato)dioxouranium(VI), $UO_2(C_5H_7O_2)_2$, which is also a moderately volatile compound of the metal has been known for a number of years.[71-74] The literature[73] method of the synthesis of this compound uses sodium hydroxide for maintaining the appropriate pH of the reaction medium. Here again, the chances of contamination of $UO_2(acac)_2$ by the alkali can not be completely ruled out. Moreover it is remarkable to note that the mass spectrum of this compound was not reported although those of some fluorinated β-diketonato complexes of Ce[75] and U[76] have been reported during the period 1983 to 1985.

It was therefore imperative to develope direct synthetic routes to acetato and acetylacetonato compounds of uranium, and to investigate $UO_2(C_5H_7O_2)_2$ mass spectrometrically.

As a sequel of the work on peroxo compounds of uranium, synthesis of $UO_2(CH_3COO)_2 \cdot 2H_2O$, A $[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4), and $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, and mass spectrometric studies of bis(acetylacetonato)dioxouranium(VI) have been carried out. Chapters 3, 4 and 5 present an account of the results of the afore-mentioned studies.

Quite apart from the studies of uranium chemistry, research involving chemistry of manganese especially with emphasis relating to its unusual oxidation states appears to be one of the areas of contemporary interest.[77-82]

Manganese is the first row group VIIB transition metal, twelfth most abundant element and constitutes about 0.085% of the earth crust.[83] Besides its various utilities in industrial as well as in laboratory purposes, the importance of manganese or some of its compounds in bio system[77,78,82,84] has also been realised. The metal also plays an important role in photosynthesis,[85-88] catalytic disproportionation of the superoxide ion[89] and in addition it can also activate enzymatic processes such as oxidative phosphorylation, synthesis of cholesterol etc.[90]

Manganese has the ground state electronic configuration, $[Ar]3d^5 4s^2$, and exhibits a wide spectrum of oxidation numbers ranging from -3 to +7. While the lower oxidation states are generally found[91] in the carbonyl, nitrosyl and organometallic

derivatives of manganese, the higher oxidation states of the metal are found in compounds which contain strong electronegative ligands like fluoride, oxide and many are unstable with respect to photochemical decomposition depending upon pH.[92,93]

An unusual oxidation state of manganese is its +3 state. This particular oxidation state has recently generated much interest not only because of its biochemical relevance but also some compounds of Mn(III) have demonstrated unusual structural and magnetic properties.[94,95,79]

Simple ion of manganese(III) does not appear to be stable, but their stability is greatly enhanced by complex formation.[96] There are relatively few simple compounds of Mn^{3+} and only the acetate salt can be prepared conveniently. This is a good oxidizing agent, particularly for organic systems.[97-98] The aquomanganese(III) ion is a strong oxidizing species but is not stable, primarily because of its disproportionation to Mn(II) ion and Mn(IV) oxide.[99] Many redox reactions have been studied involving the above mentioned species, and their kinetics and mechanism have been reported recently.[100-102] On the other hand complexes of manganese(III) are generally more stable, and their stability is even higher than the corresponding complexes of Mn(II); this is believed to be owing to the greater formation constants of Mn(III) complexes than those of Mn(II). The complexes of Mn(III),

however, are much poorer oxidizing agents than the Mn(III) ion, as they are not subjected to disproportionation. The complex formation by Mn(III) ion, usually results in a lowering of the redox potential for the Mn(III)/Mn(II) couple, dependent upon acidity and are normally of dissociative type.[103] The hydrolysis occurs at low acidic medium, but can be minimised to a considerable extent at a high acid concentration, and complexing with suitable ligands.[104,105] Thus, suitable complexing agent, for stabilizing Mn(III) is always looked for, and a little more than half a decade has been devoted by other workers in the laboratory, where the present work has been carried out, to find out suitable routes to the synthesis of Mn(III) complexes in an aqueous solution. Considering an enhanced basic character of fluoride, it was expected that, it should be able to stabilize Mn^{3+} ion leading to the formation of stable fluoromanganate(III) complexes. Accordingly, fluoride has been shown to be one of the most suitable ligands for the purpose.[94,106,107] Apart from fluoride, the ligands which can stabilize manganese(III) ion in solution include sulphate, oxalate, phosphate, pyrophosphate, EDTA etc.[99] In addition to imparting stability to the complexes of manganese(III), coordination of a fluoride ligand to Mn(III) also brings about notable changes in magnetic and structural behaviour of the complexes. It is well documented in the literature[94,108] that fluoro complexes of Mn(III) have magnetic

moments much lower than that expected for a normal Mn(III) case, owing to strong antiferromagnetic exchange interactions between the Mn(III) atoms in the polymeric structure of the compounds, whereas Mn(III) compounds with other ligands such as oxalate, sulphate etc show normal magnetic behaviour.[109] It was anticipated therefore that mixed-ligand fluoro-manganates(III) may show somewhat different magnetic behaviour from that of the binary Mn(III) compounds, in addition to exhibiting changes in other properties as well. Some of the recent results[106,110] lend support to the above view, however, further work is definitely required in this direction.

In its +3 state manganese has a $3d^4$ electronic configuration and is susceptible to Jahn -Teller distortion. The majority of complexes of Mn(III) are high spin, and magnetic moments of the apparently octahedral Mn(III) complexes show that the effect of spin-orbit coupling is almost negligible[111] and exhibit magnetic moments which are almost identical to spin-only value. Due to the presence of odd number of electrons in e_g level $\left[{}^5E_g(t_{2g}^3 e_g^1)d^4 Mn^{III}\right]$ distortion should be appreciable and might be expected to resemble the distortion of Cr^{2+} and Cu^{2+} complexes. Thus a frequent reference is made to high spin Mn(III) compounds,[79] when the subject of Jahn-Teller effect is discussed. However, as mentioned earlier in this section information concerning manganese(III) complexes are rather sparse as opposed to

those of the other tripositive first-row transition elements or other systems having a d^4 configuration. Hence studies on various aspects viz., synthesis, structural assessment, and reactivity of different types of Mn(III) complexes was felt important and it was with this perspective that an attempt was made to investigate these aspects of mixed-fluoro complexes of manganese(III).

It is known that when a solution contains a metal ion and atleast two different ligands, there exists always a finite possibility of formation of a mixed-ligand complex. In view of the potential donating ability of many counter anions and solvents, there are very few cases indeed when this possibility is out of consideration.[114] Various types of mixed-ligand complexes of other metals have been studied, methods regarding the determination of their stability constants have been worked out in details, and their importance in chemical[115,116] and biosystem[117,118] have been emphasized by others. In the area of mixed-ligand metal compounds three kinds of ternary complexes may be conveniently distinguished:

(a) complex which contains two different kinds of monodentate ligands;

(b) complexes which contains one unidentate and one multidentate ligand and

(c) complexes containing two different multidentate ligands.

Earlier reports on manganese are mainly of the type (a)[119-121] and type (c) complexes,[114,122-125] while those on the type (b) complexes containing Mn(III) being the central atom are only a few.[106,126,127,128] Accordingly, studies involving this type of complexes of manganese(III) is expected to yield valuable information and appear to be a rewarding area of investigation. A planning of synthetic strategies and working out of appropriate experimental conditions are important pre-requisites for this.

It has been mentioned in passing (vide Supra) that Mn(III) is capable of forming a complex with oxalate ion, $C_2O_4^{2-}$. Consequently such a compound namely potassium tris(oxalato)manganate(III) trihydrate,[129] $K_3[Mn(C_2O_4)_3].3H_2O$, has been known for quite sometime, and has served as a very oft-quoted example whenever the subject of inorganic photochemistry is the matter of discussion.[130] The method involving the reaction of $KMnO_4$ with oxalic acid and $K_2C_2O_4$ in the presence of an excess of K_2CO_3 is universally accepted for the synthesis of $K_3[Mn(C_2O_4)_3].3H_2O$. This method requires a very careful manipulation and also uses an excess of K_2CO_3 in order to control the pH. The chances of contamination of the end product, owing to the use of K_2CO_3 in such quantities, cannot be ruled out. A more direct method particularly without making use of any buffer is therefore highly desirable.

In line with the scope highlighted in the above discussion, studies involving chemistry of manganese(III) were undertaken as the other part of the programme (other than the uranium chemistry as mentioned earlier). A new direct method for the synthesis of photochemically important potassium tris(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$, has been developed. A number of mixed-ligand fluoromanganate(III) complexes have been synthesised, and their structural assessment has been made by various physico-chemical techniques. The results obtained on manganese(III) chemistry have been described in Chapters 6, 7 and 8.

The new results reported in the present thesis have been broadly divided into two parts viz., Part A and Part B. While Part A of the thesis containing Chapters 3, 4 and 5 presents the work on uranium, Part B deals with the results of studies involving manganese(III) (Chapters 6, 7 and 8).

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CHAPTER 2

Chapter 2

Methods of Elemental Analyses and Particulars of Instruments/ equipment Used for Characterization and Structural Assessment of Compounds

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

Elemental Analyses

Uranium[1]

Uranium was estimated gravimetrically as U_3O_8. An accurately weighed amount of an uranium compound was dissolved in a minimum volume of dilute (~5N) sulphuric acid, few drops of methyl red indicator was added, and the solution was heated to boiling. The hot solution was treated with dilute ammonia solution until the indicator just turned yellow, and a yellow precipitate was obtained in this stage. A Whatman accelerator was added and the solution was warmed for 1 to 2 min, precipitate was filtered off on a Whatman no. 541 filter paper, and washed well (3 to 4 times) with a hot 2% solution of ammonium nitrate. The wet filter paper along with the precipitate was dried in a platinum crucible over a Meker

burner at a low temperature, until the carbon was destroyed. The crucible was then heated strongly, being placed in a slanting position so as to maintain a good oxidizing condition. Crucible with its content was cooled in a desiccator and weighed, the ignition process was repeated until constant weight was attained. Uranium was finally weighed as U_3O_8.

Active Oxygen (Peroxo Oxygen)[2-4]

(i) Permanganometry[2]

An accurately weighed amount of a peroxo-uranium compound was dissolved in 7N sulphuric acid containing ca 4g of boric acid. Boric acid was used to form perboric acid to prevent any loss of active oxygen. The resulting solution was then titrated with a standard potassium permanganate solution.

1 cm^3 of 1N $KMnO_4$ = 0.01701g of H_2O_2

This method is suitable for determination of peroxide contents in peroxo-uranium compounds.

(ii) Iodometry[3]

To a freshly prepared 2N sulphuric acid solution, containing an appropriate amount of potassium iodide ($\sim$ 1g in 100 cm^3) was added an accurately weighed amount of a peroxo-uranium compound with continuous stirring. The mixture was allowed to stand for ca 15 min in CO_2 atmosphere in dark. Then the liberated amount of iodine was titrated with a standard sodium thiosulphate solution, adding 2 cm^3 of freshly

prepared starch solution, when the colour of the iodine was nearly discharged.

1 cm^3 of 1N $Na_2S_2O_3$ = 0.01701g for H_2O_2

The method is also suitable for the determination of peroxide content in peroxo-uranium compounds.

(iii) Determination of peroxide (O_2^{2-}) content by titrating with a standard Ce^{4+} solution[4]

An accurately weighed amount of a peroxo-uranium compound was dissolved in a 2N sulphuric acid solution in the presence of an excess of boric acid (~5g), peroxide was then determined by titrating with a standard Ce^{4+} solution.

Fluoride[5]

An accurately weighed amount of a fluorouranate(VI) or a fluoromanganate(III) compound was dissolved in water. The fluorouranate(VI) compound was decomposed with 20-25 cm^3 of 30% aqueous ammonia, and fluoromanganate(III) compound was decomposed by the addition of 20-25 cm^3 of 0.1N NaOH solution, the mixture was heated over steam bath for ca 10 min to ensure complete decomposition. Ammonium diuranate and hydrated manganese oxide formed due to the addition of aqueous ammonia and NaOH, respectively, was separated out by filtration and washed several times with water. The filtrate and washings were collected for fluoride estimation. To the combined washing and filtrate 2 to 3 drops of bromophenol blue indicator and 3 cm^3 of 10% sodium chloride solution were added,

and the whole was diluted to ca 250 cm^3. Dilute nitric acid was added to it until colour changed to just yellow, followed by the addition of dilute sodium hydroxide solution until the colour ultimately just changed to blue. The mixture was then treated with 1 cm^3 of concentrated hydrochloric acid and 5.0g of lead nitrate, and then heated on a steam bath. After all the lead nitrate had dissolved, 5.0g crystallised sodium acetate was added to the solution and the solution was digested on a steam bath for about half an hour with occasional stirring, and then allowed to stand overnight.

For the gravimetric estimation,[5a] the precipitate lead chloride fluoride, PbClF, was filtered through a weighed Gooch crucible (grade 4) and weighed as PbClF after drying at 140-150°C to constant weight. In the volumetric estimation,[5b] the precipitate PbClF was quantitatively collected by filtration through a Whatman 542 filter paper and washed once with cold water, then 3 to 4 times with saturated solution of lead chloride fluoride, and finally once more with cold water. The precipitate was then dissolved in 100 cm^3 of 5% (v/v) nitric acid by heating over steam bath for 4-5 min. A known excess of saturated 0.1N silver nitrate solution was then added to it, followed by digestion on a steam bath for 30 min, and then cooled at room temperature in the absence of light. The precipitated silver chloride was filtered through a sintered glass crucible and washed with cold water. The unreacted silver

nitrate in the filtrate and washings was titrated with a saturated 0.1N potassium thiocyanate solution using 1 cm^3 of ferric ion indicator solution until one drop of thiocyanate solution produced a permanent faint brown colour. The amount of silver nitrate in the filtrate, thus found, was subtracted from that originally added, and the content of fluoride was then calculated from the amount of silver nitrate consumed.

1 cm^3 1N $AgNO_3$ = 0.0190g of F.

Manganese[6]

Manganese was determined by complexometric titration with EDTA, using Eriochrome black T as an indicator.

In this procedure an accurately weighed amount of the compound was decomposed by the addition of 20-25 cm^3 of 0.1N NaOH solution, and the mixture was heated for ca 10 to 15 min on a steam bath to ensure complete decomposition. The resulting hydrated oxide of manganese was quantitatively separated by filtration and washed 3 to 4 times with cold water. The brownish black precipitate was dissolved in dilute hydrochloric acid, followed by the addition of 0.5g of hydroxylammonium chloride to prevent oxidation. The solution was diluted to 100 cm^3 and warmed slightly and was neutralized by the addition of 0.1N NaOH solution. An amount 3 cm^3 of triethanolamine was added to keep manganese in solution, when it was subsequently made alkaline by the addition of 2 cm^3 of a buffer

solution (pH = 10) and then several drops of Erio T indicator. The resulting mixture was titrated with standard 0.05M EDTA at about 40 °C, until the colour permanently changed from red to blue.

1 cm^3 0.05M EDTA = 2.747 mg of Mn

Oxalate[7]

An exactly weighed amount of the manganese(III) oxalate compound was treated with 25 cm^3 of 0.1N sodium hydroxide solution and then 100 cm^3 of water was added to it. The mixture was boiled for ca 15 min followed by filtration. The precipitated hydrated manganese oxide was washed several times with water. The filtrate and washings were collected and from which the oxalate content of the compound determined by the following method. The combined filtrate and washings was neutralized with dilute sulphuric acid. An amount of 15 cm^3 of concentrated sulphuric acid was added to the solution. The resulting solution was then titrated against standard 0.1N potassium permanganate solution maintaining the temperature of the solution at ca 60 °C.

1 cm^3 of 0.1N $KMnO_4$ = 0.044g of $C_2O_4^{2-}$

Phosphate[8]

Phosphate was determined as ammonium magnesium phosphate hexahydrate.[8a]

An accurately weighed amount of manganese(III) phosphate compound was decomposed by the addition of 15-20 cm^3 of 0.1N sodium hydroxide solution, and heated for ca 15 min to ensure complete decomposition. The resulting hydrated manganese oxide precipitate was quantitatively separated by filtration and washed with cold water. The combined filtrate and washings was collected for the estimation of phosphate content in a compound. The combined filtrate and washings was neutralized by the addition of dilute nitric acid, followed by the addition of 3 cm^3 of concentrated hydrochloric acid and a few drops of methyl red indicator. An amount of 25 cm^3 of magnesia mixture was added to the solution followed by the slow addition of concentrated aqueous ammonia with vigorous stirring, until the indicator turned yellow. Stirring was continued for a further period of 5 min and finally an excess of 5 cm^3 of concentrated aqueous ammonia was added slowly. The resulting mixture was allowed to stand in cold for 4 hrs, when the white precipitate of ammonium magnesium phosphate hexahydrate settled down. The precipitate was separated quantitatively by filtration, using a sintered glass crucible (grade 4) and washed with distilled ethanol 3 to 4 times and

finally with small portions of ether. The precipitate was dried in a vacuum desiccator for ca 20 min and finally weighed as $MgNH_4PO_4.6H_2O$.

Determination of Phosphate by indirect titration with EDTA[8b]

Phosphate content of the compound was precipitated as $Mg(NH_4)PO_4.6H_2O$, as described above. The precipitate was dissolved in hot 25 cm^3 of 1M HCl, and diluted to 100 cm^3 by the addition of water. To this mixture was added 35.0 cm^3 of 0.05M EDTA solution and then neutralized by the dropwise addition of 1M NaOH solution with stirring followed by the addition of 4 cm^3 of a buffer solution (pH = 10) and a few drops of Erio T indicator. The unreacted amount of EDTA in the solution was then titrated with a standard 0.05M magnesium chloride solution, until the colour changed from blue to wine-red.

Every 1 cm^3 difference between 1M EDTA and 1M $MgCl_2$ corresponds to 94.97 mg of PO_4^{3-}.

Sulphate[9]

A known amount of sulphatouranate(VI) compound was treated with 25 cm^3 of water, and was dissolved completely by the addition of a few drops of dilute HNO_3. A 30% solution of aqueous ammonia was added to the solution slowly with stirring,

and the mixture was heated over a steam bath for ca 30 min. The precipitated ammonium diuranate was separated by filtration, and carefully washed 2-3 times with cold water. The combined filtrate and washings was retained for estimation of sulphate. The solution was concentrated by boiling and neutralized with dilute nitric acid (volume of the solution was $\sim$230 cm^3). The solution so obtained was acidified by the addition of 0.3-0.6 cm^3 of concentrated HCl solution and was heated to boiling. A warm solution (10-12 cm^3) of 5% barium chloride (5g $BaCl_2.2H_2O$ in 100 cm^3 of water) was added from a burette or pipette drop by drop with continuous stirring, and the resultant precipitate was allowed to settle for ca 2 min. The supernatant liquid was tested for complete precipitation by adding a few drops of barium chloride solution. The process was repeated until a slight excess of barium chloride was present in the mixture to ensure complete precipitation. The mixture was kept covered over a steam bath for 1h., in order to allow time for complete precipitation of $BaSO_4$. The precipitated barium sulphate was filtered through a previously weighed sintered glass crucible (grade 4) using gentle suction. The precipitate was washed with warm water until the filtrate gave no precipitate with a few drops of silver nitrate solution. The crucible with its content was dried at ca 110°C, and heated for 10-15 min at a higher temperature (ca 600°C) followed by cooling in a desiccator.

The ignition process was continued until constant weight was attained.

The sulphate content of the sample was finally weighed as $BaSO_4$.

Sodium and Potassium

Sodium and potassium contents were determined by flame photometry. A solution containing sodium or potassium ions was acidified with hydrochloric acid. The acidified solution thus obtained was then used for flame photometry.

Rubidium and Caesium[10]

Rubidium and caesium contents in the respective salts were estimated, gravimetrically as their perchlorates. The precipitate was obtained following the standard procedure, and weighed as $AClO_4$ (A = Rb or Cs).

Carbon, Hydrogen, and Nitrogen

Carbon, hydrogen and nitrogen were estimated by micro analytical methods. The results of analyses were obtained from Amdel Australian Micro Analytical Service, Port Melbourne, Victoria 3207 Australia, and also Micro Analytical Laboratories, RSIC, NEHU, Shillong.

Particulars of Instruments/Equipment used

pH Measurement

pH of the reaction solutions, whenever required, were measured by using a SystronicsType 335 digital pH meter and also by BDH indicator paper.

Molar Conductance

Molar conductance measurements were made using Philips PR 9500 conductivity bridge. Conductivity grade water was used for the purpose.

Magnetic Susceptibility

The Gouy method was used to measure magnetic susceptibilities of the complexes. The compound $Hg[Co(NCS)_4]$ was used as the standard for calibration.

Electronic Spectra

Electronic spectral measurements of solution were made on Beckman model UV-26 and Cary model 2300 Spectrophotometers. Reflectance spectra of solids were recorded against MgO using Carl-Zeiss Jana VSU 2-P instrument.

Infrared Spectra

Infrared spectra were recorded on the following spectrophotometers;

(1) Perkin-Elmer model 297

(2) Perkin-Elmer model 983

(3) Perkin-Elmer model 125.

Laser Raman Spectra

Laser Raman (lR) spectra were recorded on a SPEX Ramalog model 1403 Raman spectrometer. The 4880 Å laser line from spectra-physics model 165 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 either in a quartz capillary or in the form of a pressed pellet. The recording was done at ambient temperatures.

Mass Spectra[11,12]

The mass spectra were recorded on a Varian MAT CH-5 spectrometer. A direct insertion probe was used to introduce the samples directly into the ion source without any prior heating. The sample was held under vacuum (inside the mass spectrometer) for ca 1h in the direct inlet probe before electron impact was initiated. The operating conditions were: electron energy, 70ev (1ev $\simeq$ 1.6 x 10^{-19}J); source temperature 100°C, resolution 10000; accelerating voltage, 8kV. The mass spectrometric observations were made with the ionising beam held constant to obtain reproducible ion intensities.

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CHAPTER 3

Chapter 3

Synthesis and Structural Assessment of Alkali-Metal and Ammonium Difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and Alkali-Metal Difluorodioxoperoxouranate(VI) Monohydrates, $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb)*

Although peroxouranate chemistry has a rather long history, reports on heteroligand peroxouranates are few. That this particular aspect of uranium chemistry is highly complicated,[1,2] owing to the formation of a host of different species with a slight variation of pH of the reaction medium, has been already accentuated in Chapter 1 of the present thesis. Simple peroxouranates containing O_2^{2-}:U ratios of 1:1, 1:2, 2:1, 3:1, 3:2 and 5:2 have been described in the literature,[1] with $UO_2(O_2).nH_2O$ (n = 2 or 4) being the best characterized example. In contrast only a limited number of heteroligand peroxouranates have reported existence, of which carbonato- and oxalato-peroxouranates are the most frequently quoted ones.[1] The only fluoroperoxouranate, known,[1] to our

*The results described in this Chapter have been published. J. Chem. Soc., Dalton Trans., 1985, 409.

knowledge, is Na $[UO_2(O_2)F(OH_2)].4H_2O$. We were unable to discern any obvious reason for the lack of information on fluoroperoxouranate, but for the one mentioned above, particularly when fluoride is also known to form complexes with uranium.

Accordingly it was believed that fluoroperoxouranates will be capable of being synthesised under suitable experimental conditions, and a systematic study involving the synthesis and structural assessment of fluoroperoxouranate compounds were undertaken. This has led to synthesise a series of novel fluoroperoxouranates, $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb). The present Chapter deals with the synthesis, characterization, and assessment of structure of the title compounds.

Experimental

The chemicals used were all reagent grade products (Loba-Chemie, Glaxo, E. Merck, S.D's, Sarabhai M).

Synthesis of Ammonium and Caesium Difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs), and Potassium and Rubidium Difluorodioxoperoxouranate(VI) Monohydrates, $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb)

As the methods of synthesis of the compounds are similar, a general procedure is described below.

An amount of 1.0g (1.99 mmol) $UO_2(NO_3)_2.6H_2O$ was dissolved in 10-15 cm^3 of water followed by addition of concentrated aqueous ammonia solution (sp.gr 0.9), or a concentrated solution of potassium hydroxide only in the case of the K^+ salt, with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off, washed free from alkali and nitrate, and then mixed with alkali-metal or ammonium fluoride, AF (A = K, Rb, Cs or NH_4) and 25 cm^3 (220.5 mmol) of 30% H_2O_2 with maintenance of the ratio of $U:F^-:H_2O_2$ as 1:4:110.8. Dropwise addition of 40% HF (1 cm^3) with constant stirring afforded a clear yellow solution (pH~ 2), the pH of the reaction mixture was raised to 6.5-7 by carefully adding 10% solution of aqueous ammonia or potassium hydroxide in the cases of the NH_4^+ and K^+ salts, respectively. and solid A_2CO_3 (A = Rb or Cs) for the Rb^+ or Cs^+ salts. An equal volume of ethanol was added with occasional stirring to obtain yellow microcrystalline $A_2[UO_2(O_2)F_2]$

(A = NH_4 or Cs) or $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb). Each compound was allowed to settle for ca 30 min, separated by centrifugation, purified by washing with ethanol, and finally dried *in vacuo* over diphosphorus pentoxide. The amounts of reagent used and the yields of the compounds are set out in Table 1.

Table 1. Amounts of Reagents used and Yields of Alkali-Metal and Ammonium Difluorodioxoperoxouranates(VI)

Compound	Yield g (%)	Amount of $UO_2(NO_3)_2.6H_2O$ g (mmol)	Amount of AF g (mmol)	Amount of H_2O_2 cm^3 (mmol)
$(NH_4)_2[UO_2(O_2)F_2]$	0.5 (67)	1 (1.99)	0.3 (8.1)	25 (220.5)
$K_2[UO_2(O_2)F_2].H_2O$	0.6 (69)	1 (1.99)	0.47 (8.1)	25 (220.5)
$Rb_2[UO_2(O_2)F_2].H_2O$	0.8 (73)	1 (1.99)	0.84 (8.0)	25 (220.5)
$Cs_2[UO_2(O_2)F_2]$	0.9 (75)	1 (1.99)	1.23 (8.1)	25 (220.5)

Elemental Analyses

Quantitative estimations of uranium, peroxide, fluoride, alkali-metals, and nitrogen were made by the methods described in Chapter 2.

The analytical data are given in Table 2.

Structurally significant IR bands and their assignments are reported in Table 3.

Results and Discussion

It is known from the literature that both fluoride[3] and peroxide (O_2^{2-})[1] can, under the appropriate conditions, coordinate to UO_2^{2+}. Thus it was rational to expect, that it would be possible to devise an appropriate method in which both fluoride and peroxide could be simultaneously made to coordinate to UO_2^{2+} center, leading to the formation of fluoroperoxouranates(VI).

Strategically most important was the evaluation of a suitable pH of the reaction medium to enable formation of the desired complexes. Accordingly the reaction of UO_2^{2+} in an aqueous solution with alkali-metal or ammonium fluoride AF, and hydrogen peroxide was carried out at pH 6.5-7 which led to the synthesis of the difluorodioxoperoxouranate(VI) complexes, $[UO_2(O_2)F_2]^{2-}$. The complex ion was isolated as its alkali-metal salts, $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb) by the addition of ethanol which facilitated precipitation. It must be emphasized that maintenance of pH of the reaction medium at ca 6.5-7 is very vital for the formation and thence successful isolation of the

Table 2. Analytical data of $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb)

Compound	Found % (Calcd. %)			
	A	U	O[a]	F
$(NH_4)_2[UO_2(O_2)F_2]$	7.55[b] (7.45)[b]	63.8 (63.3)	8.70 (8.50)	9.80 (10.1)
$K_2[UO_2(O_2)F_2].H_2O$	18.4[c] (17.95)[c]	54.9 (54.55)	7.80 (7.35)	9.10 (8.70)
$Rb_2[UO_2(O_2)F_2].H_2O$	-	45.4 (45.0)	6.40 (6.05)	7.50 (7.20)
$Cs_2[UO_2(O_2)F_2]$	-	39.8 (39.3)	5.50 (5.30)	6.10 (6.25)

[a]Peroxo-oxygen. [b]Analysis for N. [c]Analysis for K.

title compounds in the solid state. It has been observed by carrying out similar reactions at pH 2-4 that the products obtained under these conditions either donot contain peroxide at all or to a practically negligible extent suggesting thereby that acidic conditions of the reaction medium is not conducive to the formation of fluoroperoxouranate(VI) species. The compounds isolated under such conditions were found to be oxofluorouranate(VI) rather than fluoroperoxouranate(VI) complexes. Thus it is believed that the course of reaction involves the formation of oxofluorouranate(VI) first followed by an uptake of peroxide with the increase of pH of the reaction medium to ultimately produce the complex ion $\left[UO_2(O_2)F_2\right]^{2-}$ at pH ca 6.5-7. In the cases of the Rb^+ and Cs^+ salts, the pH of the reaction medium was raised to the required extent (6.5-7), by the addition of the respective carbonates, exploiting the reaction $CO_3^{2-} + 2H^+ \longrightarrow CO_2\uparrow + H_2O$, instead of aqueous ammonia which was otherwise thought to be suitable. Attempts to use aqueous ammonia solution to raise the pH to 6.5-7 in the cases of Rb^+ and Cs^+ salts resulted in the isolation of $(NH_4)_2\left[UO_2(O_2)F_2\right]$, even though the stipulated amount of RbF or CsF was used. This observation could be attributed to the relatively lower solubility of the $(NH_4)_2\left[UO_2(O_2)F_2\right]$ compound.

The synthetic reactions were monitored by IR spectroscopy. The appearance of a strong band at ca 860 cm^{-1} due to $\nu_3(O-O)$ in the IR spectrum of a small amount of the sample isolated from the reaction solutions indicated the formation of peroxouranates(VI).

Characterization and Assessment of Structure

The newly synthesised alkali-metal difluorodioxo-peroxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and alkali-metal difluorodioxoperoxouranate(VI) monohydrates, $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb) are all yellow micro-crystalline products, and can be stored for a prolong period in sealed containers. The stability of the compounds was ascertained from the results of chemical determinations of peroxide (O_2^{2-}), uranium and fluoride contents periodically. They are insoluble in common organic solvents, and very sparingly soluble in water. Owing to the sparingly soluble nature of the compounds molar conductance measurements could not be carried out. The fluoroperoxouranates, dissolve completely in a slightly acidified (H_2SO_4) solution from which uranium can be quantitatively precipitated by the addition of aqueous ammonia.

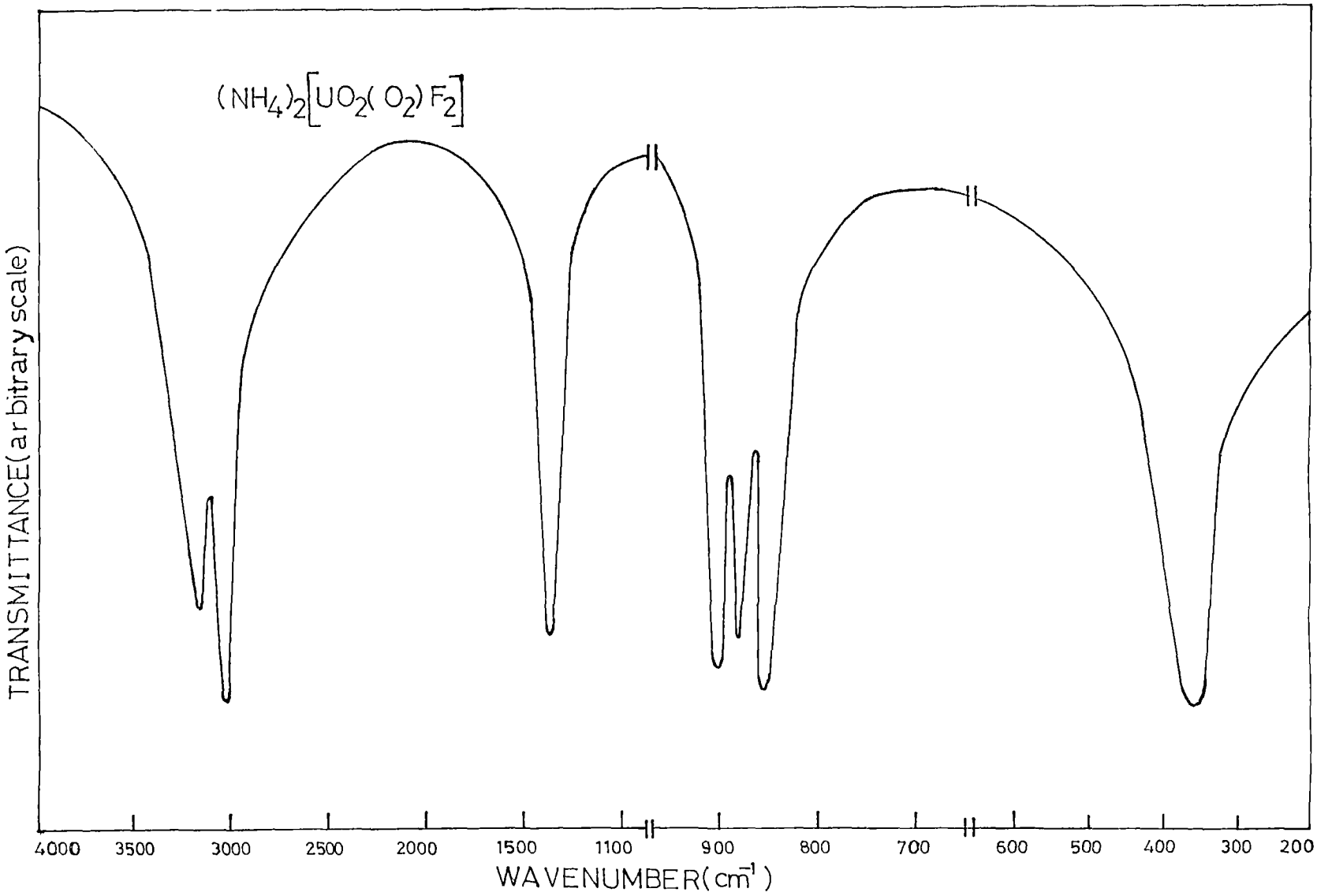
The determination of peroxide content, considered to be extremely important, to find out the number of peroxide group bonded to UO_2^{2+} center, was accomplished by redox

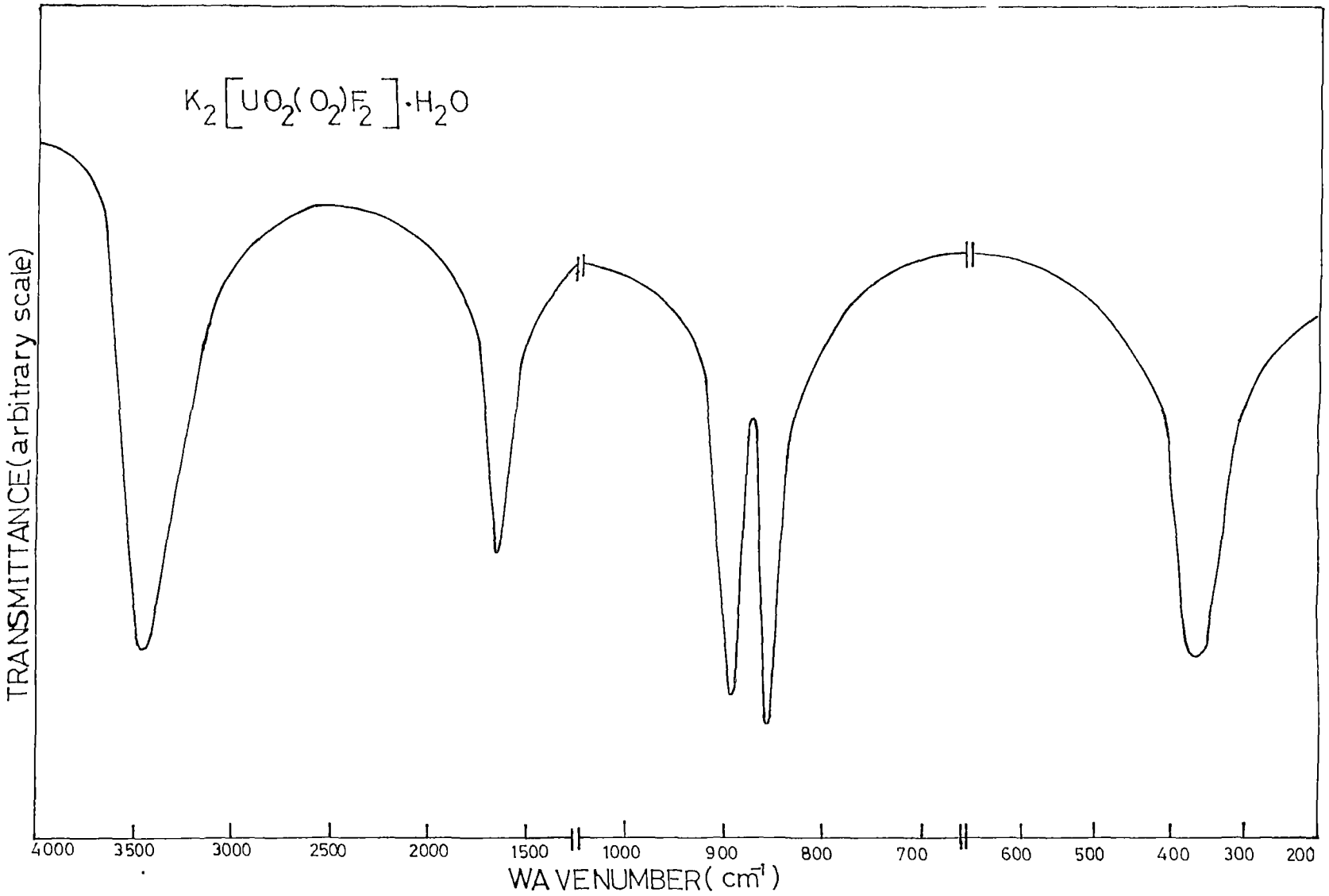
titrations with a standard Ce^{4+} solution, and also with standard $KMnO_4$ solution, in presence of boric acid to prevent any loss of active oxygen. The results of which conspicuously suggested the presence of one peroxide (O_2^{2-}) group coordinated to the UO_2^{2+} center in each of the compounds. The compounds $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb) were found to be diamagnetic in nature, as evidenced from the results of magnetic susceptibility measurements, in conformity with the occurrence of uranium in its hexavalent state.

