SOME CONTRIBUTIONS TO THE CHEMISTRY OF PEROXO COMPOUNDS OF ZIRCONIUM, THORIUM, URANIUM AND CARBON, AND ALKALI - METAL ACETYLACETONATES

ABSTRACT

CHIRA R. BHATTACHARJEE

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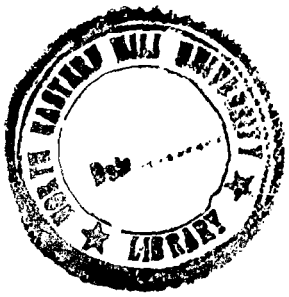

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To

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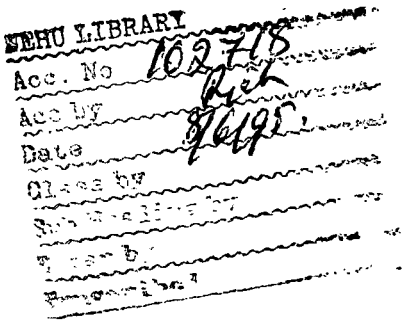

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FULFILMENT OF THE REQUIREMENT FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG
INDIA

DECEMBER, 1991

Dedicated
to
My Parents

Phone : 26593
Grams : NEHU

North - Eastern Hill University

Bijni Complex
Bhayakul, Shillong - 793003 (Meghalaya), India

Department of Chemistry

Dr. Mihir K. Chaudhuri, Dr. rer. nat. (W. Germany), FNA, FASc.
Professor of Chemistry

I certify that the thesis entitled "SOME CONTRIBUTIONS TO THE CHEMISTRY OF PEROXO COMPOUNDS OF ZIRCONIUM, THORIUM, URANIUM AND CARBON, AND ALKALI-METAL ACETYLACETONATES", submitted by Mr. Chira R. Bhattacharjee for the degree of Doctor of Philosophy of the North-Eastern Hill University, Shillong embodies the record of original investigation carried out by him under my supervision. He has been duly registered, and the thesis presented is worthy of being considered for the Ph.D. Degree. This work has not been submitted for any Degree of any other University.

Date: 12 December 1991
Place: Shillong

Signature of the Supervisor

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Department of Chemistry

This is to certify that Shri Chira R. Bhattacharjee has satisfactorily completed the following Pre-Ph.D. courses, as prescribed by the University:

1. Basic Course in German Language
2. Selected Topics in Physical Chemistry
3. Bioinorganic Chemistry
4. Medicinal Chemistry

Head
Department of Chemistry

December 1991

CONTENTS

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Bhattacharjee

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CHAPTER I

GENERAL INTRODUCTION

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 the generic designation for O_2 moiety in any of its oxidation states and can be referred to O_2 in either a free or combined state.[1] For use of this term it is essential that a covalent bond exists between the oxygen atoms. According to the rationalisation made by Vaska,[1] peroxo-compounds involve covalently bound dioxygen resembling O_2^{2-} in peroxo configuration.

Studies on the chemistry of dioxygen occurring in any of its different forms is one of the focal themes of current research.[2]

The variety of roles that the dioxygen can perform evolves from an intimate connection between the chemical reactivity of molecular oxygen and its ability to interact with metal ion centres contained in diverse state of chemical environment.[2d] Molecular oxygen has a definite role to play in the photosynthetic process.[3] In addition, it is also known to interact with a number of iron proteins involved in the physiological transport of molecular oxygen, in the oxidative metabolism of a wide variety of compounds and in the hydroxylation of a number of metabolites.[2d] Apart from these, molecular oxygen possesses the ability to form, often reversibly, adducts with a wide variety of metal-chelates or complexes in aqueous or non-aqueous media. The knowledge derived from these has been utilised in homogeneous and heterogeneous catalysis of inorganic and organic substrates by molecular oxygen, in air fuel cell electrode assemblies,[4] and to provide electronic and structural information by serving as models for various proteins involved in transport, storage and activation of molecular oxygen.[2d] Thus, the isolation and characterisation of stable dioxygen complexes, and the variety of reactions that they themselves seem to undergo have already began to yield information about bonding, structure, and reactivity of coordinated dioxygen.[2d,2i,4]

Owing to the importance of molecular oxygen as a reagent in biological and industrial processes, current research in this area has been directed not only towards the synthesis of metal dioxygen complexes, but also towards a clear understanding of the bonding properties of dioxygen and its effect upon the extent to

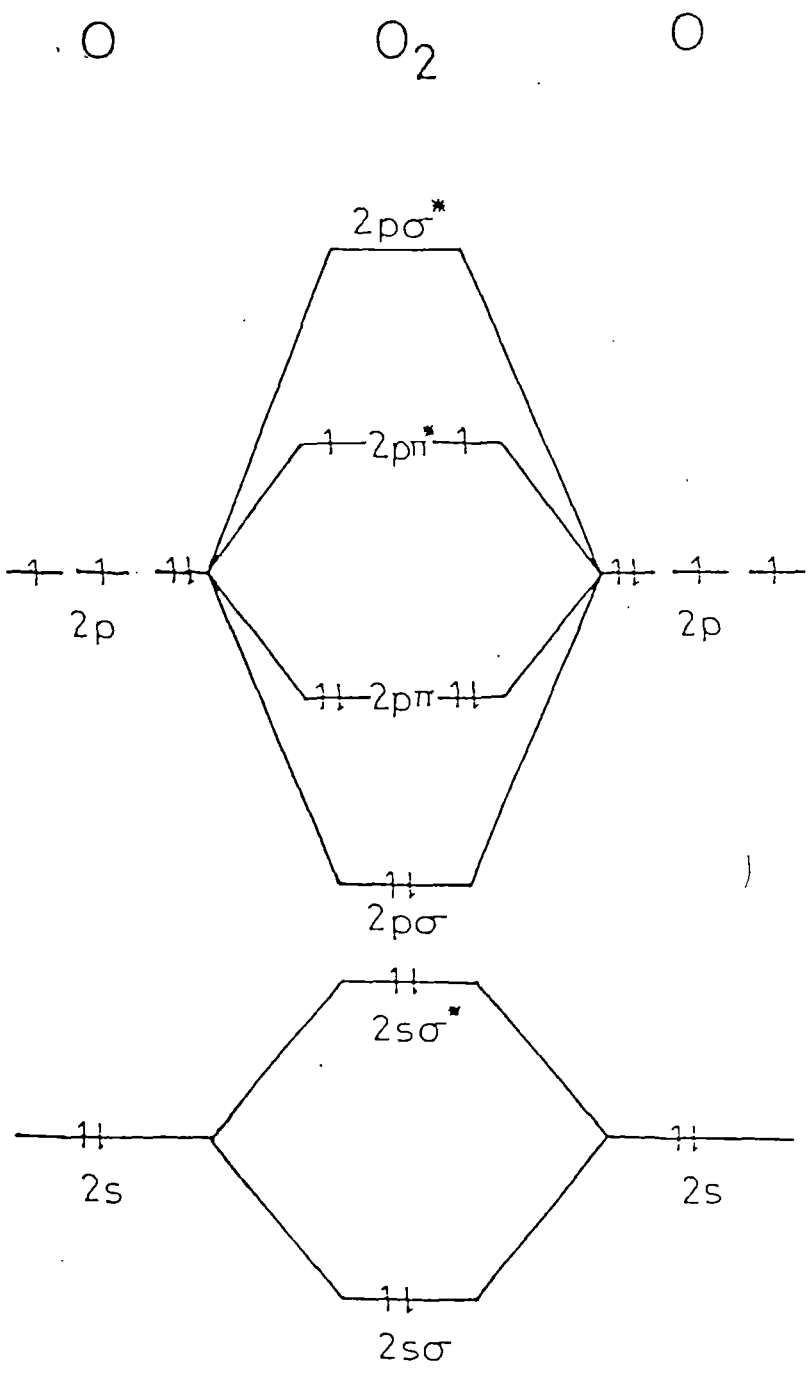


Fig.1 Molecular orbital diagram for O_2

which the O-O bond of coordinated O_2 is activated.[4]

The bonding in molecular oxygen is best described by MO theory.[5] The theory describes the bonding as arising out of the combination of the valence orbitals of the oxygen atoms ($2s^2$ $2p^4$) to give molecular orbitals, as shown in Fig.1. The ground state is predicted to be a triplet state ($^3\Sigma$) with two unpaired electrons occupying a pair of degenerate Π^* antibonding orbitals and this also is observed to be true. The configuration and energies for the ground state and first two excited states are shown in Fig.2.

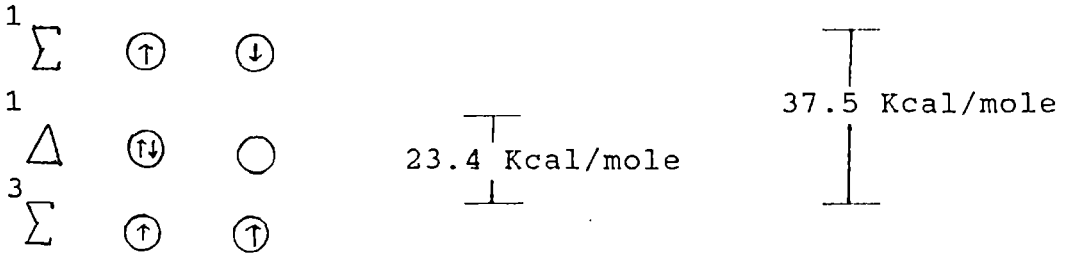


FIG.2 Π^* orbital occupancy and energies of the first two excited states of O_2

Rudimentary MO theory also predicts bond orders of 2.5, 2, 1.5 and 1 for the dioxygenyl cation O_2^+, molecular oxygen O_2, superoxide O_2^-, and peroxide O_2^{2-}, respectively.[6] As shown in Table 1.1, this results in an increase in the O-O bond order, decrease in the O-O bond energy, and a downward shift of $\nu(O_2)$ in the same order.

Table 1.1 : Some properties of O_2^+, O_2, O_2^-, and O_2^{2-}

Species	Bond Order	Compound	O-O Distance[7]	Bond Energy[5] (Kcal mole^{-1})	$\tilde{\nu}$(O-O) (cm^{-1})
O_2^+	2.5	O_2PtF_6	1.123	) -	1905[7]
O_2	2	O_2	1.207	117.2	1554[8]
O_2^-	1.5	KO_2	1.28	-	1145[9]
O_2^{2-}	1	Na_2O_2	1.49	35	842[10]

The way in which peroxo group is expected to bond to metals can range from symmetrical bidentate to a terminal monodentate position, including all the possible angles in between. The structural classification of dioxygen complexes has been rationalised by Vaska (Fig. 3).[1] The bridging peroxo could vary from cis-planar to trans-planar configuration. An unusual symmetrical double bridging was also found[11,12] in $[La_2\{N(SiMe_3)_2\}_4(O_2)(PPh_3O)_2]$ and $\{N(PhCH_2)Me_3\}_4[(UO_2Cl_3)_2(O_2)]$ in which the dioxygen ligand is bonded to the metal centres in a μ_2-peroxo fashion (M<O-O>M). However, such examples are very rare. Deviation from the ideal symmetry are also observed very often.

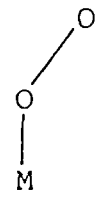
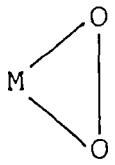
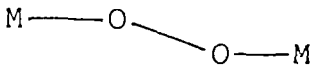
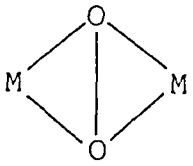
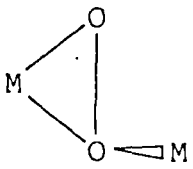
Structural type	Structural designation	Vaska Classification
	η^2 dioxygen	Type Ia (superoxo)
	η^2 dioxygen	Type IIa (peroxo)
	η^1: η^1 dioxygen	Type Ib (superoxo)
	η^1: η^1 dioxygen	Type IIb (peroxo)
	η^2: η^2 dioxygen	-
	η^1: η^2 dioxygen	-

Fig.3. Structural Classification of dioxygen complexes

Yet another manifestation of O-O bonded species is hydroperoxide ($^{-}$O-OH). Though this type is relatively more frequently encountered in non-metal chemistry, some of the metal hydroperoxide complexes have proved to be extremely important contributions owing to their unusual, but very significant reaction chemistry.[2i] For instance $VO(OOH)(Pic)_2L$ are shown to be powerful epoxidising and hydroxylating agents.[13] The discovery[14] of an efficient asymmetric epoxidation reagent ($Ti(OR)_4$, ROOH and a chiral tartarate diester) and its subsequent applications[15] in practical catalytic process have been significant contribution to the field of asymmetric synthesis. Also a Fe-OOH complex[16] is implicated in oxidation of organic substrates.

In case of non-metal peroxo compounds, however, peroxo group is found to be bonded mainly in two different fashions, viz. terminal monodentate[17,18] (i.e. end-on) and bridging transplanar configuration,[17,19-21] although in some cases for example in peroxoborates, the peroxogroup is believed to be bonded in a triangular bidentate manner.[22] In addition, peroxo group is also capable of being present as a hydroperoxide as encountered for peroxomonocarbonate[17] and peroxomonosulphate.[18,23]

Vibrational spectroscopy is a very important and useful technique for characterising complexes containing peroxo groups. For a bidentate chelated peroxide, considering C_{2v} being the local symmetry of coordinated O_2^{2-} ligand, three vibrations (two A_1 and one B_2) are expected to be IR and Raman active,[6,24] of which the

two A_1 mode (ν_1, ν_{O-O} stretching, and ν_2, $M-O_2$ symmetric stretching) are polarised, while B_2 mode (ν_3, $M-O_2$ asymmetric stretching) is depolarised in the Raman spectra. The ν_1 mode occurs normally between 800-900 cm^{-1}, the ν_2 and ν_3 modes fall generally in the region 500-600 cm^{-1}. The ν_2 and ν_3 modes can be ascertained on the basis of sharpness and intensity of the observed signals and Raman polarisation measurements on solutions. It may be mentioned that the ν_{O-O}, [(ν_1)A_1] is the most sensitive and intense one. The three modes of vibrations are governed by the nature of central metal ion and the other ligands coordinated to the metal. Further, these frequencies are influenced by the nature of environment (solvent or cavity) sorrounding the bound peroxide. The effects of these factors on vibrational frequencies has been discussed in detail by Nakamoto in a very recent review.[6] For the compounds where a peroxo group (O_2^{2-}) is bonded in an end-on fashion, the ν_{O-O} stretching frequency occurs at *ca.* 900 cm^{-1}, however, labelling studies are generally recommended[25] for complete characterisation. For a centrosymmetric bridging peroxide (M-O-O-M), the $\nu(O_2)$ and ν_s(M-O) are Raman active while ν_{as}(M-O) is IR active.[6] Thus, the results of Raman spectroscopy augment those obtained from IR studies. Moreover, Raman spectroscopy can also be easily applied to solutions and the results of which provide additional information concerning identity and structure of complex species in solutions.

Peroxo compounds can broadly be divided into two categories: the simple ones and those with heteroligand combinations. Simple peroxo compounds are those which contain peroxide, hydroperoxide

and water molecules. The heteroligand peroxo compounds, however, contain one to three coordinated peroxo groups and one or more co-ligands, including monodentate ions to bulky prophyrins (F^-, Cl^-, Br^-, CO, NO, NO_3^-, CN^-, NH_3, $C_2O_4^{2-}$, SO_4^{2-}, CO_3^{2-}, PO_4^{3-}, PPh_3, Citrate, EDTA, O-phen, 2,2'bipy, Oxine, Amino acids, Schiff bases, Pyridine 2,6-dicarboxylic acid, Prophyrins etc.).