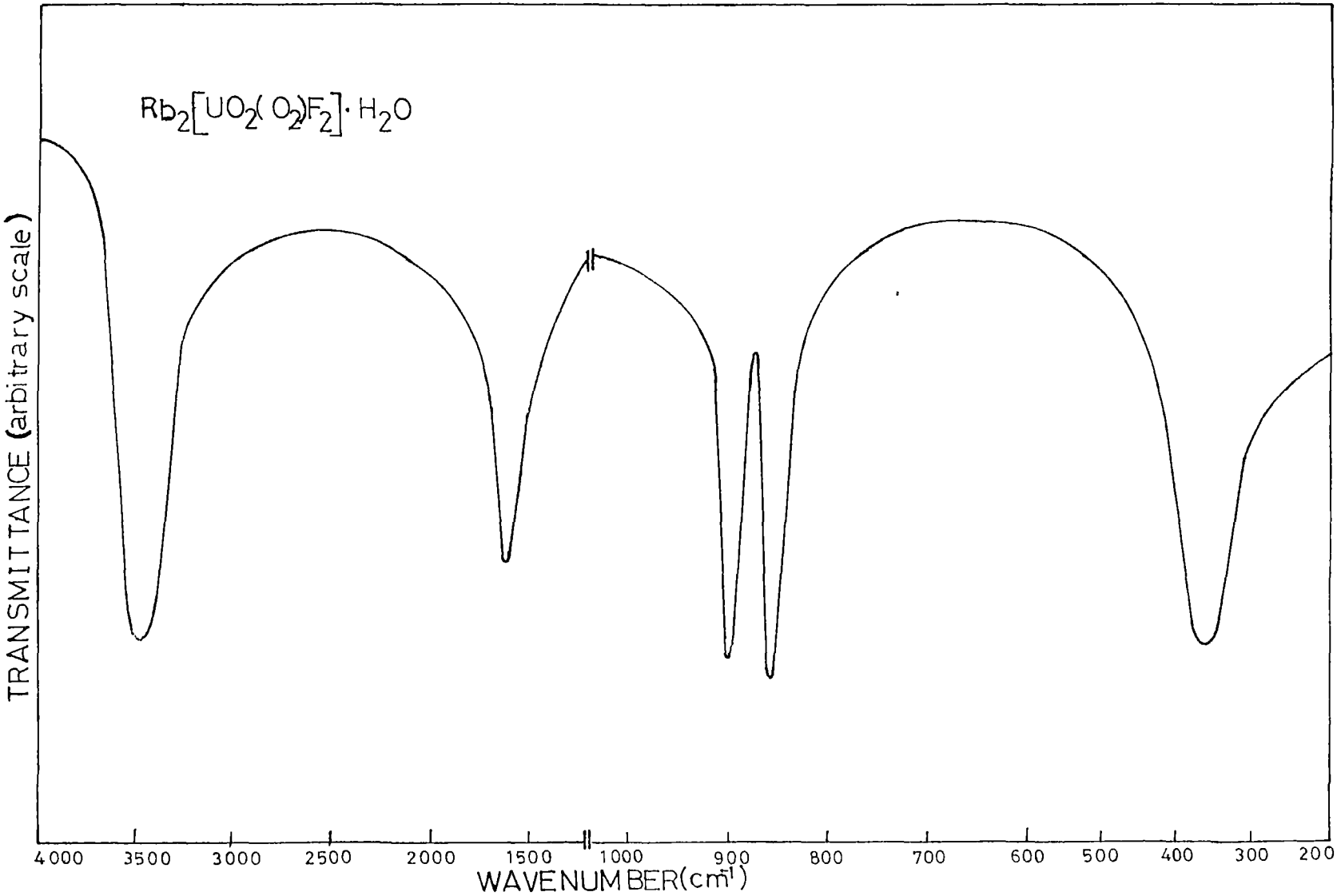
The infrared spectra of alkali-metal difluorodioxo-peroxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and alkali-metal difluorodioxouranate(VI) monohydrates, $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb) are quite characteristic. The significant features of the IR spectra of the compounds are the absorptions due to ν(U=O), coordinated peroxides and coordinated F^- ligands. The absorptions at 910-880, 870-850, and 370-350 cm^{-1} have been assigned to ν(U=O (translinked O=U=O group)[3], ν(O-O)[4,5] and ν(U-F)[6] modes, respectively. The strong and sharp band at <u>ca</u> 860 cm^{-1} due to ν(O-O) supports the view that O_2^{2-} is coordinated to the UO_2^{2+} center in a triangular bidentate (C_{2v}) manner.[4,5] The observance of ν(U=O) modes at <u>ca</u> 900 cm^{-1} are well documented in the literature[3] and suggests the presence of a translinked O=U=O group. A consistent appearance of the strong

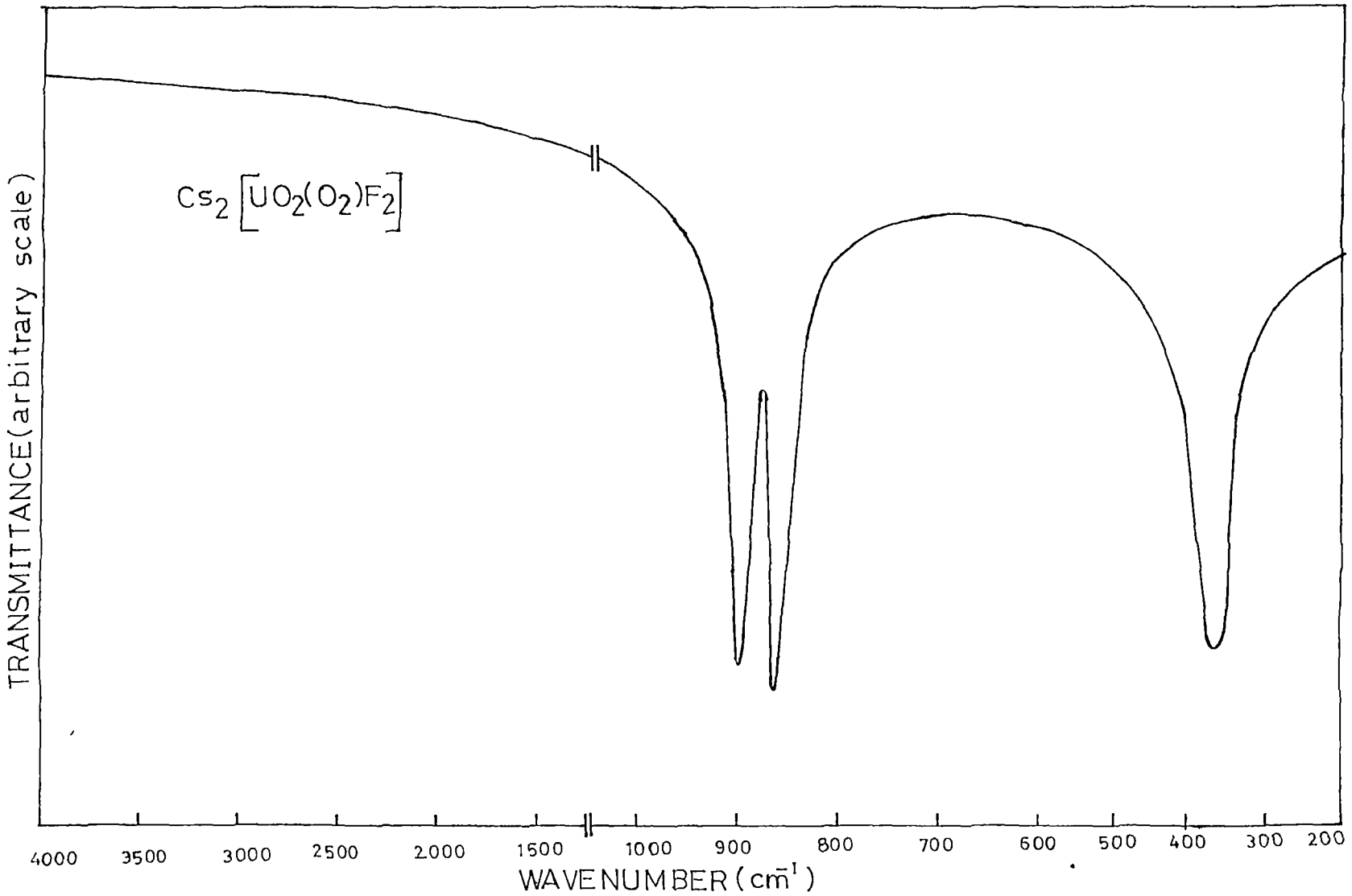
Table 3. Structurally Significant Infrared Bands of Alkali-Metal and Ammonium Difluorodioxoperoxo-uranates(VI)

Compound	IR cm^{-1}	Assignments
$(NH_4)_2[UO_2(O_2)F_2]$	885s, 900s	ν(U=O)
	855s	ν(O-O)
	350s,br	ν(U-F-U)
	3160m, 3040s, 1400s	ν_3, ν_1, ν_4 N-H
$K_2[UO_2(O_2)F_2].H_2O$	890s	ν(U=O)
	860s	ν(O-O)
	370s,br	ν(U-F-U)
	3440s	ν(O-H)
	1640m	δ(H-O-H)
$Rb_2[UO_2(O_2)F_2].H_2O$	905s	ν(U=O)
	860s	ν(O-O)
	360s, br	ν(U-F-U)
	3450s	ν(O-H)
	1640m	δ(H-O-H)
$Cs_2[UO_2(O_2)F_2]$	900s	ν(U=O)
	860s	ν(O-O)
	360s,br	ν(U-F-U)


$(NH_4)_2[UO_2(O_2)F_2]$
TRANSMITTANCE(arbitrary scale)
4000
3500
3000
2500
2000
1500
1100
900
800
700
600
500
400
300
200
WAVENUMBER(cm^{-1})


$K_2[UO_2(O_2)F_2]\cdot H_2O$
TRANSMITTANCE (arbitrary scale)
4000
3500
3000
2500
2000
1500
1000
900
800
700
600
500
400
300
200
WAVENUMBER (cm^{-1})


$Rb_2[UO_2(O_2)F_2]\cdot H_2O$
TRANSMITTANCE (arbitrary scale)
4000
3500
3000
2500
2000
1500
1000
900
800
700
600
500
400
300
200
WAVENUMBER(cm^{-1})


$Cs_2[UO_2(O_2)F_2]$
TRANSMITTANCE(arbitrary scale)
4000
3500
3000
2500
2000
1500
1000
900
800
700
600
500
400
300
200
WAVENUMBER (cm^{-1})

band at 350-370 cm^{-1} in the spectrum of each of the compounds, irrespective of the type of counter cation present, led us to assign it to ν(U-F) arising from the occurrence of coordinated fluoride. The somewhat lower value of ν(U-F) compared to those of the binary fluorouranates(VI),[6] and slightly broad nature of the band indicate the distinct possibility of fluoride acting as a bridging group. The two additional bands at ca 3440 and ca 1640 cm^{-1} in the spectra of both the K^+ and Rb^+ salts, resemble in their shapes and positions those arise from ν(O-H) and δ(H-O-H) modes, respectively, of uncoordinated water.[7] Further it was emphasized in the literature[8] that the ν(O-H) band at ca 3455 cm^{-1} is rather typical for the presence of lattice water. These results and the absence of ν(O-H) and δ(H-O-H) modes in the cases of the NH_4^+ and Cs^+ salts of the complex anion makes it clear that the water is not coordinated to the UO_2^{2+} center.

Thus it may be infered that fluoroperoxouranates, $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb) can be synthesised under the appropriate experimental conditions. The pH 6.5-7 is very crucial for the formation of $[UO_2(O_2)F_2]^{2-}$ ion. The typical pattern of the IR spectra suggests that the peroxide is bonded to the UO_2^{2+} center in triangular bidentate manner and fluoride (F^-) is also coordinated to metal center probably acting as a bridging group. The complex species $[UO_2(O_2)F_2]^{2-}$ may have a polymeric structure through -U-F-U-F-U- chains.

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CHAPTER 4

Chapter 4

Synthesis and Physico-Chemical Studies of Alkali-Metal Dioxoperoxo(carbonato)uranate(VI) Monohydrates, $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K), Alkali-Metal and Ammonium Dioxoperoxo(sulphato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4), and Molecular Complex Peroxouranates, $[UO_2(O_2)L\text{-}L]$ (L-L = ethylenediamine (en), 2,2'-bipyridine (bipy), or 1,10-phenanthroline (o-phen), and $[UO_2(O_2)glyH]$ (glyH = glycine)*

Although uranium is the most important and useful of the actinide metals and is known to form simple peroxides,[1,2] its heteroligand peroxo chemistry seems to have been practically overlooked in earlier investigations.[1,2] This is probably because of the highly complicated nature of peroxouranate chemistry[1] owing to the formation of a number of different species with a small variation of pH of the reaction solution as already mentioned in Chapter 1 and 3. Recent results,[3-6] including the ones described in Chapter 3, in the field of peroxo-metal chemistry advocate for an enhanced stability of such compounds brought about by the coordination of heteroligands.

*A major part of the work described in this Chapter has been published.
J. Chem. Soc., Dalton Trans., 1986, 709; Inorg. Chem., 1986, 25, 2354.

Peroxo(carbonato)uranate(VI), one of the text book example of complex peroxouranates, $(NH_4)_2[UO_2(O_2)(CO_3)].2H_2O$[7] being the only one for which the synthesis is available. Complex peroxo(sulphato)uranates donot seem to have any reported existence. Moreover, very little is known regarding molecular heteroligand peroxo complexes of UO_2^{2+}. An additional interest adheres to latter type of compounds because such compounds may provide a possibility of studies of reactivity of coordinated peroxide.

As a sequel of the work described in Chapter 3 the limit of heteroligand has now been extended from F^- to CO_3^{2-}, SO_4^{2-}, ethylenediamine (en), 2,2'-bipyridine (bipy), 1,10-phenanthroline (o-phen) and glycine (glyH).

Chapter 4 of the thesis presents synthesis of complex peroxouranates of the types: $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4), $[UO_2(O_2)L\text{-}L]$ (L-L = en, bipy, or o-phen), and $[UO_2(O_2)glyH]$. Also presented in this Chapter is an account of the results of structural assessment of the newly synthesised compounds made by physico-chemical studies including laser Raman (lR) spectroscopy.

Experimental

Chemicals used were all reagent grade products (Loba-Chemie, Glaxo, E. Merck, S.D's).

(i) Synthesis of Alkali-Metal Dioxoperoxo(carbonato)-uranate(VI) Monohydrates, $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K)

Since the method of synthesis of Alkali-metal Dioxoperoxo(carbonato)uranate(VI) Monohydrates, is a general one, only a representative procedure is described below.

In a typical synthesis, powdered uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$ (1g, 1.99 mmol) was dissolved in 20 cm^3 of hot water followed by the slow addition of a 20% solution of AOH (A = Na or K) with stirring until an yellow product ceased to appear. The solution was filtered hot and the yellow product washed free from alkali. To a stirred water suspension of the product, $AHCO_3$ (8 mmol; ratio $U:CO_3^{2-}$ = 1:4) was added and stirring continued for ca 20 min. An excess of 30% H_2O_2 (30 cm^3, 264.7 mmol) was added until a clear yellow solution was obtained. The pH of the reaction solution measured at that instant, was found to be 7-8. The solution was filtered to remove any undissolved residue and then cooled in an ice-bath for ca 30 min. Addition of ca 50 cm^3 of pre-cooled ethanol led to the precipitation

of yellow microcrystalline solid which was separated by filtration. The product was washed 3-4 times with ethanol, and then dried *in vacuo* over concentrated H_2SO_4.

The yield of $Na_2[UO_2(O_2)(CO_3)].H_2O$ was 0.7g (82%) and $K_2[UO_2(O_2)(CO_3)].H_2O$ was 0.8g (88%).

(ii) Synthesis of Alkali-Metal and Ammonium Dioxoperoxo-(sulphato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4)

A typical procedure

An amount of 1.0g (1.99 mmol) of uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, was dissolved in 10-15 cm^3 of water followed by addition of 25% aqueous ammonia solution or a concentrated solution of sodium hydroxide in the case of the Na^+ salt, with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off, and washed free from alkali and nitrate. To an aqueous suspension of the product was added 4 cm^3 (10 mmol) of 2.5M H_2SO_4 solution to obtain a clear solution, which was stirred for *ca* 5 min. To the clear solution, an amount of 25 cm^3 (220.5 mmol) of 30% H_2O_2 was added, while $U:SO_4^{2-}:H_2O_2$ ratio was maintained at 1:5:111, and the solution was stirred for *ca* 15 min followed by careful addition of the corresponding alkali-metal or ammonium hydroxide solution, AOH (A = Na or NH_4), until the pH of the solution was raised

to 6, where upon a yellow product just began to appear. An equal volume of ethanol was added with occassional stirring to obtain yellow microcrystalline alkali-metal or ammonium dioxoperoxo(sulphato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) in high yields. Each of the compounds was allowed to settle for ca 20 min, separated by centrifugation, and purified by washing (3-5 times) with ethanol. The product thus obtained was dried in vacuo over concentrated H_2SO_4. The amounts of reagents used for the synthesis of and the yields obtained for $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) are shown in Table 1.

Table 1. Amounts of Reagent Used for the Synthesis of and Yields Obtained for $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na)

Compound	Yield g (%)	Amount of $UO_2(NO_3)_2 \cdot 6H_2O$ g (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)	Amount of 2.5M H_2SO_4 cm^3 (mmol)
$(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$	0.8 (90)	1 (1.99)	25 (220.5)	4 (10)
$Na_2[UO_2(O_2)SO_4(H_2O)]$	0.75 (82)	1 (1.99)	25 (220.5)	4 (10)

(iii) Synthesis of Orthophenanthrolinedioxoperoxouranium(VI), $\lceil UO_2(O_2)$o-phen$\rfloor$

A 1.0g (2.36 mmol) sample of $UO_2(CH_3COO)_2.2H_2O$ was dissolved in 10-15 cm^3 of water with stirring. The solution was filtered to remove any undissolved residue, and to it was added, an ethanolic solution (10 cm^3) of 0.47g (2.36 mmol) of 1,10-phenanthroline monohydrate and the whole was stirred for ca 5 min, whereupon a light yellow product started appearing. An amount of 15 cm^3 (132.35 mmol) of 30% H_2O_2 was added maintaining the U:o-phen:H_2O_2 ratio at 1:1:56, and the mixture was stirred for ca 15 min. The pH at this stage was found to be 3.5-4. Pre-cooled ethanol (half of the original volume) was added with occassional stirring, to facilitate complete precipitation of the yellow microcrystalline $\lceil UO_2(O_2)$o-phen$\rfloor$. The compound was separated by filtration, washed 3-4 times with ethanol and finally dried in vacuo over concentrated H_2SO_4.

Yield of $\lceil UO_2(O_2)$o-phen$\rfloor$ was 1.04g (91.2%).
The method of synthesis of $\lceil UO_2(O_2)$bipy$\rfloor$ is analogous to that of $\lceil UO_2(O_2)$o-phen$\rfloor$ described above.

Starting from 1.0g (2.36 mmol) of $UO_2(CH_3COO)_2.2H_2O$ the yield of $\lceil UO_2(O_2)(bipy)\rfloor$ was found to be 1.0g (94%).

(iv) Synthesis of Ethylenediaminedioxoperoxouranium(VI) $[UO_2(O_2)en]$

Uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, 1.0g (1.99 mmol) was dissolved in 10-15 cm^3 of water, followed by addition of aqueous ammonia solution (sp.gr 0.9), until the yellow precipitate ceased to appear. The precipitate was filtered off, and washed free from alkali and nitrate. An aqueous suspension (10 cm^3) of the yellow precipitate obtained as above was dissolved by the addition of 2 cm^3 (5.0 mmol) of 5N aqueous sulphuric acid solution. This was then filtered and cooled to an ice-bath temperature. To the clear cold solution was added 3 cm^3 (49.92 mmol) of pre-cooled ethylenediamine dropwise with continuous stirring (U:en ratio at 1:25.1), while light yellow product just began to appear. To this reaction mixture an excess amount of 30% H_2O_2 solution (20 cm^3, 176.47 mmol) was added whereupon a clear orange-red solution was obtained. Stirring was continued for a further period of ca 10 min, while yellow microcrystalline ethylenediaminedioxoperoxouranium(VI), $[UO_2(O_2)en]$, started appearing. At this stage pH was found to be ca 9. A complete precipitation of the compound was, however, achieved by addition of cold ethanol in an amount not exceeding half of the original volume. The reaction container was allowed to stand for ca 30 min, and the product was isolated by

centrifugation, washed 4 times with ethanol. The compound was finally dried in vacuo over concentrated H_2SO_4. The yield of $\lceil UO_2(O_2)en \rfloor$ obtained was 0.7g (91.7%).

(v) Synthesis of glycinedioxoperoxouranium(VI), $\lceil UO_2(O_2)glyH \rfloor$

Powdered uranyl nitrate hexahydrate, $UO_2(NO_3)_2.6H_2O$, 1.0g (1.99 mmol) was dissolved in 15 cm^3 of water, followed by a slow addition of 25% solution of aqueous ammonia, until the yellow product ceased to appear. The yellow precipitate was filtered off, washed free from alkali and nitrate. To an aqueous suspension (10 cm^3) of the product was added 2 cm^3 (5.0 mmol) of 5N aqueous solution of sulphuric acid to obtain a clear solution, and stirred for ca 5 min. To the resulting clear solution 0.3g (3.99 mmol) of glycine was added, maintaining the U:glycine ratio at 1:2, and the solution was stirred for ca 5 min, followed by the addition of an excess amount of 30% H_2O_2 (15 cm^3, 132.35 mmol). Stirring was continued for a further period of ca 10 min, when a yellow product began to appear. The pH of the reaction medium was raised to ca 6.5 by the slow and careful addition of a 20% solution of KOH. Addition of 50 cm^3 of pre-cooled ethanol to the above solution led to the complete precipitation of the yellow microcrystalline $\lceil UO_2(O_2)glyH \rfloor$. The product was separated by filtration, washed with ethanol 3-4 times, and then dried in vacuo over concentrated H_2SO_4.

The yield of $[UO_2(O_2)\ glyH.]$ was found to be 0.7g (97%).

Elemental Analyses

Estimation of uranium, peroxide, sulphate, carbon, hydrogen, nitrogen were performed following the methods described in Chapter 2 of the thesis. The results of elemental analyses for $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) and $[UO_2(O_2)L\text{-}L]$ (L-L = o-phen, bipy or en), and $[UO_2(O_2)glyH]$ are given in Tables 2-4.

Table 2. Analytical data of $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K)

Compound	Found % (Calcd. %)			
	A	U	O[a]	C
$Na_2[UO_2(O_2)(CO_3)].H_2O$	10.45 (10.8)	56.2 (55.85)	7.8 (7.5)	2.85 (2.8)
$K_2[UO_2(O_2)(CO_3)].H_2O$	17.3 (17.1)	52.25 (51.95)	7.2 (7.0)	2.6 (2.6)

[a]Peroxo-oxygen

Table 3. Analytical Data of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4 or Na)

Compound	Found % (Calcd. %)			
	A or N	U	O[a]	SO_4
$(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$	6.32 (6.2)	52.38 (52.64)	7.3 (7.08)	21.62 (21.24)
$Na_2[UO_2(O_2)SO_4(H_2O)]$	9.55 (9.95)	51.82 (51.51)	7.2 (6.93)	20.93 (20.79)

[a]Peroxo-oxygen

Table 4. Analytical Data of $[UO_2(O_2)L\text{-}L]$ (L-L = o-phen, bipy or en) and $[UO_2(O_2)glyH]$

Compound	Found % (Calcd. %)				
	U	O[a]	C	H	N
$[UO_2(O_2)o\text{-}phen]$	49.51 (49.36)	6.42 (6.64)	30.12 (29.88)	1.63 (1.66)	5.79 (5.81)
$[UO_2(O_2)bipy]$	52.13 (51.95)	7.14 (6.98)	26.23 (26.21)	1.78 (1.75)	6.14 (6.11)
$[UO_2(O_2)en]$	65.67 (65.73)	8.94 (8.84)	6.66 (6.63)	2.22 (2.21)	7.92 (7.73)
$[UO_2(O_2)glyH]$	63.41 (63.12)	8.63 (8.49)	6.34 (6.37)	1.37 (1.33)	3.75 (3.71)

[a]Peroxo-oxygen

Results and Discussion

Complex Peroxo(carbonato)uranates(VI)

The reaction of hydrogen peroxide with UO_2^{2+}, leading to a complex peroxouranate(VI) of a definite composition is highly dependent on the pH of the reaction medium and it was shown very recently that a relatively higher pH favoured coordination of O_2^{2-} with UO_2^{2+} center (see Chapter 3). Thus, evaluation of an appropriate pH for successful synthesis of complex peroxouranate species is emphasized to be an important prerequisite. In the present case, pH > 6 of the reaction solution was considered conducive in order to prevent the reaction $CO_3^{2-} + 2H^+ \longrightarrow CO_2\uparrow + H_2O$. Accordingly pH ca 7 was found to be suitable for the syntheses of the desired peroxo(carbonato)uranates(VI). It is imperative to state that the products isolated at pH 4 or 5 either did not show the presence of CO_3^{2-} at all or did to a very small extent, indicating that coordination of CO_3^{2-} ligand might have just commenced. However, the reaction of UO_2^{2+} with hydrogen peroxide and alkali-metal or ammonium bicarbonate, $AHCO_3$ (A = Na or K), at pH 7-8, followed by the addition of ethanol which facilitated precipitation, afforded $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K), in very high yields. Attempts to synthesise the NH_4^+ salt of the complex ion was unsuccessful. Corresponding salts

of Rb^+ and Cs^+ could be obtained by the method analogous to that used for Na^+ and K^+. Strong desiccation of the compounds over concentrated H_2SO_4 did not remove the water of crystallization. Pyrolysis of $A_2[UO_2(O_2)(CO_3)].H_2O$ at 100°C expelled the water molecule without changing the composition of the complex ion. It is notable that peroxide was not lost at the above-mentioned temperature, unlike in the corresponding complex peroxo(carbonato)vanadates(V).[8]

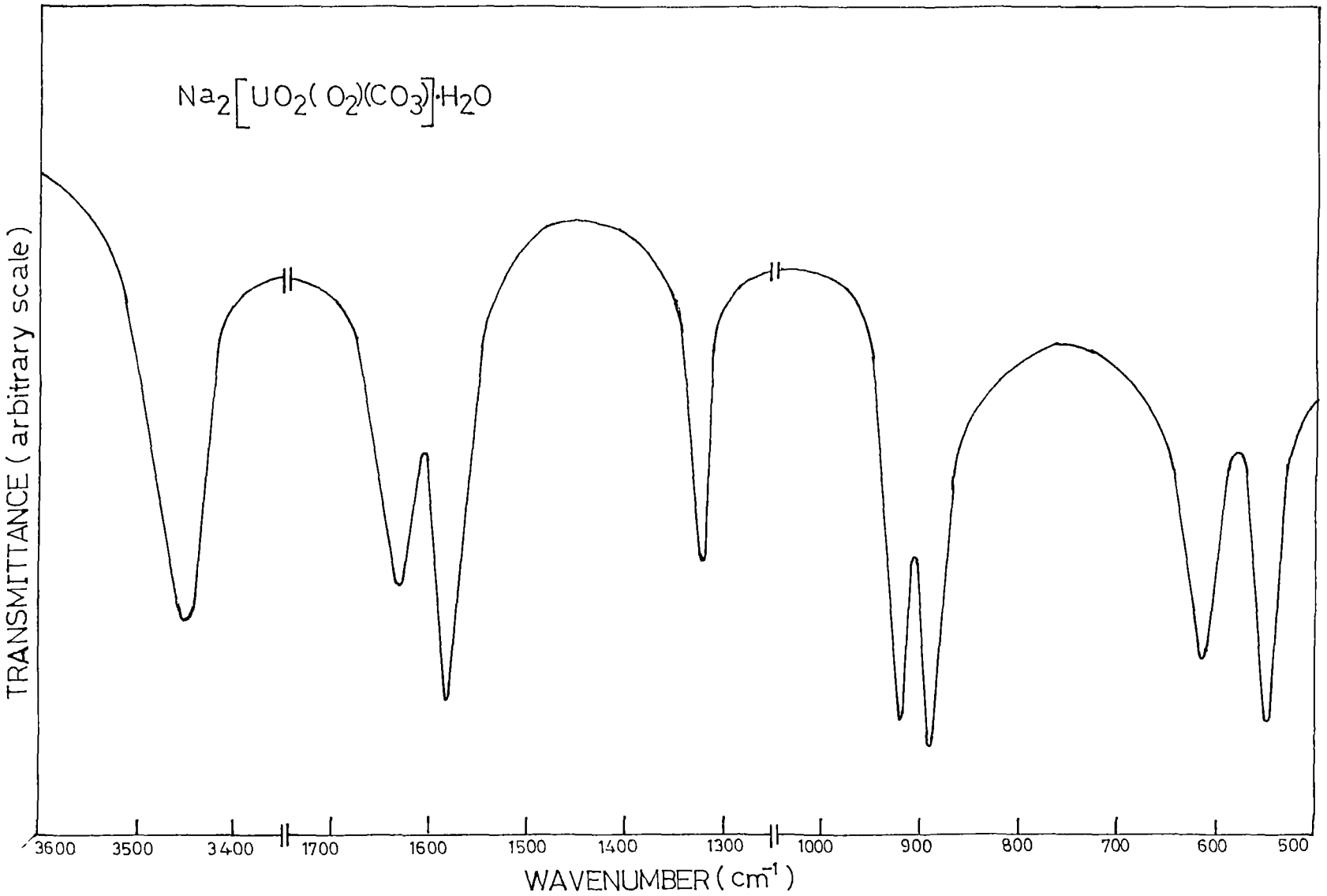
The molar conductances of $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K), measured in water, lying between 240 and 255 $\Omega^{-1}cm^2mol^{-1}$ at room temperature, are as expected and attest to the stability of the complexes. The complexes $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K) tend to absorb moisture slowly. The results of magnetic susceptibility measurement show that the compounds are diamagnetic, in conformity with the occurence of U^{VI}. The importance of estimations of active oxygen has been already emphasized in Chapter 3. The results of peroxide estimations, by redox titrations[3] involving separately standard potassium permanganate and cerium(IV) solutions, suggest the presence of one peroxide (O_2^{2-}) per U^{VI} in the complexes.

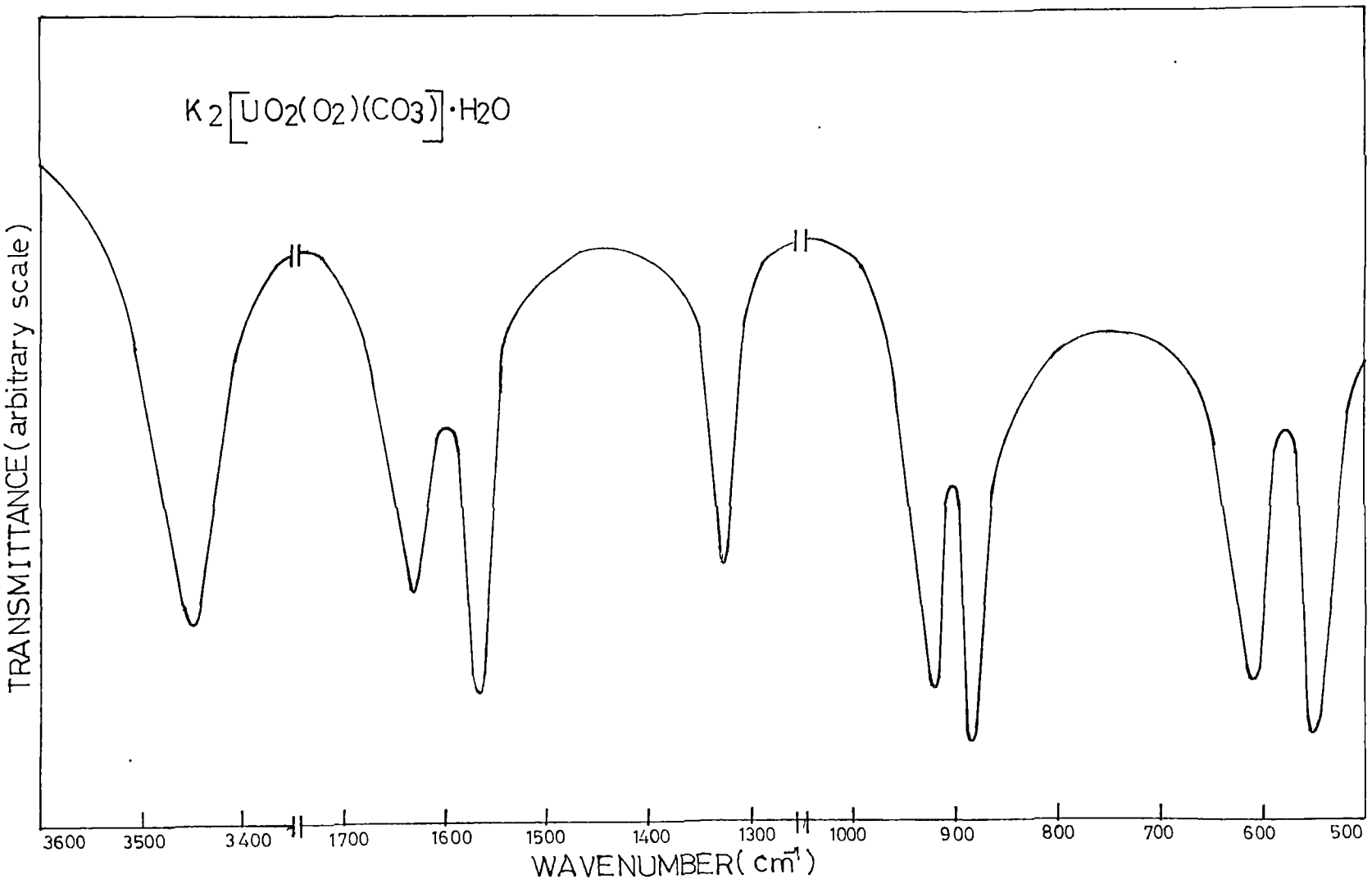
The IR spectra of $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K) show bands (Table 5), at ca 920s, ca 890s and ca 610m and ca 550s cm^{-1} due to ν(O=U=O, translinked),[9] ν(O-O) and ν(U-O_2) modes,[3,10,11] respectively, at ca 1580s, ca 1330m,

ca 1050s, ca 750m, ca 675m and at ca 415 cm^{-1} owing to ν(C-O), ν(C-O) + δ(O-C-O), ν(C-O), ring deformation + ν(U-O), δ(O-C-O) + ν(U-O) and ν(U-O), respectively, originating from the coordinated bidentate carbonate,[12] and the absorptions at ca 3445m and ca 1630s due to ν(O-H) and δ(H-O-H) modes of uncoordinated water. The laser Raman spectra, recorded in the solid state because of low solubility, exhibited peaks at ca 930 cm^{-1} assigned to ν(O=U=O),[9] at 880, ca 600, and ca 550 cm^{-1} due to ν(O-O, ν_1), ν(U-O_2, ν_3), and ν(U-O_2, ν_2), respectively,[10,11] and at ca 1570 due to ν(C-O) (ν_1,A_1) of coordinated CO_3^{2-}. The distinction between ν_2 and ν_3 modes of ν(U-O_2) was made on the basis of the sharpness and intensity of the peaks, and that at ca 550 cm^{-1} being the sharpest and most intense. The facile loss of water at 100°C and the resemblance of peak shapes and positions of δ(H-O-H) and ν(O-H) with those of uncoordinated water[13,14] suggest that the water molecules are not coordinated. The typical pattern of absorptions due to the coordinated O_2^{2-} [Ref. 3,10,11], and those due to the coordinated CO_3^{2-} [Ref. 12], especially the appreciable separation between ν_1(A_1) and ν_5(B_2) modes (Table 5) and also the appearance of a Raman peak at ca 1575 cm^{-1} due to ν(C-O) ($\nu_1 A_1$), render it certain that both the peroxide (O_2^{2-}) as well as the carbonate (CO_3^{2-}) ligands are bonded to the metal center in a bidentate chelated (C_{2v}) manner.

Table 5. Structurally Significant IR and laser Raman (LR) Bands of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ (A = Na or K)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$Na_2[UO_2(O_2)(CO_3)]\cdot H_2O$	1580s	1570	ν(C-O) ν_1, A_1
	1325m		ν(C-O) + δ(O-C-O) ν_5, B_2
	920s	930	ν(O=U=O)
	890s	880	ν(O-O) ν_1
	615m	600	ν(U-O_2) ν_3
	550s	550	ν(U-O_2) ν_2
$K_2[UO_2(O_2)(CO_3)]\cdot H_2O$	1570s	1570	ν(C-O) ν_1, A_1
	1330m		ν(C-O) + δ(O-C-O) ν_5, B_2
	925s	930	ν(O=U=O)
	885s	885	ν(O-O) ν_1
	610m	600	ν(U-O_2) ν_3
	550s	540	ν(U-O_2) ν_2


$Na_2[UO_2(O_2)(CO_3)]\cdot H_2O$
TRANSMITTANCE (arbitrary scale)
3600
3500
3400
1700
1600
1500
1400
1300
1000
900
800
700
600
500
WAVENUMBER (cm^{-1})


K2[UO2(O2)(CO3)]·H2O
TRANSMITTANCE (arbitrary scale)
3600
3500
3400
1700
1600
1500
1400
1300
1000
900
800
700
600
500
WAVENUMBER (cm⁻¹)

Complex Peroxo(sulphato)uranates(VI)

The suitable pH for bringing about coordination of both peroxide and sulphate with an uranyl center was ascertained to be 6. The compounds isolated at a relatively lower pH (eg., ca 4) on being analysed did not show the occurence of peroxide to the desired level (i.e., $U:O_2^{2-}$ as 1:1), indicating therefore that the O_2^{2-} uptake process was in progress but did not reach the $U:O_2^{2-}$ ratio of 1:1. The peroxo(sulphato)uranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) have been synthesised by carrying out reactions among UO_2^{2+}, H_2O_2, and SO_4^{2-} at pH 6 of the reaction solution maintained by addition of the corresponding alkali-metal or ammonium hydroxide, AOH. While the NH_4OH was used as a 25% solution (sp.gr 0.9), NaOH was added as a 10% solution. The peroxide uptake process was monitored through chemical determination of active oxygen (O_2^{2-}) in the product isolated from the reaction solution at different pH. The method of synthesis of complex peroxouranates is straight forward and may serve as a paradigm for an access to other heteroligand peroxouranate(VI). It is important to mention that, according to the present method, the complex peroxouranates starts appearing as soon as the solution attains pH 6, however, the addition of ethanol is required to achieve quick and nearly quantitative precipitation of the products. It must also be emphasized that

similar compounds were obtained in low yields by allowing reaction solutions, after adjusting their pH to 6, to stand for several hours at an ice-water temperature.

The $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) are yellow microcrystalline products, practically insoluble in water. Their insolubility precludes molar conductance measurements. They do not seem to be hygroscopic, and are stable for prolong periods. Pyrolysis studies showed that $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) does not suffer any loss of water upto ca 110°C leading us to state that the water molecule is rather tightly held in the compounds. The complex peroxo(sulphato)-uranates(VI) decompose in dilute sulphuric acid, liberating hydrogen peroxide quantitatively, and thus facilitate determination of active oxygen (O_2^{2-}) content of the compounds. Chemical determination of active oxygen, considered to be very crucial to ascertain the number of O_2^{2-} groups coordinated to the UO_2^{2+} center, was accomplished by the redox titrations in manners similar to those described under peroxo(carbonato)-uranate(VI). The estimation was conducted in the presence of boric acid in order to prevent any loss of active oxygen. The results suggested the occurrence of one O_2^{2-} per UO_2^{2+} center in each of the newly synthesised compounds. The compounds are all diamagnetic, in agreement with the presence of hexavalent uranium.

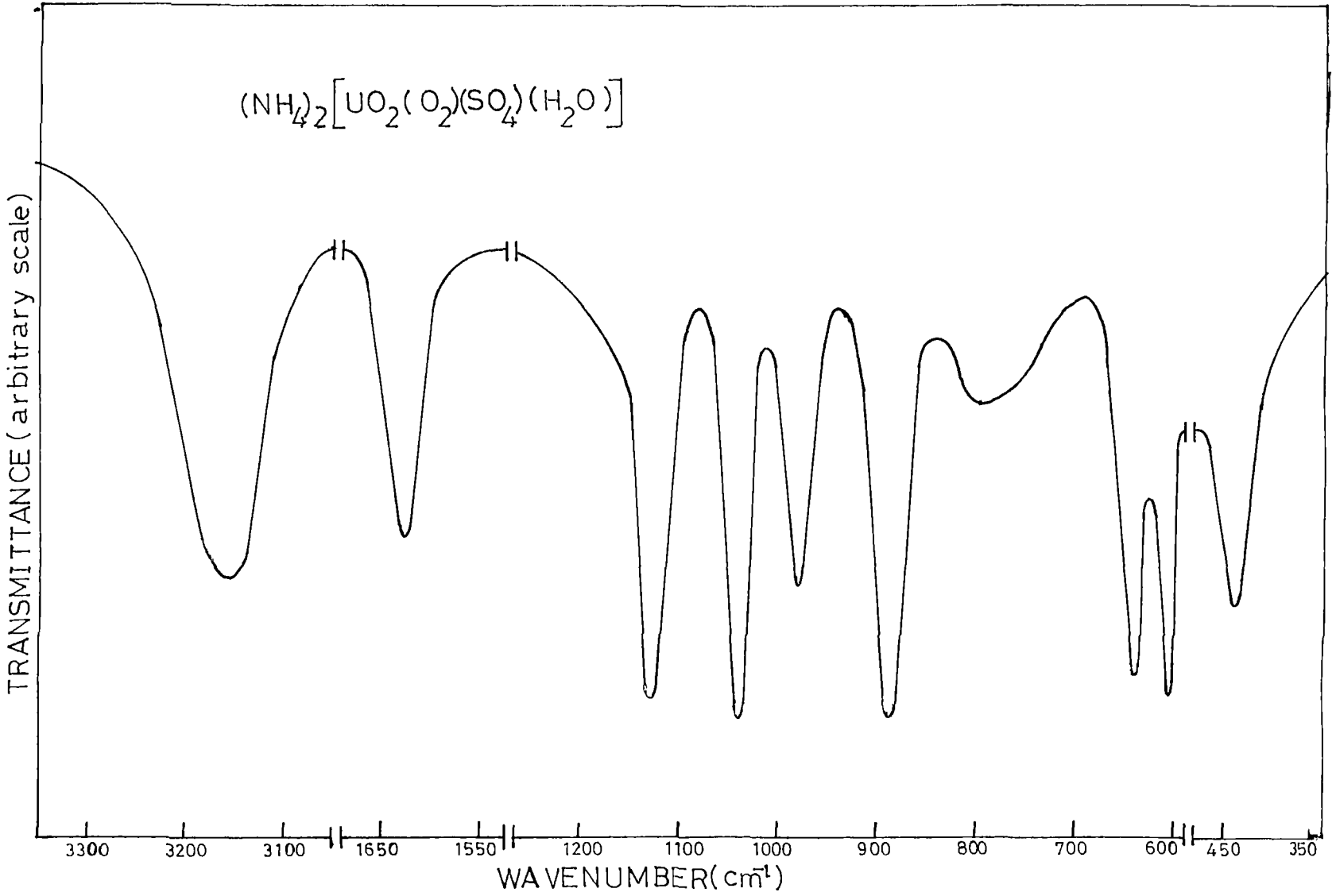
The infrared and laser Raman (IR) spectra of Dioxoperoxo(sulphato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4), were recorded in the range 4000-200 cm^{-1}, and 2000-150 cm^{-1}, respectively. Owing to the insolubility of the compounds, the IR spectra were recorded only on solids.

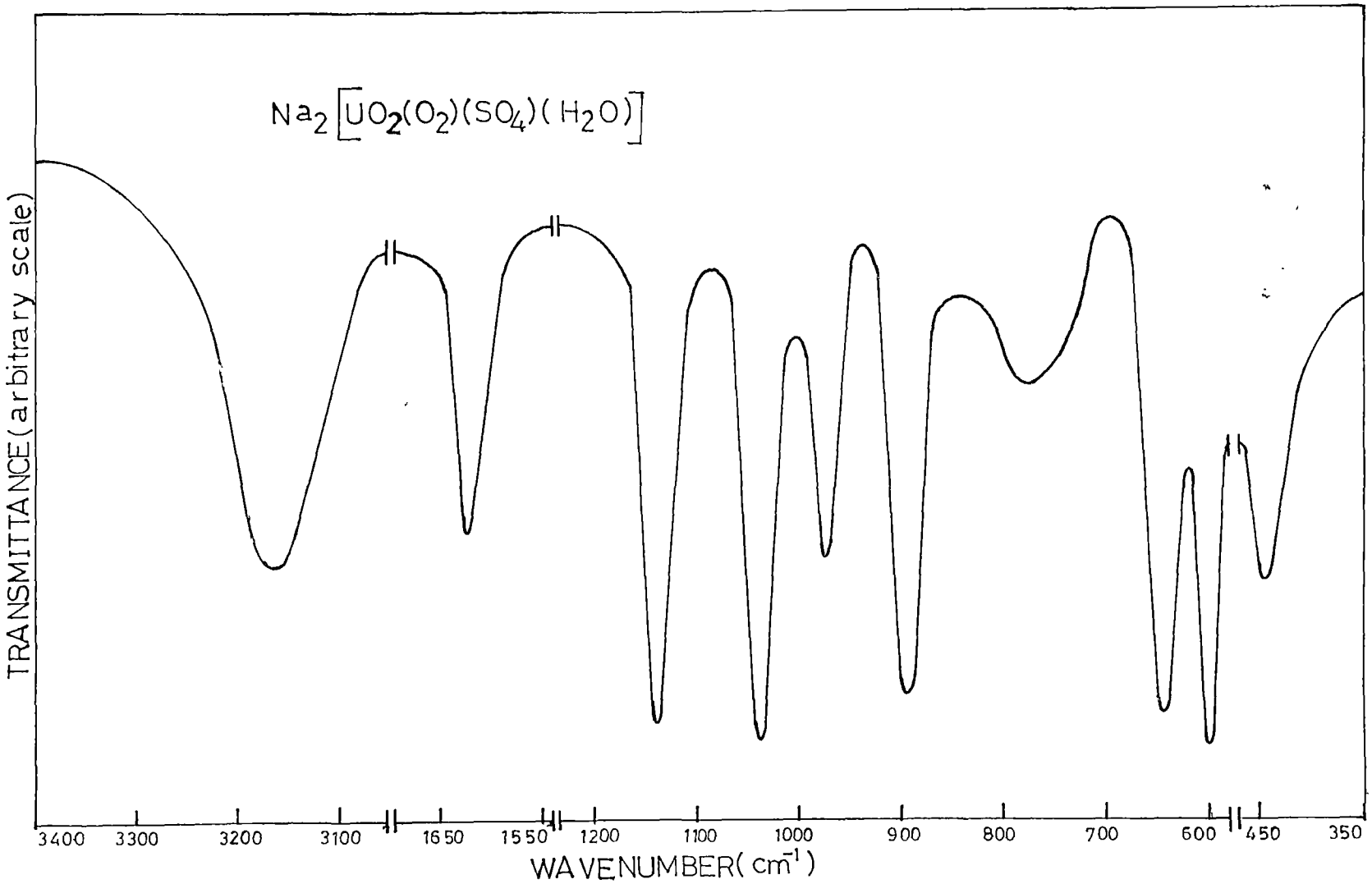
The significant features of the IR spectra of the $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) compounds involve absorptions of coordinated sulphate, coordinated water, and the U=O stretching. The appearance of medium intensity ν_1 and ν_2 modes of S-O stretchings at ca 980 and ca 450 cm^{-1}, respectively, and the splitting of ν_3 and ν_4 into two bands each (Table 6), as opposed to the absence of ν_1 and ν_2, and the presence of unsplit ν_3 and ν_4 modes in the ionic sulphate, provide strong evidence for the lowering of symmetry of SO_4^{2-} from T_d to C_{3v} and also for its occurrence as a coordinated unidentate ligand in the complex peroxo(sulphato)uranates(VI). A very strong absorption, in addition to the sulphate ligand bands, was observed at ca 895 cm^{-1} and assigned to the ν U=O stretching (translinked) O=U=O group).[9] The IR spectra of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) complement the corresponding IR spectra by exhibiting SO peaks at ca 970 and ca 440 cm^{-1} owing to ν_1 and ν_2 and at ca 1040, ca 1140, ca 600, and ca 650 cm^{-1} due to the ν_3 and ν_4 modes of SO_4^{2-} ligand coordinated in an

unidentate fashion (C_{3v}). A very strong peak observed at ca 900 cm^{-1} because of large polarizability changes involved in the U-O bond, is attributed to the νU=O (translinked O=U=O) mode. The presence of coordinated water causes the distinct appearance of ν(O-H) and δ(H-O-H) modes, which occur in the IR spectra as medium intensity bands at 3160 and 1630 cm^{-1}. The lowering of ν(O-H) frequencies and broadening of δ(H-O-H) bands relative to those of free water suggest a clear possibility of intramolecular hydrogen bonding[15,16] involving uranyl oxygens. This might be a reason for lowering of νU=O as well. Especially noteworthy, over and above the patterns just discussed, is the absence of any band in the IR or lR spectra of the peroxo(sulphato)uranates(VI) in the range 890-800 cm^{-1}, a position where ν(O-O) would appear if peroxide ligand were coordinated in the triangular bidentate (C_{2v}) manner commonly encountered in peroxo compounds of V(V),[3,5,10,11] Ti(IV)[6,10,11,17] and also in case of uranium peroxo compounds, as described earlier, for example. This causes us to infer that the O_2^{2-} (peroxide) ligand is present as a bridging group connecting the contiguous UO_2^{2+} centers through an infinite -U-O-O-U-O-O-U- chain in the crystal lattice. Fortunately the appearance of a broad rather weak band at 790-750 cm^{-1} each in the IR and lR spectra of the compounds lends support to our arguments in favour of a bridging peroxide[18] group.

Table 6. Structurally Significant IR and Raman Bands of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4 or Na)

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$	890s	900	ν(U=O)
	790w,br	780	ν(O-O)
	980m	970	ν_1
	440m	440	ν_2
	1130s	1140	ν_3
	1040s	1040	$\nu_{(S-O)}$
	640s	650	ν_4
	605s	600	
	3160m		ν(O-H)
	1630m		δ(H-O-H)
$Na_2[UO_2(O_2)SO_4(H_2O)]$	895s	950	ν(U=O)
	780w,br	780	ν(O-O)
	975m	970	ν_1
	445m	450	ν_2
	1140s	1140	ν_3
	1040s	1040	$\nu_{(S-O)}$
	645s	640	ν_4
	600s	600	
	3160m		ν(O-H)
	1630m		δ(H-O-H)


$(NH_4)_2[UO_2(O_2)(SO_4)(H_2O)]$
TRANSMITTANCE (arbitrary scale)
3300
3200
3100
1650
1550
1200
1100
1000
900
800
700
600
450
350
WAVENUMBER(cm^{-1})


$Na_2[UO_2(O_2)(SO_4)(H_2O)]$
TRANSMITTANCE (arbitrary scale)
3400
3300
3200
3100
1650
1550
1200
1100
1000
900
800
700
600
450
350
WAVENUMBER (cm^{-1})

Thus it is evident that yellow microcrystalline, diamagnetic complex peroxo(sulphato)uranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4) can be synthesised from the reaction of UO_2^{2+} and H_2O_2 with H_2SO_4 at pH 6 maintained by the addition of the corresponding AOH. The compounds are insoluble, and do not lose water upto 110°C. They decompose in dilute sulphuric acid quantitatively liberating H_2O_2.

While the peroxide group in $[UO_2(O_2)SO_4(H_2O)]$, is bonded to the UO_2^{2+} center in a bridging manner, the SO_4^{2-} occurs as a coordinated unidentate ligand, the H_2O molecule is also coordinated. The complex species very likely has a hexacoordinated polymeric structure through a -U-O-O-U-O-O-U- chain containing peroxide bridges.

Molecular Heteroligand Dioxoperoxouranium(VI), $[UO_2(O_2)bipy]$, $[UO_2(O_2)o\text{-}phen]$, $[UO_2(O_2)en]$, and $[UO_2(O_2)glyH]$

It is apparent from the results obtained so far on complex peroxouranates(VI) involving F^-, SO_4^{2-} or CO_3^{2-} as heteroligands that '$UO_2(O_2)$' is the common framework for all the newly synthesised compounds. The central atom uranium is evidently coordinatively unsaturated and permits coordination of suitable ligands or even solvent molecules leading to the synthesis of newer complex peroxouranates(VI). Thus in order to obtain molecular complexes of dioxoperoxouranium(VI)

heteroligands are to be so chosen that they could act as neutral ligands. Our choice went in favour of N-heterocyclic diamines, namely, 2,2′-bipyridine (bipy) and 1,10-phenanthroline (o-phen), an aliphatic diamine, ethylenediamine (en), and an aminocarboxylic acid, glycine (glyH).

In accord with the synthetic strategy, UO_2^{2+} in an aqueous solution could be made to react with hydrogen peroxide and each of the afore mentioned heteroligands. pH ca 3.5-4, suitable for the synthesis of $\lceil UO_2(O_2)$o-phen$\rfloor$, $\lceil UO_2(O_2)$bipy$\rfloor$ and ca 9 for that of $\lceil UO_2(O_2)$en$\rfloor$, were attained as such without any extra addition of alkali. However, pH ca 6.5 required for the synthesis of $\lceil UO_2(O_2)$glyH $\rfloor$ had to be attained by the addition of aqueous potassium hydroxide solution. Since 2,2′-bipyridine, and 1,10-phenanthroline are not soluble in water, an ethanolic solution of each of them was added to the reaction mixture in the corresponding cases. In order to bring about solubility of the yellow precipitate obtained by the addition of aqueous ammonia to a solution of $UO_2(NO_3)_2.6H_2O$, a very small amount of dilute sulphuric acid solution was added in each of the latter two cases which was followed by the direct addition of the corresponding ligands (vide Experimental). Moreover, unlike in the synthesis of 2,2′-bipyridine, 1,10-phenanthroline or ethylenediamine complexes, the pH of the reaction solution

had to be raised to ca 6.5 for the synthesis of $[UO_2(O_2)glyH]$, by the addition of alkali. Considering the relatively higher basicity of ethylenediamine (en) than bipy or o-phen ligands an enhanced pH was necessary for the successful synthesis of the $[UO_2(O_2)en]$ compound. In this way a series of four molecular heteroligand and dioxoperoxouranium(VI) compounds were obtained. The addition of ethanol was required in each case to facilitate complete precipitation of the products.

The compounds $[UO_2(O_2)bipy]$, $[UO_2(O_2)o\text{-}phen]$, $[UO_2(O_2)en]$, and $[UO_2(O_2)glyH]$ are all yellow microcrystalline products, stable for a prolong period, and their stability ascertained by estimation of active oxygen (O_2^{2-}) periodically. They are insoluble in water. In organic solvents the compounds are practically insoluble at room temperature, however, at higher temperatures they are partially soluble. The compounds are diamagnetic in nature as evident from the results of magnetic susceptibility measurements at ambient temperatures.

The IR spectra of the compounds are relatively more complicated than those of the other compounds reported in this Chapter. The complications arise mainly from the appearance of several vibrational modes owing to the presence of organic heteroligands. The common significant features of the IR spectra are the following:

(i) an absorption at ca 880s cm^{-1} assigned[3,10,11] as $\nu(O-O)$.

(ii) a band at ca 615 cm^{-1} attributed to $\nu(U-O_2)$ originating from the presence of coordinated peroxide,[3,10,11] and

(iii) a vibrational mode at ca 915s cm^{-1} assigned as $\nu_{U=O}$ (translinked O=U=O).[9]

These features attest to the notion that the '$UO_2(O_2)$', containing two oxygen atoms translinked to each other and a triangularly bonded bidentate peroxide (O_2^{2-}) ligand, is again a general framework also for the molecular peroxo compounds of uranium.

Both 2,2'-bipyridine and 1,10-phenanthroline are very commonly encountered ligands and coordination compounds of many metals involving these have been reported in the literature. These, ligands generally act as chelating groups, and metal chelates containing bipy or o-phen have typical spectral features.[19,20,21] The portions of IR spectra of the $\lceil UO_2(O_2)bipy\rfloor$ and $\lceil UO_2(O_2)o\text{-}phen\rfloor$ compounds arising from the N-heterocyclic ligand vibrations are similar to those observed for chelated bipy or o-phen ligands.[19,20,21] This causes us to infer that the bipy and o-phen ligands in the newly synthesised compounds occur as bidentate chelates. Any further discussion in this context may thus be redundant.

The IR spectrum of ethylenediamine dioxoperoxo-uranium(VI), $\lceil UO_2(O_2)en \rfloor$, exhibits in addition to the ν(U=O, translinked O=U=O), ν(O-O), and ν(U-O_2) as described above, absorptions at 1618s and at 1510m, 1340m and at 1050s cm^{-1} assigned as $\delta(NH_2)$, $\delta(CH_2)$ and ν(skeletal) modes of coordinated en[22,23] (Table 7). The observed frequencies and the pattern originating from en suggests clearly that the en ligand occurs as a bidentate one in the compound under discussion. The fact that the spectral pattern is not as simple as the one that would be observed if the en ligand were to be present as a trans-bridging group,[24] leads us to infer that en binds the uranium center as a bidentate chelate, and does not occur as a bridging group.

Besides the common features, the IR spectrum of $\lceil UO_2(O_2)glyH \rfloor$ (Table 8) show absorptions at 1630s, 1385s, ca 1112m, ca 680m, and ca 597s cm^{-1} due to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$, $\rho_r(NH_3^+)$, $\rho_w(COO^-)$ and $\delta(COO^-)$ modes, respectively.[25,26] Notably important are the (i) increase of $\nu_{as}(COO)$, (ii) decrease of $\nu_s(COO)$, and (iii)unaltered positions of N-H stretching frequencies as compared to an uncoordinated glycine. These observations strongly supports the view that glycine in the $\lceil UO_2(O_2)glyH \rfloor$ compound occurs in the Zwitterionic form[26] ($NH_3^+CH_2COO^-$) and is bonded to the metal center through its carboxylic oxygen. Thus although glycine can act as a bidentate ligand, in the present case it

Table 7. Structurally Significant IR Bands of $\lceil UO_2(O_2)en \rfloor$

Compound	IR cm^{-1}	Assignment
$\lceil UO_2(O_2)en \rfloor$	910	ν(O=U=O)
	880	ν(O-O)
	610	ν(U-O_2)
	1618s	δ(NH_2)
	1510m 1340m	δ(CH_2)
	1050s	ν(skeletal)

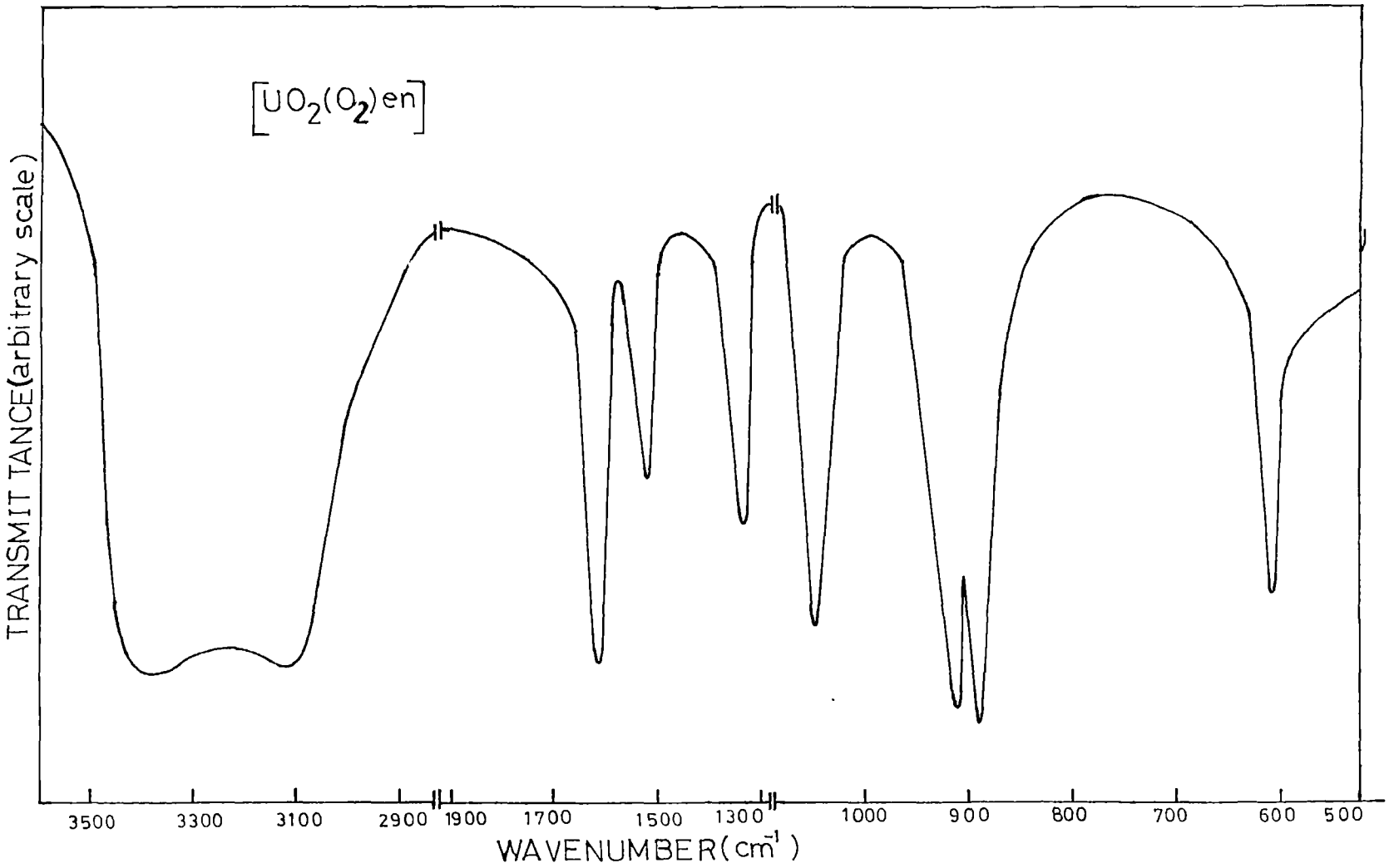
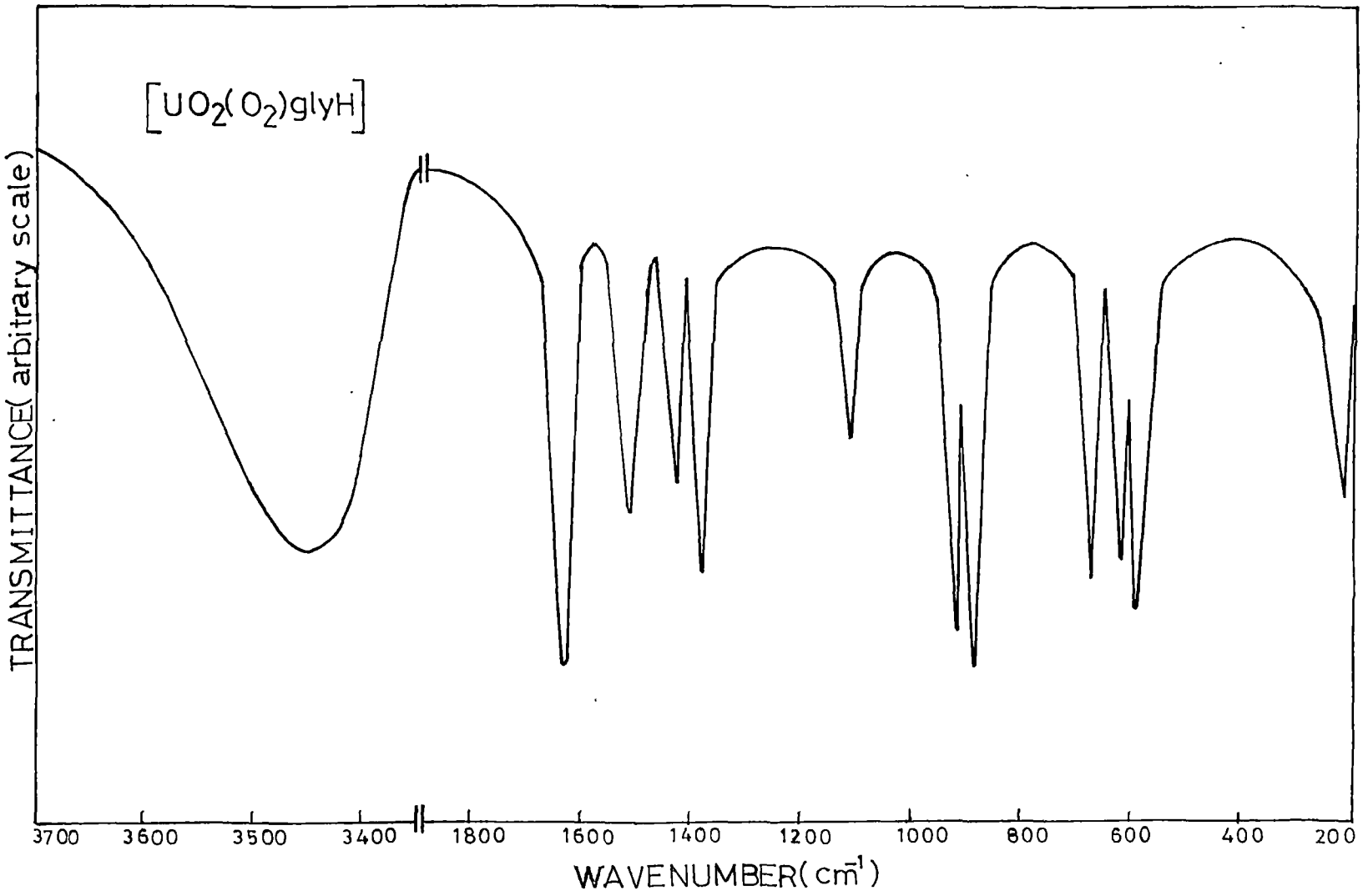

[UO2(O2)en]
TRANSMIT TANCE(arbitrary scale)
3500
3300
3100
2900
1900
1700
1500
1300
1000
900
800
700
600
500
WAVENUMBER(cm-1)

Table 8. Structurally Significant IR Bands of $\lceil UO_2(O_2)glyH \rfloor$

Compound	IR cm^{-1}	Assignment
$\lceil UO_2(O_2)glyH \rfloor$	915	ν(O=U=O)
	890	ν(O-O)
	617	ν(U-O_2)
	1630	ν_{as} (COO)
	1517	δ_s (NH_3^+)
	1427	δ (CH_2)
	1385	ν_s (COO^-)
	1112	ρ_r (NH_3^+)
	680	ρ_w (COO^-)
	597	δ (COO^-)
	215	ν(U-O)


[UO2(O2)glyH]
TRANSMITTANCE(arbitrary scale)
3700
3600
3500
3400
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER(cm-1)

appears that this ligand acts as a monodentate one being bonded in a fashion described above. This kind of bonding of glycine to a metal center is not very common, however, is not unprecedented[26] in chemical literature.

The solubility properties of $\overline{UO_2(O_2)bipy}$, $\overline{UO_2(O_2)o\text{-}phen}$, $\overline{UO_2(O_2)en}$ and $\overline{UO_2(O_2)glyH}$ indicate that each of the compounds may have a polymeric structure through a -U=O····U=O···U=O···· interaction.

The molecular heteroligand-dioxoperoxouranium(VI) compounds may show interesting oxidation chemistry in terms of activation of coordinated O-O; studies on this aspect is now in progress and will be reported elsewhere. The results of initial studies involving $\overline{UO_2(O_2)glyH}$ as the oxidant and separately involving triphenylphosphine, cyclohexene and styrene as the substrates has shown that the products obtained under acid catalysed conditions are triphenyl-phosphine oxide, 1,2 cyclohexane diol, and 1, phenylethylene-glycol, respectively.

It may only be mentioned at this stage that the preliminary results of oxidation reactions are encouraging.

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CHAPTER 5

Chapter 5

New Methods of Syntheses of Alkali-Metal Triacetatodioxouranates(VI), A $[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4), Diacetatodioxouranium(VI) Dihydrate, $[UO_2(CH_3COO)_2].2H_2O$, And Bis(acetylacetonato)dioxouranium(VI) Dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$

And

Electron Ionization Mass Spectrometric Studies of $UO_2(C_5H_7O_2)_2$*

Acetatouranate(VI) chemistry is rather complicated owing to the formation of a variety of compounds between acetic acid and UO_2^{2+} ion[1] depending upon the reaction conditions and the proportions of the reactants used. While studying some other aspects of uranium chemistry (vide Chapters 3 and 4), the need of synthesising compounds of the types A $[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4), and $[UO_2(CH_3COO)_2].2H_2O$ were felt, particularly because such compounds are capable of acting as good precursors in synthetic inorganic chemistry. Both these compounds are known,[1,2,3] but while the synthesis of the former

*The subject matter of this Chapter has been published.
Ind. J. Chem., 1986, 25A, 1048;
Int. J. Mass Spectrom. Ion Processes., 1986, 71, 109.

requires an excess of alkali-metal acetate and alkali-metal nitrate[2] where the chances of contamination of the products by acetate or nitrate cannot be ruled out, the recommended synthesis of the latter requires, UO_3, that needs extra preparation steps.

Similarly, bis(acetylacetonato)dioxouranium(VI) Dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, which is an important moderately volatile compound of the metal, is also known for a number of of years. Here again the method used in practice for its synthesis require sodium hydroxide for adjusting the pH of the medium.[4] It is possible that the end product is contaminated because of use of large amount of alkali.

In view of the above new direct methods for the syntheses of the title compounds have now been developed (present Chapter).

Acetylacetonates of metals have served, since 1966,[5] as important coordination compounds suitable for mass spectrometric investigations. McDonald and Shannon[5] reported the mass spectra of acetylacetone and several acetylacetonato metalates, and their results were supplemented by Westmore and co-workers[6] and also by others.[7] Attempts to obtain good mass spectra of some acetylacetonates of metals have not always been successful,[5,8] and mass spectrometric investigations of many heavy metal acetylacetonates have not received due attention.

As a case in point, the mass spectrum of $UO_2(C_5H_7O_2)_2$ was not known until our results were published in 1986.

In this Chapter the details of the newer syntheses of the title compounds, and an interpretative account of the results of mass spectrometric studies of $UO_2(C_5H_7O_2)_2$ are described.

Experimental

Reagent grade chemicals were used for the syntheses. (Loba-Chemie, S.D's, E. Merck, Sarabhai M).

(i) Synthesis of Alkali-metal and Ammonium Triacetatodioxouranate(VI), A$[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4)

$UO_2(NO_3)_2.6H_2O$ (1.0g, 1.99 mmol) was dissolved in 15 cm^3 of water followed by the addition of aqueous ammonia (sp.gr. 0.9), or a 15% solution of sodium hydroxide, with stirring until a yellow precipitate ceased to appear. The yellow precipitate (y) was filtered off, washed free from alkali and nitrate, and then mixed with alkali acetate ACH_3COO (A = Na, K or NH_4) (6 mmol) while maintaining the $U:CH_3COO^-$ ratio at 1:3. The mixture was stirred for 2 min followed by dropwise addition of 10% acetic acid solution under stirring until a clear solution was obtained, the pH of the reaction mixture measured at that stage was found to

be 5. The solution was filtered to remove any traces of undissolved impurity and then concentrated to nearly half the original volume by warming over a steam bath. The concentrated solution was cooled to room temperature to afford yellow crystalline alkali-metal or ammonium triacetatodioxouranates(VI), A $\left[UO_2(CH_3COO)_3\right]$ (A = Na, K or NH_4). The compound was separated by filtration, washed twice with ethanol and finally dried <u>in vacuo</u> over concentrated H_2SO_4.

The yields of $(NH_4)\left[UO_2(CH_3COO)_3\right]$, $Na\left[UO_2(CH_3COO)_3\right]$ and $K\left[UO_2(CH_3COO)_3\right]$ were 0.67g (72%), 0.76g (81%) and 0.75g (77%), respectively.

(ii) <u>Synthesis of Diacetatodioxouranium(VI) Dihydrate, $\left[UO_2(CH_3COO)_2\right].2H_2O$</u>

The yellow precipitate (y) was obtained in a manner similar to that described above by treating an aqueous solution of 1.0g (1.99 mmol) of $UO_2(NO_3)_2.6H_2O$ with aqueous ammonia. An aqueous suspension of the purified product (y) was then treated with 2.0 cm^3 (35 mmol) of glacial acetic acid to obtain a clear solution. The solution thus obtained was worked up in a analogous way described under the above synthesis. The yellow crystalline diacetatodioxouranium(VI) dihydrate, $\left[UO_2(CH_3COO)_2\right].2H_2O$, thus obtained was separated by filtration and dried <u>in vacuo</u> over concentrated H_2SO_4.

The yield of $UO_2(CH_3COO)_2 \cdot 2H_2O$ was 0.67g (80%).

Elemental Analyses

Quantitative estimations of uranium, carbon, hydrogen, nitrogen, and sodium and potassium were accomplished by the methods described in Chapter 2. The analytical data of the compounds are summarised in Table 1.

(iii) Synthesis of Bis(acetylacetonato)Dioxouranium(VI) Dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$

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

Table 1. Analytical Data of A $[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4) and $[UO_2(CH_3COO)_2].2H_2O$

Compound	Found % (Calcd. %)			
	A or N	U	C	H
$NH_4[UO_2(CH_3COO)_3]$	3.12 (3.01)	51.47 (51.16)	15.51 (15.49)	2.85 (2.82)
$Na[UO_2(CH_3COO)_3]$	4.94 (4.89)	50.52 (50.63)	15.31 (15.33)	1.89 (1.93)
$K[UO_2(CH_3COO)_3]$	8.53 (8.04)	49.12 (48.95)	14.77 (14.82)	1.89 (1.87)
$[UO_2(CH_3COO)_2].2H_2O$	-	56.21 (56.12)	11.31 (11.33)	2.45 (2.38)

The yield of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ was 0.9g (97%).

Analytical Data of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$.

Found (%) C, 23.78; H, 3.54; U, 47.52.

Calcd. (%) for $C_{10}H_{18}O_8U$: C, 23.82; H, 3.57; U, 47.22.

The IR spectral bands and their assignments for A $[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4), and $[UO_2(CH_3COO)_2] \cdot 2H_2O$ are reported in Table 2, while those of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ are given in Table 3.

The mass spectrometric features of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ are summarised in Table 4.

Results and Discussion

The reaction of uranylnitrate hexahydrate with alkali hydroxide produces sparingly soluble alkali diuranate which may serve as a very good source of the metal providing a rather easy access to the synthesis of various compounds of uranium (Chapter 3 and 4). It has now been shown that similar product can react with stoichiometric amount of alkali acetates, ACH_3COO (A = Na, K or NH_4), and a small amount of dilute acetic acid, required to dissolve the yellow precipitate, to afford triacetatodioxouranates(VI), A $[UO_2(CH_3COO)_3]$ at pH 5, in high yields. The method does not require the use of any excess alkali-metal acetate or alkali-metal nitrate unlike

the earlier methods,[1,2] and rule out the chances of contamination of the end product by acetate or nitrate. While the reactions of diuranates with stoichiometric amounts of alkali acetates and a small amount of dilute acetic acid give A $\left[UO_2(CH_3COO)_3\right]$ (A = Na, K or NH_4) compounds, the reaction of ammonium diuranate with glacial acetic acid produces pure diacetatodioxouranium(VI) dihydrate, $\left[UO_2(CH_3COO)_2\right].2H_2O$, in a very high yield. The method described is a direct one and may be used as a paradigm for the synthesis of other molecular complexes. Indeed, it has been shown in the present Chapter (vide Experimental) that the reaction of ammonium diuranate with acetylacetone ($C_5H_8O_2$, acacH), in absence of any buffer, gives bis(acetylacetonato)-dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$, thereby justifying the scope of the method.

The compounds A $\left[UO_2(CH_3COO)_3\right]$ (A = Na, K or NH_4) and $\left[UO_2(CH_3COO)_2\right].2H_2O$ are all yellow crystalline solids which are stable for prolong periods. The molar conductance of $\left[UO_2(CH_3COO)_2\right].2H_2O$ in methanol at ambient temperatures was found to be very low indicating the non-electrolytic nature of the compounds in agreement with the observation made earlier.[9] The compound $\left[UO_2(CH_3COO)_2\right].2H_2O$ can be dehydrated and annydrous $\left[UO_2(CH_3COO)_2\right]$ has been obtained by heating the dihydrate between 110-120°C. The compounds are diamagnetic in nature in conformity with the occurrence of U(VI) in each of them.

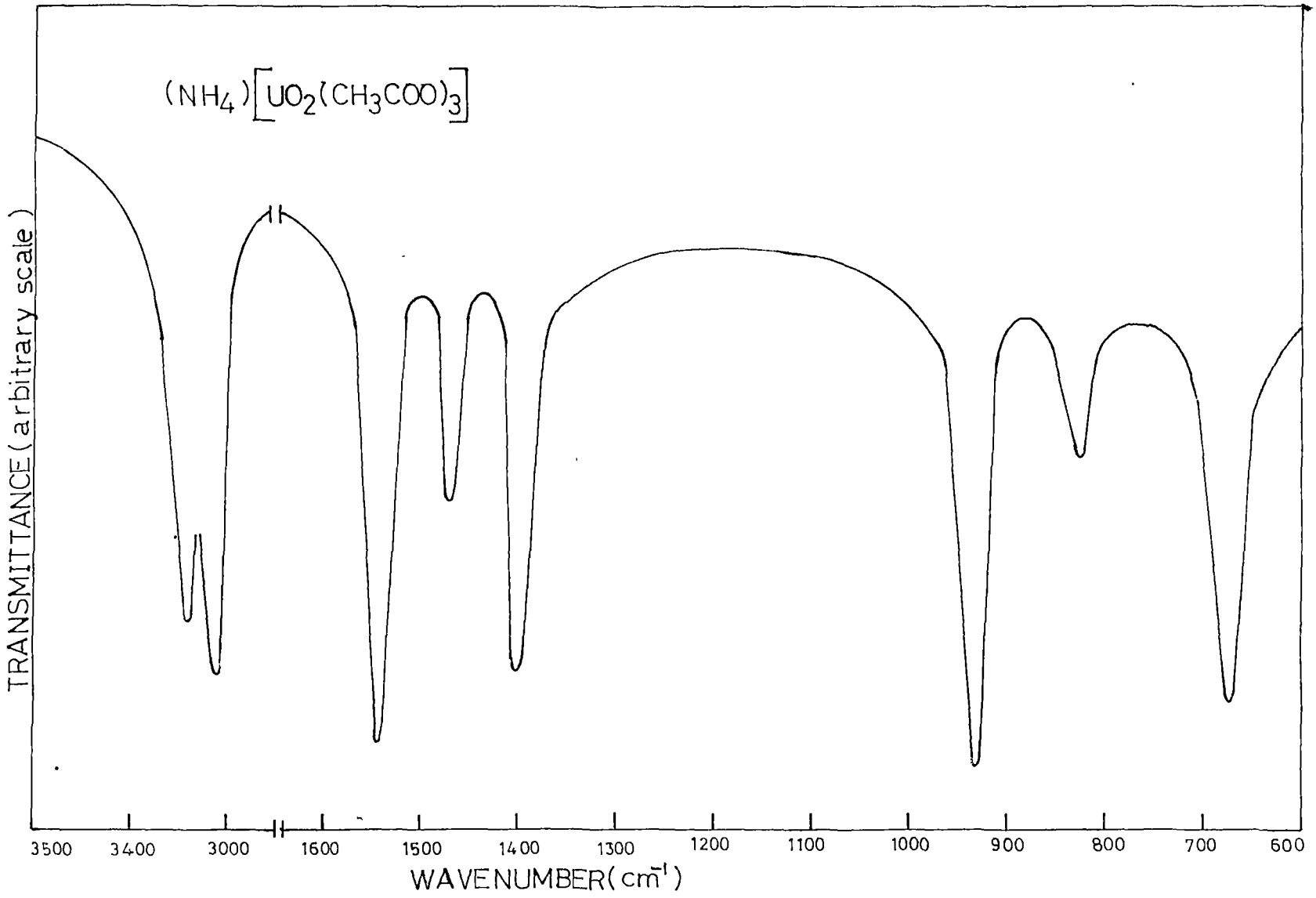
The IR spectra of the compounds A $[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4) and $[UO_2(CH_3COO)_2].2H_2O$ are quite characteristic. The significant features in the spectra of the compounds involve the bands due to $\nu_{as}(OUO)$, $\nu_s(OUO)$, $\nu_{as}(OCO)$, $\nu_s(OCO)$, and $\delta(OCO)$ which have been observed at ~930, ~850, ~1540, ~1470, and ~675 cm^{-1}, respectively, which are similar to those reported in literature[2,10,11] for these types of compounds. These results and those of chemical analyses are in excellent agreement with the formula of the compounds suggesting that the compounds are the same as those reported earlier in the literature.[1,2,3]

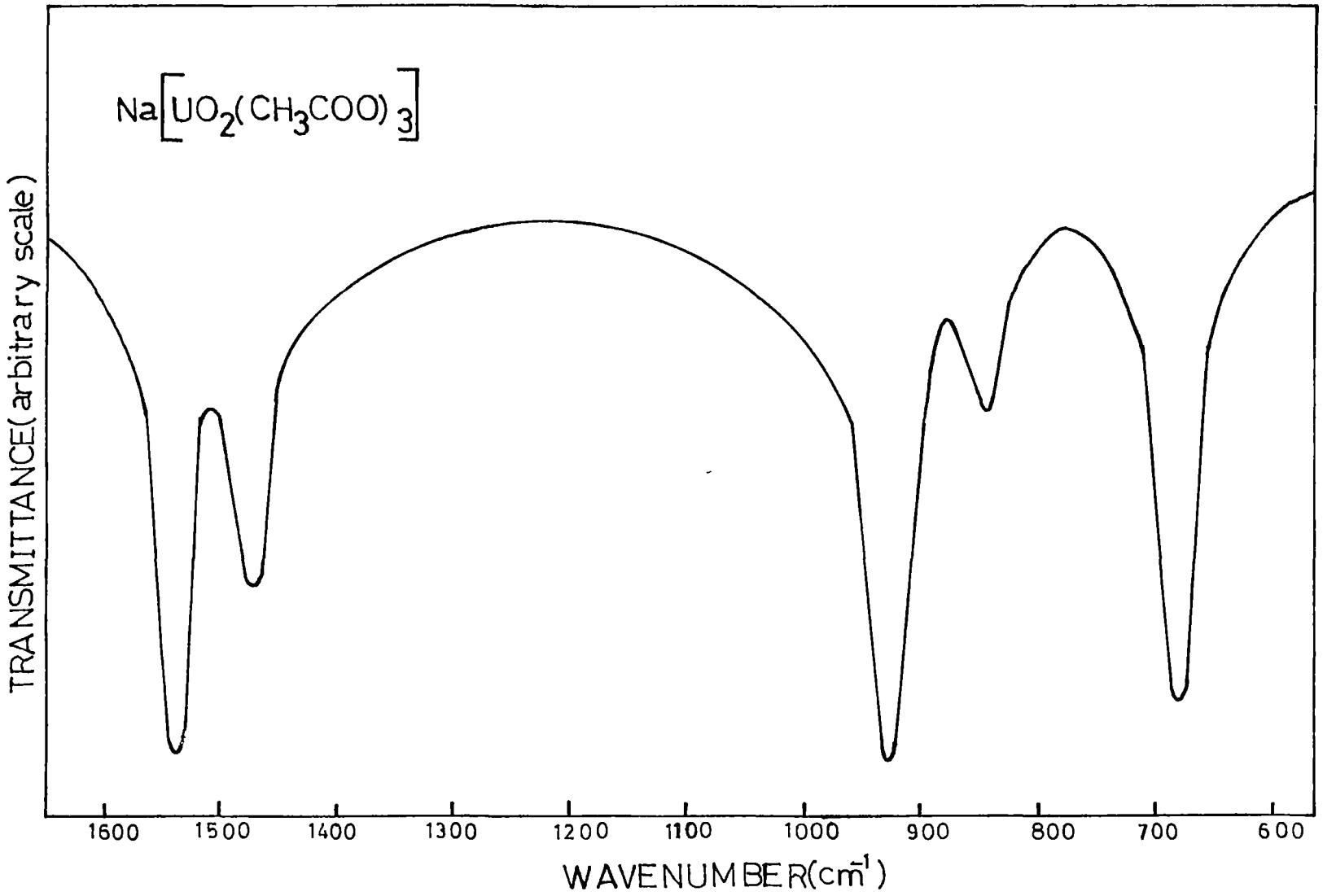
Thus it is evident that A $[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4) can be synthesised from the reaction of the product, obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with the corresponding alkali, with a stoichiometric amount of alkali acetate ACH_3COO, and a small amount of alkali dilute acetic acid at pH 5. The diacetato compound $[UO_2(CH_3COO)_2].2H_2O$ can be obtained directly from the reaction of the product, obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with aqueous ammonia, with glacial acetic acid. The new methods give the compounds in very high yields.