Peroxo compounds can be synthesised either by activation of oxygen or by the interaction of peroxide with an appropriate starting material.[26]

The stability of peroxo complexes is generally enhanced by heteroligand environment.[27] Many simple peroxides often explodes spontaneously, some are sensitive to shock or decompose above 0°C, and several do not exist at all as stoichiometric compounds,[28] but many heteroligand peroxo complexes, on the other hand, survive recrystallisation from boiling aqueous solutions, heating *in vacuo*, and remain unchanged for prolong periods in closed containers.[27,29]

The research leading to gain an insight into the roles of peroxo-transition metal compounds in the storage and transport of oxygen and oxidas functions in biological systems is of growing interest.[2e, 2g, 2j, 2k, 13, 30-32] Although the importance of dioxygen complexes in biochemistry is well known,[2c,26] but the biochemical connection of the metal peroxo complexes with biological processes is yet to be clearly understood. The metals Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Y, Zr, Nb, Mo, Ru, Rh, Pd, Hf, Ta, W, Os, Ir, Pt, Ce, Th, and U form stable heteroligand peroxo

complexes, and evidence shows that some of these metals have significant biological roles.[2c, 33]

Peroxo complexes besides having an intrinsic interest of their own,[4,34-56] constitute an important class of reactive intermediates in catalytic oxidation reactions.[2h,13,57-61] Results of studies indicate that some are highly active and stereoselective in the oxidation of various organic substrates.[13] In a recent report,[2h] Mimoun et al. have furnished a good account of the synthesis of oxo-[N-(2-oxodiphenyl)salicylidenaminato]vanadium(V) alkyl peroxides, their use in the selective epoxidation of olefins, and discussed the results in relation to the mechanism of Halcon epoxidation process.[2h] In addition, peroxo complexes are potential oxygen donors to organic and inorganic substrates[2i,59] which make them highly useful in industry as well as in the laboratory for obtaining a number of valuable oxygenated products, such as, alcohols, ketones, epoxides, glycols, and phenols etc. Apart from this, the intramolecular electron-transfer in a 'metal-peroxo' moiety leads to weakening of bonds to coordinated ligand, and superoxide ion generated in the process could trigger further biological events.[33] Current evidence suggests that even in biological oxidation, metal-dioxygen complexes may be precursors of catalytically active species.[60]

Considerable variation exists in the reactivity of metal-dioxygen complexes depending on different structural type dioxygen and metal oxidation states. The binding of dioxygen to a metal is accompanied by (i) reduction in the number of unpaired electrons

on the oxygen (to 1 or 0) and (ii) transfer of charge density to the dioxygen. The kinetic barrier to spin changes in dioxygen reaction is thus lifted and the dioxygen ligand acquires some basic or nucleophilic character. This enables the dioxygen complexes to exhibit some typical reactions with diamagnetic electrophiles. Gubelmann and Williams[2e] have summarised the reactions of various types of dioxygen complexes with a variety of substrates. Of the various types, reactions of η^2 coordinated dioxygen have been studied rather extensively and their chemistry received comparatively more attention.[2e, 2i]

Peroxo-metal complexes, may act as 1,3-dipolar reagents, M^+-O-O^-, in which the positive charge is localised on the metal and the negative charge on the terminal oxygen atom of the opened peroxo group. They can react with both electrophilic and nucleophilic substrates.[2e,59]

A comprehension of the results of a non-exhaustive study suggested that three reactivity zones might be identified in case of peroxo-metal complexes. Thus, (i) Mo(VI) and W(VI) peroxo complexes which act as heterolytic alkene epoxidation reagents, (ii) V(V)-peroxo and alkyl peroxo complexes which act as heterolytic alkene epoxidation reagents and Cr(VI)-peroxo complexes which act as homolytic hydrooxylation reagent, and (iii) Rh(III)-peroxo complexes and alkyl or hydroperoxo complexes of Rh(III), Ir(III), Pd(III), and Pt(III), which act as heterolytic alkene ketonisation reagents.[57]

The reactivity of coordinated dioxygen in low valent transition metal compounds has received a considerable attention in recent years, particularly with respect to its ability to oxidise organic and inorganic substrates, viz olefins,[62-65] carbon dioxide,[66] sulphur dioxide,[67-73] and nitric oxide.[68] In most cases, the coordinated dioxygen behaves as a nucleophile.[65] It is evident from these reports that the coordinated peroxide shows a characteristic reactivity pattern towards inorganic polar substrates like SO_2, CO_2, NO_2, and NO etc. by way of producing coordinated sulphate,[4,67] carbonate and nitrate, respectively. Formation of coordinated sulphate from coordinated O_2 can be adequately summarised by the equation:

Coordinated (O_2^{2-}) + SO_2 ———> coordinated (SO_4^{2-})

Corresponding theoretical studies on the mechanistic details of the steps involved in the formation of SO_4^{2-} were also carried out.[72] In addition, there have been a number of reports specifically devoted to interaction of SO_2 (g) with dioxygen-metal complexes.[67,69,71,73] Despite this progress, there did not exist any information concerning the reactions of a highly peroxygenated metal complex with inorganic polar substrates viz., $SO_2(g)$, $NO_2(g)$, or $CO_2(g)$ etc. until a report[73] on the reactivity of $[V(O_2)_3]^-$ with $SO_2(g)$ appeared in 1989. Equally significant is that barring one report involving titanium[71] and the one on vanadium[73] as mentioned above, reactions of peroxometallates with such substrates were confined to Group VIII metals only. Moreover, except for a report by Sykes et al.[70] and

the one from this laboratory,[73] earlier results were all derived from studies conducted in nonaqueous medium.

Interestingly, other than cobalt, only a few examples of η^1: η^1 type dioxygen complexes have been known. Accordingly, information on their reactivity is practically lacking. The best established reaction of dinuclear dioxygen complexes is the peroxo-superoxo conversion.[74] Among the bridged dioxygen complexes, however, a notable feature is the difference in reactivity that a mono-bridged dinuclear and a di-bridged dioxygen complex exhibit.[74] It is evident, therefore, that an important issue addresses to the pattern of reactivity of peroxo-metal species with metal: O_2 being 1:>1 towards inorganic substrates like $SO_2(g)$, $CO_2(g)$, or $NO_2(g)$ etc. in an aqueous medium. It was considered worthwhile to select $SO_2(g)$, $NO_2(g)$, and $CO_2(g)$ as substrates, in part, owing to a recognition of the fact that these molecules, especially $SO_2(g)$, are objectionable atmospheric pollutants which have detrimental effects also on metallo-enzymes in biological systems. Thus, it was imperative to investigate the reactions of these molecules with metal dioxygen system, not only with metal:O_2 as 1:>1 but also with those of monoperoxo complexes, and rationalise the reaction sequence by isolation of products at different stages.

From the foregoing discussion it is evident that although a considerable progress, in the context of both synthesis and reactivity of peroxocompounds of lighter metals, has been registered, research on similar aspects of heavier metals and non-metals, received far less attention. Incidentally, different

aspects of peroxo-element chemistry have been persued in the laboratory where the work presented herein was performed. While the predecessors of the group dealt mostly with lighter metals, for instance, Ti, V, and Cu, the metals identified for the present Ph.D. research on the chosen theme were Zr, Th, and U.

In inviting reference to the non-metal peroxo chemistry, it is of relevance to mention that some success was achieved in this laboratory involving boron (B)[22] and phosporus (P).[75] Remarkable are the first chemical synthesis of a fluorinated peroxophosphate, $(NH_4)_2[PO_2(O_2)F].2H_2O$,[75] and the ability of a few newer peroxophosphorus compounds to demonstrate reactions typical of `alkaline-$H_2O_2$' reagent towards a number organic substrates.[76] As a sequel to the work on non-metal peroxo chemistry, attention of the present worker was drawn to also undertake studies on some chosen aspects of `peroxo-carbon' chemistry.

Having identified some of the selective aspects of peroxo-element chemistry for the present Ph.D. research, a good part of the attention was engaged to studies addressed to:

(i) The synthesis, isolation in the solid state, evaluation of properties, characterisation, and making structural assessment, involving a variety of physical techniques, of peroxo compounds of Zirconium (Zr), Thorium (Th), and Uranium (U), and Carbon (C).

(ii) Investigation of reactivity profiles of a few selected peroxo compounds of zirconium and uranium with inorganic substrates like $SO_2(g)$, $CO_2(g)$, or $NO_2(g)$ in an aqueous medium,

to provide an interpretative account, and make an internal comparison of the results.

(iii) Reactions of peroxo-carbon compounds in an aqueous medium with a few chosen organic substrates.

In order to pin point the specific problems selected for the present work related to peroxo-element chemistry, it is appropriate that relevant familiar chemistry of the chosen elements are highlighted.

Zirconium, a metal of our interest for the present work, albeit has oxidation states ranging from zero to +4, the lower oxidation states are of minor importance. There are a few authenticated compounds of zirconium, except those of its tetravalent state.[77,78] Because of a lesser tendency of the metal towards complete hydrolysis, there exists an extensive aqueous chemistry. Nevertheless, hydrolysis does occur and the hydrolysed ion often referred to as the "zirconyl" ion and written as ZrO^{2+} is formed. Zirconyl salts are known to form peroxozirconium compounds with varying Zr(IV): O_2^{-2} stoichiometry under different conditions. Only a few peroxozirconium compounds, with coligands like sulphate,[79] e.g. $Zr_2(O_2)_3SO_4(H_2O)_{8-10}$, oxalate,[80] e.g. $K_2[Zr(O_2)(C_2O_4)_2].2H_2O$, fluoride,[24a,81] e.g. $(NH_4)_2[Zr(O_2)F_5]$, and neutral organic ligands,[82] e.g. $[Zr(O_2)(C_5H_4NCOO)_2]$ have been known in the literature. Practically very little is, however, documented regarding reactivity of peroxo-zirconium compounds. Some attempts were certainly made by other group of workers[82,83] to explore

reactivity of such compounds, but the attempts were not always successful.

If one turns attention to the peroxo-chemistry of its congener, titanium, one finds that far more is known and relatively much better understood. Thus, research on various aspects of peroxozirconium(IV) chemistry warrants a greater attention and a systematic approach in order to gain a clearer insight.

In light of the above, work on peroxo-zirconium(IV) chemistry has very recently been initiated[84] in our laboratory and two series of peroxo(fluoro)zirconate(IV) complexes viz. $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$ have been synthesised. As a part of the present Ph.D. programme one such complex, ie., $(NH_4)_2[ZrO(O_2)F_2]$, was chosen as a typical case for investigating its reaction especially with $SO_2(g)$ in aqueous medium. The specific concern was to examine if SO_2 insertion into the O-O bond would take place, and then to ascertain the nature of interaction of the oxidised substrate (anticipated to be SO_4^{2-}) with the metal centre. An account of the results of this investigation is presented in Chapter III.

Like transition metals, actinides too are known to form simple peroxides but owing to a much higher degree of complexities involved,[77,85] the peroxo-chemistry of actinides has been far less investigated let alone their reactivity.

For instance, addition of H_2O_2, ozone, or peroxodisulphate to a neutral or weakly acid solutions of thorium salts produces a

poorly characterised compound of variable composition containing anions from the solution.[77] A peroxonitratothorium(IV) complex, $Th_6(O_2)_{10}(NO_3)_4 . 10H_2O$, peroxochloro complexes with Cl^-: Th ratio as 2:3 and 1:3 and, a peroxo-sulphato complex, $Th(O_2)SO_4.3H_2O$, have been known in the literature[77] with $Th(O_2)SO_4.3H_2O$ being the best characterised and thermally most stable compound. Later on, a few peroxothorium complexes, with carboxylato and phenoxo type ligands[82,86] and more recently some with Shiff-bases[86,87] have been reported. And till date there are only a very few publications[87] addressing to reactivity of peroxothorium compounds. The limited reactivity experiments were conducted[87] involving only organic substrates.

Somewhat like that of zirconium, the chemistry of thorium is mostly that of its +4 oxidation state and compounds of thorium(III) seem to be non-existent.[77,85] Synthesis of thorium complexes involving 'peroxide' as the ligand, or a combination of peroxide and a heteroligand have scarcely been investigated. In an appreciation of this problem, it was considered worthwhile to undertake studies on peroxothorium chemistry with a hope of making some headway in the area. The specific aim was to evaluate conditions appropriate for the synthesis of peroxothorium(IV) compounds containing one or more than one peroxo groups per metal centre, and sulphate, oxalate, or fluoride as coligands. Fortunately, some success has been achieved in the afore-said direction and the outcome of effort including synthesis and spectroscopic evaluation of structural motifs of new peroxo-thorium(IV) complexes constitute the subject matter of Chapter IV of the thesis. Also included in this

Chapter is a comparison of the new results with those of its congeners, titanium[88] and zirconium.[84]

Like thorium, uranium the fourth member of the actinide series, is known to form a host of simple peroxides.[28,77] But the chemistry of the metal, in general, shows a considerable difference from that of its preceding members of the series. Stable oxidation states of the metal range progressively from +3 to +6, with uranium(VI) oxidation level being the most stable. The ligands that stabilise this particular oxidation state include halides, nitrates, carboxylates, sulphate, β-diketonates, and peroxides etc. In simple compounds, the hexavalent state occurs only in hexafluoride, UF_6, and hexachloride, UCl_6.[77] The principal chemistry of +6 state, both in solids as well as in solution, is that of the dioxo cation, UO_2^{2+}, which forms a variety of complexes. The oxo cation is generally linear[77] in crystalline compounds as well as in solutions. The uranyl ion (UO_2^{2+}), characteristic of +6 state, forms a great variety of complexes with anionic and neutral ligands. Some of these complexes are important from the point of view that they may have applications in solar energy conversion system due to their inherent spectral properties,[89] and may be of potential use in photogeneration[90] of oxygen which is of great importance for the photocleavage of water. Uranyl systems with nitrate, sulphate, and carbonate as ligands are of technological importance.[91a] For instance, uranyl-carbonato complexes and related chemistry are of relevance in the context of carbonate leaching in the hydrometallurgy of the metal. Such compounds are also useful

intermediates for accessing uranium and uranium-plutonium ceramics.[91b]

As mentioned earlier, peroxide (O_2^{2-}) is capable of acting as a stabilising ligand for uranium(VI) [or UO_2^{2+}] and a host of different peroxo compounds of the metal with O_2^{2-}: U stoichiometry being 1:1, 1:2, 2:1, 3:1, 3:2, and 5:2 have been mentioned in the literature.[28,77] The complexity involved in the peroxo-uranium chemistry is an acknowledged problem,[28,77,92] and the system is exceedingly complicated owing to the formation of a number of peroxouranate(VI) species with a slight variation of pH of the reaction medium. Among these peroxouranates, however, $UO_2(O_2).nH_2O$(n=2 or 4) appears to be one of the best characterised compositions. This species has been known since 1876, and was a subject of extensive investigation. Nevertheless, its constitution was not well established until 1961 when Gordon and Taube[93] showed it to be a true peroxide hydrate based on an isotopic tracer studies on thermal decomposition of uranium-peroxide system. Despite a long history of peroxo-uranium chemistry, reports on peroxouranates, with more than one O_2^{2-} per UO_2^{2+} centre, containing both terminal and μ-peroxo groups, are far less. It is also significant to note that reactivity involving peroxo-uranium systems particularly towards inorganic substrates in both non-aqueous and aqueous medium has remained almost unattended to, although the ability of such system as potential oxidants may not be underestimated.[94]

In view of the above nonexhaustive discussion, a combination of the synthesis and structural assessment of a dinuclear uranium(VI) complex having a μ-peroxo linkage, study of its reactivity profiles with inorganic polar substrates viz., $SO_2(g)$, $CO_2(g)$ and $NO_2(g)$ in aqueous medium, and making an internal comparison of the results was set as one of the major targets for the present Ph.D. research programme.

A few years back, the first full series of fluoro(peroxo)-uranates(VI) of the type $A_2[UO_2(O_2)F_2].nH_2O$ (A=NH_4, Na, K, Rb or Cs) was reported[95] from this laboratory. The synthesis was based upon the reaction of diuranate of uncertain composition, $U_2O_7^{2-}$(!), with H_2O_2 and hydrofluoric acid. In the context of the present reactivity studies, it became necessary to resynthesise these compounds. Meanwhile, the knowledge gathered from some of the ongoing research in our laboratory on peroxo-element chemistry, it was perceived that a relatively more convenient synthesis could be possible involving a well defined starting material and without using hydrofluoric acid.

Chapter V of the thesis addresses to a practical synthesis of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$, a straight-forward route to $A_2[UO_2(O_2)F_2].nH_2O$ (A=NH_4, n=0; K, n = 1), and studies of reactions of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$[17] with $SO_2(g)$, $CO_2(g)$, and $NO_2(g)$, and of $(NH_4)_2[UO_2(O_2)F_2]$ with $SO_2(g)$ followed by rationalisation of reaction sequence by isolation of products at different stages. A comparative account of the results of present investigation with those obtained in the cases of V-

peroxo[73] and Zr-peroxo (present thesis, vide Chapter III) compounds is also incorporated in this Chapter.

A scrutiny of the literature related to peroxo-element chemistry, further reveals that while a lot is yet to be explored regarding synthesis, structure, and reactivity of `peroxometal' systems, development on similar aspects of `non-metal peroxo' systems has long been delayed. Consequently, compared to a good number of reports dealing with various facets of peroxo-metallates, far less is documented on peroxo-nonmetallates. Some peroxo compounds of non-metals like peroxodicarbonate,[17] peroxomonocarbonate,[17] peroxodisulphate,[96,97] peroxomonosulphate,[18,98] peroxonitrous acid,[99] peroxodiphosphates,[100] and peroxomonophosphoric acid,[100] have been known, and are widely used[100-105] in both research as well as industry. Unfortunately, methods of synthesis of many of the aforementioned compounds involve complicated reaction manipulations.

As a part of the present work, it was decided to investigate some aspects of peroxo-carbon chemistry. Carbon-peroxo compounds or the `percarbonates' are categorised into two classes: (i) the `perhydrates' and (ii) the `peroxocarbonates'. The perhydrates contain hydrogen peroxide of crystallisation and, on the other hand, the `peroxocarbonates' contain C-O-O linkage, as in organic peroxides.[17] Interestingly `percarbonates' have long been known,[106] and their role in industry as bleaching agents,[107] and as active intermediates (e.g. HCO_4^-, $C_2O_6^{2-}$) in biochemical reactions[108] recognised from an early date, yet no simple routes to their synthesis existed. Like for many other non-metals,

preparation of peroxocarbonates often require rather difficult reaction conditions. For instance, peroxocarbonates are synthesised by the reaction of alkali-metal hydroxide with H_2O_2 and CO_2 or by the anodic oxidation of carbonates at low temperature.[17] The perhydrates are obtained by simple recrystallisation of alkali-metal or ammonium carbonate with H_2O_2. Recently evidence[109] has been furnished for the presence of a peroxocarbonate species believed to be HCO_4^- or CO_4^{2-} formed in a highly alkaline solution of bicarbonate and H_2O_2. Prior to this report, alkali-metal salts of HCO_4^- were synthesised following a different route. The compound $NH_4[HCO_4]$ was not reported, however. It may be noted that synthesis of an ammonium salt from a very highly alkaline medium is difficult because of a higher concentration of NH_3 over that of NH_4^+. In light of this consideration, it appeared a sort of a challenge to try out the synthesis of $NH_4[HCO_4]$ and to demonstrate that peroxo-carbon compounds could be synthesised in a rather simple way. It was also deemed necessary to reinvestigate the synthesis of the perhydrate, $(NH_4)_2[CO_3].H_2O_2$, so that a comparative scenario could be presented. It might be necessary to add that the reported[17] synthesis of the above species requires a very long reaction time (3-4d). The possibility of rapid synthesis was perceived.

Reactions involving peroxo-carbon systems were not conducted by others presumably owing to their insolubility in organic solvents. Although it is true that such compounds are insoluble in organic solvents, the scope of investigating their reactivity

in aqueous solution remains open. The interest, in particular, was to examine if the compounds $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$ could effect oxidation reactions similar to those brought about by alkaline—H_2O_2 reagent.

Chapter VI of the thesis has been devoted to the first synthesis of $NH_4[HCO_4].3H_2O$ and a new synthesis of $(NH_4)_2[CO_3].H_2O_2$. The results of studies of reactions of these compounds with a few selected substrates in aqeuous medium have also been incorporated in the same **Chapter.**

Interestingly, like peroxo-element compounds highlighted above, 'peroxo-metal' —— acetylacetone (acacH) systems[110] also exhibit remarkable reaction chemistry. Thus, quite apart from the study of peroxo-element chemistry, studies on metal derivatives of β-diketone embraces a fascinating area of research.* Complexes with 1,3-diketones, particularly involving acetylacetone, have been reported for almost all of the non-radioactive metallic or metalloid elements in the periodic table[111,112] and can be broadly grouped into two categories, viz. molecular and ionic complexes. It is perhaps appropriate at this juncture to briefly enumerate the vast potential and importance that such complexes hold. The role of metal-acetylacetonates as catalysts in important organic reactions such as oligomerisation, polymerisation, hydrogenation, isomerisation of olefins,

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*A short review on the current status of metal-actylacetonate chemistry has been made and published:
Proc. Ind. natn. Sci. Acad., 1989, 55, 194.

hydrosylylation of alkynes, and coupling of organic halides is well recognised.[113] Metal — acetylacetonato complexes have also found application in various industrial processes, e.g., in rubber technology for vulcanisation,[114] in polymer, plastic,[115,116] and paints industries as additives, and for metal plating from organic solvents,[114] and for extraction, separation of metals,[117-119] and also as semiconductors,[120,121] and antioxidants[122] etc. Their ability to function as probes for NMR spectroscopic studies has rendered them a useful class of NMR shift reagents.[123,124] Two important properties viz., volatility and solubility in organic solvents are significant. While the former renders this class of compounds as suitable probes amenable to mass spectroscopic and other gas phase studies, the latter causes them to be useful synthetic precursors for organometallic synthesis. In addition, it has been proved[125,126] that metal-chelates of β-diketonates, under certain specific conditions, are capable of laser emission. Work in this regard has confirmed the fact that the metal-chelate anion is responsible for laser action in a number of such complexes. Many acetylacetonates for that matter have also been found to exhibit quenching effect of triplet state.[127] It is believed that the effect is due to the presence of unsaturated ligands. Based upon their volatile nature, yet another application of metal-β-diketonato complexes has very recently attracted an active attention of researchers. This involves Chemical Vapour Deposition (CVD) technique for making high quality film superconductors, or superconducting ceramics and materials for microelectronics application.[128,129] Consequent upon the applied

need as well as the interest in academic research, metal β-diketonates in general and acetylacetonato-metal, in particular, have always engaged the attention of several groups of workers over the years. A sustained endeavour of this laboratory for a decade on acetylacetonato-metal chemistry has led to two direct and general methods, based on (i) Acid-Base and (ii) Electron-transfer (Redox) concepts, for the synthesis of a number of acetylacetonato-metal with M : acac stoichiometry being 1:2,[130] 1:3,[131,132] 1:4,[133] and enabled an extensive investigation of their EI-induced mass spectra. Despite such progress, 1:1 type acetylacetonato-alkali-metal complexes appear to have drawn far less attention. For instance, Rb(acac) does not seem to have any reported existence until date although a corresponding fluorinated acetylacetonate, $Rb(C_5F_6HO_2)$, was reported in the literature.[134] In addition, the method of preparation of Cs(acac) is rather cumbersome.[135]

It was therefore imperative to attend to the identified problems related to alkali-metal-acetylacetonato chemistry. Our principal concerns were to develop the first synthetic methodology for the missing member of the A(acac) series, Rb(acac), and to provide a direct access to Cs(acac). It was also of an equal importance to us to furnish experimental evidence enabling comments on covalent-like character of alkali-metal-acetylacetonato compounds, A(acac) (A=Li, Na, K, Rb, or Cs).

In line with the proposition, experiments were designed and conducted. An account of this work is presented in Chapter VII, the concluding Chapter of the thesis.

While the Chapter in hand presents a non-comprehensive account pertaining the kind of work chosen for the present Ph.D. research and highlights the scope of work in the field, Chapter II provides details of the particulars of instruments/equipment used for characterisation and structural assessment, and the methods of elemental analyses. The procedure for obtaining deoxygenated water required for the reactivity experiments and the methods for generating $SO_2(g)$, $CO_2(g)$, and $NO_2(g)$ are also described in the same Chapter. Chapters III to VII incorporate the results of studies on the chosen problems. In order to make each of the Chapters III to VII a self-contained one, providing a brief introduction, sections on experimental and results and discussion followed by relevant bibliography some repetitions became inevitable, however, sincere attempts have been made to keep this to a minimum. A major part of the new results has been published while rest is under communication.

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CHAPTER II

PARTICULARS OF INSTRUMENTS/EQUIPMENT USED AND METHODS OF ELEMENTAL ANALYSES FOR CHARACTERISATION AND STRUCTURAL ASSESSMENT OF COMPOUNDS

The present Chapter deals with the details of the method employed for the quantitative analysis of various constituents and relevant particulars of the instruments/equipment used for the characterisation and structural assessment of the newly synthesised compounds.

PARTICULARS OF INSTRUMENTS/EQUIPMENT USED

pH Measurement

The pH values of the reaction solutions were measured by using a Systronics Type 335 digital pH meter.

Conductance

The conductance values were measured in conductivity grade water using a Wayne Kerr Automatic Precision Bridge B 905 conductometer and a Systronics Type 304 digital Direct Reading conductivity meter.

Magnetic Susceptibility

Magnetic susceptibilities of the complexes were measured using the Gouy method. The compound $Hg[Co(NCS)_4]$ was used as the calibrant.

Infrared Spectra

The infrared (IR) spectra were recorded in KBr as well as in nujol mull on the following spectrophotometers:

(i) Perkin-Elmer model 297

(ii) Perkin-Elmer model 983

Laser Raman Spectra

Laser Raman (LR) spectra were recorded on a SPEX Ramalog model 1403 Raman Spectrometer. The 4880 A laser line from Spectra-Physics model 165-09 Argon laser and 5145 A laser line from Spectra-Physics model 165 Argon laser were used as the excitation sources. 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.

^1H NMR Spectra

^1H NMR spectra were recorded on a Varian 390, 90 MHz spectrometer. Tetramethylsilane (TMS) was used as the internal standard.

ESR Spectra

ESR spectra of the compounds were recorded in the form of polycrystalline solid using Varian E109, X-band ESR Spectrometer.

Atomic Absorption Spectrometry

Perkin-Elmer 2380 Atomic Absorption Spectrometer was used for the determination of Potassium, Rubidium, Caesium, Zirconium, and Uranium.

Flame Photometry

Sodium and Potassium were determined by a Flame Photometer using an acidified (hydrochloric acid) solution of the sample.

Melting Point

Melting points of the compounds, whenever required, were measured using a Toshniwal CL 0302 melting point/boiling point apparatus.

ELEMENTAL ANALYSES

Active Oxygen (Peroxo Oxygen)[1]

(i) Permanganometry[1]

An accurately weighed amount of a peroxo compound of Zirconium, Thorium, Uranium, or Carbon was dissolved in 7N sulphuric acid in the presence of boric acid (4g). Boric acid was used to prevent any loss of active oxygen by forming perboric acid. The

resulting solution was then titrated with a standard solution of potassium permanganate.

$$1cm^3 \text{ of } 1N\ KMnO_4 \equiv 0.01701g \text{ of } H_2O_2$$

This method is suitable for determination of peroxide contents of peroxo compounds of zirconium, thorium, uranium and carbon.

(ii) Iodometry[2]

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

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

The method is particularly suitable for the determination of peroxide content of peroxo-uranium compounds. This method was also employed in determining active oxygen content in other peroxo compounds.

(iii) Cerimetry[3]

An accurately weighed amount of a peroxo compound was dissolved in 2N sulphuric acid solution containing boric acid (*ca.* 5g). Peroxide was determined by titrating with standard Ce^{+4} solution.

(iv) Fluoride[4]

An accurately weighed amount of a fluoro-compound was dissolved in dilute nitric acid (0.1N, 25 cm^3). The resulting solution was then made alkaline by the addition of 0.1N NaOH (50 cm^3). The mixture was heated for *ca.* 20 min. to ensure complete decomposition. The hydrated metal oxide thus formed was separated by filtration and washed several times with water. The filtrate and washings were collected for fluoride estimation.

To the combined washings and filtrate, a pinch 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 an digested on a steam-bath for about half an hour with occasional stirring, and then allowed to stand overnight.

For the gravimetric estimation, the precipitated lead chloride fluoride, PbClF, was filtered through a Gooch crucible (grade 4) and weighed as PbClF after drying at 140-150°C to constant weight. In the volumetric estimation 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 a 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 a steam-bath for 4-5 min. A known excess of standard 0.1N silver nitrate solution was then added to it followed by digestion on a steam-bath for 30 min and then cooled to room temperature in the dark. The precipitated silver chloride was filtered through a sintered glass crucible and washed with cold water. The excess of silver nitrate was then titrated with a standard 0.1N potassium thiocyanate solution using ferric ion indicator. 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.

$$1\ cm^3\ 1N\ AgNO_3 \equiv 0.0190g\ of\ F^-$$

(v) Sulphate[5]

A known amount of a zirconium-, thorium-, or uranium-, sulphato compound was treated with 25 cm^3 of water, and was completely dissolved 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 hydrated, ThO_2, ZrO_2 or 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 neutralised with dilute nitric acid (volume of the solution was ~ 230 cm^3). The solution so obtained was acidified by the addition of 0.3-0.6 cm^3 of concentrated HCl solution and

heated to boiling. A warm solution (10-12 cm^3) of 5% barium chloride (5g of $BaCl_2.2H_2O$ in 100 cm^3 of water) was added from a burette or a 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 $BaSO_4$.

(vi) Oxalate[6]

An accurately weighed amount of the thorium-peroxo-oxalato compound was dissolved in 0.1N sulphuric acid (25 cm^3). To the solution was added 30 cm^3 of 0.1N NaOH solution followed by dilution to *ca.* 100 cm^3. The mixture was then boiled for *ca.* 15 min. followed by filtration. The yellow precipitate was washed 3 to 4 times with cold water and the filtrate and washings were collected for the determination of oxalate. The combined filtrate and washings was neutralised 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 $KMnO_4$ solution maintaining the temperature of the solution at *ca.* 60°C.

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

(vii) Zirconium[7]

Zirconium was determined gravimetrically as zirconium oxide, ZrO_2.

In this procedure, an accurately weighed amount of the compound was dissolved in 0.1N nitric acid (20 ml) and the mixture was heated for *ca.* 10 min. The resulting solution was then made alkaline by the addition of 0.1N NaOH solution (30 cm^3) followed by heating for *ca* 10 min to ensure complete decomposition. The precipitated hydrated zirconium dioxide was filtered off and washed several times with cold water. The gelatinous precipitate was then dissolved in 20% hydrochloric acid (v/v) followed by the addition of 50 cm^3 of 16% aqueous mandelic acid solution. The mixture was heated to 85°C over a steam-bath for *ca* 20 min. The resulting precipitate was then filtered off and washed with a hot solution containing 2% of hydrochloric acid and 5% mandelic acid. The filter paper and the precipitate was ignited to the oxide in an usual manner in a silica crucible, and finally weighed as ZrO_2.

(viii) Thorium[8]

Thorium was estimated gravimetrically as thoria, ThO_2. An accurately weighed amount of the sample was dissolved in

ca. 25 cm^3 of dilute hydrochloric acid by warming and heated to boiling to ensure complete decomposition of the peroxide. To the hot solution was then added 25% potassium hydroxide until a white precipitate ceases to appear. The precipitated hydrated thorium oxide was filtered off and washed several times with cold water. The gelatinous precipitate was then dissolved in 20% hydrochloric acid (v/v). The solution was heated to boiling and to it then was added 10% solution of oxalic acid to combine with all the thorium. An excess of 20 cm^3 of oxalic acid solution was then added. The solution was cooled and kept overnight. The precipitate was filtered through Whatman 41 filter paper and washed with a solution containing 3.5 cm^3 of concentrated hydrochloric acid and 2.5g of oxalic acid per 100 cm^3 and then ignited in a weighed platinum crucible in an electric muffle furnace at 700-800°C, and finally weighed as ThO_2.

(ix) Uranium[9]

Uranium was estimated gravimetrically as U_3O_8. An accurately weighed amount of an uranium compound was dissolved in *ca.* 25 cm^3 of dilute sulphuric acid and the solution was heated to boiling. To the hot solution was then added a few drops of methyl red indicator followed by a slow addition of dilute ammonia until the indicator turned yellow, and a yellow precipitate was obtained at this stage. A Whatman accelerator was added and the solution warmed for 1 to 2 min. The precipitate was filtered off on a Whatman 541 filter paper and washed 4 to 5 times with a hot 2% solution of ammonium nitrate. The filter paper alongwith the

precipitate was then ignited over a Meker burner in a platinum crucible and finally the uranium content was weighed as U_3O_8.

Carbon, Hydrogen and Nitrogen

Carbon, hydrogen, and nitrogen were estimated by microanalytical methods. The results of analyses were obtained from Micro Analytical Laboratory, Department of Chemistry, North-Eastern Hill University, Shillong.

Preparation of deoxygenated water for reactivity studies

The water used for reactivity studies was deoxygenated by first boiling the water sample for *ca.* 30 min under N_2 atmosphere and cooling to room temperature followed by bubbling of N_2 gas through it for a period of *ca.* 15 min.

The deoxygenated water was stored in an airtight container. The water thus obtained has been used in reactivity studies throughout.

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9. Ref. 5, p. 539.