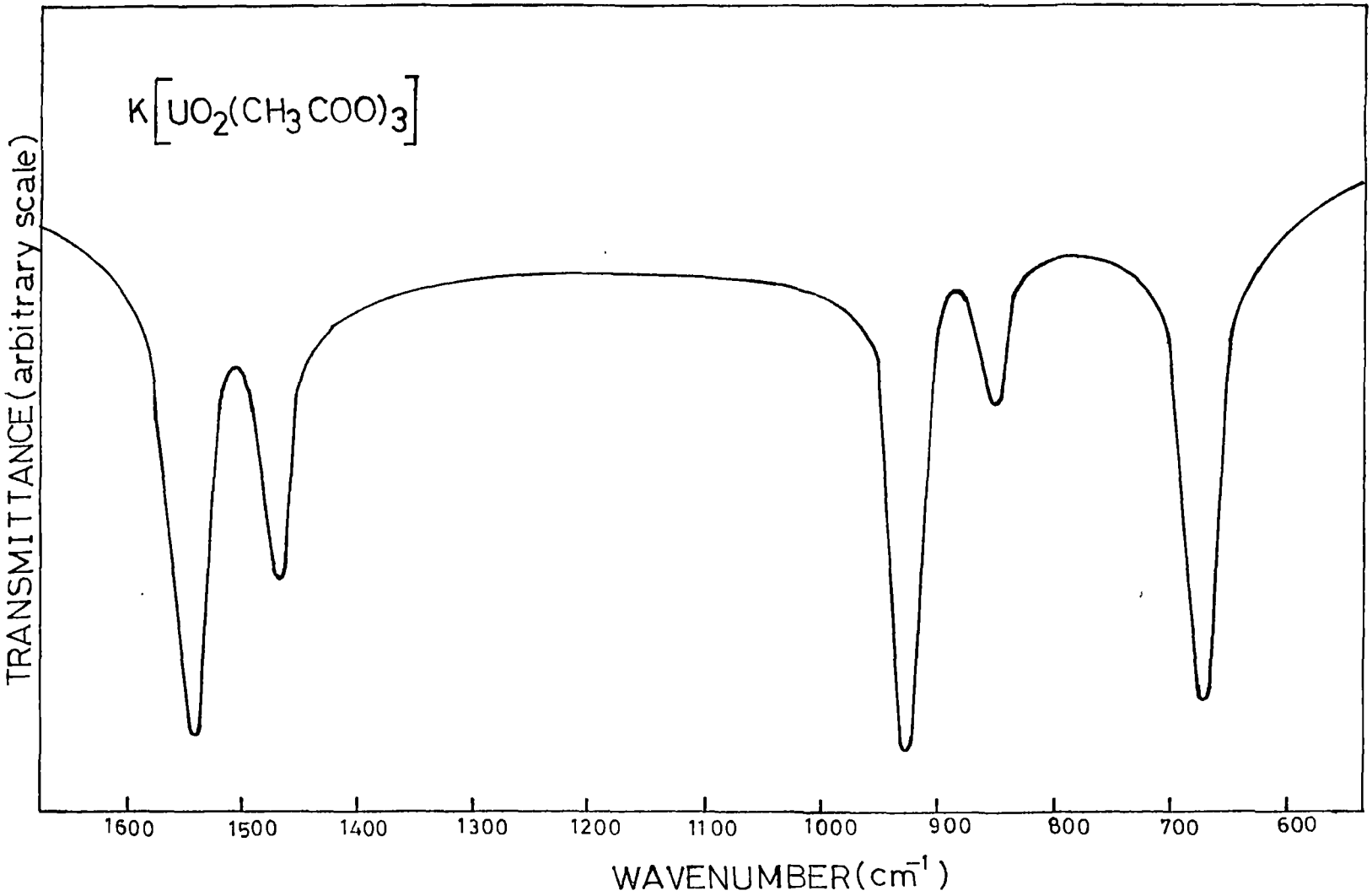
The importance of bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$, and the limitations of its methods

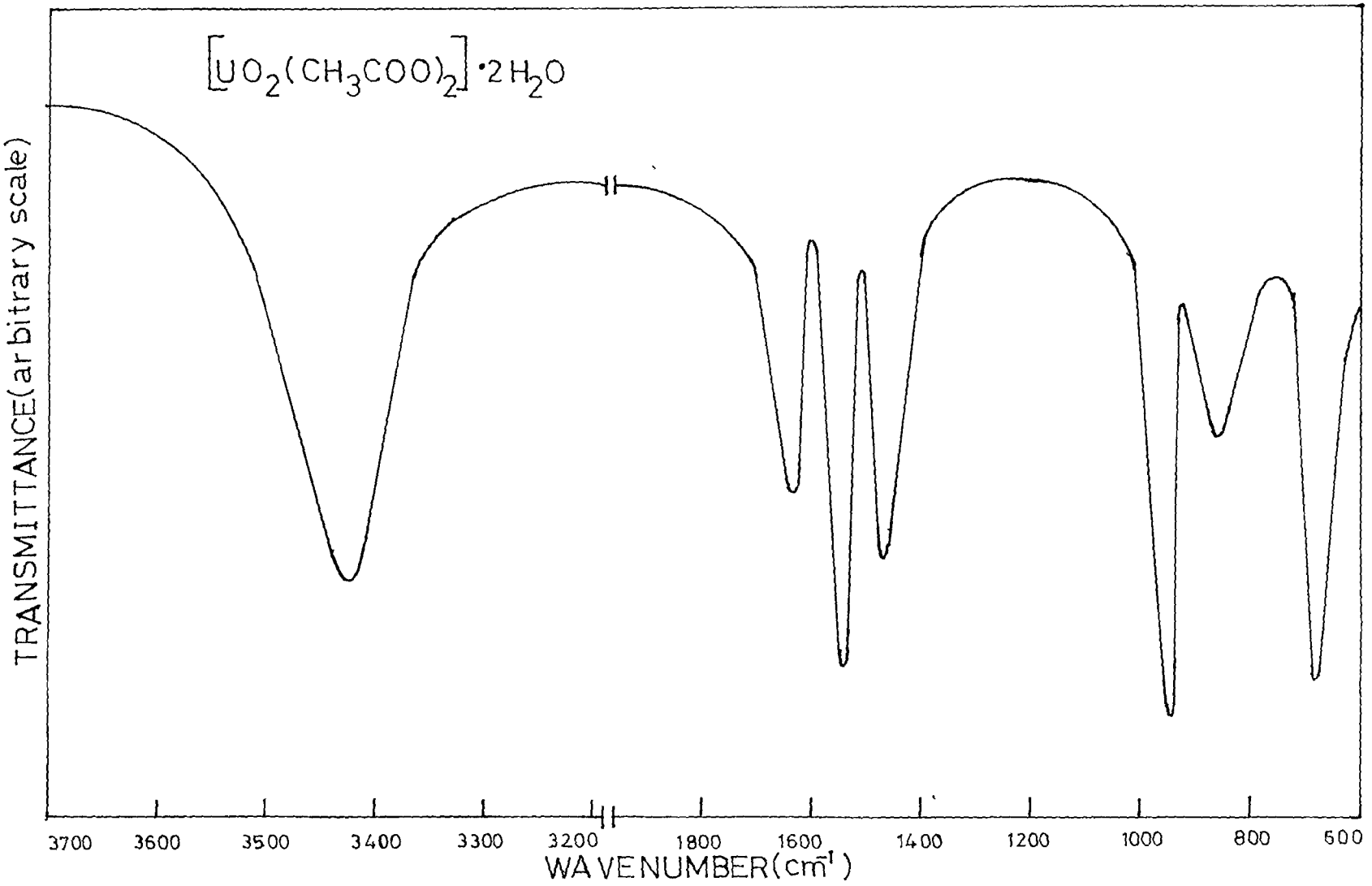
Table 2. Structurally Significant IR Bands of A $[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4) and $[UO_2(CH_3COO)_2].2H_2O$

Compound	IR cm^{-1}	Assignment
$(NH_4)[UO_2(CH_3COO)_3]$	930s	ν_{as} (O–U–O)
	850w	ν_{s} (O–U–O)
	1542s	ν_{as} (O–C–O)
	1470m	ν_{s} (O–C–O)
	675s	δ (O–C–O)
$Na[UO_2(CH_3COO)_3]$	932s	ν_{as} (O–U–O)
	845w	ν_{s} (O–U–O)
	1540s	ν_{as} (O–C–O)
	1470m	ν_{s} (O–C–O)
	680s	δ (O–C–O)
$K[UO_2(CH_3COO)_3]$	930s	ν_{as} (O–U–O)
	850w	ν_{s} (O–U–O)
	1545s	ν_{as} (O–C–O)
	1470m	ν_{s} (O–C–O)
	675s	δ (O–C–O)
$[UO_2(CH_3COO)_2].2H_2O$	940s	ν_{as} (O–U–O)
	865w	ν_{s} (O–U–O)
	1540s	ν_{as} (O–C–O)
	1470s	ν_{s} (O–C–O)
	680s	δ (O–C–O)
	1635	δ (H–O–H)
	3445	ν (O–H)


(NH4)[UO2(CH3COO)3]
TRANSMITTANCE (arbitrary scale)
3500
3400
3000
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
WAVENUMBER (cm⁻¹)


Na[UO2(CH3COO)3]
TRANSMITTANCE(arbitrary scale)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
WAVENUMBER(cm-1)

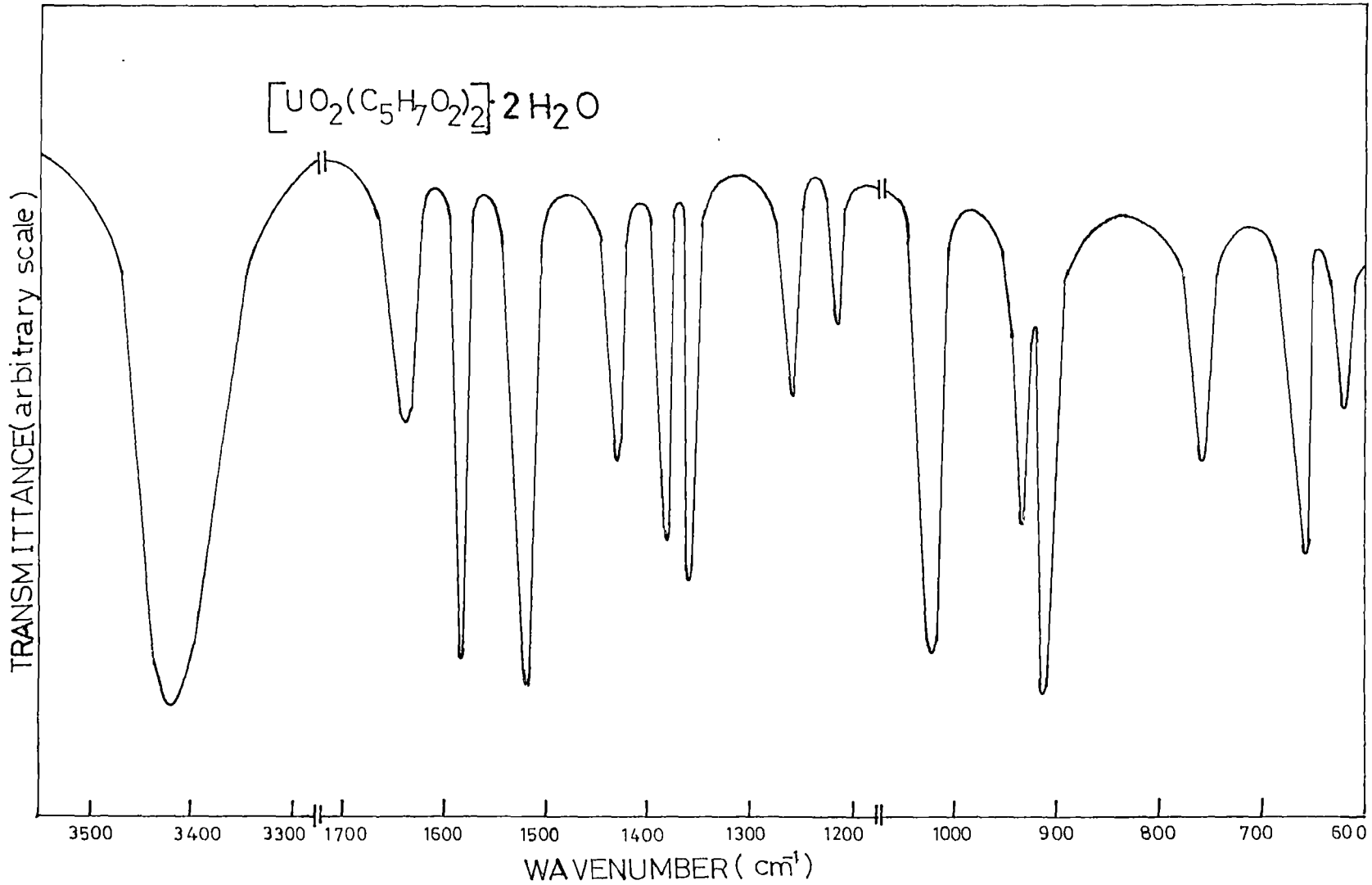

K[UO2(CH3COO)3]
TRANSMITTANCE (arbitrary scale)
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
WAVENUMBER (cm-1)


$[UO_2(CH_3COO)_2]\cdot 2H_2O$
TRANSMITTANCE(arbitrary scale)
3700
3600
3500
3400
3300
3200
1800
1600
1400
1200
1000
800
600
WAVENUMBER(cm^{-1})

of synthesis have been highlighted earlier in this Chapter as well as in Chapter 1. In order to overcome the existing difficulties involved in the recommended method of synthesis, as well as the necessity of high purity of samples for mass spectrometric studies, a direct method has been developed for the synthesis of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$. The method described (vide Experimental) does not require any alkali for adjusting the pH of the reaction solution. The pH of the solution recorded immediately after formation of the product was found to be ca 5, a condition conducive to the synthesis of metal-acetylacetonates. The yields of the product obtained was very high. The orange yellow crystalline $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, is soluble in many organic solvents and much less soluble in water. It is capable of being stored for a long period. The infra red spectra of bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, is similar to that reported for the compound in the literature[12] and conforms to the occurrence of chelated acetylacetonates. The significant IR absorption bands are given in Table 3. The results of IR spectral measurements and chemical analyses attest to the identity of the compound. It is therefore clear that $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ can be obtained in a high yield without the use of alkali by the adaptation of the new method.

Table 3. Infrared Band positions (and their assignments) of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$

IR cm^{-1}	Assignment
1585	C=C str. (ν_8) + C=O str. (ν_1)
1520 1430	C=O str + CH bend (ν_9)
1380	CH_3 def.
1360	CH_3 sym. def.
1260	C-C str. + C-CH_3 str. (ν_2)
1215	C-H in-plane bend (ν_{10})
1020	CH_3 rock.
930	C-CH_3 str. + CO str. (ν_3) + C-CH_3 str. (ν_{11})
760	CH out of plane bend
915	ν(O=U=O)
660	Ring def.
620	ν(U-O_2)
1640	δ(H-O-H)
3420	ν(O-H)


$[UO_2(C_5H_7O_2)_2]\cdot 2H_2O$
TRANSMITTANCE(arbitrary scale)
3500
3400
3300
1700
1600
1500
1400
1300
1200
1000
900
800
700
600
WAVENUMBER (cm^{-1})

Mass Spectrometric Studies

One of our main interest on $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ was to study the compound mass spectrometrically.

The importance of direct insertion technique has been emphasized in some recent reports on mass spectrometric studies,[7,13,14] and it is reiterated from the results of large number of measurements that this technique is particularly suitable for inorganic mass spectrometry, especially because of the following advantages: (i) it allows introduction of samples straight into the ion-source without any prior heating which helps to overcome the problems of any decomposition, particularly high temperature metal catalysed ones, of the sample molecules before their ionization, and (ii) it also permits removal of H_2O from hydrated inorganic molecules prior to their ionization, which is especially important, but has seldom been realised, for the type of the compound involved in the present case, because H_2O elimination from coordinated acetylacetone ($acac^-$, $C_5H_7O_2^-$) constitutes, in some cases, an integral part of the fragmentation pattern.

The mass spectrum of $UO_2(C_5H_7O_2)_2$, was recorded with the ion source temperature being maintained at 100°C and the sample was introduced into the spectrometer, using a direct insertion probe, without prior heating to avoid any pyrolytic effects prior to its coming in contact with ionizing electron

beam. The electron ionization mass spectrum of $UO_2(C_5H_7O_2)_2$ (Table 4), exhibited parent ion signal of medium intensity at m/z 468 due to $\lceil UO_2(C_5H_7O_2)_2\rfloor^{+\cdot}$ followed by signals of equal intensity at m/z 453 and 426 due to the fragment ions $\lceil UO_2(C_5H_7O_2)\ (C_4H_4O_2)\rfloor^{+}$ and $\lceil UO_2(C_5H_7O_2)(C_3H_5O)\rfloor^{+\cdot}$, respectively, originating from the $\lceil UO_2(C_5H_7O_2)_2\rfloor^{+\cdot}$ ion through the loss of a $CH_3^{\cdot}$ radical and the loss of a ketene molecule ($OCCH_2$). Since no signal appeared beyond m/z 468, it may be safe to infer that the molecule does not undergo association in the gaseous state, and it exists as a monomer. Fragmentation of the parent ion of $UO_2(C_5H_7O_2)_2$ to $\lceil UO_2(C_5H_7O_2)(C_4H_4O_2)\rfloor^{+}$ and $\lceil UO_2(C_5H_7O_2)(C_3H_5O)\rfloor^{+\cdot}$ with an equal probability, as evidenced from their intensities (Table 4), is an unique feature of the spectrum. This kind of behaviour has not been observed in the cases of other relatively heavy metal acetylacetonates.[14] While the $CH_3^{\cdot}$ radical loss from the molecular ion $\lceil UO_2(C_5H_7O_2)_2\rfloor^{+\cdot}$ involves simply the cleavage of C-CH_3 bond to produce the even-electron ion $\lceil UO_2(C_5H_7O_2)(C_4H_4O_2)\rfloor^{+}$, the loss of an even-electron species $OCCH_2$ from $\lceil UO_2(C_5H_7O_2)_2\rfloor^{+\cdot}$ must involve a rearrangement in the ligand to give the odd-electron ion $\lceil UO_2(C_5H_7O_2)(C_3H_5O)\rfloor^{+\cdot}$. This difference between $UO_2(C_5H_7O_2)_2$ and the bis(acetylacetonato) complexes of the first row transition metals may in part, owe its origin to the $5f^{\circ}$ $6d^{\circ}$ configuration of U in $UO_2(C_5H_7O_2)_2$ as opposed to a

Table 4. Mass Spectrometric Data for $UO_2(C_5H_7O_2)_2$

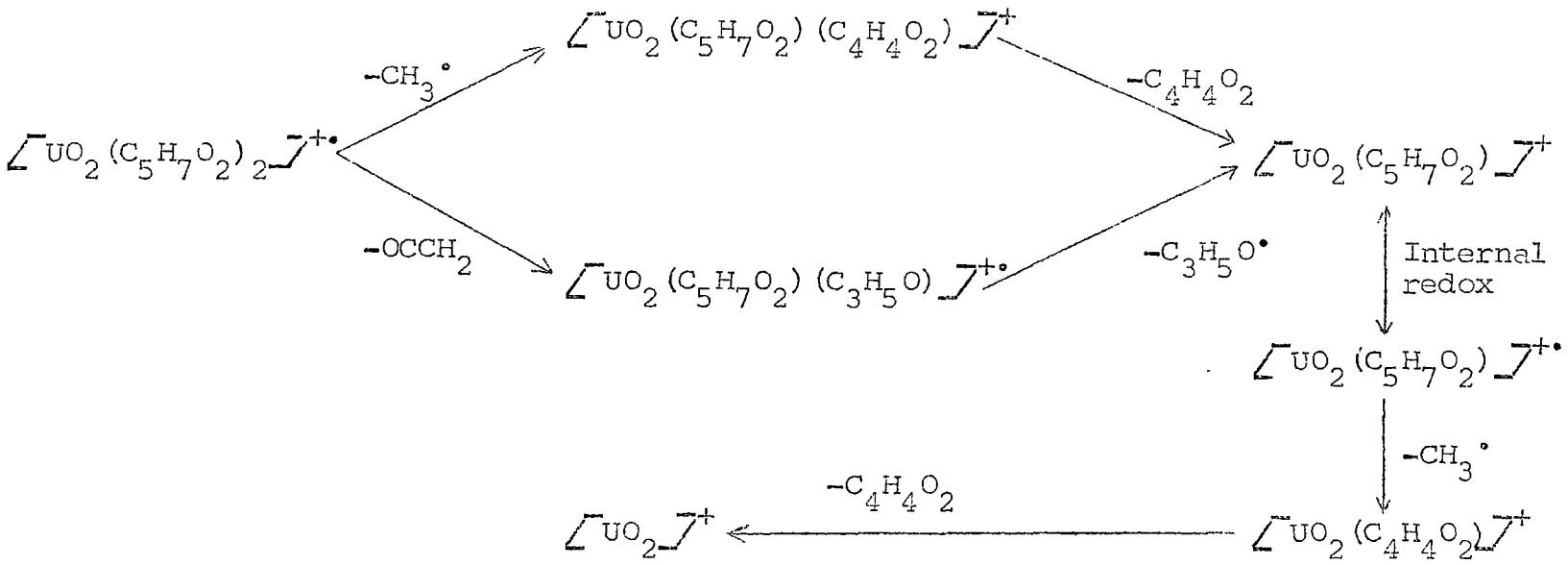
a) Major peaks

Assignment	m/z	Intensity (%)
$[UO_2(C_5H_7O_2)_2]^+$	468	54
$[UO_2(C_5H_7O_2)(C_4H_4O_2)]^+$	453	10
$[UO_2(C_5H_7O_2)(C_3H_5O)]^+$	426	10
$[UO_2(C_5H_7O_2)]^+$	369	100
$[UO_2(C_4H_4O_2)]^+$	354	14
$[UO_2(C_5H_5O)]^+$	351	4
$[UO_2]^+$	270	47

b) Metastable transitions

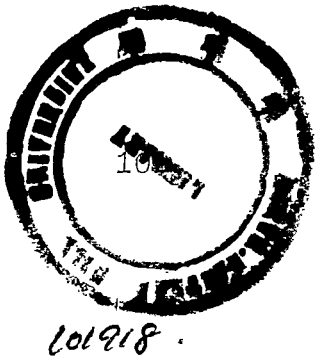
m^*/z			
Observed	Calculated	Process	Fragment lost
438.4	438.48	468 → 453	CH_3
387.8	387.77	468 → 426	CH_2CO
319.6	319.63	426 → 369	C_3H_5O
300.6	300.58	453 → 369	$C_4H_4O_2$
339.6	339.61	369 → 354	CH_3
205.6	205.93	354 → 270	$C_4H_4O_2$

d^n configuration of the metal in the latter. The ions $[UO_2(C_5H_7O_2)(C_4H_4O_2)]^+$ and $[UO_2(C_5H_7O_2)(C_3H_5O)]^{+\bullet}$ lose $C_4H_4O_2$ and $C_3H_5O^\bullet$ species, respectively, to form the most dominant ion (100% relative intensity) at m/z 369 assigned as $[UO_2(C_5H_7O_2)]^+$, which again fragments in two different ways by the loss of H_2O and $CH_3^\bullet$, respectively, to give $[UO_2(C_5H_5O)]^+$ and $[UO_2(C_4H_4O_2)]^+$ ions, as is evident from the appearance of signals at m/z 351 and 354. The weak nature of the signal at m/z 351 points to a relatively lower ease of H_2O loss from the $[UO_2(C_5H_7O_2)]^+$ ion over the loss of a $CH_3^\bullet$ radical . The loss of a $CH_3^\bullet$ radical, at this stage, can be rationalised in the light of the valency change concept and accordingly the even-electron ion $[U(VI)O_2(C_5H_7O_2)]^+$ changes to the odd-electron ion $[U(V)O_2(C_5H_7O_2)]^{+\bullet}$ which then expels a $CH_3^\bullet$ radical to produce $[UO_2(C_4H_4O_2)]^+$. This even-electron ion ultimately cracks down to the bare $[UO_2]^+$ ion (m/z 270). The last two steps of fragmentation involving loss of $CH_3^\bullet$ and $C_4H_4O_2$ from the $[UO_2(C_5H_7O_2)]^{+\bullet}$ fragment resemble those generally observed for the corresponding $[M(C_5H_7O_2)]^+$ where M = Mn, Fe or Co, recorded under analogous conditions. Methyl transfer from the ligand to uranyl (UO_2) center, unlike that of $MoO_2(C_5H_7O_2)_2$,[14] could not be observed in the case of $UO_2(C_5H_7O_2)_2$. The most probable fragmentation pattern of $UO_2(C_5H_7O_2)_2$, in conformity with the experimental obsevations, is shown in Scheme 1.


$[UO_2(C_5H_7O_2)_2]^{+\bullet}$
$-CH_3^\bullet$
$-OCCH_2$
$[UO_2(C_5H_7O_2)(C_4H_4O_2)]^{+}$
$[UO_2(C_5H_7O_2)(C_3H_5O)]^{+\bullet}$
$-C_4H_4O_2$
$-C_3H_5O^\bullet$
$[UO_2(C_5H_7O_2)]^{+}$
Internal redox
$[UO_2(C_5H_7O_2)]^{+\bullet}$
$-CH_3^\bullet$
$[UO_2(C_4H_4O_2)]^{+}$
$-C_4H_4O_2$
$[UO_2]^{+}$

Scheme 1

In order to obtain further support for the mode of fragmentation of $UO_2(C_5H_7O_2)_2.2H_2O$, metastable transition studies were undertaken. Metastable transition peaks were observed at m^*/z 387.8, 438.4, 319.6, 300.6, 339.6 and 205.6. The observed metastable transition peaks are consistent with the suggested fragmentation pattern of the compound. Mass spectrometric study shows that bis(acetylacetonato)dioxouranium(VI), $UO_2(C_5H_7O_2)_2$, exists as a monomer in the gaseous state, and does not undergo any association. The electron ionisation mass spectrum of the compound provides evidence for the simultaneous loss of both $CH_3^\bullet$ and ketene ($OCCH_2$) from the molecular ion. No methyl or hydrogen migration from ligand to the UO_2 center could be observed. The observation of enough number of metastable transition peaks lends support to the suggested fragmentation pattern.



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PART B

CHAPTER 6

Chapter 6

Direct Synthesis of Potassium Tris(oxalato)manganate(III) Trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$, And Evidence for the Existence of $[Mn(C_2O_4)_3]^{3-}$ in Solutions in the Presence of Countercations like Na^+, Rb^+, Cs^+ or NH_4^+ *

The compound Potassium tris(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$, is known for quite some time.[1] As mentioned in Chapter 1, this compound is particularly interesting because it has served as a very oft-quoted example whenever the subject of inorganic photochemistry is discussed.[2] However, the literature method of synthesis of the title compound[1] poses some problems. The method involving the reaction of $KMnO_4$ with oxalic acid and $K_2C_2O_4$ in the presence of an excess of K_2CO_3 is universally accepted for the synthesis of $K_3[Mn(C_2O_4)_3].3H_2O$. This method not only requires very careful manipulation, but also it uses an excess of potassium carbonate, K_2CO_3, in order to control the pH. The chances of contamination of the end product, owing to the use of K_2CO_3 in such quantities, can not be ruled out. Our contention was to develope a new synthetic

*This work has been published.
Inorg. Chem., 1985, 24, 447.

route leadingto the above-mentioned compound, and also to explore the possibility of synthesis of various other salts of the complex ion $\left[Mn(C_2O_4)_3\right]^{3-}$ with countercations like Na^+, Rb^+, Cs^+ or NH_4^+.

It is shown in this Chapter that it is possible to synthesise potassium tris(oxalato)manganate(III) trihydrate, $K_3\left[Mn(C_2O_4)_3\right].3H_2O$ in a more nearly quantitative way directly from MnO(OH) without making use of any buffer. It will also be shown that $\left[Mn(C_2O_4)_3\right]^{3-}$ can exist in solutions in the presence of countercations like Na^+, Rb^+, Cs^+ or NH_4^+.

Experimental

The chemicals used were all reagent grade products (Sarabhai M, Glaxo, S.D's, E. Merck).

The compound MnO(OH) was prepared by the oxidation of $Mn(OH)_2$ with hydrogen peroxide.[3] In a typical preparation, a solution of 2.2g (10 mmol) $MnSO_4.4H_2O$ in 350 cm^3 of water was treated with 34 cm^3 of a 3% H_2O_2 (30 mmol) solution. An amount of 50 cm^3 of a 0.2M ammonia solution (10 mmol) was added under constant stirring. The mixture was boiled for about 5 min and then filtered. The dark-brown compound was washed with about 1.5 lit of hot water on the filter and then dried over phosphorous pentoxide in vacuo.

Synthesis of Potassium Tris(oxalato)manganate(III) Trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$

To a water suspension (20 cm^3) of 0.89g (10.1 mmol) of MnO(OH) was added a concentrated solution of 2.82g (15.3 mmol of $K_2C_2O_4$. The mixture was cooled in an ice bath for ca 15 min, followed by addition of concentrated solution of 1.93g (15.3 mmol) of oxalic acid and the whole was stirred for ca 50 min in an ice bath. The solution, which became cherry-red, was filtered quickly, and an excess of precooled (~0°C) ethanol (about 1/1 v/v) was added with stirring to obtain the cherry-red $K_3[Mn(C_2O_4)_3].3H_2O$. The microcrystalline compound was isolated by quick filtration, washed twice with precooled ethanol, and finally dried in vacuo in the absence of light.

The yield of $K_3[Mn(C_2O_4)_3].3H_2O$ was 3.1g (62.5%).

Attempted Preparation of Solid $A_3[Mn(C_2O_4)_3]$ (A = Na, Rb, Cs or NH_4). Evidence for the Existence of $[Mn(C_2O_4)_3]^{3-}$ in Solutions in the Presence of Na^+, Rb^+, Cs^+ or NH_4^+

The reaction of MnO(OH), alkali-metal or ammonium oxalate, $A_2C_2O_4$ (A = Na, Rb, Cs or NH_4), and oxalic acid in the mole ratio 1:1.5:1.5 were carried out in a manner analogous to that described above under the synthesis of potassium tris(oxalato)manganate(III) trihydrate. In each case cherry-red solution was obtained which was found to be stable at ca 0°C in

the dark for a period of at least 7 days. The electronic spectrum of each of the solutions showed characteristic maximum absorption at ca 19,050 cm^{-1} providing evidence for the existence of the complex species $[Mn(C_2O_4)_3]^{3-}$.

Attempts to isolate $A_3[Mn(C_2O_4)_3]$ (A = Na, Rb, Cs or NH_4) in the solid state either by the addition of ethanol or by slow concentration at ca 0°C under reduced pressure in the dark have resulted in the formation of white decomposition products.

Elemental Analyses

Manganese, oxalate, and potassium contents were determined by the methods described in Chapter 2.

Analytical data of $K_3[Mn(C_2O_4)_3].3H_2O$:

Found: K, 23.81; Mn, 11.41; C_2O_4, 53.76.

Calcd. for $K_3[Mn(C_2O_4)_3].3H_2O$; K, 23.92; Mn, 11.21; C_2O_4, 53.86.

Estimated oxidation state of Mn, 3.0;

μ_{eff}: 4.92 μ_B

Chemical Determination of the Oxidation State of Manganese

The oxidation state of manganese was determined idometrically by treating a freshly prepared ice-cold potassium iodide solution, acidified with dilute sulphuric acid, with the compound followed by titration of the liberated iodine with a standard sodium thiosulphate solution. The iodine titration was done under an ice - cold condition.

Results and Discussion

In order to overcome the difficulties involved in the synthesis[1] of the classic oft-quoted, potassium tris(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$, a direct method has now been improvised. The new method involves two steps. First, the reaction of MnO(OH) with 1:1.5:1.5 stoichiometric amounts of $H_2C_2O_4$ and $K_2C_2O_4$ leading to the synthesis of $K_3[Mn(C_2O_4)_3]$ in solution.

$$MnO(OH) + 1.5\ H_2C_2O_4 + 1.5\ K_2C_2O_4 \longrightarrow K_3[Mn(C_2O_4)_3] + 2H_2O$$

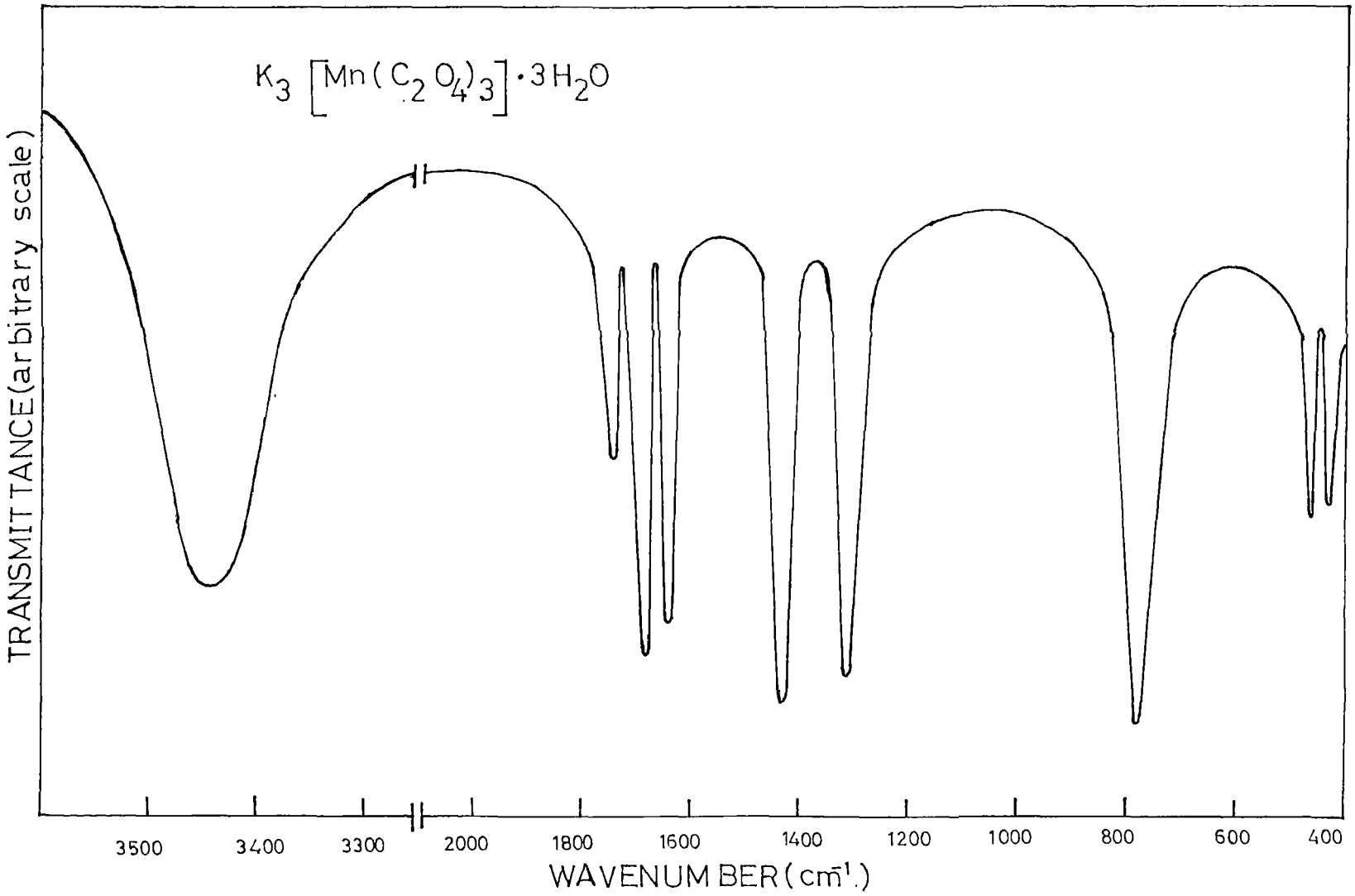
Second, isolation of $K_3[Mn(C_2O_4)_3]$ in the solid state by the addition of ethanol, which facilitated precipitation. The strategy for the present synthesis was that MnO(OH) would react with oxalic acid to generate Mn^{3+}, which would be trapped immediately by the $C_2O_4^{2-}$ ions, arising out of $H_2C_2O_4$ and $K_2C_2O_4$, affording the complex $[Mn(C_2O_4)_3]^{3-}$ in the presence of K^+. The method is rapid, giving potassium tris(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$ in a higher yield than the earlier method.[1]

The pink crystalline $K_3[Mn(C_2O_4)_3].3H_2O$ is stable only in the dark. In the presence of light it decomposes to a white product, a property which is typical of the compound. The chemically estimated oxidation state of manganese was found to be 3.0 in accord with the notion that the metal occurs

in its +3 state. The room temperature magnetic susceptibility measurement yielded a value of the magnetic moment of 4.92 μ_B in conformity with that reported in the literature.[1] The IR spectrum of the compound is unambiguous and shows the characteristics of chelated oxalato groups.[4] The electronic spectra of a solution of $K_3[Mn(C_2O_4)_3]$ showed the maximum absorption, a characteristic of the $[Mn(C_2O_4)_3]^{3-}$ ion, at 19050 cm^{-1}, while the reflectance spectrum showed a broad band at 9200, a shoulder at 19050, and a peak at 20500 cm^{-1} assigned[5] to the transitions $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$, and $^5B_{1g} \longrightarrow {}^5E_g$, respectively, lending support to the identity of the compound.

Reactions of MnO(OH) with $A_2C_2O_4$ (A = Na, Rb, Cs or NH_4) and $H_2C_2O_4$ gave a cherry-red solution, stable at ca 0°C in the dark, showing the electronic spectral absorption at 19050 cm^{-1}, and allowing to infer the formation and existence of the $[Mn(C_2O_4)_3]^{3-}$ ion. However, attempts to isolate the corresponding compounds in the solid state resulted in the formation of white decomposition products.

To control photochemical decomposition, it was expected that the stability of the Mn(III) - oxalate system could be enhanced by the presence of F^- ions, since fluoromanganates(III) are stable. It was observed by a co-worker[6] of our laboratory, in line with the contention, that addition


$K_3[Mn(C_2O_4)_3]\cdot 3H_2O$
TRANSMITTANCE (arbitrary scale)
3500
3400
3300
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER (cm^{-1})

of 40% HF to the afore-mentioned reaction greatly increased the stability of the solutions as evidenced by their unaltered colour at ca 20 °C in light. Accordingly, the reaction of MnO(OH) with 40% HF and $A_2C_2O_4$ (A = Na, K, or NH_4) in the ratio of $Mn:F^-:C_2O_4^{2-}$ at 1:4-5:1 at any temperature between 0 and 20 °C gave a pink solution from which the deep pink microcrystalline $A_2[MnF_3(C_2O_4)]$ was isolated[6] by the addition of ethanol.

Thus it appears from the present studies that the classic oft-quoted $K_3[Mn(C_2O_4)_3].3H_2O$ can be synthesised in a high yield directly from MnO(OH) without making use of any buffer. The tris(oxalato)manganate(III) anion, $[Mn(C_2O_4)_3]^{3-}$ can exist in solutions in the presence of countercations like Na^+, Rb^+, Cs^+ and NH_4^+, but these salts are not capable of being isolated in the solid state. Manganese(III)——oxalate system can, however, be stabilised by fluoride ions.

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CHAPTER 7

Chapter 7

New Mixed-Ligand Fluoro Complexes of Manganese(III). Synthesis and Assessment of Structure of Complexes of the Types $A_3[MnF_2L_2].3H_2O$ ($L = C_2O_4^{2-}$, A = K; $L = HPO_4^{2-}$, A = Na, K or NH_4) And $A[MnF_4L_n].3H_2O$ (L = EDTA, n = 1, A = K; L = glyH , n = 2, A = Na, K or NH_4)

It has been emphasized in the literature[1-4] and also in Chapter 6 of the thesis that fluoride ions can act as stabilizing ligands for tripositive manganese, and fluoromanganates(III) exhibits interesting structural and magnetic properties.[5,6] Consequently this has generated a considerable interest in studies involving synthesis and structural aspects of fluoromanganates(III) over the years.[7-19] In contrast, information on mixed-ligand fluoro complexes of manganese(III) are restricted to only few reports.[20-23] Mixed-ligand complexes may be important particularly because a combination of suitable ligands might lead to a sharp increase in the stability of Mn(III) in solutions as well as in the solid state. Further, a marked variation in magnetic properties of the mixed-ligand complexes may also be expected since some of the binary fluoromanganates(III) display strong antiferromagnetism whereas other manganese(III) complexes, in general, have straight forward magnetic behaviour.

Recently,[22] it has been shown that the stability of Mn(III)——oxalate system can be enhanced to a large extent by the partial replacement of oxalate ligands in the complex $\left[Mn(C_2O_4)_3\right]^{3-}$ ion by F^- ligands leading to the formation of a stable mono(oxalato)trifluoromanganate(III) species $\left[MnF_3(C_2O_4)\right]^{2-}$. The magnetic properties of the mixed-fluoro(oxalato)manganates(III), $A_2\left[MnF_3(C_2O_4)\right]$ were found to be similar to those of $A_2\left[MnF_3(SO_4)\right]$, but different from both the binary oxalatomanganates(III) and the binary fluoro-manganates(III). In this context it appeared interesting to see the effect of replacing one $C_2O_4^{2-}$ ligand by two F^- ligands in the complex ion $\left[Mn(C_2O_4)_3\right]^{3-}$. A survey of literature reveals that information regarding the dioxalato-manganates(III) is very scanty,[24,25] apparently owing to instability of such complexes. Similarly, the EDTA (ethylene-diamine-tetraacetic acid) complex of Mn(III) is known[26] to be unstable against heat and light. It was thought that introduction of some F^- ligands in the coordination sphere of Mn(III) would result into the formation of stable mixed-fluoro-EDTA complex of tripositive manganese. Coordination compounds of transition metals containing orthophosphate ion as the ligand have not been investigated in detail. The multivalent nature of orthophosphate ion and its potential for multidentate coordination were expected to show an interesting variety of coordination modes. It has been reported[27] that acid orthophosphate

complex of Mn(III) is known only in solution, although the olive green $MnPO_4.H_2O$ species is well characterised.[28] It may therefore be anticipated that fluoride ion will contribute significantly in stabilizing acid orthophosphate-Mn(III) system providing means for the synthesis and related investigation of fluoro-acid phosphatomanganates(III).

As opposed to aminopolycarboxylate complexes of manganese(III),[25] complexes containing aminomonocarboxylic acid, for instance, glycine (glyH) do not seem to have been studied by previous workers. Here again the problem of stabilization of Mn(III) by glyH alone may not be a reasonable proposition, however, there seems to be a finite possibility of formation of stable mixed-fluoro-glycine complexes of manganese(III).

In view of the above, a research programme aimed at synthesis and structural studies, of mixed-ligand fluoromanganates(III) was chalked out. The present Chapter of thesis describes the first synthesis, characterization and structural assessment of potassium difluorobis(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_2F_2].3H_2O$, potassium tetrafluoro-(ethylenediaminetetraacetic acid)manganate(III) trihydrate, $K[Mn(EDTA)F_4].3H_2O$, alkali-metal or ammonium difluorobis-(hydrogen orthophosphato)manganate(III) trihydrates of the type $A_3[Mn(HPO_4)_2F_2].3H_2O$ (A = Na, K or NH_4), and alkali-metal

or ammonium tetrafluorobis(glycine)manganate(III) trihydrates A $[Mn(glyH)_2F_4].3H_2O$ (A = Na, K or NH_4). An attempt has also been made in this Chapter to put in record of a set of internally consistent data concerning the effect of mixed-ligands on the magnetic properties of fluoromanganates(III).

Experimental

Reagent grade chemicals were used (Sarabhai M, Glaxo, E. Merck, S.D's).

The compound MnO(OH) was prepared by the oxidation of $Mn(OH)_2$ with hydrogen peroxide as described in Chapter 6.

(i) Synthesis of Potassium Difluorobis(oxalato)Manganate(III) Trihydrate, $K_3[Mn(C_2O_4)_2F_2].3H_2O$

To an aqueous solution (20 cm^3) of 1g (6.33 mmol) of $KMnO_4$, kept in an ice-bath and protected from light, was added an aqueous solution of 3.2 (25.38 mmol) of oxalic acid ($H_2C_2O_4.2H_2O$). The resulting solution was stirred in an ice-bath for ca 20 min followed by rapid filtration to remove any undissolved residue. To the cherry-red filtrate was added 0.74g (12.74 mmol) of solid potassium fluoride, KF and stirred for a further period of ca 20 min. An equal volume of pre-cooled (0°C) ethanol was added with continuous stirring. A very light pink microcrystalline product that precipitated out at this

stage was filtered off. To the cherry-red filtrate, again an excess of pre-cooled ethanol (twice the volume of the filtrate) was added to obtain the cherry-red coloured microcrystalline $K_3[Mn(C_2O_4)_2F_2].3H_2O$. The compound was then isolated by quick filtration, washed twice with pre-cooled ethanol, and finally dried in vacuo over concentrated H_2SO_4 in the absence of light.