CHAPTER III

REACTIVITY OF COMPLEX PEROXOZIRCONATE. REACTION OF AMMONIUM OXOMONOPEROXODIFLUORO-ZIRCONATE(IV), $(NH_4)_2[ZrO(O_2)F_2]$, WITH SULPHUR DIOXIDE, $SO_2(g)$, IN AQUEOUS MEDIUM. AN ACCESS TO A NEW TERNARY COMPLEX OF ZIRCONIUM(IV), $[ZrO(SO_4)F_2]^{2-}$*

The importance of peroxo-metal compounds and their reactivity have been highlighted in Chapter I of the thesis. Interest in the studies of peroxo-metal chemistry, stems mainly from an intrinsic biochemical connection,[1,2-5] fascinating coordination chemistry as well as the role and use of peroxo-metal compounds

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* The work described herein has been published. Polyhedron, 1990, 9, 1653.

in the oxidation chemistry,[6-13,14] and the extent of activation of coordinated peroxide (O_2^{2-}) in such compounds. Synthesis followed by characterisation of peroxo-metal compounds are undisputedly the prerequisite for a systematic approach to this field. Although a commendable progress has been made on this aspect of first-row transition metals, much less has been investigated involving, that of the second-row transition metals. As a case in point, information on peroxozirconium(IV) compounds is rather scant.[15-19] Based on the above rationale, a programme aimed at synthesis and assessment of structure of peroxozirconium(IV) compounds was taken up in this laboratory as the first step towards accessing the chosen field. Adopting a suitable reaction strategy, ZrO^{2+} was allowed to interact with O_2^{2-} and F^- in presence of each other at an appropriate pH. This enabled the synthesis of one series each of monoperoxofluorozirconates(IV), $A_2[ZrO(O_2)F_2]^{2-}$ ($A=NH_4$, Na, K) and diperoxofluorozirconates(IV), $A_3[ZrO(O_2)_2F]^{3-}$ ($A=NH_4$, Na, or K), with zirconyl (ZrO^{2+}) core being the centre of coordination.[20] Pertinent here is to mention that the occurrence of ZrO^{2+} is not a very common phenomenon, though not unprecedented.[21] Following the successful synthesis, we were rather keen in investigating the reactivity profile of such a compound towards small inorganic molecules. This was considered important since the earlier reports involved mainly Group VIII metal-peroxo species and the reactions were conducted in non-aqueous medium. In the case of peroxozirconium chemistry, while oxygen atom transfer capability of such complexes towards organic substrate was tested[17,19] with some success, reports dealing with

reaction towards inorganic substrates appeared to be nonexistent. It was thus imperative to study the reactions of the peroxozirconium(IV) complexes synthesised in this laboratory toward small inorganic polar substrates. Accordingly, the study of reaction of monoperoxofluorozirconate(IV), $(NH_4)_2[ZrO(O_2)F_2]$, with $SO_2(g)$ in aqueous medium was undertaken as a typical case. The concerns in this regard was also to examine if SO_2 insertion would take place into the O-O bond leading to newer ternary complexes of Zr(IV) and to rationalise the reaction by isolation and subsequent characterisation of the reaction product. The results of the aforementioned investigation constitute the subject matter of the present Chapter.

EEXPERIMENTAL

Reagent grade chemicals were used throughout the present work.

Synthesis of the Precursor Compound, Ammonium Oxomonoperoxo-difluorozirconate(IV), $(NH_4)_2[ZrO(O_2)F_2]$ [20]

A 1.0g (4 mmol) sample of $ZrO(NO_3)_2.H_2O$ was dissolved in water (15-20 cm^3) followed by the addition of aqueous ammonia (sp.gr.0.9) until the white hydrated zirconium dioxide precipitate ceased to appear. The product was filtered off and washed free from ammonia and nitrate. To the water suspension of hydrated zirconium oxide was added 15 cm^3 (132.36 mmol) of 30% H_2O_2 with continuous stirring followed by a slow addition of 1 cm^3 (24 mmol) of 48% HF, whereupon a clear solution resulted. The solution was stirred further for a period of *ca.* 15 min. and filtered to remove any undissolved residue. The pH of the

reaction solution was raised to 6 by careful addition of aqueous ammonia (sp. gr. 0.9). A small amount of white product appeared at this pH. To ensure complete precipitation, *ca.* 50 cm^3 of pre-cooled ethanol was added, and finally dried *in vacuo* over P_4O_{10}. The yield of the compound $(NH_4)_2[ZrO(O_2)F_2]$ was 0.75g (87%). The analytical data are presented in Table 3.1.

Reaction of $(NH_4)_2[ZrO(O_2)F_2]$ with $SO_2(g)$ In Aqueous Medium - Synthesis of Ammonium Oxomonosulphatodifluorozirconate(IV) Heptahydrate, $(NH_4)_2[ZrO(SO_4)F_2].7H_2O$

Reactivity grade water (Chapter II) was used in the following reaction.

Through an aqueous suspension of $(NH_4)_2[ZrO(O_2)F_2]$ (1.g, 4.69 mmol), $SO_2(g)$ was slowly bubbled until the solution registered a pH value of 2-1. This was filtered and ethanol was added to initiate precipitation. It was allowed to stand for 2h and then filtered to isolate the white crystalline product. The compound was washed with ethanol and finally dried *in vacuo* over conc. H_2SO_4. The yield of $(NH_4)_2[ZrO(SO_4)F_2].7H_2O$ was 0.97 (47%).

Elemental Analysis

Methods of chemical analyses and the details of equipment used for characterisation have been elaborated in Chapter II.

RESULTS AND DISCUSSION

As emphasised in the preamble of this Chapter, our present interest has been mainly to conduct an electron-transfer reaction

between one of the peroxofluorozirconate(IV) complex, $[ZrO(O_2)F_2]^{2-}$, and $SO_2(g)$ in an aquous medium and explore the possibility of obtaining a hitherto unreported mixed-ligand fluoro(sulphato)zirconate(IV) species. It was expected that this would be possible through an insertion of SO_2 into the O-O bond of coordinated peroxide.

Thus, strategically a suspension of $(NH_4)_2[ZrO(O_2)F_2]$ in aqueous solution was reacted with $SO_2(g)$ until a clear colourless solution was obtained, which on addition of ethanol afforded a white product. The reaction solution at the stage of isolation of the product registered a pH value of 2-1.

The compound is diamagnetic in nature and sparingly soluble in water. Chemical tests confirmed the absence of O_2^{2-} and the presence of SO_4^{2-} in it. These were also ascertained from the IR spectrum of the compound. The results of chemical analyses (Table 3.1) suggested the stoichiometry of $Zr:SO_4^{2-}:F^-$ as 1:1:2. Based on this and the vibrational spectroscopic studies as discussed below, the white compound was characterised as ammonium oxomono(sulphato)difluorozirconate(IV) heptahydrate, $(NH_4)_2[ZrO(SO_4)F_2].7H_2O$.

The IR spectroscopic signatures (Table 3.2) of the compound provided clear evidence for the occurrence of a zirconyl core, (ZrO^{2+}), coordinated fluoride and coordinated sulphate. While the $\nu_{Zr=O}$ appeared at 980s cm^{-1}, the ν_{Zr-F} was observed at 460m cm^{-1}. sulphate, the appearance of medium intensity ν_1 (970m cm^{-1}, ν_{S-O}) and ν_2 (470m, ν_{S-O}) modes, and the splitting of ν_3 and ν_4

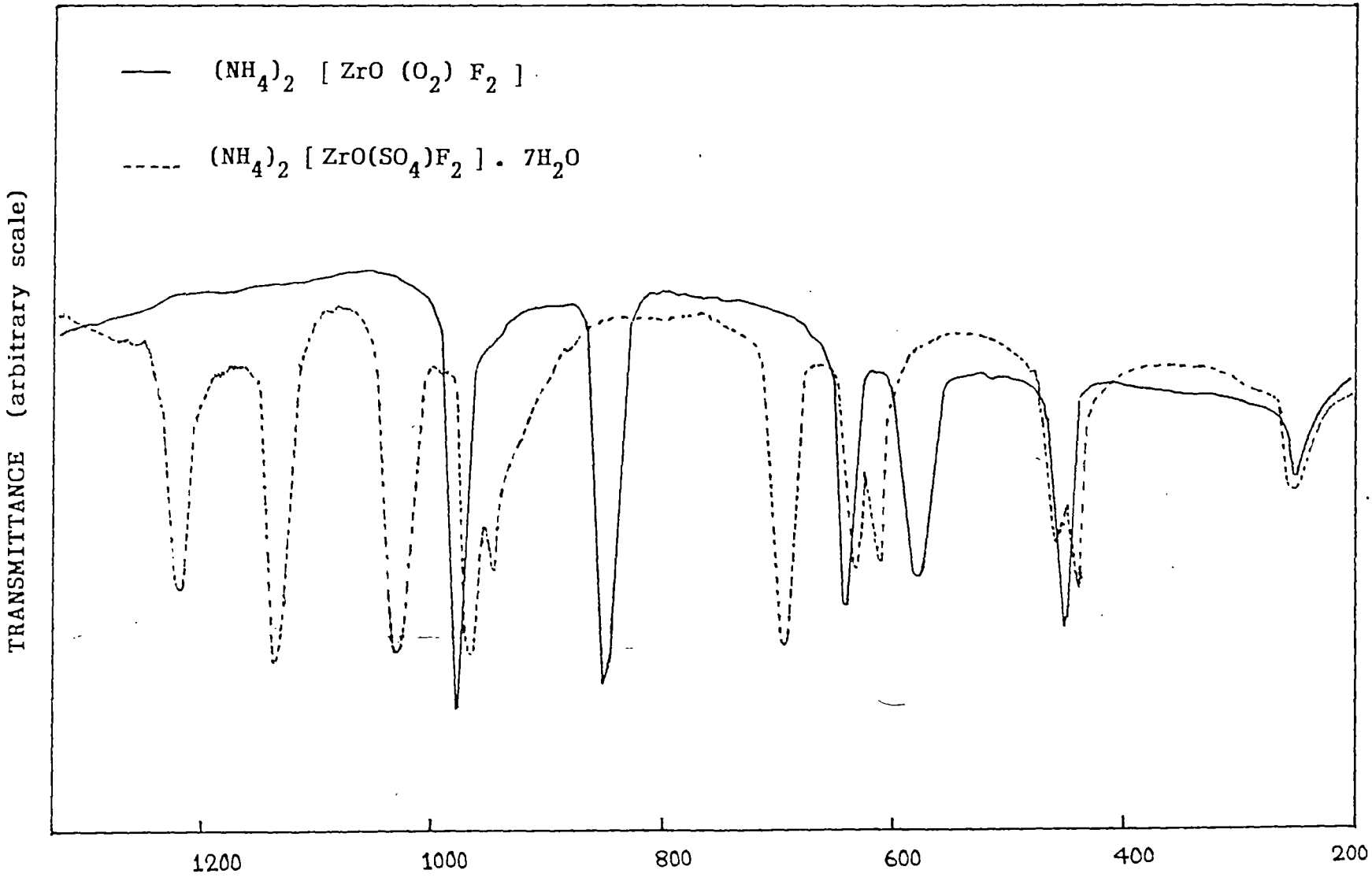
Table 3.1 : Analytical data of $(NH_4)_2[ZrO(O_2)F_2]$ and $(NH_4)_2[ZrO(SO_4)F_2].7H_2O$.

Compound	Analysis[a] (%)				
	N	Zr	O_2^{2-}	SO_4^{2-}	F^-
$(NH_4)_2[ZrO(O_2)F_2]$	13.0 (13.1)	42.1 (42.8)	15.3 (15.0)	-	18.1 (17.8)
$(NH_4)_2[ZrO(SO_4)F_2].7H_2O$	6.9 (6.9)	22.3 (22.6)	-	24.2 (23.8)	9.2 (9.4)

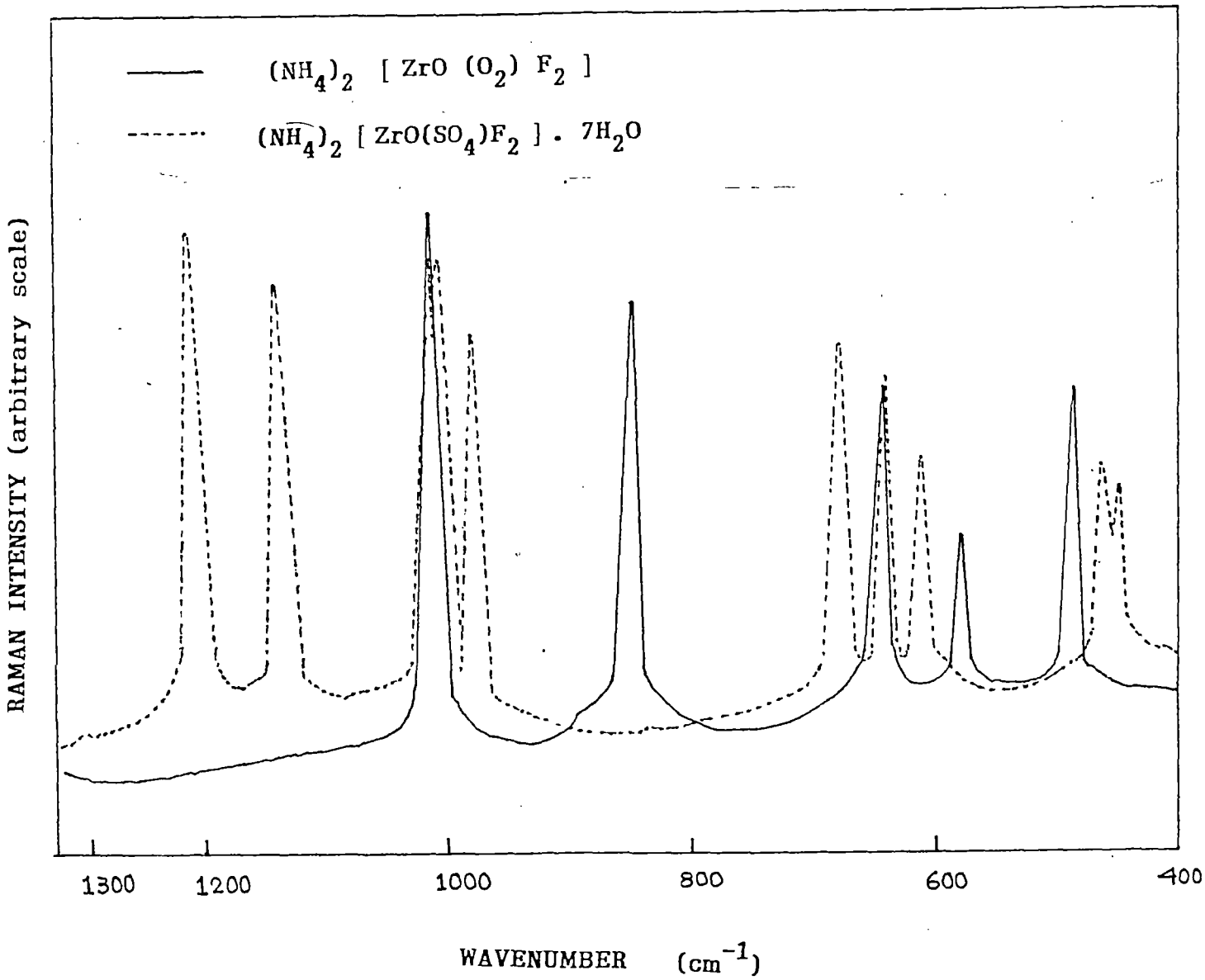
[a] Calculated values are in parenthesis.