The yield of $K_3[Mn(C_2O_4)_2F_2].3H_2O$ was 1.7g (61%).

(ii) Synthesis of Potassium Tetrafluoro(ethylenediaminetetra-acetic acid)Manganate(III) Trihydrate, $K[Mn(EDTA)F_4].3H_2O$

Freshly prepared MnO(OH) was dissolved in 48% HF (2.5 cm^3, 60.0 mmol of HF/0.89g, 10.11 mmol of MnO(OH)) and stirred for ca 10 min. The mixture was placed in an ice-bath; to it was added an aqueous solution of 2.96g (10.11 mmol) of ethylenediaminetetraacetic acid (EDTA, H_4Y) slowly with continuous stirring (EDTA was dissolved in water by the addition of 2-3 drops of 10% KOH solution). To the resulting deep pink solution was added 2.35g (40.45 mmol) of solid KF (Mn:KF as 1:4) and the solution thus obtained was stirred for a further period of ca 30 min in an ice-bath. The pH was found to be ca 2. The solution was filtered, to remove any undissolved residue, followed by the addition of an equal volume of diethylether to the filtrate with thorough stirring. The organic layer became red-pink in colour with the aqueous layer being practically

colourless. To the above mixture was added an equal volume of a mixture of ethanol and acetone (1/1,v/v) and the whole was kept in a freezer for ca 3h. A deep pink coloured oily mass was formed which was separated by decantation. The oily mass was treated 3-4 times with acetone, and finally dried in vacuo to obtain the solid pink coloured $K\left[Mn(EDTA)F_4\right].3H_2O$.

Starting from 0.89g of MnO(OH) the yield of $K\left[Mn(EDTA)F_4\right].3H_2O$ obtained was 1.35g (25.8%).

(iii) Synthesis of Difluorobis(hydrogen orthophosphato)-Manganate(III) Trihydrates, $A_3\left[Mn(HPO_4)_2F_2\right].3H_2O$ (A = Na, K or NH_4)

To an aqueous suspension (25 cm^3) of 0.89g (10.11 mmol) of MnO(OH) was added alkali-metal or ammonium fluoride, AF (A = Na, K or NH_4), with the maintenance of MnO(OH) to AF ratio at 1:3, and the resulting mixture was stirred for ca 5 min. To it was added 8 cm^3 (142.9 mmol) of orthophosphoric acid, H_3PO_4 (88-93%, wt. per cm^3 at 20°C, 1.75g), slowly with continuous stirring to obtain a violet colour solution. Stirring was continued, for a further period of ca 10 min. To the violet solution, obtained as above, equal volumes (in each case equal to that of the violet solution) of ethanol and acetone were added with continuous stirring. This resulted in the precipitation of pink-brown microcrystalline

$A_3[Mn(HPO_4)_2F_2].3H_2O$ (A = Na, K or NH_4). The compound was separated by filtration, and purified by washing 3-4 times with acetone, and finally dried in vacuo over concentrated H_2SO_4.

The yields of $Na_3[Mn(HPO_4)_2F_2].3H_2O$, $K_3[Mn(HPO_4)_2F_2].3H_2O$, and $(NH_4)_3[Mn(HPO_4)_2F_2].3H_2O$ were 2.2g (53%), 2.4g(52%), 2.1g (53%), respectively.

(iv) Synthesis of Ammonium and Alkali-Metal Tetrafluorobis-(glycine)Manganate(III) Trihydrates, A $[Mn(glyH)_2F_4].3H_2O$, (A = Na, K or NH_4)

An amount of 0.89g (10.11 mmol) of freshly prepared MnO(OH) was dissolved by the addition of 2.0 cm^3 (40.0 mmol) of 40% HF, maintaining the molar ratio between MnO(OH) and HF at 1:4. The solution was stirred for ca 10 min followed by the addition of 1.52g (20.2 mmol) of glycine, keeping MnO(OH):glycine ratio at 1:2, and the resulting solution was stirred for a period of ca 15 min. To this was added a stipulated amount of A_2CO_3 (A = Na, K or NH_4) (MnO(OH):A_2CO_3 as 1:0.5) with stirring. The whole was then concentrated over a steam bath followed by the slow addition of acetone whereupon pink microcrystalline, A $[Mn(glyH)_2F_4].3H_2O$ (A = Na, K or NH_4) was precipitated out. The compound was isolated by centrifugation, washed 3 times with acetone, and then dried in vacuo over concentrated H_2SO_4.

The yields of Na $\left[Mn(glyH)_2F_4\right].3H_2O$, K $\left[Mn(glyH)_2F_4\right].3H_2O$, and (NH_4) $\left[Mn(glyH)_2F_4\right].3H_2O$ were 3.16g (87.3%), 3.5g (92%) and 3g (85%), respectively.

Elemental Analyses

Determination of manganese, fluoride, oxalate, phosphate, and C, H and N, and sodium and potassium contents of the various compounds described in this Chapter have been made by the methods already described in Chapter 2.

The analytical data for $K_3\left[Mn(C_2O_4)_2F_2\right].3H_2O$ and K $\left[Mn(EDTA)F_4\right].3H_2O$ are given in Table 1, while those for $A_3\left[Mn(HPO_4)_2F_2\right].3H_2O$ (A = Na, K or NH_4), and A $\left[Mn(glyH)_2F_4\right].3H_2O$ (A = Na, K or NH_4) are reported in Tables 2 and 3, respectively.

Chemical Determination of Oxidation State of Manganese

The oxidation state of manganese was determined chemically by iodometry. An accurately weighed amount of the manganese compound was added to an ice-cold potassium iodide solution acidified with dilute sulphuric acid and kept in the dark for about 10 min. The liberated iodine was then titrated with a standard sodium thiosulphate solution using starch as the indicator.

Table 1. Analytical Data of $K_3[Mn(C_2O_4)_2F_2].3H_2O$ and $K[Mn(EDTA)F_4].3H_2O$

Compound	Found % (Calcd. %)						
	K	Mn	F	C_2O_4	C	H	N
$K_3[Mn(C_2O_4)_2F_2].3H_2O$	26.75 (26.64)	12.51 (12.48)	8.82 (8.63)	39.65 (39.98)	10.87 (10.91)	1.38 (1.36)	-
$K[Mn(EDTA)F_4].3H_2O$	7.73 (7.57)	10.77 (10.64)	14.81 (14.72)	-	23.29 (23.26)	4.23 (4.26)	5.46 (5.42)

Table 2. Analytical Data of $A_3[Mn(HPO_4)F_2].3H_2O$ (A = Na, K or NH_4)

Compound	Found % (Calcd. %)			
	A or N	Mn	F	PO_4
$(NH_4)_3[Mn(HPO_4)_2F_2].3H_2O$	10.72 (10.69)	14.22 (13.98)	9.87 (9.67)	48.7 (48.35)
$Na_3[Mn(HPO_4)_2F_2].3H_2O$	17.21 (16.91)	13.68 (13.47)	9.44 (9.32)	46.8 (46.57)
$K_3[Mn(HPO_4)_2F_2].3H_2O$	25.56 (25.71)	12.22 (12.04)	8.58 (8.33)	41.5 (41.64)

Table 3. Analytical Data of A $\lceil Mn(glyH)_2F_4 \rfloor .3H_2O$

(A = Na, K or NH_4)

Compound	Found % (Calcd. %)					
	A	Mn	F	C	H	N
$(NH_4)\lceil Mn(glyH)_2F_4 \rfloor .3H_2O$		15.73 (15.56)	21.41 (21.52)	13.67 (13.61)	5.68 (5.66)	11.78 (11.89)
$Na\lceil Mn(glyH)_2F_4 \rfloor .3H_2O$	6.53 (6.42)	15.21 (15.34)	21.54 (21.22)	13.61 (13.42)	4.53 (4.47)	7.84 (7.82)
$K\lceil Mn(glyH)_2F_4 \rfloor .3H_2O$	10.55 (10.45)	14.82 (14.68)	20.62 (20.31)	12.88 (12.84)	4.32 (4.28)	7.46 (7.48)

Results and Discussion

The main problem, that one encounters in the synthesis of manganese(III) complexes from aqueous solutions, lies in the ease with which Mn(III) disproportionates to Mn(IV) and Mn(II).[29,30] Synthesis of manganese(III) compounds may not, however, be difficult provided the above-mentioned disproportionation process is inhibited. It is evident from earlier work done in the laboratory, where the present work was carried out, that manganese(III) can be well stabilized in an acidic medium containing fluoride ions, and accordingly some binary fluoro- and mixed-ligand fluoro-complexes of manganese(III were synthesised.[16,21,22] Apart from fluoride, ligands like oxalate, phosphate, carboxylates etc also seem to form complexes with manganese(III) in solutions with varying stabilities.[31] It was therefore rational to think that mixed fluoromanganate(III) complexes containing oxalate, EDTA, acidphosphate or an amino-acid like glycine could be stabilized in solutions and thence isolated in the solid state to get an access to a host of manganese(III) complexes. Potassium permanganate, $KMnO_4$, or a manganese compound already containing manganese in its +3 state can be chosen as a source of the metal depending upon the redox property of the ligand itself. If a ligand is capable of reducing manganese(VII), $KMnO_4$ can be taken as a starting material, where as in the cases where ligands donot

posses such a property a manganese(III) compound may be suitable. Oxalic acid is known to reduce manganese(VII) ultimately to manganese(II). This reduction is assisted by heat. It was believed that such a reduction of manganese(VII), if carried out at a relatively lower temperature (say $\sim$ 0°C) particularly in the presence of a limited amount of fluoride ions using an excess of oxalic acid might lead to the synthesis of mixed-fluorooxalatomanganates(III). In accord with this a reaction of $KMnO_4$ with potassium fluoride, KF, and oxalic acid in the ratio of 1:2:4 at 0°C in the dark followed by the addition of etnanol has led to the successful synthesis of potassium difluorobis(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_2F_2].3H_2O$

$$KMnO_4 + 4H_2C_2O_4 + 2\ KF \longrightarrow K_3[Mn(C_2O_4)_2F_2] + 4\ CO_2 + 4\ H_2O$$

Success of the above synthesis lies on:

(i) maintaining of a low temperature (0°C) of the reaction;

(ii) using of the appropriate amounts of both oxalate and fluoride, remembering that while a part of $C_2O_4^{2-}$ is utilised to reduce manganese(VII) to manganese(III), the rest is used for coordinating to the metal center;

(iii) avoiding an excess of fluoride ions in the medium to check the formation of $[MnF_5]^{2-}$; and

(iv) carrying out of the reaction in the dark.

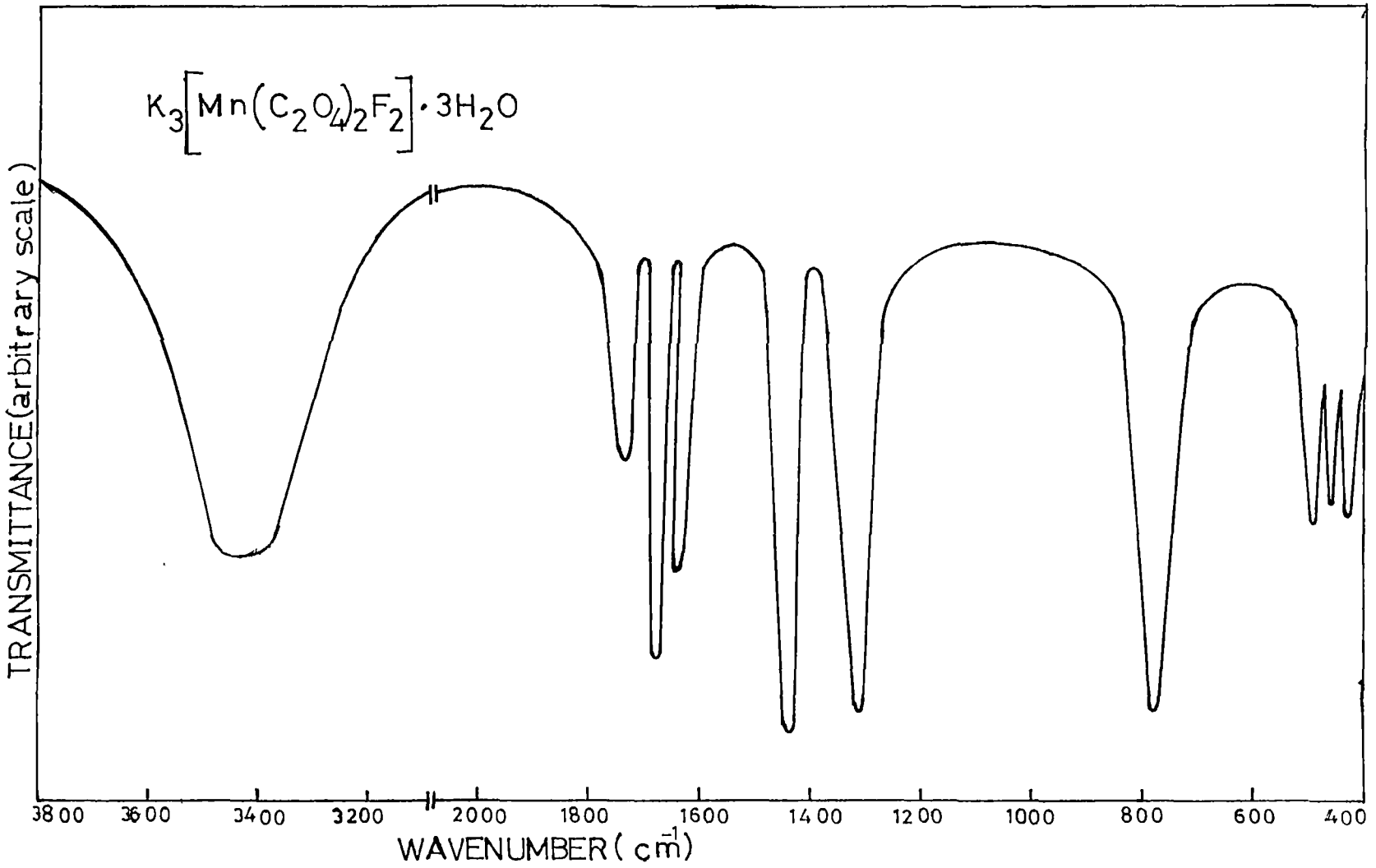
The role of ethanol was to bring about precipitation of the desired product. An alternative route starting with MnO(OH) (a manganese(III) compound) was not found suitable since an already known[22] compound $K_2[MnF_3(C_2O_4)]$ was obtained instead of the compound looked for.

The cherry-red $K_3[Mn(C_2O_4)_2F_2].3H_2O$ compound was obtained in a microcrystalline form and was found to be unstable both in the solid state as well as in a solution. The compound is relatively less stable than the potassium tris(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_3].3H_2O$, (described in Chapter 6). Owing to its instability neither molar conductance nor even a satisfactory magnetic susceptibility measurement could be made. The chemically estimated oxidation state of manganese, determined iodometrically immediately after synthesising a sample of the compound, was found to be 3.1 in conformity with the occurrence of manganese(III). The electronic spectrum of a freshly prepared sample of the compound, recorded immediately after making a solution in water containing a small amount of HF, shows bands at 11950, 19800, and 22220 cm^{-1} which have been assigned to $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$, and $^5B_{1g} \longrightarrow {}^5E_g$ transitions, respectively, suggesting a distorted octahedral environment of manganese(III)[32,33] in the compound. The observed pattern also points to an appreciable splitting of the ^5E_g ground state

of Mn^{3+} probably owing to Jahn-Teller effect. The IR spectrum of the compound shows absorptions characteristic for the presence of coordinated oxalate and fluoride ligands (Table 4). Ionic oxalate has a planar, symmetrical structure with all C-O bonds of equal length. For a chelated oxalate, all the C-O vibrations become infrared active, with asymmetric (O-C-O) stretching shifting to higher frequency and the symmetric stretching to lower.[34] The oxalato modes for the present compound occur in the region 1680-1750 cm^{-1} and at 1435 cm^{-1} the positions stipulated for a chelated $C_2O_4^{2-}$ group[35] leading us to state that the oxalate ligand in $K_3[Mn(C_2O_4)_2F_2].3H_2O$ is bonded to manganese in a chelated fashion. A comparison of the IR spectrum of the present compound with that of $K_2[MnF_3(C_2O_4)]$[22] shows a distinct difference in so far as the mode of coordination of oxalate is concerned. Unlike the presence of a bridging $C_2O_4^{2-}$ group in $K_2[MnF_3(C_2O_4)]$,[22] the $C_2O_4^{2-}$ ligands in $K_3[Mn(C_2O_4)_2F_2].3H_2O$ occur as chelated ones. The band at 490 cm^{-1} originates from the presence of coordinated fluoride and is attributed to ν(Mn-F). The absence of any splitting of this band as well as appearance of no other band close to 490 cm^{-1} suggest[36,37] that the two F^- ligands occupy positions trans to each other around manganese(III), and the complex species $[Mn(C_2O_4)_2F_2]^{3-}$ most likely has a distorted octahedral structure with a D_{4h} symmetry. The two additional bands occurring at 3460 and

Table 4. Structurally Significant IR Bands of $K_3[Mn(C_2O_4)_2F_2]\cdot 3H_2O$

Compound	IR cm^{-1}	Assignment
$K_3[Mn(C_2O_4)_2F_2]\cdot 3H_2O$	1730m	ν_{as} (C=O) · ν_7
	1680s	ν_{as} (C=O) · ν_1
	1435s	ν(C-O+C-C) ν_2
	1315s	ν(C-O) + ν_8 δ(O-C-O)
	780s	δ(O-C-O) + ν_9
	460m	ring def. + ν_{10} δ(O-C-O)
	430m	ring def. + ν_{11} δ(O-C-O)
	490m	ν(Mn-F)
	3460m	ν(O-H)
	1640s	δ(H-O-H)


$K_3[Mn(C_2O_4)_2F_2]\cdot 3H_2O$
TRANSMITTANCE(arbitrary scale)
3800
3600
3400
3200
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER (cm^{-1})

1640 cm^{-1} resemble in their shapes and positions to those observed for other fluoromanganate(III) complexes[16] containing uncoordinated water, and accordingly these modes have been assigned to ν(O-H) and δ(H-O-H), respectively.

It is evident therefore that potassium difluorobis-(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_2F_2].3H_2O$, can be synthesised by the method developed now (vide Experimental). The compound is not very stable. The complex species $[Mn(C_2O_4)_2F_2]^{3-}$ containing coordinated fluorides and chelated oxalato groups most probably has a distorted octahedral structure.

The problems regarding the stability of manganese(III)-EDTA system has been already stressed earlier in this Chapter. In view of the earlier problems[26] and also because of our interest in mixed-ligand fluoromanganates(III), the synthesis of mixed-fluoro-EDTA-manganese(III) complexes was undertaken. A redox reaction between Mn(VII) and EDTA was not considered to be a viable method. Thus a reaction of MnO(OH) in 40% HF with a solution of ethylenediaminetetraacetic acid (EDTA) containing a very small amount of KOH, and potassium fluoride, KF, in the ratio of Mn:EDTA:KF as 1:1:4, was carried out in a manner described in the experimental section. The product isolated from this was found to be pink microcrystalline $K[Mn(EDTA)F_4].3H_2O$. That the condition described

herein for the synthesis of the above compound is appropriate was ascertained from the results of similar reactions carried out under higher pH (~ 7 or slightly above). The products obtained from such reactions were found to be contaminated ones. It is necessary to mention that an higher amount of fluoride, higher than the one used in the present case, is detrimental because this leads to the formation of $[MnF_5]^{2-}$.

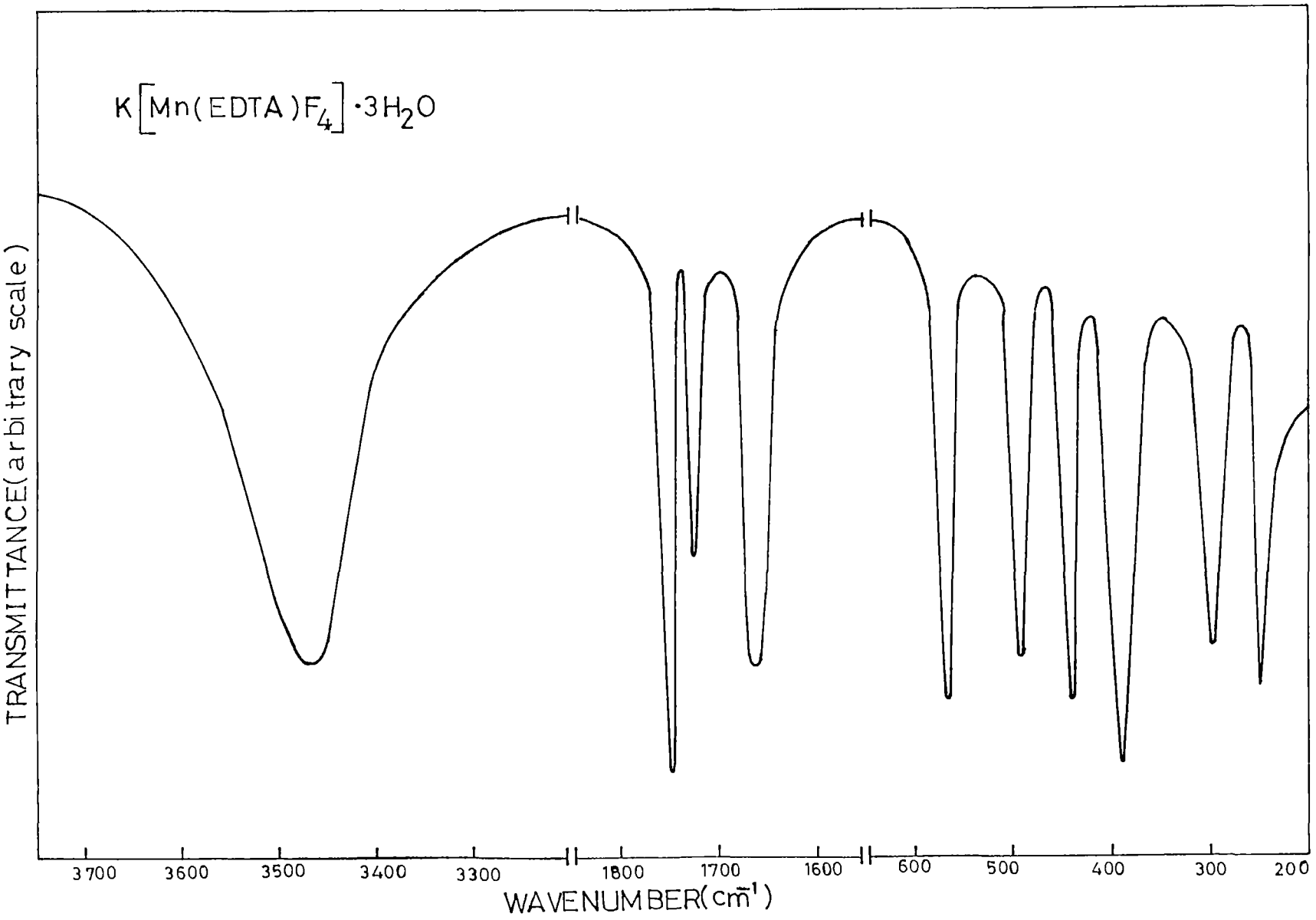
Potassium tetrafluoro(ethylenediaminetetraacetic acid) manganate(III) trihydrate, $K[Mn(EDTA)F_4].3H_2O$, is stable, unlike the $K_3[Mn(C_2O_4)_2F_2].3H_2O$, and can be stored for a prolong period, and its stability can be ascertained by estimating manganese and recording its IR spectrum. The chemically estimated oxidation state of manganese in this compound was found to be 3.0, while the room temperature magnetic susceptibility measurement gave a value of the magnetic moment as 4.92 μ_B (at 300K). These two results unambigously showed the occurrence of manganese(III) in the compound under discussion.

The electronic spectrum of the compound, recorded in the region 11000-40000 cm^{-1} immediately after making a solution exhibited bands at 22200, 19800, and 11800 cm^{-1} assigned to $^5B_{1g} \longrightarrow {}^5E_g$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5A_{1g}$ transitions, respectively. This feature is similar to that observed for $K_3[Mn(C_2O_4)_2F_2].3H_2O$ and also for other manganese(III)

complexes suggesting thereby that the complex species $[Mn(EDTA)F_4]^-$ may have a distorted octahedral structure. The infrared spectral band positions along with their assignments are set out in Table 5. It is notable that the absence of any band in the region 1590-1650 cm^{-1} points to the occurrence of the EDTA ligand as an unionized one and accordingly rules out the possibility of coordination of EDTA through its O atoms.[38] This view is further supported by the observation of bands at 1738 and 1723 cm^{-1} attributed to antisymmetric (O-C-O) stretchings arising from the presence of -COOH groups.[26] This therefore suggests that the EDTA ligand is coordinated to the manganese(III) center through nitrogen only.[26,38] Since the reactions were carried out in an acidic condition, protons from the carboxylic acid groups of EDTA could not be removed as this is now more evident from the IR spectrum of the newly synthesised compound. The frequencies at 444 and 390 cm^{-1} have been assigned to ν(Mn-N) modes, and those at 298 and 245 cm^{-1} to δ(N-Mn-N) further support the notion concerning the presence of N-bonded[26] EDTA in present case. Another important feature of the IR spectrum of $K[Mn(EDTA)F_4].3H_2O$ is the appearance of two bands at 562 and 494 cm^{-1} due to ν(Mn-F) vibrations of the coordinated fluoride ligands.[37] The additional bands at 3440 and 1640 cm^{-1} assignable to ν(O-H) and δ(H-O-H), respectively, are

Table 5. Structurally Significant IR Bands of $K[Mn(EDTA)F_4] \cdot 3H_2O$

Compound	IR cm^{-1}	Assignment
$K[Mn(EDTA)F_4] \cdot 3H_2O$	1738, 1723	ν_{as} (O-C-O)
	440, 390	ν(Mn-N)
	298, 245	δ (N-Mn-N)
	562, 494	ν(Mn-F)
	3450	ν(O-H)
	1660	δ (H-O-H)


K[Mn(EDTA)F4]·3H2O
TRANSMITTANCE(arbitrary scale)
3700
3600
3500
3400
3300
1800
1700
1600
600
500
400
300
200
WAVENUMBER(cm⁻¹)

typical for the presence of lattice water supporting the view that the water molecules are not coordinated to the metal center.

It is evident from the above results that a stable mixed-ligand fluoro-EDTA-manganese(III) complex, $K\left[Mn(EDTA)F_4\right].3H_2O$ can be synthesised from the reaction of MnO(OH) with 48% HF, EDTA and KF. The complex species $\left[Mn(EDTA)F_4\right]^-$ most probably has a distorted octahedral structure.

As mentioned in the opening section of this Chapter, we were also interested to synthesise mixed-fluoromanganate(III) containing acid phosphate as the heteroligand. The synthetic strategy for achieving this goal was somewhat different from the one adapted for that of $K\left[Mn(EDTA)F_4\right].3H_2O$. Instead of dissolving MnO(OH) in 48% HF, a mixture of MnO(OH) and AF (A = Na, K or NH_4) was dissolved in orthophosphoric acid (H_3PO_4), while the $Mn:F^-$ ratio was maintained at 1:3. The reaction took place as indicated by the appearance of a violet colour of the reaction solution. Addition of a mixture of ethanol and acetone (1/1,v/v) gave pink-brown micro-crystalline $A_3\left[Mn(HPO_4)_2F_2\right].3H_2O$ (A = Na, K or NH_4). Thus it is clear that the synthesis of the desired compound could be achieved without making use of hydrofluoric acid. The method is a straight one and leads to the synthesis of a series of salts of the complex ion $\left[Mn(HPO_4)_2F_2\right]^{3-}$.

The $A_3[Mn(HPO_4)_2F_2].3H_2O$ (A = Na, K or NH_4), compounds are quite stable, in the absence of moisture, for a long period. The stability of the compounds were ascertained in a manner similar to that described earlier for the $K[Mn(EDTA)F_4].3H_2O$ case. The compounds donot dissolve in water instead they decompose. The chemically determined oxidation state of manganese was found to lie between 2.9 and 3.1 in conformity with the occurrence of manganese(III) in each of them. The room temperature magnetic moments of the compounds lying in the range 4.8-4.9 μ_B give further support with regard to the presence of manganese(III) in the newly synthesised compounds. The observed magnetic moments are normal for a d^4 system and donot indicate any antiferromagnetic exchange interaction in the compounds.

Owing to their instability in water, solution electronic spectra could not be recorded. The reflectance spectra of $A_3[Mn(HPO_4)_2F_2].3H_2O$ (A = Na, K or NH_4) resemble each other very closely showing absorptions at ca 11000, ca 18200 and ca 20800 cm^{-1} owing, respectively, to the transitions $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$, and $^5B_{1g} \longrightarrow {}^5E_g$. These absorptions are quite representative for a distorted octahedral manganese(III) complex.[32]

The IR spectra of phosphato complexes of metals are generally complex particularly because of the broadness of peaks and poor resolution of the spectra making it difficult to precisely identify the peak positions let alone their assignments.[39] These problems become more pronounced when phosphate occurs as an acid phosphate and more so when lattice water is also present in the same compound. The presence of lattice water and hydrogen bonding largely effect the internal modes of vibrations of the anion with the ν(O-H) shifting appreciably to lower frequencies.[39] These difficulties were also encountered for the present compounds, The IR spectra of $A_3[Mn(HPO_4)_2F_2].3H_2O$ (A = Na, K, or NH_4) complexes, though poorly resolved, indicate the presence of coordinated acid phosphate ligand. A strong but broad absorption in the region 1050-1250 cm^{-1}, and a weak broad absorption at 2750-2925 cm^{-1} were observed in the IR spectrum of each of the compounds. These are regarded as characteristics for the presence of coordinated acid orthophosphate ligands[39-42] causing us to infer that the complexes under discussion contain HPO_4^{2-} coordinated through O atoms to the manganese(III) center. This view is further supported by the observance of a medium intensity band at ca 350 cm^{-1} which has been assigned to Mn-O stretching mode originating from the coordination of HPO_4^{2-} ligands through their O atoms. The band at ca 510 cm^{-1} has been assigned to the ν(Mn-F) mode arising from the

presence of coordinated fluoride ligands. The IR spectra also show bands at ca 1640 and around 3450 cm^{-1} attributed to δ(H-O-H) and ν(O-H) modes of uncoordinated water similar to those observed for the other manganese(III) compounds described in this Chapter. The weak nature and broadness of the ν(O-H) mode in addition to its lowering point to the involvement of hydrogen bonding as expected.

The results of pyrolytic studies involving $K_3[Mn(HPO_4)_2F_2].3H_2O$ show that the compound first loses water molecules in two steps. While one molecule of H_2O was lost at 120°C the rest two molecules of H_2O were lost at 190-200°C. It is believed that a relatively higher temperature, required for the removal of last two molecules of water was probably because of their involvement in hydrogen bonding. The dehydrated material on being heated at 300°C underwent a loss in its weight corresponding to the loss of two molecules of HF. The formation of HF owes its origin to the occurrence of HPO_4^{2-}, from which the H^+ is abstracted by a F^- ligand followed by the loss of HF. The above observations further support the formulation of the compounds.

Thus mixed-fluoromanganates(III) containing acid phosphate of the type $A_3[Mn(HPO_4)_2F_2].3H_2O$ (A = Na, K or NH_4) can be obtained under the experimental conditions described herein. The complexes are stable. It appears from

the results of various physical studies that the complex species $[Mn(HPO_4)_2F_2]^{3-}$ may have a distorted octahedral structure.

In our attempts to synthesise mixed-ligand fluoromanganate(III) containing glycine, a freshly prepared sample of MnO(OH) was allowed to react with 40% HF and glycine (glyH) with the ratio of $Mn:F^-$:glyH being maintained at 1:4:2. In order to provide counter cations, alkali-metal or ammonium carbonate, in lieu of the corresponding alkali-metal or ammonium fluoride, was added to the reaction solutions. The use of alkali-metal or ammonium fluoride had to be avoided in order to inhibit the formation of $[MnF_5]^{2-}$ species instead of the desired one. Another point of importance in the context of the synthesis of mixed-fluoro(glycine)manganate(III) complexes is that the reaction solution requires concentration prior to precipitating out the compounds by the addition of acetone. The compounds synthesised in this way were found to be A $[Mn(glyH)_2F_4].3H_2O$ with A being Na, K or NH_4.

The alkali-metal or ammonium tetrafluorobis(glycine)-manganate(III) trihydrates, A $[Mn(glyH)_2F_4].3H_2O$ (A = Na, K or NH_4), were obtained as pink microcrystalline products. They are stable in the absence of moisture. Like the fluorophosphatomanganate(III) described above, these compounds are also insoluble in common organic solvents. The chemically

estimated oxidation state of manganese in the compounds was found to lie between 2.9 and 3.1 in conformity with the occurrence of manganese(III) in each of the compounds. The results of magnetic susceptibility measurements on $A[Mn(glyH)_2F_4].3H_2O$ (A = Na, K or NH_4) gave the magnetic moments falling in the range 4.78 to 4.80 μ_B (300K). These values are normal for d^4 systems occurring in an octahedral or a distorted octahedral environment.

Owing to their instability in water, solution electronic spectra could not be recorded. The reflectance spectra of the compounds exhibit bands at ca 12000, ca 19800 and ca 21300 cm^{-1}. The observed pattern is rather typical of an octahedral or a distorted octahedral Mn^{3+} complex, and the bands have been accordingly assigned to the transitions $^5B_{1g} \longrightarrow {}^5A_{1g}$, $^5B_{1g} \longrightarrow {}^5B_{2g}$, and $^5B_{1g} \longrightarrow {}^5E_g$, respectively.[32] This also indicates an appreciable splitting of ^5E_g ground state of manganese(III) in the complex ion. The significant features of infrared spectra of the compounds are absorptions due to coordinated glycine and fluoride ligands (Table 6). The mode of bonding of glycine to a metal center can be ascertained from the IR spectra of such compounds. The COO stretching band near 1710 cm^{-1} occurs[43] when glycine is coordinated to a metal center in its unionized form, while for an ionized glycine being coordinated shows the COO stretching band near

1610 cm^{-1}. If, however, glycine acts as a chelated ligand an absorption at 1640 cm^{-1}, different from the one mentioned above, becomes a characteristic feature of its IR spectrum.[44] The IR spectra of the present compound show this absorption at ca 1715 cm^{-1} consistent with the coordination of glycine in its unionized form. It is therefore reasonable to assume that the coordination of glycine has taken place through its nitrogen lone pair electrons. Accordingly, the corresponding ν(Mn-N) and δ(N-Mn-N) modes have been observed at ca 505 and ca 355 cm^{-1}, respectively. Unfortunately in the present case, the ν(Mn-F) mode could not be identified clearly, however, increase in intensity and broadening of the band at ca 505 suggest the overlapping of ν(Mn-F) mode with that of the ν(Mn-N). The presence of uncoordinated water is unambiguous in the present cases and the corresponding ν(O-H) and δ(H-O-H) modes of water were observed in positions similar to those observed in various other cases containing lattice water making any further discussion redundant. It is evident from the IR spectra that glycine in the present complexes coordinate to the metal center in its unionized form through its nitrogen atom. This also appears reasonable in view of an acidic condition maintained for the syntheses of the present series of compounds.

Table 6. Structurally Significant Infrared Bands of $A\,[Mn(glyH)_2F_4].3H_2O$ (A = Na, K or NH_4)

Compound	IR cm^{-1}	Assignment
$(NH_4)\,[Mn(glyH)_2F_4].3H_2O$	1715	$\nu_{as}(COOH)$
	1596	$\delta(NH_2)$
	1445	$\delta(CH_2)$
	1411	$\nu(C-O)$
	1335	$\rho_w(CH_2)$
	1256	$\rho_t(NH_2)$
	1130	$\rho_r(NH_2)$
	1027	$\rho_w(NH_2)$
	913	$\rho_r(CH_2)$
	888, 871	$\nu_s(CCN)$
	740	$\delta(C=O)$
	606	$\pi(C=O)$
	505br	$\nu(Mn-N)$ + $\nu(Mn-F)$
	355	$\delta(N-Mn-N)$
	3445	$\nu(O-H)$
	1640	$\delta(H-O-H)$

continued..

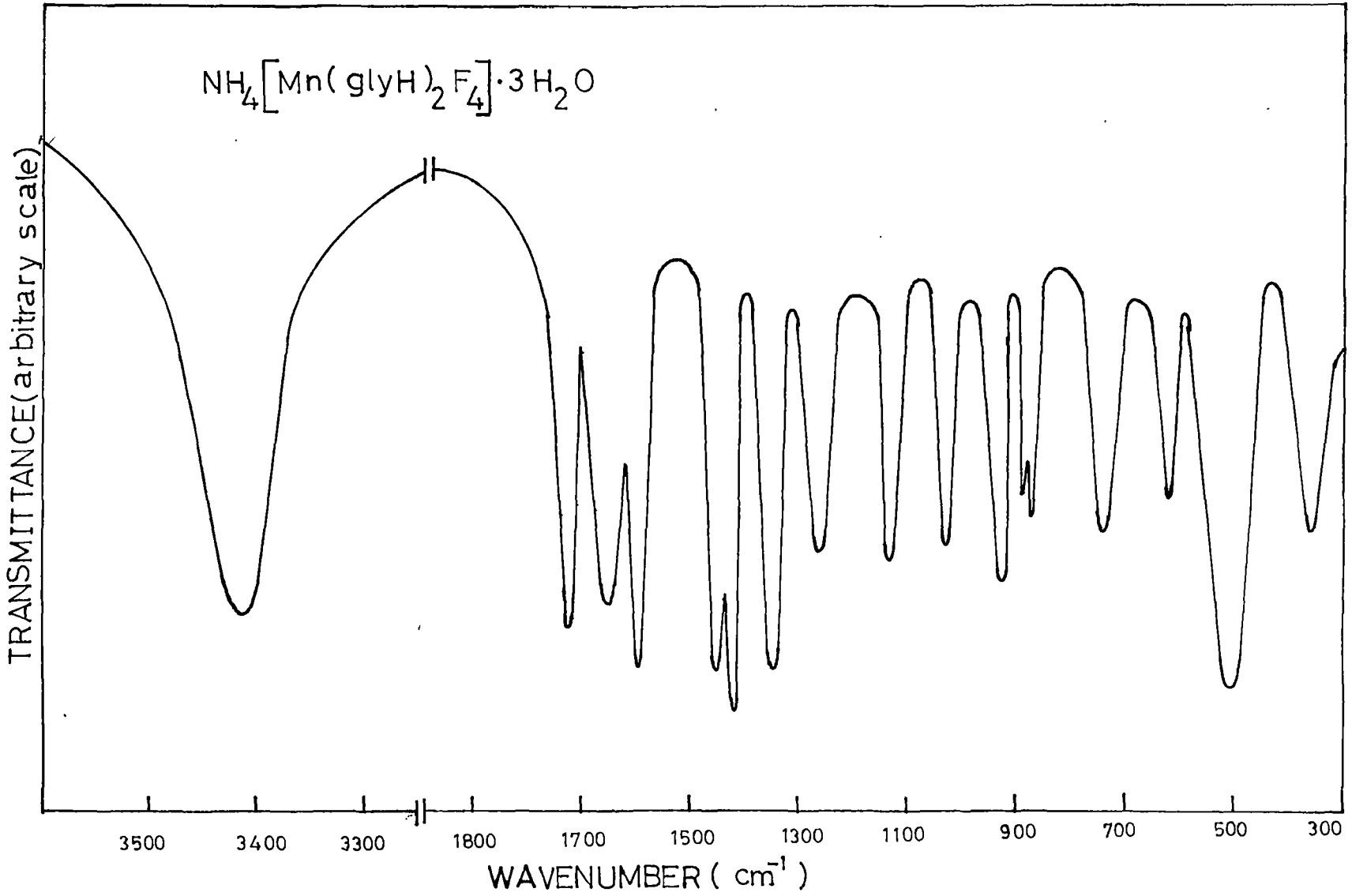

NH4[Mn(glyH)2F4]·3H2O
TRANSMITTANCE(arbitrary scale)
3500
3400
3300
1800
1700
1500
1300
1100
900
700
500
300
WAVENUMBER (cm-1)

Table 6 continued

Compound	IR cm^{-1}	Assignment
$Na\,[Mn(glyH)_2F_4]\cdot 3H_2O$	1710	$\nu_{as}(COOH)$
	1590	$\delta(NH_2)$
	1450	$\delta(CH_2)$
	1410	$\nu(C-O)$
	1330	$\rho_w(CH_2)$
	1255	$\rho_t(NH_2)$
	1128	$\rho_r(NH_2)$
	1030	$\rho_w(NH_2)$
	915	$\rho_r(CH_2)$
	890 875	$\nu_s(CCN)$
	745	$\delta(C=O)$
	610	$\pi(C=O)$
	500br.	$\nu(Mn-N) + \nu(Mn-F)$
	360	$\delta(N-Mn-N)$
	3450	$\nu(O-H)$
	1640	$\delta(H-O-H)$

continued..

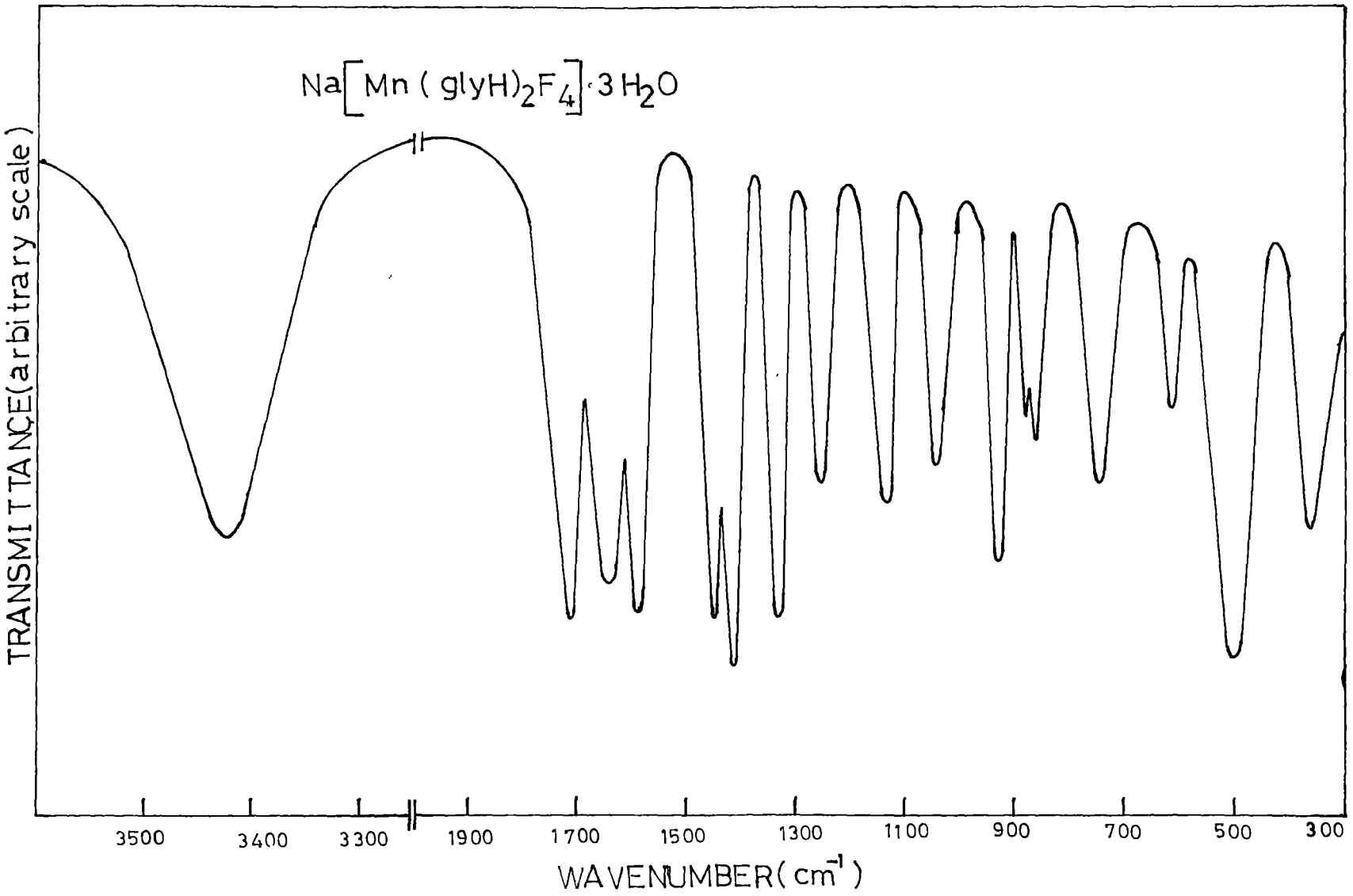
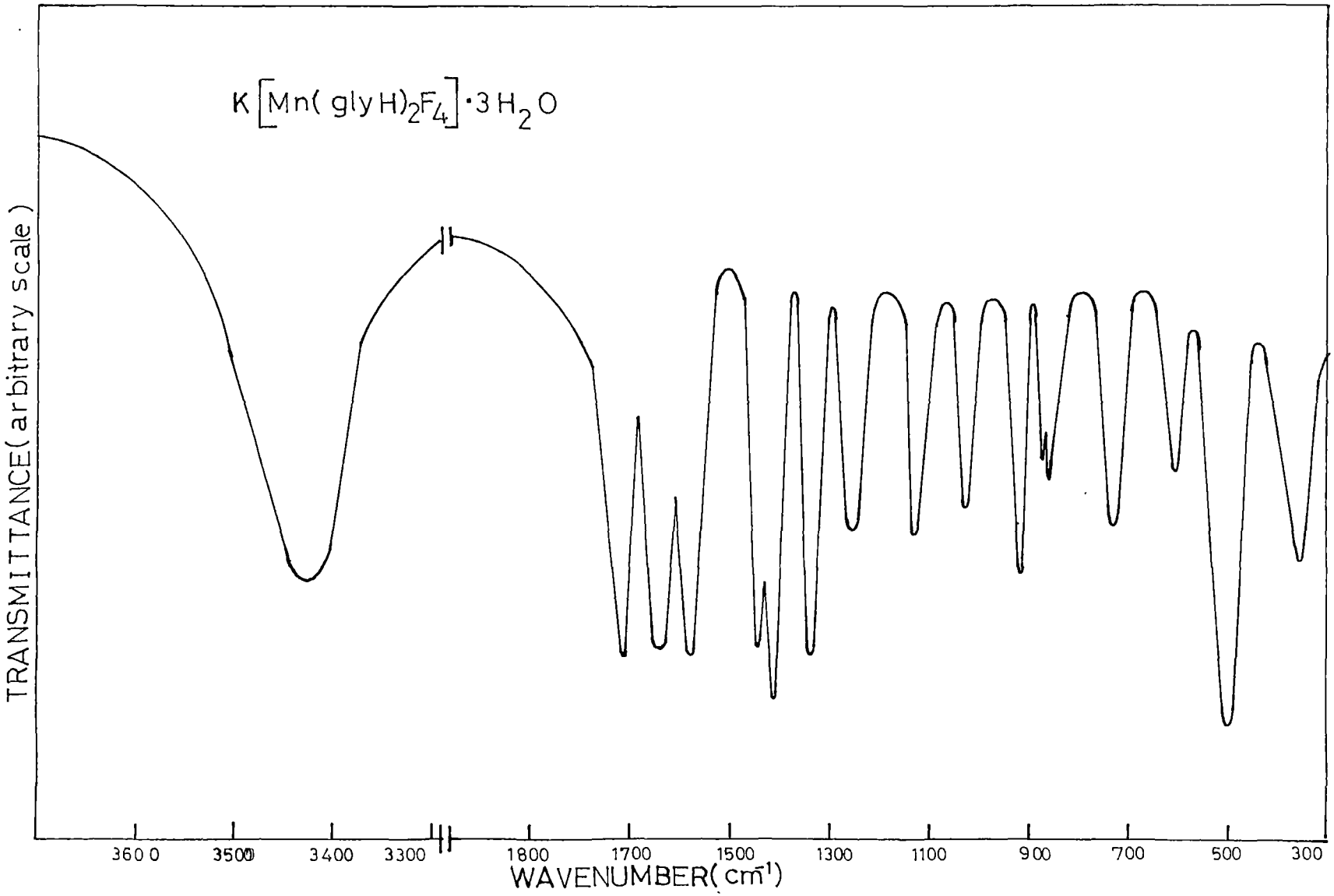

Na[Mn(glyH)2F4]·3H2O
TRANSMITTANCE(arbitrary scale)
3500
3400
3300
1900
1700
1500
1300
1100
900
700
500
300
WAVENUMBER(cm-1)

Table 6 continued

Compound	IR cm^{-1}	Assignment
$K[Mn(glyH)_2F_4] \cdot 3H_2O$	1715	$\nu as(COOH)$
	1595	$\delta(NH_2)$
	1445	$\delta(CH_2)$
	1411	$\nu(C-O)$
	1330	$\rho_w(CH_2)$
	1255	$\rho_t(NH_2)$
	1128	$\rho_r(NH_2)$
	1025	$\rho_w(NH_2)$
	910	$\rho_r(CH_2)$
	888 | 875	$\nu_s(CCN)$
	740	$\delta(C=O)$
	605	$\pi(C=O)$
	505br	$\nu(Mn-N) + \nu(Mn-F)$
	355	$\delta(N-Mn-N)$
	3445	$\nu(O-H)$
	1645	$\delta(H-O-H)$


K[Mn(glyH)2F4]·3H2O
TRANSMITTANCE(arbitrary scale)
3600
3500
3400
3300
1800
1700
1500
1300
1100
900
700
500
300
WAVENUMBER(cm-1)

Considering the results of chemical determination of oxidation state of manganese, magnetic susceptibility measurements, reflectance, and infrared spectral studies that the complex species has the formula $[Mn(glyH)_2F_4]^-$ with the manganese(III) being in a distorted octahedral environment.

To conclude this Chapter the following points may be emphasized that,

(i) a number of mixed-ligand fluoro complexes of Mn(III) containing O- and N-donor ligands have been synthesised by proper choice of the reaction conditions;

(ii) all the newly synthesised compounds have been synthesised in aqueous media;

(iii) of all the compounds reported in this Chapter $K_3[Mn(C_2O_4)_2F_2].3H_2O$ is the only example which is a very unstable one, while the rest are stable for prolong period in the absence of moisture; and

(iv) the magnetic moments of all the newly synthesised complexes, except $K_3[Mn(C_2O_4)_2F_2].3H_2O$ for which magnetic susceptibility could not measured owing to its instability, are normal unlike those of the $A_2[MnF_3(SO_4)]$[21] and $A_2[MnF_3(C_2O_4)]$[22] (A = alkali metal or NH_4) complexes.

Moreover, a comparison of magnetic properties of the binary fluoro complexes of manganese(III) namely $A_2[MnF_5]$ with those of the newly synthesised compounds described in the present work shows that whereas $A_2[MnF_5]$ compounds

exhibit strong antiferromagnetic interactions, the magnetic moments of K $[Mn(EDTA)F_4].3H_2O$, $A_3[Mn(HPO_4)_2F_2].3H_2O$ and $A[Mn(glyH)_2F_4].3H_2O$ have been found to be normal expected for (d^4) manganese(III) systems. In view of the present results we tend to also believe that manganese(III) compounds involving -Mn····· Mn- ····· interactions either through bridging fluoride or through double bridges like in the cases $A_2[MnF_3(SO_4)]$[20,21] and $A_2[MnF_3(C_2O_4)]$[22] lead to the operation of super exchange phenomenon giving rise to antiferromagnetism to a variable extent. Further the synthesis of stable manganese(III) complexes $K[Mn(EDTA)F_4].3H_2O$ and $A[Mn(glyH)_2F_4].3H_2O$, provides evidence for the capability of manganese(III) complexes containing N-donor ligands being synthesised. The examples of manganese(III) complexes containing nitrogen donor ligands are scanty.[45,46]

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CHAPTER 8

Chapter 8

Molecular Complexes of Manganese(III). Synthesis And Physico-Chemical Studies of $[Mn(o\text{-phen})F_3(H_2O)].2H_2O$, $[Mn(bipy)F_3(H_2O)].2H_2O$, And $[Mn(urea)_2F_3].3H_2O$

Fluoride assisted stabilization of manganese(III) in aqueous solutions ultimately allowing the synthesis of a good number of mixed-ligand fluoromanganate(III) complexes has been described in the previous Chapter. A few molecular mixed-ligand chloro complexes of manganese(III) were reported by earlier workers,[1,2] and the only molecular mixed ligand fluoro complex of manganese(III) known to our knowledge is $[Mn(o\text{-phen})F_3(H_2O)]$.[2] It was also reported[2] that the corresponding 2,2'-bipyridine complex could not be synthesised. As a sequel of the studies described in Chapter 7, we were curious also to synthesise molecular mixed-ligand fluoro complexes of manganese(III) and to study their properties. In view of this attention was directed to synthesise the proposed type of manganese(III) compounds.

The present Chapter deals with the synthesis, characterization, and structural assessment of three molecular mixed ligand fluoro complexes of manganese(III).

Experimental

Reagent grade chemicals were used (Sarabhai M, S.D's, E. Merck, Glaxo, Sisco).

The compound MnO(OH) was prepared by the oxidation of $Mn(OH)_2$ with hydrogen peroxide as described in Chapter 6.

(i) Synthesis of Trifluoroaquo(1,10-phenanthroline)-Manganese(III) Dihydrate, $[Mn(o\text{-phen})F_3(H_2O)].2H_2O$

An aqueous suspension (20 cm^3) of freshly prepared 0.89g (10.11 mmol) of MnO(OH) was dissolved in 3 cm^3 (72 mmol) of 48% HF with continuous stirring. To the clear solution an ethanolic solution of 1,10-phenanthroline (2.0g, 10.11 mmol) was added slowly, maintaining Mn:o-phen ratio at 1:1. The solution was stirred for ca 20 min, whereupon a dull orange compound started appearing. Stirring was continued for a further period of ca 10 min followed by the addicion of about 10 cm^3 of ethanol (ethanol was added to achieve nearly complete precipitation of the product). The compound $[Mn(o\text{-phen})F_3(H_2O)].2H_2O$ was filtered, and washed 3 to 4 times with ethanol, dried *in vacuo* over concentrated H_2SO_4.

Yield of $[Mn(o\text{-phen})F_3(H_2O)].2H_2O$ was found to be 2.5g (71.4%).

(ii) Synthesis of Trifluoroaquo(2,2′-bipyridine)Manganese(III) Dihydrate $[Mn(bipy)F_3(H_2O)].2H_2O$

Freshly prepared 0.89g (10.11 mmol) of MnO(OH) was dissolved in 3 cm^3 (72 mmol) of 48% HF with stirring to obtain a clear solution. To the above reaction solution was added a concentrated ethanolic solution of 1.58g (10.11 mmol) of 2,2′-bipyridine and the whole was stirred for ca 10 min, a reddish-brown colour was developed. This was then concentrated over a steam bath to nearly half of its original volume. Acetone (half of the original volume) was added slowly, to the above concentrated solution, which precipitated out dull orange $[Mn(bipy)F_3(H_2O)].2H_2O$. The compound was isolated by filtration, followed by washing with acetone 2 to 3 times and dried in vacuo over concentrated H_2SO_4.

Yield of the compound $[Mn(bipy)F_3(H_2O)].2H_2O$ was 2g (61.4%).

(iii) Synthesis of Trifluorobis(urea)Manganese(III) Trihydrate, $[Mn(urea)_2F_3].3H_2O$

An aqueous suspension of 0.89g (10.11 mmol) of freshly prepared MnO(OH) was dissolved by the slow addition of 3 cm^3 (72 mmol) of 48% HF with continuous stirring. To the clear reaction solution 1.82g (30.34 mmol) of solid urea was added slowly with the maintenance of Mn:urea ratio at 1:3, and stirring was continued for a further period of ca 20 min.

The resultant reddish-brown solution was concentrated over a steam bath, and to the concentrated reaction mixture was added acetone slowly, when chocolate colour microcrystalline $[Mn(urea)_2F_3].3H_2O$ precipitated out. The compound was filtered, and purified by washing 2-3 times with acetone. The product $[Mn(urea)_2F_3].3H_2O$ was dried in vacuo over concentrated H_2SO_4.

Yield of $[Mn(urea)_2F_3].3H_2O$ was found to be 1.2g (41.5%).

Elemental Analyses

Quantitative estimations of manganese, fluoride, carbon, hydrogen, and nitrogen were accomplished by the methods described in Chapter 2.

The results of elemental analyses and chemically estimated oxidation state of manganese in the newly synthesised compounds are reported in Table 1.

Chemical Determination of oxidation state of Manganese

The estimation of oxidation state of manganese was made chemically by the method already described in Chapter 7.

Table 1. Analytical Data of $[Mn(o\text{-phen})F_3(H_2O)]\cdot 2H_2O$, $[Mn(bipy)F_3(H_2O)]\cdot 2H_2O$, and $[Mn(urea)_2F_3]\cdot 3H_2O$

Compound	Estimated oxidation state of Mn	Found % (Calcd. %)				
		Mn	F	C	H	N
$[Mn(o\text{-phen})F_3(H_2O)]\cdot 2H_2O$	2.9	15.77 (15.87)	16.81 (16.47)	41.54 (41.63)	4.11 (4.04)	8.12 (8.09)
$[Mn(bipy)F_3(H_2O)]\cdot 2H_2O$	3.0	17.51 (17.06)	17.62 (17.69)	37.32 (37.28)	4.37 (4.35)	8.82 (8.69)
$[Mn(urea)_2F_3]\cdot 3H_2O$	3.1	18.92 (19.21)	19.81 (19.93)	8.43 (8.39)	4.85 (4.89)	19.64 (19.58)

Results and Discussion

In the context of some studies involving manganese(III), it was suggested in 1982[3] that MnO(OH) when dissolved in 40% HF produced MnF_3 in solution. It was thought in the present context that a further reaction of MnF_3, generated *insitu*, with ligands like 1,10-phenanthroline, 2,2'-bipyridine or urea, which are capable of acting as neutral ligands for transition metal would be a reasonable strategy for the synthesis of the kind of compounds looked for. Accordingly a solution of MnO(OH) in 48% hydrofluoric acid was reacted separately with o-phen, bipy and urea (vide Experimental), from which $[Mn(o\text{-}phen)F_3(H_2O)].2H_2O$, **1**, $[Mn(bipy)F_3(H_2O)].2H_2O$, **2**, and $[Mn(urea)_2F_3].3H_2O$, **3**, respectively, were obtained in high yields. While $[Mn(o\text{-}phen)F_3(H_2O)].2H_2O$ was precipitated out from a dilute solution, the other two compounds required concentration of the reaction solution by heating on a steam bath followed by the addition of acetone required for bringing about precipitation of the compounds. These results again support the view concerning the formation of MnF_3 in the reaction of MnO(OH) with aqueous hydrofluoric acid. The methods described are direct and the strategy used herein can be used as a paradigm for the synthesis of similar mixed-ligand fluoromanganate(III) compounds to provide a rather easy access to them.

Whereas $[Mn(o\text{-phen})F_3(H_2O)]\cdot 2H_2O$, 1, and $[Mn(bipy)F_3(H_2O)]\cdot 2H_2O$, 2, were dull orange in colour, the $[Mn(urea)_2F_3]\cdot 3H_2O$, 3, was obtained as a chocolate colour product. The compounds are stable and can be stored in polyethylene sample containers. Their stability can be ascertained by estimation of manganese and also by chemical determination of its oxidation state. The compounds slowly decompose in water, however, they dissolve partly in polar organic solvents. The chemically estimated oxidation state of manganese was found to lie in the range 2.9 to 3.1 (Table 1) suggesting the occurence of manganese(III) in each of the compounds. Chemical determination of oxidation state of the metal in such compounds is very crucial particularly because their magnetic moments may not always be very straight forward leading to confusion concerning the formal oxidation state of the central metal atom.

The results of room temperature (300K) magnetic susceptibility measurements showed that the compounds are paramagnetic with the magnetic moments of $[Mn(o\text{-phen})F_3(H_2O)]\cdot 2H_2O$, 1, $[Mn(bipy)F_3(H_2O)]\cdot 2H_2O$, 2, and $[Mn(urea)_2F_3]\cdot 3H_2O$, 3, being 5.0, 4.9 and 4.3 μ_B, respectively. Thus it is evident that the magnetic moment values of the compounds 1 and 2 are normal, whereas that of the compound 3, is relatively low. This suggests that $[Mn(urea)_2F_3]\cdot 3H_2O$ is weakly antiferromagnetic. From the observed magnetic moment values alone, it

may be said that the complex unit in $\lceil Mn(o\text{-phen})F_3(H_2O)\rfloor.2H_2O$ and $\lceil Mn(bipy)F_3(H_2O)\rfloor.2H_2O$ are very likely monomeric with distorted octahedral structures, but the $\lceil Mn(urea)_2F_3\rfloor.3H_2O$ may have a polymeric structure through -Mn-F-Mn- interactions enabling super exchange to be operative leading to lowering of magnetic moments as observed. The manganese(III) center in this compound may also find itself in a distorted octahedral environment. The solution electronic spectra also support the view. The electronic spectra of $\lceil Mn(o\text{-phen})F_3(H_2O)\rfloor.2H_2O$, 1, and $\lceil Mn(bipy)F_3(H_2O)\rfloor.2H_2O$, 2, were recorded in DMSO solutions, and of $\lceil Mn(urea)_2F_3\rfloor.3H_2O$, 3, was recorded in a methanol solution. While the spectra of 1 and 2 showed absorptions at ca 23250, 19000, and 13750 cm^{-1} assigned to $^5B_{1g} \longrightarrow {}^5E_g$, $^5B_{1g} \longrightarrow {}^5B_{2g}$ and $^5B_{1g} \longrightarrow {}^5A_{1g}$ transitions, respectively, that of 3 exhibited the corresponding bands at 20620, 17240, and 10810 cm^{-1}, respectively. The pattern is typical[4] for manganese(III) occurring in a distorted octahedral environment with appreciable splitting of ^5E_g ground term of Mn(III). This again adduce support to the notion that each of the compounds 1, 2 and 3, has a distorted octahedral structure.

The IR spectra of $\lceil Mn(o\text{-phen})F_3(H_2O)\rfloor.2H_2O$, 1, and $\lceil Mn(bipy)F_3(H_2O)\rfloor.2H_2O$, 2, showed the characteristics of coordinated o-phen and bipy ligands, respectively.[1,5-7] The Mn-N stretching modes originating from the coordinated

N-heterocyclic ligands for 1 and 2 were observed at 296m and 245s, and 282s and 233m cm^{-1}, respectively,[6,8] providing further support to the occurrence of coordinated o-phen and bipy ligands in the corresponding compounds. The band at ca 480 cm^{-1} has been assigned to ν(Mn-F) of the coordinated F^- ligands.[9,10] A notable feature of the IR spectra of 1 and 2 is the band at ca 725 cm^{-1} which has been assigned to the rocking mode of coordinated water. This is particularly important because the formula of 1 and 2 contain both coordinated as well as lattice water. Owing to the presence of lattice water the information obtainable from the ν(O-H) and δ(H-O-H) positions are not very significant in the present cases as far as the distinction between the two kinds of water molecule is concerned. Fortunately the occurrence of rocking mode of water as mentioned above supports the occurrence of coordinated water. Taking into account of the observed magnetic moment values of 1 and 2 together with the results obtained from their IR spectroscopic studies now cause us to infer that while one molecule of water is coordinated to the manganese center in each case, the other two molecules are present as lattice water. Thus the complexes 1 and 2 acquire distorted octahedral structures, and the involvement of polymer formation through a bridging ligand is not required to account for the experimentally obtained results.

The significant features of the IR spectrum of trifluorobis(urea)manganese(III) trihydrate, $[Mn(urea)_2F_3].3H_2O$, 3, are absorptions due to coordinated urea, coordinated fluoride, and lattice water. The important bands arising from coordinated urea were observed at 3424s and 1535s cm^{-1} attributed to $\nu(NH_2)$ and $\nu(C=O)$ vibrational modes,[11,13] respectively. The fact that $\nu(NH_2)$ occur in a position stipulated for such a mode[12,13] of free urea, and a significant lowering of the $\nu(C=O)$ frequency compared to that of free urea[12,13] strongly suggest that the urea ligands are coordinated to the metal center through its oxygen atom only. Therefore it is evident that each of the two urea ligands coordinate in a monodentate manner. Unlike in the cases of 1 and 2, the $\nu(Mn-F)$ mode for 3 was observed at 453 cm^{-1}. Lowering in position of this mode accompanied by its broadening lead us to believe that the coordinated fluorides might also be involved in bridge formation among the contiguous Mn atoms in the crystal lattice. The complex $[Mn(urea)_2F_3].3H_2O$ may have a distorted octahedral structure attained through -Mn-F-Mn-F-Mn- interactions. Such a proposition is not irrational in view of the earlier reports $[MnF_3(SO_4)]^{2-}$ [ref. 14,15] and $[MnF_3(C_2O_4)]^{2-}$ [ref. 16]. Moreover, this arrangement will also support the possibility of the compound 3 being slightly antiferromagnetic through super-exchange leading to lowering of magnetic moments as observed,

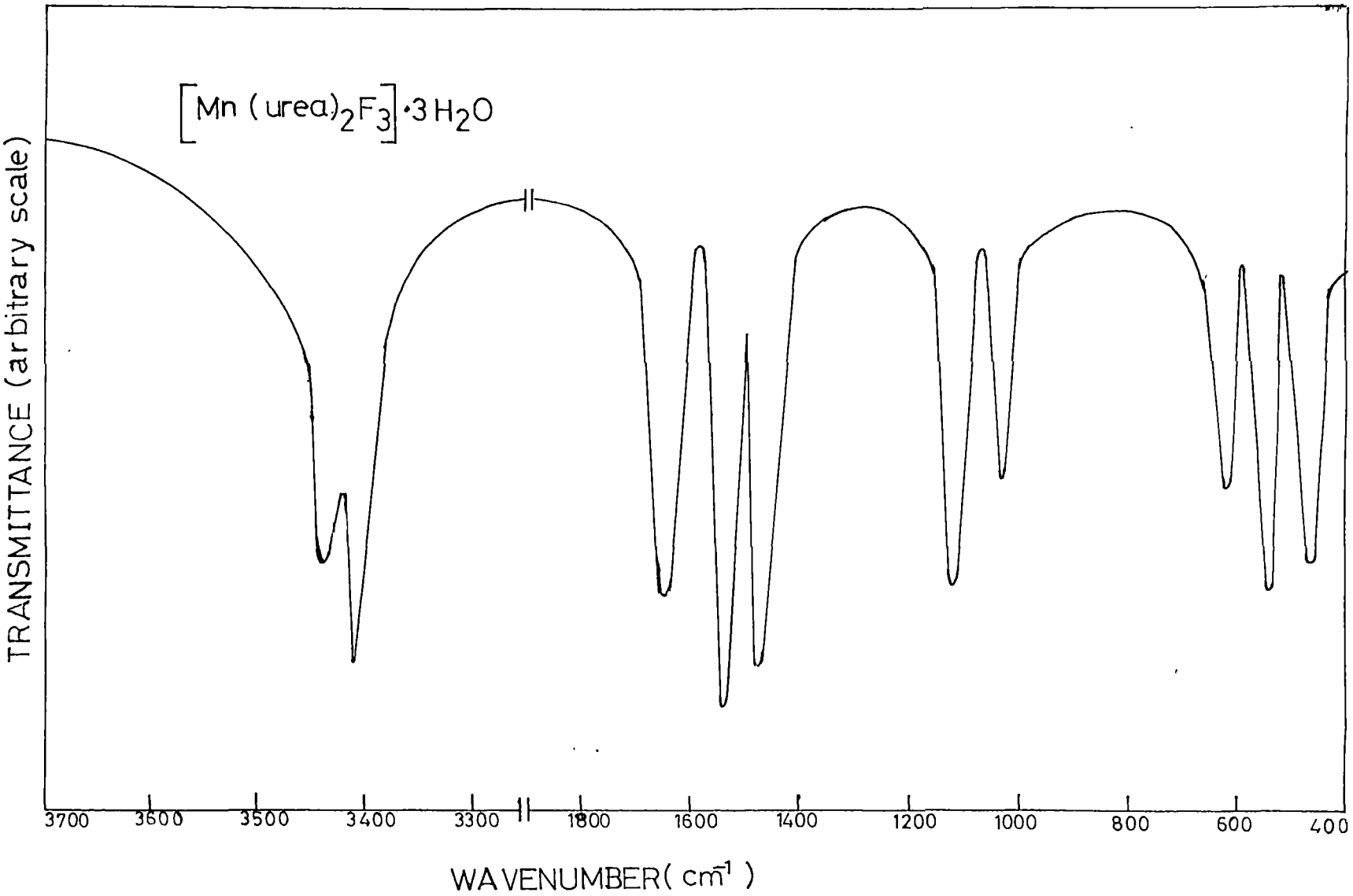
The bands at 3440 and 1645 cm^{-1} in the IR spectrum of 3 have been assigned to ν(O-H) and δ(H-O-H) modes, respectively. The absence of any band at ca 720 cm^{-1}, and the positions and shapes of ν(O-H) and δ(H-O-H) bands further support the occurrence of water molecule as lattice water only. The presence of lattice water in fluoromanganates(III) are well precedented.[10,17]

It may be stated therefore that $[Mn(urea)_2F_3].3H_2O$, 3, may have a distorted octahedral structure involving -Mn-F-Mn-F-Mn- interactions and the water molecules are not coordinated to the manganese(III) center.

Thermogravimetric analysis (TGA) of trifluorobis(urea)-manganese(III) trihydrate, $[Mn(urea)_2F_3].3H_2O$, 3, was carried out in the range 40-800°C. The thermogram of the compound shows that the compound starts losing its weight from about 140°C and continues until 210°C giving a horizontal at 210-240°C. The loss of weight in this process was found to be 19.2% corresponding to the loss of three molecules of H_2O (calc. 18.9) giving anhydrous $[Mn(urea)_2F_3]$ as an intermediate. This undergoes further decomposition in two stages showing horizontals at 330-360°C and 470°C onwards, respectively, with the corresponding weight losses being 40.1% and 62.1% which in turn correspond to the loss of one urea at each step (Calc. 39.9 and 60.8, respectively), finally

Table 2. Structurally Significant IR bands of $[Mn(urea)_2F_3].3H_2O$

Compound	IR cm^{-1}	Assignment
$[Mn(urea)_2F_3].3H_2O$	1535	ν(C=O)
	3424	$\nu(NH_2)$
	1480	ν_{as} (CN)
	1152	NH_2 rocking
	1030	ν_s (CN)
	610	δ(NCO)
	532	δ(NCN)
	453	ν(Mn-F)
	3445	ν(O-H)
	1645	δ(H-O-H)


[Mn (urea)2F3]·3H2O
TRANSMITTANCE (arbitrary scale)
3700
3600
3500
3400
3300
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER(cm-1)

producing MnF_3. No loss of weight beyond 470°C till 800°C suggest that MnF_3 once formed, from $[Mn(urea)_2F_3].3H_2O$ at ca 470°C, does not undergo any change, atleast within the range of temperature involved in the present TGA experiment. The mode of thermal decomposition may be depicted in the following way:

$$[Mn(urea)_2F_3].3H_2O \xrightarrow{\text{ca } 220\,^\circ C} [Mn(urea)_2F_3] \xrightarrow{\text{ca } 350\,^\circ C} [Mn(urea)F_3] \xrightarrow{\text{ca } 470\,^\circ C} MnF_3$$

The information gathered from the thermogravimetric analysis (TGA) may be useful in the context of obtaining the intermediates, viz., $[Mn(urea)_2F_3]$ and $[Mn(urea)F_3]$, by the pyrolysis of 3 at the temperatures given above, for further studies involving them. Moreover, heating of $[Mn(urea)_2F_3].3H_2O$ at ca 470°C under nitrogen leading to the formation of MnF_3 may be an useful way of preparing this compound. The importance of MnF_3 as a powerful fluorinating agent is well known.[18]

In order to evaluate the potentiality of 1, 2 and 3 as oxidants, oxidation reactions involving the newly synthesised compounds were carried out. The results of our initial studies reveal that the compounds can oxidize substrates like benzyl alcohol, anthracene etc. Further studies are now being carried

out by other workers of our laboratory in this direction and the results will be reported elsewhere.

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APPENDIX

APPENDIX

LIST OF PUBLICATIONS

1. Synthesis and Structural Assessment of Ammonium and Caesium Difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and Alkali-metal Difluorodioxoperoxouranate(VI) Monohydrates, $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb), M.N. Bhattacharjee, M.K. Chaudhuri, and R.N. Dutta Purkayastha. J. Chem. Soc. Dalton Trans., 1985, 409.

2. First Synthesis and Structural Assessment of Alkali-metal carbonatodioxoperoxouranate(VI) Monohydrates, $A_2[UO_2(O_2)(CO_3)].H_2O$, and carbonatooxodiperoxovanadate(V) Trihydrates, $A_3[VO(O_2)_2(CO_3)].3H_2O$, J.K. Basumatary, M.K. Chaudhuri, R.N. Dutta Purkayastha, and Z. Hiese J. Chem. Soc., Dalton Trans., 1986, 709.

3. Complex peroxyuranates. Synthesis and structural Assessment of Alkali-metal and Ammonium Dioxoperoxy (Sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), and Alkali-metal and Ammonium Dioxo-peroxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4].H_2O$, M. Bhattacharjee, M.K. Chaudhuri, and R.N. Dutta Purkayastha, Inorg. Chem., 1986, 25, 2354.

4. New Methods of Syntheses of Ammonium, Sodium and Potassium Triacetatodioxouranates(V) and Diacetatodioxouranium(VI) Dihydrate
M.K. Chaudhuri and R.N. Dutta Purkayastha,
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5. Mass Spectrometry of Metal Compounds IV. Electron Ionisation Mass Spectra of Bis(Acetylacetonato)dioxo-uranium(VI), $UO_2(C_5H_7O_2)_2$, And a Comparison with those of Bis(acetylacetonato)complexes of First Row Transition Metals, $M(C_5H_7O_2)_2$ (M = Mn, Fe, Co, Ni or Cu),
M.N. Bhattacharjee, M.K. Chaudhuri, M. Devi,
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6. Direct Synthesis of Potassium Tris(oxalato)Manganate(III) and First Synthesis of Alkali-Metal and Ammonium Trifluoro(oxalato)Manganates(III).
M.N. Bhattacharjee, M.K. Chaudhuri, and R.N. Dutta Purkayastha,
Inorg. Chem., 1985, 24, 447.

Synthesis and Structural Assessment of Ammonium and Caesium Difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs), and Alkali-metal Difluorodioxoperoxouranate(VI) Monohydrates, $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb)

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The product obtained by treating an aqueous solution of $UO_2(NO_3)_2\cdot 6H_2O$ with NH_4OH or KOH reacts with AF (A = NH_4, Rb, or Cs) or KF, 30% H_2O_2, and a very small amount of 40% HF, in the mol ratio $UO_2(NO_3)_2\cdot 6H_2O$: AF : H_2O_2 of 1 : 4 : 110.8, at pH 6.5—7 to afford ammonium and caesium difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs), and potassium and rubidium difluorodioxoperoxouranate(VI) monohydrates, $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb). The i.r. spectra suggest that the peroxo-ligand is bonded to the UO_2^{2+} centre in a triangular bidentate (C_{2v}) manner.

Peroxouranate chemistry is highly complicated[1,2] owing to the formation of a host of different species with a slight variation of pH of the reaction medium. Peroxouranates containing O_2^{2-} : U ratios of 1:1, 1:2, 2:1, 3:1, 3:2, and 5:2 have been described in the literature,[1] of which $UO_2(O_2)_2\cdot nH_2O$ (n = 2 or 4) is the best characterised example. Reports on heteroligand peroxouranates are few, except for some on carbonato- and oxalato-peroxouranates.[1] The only fluoro-peroxouranate known,[1] to our knowledge, is $Na[UO_2(O_2)F(OH_2)]\cdot 4H_2O$. Our interest in the area of peroxo-metal chemistry[3] has now led us to synthesise a series of novel compounds $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb), the first full series of fluoroperoxouranate compounds. The present paper reports the synthesis, characterisation, and assessment of the structure of the title compounds.

Experimental

All chemicals were of reagent grade. I.r. spectra were recorded on a Perkin-Elmer model 683 spectrophotometer. Magnetic susceptibility measurements were made by the Gouy method; $Hg[Co(NCS)_4]$ was used as calibrant. The pH of the reaction solutions was measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper.

Synthesis of $A_2[UO_2(O_2)F_2]$ (A = NH_4 *or* Cs) *and* $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K *or* Rb).—$UO_2(NO_3)_2\cdot 6H_2O$ (1.0 g, 1.99 mmol) was dissolved in water (10—15 cm^3) followed by addition of 25% ammonium hydroxide solution, or a concentrated solution of potassium hydroxide only in the case of the K^+ salt, with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off, washed free from alkali and nitrate, and then mixed with alkali-metal or ammonium fluoride, AF (A = NH_4, Rb, Cs, or K) and 30% H_2O_2 (25 cm^3, 220.5 mmol) while maintaining the U : F^- : H_2O_2 ratio at 1:4:110.8. Dropwise addition of 40% HF (1 cm^3) with constant stirring afforded a clear yellow solution (pH ~ 2), the pH of which was raised to 6.5—7 by carefully adding a 10% solution of ammonium or potassium hydroxide in the cases of the NH_4^+ and K^+ salts respectively and solid A_2CO_3 (A = Rb or Cs) for the Rb^+ or Cs^+ salts. An equal volume of ethanol was added with occasional stirring to obtain yellow microcrystalline $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) or $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb). Each compound was allowed to settle for *ca.* 30 min, separated by centrifugation, purified by washing with ethanol, and finally dried *in vacuo* over diphosphorus pentaoxide.

The amounts of reagents used and the yields of the compounds are set out in Table 1.

Elemental Analysis.—Uranium was estimated gravimetrically as U_3O_8.[4] The peroxide content was determined by redox titration with standard solutions of $KMnO_4$[5] or Ce^{4+}.[6] Fluoride was estimated gravimetrically as lead chloride fluoride, PbClF.[7] Nitrogen and potassium were estimated by methods described in previous papers.[3]

The analytical data and structurally significant i.r. bands and their assignments are summarised in Table 2.

Results and Discussion

Both fluoride[8] and peroxide[1] can, under the appropriate conditions, co-ordinate to UO_2^{2+}. Accordingly we carried out the reaction of UO_2^{2+} with alkali-metal or ammonium fluoride, AF, and H_2O_2 at pH 6.5—7 which enabled us to synthesise the difluorodioxoperoxouranate(VI) compounds, $[UO_2(O_2)F_2]^{2-}$, in aqueous medium. The complex ion was isolated as its alkali-metal and ammonium salts, $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2]\cdot H_2O$ (A = K or Rb) by the addition of ethanol which facilitated precipitation. It must be emphasised that maintenance of the pH at 6.5—7 is vital for the formation and thence successful isolation of the compounds in the solid state. It has been observed by carrying out similar reactions at pH 2—4 that the products obtained under these conditions either do not contain peroxide at all or do to a practically negligible extent, suggesting thereby that acidic conditions are not conducive to the desired synthesis. The compounds isolated under such conditions were found to be oxofluoro- rather than fluoroperoxo-uranates(VI). Thus we believe that the course of reaction involves the formation of oxofluorouranate(VI) first followed by uptake of peroxide with the increase in pH of the medium to produce ultimately the complex ion $[UO_2(O_2)F_2]^{2-}$. In the cases of the Rb^+ and Cs^+ salts, the pH of the reaction medium was raised to 6.5—7 by the addition of the respective carbonates, exploiting the reaction $CO_3^{2-} + 2H^+ \rightarrow CO_2\uparrow + H_2O$, instead of NH_4OH which was otherwise thought to be suitable. Attempts to use ammonia solution to raise the pH to 6.5—7 resulted in the isolation of $[NH_4]_2[UO_2(O_2)F_2]$ even though the stipulated amount of RbF or CsF was used. This could be due to the relatively lower solubility of $[NH_4]_2[UO_2(O_2)F_2]$.

Table 1. Amounts of reagents used and yields of alkali-metal and ammonium difluorodioxoperoxouranates(VI)

Compound	Yield/g (%)	Amount of $UO_2(NO_3)_2 \cdot 6H_2O$/g (mmol)	Amount of AF/g (mmol)	Amount of H_2O_2/cm^3 (mmol)
$[NH_4]_2[UO_2(O_2)F_2]$	0.5	1	0.3	25
	(67)	(1.99)	(8.1)	(220.5)
$K_2[UO_2(O_2)F_2] \cdot H_2O$	0.6	1	0.47	25
	(69)	(1.99)	(8.1)	(220.5)
$Rb_2[UO_2(O_2)F_2] \cdot H_2O$	0.8	1	0.84	25
	(73)	(1.99)	(8.0)	(220.5)
$Cs_2[UO_2(O_2)F_2]$	0.9	1	1.23	25
	(75)	(1.99)	(8.1)	(220.5)

Table 2. Analytical data and structurally significant i.r. bands of alkali-metal and ammonium difluorodioxoperoxouranates(VI)

	Analysis[a] (%)					
Compound	A	U	O[b]	F	I.r. (cm^{-1})	Assignments
$[NH_4]_2[UO_2(O_2)F_2]$	7.55[c]	63.8	8.70	9.80	885s, 900s	ν(U=O)
	(7.45)[c]	(63.3)	(8.50)	(10.1)	855s	ν(O–O)
					350s,br	ν(U–F–U)
					3 160m	ν_3 N–H
					3 040s	ν_1 N–H
					1 400s	ν_4 N–H
$K_2[UO_2(O_2)F_2] \cdot H_2O$	18.4[d]	54.9	7.80	9.10	890s	ν(U=O)
	(17.95)[d]	(54.55)	(7.35)	(8.70)	860s	ν(O–O)
					370s,br	ν(U–F–U)
					3 440s	ν(O–H)
					1 640m	δ(H–O–H)
$Rb_2[UO_2(O_2)F_2] \cdot H_2O$		45.4	6.40	7.50	905s	ν(U=O)
		(45.0)	(6.05)	(7.20)	860s	ν(O–O)
					360s,br	ν(U–F–U)
					3 450s	ν(O–H)
					1 640m	δ(H–O–H)
$Cs_2[UO_2(O_2)F_2]$		39.8	5.50	6.10	900s	ν(U=O)
		(39.3)	(5.30)	(6.25)	860s	ν(O–O)
					360s,br	ν(U–F–U)

[a] Calculated values are in parentheses. [b] Peroxo-oxygen. [c] Analysis for N. [d] Analysis for K.

Characterisation and Assessment of Structure.—The newly synthesised compounds are insoluble in common organic solvents, and very sparingly soluble in water. They dissolve completely in a slightly acidified (H_2SO_4) solution from which uranium can be quantitatively precipitated by the addition of ammonium hydroxide. The determination of peroxide content, considered to be extremely important, was accomplished by redox titrations with a standard Ce^{4+} solution, and also with a standard $KMnO_4$ solution, in the presence of boric acid to prevent any loss of active oxygen; results conspicuously suggested the presence of one O_2^{2-} group co-ordinated to the UO_2^{2+} centre in each of the compounds. The occurrence of hexavalent uranium has been confirmed by the diamagnetic nature of the compounds. It may be noted that while the ammonium and caesium salts of the $[UO_2(O_2)F_2]^{2-}$ ion are anhydrous, those of the potassium and rubidium are monohydrates.