Table 3.2 : Structurally significant IR and Raman bands of $(NH_4)_2[ZrO(O_2)F_2]$ and $(NH_4)_2[ZrO(SO_4)F_2].7H_2O$

Compound	IR(cm^{-1})	LR(cm^{-1})	Assignment
$(NH_4)_2[ZrO(O_2)F_2]$	981s	1020	$\nu_{Zr=O}$
	850s	847	$\nu_{O-O}(\nu_1$
	640s	650	$\nu_2(Zr-O_2)$
	585m	590	$\nu_3(Zr-O_2)$
	460s	480	ν_{Zr-F}
	249		ν_{Zr-F} def.
$(NH_4)_2[ZrO(SO_4)F_2].7H_2O$	980s	1010	$\nu_{Zr=O}$
	970m	990	ν_1
	470m	470	ν_2
	1220s	1215	
	1145s	1145	ν_3 SO_4^{2-} modes
	1030s	1020	
	685s	680	
	635s	640	ν_4
	605s	610	
	460m	460	ν_{Zr-F}


—— $(NH_4)_2$ [ZrO (O_2) F_2]
----- $(NH_4)_2$ [$ZrO(SO_4)F_2$] . $7H_2O$
TRANSMITTANCE (arbitrary scale)
1200
1000
800
600
400
200
WAVENUMBER (cm^{-1})

IR SPECTRUM


$(NH_4)_2$ [ZrO (O_2) F_2]
$(NH_4)_2$ [$ZrO(SO_4)F_2$] . $7H_2O$
RAMAN INTENSITY (arbitrary scale)
1300
1200
1000
800
600
400
WAVENUMBER (cm^{-1})

LR SPECTRUM

vibrations into three bands each (Table 3.2), in contrast to the absence of ν_1 and ν_2 and unsplit ν_3 and ν_4, suggested the lowering of the symmetry of SO_4^{2-} from T_d to C_{2v}, and its presence as a chelated ligand in the complex.[23] The formation of the sulphato complex is explained in terms of insertion of SO_2 into the O-O bond of the coordinated peroxide, without causing any reduction of the metal centre. Two additional IR bands at 1640s cm^{-1} (δ_{H-O-H}) and 3460s cm^{-1} (ν_{O-H}) are unambiguous in their shapes and positions and owe their origins to lattice water.[24,25] In order to gain further support regarding the structural motifs of the compound, laser Raman spectroscopic investigation were undertaken. The complementary singals in the LR spectrum of the fluorosulphatozirconate(IV) compound were observed at 1010 ($\nu_{Zr=O}$); 990 (ν_1, ν_{S-O}), 470(ν_2, ν_{S-O}); 1215, 1145, 1020(ν_3, ν_{S-O}); and 680; 640, 610 (ν_4, ν_{S-O}) and 460 cm^{-1}(ν_{Zr-F}).

It may be inferred from the results of the present investigation that under appropriate experimental conditions, the monoperoxofluoro compound, $(NH_4)_2[ZrO(O_2)F_2]$, reacts with $SO_2(g)$ in aqueous medium to afford a new ternary complex of Zr(IV), $(NH_4)_2[ZrO(SO_4)F_2].7H_2O$. The formation of a mono(sulphato)-fluorozirconate(IV) complex demonstrated that coordinated F- ligands were not affected thus indicating a rather strong Zr-F bond in the compound. The zirconyl 'ZrO^{2+}' core in the starting peroxozirconate(IV) complex is retained in the final product. The reaction is interesting because it not only provides an access to a new ternary complex of zirconium(IV) as obtained, but

also this route prevents the formation of a binary fluorozirconate(IV) which is a normally encountered problem in the synthesis of mixed-fluorozirconates(IV).

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CHAPTER IV

SYNTHESIS, CHARACTERISATION AND STRUCTURAL ASSESSMENT OF NEW HETEROLIGAND PEROXOTHORATES(IV) OF THE TYPE $A_2[Th(O_2)F_2(OH)_2].nH_2O$ (A=NH_4, n=3; A=Na or K, n=1) AND MOLECULAR PEROXOTHORIUM(IV) COMPLEXES $[Th_2(O_2)_3L(H_2O)_4].5H_2O$(L=$C_2O_4$ or SO_4)*

Although one of the active areas of research in contemporary inorganic chemistry addresses to studies on compounds that contain peroxo ligands, the peroxochemistry of heavier metals especially actinides do not appear to have received due attention compared to that of lighter metals. This could, in part, be due to the very complicated nature of peroxo-actinide chemistry as noted earlier in Chapter I. For instance, thorium forms a poorly

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* The work described herein has been published:
Inorg. Chim. Acta., 1989, 160, 147.

characterised compound of variable composition containing anions from solution when H_2O_2, ozone or peroxodisulphate is added to a neutral or weakly acidic solution of thorium salts.[1] Normally, similar is not the observation with a lighter transition metal.

Consequently, reports on hetero-ligand peroxothorium compounds are rather scarce, except for the ones on peroxonitrato-,[2] peroxochloro-,[3] and peroxosulphato— thorates (IV).[4] Of these, the peroxosulphato complex, $Th(O_2)SO_4.3H_2O$, seems to be one of the best characterised and thermally most stable species. Incidentally, recent reports[5] still describe that molecular complexes of peroxoactinides are only a very few although actinides have long been known to form peroxo-compounds. A few peroxothorium complexes with carboxylato- and phenoxo- type ligands were known in the literature[6] and some with Schiff bases were reported[7] only recently. As a sequal to the endeavour of the group[8-13] at NEHU in the field of peroxo-metal chemistry, and also in view of the fact that far less has been known regarding this aspect of thorium, it was considered worthwhile to evaluate appropriate reaction conditions in order to develope an access to some hitherto unreported heteroligand peroxothorium(IV) complexes. It was expected that the new results would enable an internal comparison with those obtained in the case of peroxozirconium.[14]

Accordingly, the present Chapter describes the synthesis, characterisation, and structural assessment of new heteroligand peroxothorates(IV) of the type $A_2[Th(O_2)F_2(OH)_2].nH_2O$ ($A=NH_4$, $n=3$; A=Na or K, $n=1$) and molecular peroxothorium(IV) compounds of the type $[Th(O_2)L(H_2O)_4].5H_2O$ ($L=C_2O_4$ or SO_4).

EXPERIMENTAL

Reagent grade chemicals were used for the present investigation. All the manipulations pertaining to the synthesis of $A_2[Th(O_2)F_2(OH)_2].nH_2O$ were carried out in polyethylene apparatus.

(i) Synthesis of Alkali-metal and Ammonium Difluorodihydroxo-monoperoxothorate(IV) Hydrates, $A_2[Th(O_2)F_2(OH)_2].nH_2O$ (A=NH_4, n=3; A=Na or K, n=1)

Following a typical procedure, representative of the general method, to a solution of 1g (1.70 mmol) $Th(NO_3)_4.6H_2O$ in 15 cm^3 of water was added 25% aqueous solution of AOH (A=Na or K) until the white gelatinous precipitate of hydrated thorium oxide ceased to appear. Hydrated thorium oxide was then washed free from the alkali or nitrate. To a water suspension of hydrated oxide was added 15 cm^3 (132.25 mmol) of 30% H_2O_2 solution and the mixture was stirred for *ca.* 15 min. followed by the addition of 4 cm^3 (96.0 mmol) of 48% HF drop by drop with continuous stirring to obtain a clear solution. The pH of the reaction solution at this stage was found to be *ca.* 2. This was slowly raised to 10-11 by addition of the corresponding alkali-metal hydroxide solution or aqueous ammonia. Stirring was continued for a further period of 10 min. A small volume of ethanol (20 cm^3) was added to facilitate precipitation of alkali-metal or ammonium difluorodihydroxomonoperoxothorate(IV) hydrates. The compound was isolated by filtration and dried *in vacuo* over conc. H_2SO_4. Starting from 1g of $Th(NO_3)_4.6H_2O$, in each case the yields were recorded as: $(NH_4)_2[Th(O_2)F_2(OH)_2].3H_2O$, 0.58g (74%);

$Na_2[Th(O_2)F_2(OH)_2].H_2O$, 0.51g (75%); $K_2[Th(O_2)F_2(OH)_2].H_2O$, 0.6g (80%).

(ii) Synthesis of Diperoxotetra-aquo-μ-peroxo-μ-oxalato-dithorium(IV) Pentahydrate, $[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$

To a solution of 1g (1.70 mmol) of $Th(NO_3)_4.6H_2O$ in 20 cm^3 of water was added a solution of 0.20g (1.70 mmol) of oxalic acid in 15 cm^3 (132.35 mmol) of 30% H_2O_2. A white gelatinous mass that appeared was stirred for *ca.* 10 min. followed by raising pH of the medium to 7-8 by the addition of aqueous ammonia (sp.gr. 0.9) or 15% AOH (A=Na or K) solution. The whole was again stirred for *ca.* 5 min. and then the product was isolated by filtration, washed with water, and portions of ethyl alcohol 3-4 times, and finally dried *in vacuo* over conc.H_2SO_4.

Yield of the compound $[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$ was 1g (73%)>

(iii)Synthesis of Diperoxotetra-aquo-μ-peroxo-μ-sulphato dithorium(IV) Pentahydrate,$[Th_2(O_2)_3SO_4(H_2O)_4].5H_2O$

To a solution of 1g (1.70 mmol) $Th(NO_3)_4.6H_2O$ in 20 cm^3 of water was added 1.70 mmol of A_2SO_4 (A=NH_4, Na or K) and the whole was stirred or *ca.* 10 min. until a clear solution was obtained. To this was added 15 cm^3(132.35 mmol) of 30% H_2O_2 whereupon a white product appeared. Stirring was continued for a further period of 10 min. Isolation, purification, and drying of the compound was accomplished in similar ways to those mentioned under (ii).

The yield of the compound $[Th_2(O_2)_3\ SO_4(H_2O)_4].5H_2O$ was 0.9g (65%)

Elemental Analyses

The methods of quantitative estimation of thorium, fluoride, peroxide, oxalate, sulphate, sodium, potassium, carbon, nitrogen, and hydrogen were described in Chapter II. The results of elemental analyses are displayed in Table 4.1.

RESULTS AND DISCUSSION

That the peroxo-metal compounds can be stabilised under suitably chosen heteroligand environment has been earlier emphasised by us.[8,9, 11-13] In order to gain an access to the synthesis of newer heteroligand peroxothorates(IV), simple heteroligands viz., fluoride (F^-), oxalate ($C_2O_4^{2-}$), and sulphate (SO_4^{2-}) were chosen for the present work as these ligands are not only known to stabilise Th(IV) oxidation level but their detection and determination are rather easy. Moreover, IR spectroscopic detection of peroxide (O_2^{2-}) in such systems is not expected to be difficult in the presence of the chosen ligands. Thus, a clean characterisation was anticipated to be rather easy. Since each of the aforementioned heteroligands and peroxide (O_2^{2-}), independent of each other, forms stable compounds[15] with the chosen metal, it was rational to expect that under appropriate experimental conditions both the selected heteroligands and peroxide could be made to simultaneously coordinate with the metal centre.

Table 4.1 : Analytical data of $A_2[Th(O_2)F_2(OH)_2].nH_2O$ (A=NH_4, n=3; A=Na or K, n=1) and $[Th_2(O_2)_3L(H_2O)_4].5H_2O$ (L=C_2O_4 or SO_4)

Compounds	Analysis[a] (%)					
	A or N	Th	O_2^{2-}	$C_2O_4^{2-}$	SO_4^{2-}	F^-
$(NH_4)_2[Th(O_2)F_2(OH)_2].3H_2O$	6.58 (6.62)	54.9 (54.83)	7.3 (7.56)	-	-	8.65 (8.98)
$Na_2[Th(O_2)F_2(OH)_2].H_2O$	11.7 (11.52)	58.32 (58.14)	7.8 (8.02)	-	-	9.48 (9.52)
$K_2[Th(O_2)F_2(OH)_2].H_2O$	17.83 (18.13)	53.3 (53.80)	7.1 (7.42)	-	-	8.67 (8.81)
$[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$	-	58.22 (57.92)	11.68 (11.98)	10.62 (10.92)	-	-
$[Th_2(O_2)_3SO_4(H_2O)_4].5H_2O$	-	57.81 (57.34)	11.65 (11.89)	-	12.07 (11.87)	-

[a] Calculated values in parenthesis.

While freshly prepared hydrated thorium oxide, $ThO_2.nH_2O$, was used in the synthesis of fluoroperoxothorates(IV), aqueous solutions of thorium nitrate, hexahydrate, $Th(NO_3)_4.6H_2O$, were used for the preparation of the molecular complexes described herein. An important requirements for the successful synthesis of peroxometallate is the evaluation of an appropriate pH of the reaction medium. Accordingly, it was found that the reaction of hydrated thorium oxide with hydrogen peroxide, and hydrofluoric acid leading to the synthesis of the fluoroperoxo complex of thorium, was successful at a pH value 10-11. The conducive reaction medium pH for the synthesis of peroxo-oxalato complex of thorium was, however, found to be 7-8, while for the peroxo-sulphato complex it was found to be 2. The strategy for the reaction was that hydrated thorium oxide would first react with H_2O_2 to form a thorium peroxo species which in turn would interact with F^- to afford the desired compound. Notably important is the order of addition of the reagents, since a reverse order of addition of the reactants is detrimental to the successful synthesis of fluoroperoxothorates(IV) owing to the formation of a sparingly soluble binary fluoro complex of thorium(IV).

The white gelatinous mass, resulting from the addition of hydrogen peroxide to hydrated thorium oxide, was dissolved by careful addition of aqueous HF. The pH value of the reaction solution was then raised slowly by dropwise addition of aqueous ammonia or alkali-metal hydroxides until the $Th:O_2^{2-}$ ratio in the product isolated therefrom reached a 1:1 stoichiometry. Products

isolated at a pH relatively lower than 10-11, on being analysed, gave a nonstoichiometric composition of thorium, O_2^{2-}, and F^-. It is therefore evident that although the O_2^{2-} uptake process might have been in progress at a lower pH, a compound of definite stoichiometry could only be synthesised at pH 10-11. However, apart from O_2^{2-} and F^- being coordinated to the Th(IV) centre, two hydroxyl (OH^-) groups per thorium were also found to be present in the compounds synthesised under the conditions enumerated (vide experimental). Thus, it is evident that although a high concentration of alkali media is unavoidable for the synthesis of peroxofluorothorates(IV), at a high pH OH^- seems to effectively compete with O_2^{2-} and F^- for coordination with metal centre thereby resulting into the formation of hydroxofluoroperoxothorates(IV), as obtained. Incorporation of OH^- groups is explained in terms of an extensive hydrolysis of the Th^{4+} ion in aqueous solution at a high pH.[1,16]

The diperoxotetra-aquo-μ-peroxo-μ-oxalato dithorium(IV) pentahydrate, $[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$, and diperoxo-tetra-aquo-μ-peroxo-μ-sulphatodithorium(IV) pentahydrate, $[Th_2(O_2)_3SO_4(H_2O)_4].5H_2O$, were synthesised directly from the reaction of an aqueous solution of $Th(NO_3)_4.6H_2O$ with $A_2C_2O_4$ and A_2SO_4 (A=Na, K or NH_4), respectively, and H_2O_2. The appropriate pH required for the synthesis of $[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$ was ascertained to be 7-8, maintained by the addition of aqueous ammonia or 15% solution of AOH (A=Na or K). The reaction leading to the corresponding sulphato complex was, however, found to be complete at pH 2, attained spontaneously. In order to ascertain the effect of pH, similar reactions were conducted between pH 2

and 9, however, the products isolated were found to be similar to the one obtained at a pH value of 2. This causes us to state that the dimeric $[Th_2(O_2)_3SO_4(H_2O)_4].5H_2O$ compound once formed at pH 2 does not undergo any change in its composition within the aforesaid pH range.

A point worth commenting on at this stage is that while fluoroperoxothorates(IV) contain hydroxo ligands, the molecular heteroperoxo complexes containing either oxalato or sulphato involve aquo ligands. Evidently, this difference must be owing to the fact that the latter compounds were synthesised at a pH considerably lower than that of the fluoroperoxothorates(IV). It is believed that at a pH lower than that mentioned for the synthesis of fluoroperoxothorates(IV), Th(IV) exists as aquated species and partial substitution of H_2O molecules by O_2^{2-} and SO_4^{2-} or $C_2O_4^{2-}$ leads to the kind of compounds obtained herein. In this way, the synthesis of heteroligand peroxothorium(IV) complexes of the types $A_2[Th(O_2)F_2(OH)_2].nH_2O$ (A=NH_4, n=3; A=Na or K, n=1) and $[Th_2(O_2)_3L(H_2O)_4].5H_2O$ (L=C_2O_4 or SO_4) has been achieved.