The principal features of the i.r. spectra are the absorptions at 910—880, 870—850, and 370—350 cm^{-1}, which have been assigned to ν(U=O) (*trans*-linked O=U=O group),[8] ν(–O–O–),[3,9] and ν(U–F)[10] modes respectively. The strong and sharp ν(–O–O–) band at *ca.* 860 cm^{-1} supports the view that the O_2^{2-} is co-ordinated to the UO_2^{2+} centre in a triangular bidentate (C_{2v}) manner.[3,9] The somewhat lower value of ν(U–F), compared to those of binary fluorouranates(VI),[10] and slightly broad nature of the band indicate the distinct possibility of fluoride acting as a bridging group. The two bands at *ca.* 3 440 and at *ca.* 1 640 cm^{-1} in the spectra of both the K^+ and Rb^+ salts resemble in their shapes and positions those from the ν(O–H) and δ(H–O–H) modes of unco-ordinated water.[11]

Conclusions

It is evident that fluoroperoxouranates, $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2] \cdot H_2O$ (A = K or Rb), can be synthesised under the appropriate conditions. The pH of 6.5—7 is very crucial for the formation of the $[UO_2(O_2)F_2]^{2-}$ ion. The peroxide is bonded to the UO_2^{2+} in a triangular bidentate manner. The complex $[UO_2(O_2)F_2]^{2-}$ may have a polymeric structure through –U–F–U– chains.

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Notes

First Synthesis and Structural Assessment of Alkali-metal Carbonatodioxoperoxouranate(VI) Monohydrates, $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$, and Carbonatooxodiperoxovanadate(V) Trihydrates, $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$

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The complexes $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ (A = Na or K) have been synthesised from the reaction of the product obtained by treating $UO_2(NO_3)_2\cdot 6H_2O$ with AOH and $AHCO_3$ (ratio $U:CO_3^{2-} = 1:4$) with an excess of 30% H_2O_2 at pH 7—8, and $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ (A = Na or K) have been synthesised by treating V_2O_5 with A_2CO_3 (ratio $V:CO_3^{2-} = 1:1.5$) and an excess of 30% H_2O_2 at pH *ca.* 7. They were precipitated with ethanol. The occurrence of *trans* O=U=O and terminal V=O in the $[UO_2(O_2)(CO_3)]^{2-}$ and $[VO(O_2)_2(CO_3)]^{3-}$ ions, respectively, and the presence of triangular bidentate O_2^{2-} and chelated bidentate CO_3^{2-} groups, have been ascertained from i.r. and laser Raman spectra. The complexes $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ can be dehydrated at *ca.* 100 °C, a temperature at which $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ starts to decompose.

The complexity involved in the field of peroxouranates is an acknowledged problem.[1,2] Few examples of peroxouranates have been reported, $[NH_4]_2[UO_2(O_2)(CO_3)]\cdot 2H_2O$[3] being the only one for which the synthesis is available. In contrast, relatively more is known about complex peroxovanadates,[4,5] and some peroxovanadates containing co-ordinated N-heterocyclic ligands have been very well characterised.[5] However, $[VO(O_2)_2C_2O_4]^{3-}$ is to our knowledge the only peroxovanadate having an oxygen-containing ligand.[5,6] Attempts to co-ordinate SO_4^{2-} with V^V in the presence of O_2^{2-} were unsuccessful,[7] however, the simultaneous co-ordination of CO_3^{2-} and O_2^{2-} to V^V appeared to be possible under appropriate conditions.

Experimental

The chemicals used were all reagent-grade products. Magnetic susceptibilities and the pH of the reaction solutions were measured as described earlier.[4,8] Molar conductances were measured using a Philips PR 9500 conductivity bridge. I.r. spectra were recorded on a Perkin-Elmer model 983 instrument. The laser Raman spectra were recorded at ambient temperatures on a SPEX Ramalog 1403 spectrometer using the line at 4 880 Å from a Spectra Physics model 165 argon laser as the excitation source. The sample was held either in a quartz capillary or in the form of a pressed pellet.

Synthesis of Alkali-metal Carbonatodioxoperoxouranate(VI) *Monohydrates*, $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ (A = Na *or* K).—Powdered $UO_2(NO_3)_2\cdot 6H_2O$ (1 g, 1.99 mmol) was dissolved in hot water (20 cm^3) and a 20% solution of AOH (A = Na or K) was added slowly with stirring until a yellow product ceased to appear. The solution was filtered while hot and the yellow product washed free from alkali. To a stirred water suspension of the product, $AHCO_3$ (8 mmol; ratio $U:CO_3^{2-} = 1:4$) was added and stirring continued for *ca.* 20 min. An excess of 30% H_2O_2 (30 cm^3, 264.7 mmol) was added until a clear yellow solution was obtained. The pH of the solution was found to be 7—8. The solution was filtered and then cooled in an ice-bath for *ca.* 30 min. Addition of pre-cooled ethanol (*ca.* 50 cm^3) led to the precipitation of a yellow microcrystalline solid which was filtered off, washed 3—4 times with ethanol, and then dried *in vacuo* over concentrated H_2SO_4. The yields of $Na_2[UO_2(O_2)(CO_3)]\cdot H_2O$ and $K_2[UO_2(O_2)(CO_3)]\cdot H_2O$ were 0.7 (82) and 0.8 g (88%) respectively.

Synthesis of Alkali-metal Carbonato-oxodiperoxovanadate(V) *Trihydrates*, $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ (A = Na *or* K).—In a typical synthesis a mixture of V_2O_5 (1 g, 5.5 mmol) and A_2CO_3 (16.5 mmol; ratio $V:CO_3^{2-} = 1:1.5$) was dissolved in 30% H_2O_2 (15 cm^3, 132.4 mmol) giving a clear yellow solution. The solution was filtered and the filtrate cooled in an ice-bath for *ca.* 15 min. An excess of pre-cooled ethanol was added with stirring until the yellow microcrystalline $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ (A = Na or K) was completely precipitated. The stirring and cooling were continued for another 30 min. The compounds were isolated, purified, and dried similarly to the peroxouranates. The yields of $Na_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ and $K_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ were 3 (87) and 3.2 g (80%) respectively.

Elemental Analysis.—The determinations of uranium,[8] and of vanadium, peroxide, carbon, sodium, and potassium,[4] were as described earlier. The elemental analyses, molar conductances, and structurally significant i.r. and Raman bands are summarised in the Table.

Results and Discussion

The importance of the pH for the successful synthesis of peroxometal compounds has been emphasised,[4,9,10] and it was shown very recently that a relatively high pH favoured co-ordination of O_2^{2-} with UO_2^{2+} (ref. 8) and VO^{3+}.[4,10] In the present case, pH > 6 was considered conducive in order to prevent the reaction $CO_3^{2-} + 2H^+ \longrightarrow CO_2 + H_2O$. Thus pH *ca.* 7 was found to be suitable for the syntheses. It is imperative that the products isolated at pH 4 or 5 either did not show the presence of CO_3^{2-} at all or did to a very small extent, indicating that co-ordination of the CO_3^{2-} ligand might have just commenced. However, the reaction of UO_2^{2+} with hydrogen peroxide and $AHCO_3$ (A = Na or K) at pH 7—8, and that of V_2O_5 with H_2O_2 and A_2CO_3 at pH 7, followed by the addition of alcohol which facilitated precipitation, afforded $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ respectively in very high yields. Attempts to synthesise the ammonium salts of the complex ions were not successful. Corresponding salts of Rb^+ and

Table. Analytical data, molar conductances, structurally significant i.r. and laser Raman bands of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ (A = Na or K)

Compound	Molar conductance[a]/ Ω^{-1} cm^2 mol^{-1}	Analysis[b]/(%) A	U or V	O[c]	C	I.r. (cm^{-1})	Laser Raman (cm^{-1})	Assignment
$Na_2[UO_2(O_2)(CO_3)]\cdot H_2O$	255(20)	10.45 (10.8)	56.2 (55.85)	7.8 (7.5)	2.85 (2.8)	1 580s	1 570	ν(C–O) ν_1, A_1
						1 325m		ν(C–O) + δ(O–C–O) ν_5, B_2
						920s	930	ν(O=U=O)
						890s	880	ν(O–O) ν_1
						615m	600	ν(U–O_2) ν_3
						550s	550	ν(U–O_2) ν_2
$K_2[UO_2(O_2)(CO_3)]\cdot H_2O$	245(20)	17.3 (17.1)	52.25 (51.95)	7.2 (7.0)	2.6 (2.6)	1 570s	1 570	ν(C–O) ν_1, A_1
						1 330m		ν(C–O) + δ(O–C–O) ν_5, B_2
						925s	930	ν(O=U=O)
						885s	885	ν(O–O) ν_1
						610m	600	ν(U–O_2) ν_3
						550s	540	ν(U–O_2) ν_2
$Na_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$	370(7)	23.2 (21.95)	16.7 (16.2)	20.65 (20.4)	3.85 (3.8)	1 580s	1 580	ν(C–O) ν_1, A_1
						1 340s		ν(C–O) + δ(O–C–O) ν_5, B_2
						940s	940	ν(V=O)
						865s	870	ν(O–O) ν_1
						620s	600	ν(V–O_2) ν_3
						525s	530	ν(V–O_2) ν_2
$K_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$	375(7)	32.6 (32.4)	14.55 (14.05)	18.2 (17.65)	3.35 (3.3)	1 585s	1 580	ν(C–O) ν_1, A_1
						1 335s		ν(C–O) + δ(O–C–O) ν_5, B_2
						945s	940	ν(V=O)
						865s	865	ν(O–O) ν_1
						625s	600	ν(V–O_2) ν_3
						520s	530	ν(V–O_2) ν_2

[a] Temperature (°C) in parentheses. [b] Calculated values are in parentheses. [c] Peroxo-oxygen.

Cs^+ could be obtained by the method analogous to that used for Na^+ and K^+. Strong desiccation of the compounds over concentrated H_2SO_4 did not remove the water of crystallisation. Pyrolysis of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ at 100 °C expelled the water molecule without changing the composition of the complex ion, while at the same temperature the $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ started to decompose through the loss of both O_2^{2-} and H_2O.

The molar conductances of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$, lying in the range 240—255 Ω^{-1} cm^2 mol^{-1} at room temperature, are as expected and attest to the stability of the complexes. The room-temperature molar conductances of $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ were higher than the expected values, indicating rapid decomposition. The values obtained at *ca.* 7 °C, *ca.* 370 Ω^{-1} cm^2 mol^{-1} were, however, as expected, suggesting that the complex peroxovanadates are stable in solution only at low temperatures.

The complexes $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ and $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ tend to absorb moisture slowly. The compounds are diamagnetic, in conformity with the occurrence of U^{VI} and V^V respectively. The results of the peroxide estimations, by redox titrations[4,8,10] involving separate standard potassium permanganate and cerium(IV) solutions, suggest the presence of one peroxide per U^{VI} and two peroxides per V^V in the corresponding complexes.

The i.r. spectra of $A_2[UO_2(O_2)(CO_3)]\cdot H_2O$ show bands at *ca.* 920s, *ca.* 890s, and *ca.* 610m and *ca.* 550s cm^{-1} due to ν(O=U=O, *trans*),[8,11] ν(O–O), and ν(U–O_2) modes[8,10,12] respectively, at *ca.* 1 580s, *ca.* 1 330m, *ca.* 1 050s, *ca.* 750m, *ca.* 675m, and *ca.* 415 cm^{-1} due to ν(C–O), ν(C–O) + δ(O–C–O), ν(C–O), ring deformation + ν(U–O), δ(O–C–O) + ν(U–O), and ν(U–O) respectively originating from the co-ordinated bidentate carbonate,[13] and at *ca.* 3 455m and *ca.* 1 630s cm^{-1} due to ν(O–H) and δ(H–O–H) modes of unco-ordinated water. The laser Raman spectra, recorded in the solid state because of low solubility, exhibited peaks at *ca.* 930 cm^{-1} assigned to ν(O=U=O),[8,11] at 880, *ca.* 600, and *ca.* 550 cm^{-1} due to ν(O–O, ν_1), ν(U–O_2, ν_3), and ν(U–O_2, ν_2) respectively,[12] and at *ca.* 1 570 cm^{-1} due to ν(C–O) (ν_1, A_1) of co-ordinated CO_3^{2-}. The distinction between the ν_2 and ν_3 modes of ν(U–O_2) was made on the basis of the sharpness and intensity of the peaks, that at *ca.* 550 cm^{-1} being the sharpest and most intense. The i.r. spectra of $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ show ν(V=O, terminal) at *ca.* 940s cm^{-1}, ν(O–O, ν_1) at 865s cm^{-1}, and the two ν(V–O_2, ν_2, and ν_3) modes at *ca.* 525s and *ca.* 620s cm^{-1} due to co-ordinated O_2^{2-} groups. The bands at *ca.* 1 585s, *ca.* 1 340s, *ca.* 1 050s, *ca.* 740m, *ca.* 695w, and *ca.* 395m cm^{-1} have been attributed to ν(C–O), ν(C–O) + δ(O–C–O), ν(C–O), ring deformation + ν(V–O), δ(O–C–O) + ν(V–O), and ν(V–O) modes[13] respectively, while those at *ca.* 1 640s and *ca.* 3 450m cm^{-1} have been assigned to δ(H–O–H) and ν(O–H) modes of unco-ordinated water.[14] The laser Raman spectra of $A_3[VO(O_2)_2(CO_3)]\cdot 3H_2O$ exhibit a strong peak at 940 cm^{-1} assigned to ν(V=O), peaks at *ca.* 870, *ca.* 600, and *ca.* 530 cm^{-1} attributed to the ν(O–O, ν_1), ν(V–O_2, ν_3), and ν(V–O_2, ν_2) modes[12] respectively of the co-ordinated O_2^{2-}, and a peak at *ca.* 1 580 cm^{-1} assigned to the ν(C–O, ν_1, A_1) mode of co-ordinated CO_3^{2-}. The facile loss of water at 100 °C and the resemblance of the peak shapes and positions of δ(H–O–H) and ν(O–H) with those of unco-ordinated water[14,15] suggest that the water molecules are not co-ordinated. The typical pattern of absorptions due to the co-ordinated O_2^{2-},[4,8,12] and those due to co-ordinated CO_3^{2-},[13] especially the appreciable separation between $\nu_1(A_1)$ and $\nu_5(B_2)$ modes (Table) and also the appearance of a Raman peak at *ca.* 1 575 cm^{-1} due to ν(C–O) (ν_1, A_1), render it certain that both the peroxide (O_2^{2-}) as well as the carbonate (CO_3^{2-}) ligands

are bonded to the metal centres in a bidentate chelated (C_{2v}) manner.

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Contribution from the Department of Chemistry, North-Eastern Hill University, Shillong 793003, India

Complex Peroxyuranates. Synthesis and Structural Assessment of Alkali-Metal and Ammonium Dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), and Alkali-Metal and Ammonium Dioxoperoxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$

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Yellow microcrystalline alkali-metal and ammonium dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), and alkali-metal and ammonium dioxoperoxy(oxalato)uranate(VI) hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K), have been synthesized from the reaction of the product obtained by treating an aqueous solution of $UO_2(NO_3)_2\cdot 6H_2O$ with alkali-metal or ammonium hydroxide, AOH, with 30% H_2O_2 and aqueous sulfuric acid and oxalic acid solution, respectively, in the mole ratio $UO_2(NO_3)_2\cdot 6H_2O$ H_2O_2 SO_4^{2-} or $C_2O_4^{2-}$ of 1 111 5 or 1, at pH 6 maintained by the addition of the corresponding alkali-metal or ammonium hydroxide Precipitation was completed by the addition of ethanol IR and laser Raman spectra suggest that the O_2^{2-} and SO_4^{2-} ions in $[UO_2(O_2)SO_4(H_2O)]^{2-}$ are bonded to the UO_2^{2+} center in a bridging and in a monodentate manner, respectively, while both the O_2^{2-} and $C_2O_4^{2-}$ ions in $[UO_2(O_2)C_2O_4]^{2-}$ bind the uranyl center in a bidentate chelated fashion The complex peroxyuranates are diamagnetic and insoluble The $A_2[UO_2(O_2)SO_4(H_2O)]$ compounds unlike $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ are stable up to 110 °C Whereas H_2O in $A_2[UO_2(O_2)SO_4(H_2O)]$ is coordinated to the UO_2^{2+} center it occurs as a water of crystallization in the corresponding peroxy oxalato compounds

Introduction

Although uranium is the most important and useful of the actinide metals and is known to form simple peroxides,[1,2] its heteroligand peroxy chemistry seems to have been practically overlooked in earlier investigations [1,2] This is probably because of the highly complicated nature of peroxyuranate chemistry[1] owing to the formation of a number of different species with a small variation of pH of the reaction solution Peroxyuranates containing O_2^{2-} U ratios of 1 1, 1 2 2 1 3 1, 3 2, and 5 2 were described in the literature,[1,2] of which $UO_2(O_2)\cdot nH_2O$ (n = 2 4) appears to be the best characterized one Recent experience in the field of peroxy–metal chemistry[3-6] advocates an enhanced stability of such compounds brought about by the coordination of heteroligands Reports on heteroligand peroxyuranate compounds are rather scanty, except for the ones on (carbonato)- and (oxalato)peroxyuranates [1]

The present work was undertaken to synthesize hitherto unknown peroxy(sulfato)uranates(VI) and improvise a direct route to peroxy(oxalato)uranates(VI), to make an assessment of their structures and to rationalize the IR and laser Raman spectra in terms of the modes of binding of O_2^{2-} and SO_4^{2-} or $C_2O_4^{2-}$ with the UO_2^{2+} center, and to make an internal comparison of the results to correlate with that of the previously reported $(NH_4)_2UO_4C_2O_4\cdot 3H_2O$ [7]

Experimental Section

The chemicals used were all reagent grade products IR and laser Raman (LR) spectra were recorded on the instruments and by the methods described in our earlier papers [3,6,8] LR spectra were recorded on solids owing to the insolubility of the compounds Magnetic susceptibility measurements were made by the Gouy method, $Hg[Co(NCS)_4]$ was the calibrant The pH of the reaction solutions was measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper

Synthesis of Alkali-Metal and Ammonium Dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na). A 1 0-g (1 99-mmol) sample of $UO_2(NO_3)_2\cdot 6H_2O$ was dissolved in water (10–15 cm^3) followed by addition of 25% ammonium hydroxide solution or a concentrated solution of sodium hydroxide in the case of the Na^+ salt with stirring until the yellow precipitate ceased to appear The yellow precipitate was filtered off and washed free of alkali-metal ion or ammonium ion and nitrate To an aqueous suspension of the product was added 4 cm^3 (10 mmol) of 2 5 M H_2SO_4 solution to obtain a clear solution, which was stirred for ca 5 min A 25-cm^3 (220 5-mmol) sample of 30% H_2O_2 was added, while the U SO_4^{2-} H_2O_2 ratio was maintained at 1 5 111, and the solution was stirred for ca 15 min followed by careful addition of the corresponding alkali-metal or ammonium hydroxide solution, AOH (A = NH_4, Na), until the pH was raised to 6, whereupon a yellow product just began to appear An equal volume of ethanol was added with occassional stirring to obtain yellow microcrystalline alkali-metal or ammonium dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), in high yields Each compound was allowed to settle for ca 20 min, separated by centrifugation, purified by washing with ethanol (3–5 times), and finally dried in vacuo over concentrated H_2SO_4

Synthesis of Alkali-Metal and Ammonium Dioxoperoxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K). The $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ compounds were prepared in a manner analogous to that described above for the synthesis of the peroxy(sulfato)uranate compounds The two points of differences are that (i) a concentrated solution of oxalic acid ($H_2C_2O_4\cdot 2H_2O$) was used in lieu of the 2 5 M H_2SO_4 solution and (ii) a U $C_2O_4^{2-}$ H_2O_2 ratio of 1 1 111 was maintained for the synthesis

The amounts of reagents used for the syntheses and the yields of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A

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Table I. Amounts of Reagents Used for the Syntheses of and the Yields Obtained for $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K)

compd	yield, g (%)	amt of $UO_2(NO_3)_2\cdot 6H_2O$, g (mmol)	amt of 30% H_2O_2, cm^3 (mmol)	amt of 2.5 M H_2SO_4, cm^3 (mmol)	amt of $H_2C_2O_4\cdot 2H_2O$ g (mmol)
$(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$	0.8 (90)	1 (1.99)	25 (220.5)	4 (10)	
$Na_2[UO_2(O_2)SO_4(H_2O)]$	0.75 (82)	1 (1.99)	25 (220.5)	4 (10)	
$(NH_4)_2[UO_2(O_2)C_2O_4]\cdot H_2O$	0.8 (91)	1 (1.99)	25 (220.5)		0.25 (1.98)
$Na_2[UO_2(O_2)C_2O_4]\cdot H_2O$	0.8 (89)	1 (1.99)	25 (220.5)		0.25 (1.98)
$K_2[UO_2(O_2)C_2O_4]\cdot H_2O$	0.85 (87)	1 (1.99)	25 (220.5)		0.25 (1.98)

= NH_4, Na, K) compounds are summarized in Table I.

Elemental Analyses. Uranium was estimated gravimetrically as U_3O_8.[9a] The peroxide content was determined by redox titration with standard solutions of $KMnO_4$[9b] or Ce^{4+}.[9c] While sulfate was estimated gravimetrically as $BaSO_4$,[9d] oxalate was estimated volumetrically.[9e] Nitrogen, sodium and potassium were estimated by the methods described in previous papers.[3]

Results and Discussion

The reaction of hydrogen peroxide with UO_2^{2+} leading to a complex peroxyuranate(VI) of a definite composition is highly dependent on the pH of the reaction medium. Thus, evaluation of an appropriate pH for successful synthesis of a peroxyuranate species is emphasized to be an important prerequisite. The suitable pH for bringing about coordination of both peroxide and sulfate or oxalate with the uranyl center was ascertained to be 6. The compounds isolated at a relatively lower pH (e.g., ca. 4) on being analyzed did not show the occurrence of peroxide to the desired level (i.e., U:O_2^{2-} as 1:1), indicating therefore that the O_2^{2-} uptake process was in progress but did not reach the U:O_2^{2-} ratio of 1:1. The peroxy(sulfato)uranates(VI) and peroxy(oxalato)uranates(VI) of the types $A_2[UO_2(O_2)SO_4(H_2O)]$ and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = alkali metal or ammonium) have been synthesized by carrying out reactions among UO_2^{2+}, H_2O_2, and SO_4^{2-} and $C_2O_4^{2-}$, respectively, at pH 6 of the reaction solution maintained by addition of the corresponding alkali-metal or ammonium hydroxide, AOH. While ammonium hydroxide was used as a 25% solution (sp gr 0.88), sodium and potassium hydroxides were added as 10% solutions. The peroxide uptake process was monitored through chemical determination of active oxygen (O_2^{2-}) in the products isolated from the reaction solution at different pH. The method of synthesis of the complex peroxyuranates described in the present work is straightforward, does not involve any extra preparation step unlike in the method previously reported for the synthesis of peroxy(oxalato)uranates(VI)[7] (which required ammonium uranyl oxalate), and may serve as a paradigm for an access to other heteroligand peroxyuranates(VI). It is imperative to mention that, according to the present method, the complex peroxyuranates(VI) start appearing as soon as the solution attains pH 6, however, the addition of ethanol is required to achieve quick and nearly quantitative precipitation of the products. It must also be mentioned that similar compounds were obtained in low yields by allowing the reaction solutions, after adjusting their pH to 6, to stand for several hours at an ice–water temperature.

Characterization and Assessment of Structure. The $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K) compounds are all yellow microcrystalline products, practically insoluble in water. Their insolubility precludes molar conductance measurements. They do not seem to be hygroscopic, and while the $A_2[UO_2(O_2)SO_4(H_2O)]$ compounds are stable for a prolonged period, the oxalato compounds, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$, start losing active oxygen with time (in days). Pyrolysis studies showed that $A_2[UO_2(O_2)SO_4(H_2O)]$ does not suffer any loss of water up to ca. 110 °C, whereas $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ begins to expel water around the same temperature, leading us to state that the H_2O molecule is rather loosely held in the latter compound. Both types of complex peroxyuranates(VI) readily decompose in dilute sulfuric acid, liberating hydrogen peroxide quantitatively, and thus facilitate determination of active oxygen content of the compounds. Chemical determination of active oxygen, considered to be very crucial to ascertain the number of O_2^{2-} groups coordinated to the UO_2^{2+} center, was accomplished by redox titrations involving a standard Ce^{4+} solution, and also separately with a standard $KMnO_4$ solution. The estimation was conducted in the presence of boric acid in order to prevent any loss of active oxygen. The results suggested the occurrence of one O_2^{2-} group per UO_2^{2+} center in each of the newly synthesized compounds. The compounds are all diamagnetic, in conformity with the presence of hexavalent uranium.

Albeit complex peroxy(oxalato)uranates(VI) have been reported,[7] we became interested in them not only to explore the feasibility of their being obtained by a method analogous to that improvised for the hitherto unknown peroxy(sulfato)uranates(VI) but also to spectroscopically evaluate the mode of bonding of O_2^{2-} with UO_2^{2+} in the compounds. The infrared and laser Raman spectra of all the compounds were recorded in the range 4000–200 and 2000–150 cm^{-1}, respectively. The significant features of the IR spectra of the $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) compounds involve absorptions of coordinated sulfate, coordinated water, and the U=O stretch. The appearance of medium-intensity ν_1 and ν_2 modes of S–O stretchings at ca. 980 and ca. 450 cm^{-1}, respectively, and the splitting of ν_3 and ν_4 into two bands each (Table II), as opposed to the absence of ν_1 and ν_2 and the presence of unsplit ν_3 and ν_4 modes in the ionic sulfate, provide strong evidences for the lowering of the symmetry of SO_4^{2-} from T_d to C_{3v} and also for its occurrence as a coordinated unidentate ligand in the complex peroxy(sulfato)uranates(VI). A very strong absorption, in addition to the sulfate ligand bands, was observed at ca. 895 cm^{-1} and assigned to the $\nu_{U=O}$ stretching (trans-linked O=U=O group).[1] The LR spectra of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) complement the IR spectra by exhibiting SO peaks at ca. 970 and ca. 440 cm^{-1} owing to ν_1 and ν_2 and at ca. 1040, ca. 1140, ca. 600, and ca. 650 cm^{-1} due to the ν_3 and ν_4 modes of a coordinated SO_4^{2-} (C_{3v}) ligand. A very strong peak observed at ca. 900 cm^{-1}, because of large polarizability changes involved in the U–O bond, is attributed to the $\nu_{U=O}$ (trans-linked O=U=O) mode. The presence of coordinated water causes the distinct appearance of ν_{O-H} and δ_{H-O-H} modes which occur in the IR spectra as medium-intensity bands at 3460 and 1630 cm^{-1}. The lowering of ν_{O-H} frequencies and broadening of δ_{H-O-H} bands relative to those of free water suggest a clear possibility of intramolecular hydrogen bonding[1,10-13] involving uranyl oxygens. This might be a reason for lowering of $\nu_{U=O}$ as well. Especially noteworthy, over and above the patterns just discussed, is the absence of any band in the IR or LR spectra of the peroxy(sulfato)uranates(VI) in the range 890–800 cm^{-1}, a position where ν_{O-O} would appear if peroxide ligand were coordinated in the triangular bidentate (C_{2v}) manner commonly encountered in peroxy compounds of V(V)[3c,14] and Ti(IV),[6,14,15] for example. This causes us to infer that the O_2^{2-} ligand is present as a bridging group.

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Table II Analytical Data and Structurally Significant IR and Raman Bands of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K)

compd	% found (% calcd) A or N	U	O_2[a]	SO_4 or C_2O_4	IR cm^{-1}	Raman cm^{-1}	assignt
$(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$	6.32 (6.2)	52.38 (52.64)	7.3 (7.08)	21.62[b] (21.24)[b]	890 (s)	900	$\nu_{U=O}$
					790 (w, br)	780	ν_{O-O}
					980 (m)	970	(ν_1)
					440 (m)	440	(ν_2)
					1130 (s)	1140	(ν_3) ν_{S-O}
					1040 (s)	1040	
					640 (s)	650	(ν_4)
					605 (s)	600	
					3160 (m)		ν_{O-H}
					1630 (m)		δ_{H-O-H}
$Na_2[UO_2(O_2)SO_4(H_2O)]$	9.55 (9.95)	51.82 (51.51)	7.2 (6.93)	20.93[b] (20.79)[b]	895 (s)	950	$\nu_{U=O}$
					780 (w, br)	780	ν_{O-O}
					975 (m)	970	(ν_1)
					445 (m)	450	(ν_2)
					1140 (s)	1140	(ν_3) ν_{S-O}
					1040 (s)	1040	
					645 (s)	640	(ν_4)
					600 (s)	600	
					3160 (m)		ν_{O-H}
					1630 (m)		δ_{H-O-H}
$(NH_4)_2[UO_2(O_2)C_2O_4]\ H_2O$	6.34 (6.31)	53.82 (53.59)	7.5 (7.2)	20.11[c] (19.82)[c]	880 (s)	890	$\nu_{U=O}$
					860 (s)	850	ν_{O-O}
					610 (s)	600	ν_{U-O_2}
					3455 (m)		ν_{O-H}
					1640 (s)		δ_{H-O-H}
$Na_2[UO_2(O_2)C_2O_4]\ H_2O$	10.42 (10.13)	52.73 (52.42)	7.3 (7.05)	19.63[c] (19.39)[c]	890 (s)	890	$\nu_{U=O}$
					860 (s)	860	ν_{O-O}
					600 (s)	600	ν_{U-O_2}
					3460 (m)		ν_{O-H}
					1640 (s)		δ_{H-O-H}
$K_2[UO_2(O_2)C_2O_4]\cdot H_2O$	16.33 (16.08)	48.66 (48.95)	6.8 (6.58)	18.4[c] (18.1)[c]	890 (s)	880	$\nu_{U=O}$
					850 (s)	860	ν_{O-O}
					600 (s)	600	ν_{U-O_2}
					3455 (m)		ν_{O-H}
					1640 (m)		δ_{H-O-H}

[a] Peroxy oxygen [b] SO_4 [c] C_2O_4

connecting the contiguous UO_2^{2+} centers through an infinite -U-O-O-U-O-O-U- chain in the crystal lattice. Fortunately the appearance of a broad, rather weak band at 790–750 cm^{-1} in the IR and LR spectra of the compounds lends support to our arguments in favor of a bridging peroxide[16] group.

The IR and LR spectra of the complex peroxy(oxalato)uranates(VI), $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K), were studied particularly to ascertain the mode of bonding of the O_2^{2-} ligand to the UO_2^{2+} center in the complex. It is pertinent to mention here that the earlier reports on peroxy(oxalato)uranates(VI)[7] suggested the presence of a bridging peroxide. The IR and LR spectra of the newly synthesized peroxy(oxalato)-uranates(VI) showed distinctly strong and sharp bands at ca. 890, ca. 860, and ca. 600 cm^{-1}, in each of the compounds, which have been assigned to the $\nu_{U=O}$ (trans-linked O=U=O)[11] and peroxy modes[3,5,14,15] ν_{O-O} and ν_{U-O_2} respectively. The definite presence, shapes, and positions of ν_{O-O} and the complementary ν_{U-O_2} modes in the regions stipulated for the presence of triangularly bonded bidentate peroxide led us to draw an inference that the O_2^{2-} group is bonded to the UO_2^{2+} center, in each of the $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ compounds, in a triangular bidentate (C_{2v}) manner. The IR modes due to the coordinated $C_2O_4^{2-}$ ligand are quite straightforward and unequivocal, showing the presence of a chelated oxalto group,[17,18] and thus further discussion on this is redundant. The ν_{O-H} and δ_{H-O-H} bands in the IR spectra of the compounds resemble in their shapes and positions those generally observed for uncoordinated water.[19,20] This result, as well as the facile loss of water as evident from the pyrolysis studies, suggest that the H_2O molecule in $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ occurs as lattice water and probably is not coordinated to the uranyl center. The solubility property of the compounds suggests a fair possibility of a polymeric structure of the complex species $[UO_2(O_2)(C_2O_4)]^{2-}$ through a -U=O···U=O···U=O··· interaction.

Conclusions

Yellow microcrystalline, diamagnetic complex peroxyuranates(VI) $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) and $A_2[UO_2(O_2)C_2O_4]\ H_2O$ (A = NH_4, Na, K) can be synthesized from the reaction of UO_2^{2+} and H_2O_2 with H_2SO_4 and $H_2C_2O_4\cdot 2H_2O$, respectively, at pH 6 maintained by the addition of the corresponding AOH (A = NH_4, Na, K). The compounds are insoluble.

The peroxy(sulfato)uranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$, are comparatively more stable than the corresponding peroxy(oxalato)uranates(VI), $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$, the former does not lose H_2O upto 110 °C, a temperature at which the latter undergoes dehydration. Both compounds decompose in dilute sulfuric acid, quantitatively liberating H_2O_2.

The peroxide group in $[UO_2(O_2)SO_4(H_2O)]^{2-}$ is bonded to the UO_2^{2+} center in a bridging manner, while the O_2^{2-} in $[UO_2(O_2)C_2O_4]^{2-}$ is bound to UO_2^{2+} in a triangular bidentate fashion. The SO_4^{2-} in the peroxy(sulfato)uranates(VI) occurs as a coordinated unidentate ligand, whereas the $C_2O_4^{2-}$ in the corresponding peroxy(oxalato)uranates(VI) acts as a bidentate chelating ligand.

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The H_2O molecule in the former complex is coordinated, but in the $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ case it is present as lattice water

The complex species $[UO_2(O_2)SO_4(H_2O)]^{2-}$ very likely has a hexacoordinated polymeric structure through a –U–O–O–U–O–O–U– chain containing peroxide bridges The complex $[UO_2(O_2)C_2O_4]^{2-}$ ion may be a hexacoordinated monomer, however, the possibility of a polymeric structure through a weak –U=O···U=O··· interaction cannot be totally ruled out

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Registry No $(NH_4)_2[UO_2(O_2)SO_4(H_2O)]$, 102149-54 2, $Na_2[UO_2(O_2)SO_4(H_2O)]$, 102149-56-4, $(NH_4)_2[UO_2(O_2)C_2O_4]$, 94535 39 4, $Na_2[UO_2(O_2)C_2O_4]$, 102149-57-5, $K_2[UO_2(O_2)C_2O_4]$, 102149 58-6

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Redox and Spectral Properties of the Cis and Trans Isomers of the Osmium(VI) Dioxo Complex $[(bpy)_2Os(O)_2](ClO_4)_2$

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The cis and trans isomers of $[(bpy)_2Os(O)_2](ClO_4)_2$ (bpy = 2,2′-bipyridine) have been prepared and characterized and their redox properties in aqueous solution investigated by using electrochemical techniques Plots of $E_{1/2}$ vs pH for a series of redox couples that appear involving oxidation states II–VI are revealing both in terms of the relative stabilities of the various oxidation states for each isomer and in terms of the relative stabilities of the cis and trans isomers in different oxidation states The cis isomer undergoes bpy ligand loss in aqueous solution on a time scale of minutes by chelate ring opening followed by ligand loss Upon reduction to Os(III) or Os(II) the trans isomer is unstable with respect to isomerization to the cis isomer Comparisons of the redox properties of the isomeric pair give insight into the factors that dictate the relative stabilities of oxidation states and suggest possibilities for the control of the redox potentials, which play a key role in the ability of polypyridyl oxo complexes of ruthenium and osmium to act as redox catalysts

Introduction

In recent work we have shown that access to a series of metal oxo complexes of Ru and Os is possible based on oxidation of the corresponding aqua complexes, e g , reaction 1 (b = bpy 2,2′-bipyridine) [1] In most accessible pH domains, the oxidation process

$$[b_2(py)Ru^{II}\text{–}OH_2]^{2+} \xrightarrow{-e\ -H^+} [b_2(py)Ru^{III}\text{–}OH]^{2+} \xrightarrow{-e\ H^+} [b_2(py)Ru^{IV}{=}O]^{2+} \quad (1)$$

is accompanied by proton loss and stabilization of higher oxidation states by electronic donation from bound hydroxo or oxo groups Synthetically, this approach to the preparation of metal oxo complexes has the advantage of starting with the synthetically accessible lower oxidation states to give higher oxidation states that are frequently good stoichiometric or even catalytic oxidants

In a preliminary communication we noted an extensive redox chemistry of this kind based on $[(bpy)_2M(OH_2)_2]^{2+}$ (M = Ru or Os) which extended from oxidation states II through VI [1c] In this paper we elaborate on the Os chemistry and note the existence of cis and trans isomers of $[(bpy)_2Os^{VI}(O)_2]^{2+}$ The cis isomer appears to be the first example of a d^2 *cis*-dioxo complex

Experimental Section

Materials. Burdick and Jackson spectrograde acetonitrile was distilled under argon over P_2O_5 on a Vigreaux column Ce(IV) perchlorate in perchloric acid solution (0 5 N) was purchased from G F Smith Chemical Co Buffer solutions for electrochemical and spectroscopic measurements were prepared from $HClO_4$ acid solutions with $LiClO_4$ added as additional electrolyte (pH 0–2) and mono-, di-, and tribasic phosphate (pH 3–12) to maintain a minimum ionic strength of 0 1 M The pH measurements were made with a radiometer pHM62 pH meter All other materials were obtained as reagent grade and used without further purification

Elemental Analysis. Microanalyses were conducted by Galbraith Laboratories Knoxville, TN

Preparations. The syntheses of $(bpy)_2OsCO_3$ and $(phen)Os(O)_2(OH)_2$ have been described previously [2,3]

cis $[(bpy)_2Os(O)_2](ClO_4)_2$. To 10 mL of 2 M $HClO_4$ was added 50 mg (0 089 mmol) of bpy_2OsCO_3 The resulting solution was degassed with argon for 15 min and then filtered through a medium glass frit To the stirred filtrate was added 1 mL of 0 5 N cerium(IV) perchlorate in perchloric acid solution The green microcrystalline precipitate was filtered off, washed with 3 × 3 mL portions of ether, and then dried in vacuo Yield 34 mg, 52% Anal Calcd for $OsC_{10}H_{16}O_{10}Cl_2$ C, 32 71, H, 2 18, N, 7 63, Cl, 9 68 Found C, 32 57, H, 2 35, N, 7 39, Cl, 9 58

trans $[(bpy)_2Os(O)_2](ClO_4)_2$ To 20 mL of rigorously dry acetonitrile was added 50 mg (0 068 mmol) of *cis*-$[(bpy)_2Os(O)_2](ClO_4)_2$ The solution was heated at gentle reflux for 20 min with magnetic stirring under an inert argon atmosphere After this time the solution was allowed to cool to room temperature and the resulting precipitate filtered onto a medium glass frit Dry conditions are essential as bipyridine loss from *cis*-$[(bpy)_2Os(O)_2]^{2+}$ and subsequent dimer formation upon heating to yield the dioxo-bridged dimer $[(bpy)(O)_2Os]_2O_2^{4+}$ is competitive with isomerization The beige solid was washed with 1 mL of ether and dried in vacuo Yield 24 mg, 48% Anal Calcd for $OsC_{10}H_{16}O_{10}Cl_2$ C, 32 71, H, 2 18, N, 7 63, Cl, 9 68 Found C, 32 83, H, 2 18, N, 7 65, Cl, 9 46

Measurements. Aqueous solutions of *cis*-$[(bpy)_2Os(OH_2)_2]^{2+}$ were prepared by dissolving the appropriate amount of $(bpy)_2OsCO_3$ in acidic solution The diaqua complex is formed by protonation and loss of carbonate as CO_2

$$(bpy)_2Os(CO_3) + 2H^+ + H_2O \rightarrow [(bpy)_2Os(OH_2)_2]^{2+} + CO_2$$

Spectroscopy. Routine UV–vis spectra were recorded in quartz cells at room temperature on a Bausch and Lomb Model 210 spectrophotometer Proton NMR spectra were recorded on a Bruker 250-MHz Fourier transform spectrometer and referenced to either Me_4Si or DSS accordingly Spectra were recorded within $^1/_2$ h of sample preparation IR measurements were obtained as KBr pellets or Nujol mulls on a Nicolet Model 20 DX FTIR

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MASS SPECTROMETRY OF METAL COMPOUNDS. IV. ELECTRON IONISATION MASS SPECTRA OF BIS(ACETYLACETONATO)DIOXOURANIUM(VI), $UO_2(C_5H_7O_2)_2$, AND A COMPARISON WITH THOSE OF BIS(ACETYLACETONATO) COMPLEXES OF FIRST ROW TRANSITION METALS, $M(C_5H_7O_2)_2$ (M = Mn, Fe, Co, Ni, or Cu)

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ABSTRACT

Electron ionisation mass spectra are reported for the first time for $UO_2(C_5H_7O_2)_2$, **1**, and the results compared with those of $M(C_5H_7O_2)_2$ (M = Mn, Fe, Co, Ni or Cu) recorded under identical experimental conditions. The EI mass spectra of **1** showed a molecular ion signal at *m/z* 468 without indicating any association in the gaseous state. The molecular ion $[UO_2(C_5H_7O_2)_2]^{+\cdot}$ loses either $CH_3^{\cdot}$ and $C_4H_4O_2$, or $OCCH_2$ and $C_3H_5O^{\cdot}$ to produce $[UO_2(C_5H_7O_2)]^+$, which undergoes internal reduction to give $[UO_2(C_5H_7O_2)]^{+\cdot}$. The radical ion $[UO_2(C_5H_7O_2)]^{+\cdot}$ suffers a sequential loss of $CH_3^{\cdot}$ and $C_4H_4O_2$ to produce ultimately the bare species $[UO_2]^+$. A comparative account of the results of mass spectrometric studies of **1** and $M(C_5H_7O_2)_2$ is presented.

INTRODUCTION

There has been a continued interest in the mass spectrometric studies of acetylacetonate complexes of metals [1–6] and such complexes of first row transition metals have received comparatively more attention [1,2,4,5] than those of the heavy metals. As a case in point, the mass spectrum of $UO_2(C_5H_7O_2)_2$, **1**, an important compound of uranium, has not been reported to date, although those of some fluorinated β-diketonate complexes of cerium [7] and uranium [8] have been reported recently.

The present study was undertaken to obtain the electron ionisation mass

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spectrum of $UO_2(C_5H_7O_2)_2$, **1**, and to record the spectra of $M(C_5H_7O_2)_2$ (M = Mn, Fe, Co, Ni or Cu) under mass spectrometrically analogous conditions, to rationalise the spectrum of **1** in terms of its fragmentation behaviour, and to compare this spectrum and fragmentation pattern with those of the analogous bis(acetylacetonato) complexes of the first row transition metals.