Characterisation and Structural Assessment

All the compounds were obtained as white microcrystalline products and were found to be stable for a prolonged period. The stability of the compounds was checked by the analysis of O_2^{2-} content from time to time. Recording of ESR spectra on solids at room temperature and results of magnetic susceptibility measurements provide evidence for the diamagnetic nature of the

products concurrent with the occurrence of Th(IV) in each of the compounds. The compounds are practically insoluble in water thus precluding their molar conductance measurements. Unlike the fluoroperoxothorates(IV) the peroxo-oxalato and peroxosulphato compounds were obtained as molecular complexes. All the peroxothorium compounds mentioned herein slowly decompose in dilute sulphuric acid, liberating hydrogen peroxide quantitatively, and thus facilitate determination of active oxygen content. The importance of the chemical determination of active oxygen content has been emphasised earlier.[17,18] In the present work, this was accomplished by redox titration separately involving standard Ce^{4+} solution as well as standard $KMnO_4$ solution. Redox titrations were performed in the presence of boric acid in order to prevent any loss of active oxygen. The results of chemical analyses of fluoroperoxothorates gave $Th:F:O_2^{2-}$ as 1:2:1 while those for molecular complexes $Th:L(C_2O_4^{2-}$ or $SO_4^{2-}): O_2^{2-}$ were found to be 2:1:3 in accord with their formulae.

Infrared and laser Raman spectroscopic studies were carried out on all the compounds and the results (Table 4.2) were found to be in order with the assigned formulae. The significant features of the IR spectra of $A_2[Th(O_2)F_2(OH)_2].nH_2O$ ($A=NH_4$, n=3; A=Na or K, n=1) involve absorptions due to coordinated fluoride, coordinated peroxide, coordinated OH^- and those of uncoordinated water. The band at *ca.*850 cm^{-1}, though weak in intensity, is typical of the ν_{O-O} mode of O_2^{2-} and is indicative of triangularly bonded bidentate chelating O_2^{2-} (C_{2v}) group,

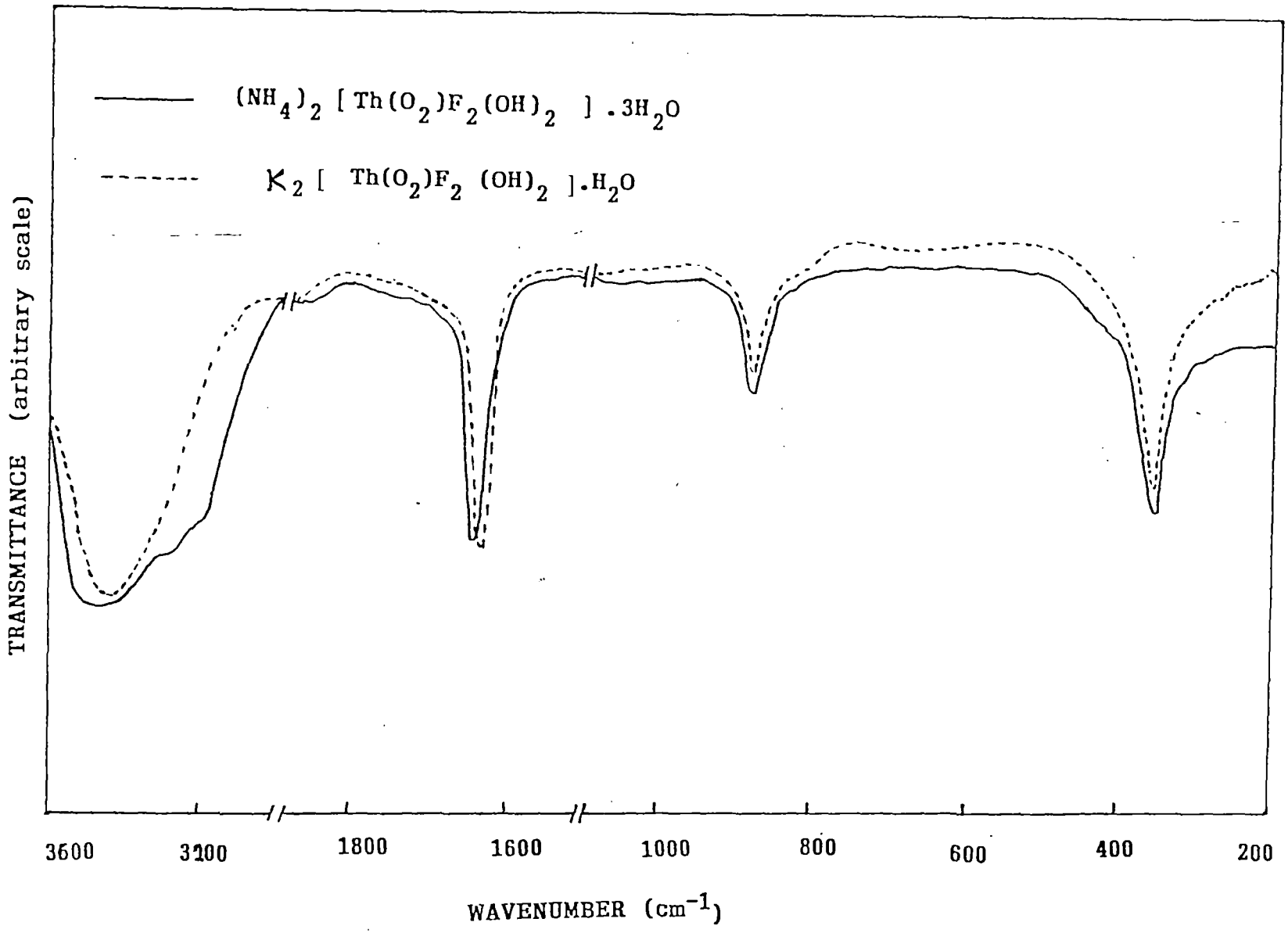
Table 4.2 : Structurally significant IR and LR bands of $A_2[Th(O_2)F_2(OH)_2].nH_2O$ (A=NH_4, n=3; A=Na or K, n=1) and $[Th_2(O_2)_3L(H_2O)_4].5H_2O$. (L = C_2O_4 or SO_4)

Compound	IR(cm^{-1})	LR(cm^{-1})	Assingments
$(NH_4)_2[Th(O_2)F_2(OH)_2].3H_2O$	850w	850	ν_{O-O}
	355m		ν_{Th-F}
	3560s		$\nu_{O-H}(OH^-)$
	3420s		$\nu_{O-H}(H_2O)$
	1640s		δ_{H-O-H}
$Na_2[Th(O_2)F_2(OH)_2].H_2O$	845w	845	ν_{O-O}
	355m		ν_{Th-F}
	3555s		$\nu_{O-H}(OH^-)$
	3415s		$\nu_{O-H}(H_2O)$
	1638s		δ_{H-O-H}
$K_2[Th(O_2)F_2(OH)_2].H_2O$	850w	845	ν_{O-O}
	360m		ν_{Th-F}
	3565s		$\nu_{O-H}(OH^-)$
	3425s		$\nu_{O-H}(H_2O)$
	1635s		δ_{H-O-H}

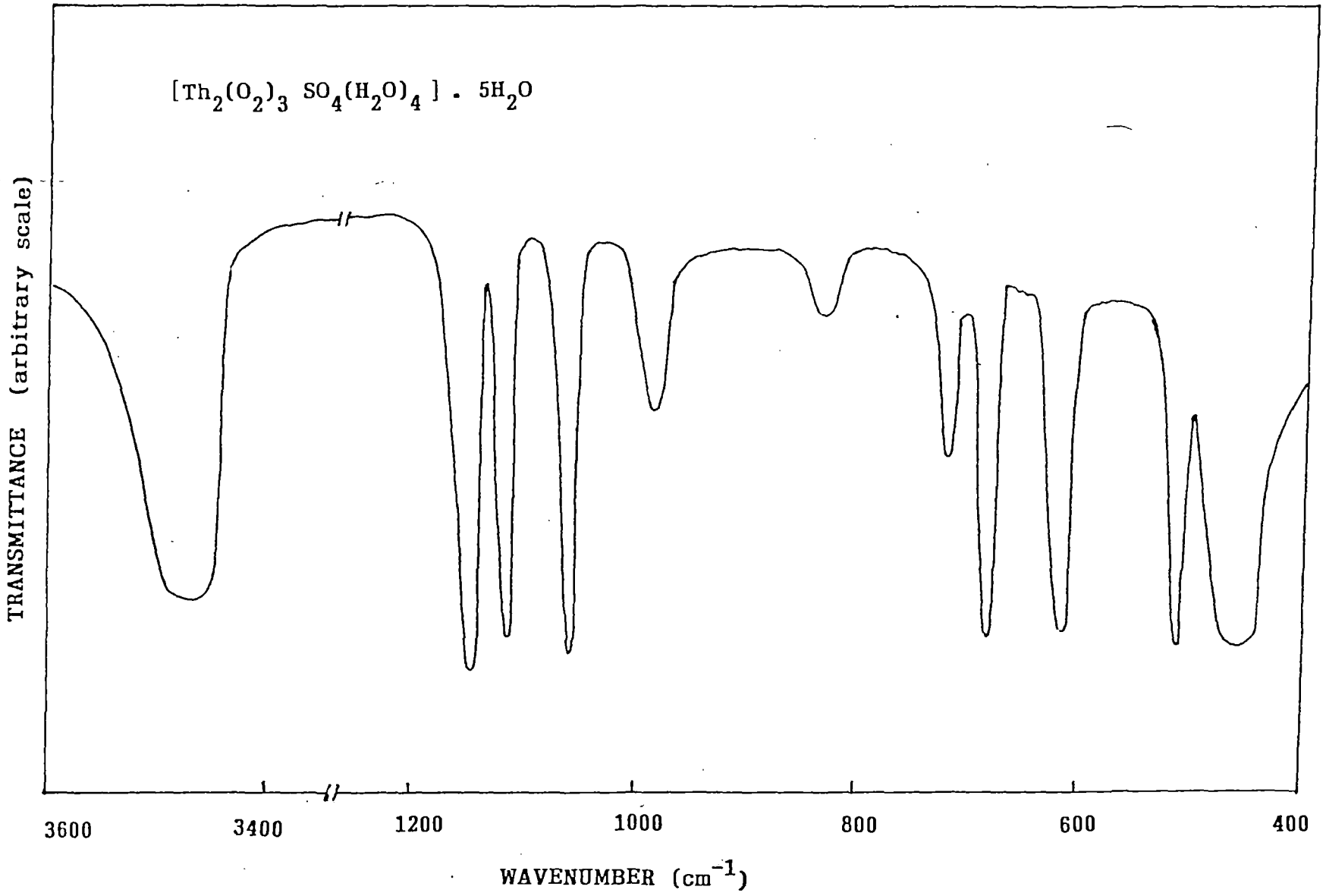
Table 4.2 (Contd.)

$[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$	835w	835	ν_{O-O}
		845	
	725m		$\rho_r(H_2O)$
	1640s		δ_{H-O-H}
	3455s		ν_{O-H}
	1670s		$\nu_{as}(O-C-O)$
	1360w		
	1320m		$\nu_s(O-C-O)$
	780m		
	750w		δ_{O-C-O}
$[Th_2(O_2)_3SO_4(H_2O)_4].5H_2O$	830w	835	ν_{O-O}
		845	
	728m		$\rho_r(H_2O)$
	1635s		δ_{H-O-H}
	3460s		ν_{O-H}
	1155s	1150	
	1115s	1120	ν_3
	1060s	1050	
	990m	975	ν_1
	677s	660	
	618	610	ν_4
	520s	550	
	460s,br	460	ν_2

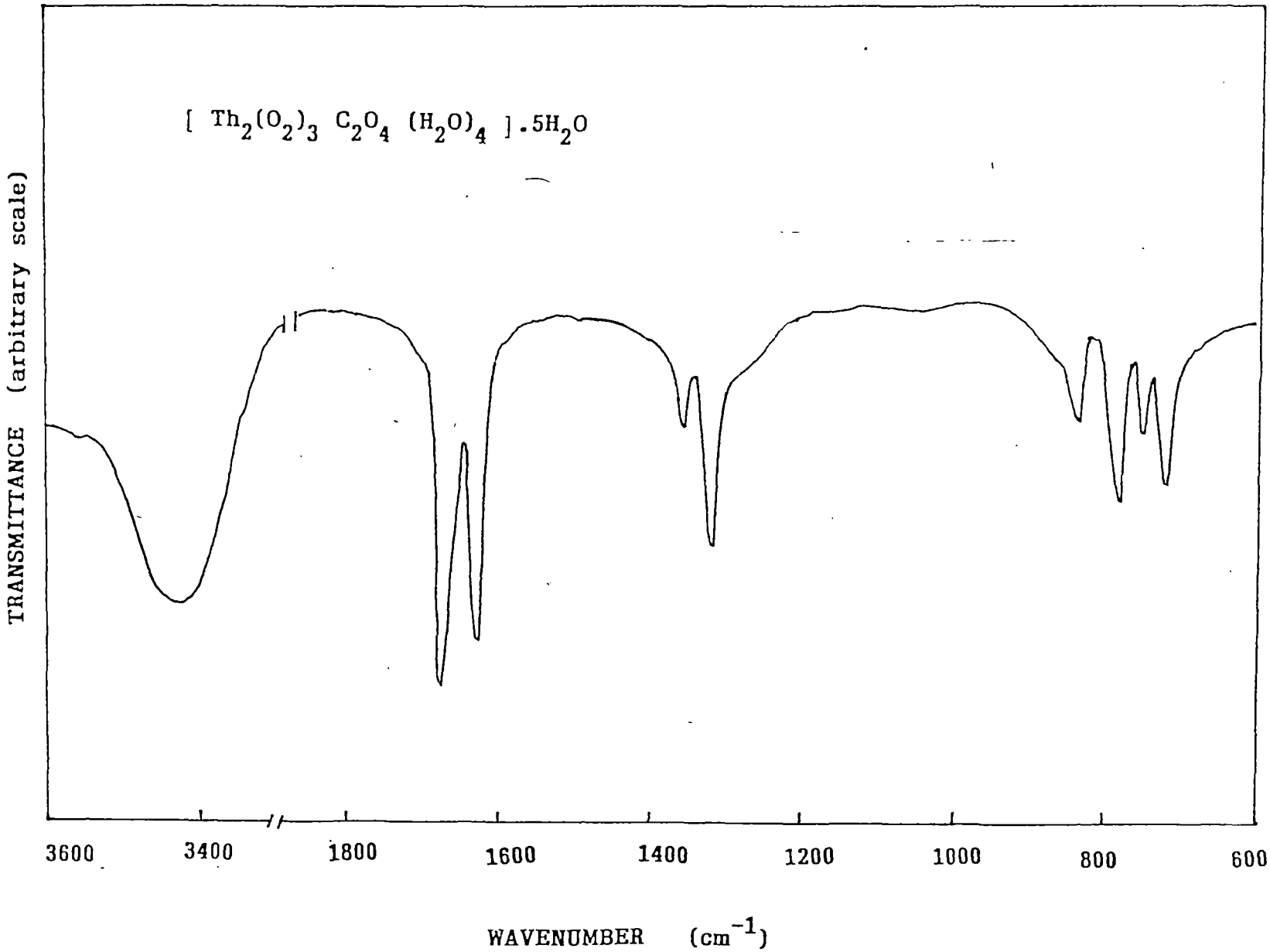
ν_{S-O}


$(NH_4)_2[Th(O_2)F_2(OH)_2].3H_2O$
$K_2[Th(O_2)F_2(OH)_2].H_2O$
TRANSMITTANCE (arbitrary scale)
3600
3200
1800
1600
1000
800
600
400
200
WAVENUMBER (cm^{-1})