EXPERIMENTAL

New methods of synthesis of bis(acetylacetonato)dioxouranium(VI). $UO_2(C_5H_7O_2)_2$, **1**, and $M(C_5H_7O_2)_2 \cdot 2H_2O$ (M = Mn, Fe, Co, Ni or Cu) have been developed. The synthetic procedures are described below.

Synthesis of $UO_2(C_5H_7O_2)_2$

$UO_2(NO_3)_2 \cdot 6H_2O$ (1.0 g, 1.99 mmol) was dissolved in ca. 15 cm^3 of water followed by the addition of 25% aqueous ammonia with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off, washed free from alkali and nitrate, and then mixed with distilled acetylacetone (10 cm^3, 100 mmol). Stirring was continued for ca. 15 min while the yellow precipitate dissolved completely. The solution was filtered to remove any traces of undissolved impurity and the pH of the solution was found to be 5–6. The clear filtrate was concentrated by heating on a steam bath for ca. 1 h and then cooled at ca. 0 °C for ca. 2 h. The orange yellow crystalline $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, **1**, thus obtained was separated by decantation, dried on a filter paper, and finally dried in vacuo over concentrated H_2SO_4. The compound was recrystallised from dichloromethane. The yield of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ was 0.9 g (97% yield). The results of chemical analysis and infrared spectra studies compared very well with those of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$ obtained by the reported method [9].

Synthesis of $M(C_5H_7O_2)_2 \cdot 2H_2O$ (M = Co, Ni or Cu)

20.0 mmol of freshly prepared alkali-free metal hydroxide, $M(OH)_2$ (M = Co, Ni or Cu), was taken as an aqueous suspension (in ca. 15 cm^3 of water). To this was added 80.0 mmol of distilled acetylacetone with stirring. The mixture was warmed on a steam bath for ca. 30 min to obtain a clear coloured solution or, in the case of nickel, a green-blue microcrystalline product. The whole was cooled at ca. 0 °C, and then the product was separated by filtration. The compound thus obtained was first washed 3 or 4 times with a 1 : 1 acetylacetone–water mixture, then twice with ethanol, and finally dried in vacuo over concentrated H_2SO_4. The compounds were recrystallised from methanol or, for the nickel complex, boiling acetone by

the addition of light petroleum (b.p. 40–60 °C), and subsequent cooling at ca. 0 °C. The $M(C_5H_7O_2)_2 \cdot 2H_2O$ (M = Co, Ni or Cu) was obtained in a highly crystalline form. The yields of orange crystalline $Co(C_5H_7O_2)_2 \cdot 2H_2O$, green-blue platelet $Ni(C_5H_7O_2)_2 \cdot 2H_2O$, and deep blue crystalline $Cu(C_5H_7O_2)_2 \cdot 2H_2O$ were 90, 92 and 95%, respectively.

Synthesis of $M(C_5H_7O_2)_2 \cdot 2H_2O$ (M = Mn or Fe)

Bis(acetylacetonato)manganese(II) dihydrate, $Mn(C_5H_7O_2)_2 \cdot 2H_2O$, and bis(acetylacetonato)iron(II) dihydrate, $Fe(C_5H_7O_2)_2 \cdot 2H_2O$, were synthesised by following the general procedure described above for those of the other $M(acac)_2 \cdot 2H_2O$ complexes. The only difference was that the syntheses were carried out in the presence of 2.5–3.0 cm^3 of 38% formaldehyde solution to prevent undesirable oxidation of manganese(II) and iron(II). The yields of $Mn(C_5H_7O_2)_2 \cdot 2H_2O$ and $Fe(C_5H_7O_2)_2 \cdot 2H_2O$ were 75 and 65%, respectively.

The results of chemical analyses, magnetic susceptibility measurements, and spectroscopic studies compare very well with those of $Mn(C_5H_7O_2)_2 \cdot 2H_2O$ [10], $Fe(C_5H_7O_2)_2 \cdot 2H_2O$ [11], $Co(C_5H_7O_2)_2 \cdot 2H_2O$ [12], $Ni(C_5H_7O_2)_2 \cdot 2H_2O$ [13], and $Cu(C_5H_7O_2)_2 \cdot 2H_2O$ [14] reported in the literature.

The mass spectra were recorded on a Varian MAT CH-5 spectrometer [6]. A direct insertion probe was used to introduce the samples directly into the ion source without any prior heating. The samples were held under vacuum (inside the mass spectrometer) for ca. 1 h in the direct inlet probe before electron impact was initiated. The operating conditions were: electron energy, 70 eV (1 eV $\approx 1.6 \times 10^{-19}$ J); source temperature, 100 °C, resolution 10000; accelerating voltage, 8 kV. The mass spectrometric observations were made with the ionising beam held constant to obtain reproducible ion intensities. The essential mass spectrometric features of $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, and $M(C_5H_7O_2)_2 \cdot 2H_2O$, are summarized in Tables 1–6.

RESULTS AND DISCUSSION

The methods currently used in practice for the synthesis of bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, **1**, require sodium hydroxide for adjusting the pH of the medium. Similarly, the recommended methods of synthesis of the bis(acetylacetonato) complexes of the first row transition metals, $M(C_5H_7O_2)_2 \cdot 2H_2O$ (M = Mn, Fe, Co, Ni or Cu) [10–14] require, in each case, a large excess of sodium acetate buffer for the maintenance of a suitable pH. The chances of contamination of the end products owing to the use of such large amounts of alkali or buffer cannot be ruled out.

TABLE 1

Mass spectrometric data for $UO_2(C_5H_7O_2)_2$

Assignment	m/z	Intensity (%)
$[UO_2(C_5H_7O_2)_2]^+$	468	54
$[UO_2(C_5H_7O_2)(C_4H_4O_2)]^+$	453	10
$[UO_2(C_5H_7O_2)(C_3H_5O)]^+$	426	10
$[UO_2(C_5H_7O_2)]^+$	369	100
$[UO_2(C_4H_4O_2)]^+$	354	14
$[UO_2(C_5H_5O)]^+$	351	4
$[UO_2]^+$	270	47

It is because of this, as well as he necessity of high-purity of samples for mass spectrometric studies, that direct methods have been developed for the syntheses of **1** and $M(C_5H_7O_2)_2 \cdot 2H_2O$ (M = Mn, Fe, Co, Ni or Cu). The methods described above do not require any alkali or buffer. The pH of the solution recorded immediately after the formation of the products was found to be ca. 5, a condition conducive to the synthesis of metal acetylacetonates. The yields of the products are very high.

In order to enable a good internal consistency, the spectra were recorded under analogous experimental conditions. The importance of the direct insertion technique has been emphasised [5,6,15] and it is confirmed by the results of a large number of measurements that this technique is particularly suitable for inorganic mass spectrometry.

The electron ionisation mass spectrum of $UO_2(C_5H_7O_2)_2$ (Table 1) exhibited a parent ion signal of medium intensity at m/z 468 due to $[UO_2(C_5H_7O_2)_2]^{+\cdot}$ followed by the signals of equal intensity at m/z 453 and 426 due to the fragment ions $[UO_2(C_5H_7O_2)(C_4H_4O_2)]^+$ and $[UO_2(C_5H_7O_2)(C_3H_5O)]^+$, respectively, originating from the $[UO_2$

TABLE 2

Mass spectral data for $Mn(C_5H_7O_2)_2$

Assignment	m/z	Intensity (%)
$[Mn(C_5H_7O_2)_2]^+$	253	71
$[Mn(C_5H_7O_2)(C_4H_4O_2)]^+$	238	47
$[Mn(C_5H_7O_2)(C_3H_5O)]^+$	211	4
$[Mn(C_5H_7O_2)]^+$	154	100
$[Mn(C_4H_4O_2)]^+$	139	5
$[Mn(C_5H_5O)]^+$	136	4
$[Mn(C_3H_5O)]^+$	112	3
$[Mn(CH_3)]^+$	70	15
$[Mn]^+$	55	18

TABLE 3

Mass spectral data for $Fe(C_5H_7O_2)_2$

Assignment	m/z	Intensity (%)
$[Fe(C_5H_7O_2)_2]^+$	254	70
$[Fe(C_5H_7O_2)(C_4H_4O_2)]^+$	239	45
$[Fe(C_5H_7O_2)(OH)]^+$	172	8
$[Fe(C_5H_7O_2)]^+$	155	100
$[Fe(C_4H_4O_2)]^+$	140	11
$[Fe]^+$	56	19

$(C_5H_7O_2)_2]^{+\cdot}$ ion through the loss of a $CH_3^{\cdot}$ radical and the loss of a ketene molecule ($OCCH_2$). Since no signal appeared beyond m/z 468, it may be safe to infer that the molecule does not undergo association in the gaseous state and that it exists as a monomer. Fragmentation of the parent ion of **1** to $[UO_2(C_5H_7O_2)(C_4H_4O_2)]^+$ and $[UO_2(C_5H_7O_2)(C_3H_5O)]^{+\cdot}$ with an equal probability, as evidenced from their relative intensities (Table 1), is a unique feature of the spectrum. While the $CH_3^{\cdot}$ radical loss from the molecular ion $[UO_2(C_5H_7O_2)_2]^{+\cdot}$ involves simply the cleavage of a C–CH_3 bond to produce the even-electron ion $[UO_2(C_5H_7O_2)(C_4H_4O_2)]^+$, the loss of an even-electron species $OCCH_2$ from $[UO_2(C_5H_7O_2)_2]^{+\cdot}$ must involve a rearrangement in the ligand to give the odd-electron ion $[UO_2(C_5H_7O_2)(C_3H_5O)]^{+\cdot}$. This difference between **1** and the bis(acetylacetonato) complexes of the first row transition metals may, in part, owe its origin to the $5f^o6d^o$ configuration of U in **1** as opposed to a d^n configuration of the metal in the latter. The ions $[UO_2(C_5H_7O_2)(C_4H_4O_2)]^+$ and $[UO_2(C_5H_7O_2)(C_3H_5O)]^{+\cdot}$ lose $C_4H_4O_2$ and $C_3H_5O^{\cdot}$ species, respectively, to form the most dominant ion at m/z 369 assigned as $[UO_2(C_5H_7O_2)]^+$, which again fragments in two different ways by the loss of H_2O and $CH_3^{\cdot}$, respectively, to give $[UO_2(C_5H_5O)]^+$ and $[UO_2(C_4H_4O_2)]^+$ ions, as is evident from the appearance of signals at m/z 351 and 354. The weak nature of the signal at m/z 351 points to a relatively lower ease of H_2O loss from

TABLE 4

Mass spectral data for $Co(C_5H_7O_2)_2$

Assignment	m/z	Intensity (%)
$[Co(C_5H_7O_2)_2]^+$	257	85
$[Co(C_5H_7O_2)(C_4H_4O_2)]^+$	242	80
$[Co(C_5H_7O_2)]^+$	158	100
$[Co(C_4H_4O_2)]^+$	143	15
$[Co]^+$	59	7

TABLE 5

Mass spectral data for $Ni(C_5H_7O_2)_2$

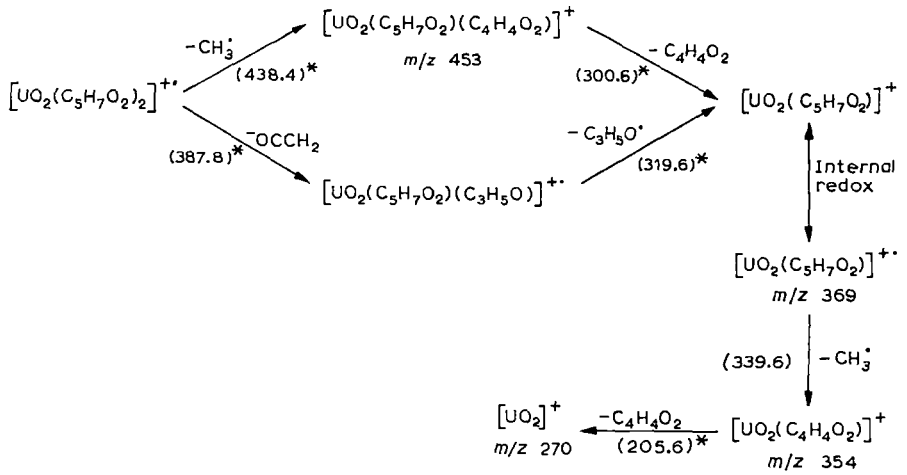
Assignment	m/z	Intensity (%)
$[Ni(C_5H_7O_2)_2]^+$	256	100
$[Ni(C_5H_7O_2)(C_4H_4O_2)]^+$	241	95
$[Ni(C_5H_7O_2)(OCCH_2)]^+$	199	5
$[Ni(C_5H_7O_2)H]^+$	158	40
$[Ni(C_5H_7O_2)]^+$	157	90
$[Ni(C_4H_4O_2)]^+$	142	30
$[Ni(C_4H_3O_2)]^+$	141	25
$[Ni(C_3H_4O)]^+$	114	5
$[Ni(OCCH_2)]^+$	100	55
$[Ni(CO)]^+$ or $[Ni(C_2H_4)]^+$	86	70
$[Ni]^+$	58	18

the $[UO_2(C_5H_7O_2)]^+$ ion over the loss of a $CH_3^{\cdot}$ radical. The loss of a $CH_3^{\cdot}$ radical, at this stage, can be rationalised in the light of the valency change concept and accordingly the even-electron ion $[U(VI)O_2(C_5H_7O_2)]^+$ changes to the odd-electron ion $[U(V)O_2(C_5H_7O_2)]^{+\cdot}$ which then expels a $CH_3^{\cdot}$ radical to produce $[UO_2(C_4H_4O_2)]^+$. This even-electron ion ultimately cracks down to the bare $[UO_2]^+$ ion (m/z 270). The last two steps of fragmentation involving loss of $CH_3^{\cdot}$ and $C_4H_4O_2$ from the $[UO_2(C_5H_7O_2)]^{+\cdot}$ fragment resemble those generally observed for the corresponding $[M(C_5H_7O_2)]^+$ where M = Mn, Fe or Co, as discussed below. Methyl transfer from the ligand to the uranyl (UO_2) centre, unlike that of $MoO_2(C_5H_7O_2)_2$ [6], could not be observed in the case of **1**. The most probable fragmentation pattern of **1**, in conformity with the experimental observations, is shown in Scheme 1.

TABLE 6

Mass spectral data for $Cu(C_5H_7O_2)_2$

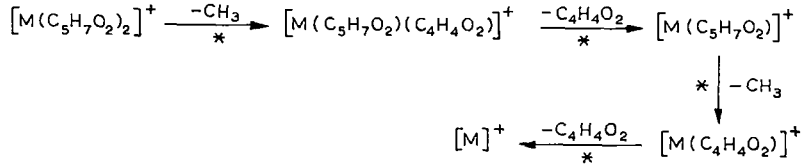
Assignment	m/z	Intensity (%)
$[Cu(C_5H_7O_2)_2]^+$	261	100
$[Cu(C_5H_7O_2)(C_4H_4O_2)]^+$	246	58
$[Cu(C_4H_4O_2)_2]^+$	231	45
$[Cu(C_5H_7O_2)(C_3H_5O)]^+$	219	5
$[Cu(C_5H_7O_2)H]^+$	163	12
$[Cu(C_5H_7O_2)]^+$	162	55
$[Cu(C_4H_4O_2)]^+$	147	80
$[Cu(OCCH_2)]^+$	105	45
$[Cu]^+$	63	37



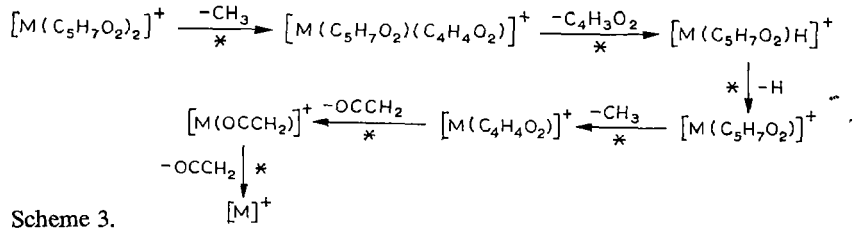
Scheme 1.

The observed metastable transition peaks (indicated by * in Scheme 1) are consistent with the suggested fragmentation pattern of **1**.

Mass spectra of bis(acetylacetonato)metal(II), of the type $M(C_5H_7O_2)_2$ with M being Mn, Fe, Co, Ni or Cu, have been reported by earlier workers [1,4,16]. It is mainly in order to collate the mass spectrometric results of these compounds with that of **1** that we recorded the spectra of all the compounds under mass spectrometrically identical conditions. The spectra of the $M(C_5H_7O_2)_2$ compounds synthesised by the new methods (described above) are generally similar to those previously reported [1,4,16]. The salient points of difference in the fragmentation behaviour of **1** and $M(C_5H_7O_2)_2$ have been highlighted in the preceding discussion. A perusal of the mass spectra of $M(C_5H_7O_2)_2$ revealed some basic differences in their fragmentation patterns as shown in Schemes 2 (M = Mn, Fe, or Co) and 3 (M = Ni or Cu) where * indicates metastable supported transitions.



Scheme 2.



Scheme 3.

Mass spectrometrically, $M(C_5H_7O_2)_2$ compounds may be classified into two groups with M = Mn, Fe or Co forming one, and M = Ni or Cu the other. The molecular ion $[M(C_5H_7O_2)_2]^+$ in each case loses $CH_3^{\cdot}$ to produce $[M(C_5H_7O_2)(C_4H_4O_2)]^+$. However, the subsequent fragmentation of $[M(C_5H_7O_2)(C_4H_4O_2)]^+$ with M being Mn, Fe or Co is distinctly different from that with M being Ni or Cu. Whereas in the former case the fragment ion undergoes a loss of $C_4H_4O_2$ to produce the most dominant ion $[M(C_5H_7O_2)]^+$, in the latter case it fragments involving an extensive H migration to the metal, especially to give $[M(C_5H_7O_2)H]^+$, with the loss of $C_4H_3O_2$. Further, hydrogen atom migration appears to be more facile in the case of $Ni(C_5H_7O_2)_2$ than the corresponding copper complex. Facile H migration in the case of nickel is rationalised in terms of the formation of a strong nickel–hydrogen bond and may be related to the catalytic activity of the metal in hydrogenation reactions. Hydrogen transfer to the metal, rather than to an oxygen atom of the other ligand as proposed by others [17], is considered to be a more likely alternative explanation because if H migration to any other sites were involved, this type of ion (cf. $[M(C_5H_7O_2)H]^+$) should be well observed for acetylacetonato complexes of other metals. The fragment ion $[M(C_5H_7O_2)H]^+$ then loses H to produce $[M(C_5H_7O_2)]^+$ (M = Ni or Cu) which undergoes a stepwise loss of $CH_3^{\cdot}$, $OCCH_2$ and again another $OCCH_2$ ultimately to give the $[M]^+$ ion as shown in Scheme 3.

A comparison of the Schemes 2 and 3 shows that the mode of fragmentation of the $[M(C_5H_7O_2)]^+$ ion is different in the two cases. While for M = Mn, Fe or Co, the $[M(C_5H_7O_2)]^+$ first expels $CH_3^{\cdot}$ and then a $C_4H_4O_2$ moiety to produce the bare $[M]^+$ ion, for M = Ni or Cu three steps are involved as depicted in the Scheme 3. Another point of difference lies in the appearance of the base peaks. Whereas the $[M(C_5H_7O_2)]^+$ ion is the most dominant fragment in the spectra of Mn, Fe and Co complexes, the molecular ion $[M(C_5H_7O_2)_2]^+$ appears to provide the base peak in the spectra of the corresponding complexes of Ni or Cu. Enough metastable ion peaks have been observed in support of Schemes 2 and 3 to lend credence to the suggested modes of fragmentation.

CONCLUSIONS

Bis(acetylacetonato)dioxouranium(VI), $UO_2(C_5H_7O_2)_2$, **1**, exists as a monomer in the gaseous state and does not undergo any association. The electron ionisation mass spectrum of **1** provides evidence for the simultaneous loss of both $CH_3^{\cdot}$ and ketene ($OCCH_2$) from the molecular ion. Fragmentation beyond $[UO_2(C_5H_7O_2)]^{+\cdot}$ resembles that of the bis(acetylacetonato) complexes of Mn, Fe and Co. No methyl or hydrogen migration from ligand to the UO_2 centre could be observed for **1**.

The electron ionisation mass spectra of $M(C_5H_7O_2)_2$ (M = Mn, Fe, Co, Ni or Cu), synthesised by new methods, generally resemble those reported earlier [1,14,16]. An alternative explanation for the hydrogen atom migration from ligand to the nickel centre to form $[Ni(C_5H_7O_2)H]^+$ ion is provided.

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New Methods of Syntheses of Ammonium, Sodium & Potassium Triacetatodioxouranates (VI) & Diacetatodioxouranium (VI) Dihydrate

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The product obtained by treating an aqueous solution of $UO_2(NO_3)_26H_2O$ with ammonia or NaOH or KOH solution reacts with ACH_3COO (A = NH_4, Na or K) and a small amount of 10% acetic acid in 1:3 mol ratio $\{UO_2(NO_3)_2.6H_2O : ACH_3COO\}$ at *p*H to afford the compounds $A[UO_2(CH_3COO)_3]$ (A = NH_4, Na at *p*H 5 to afford the compounds $A[UO_2(CH_3COO)_2.2H_2O$ has been achieved by the reaction of the product obtained by treating a solution of $UO_2(NO_3)_2.6H_2O$ with aqueous ammonia, with an excess of glacial acetic acid in the ratio 1:17.5 $\{UO_2(NO_3)_2.6H_2O:CH_3COOH\}$.

Acetatouranate (VI) chemistry is rather complicated owing to the formation of a variety of compounds between acetic acid and UO_2^{2+} ion[1] depending upon the reaction conditions and the proportions of the reactants used. Recently, while studying some aspects of uranium chemistry[2-4] we felt the need of synthesising compounds of the types $A[UO_2(CH_3COO)_3]$ where A = NH_4, Na or K and $UO_2(CH_3COO)_2.2H_2O$. Both these compounds are known[1,5,6], but while the synthesis of the former requires an excess of alkali acetate and alkali nitrate[5] where the chances of contamination of products by acetate and nitrate cannot be ruled out, the recommended synthesis of the latter requires uranium trioxide, UO_3, that needs extra preparation steps. We report here the direct syntheses of the title compounds which provide an easy access to these important compounds of uranium.

Reagent grade chemicals were used in the present studies. IR spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. Molar conductances were measured using a Philips PR 9500 conductivity bridge.

Uranium[2-4], carbon, hydrogen, nitrogen, sodium and potassium[3,7] were determined by methods described earlier.

Synthesis of alkali triacetatodioxouranate (VI) $A[UO_2(CH_3COO)_3]$*(A = NH_4, Na or K)*

$UO_2(NO_3)_2.6H_2O$ (1.0 g, 1.99 mmol) was dissolved in 15 cm^3 of water followed by the addition of aq. ammonia (sp. gr. 0.9), or a 15% solution of sodium hydroxide or potassium hydroxide, with stirring until a yellow precipitate ceased to appear. The yellow precipitate (Y) was filtered off, washed free from alkali and nitrate, and then mixed with alkali acetate, ACH_3COO (A = NH_4, Na or K) (6 mmol) while maintaining the $U:CH_3COO^-$ ratio at 1:3. The mixture was stirred for 2 min followed by dropwise addition of 10% acetic acid solution under stirring until a clear solution was obtained (*p*H 5). The solution was filtered and then concentrated to nearly half the original volume by warming over a steam-bath. The concentrated solution was cooled to room temperature to afford yellow crystalline alkali triacetatodioxouranates (VI), $A[UO_2(CH_3COO)_3]$ (A = NH_4, Na or K). The compound was separated by filtration, washed twice with ethanol and dried *in vacuo* over conc. H_2SO_4. The yields of $NH_4[UO_2(CH_3COO)_3]$, $Na[UO_2(CH_3COO)_3]$ and $K[UO_2(CH_3COO)_3]$ were 0.67 g (72%), 0.76 g, (81%) and 0.75 g, (77%) respectively.

Synthesis of diacetatodioxouranium (VI) dihydride, $UO_2(CH_3COO)_2.2H_2O$

The yellow precipitate (Y) was obtained in a manner similar to that described above by treating an aqueous solution of 1.0 g (1.99 mmol) of $UO_2(NO_3)_2.6H_2O$ with aqueous ammonia. An aqueous suspension of the purified product (Y) was then treated with 2.0 cm^3 (35 mmol) of glacial acetic acid to obtain a clear solution. The solution thus obtained was worked up in an analogous way as described under the above synthesis. The yellow crystalline diacetatodioxouranium (VI) dihydrate, $UO_2(CH_3COO)_2.2H_2O$ thus obtained was separated by filtration, and dried *in vacuo* over conc. H_2SO_4, yield 0.67 g (80%).

The analytical data of the compounds are summarised in Table 1.

Table 1—Analytical Data of the Uranium Complexes

	Found (Calc.) %			
	A or N	U	C	H
$NH_4[UO_2(CH_3COO)_3]$	3.12 (3.01)	51.47 (51.16)	15.51 (15.49)	2.85 (2.82)
$Na[UO_2(CH_3COO)_3]$	4.94 (4.89)	50.52 (50.63)	15.31 (15.33)	1.89 (1.93)
$K[UO_2(CH_3COO)_3]$	8.53 (8.04)	49.12 (48.95)	14.77 (14.82)	1.89 (1.87)
$UO_2(CH_3COO)_2.2H_2O$	—	56.31 (56.12)	11.31 (11.33)	2.45 (2.38)

The reaction of uranyl nitrate hexahydrate with alkali hydroxide produces sparingly soluble alkali diuranate which may serve as a very good source of the metal providing a rather easy access to the synthesis of various compounds of uranium[2-4]. It has been now shown that similar products can react with stoichiometric amounts of alkali acetates, ACH_3COO ($A=NH_4$, Na or K), and a small amount of dilute acetic acid to yield triacetatodioxouranates (VI) at *p*H 5. The method does not require the use of any excess alkali acetate or alkali nitrate unlike the earlier methods[1,5]. While the reactions of diuranates with stoichiometric amounts of alkali acetates and a small amount of dilute acetic acid give $A[UO_2(CH_3COO)_3]$ compounds, the reaction of ammonium diuranate with glacial acetic acid produces pure diacetatodioxouranium (VI) dihydrate, $UO_2(CH_3COO)_2.2H_2O$, in a very high yield. The method is a direct one and may be used as a paradigm for the synthesis of other molecular complexes. Indeed, it has been shown very recently[8] that the reaction of ammonium diuranate with acetylacetone ($C_5H_8O_2$, acacH), in the absence of any buffer, gives bis(acetylacetonato)dioxouranium (VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$[8], thereby justifying the scope of the method.

The compounds $A[UO_2(CH_3COO)_3]$ ($A=NH_4$, Na or K) and $UO_2(CH_3COO)_2.2H_2O$ are yellow crystalline solids which are stable for long periods. The molar conductance of $UO_2(CH_3COO)_2.2H_2O$ in methanol at ambient temperature was found to be very low indicating the non-electrolytic nature of the compound which was in agreement with the observation made earlier[9]. Anhydrous $UO_2(CH_3COO)_2$ was obtained by heating the dihydrate to 110-120°C.

The characteristic features of the IR spectra of $A[UO_2(CH_3COO)_3]$ and $UO_2(CH_3COO)_2.2H_2O$ are the ν_{as}(OUO), ν_s(OUO), ν_{as}(OCO), ν_s(OCO), and δ(OCO) bands which have been observed at ~930, ~850, ~1540, ~1470, and ~675 cm^{-1}, respectively[5,10,11]. These features are the most significant ones and typical of the compounds described in the present report. IR spectra of the compounds are similar to those reported in the literature[5,10,11] for these types of compounds.

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Direct Synthesis of Potassium Tris(oxalato)manganate(III) and First Synthesis of Alkali-Metal and Ammonium Trifluoro(oxalato)manganates(III)

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The compound $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$, known for quite some time,[1] has served as a very oft-quoted example whenever the subject of inorganic photochemistry is discussed.[2] The method involving the reaction of $KMnO_4$ with oxalic acid and $K_2C_2O_4$ in the presence of an excess of K_2CO_3 is universally accepted for the synthesis of $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$. This method requires very careful manipulation and uses an excess of K_2CO_3 in order to control the pH. The chances of contamination of the end product, owing to the use of K_2CO_3 in such quantities, cannot be ruled out. It is possible to synthesize $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ in a more nearly quantitative way directly from MnO(OH) without making use of any buffer. It will also be shown that $[Mn(C_2O_4)_3]^{3-}$ can exist in solutions in the presence of countercations like Na^+, Rb^+, Cs^+ or NH_4^+. Attempts to stabilize manganese(III)–oxalate systems have now led to the first synthesis of alkali-metal and ammonium trifluoro(oxalato)manganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K or NH_4), providing a very good opportunity to demonstrate the enhanced stability of (oxalato)manganates(III) and to obtain a set of internally consistent data concerning the effect on the magnetic properties of trivalent manganese on going from $K_3[Mn(C_2O_4)_3]$ to $A_2[MnF_5]$ via $A_2[MnF_3(C_2O_4)]$.

Experimental Section

The chemicals used were all reagent grade products. The compound MnO(OH) was prepared by the oxidation of $Mn(OH)_2$ with hydrogen peroxide.[3]

Infrared spectra were recorded on a Perkin-Elmer Model 683 spectrophotometer. Electronic spectra were recorded on a Beckman Model UV-26 spectrophotometer. The Gouy method was used to measure the magnetic susceptibility of the complexes using $Hg[Co(NCS)_4]$ as the standard.

Syntheses. Potassium Tris(oxalato)manganate(III) Trihydrate, $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$. To a water suspension (20 cm^3) of 0.89 g (10.1 mmol) of MnO(OH) was added a concentrated solution of 2.82 g (15.3 mmol) of $K_2C_2O_4$. The mixture was cooled in an ice bath for ca. 15 min, followed by addition of a concentrated solution of 1.93 g (15.3 mmol) of oxalic acid. The solution was stirred for ca. 50 min in an ice bath. The solution, which became cherry red, was filtered quickly, and an excess of precooled (~0 °C) ethanol (about 1/1 v/v) was added with stirring to obtain the cherry red $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$. The microcrystalline compound was isolated by quick filtration, washed twice with precooled ethanol, and finally dried in vacuo in the absence of light. The yield of $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ was 3.1 g (62.5%).

Alkali-Metal and Ammonium Trifluoro(oxalato)manganates(III), $A_2[MnF_3(C_2O_4)]$ (A = Na, K, NH_4). Representative Procedure. Freshly prepared MnO(OH) was dissolved in 40% HF with maintenance of the molar ratio of MnO(OH) to HF at 1/4–5 (2.5 cm^3, 40% HF/1 g of MnOOH), and the solution was warmed at ca. 100 °C for ca. 5 min, followed by filtration. The filtrate was cooled to room temperature, and a concentrated solution of $A_2C_2O_4$ (A = Na, K, NH_4) was slowly added with stirring, with the molar ratio of MnO(OH) to $A_2C_2O_4$ being maintained at 1/1. The solution was stirred for a further period of ca. 10 min at room temperature (ca. 20 °C). Addition of an excess of ethanol, in an amount not exceeding half of the original volume of the solution, precipitated pink alkali-metal or ammonium trifluoro(oxalato)manganage(III), $A_2[MnF_3(C_2O_4)]$. The compound was separated by filtration, washed thrice with ethanol, and finally dried in vacuo. Starting from 1.0 g of MnO(OH) in each case, the yields of $Na_2[MnF_3(C_2O_4)]\cdot 5H_2O$, $K_2[MnF_3(C_2O_4)]\cdot H_2O$, and $(NH_4)_2[MnF_3(C_2O_4)]$ were 3.4 g (89%), 3.2 g (94%), and 2.4 g (90%), respectively. Anal. Calcd for

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$Na_2[MnF_3(C_2O_4)]\cdot 5H_2O$; Na, 13.69; Mn, 16.37; C_2O_4, 26.19; F, 16.96. Found: Na, 13.9; Mn, 16.7; C_2O_4, 26.5; F, 17.2. Estimated oxidation state of Mn: 3.0. μ_{eff}: 4.3 μ_B. IR: 1670 s (ν_{as}(O–C–O)), 1365 w and 1320 m (ν_s(O–C–O)), 778 m and 755 w (δ(O–C–O)), 425 s (ν(Mn–O)), 495 m (ν(Mn–F)), 3455 m (ν(O–H)), 1640 s cm^{-1} (δ(H–O–H)). Anal. Calcd for $K_2[MnF_3(C_2O_4)]\cdot H_2O$: K, 26.35; Mn, 18.58; C_2O_4, 29.73; F, 19.26. Found: K, 26.1; Mn, 18.8; C_2O_4, 29.7; F, 19.4. Estimated oxidation state of Mn; 3.1. μ_{eff}: 4.3 μ_B. IR: 1672 s (ν_{as}(O–C–O)), 1365 w and 1320 m (ν_s(O–C–O)), 778 m and 750 w (δ(O–C–O)), 425 s (ν(Mn–O)), 490 m (ν(Mn–F)), 3460 m (ν(O–H)), 1640 s cm^{-1} (δ(H–O–H)). Electronic spectra: 19 800 ($^5B_{1g} \rightarrow {}^5B_{2g}$), 22 700 cm^{-1} ($^5B_{1g} \rightarrow {}^5E_g$). Anal. Calcd for $(NH_4)_2[MnF_3(C_2O_4)]$: N, 11.86; Mn 23.31; C_2O_4, 37.29; F, 24.15. Found: N, 11.4; Mn, 23.2; C_2O_4, 37.6; F, 24.4. Estimated oxidation state of Mn: 3.1. μ_{eff}: 4.2 μ_B. IR: 1670 s (ν_{as}(O–C–O)), 1360 w and 1315 m (ν_s(O–C–O)), 780 m and 750 s (δ(O–C–O)), 425 s (ν(Mn–O)), 490 m (ν(Mn–F)), 3160 m, 3040 s, and 1400 s cm^{-1} (ν_3, ν_1, and ν_2 modes of NH_4^+). Electronic spectra: 19 500 ($^5B_{1g} \rightarrow {}^5B_{2g}$), 22 500 cm^{-1} ($^5B_{1g} \rightarrow {}^5E_g$).

Elemental Analyses. Manganese was estimated volumetrically by complexometric titration with EDTA[4] using Erio T as the indicator. Oxalate was estimated by redox titration with a standard potassium permanganate solution.[5] Fluoride was precipitated, after destroying oxalate, as lead chloride fluoride, PbClF, and chloride was estimated by Volhard's method, from which the fluoride content was calculated.[6] Sodium, potassium, and nitrogen were determined by the methods described in a previous paper.[7]

Chemical Determination of the Oxidation State of Manganese. The oxidation state of manganese was determined iodometrically by treating a freshly prepared ice-cold potassium iodide solution, acidified with dilute sulfuric acid, with the compound followed by titration of the liberated iodine with a standard sodium thiosulfate solution. The iodine titration was done under an ice-cold condition.

Results and Discussion

In order to overcome the difficulties involved in the synthesis[1] of the classic, oft-quoted, $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$, a direct method has now been improvised. The new method involves two steps. First, the reaction of MnO(OH) with 1/1.5/1.5 stoichiometric amounts of $H_2C_2O_4$ and $K_2C_2O_4$ leading to the synthesis of $K_3[Mn(C_2O_4)_3]$ in solution.

$$MnO(OH) + 1.5H_2C_2O_4 + 1.5K_2C_2O_4 \rightarrow K_3[Mn(C_2O_4)_3] + 2H_2O$$

Second, isolation of $K_3[Mn(C_2O_4)_3]$ in the solid state by the addition of ethanol, which facilitated precipitation. The strategy for the present synthesis was that MnO(OH) would react with oxalic acid to generate Mn^{3+}, which would be trapped immediately by the $C_2O_4^{2-}$ ions, arising out of $H_2C_2O_4$ and $K_2C_2O_4$, affording the complex $[Mn(C_2O_4)_3]^{3-}$ in the presence of K^+. The method is rapid, giving $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ in a higher yield than the earlier method.[1] The room-temperature magnetic moment was found to be 4.92 μ_B in conformity with that reported in the literature.[1] The IR spectrum is unambiguous and shows the characteristics of chelated oxalato groups. The electronic spectrum of a solution of $K_3[Mn(C_2O_4)_3]$ showed the maximum absorption, a characteristic[1] of the $[Mn(C_2O_4)_3]^{3-}$ ion, at 19 050 cm^{-1}, while the reflectance spectrum showed a broad band at 9200, a shoulder at 19 050, and a peak at 20 500 cm^{-1} assigned[8] to the transitions $^5B_{1g} \rightarrow {}^5A_{1g}$, $^5B_{1g} \rightarrow {}^5B_{2g}$, and $^5B_{1g} \rightarrow {}^5E_g$, respectively, lending support to the identity of the compound.

Reactions of MnO(OH) with $A_2C_2O_4$ (A = Na, Rb, Cs, NH_4) and $H_2C_2O_4$ gave a cherry red solution, stable at ca. 0 °C in the dark, showing the electronic spectral absorption at 19 050 cm^{-1}, and allowing us to infer the formation and existence of the $[Mn(C_2O_4)_3]^{3-}$ ion. However, attempts to isolate the corresponding compounds in the solid state resulted in the formation of white decomposition products.

To control photochemical decomposition, it was expected that the stability of the manganese(III)–oxalato system can be enhanced by the presence of F^- ions, since fluoromanganates(III) are stable. It was observed, in line with the contention, that addition of 40% HF to the aforementioned reactions greatly increased the stability of the solutions as evidenced by their unaltered color at ca. 20 °C in light. Accordingly, the reaction of MnO(OH) with 40% HF and $A_2C_2O_4$ (A = Na, K, NH_4) in the ratio of $Mn/F^-/C_2O_4^{2-}$ at 1/4–5/1 at any temperature between 0 and 20 °C gave a pink solution from which the deep pink microcrystalline $A_2[MnF_3(C_2O_4)]$ was isolated by the addition of ethanol that facilitated precipitation. It is believed that MnF_3 is first formed in the solution, which then reacts with $C_2O_4^{2-}$ to generate the complex $[MnF_3(C_2O_4)]^{2-}$ ion, and weak acidity is conducive to the process while the application of heat annihilates the complex ion.

The compounds $A_2[MnF_3(C_2O_4)]$ are comparatively more stable than $K_3[Mn(C_2O_4)_3]\cdot 3H_2O$ and can be stored in sealed polyethylene bags. The chemical determination of oxidation states of manganese in such compounds is emphasized because many Mn^{3+} compounds show abnormal magnetic moments,[9-11] leading to confusion regarding the actual oxidation state of the metal. The chemically estimated oxidation state was found to fall between 3.0 and 3.1, suggesting that manganese occurs in its +3 state. The room-temperature magnetic moments of the compounds, lying between 4.2 and 4.3 μ_B, suggest the possibility of a polymeric structure of $[MnF_3(C_2O_4)]^{2-}$ in the solid state, through –Mn–F–Mn– linkage or involving both F^- and $C_2O_4^{2-}$ as the bridging groups, allowing a weak antiferromagnetic interaction between the contiguous Mn^{3+} ions to be operative. Similar observations were recently made in the case of $A_2[MnF_3(SO_4)]$.[11] It is therefore apparent that antiferromagnetic interaction in manganese(III) complexes sets in with the partial replacement of $C_2O_4^{2-}$ by F^- ligands and becomes fully operative on complete removal of the $C_2O_4^{2-}$ ligands by F^- as evidenced by the lowering of magnetic moments on going from $[Mn(C_2O_4)_3]^{3-}$ through $[MnF_3(C_2O_4)]^{2-}$ (present work) to $[MnF_5]^{2-}$.[9,10]

The electronic spectra of $A_2[MnF_3(C_2O_4)]$ (A = K, NH_4) recorded in solution containing a small amount of 40% HF, required to check hydrolysis, show bands at ca. 19 600 and ca. 22 600 cm^{-1}, assigned to the transitions[8] $^5B_{1g} \rightarrow {}^5B_{2g}$ and $^5B_{1g} \rightarrow {}^5E_g$, respectively. This suggests an appreciable splitting of the ^5E_g ground state of Mn^{3+} in $[MnF_3(C_2O_4)]^{2-}$ as a consequence of Jahn–Teller effects. The infrared spectra of the compounds are similar and show characteristic absorptions for the coordinated $C_2O_4^{2-}$ and F^- groups. The band observed between 490 and 495 cm^{-1} has been assigned to the ν_{Mn-F} mode of coordinated fluoride. The absorptions due to the $C_2O_4^{2-}$ group imply the presence of a bridging oxalato group. Particularly significant is the absence of any band at 1680–1750 cm^{-1}, which is regarded as typical for a chelated oxalato ligand. Thus, the following assignments, which are also in agreement with those of Curtis,[12-14] were made in the present case: ν_{as}(O-C-O) at ~1670 s, ν_s(O–C–O) at ~1360 w and ~1320 m, δ(O-C-O) at ~780 m, and ~750 w cm^{-1}. The two additional bands at ca. 3455 m and ca. 1640 cm^{-1} in each of the sodium and potassium salts resemble in their shapes and positions those of the uncoordinated water in $K_2[MnF_5]\cdot H_2O$[10,15] and have been assigned to ν(O–H) and δ(H–O–H) modes. Further, it was emphasized in the literature[14] that the ν(O–H) band at 3455 cm^{-1} is rather typical of lattice water. These and the absence of any water in the $(NH_4)_2[MnF_3(C_2O_4)]$ compound lead us to infer that the water is not coordinated to the Mn^{3+} center. The three extra bands at 3160 m, 3040 s, and 1400 s cm^{-1} in the case of $(NH_4)_2[MnF_3(C_2O_4)]$ have been assigned to the ν_3, ν_1, and ν_2 modes of NH_4^+. It is presumed, on the basis of the present results, that the structure of and Jahn–Teller effect in the

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complex $[MnF_3(C_2O_4)]^{2-}$ are essentially analogous to those of the $[MnF_3(SO_4)]^{2-}$ complex.[16]

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Registry No. $K_3[Mn(C_2O_4)_3]$, 14874-30-7; $Na_2[MnF_3(C_2O_4)]$, 94138-06-4; $K_2[MnF_3(C_2O_4)]$, 94138-07-5; $(NH_4)_2[MnF_3(C_2O_4)]$, 94138-08-6.

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