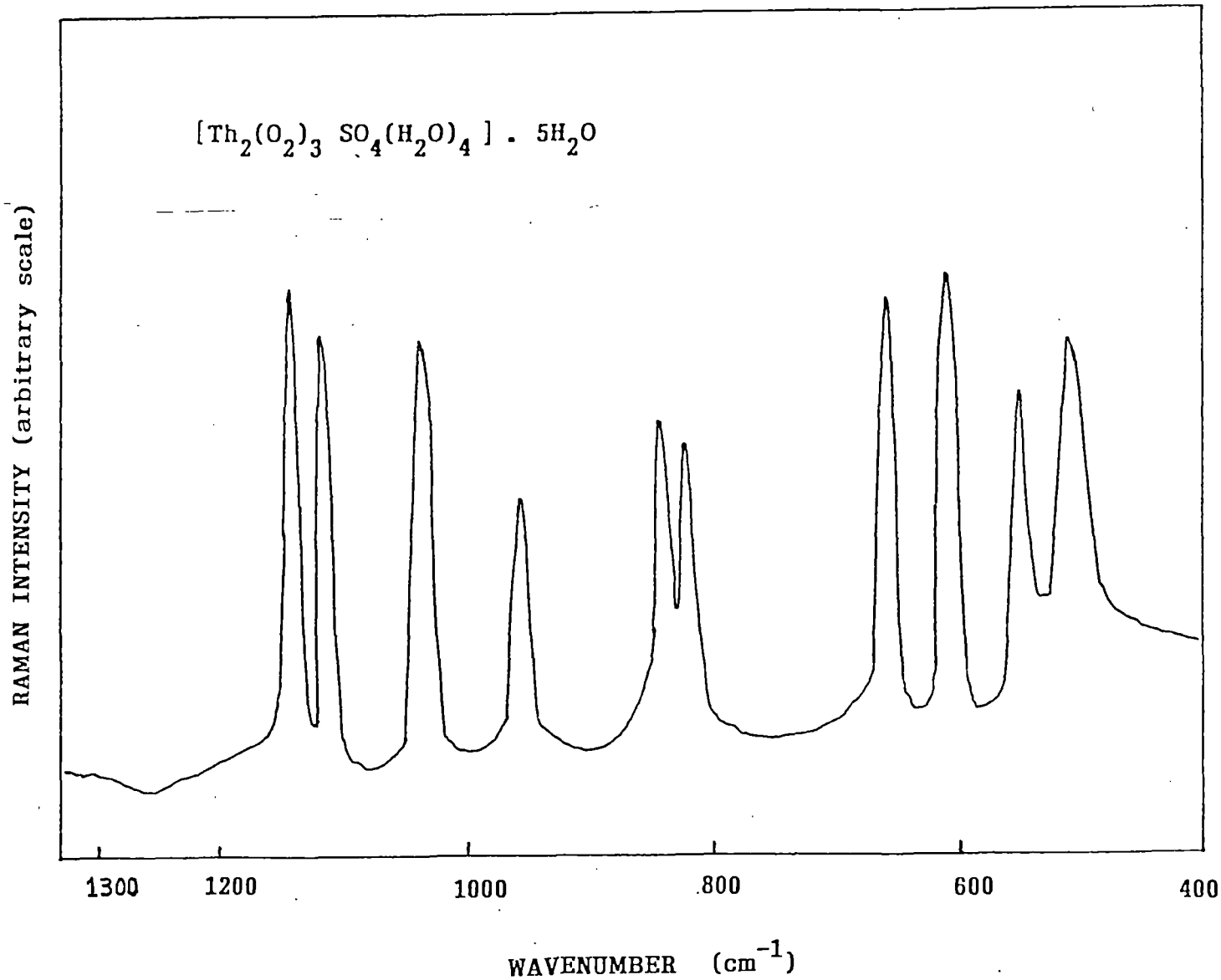
IR SPECTRUM


$[Th_2(O_2)_3\ SO_4(H_2O)_4]\ .\ 5H_2O$
TRANSMITTANCE (arbitrary scale)
3600
3400
1200
1000
800
600
400
WAVENUMBER (cm^{-1})

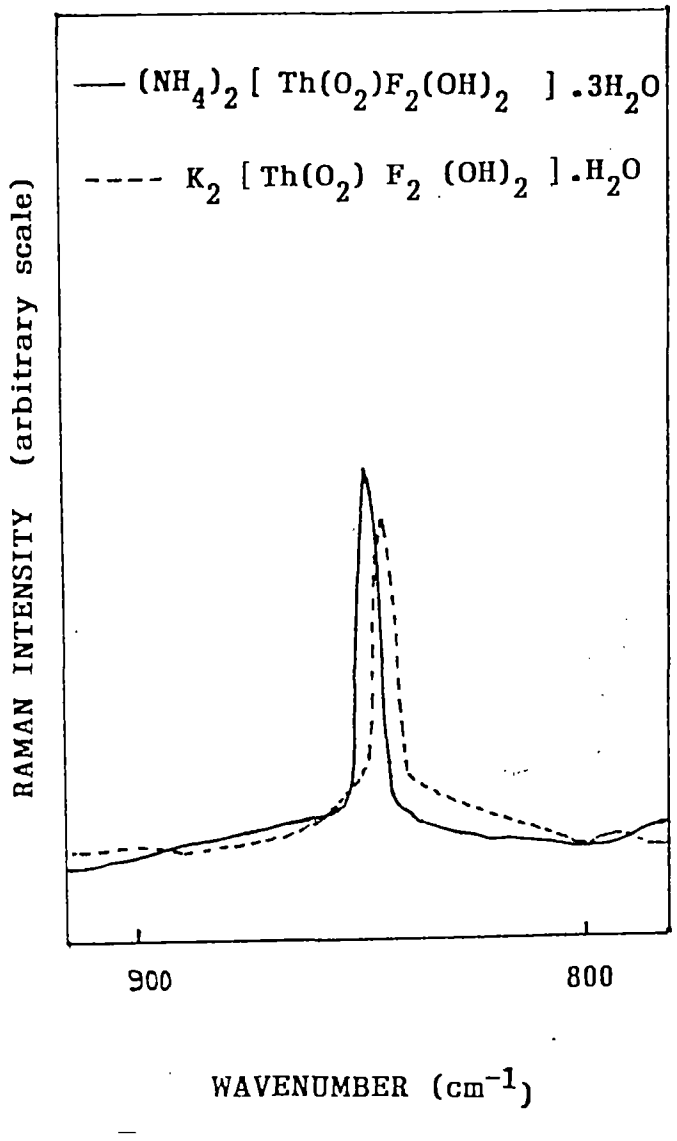
IR SPECTRUM


[Th2(O2)3 C2O4 (H2O)4].5H2O
TRANSMITTANCE (arbitrary scale)
3600
3400
1800
1600
1400
1200
1000
800
600
WAVENUMBER (cm-1)

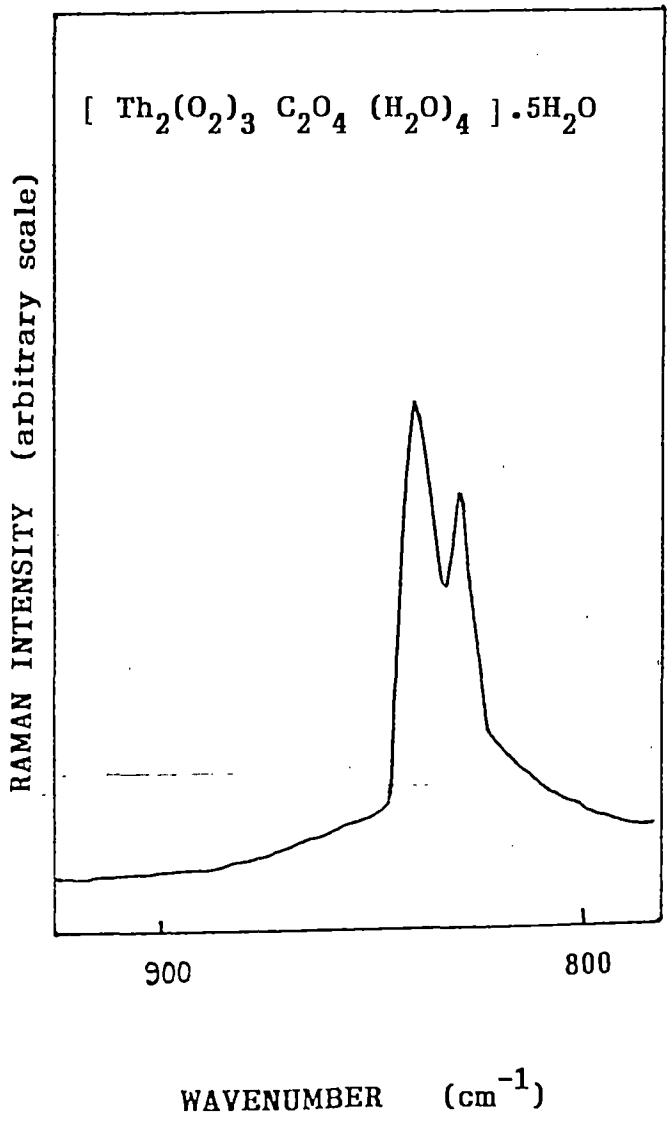
IR SPECTRUM


$[Th_2(O_2)_3\ SO_4(H_2O)_4]\ .\ 5H_2O$
RAMAN INTENSITY (arbitrary scale)
1300
1200
1000
800
600
400
WAVENUMBER (cm^{-1})

LR SPECTRUM



LR SPECTRUM

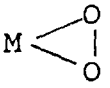


LR SPECTRUM

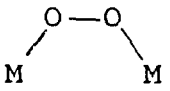
commonly encountered in peroxo-metallates.[17,18,19,20] This is complemented by a band at *ca.*850 cm^{-1} in the IR spectra. The IR absorption at *ca.* 360 cm^{-1} is attributed to the ν_3(Th-F) mode arising from the terminally coordinated F^- ligand.[21] The consistent appearance of a broad band at *ca.*3560 cm^{-1} led us to assign it to the O-H stretching mode of coordinated OH^- groups.[22a] The assignments of Th-O_2 stretching modes due to coordinated peroxide, however, were not attempted. The presence of several modes owing to Th-OH, Th-O_2 and Th-F in the low energy region make this task a difficult one. Over and above the band due to coordinated OH^- groups two other bands at *ca.* 3420 (ν_{O-H}) and *ca.* 1640 (δ_{H-O-H}) cm^{-1} were observed in the IR spectra of fluoroperoxothorium complexes which are typical of the ones expected for uncoordinated water molecules.[22b] In the ammonium salt, however, one additional sharp band appears at 1400 cm^{-1} which is clearly due to the N-H deformation mode of NH_4^+ ion. The ν_{N-H} modes arising from NH_4^+ could not be identified clearly owing to their overlap with the ν_{O-H} modes originating from the lattice water. Thus leaving aside the modes due to the NH_4^+ ion of $(NH_4)_2[Th(O_2)F_2(OH)_2].3H_2O$, the IR spectrum of all the compounds display a general feature.

The common features of the IR spectra of $[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$ and $[Th_2(O(_3)SO_4(H_2O)_4].5H_2O$ are the bands at *ca.* 835 w, *ca.* 725m, *ca.* 1640s and *ca.* 3455 cm^{-1} which owe their origins to ν_{O-O} (O_2^{2-}), ρ_r (coordinated water), δ_{H-O-H} and ν_{O-H}, respectively. Although from the appearance and observed positions for the δ_{H-O-H} and ν_{O-H} modes of water no

clear inference can be made regarding the nature of the water molecules, the consistent appearance of a distinct band at *ca.* 725 cm^{-1} provides evidence for the notion that at least some water molecules are coordinated[23] to the metal centres, in line with the formula assigned. Appearance of signals at *ca.* 830 and 845 cm^{-1} in the laser Raman (LR) spectra of both the compounds are indicative of the presence of two types of peroxo groups[20] viz. triangular bidentate type



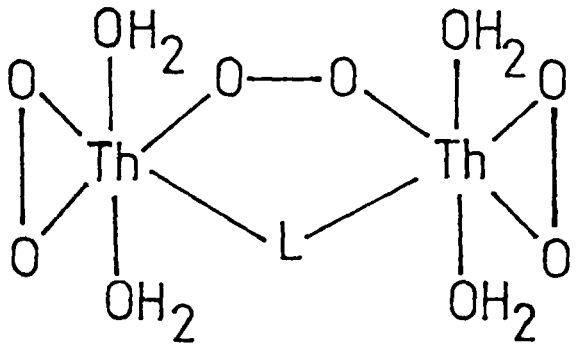
and bridging type



The IR spectrum of $[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$, in addition to the common features enumerated above, also exhibits patterns at 1670s (ν_{as},O-C-O), 1630w and 1320m (ν_3,O-C-O), 780m and 750w (δ_{O-C-O}) cm^{-1} which are in conformity with the occurrence of a bridging oxalato group. These assignments are in good agreement with those described in the literature.[25,26] That the oxalato group occurs as a bridging ligand is further augmented by the absence of any band at 1680-1750 cm^{-1} which is expected of a chelated oxalato group. Like for $[Th_2(O_2)_3C_2O_4(H_2O)_4].5H_2O$, the IR spectrum of the $[Th_2(O_2)_3SO_4(H_2O)_4].5H_2O$ complex also shows characteristic patterns for the occurrence of a bridging sulphato ligand. The bands arising from SO_4^{2-} are observed at 1155s, 1115s, 1060s cm^{-1} due to ν_3, at 990m cm^{-1} due to ν_1, at 677s, 618s and 520s cm^{-1} due to ν_4, and at 460s br due to ν_2 of the

coordinated sulphate.[24,27-29] The IR spectrum recorded on solids exhibited signals at 1150,1120,1050 cm^{-1} due to ν_3, at 975 cm^{-1} due to ν_1, at 660, 610 and 550 cm^{-1} due to ν_4 and 460 due to ν_2 of the sulphato ligand. The IR and LR spectral patterns particularly the appearance of ν_1 and ν_2 vibrations, the splitting of ν_3 and ν_4 into three bands each and the observation of ν_3 bands at a lower energy than generally observed for a chelated SO_4^{2-} ligand, supports the contention that SO_4^{2-} occurs as a bridging ligand in the compound under study.

Pyrolysis studies yielded similar results for both the molecular complexes. The results show that at about 100°C the compound starts losing weight and between 125-130°C almost all the peroxy oxygen is lost along with 4.5-5 water molecules. The remaining water molecules were lost above 150°C. The thermal studies therefore clearly suggest the presence of four coordinated water molecules and five uncoordinated water molecules in each of the compounds. Thus, on the basis of chemical analyses in conjuction with IR, lR, ESR and pyrolysis studies the following structure can be put to represent the complexes.



A similar structural representation was proposed[24] for $[Zr_2(O_2)_3SO_4(H_2O)_4].6H_2O$. The number of water molecules associated with such complexes needs to be characterised carefully as vibrational spectroscopy alone makes it very difficult to distinguish between lattice and coordinated water.[30]

The successful synthesis of peroxothorates(IV) calls for an internal comparison to be made with that of an earlier work on peroxotitanates(IV),[9,31] and peroxozirconates(IV),[14] reported from this laboratory, particularly because Ti, Zr and Th all belong to group IVB of the periodic table. The points that emerge out of the comparative studies are listed below.

(i) While the mono- and di-peroxofluoro complexes can be obtained for Ti[9,31] and Zr,[14] no diperoxofluorothorates could be obtained under the present experimental conditions.

(ii) All three elements Ti, Zr and Th permit synthesis of fluoroperoxo compounds. However, while the fluoroperoxo-titanates(IV),[9,31] contain a Ti(IV) centre and fluoroperoxozirconates(IV)[14] contain a zirconyl (ZrO^{2+}) centre, the fluoroperoxothorates(IV) (present work) have been shown to contain hydroxo(OH^-) groups bonded to the metal centre.

Thus from the results of the present investigation, it is evident that under the appropriate reaction conditions, it is not only possible to accomplish the synthesis of both heteroligand peroxothorates as well as molecular peroxothorium complexes but such a reaction strategy may also serve as a paradigm for the synthesis of new heteroligand peroxothorium(IV) compounds.

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CHAPTER V

COMPLEX PEROXOURANATES. A PRACTICAL SYNTHESIS AND ASSESSMENT OF STRUCTURE OF $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$, STUDY OF ITS REACTION PROFILE WITH $SO_2(g)$, $CO_2(g)$, AND $NO_2(g)$ IN AQUEOUS MEDIUM AND A DIRECT SYNTHESIS OF $A_2[UO_2(O_2)F_2].nH_2O$ ($A=NH_4$, $n=0$; $A=K$, $n=1$) AND STUDY OF REACTION OF $(NH_4)_2[UO_2(O_2)F_2]$ WITH $SO_2(g)$

The relevance of research in the area of peroxo-element chemistry has been elaborated in Chapter I. It has been noted in Chapter I and subsequently in Chapter III and Chapter IV that peroxo-chemistry of heavier metals, particularly actinides, have been rather sparsely dealt with. This may, in part, be owing to the

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A part of the work described herein is under revision:
J.Chem.Soc., Dalton Trans.

complexity involved in peroxo-actinide chemistry.[1] As a case in point, peroxo-uranium chemistry is rather complex. Consequently, reports on heteroligand peroxouranates is rather scant except for those of carbonato-,[2,3] oxalato-,[2,4] sulphato-,[2,4] and fluoroperxouranates.[2,5] A series of fluoro(peroxo)uranates(VI) have been reported from this laboratory only in 1985.[5] In addition, a few molecular peroxouranium compounds are known which include $UO_2(O_2).nH_2O$[6] (n=2 or 4), $UO_2(O_2)L$[7] (L=Ph_3PO, Ph_3AsO, or pyNO), and dioxoperoxouranium(VI) complexes containing glycine, EDTA, 1,10 phenanthroline, 2,2'bipyridyl as coligands[8] and few more with other organic ligands[9,10] and Schiff bases.[11] A perusal of literature revealed that in contrast to monoperoxouramates(VI), such complexes with $U:O_2^{2-}$ ratio 1:>1 have been far less dealt with. Guided by these considerations, our interest was particularly drawn to dinuclear "peroxo-uranium" systems with O_2^{2-}:U being 3:2. The reason was threefold, first, to provide an access to such a compound, second, to spectroscopically ascertain the modes of coordination of peroxide ligands to the metal centre and third, to investigate the reaction profiles of the compound with polar inorganic substrates in aqueous medium and to rationalise the reaction sequence by isolation of products at different stages of the reaction.

In addition, as a sequel to our interest in investigating the reactivity of non-group VIII metal-peroxides towards small inorganic molecules in aqueous medium (Chapter III), it became necessary to synthesise the complex species $[UO_2(O_2)F_2]^{2-}$. It was also of interest to explore the possibility of obtaining fluorosulphato complex of the metal. The synthesis of the

complex, however, was not very simple as it required at least two delicate manipulations; first, the use of alkali-free moist dioxouranium(IV). species, $U_2O_7^{2-}$, and second, the involvement of hydrofluoric acid which requires a careful handling. Therefore developing a rather straight synthetic route to the complex also became imperative.

A striking feature in the context of reactivity of peroxoactinide chemistry is that reports concerning investigation of reactivity of peroxouranate towards small inorganic molecules appear to be non-existent. The potential of peroxouranium compound as an efficient oxidant for organic substrate was, however, been demonstrated. The strategy of the present reactivity studies was anticipated to provide a methodology for a smooth access to binary and mixed ligand fluoro complexes.

Accordingly, the Chapter under discussion presents an account of the synthesis of a new peroxouranates(VI), $(NH_4)_2[U_2O_4\cdot(O_2)_3(H_2O)_2].4H_2O$ followed by an investigation of its reactivity in aqueous medium with $SO_2(g)$, $CO_2(g)$, and $NO_2(g)$. Also included in this Chapter is a description of an improved synthesis of $A_2[UO_2(O_2)F_2].nH_2O$(A = NH_4, n=0; A=K, n=1) and the reaction of the ammonium salt of the complex, as a typical case, with $SO_2(g)$. The course of each reaction has been rationalised based upon isolation and characterisation of the products at different stages of the reactions. An interpretative account of interesting H-bonding feature in the uranyl fluoro complexes has also been presented.

EXPERIMENTAL

Chemicals used were all of reagent grade quality.

(i) Synthesis of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$

To 1g (2.79 mmol) of $UO_3.4H_2O$, 12 cm^3 (105.78 mmol) of 30% H_2O_2 was added. The mixture was stirred for 5 min. followed by dropwise addition of aqueous ammonia (sp. gr. 0.9) until a clear dark orange coloured solution was obtained. The pH value of the solution recorded at this stage was 8-9. Stirring was continued for a further period of *ca.* 10 min, and then a yellow microcrystalline product was precipitated out by the addition of ice-cold ethanol (*ca.* 20 cm^3). The product, after being left to stand for 30 min., was isolated by filtration, washed 3 or 4 times with ethanol and finally dried *in vacuo* over conc.H_2SO_4. The yield of the compound, $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$, was 0.8g (74%).

(ii) Reaction of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ with $SO_2(g)$, $CO_2(g)$, and $NO_2(g)$

(a) *Isolation of yellow Dioxo(monoperoxo)uranium(VI) Tetrahydrate,* $UO_2(O_2).4H_2O$

The yellow $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ (1g, 1.28 mmol) was dissolved in 20 cm^3 of deoxygenated water. The aliquot of water used for reactivity studies was purged with the substrate gas prior to dissolving the complex in order to avoid any decomposition of the compound before its coming into contact with the substrates. In three separate

experiments, $SO_2(g)$, $CO_2(g)$, and $NO_2(g)$ was bubbled through the yellow solution under constant stirring until a microcrystalline product was thwarted from the solution. The pH value of the reaction solution at this stage was *ca.*5. The compound was separated by filtration, washed repeatedly with ethanol, and then dried *in vacuo* over conc. H_2SO_4. The yield of $UO_2(O_2).4H_2O$ was 0.7g (73%).

(b) *Isolation of yellow* $(NH_4)_2[UO_2(SO_4)_2].2H_2O$, $(NH_4)_2[UO_2(CO_3)_2].5H_2O$, *and a nitrato product*

Through a solution of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ (1g, 1.28 mmol) in 20 cm^3 of pretreated (as described under (a)) deoxygenated water, $SO_2(g)$, $CO_2(g)$ or $NO_2(g)$ was bubbled through until the yellow intermediate $UO_2(O_2).4H_2O$, which appeared at pH *ca.*5, dissolved completely resulting into a clear solution. The pH at this point of the reaction was recorded to be *ca.* 2 for $SO_2(g)$ and *ca.*3 for $CO_2(g)$ or $NO_2(g)$ reactions. Addition of precooled ethanol in each case resulted into the precipitation of a yellow microcrystalline compound. Starting from 1.0g of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$, the yield of $(NH_4)_2[UO_2(SO_4)_2].2H_2O$, was 1.1g (80%;), and that of $(NH_4)_2[UO_2(CO_3)_2].5H_2O$ was 1g (73%). The uranyl-nitrato product obtained from the reaction of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ and $NO_2(g)$ could not be assigned a definite formula.

(iii) Synthesis of $(NH_4)_2[UO_2(O_2)F_2]$ **and** $K_2[UO_2(O_2)F_2].H_2O$

A 1.0g (2.79 mmol) sample of $UO_3.4H_2O$ and 2.0g (35.05 mmol) of

NH_4HF_2 or 2.73g (35.05 mmol) KHF_2 were mixed together and the mixture was dissolved in 20 cm^3 of water in a 250 cm^3 polyethylene beaker by slight warming over a steam-bath. The solution was filtered to remove any undissolved residue and cooled to room temperature. To this solution was added 24 cm^3 (211.78 mmol) of 30% H_2O_2 with stirring. The pH value of the reaction solution was then raised to 6 by dropwise addition of aqueous ammonia (sp. gr. 0.9) whereupon a yellow compound began to appear. On addition of 25 cm^3 of ethanol, the complete precipitation of the product was achieved. The yellow product is collected by suction filtration and washed with ethanol (4x10cm^3) and finally dried *in vacuo*. The yield of $(NH_4)_2[UO(O_2)F_2]$ was 1.0g (95%), while that of $K_2[UO_2(O_2)F_2].H_2O$ was 1.1g (88%).

(iv) Reaction of $(NH_4)_2[UO_2(O_2)F_2]$ with $SO_2(g)$

Through a suspension of $(NH_4)_2[UO_2(O_2)F_2]$ (1g, 2.65 mmol) in 20 cm^3 of deoxygenated water, $SO_2(g)$ was passed under constant stirring until a clear yellow solution was obtained. The pH value of the reaction solution at this stage was *ca.* 2. The solution thus obtained was concentrated, to half of its volume, over steam-bath and a yellow crystalline product was then isolated by the addition of precooled ethanol. The product was separated by filtration, washed with ethanol, and then dried *in vacuo* over conc. H_2SO_4. The yield of $(NH_4)_2[UO_2(SO_4)F_2].H_2O$ was 9.4g (77%).

Elemental Analysis

The results of elemental analysis have been given in Table 5.1, while the spectral data are provided in Table 5.2.

Table 5.1 : Analytical data of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$; $UO_2(O_2).4H_2O$; $(NH_4)_2[UO_2(SO_4)_2].2H_2O$; $(NH_4)_2[UO_2(CO_3)_2].5H_2O$; $A_2[UO_2(O_2)F_2].nH_2O$ (A=NH_4, n=0; A=K, n=1) and $(NH_4)_2[UO_2(SO_4)F_2].H_2O$

Compound	Analysis [a] (%)				
	A or N	U	O_2^{2-}	SO_4^{2-} or C	F^-
$(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$	3.54	61.31	12.41		
	(3.59)	(61.01)	(12.30)	(-)	(-)
$UO_2(O_2).4H_2O$		63.54	8.58		
	(-)	(63.63)	(8.55)	(-)	(-)
$(NH_4)_2[UO_2(SO_4)_2].2H_2O$	5.37	44.51		36.23	
	(5.24)	(44.55)	(-)	(35.96)	(-)
$(NH_4)_2[UO_2(CO_3)_2].5H_2O$	6.72	44.57		4.58	
	(6.76)	(44.54)	(-)	(4.5)	(-)
$(NH_4)_2[UO_2(O_2)F_2]$	7.55	63.80	3.38	9.82	
	(7.45)	(63.29)	(8.51)	(-)	(10.10)
$K_2[UO_2(O_2)F_2].H_2O$	18.10	54.72	6.93	8.02	
	(17.93)	(54.56)	(7.34)	(-)	(8.71)
$(NH_4)_2[UO_2(SO_4)F_2].H_2O$	5.82	52.16		20.14	7.95
	(6.12)	(51.95)	(-)	(20.96)	(8.29)

[a] Calculated values are in parenthesis.

RESULTS AND DISCUSSION

Uranyl, UO_2^{2+} seems to form complexes with peroxide rather easily. But the UO_2^{2+} ——— H_2O_2 system is very complicated since a number of peroxouranate species with a variety of compositions are formed under slightly varying experimental conditions.[1,2] In an earlier work, conducted in this laboratory, it was shown that a monoperoxo complex of UO_2^{2+} predominantly existed upto a pH value of *ca.*7. [4] It thus appeared logical to anticipate the formation of a peroxouranate complex with UO_2^{2+}:O_2^{2-} ratio of 1:>1 at a relatively higher pH value (pH>7) of the reaction medium. We expected that such a reaction strategy might conduce formation of the kind of a compound looked for. As a follow up of the elicit strategy, the reaction of $UO_3.4H_2O$ with H_2O_2 was conducted at a pH value of 8-9 of the reaction medium which led to the successful synthesis of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$. The pH of the reaction solution was raised by the addition of aqueous ammonia which also served as the source of the counter-cation (NH_4^+). In this way a convenient access to the complex $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ has been provided. A very high yield and high purity of the product are additional advantages of the method.

The compound is yellow in colour and has been obtained as microcrystals. It is stable for days in the solid state. The compound is diamagnetic in nature, as expected.

The infrared spectra of the compound revealed structurally very significant informations (Table 5.2). While the $\nu_{U=O}$ band was

observed at 900s cm^{-1} in line with the presence of trans-linked O=U=O moiety,[13] the coordinated peroxides, however, exhibited two distinct ν_{O-O} absorptions at 860s [14-16] and 795w, br cm^{-1} (17) originating, respectively, from chelated and bridged peroxide groups. The observed positions and the intensities are in order with the assignments. The ν_2 and ν_3 modes of O_2^{2-} were observed in the 500-400 cm^{-1} region (Table 5.2). A notable point in this context is the small separation between the ν_2 and ν_3 modes which often resulted into a broad band, especially if the scanning in the region was fast. The IR signatures in support of the coordinated water was observed at 728w cm^{-1} due to the rocking mode of bonded water. The ν_{O-H} and δ_{H-O-H} modes for H_2O were observed in the expected regions. The ν_{O-H} region, however, was complicated owing to the presence of both coordinated and lattice water. In addition, the occurrence of ν_1 and ν_3 modes of NH_4^+, in the region where ν_{O-H} also appears, makes the pattern further complicated. The ν_4 mode of NH_4^+ was clearly located at 1400 cm^{-1}. Fortunately, absence of any other absorptions in the region enabled an unambiguous assignment of the observed band. Laser Raman(LR) spectrum of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ was recorded on solid. The LR signals at 905 cm^{-1} ($\nu_{U=O}$, trans-linked O=U=O), 855 cm^{-1} (ν_{O-O}, ν_1, chelated O_2^{2-}), 798 cm^{-1} (ν_{O-O}, ν_1, bridged O_2^{2-}), and at 495 cm^{-1} and 460 cm^{-1} due to ν_2 and ν_3 modes, respectively, of chelated peroxide are in conformity with the formula of the compound. These results enable the complex, $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$, to be envisioned as a dinuclear species with UO_2^{2+} centres being bridged by a O_2^{2-} ligand. In

addition, each of the UO_2^{2+} centres is also bound to a chelated peroxo and an aqua ligand (Fig. 1).

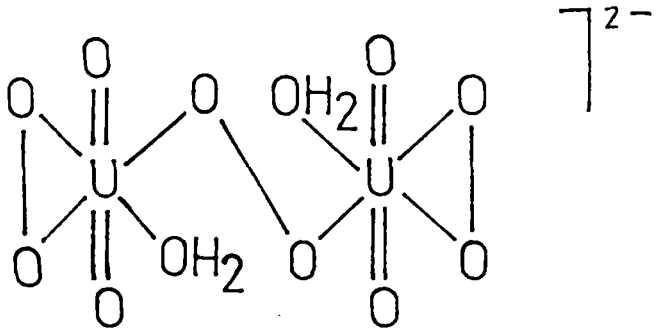


Fig. 1. Tentative structure of $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$

As noted in the introduction section of this Chapter, it was also of interest to synthesise $[UO_2(O_2)F_2]^{2-}$ and invdlve the species in reactivity studies. Based upon HSAB principle, it was perceived that besides O_2^{2-}, fluoride (F^-) would also coordinate simultaneously to uranyl (UO_2^{2+}) centre in the presence of each other to provide a direct access to stable fluoro(peroxo)-uranates(VI). With this in view, and also taking note of the problems (vide infra) encountered in the earlier synthesis,[5] a direct reaction between $UO_3.4H_2O$ and H_2O_2 in the presence of AHF_2 (A=NH_4 or K) at pH 5-6 was carried out. This has now led to a new and straight forward route the complex, $[UO_2(O_2)F_2]^{2-}$, species. One of the most significant point in the context of synthesis of $[UO_2(O_2)F_2]^{2-}$ has been the redundancy of aqueous hydrofluoric acid.

The compounds $A_2[UO_2(O_2)F_2].nH_2O$ (A = NH_4, n=0; K, n=1) are all yellow microcrystalline products. They can be stored in

polyethylene envelopes for years and their stability ascertained by estimating active oxygen contents periodically. Insolubility precluded their molar conductance measurements.

The IR spectral characteristics (Table 5.2) of the compounds bear one to one correspondence with those reported earlier.[5] Interestingly there are certain features in respect of N-H modes observed in the spectrum of $(NH_4)_2[UO_2(O_2)F_2]$ which, however, were not addressed to earlier. These features are now interpreted in terms of the occurrence of appreciable H-bonding involving N-H of NH_4^+ and coordinated F^-.

Symmetry consideration of both NH_4^+ ion and the surrounding acceptors is a crucial factor to the existence and extent of H-bonding. Information on geometric data of H-bond is largely based on X-ray diffraction studies and therefore are not very precise.[18] Vibrational spectroscopy, however, has proved to be rather a powerful technique to unravel H-bonding phenomenon[18,19]. Thus, the appearance of two bands at 1430 and 1470 cm^{-1} of approximately equal intensities in case of $(NH_4)_2[UO_2(O_2)F_2]$ connected with the ν_4 deformation frequency and the shift to slightly higher wave numbers than is usually observed for ammonium ion suggest the existence of hydrogen bonding in the complex.[20] In addition, the occurrence of a weak combination bond $(\nu_4+\nu_6)$[20] at 1715 cm^{-1} (which is absent in the spectrum of the corresponding $K_2[UO_2(O_2)F_2].H_2O$ provides a strong evidence for H-bonding involving NH_4^+ as the acceptor. The split of ν_4 mode into two well separated bands in the diammonium complex $(NH_4)_2[UO_2(O_2)F_2]$ can be explained in terms of occupance of two

unequivalent lattice sites by the ammonium ions rather than a mere distortion of the same[20]. That the broad band assigned to U-F vibrational mode appears appreciably lower (~ 350 cm^{-1}) than that in the spectrum of corresponding[5] K-salt or those of the salts of Rb or Cs (*ca.* 365 cm^{-1}) is a definite indication of involvement of F^- in N-H .... F type H — bonding. The spectral features for $\nu_{U=O}$ and ν_{O-O}, on the contrary, remains practically unaffected. This then, will lead one to expect a rather similar type of H-bonding in the ammonium salt of oxofluorouranates(VI).[21] Its IR spectrum, however, displayed an unsplit band owing to ν_4 mode of NH_4^+. Moreover no lowering of ν_{U-F} position was observed. It may therefore be inferred that if there is hydrogen bonding in $(NH_4)_2[UO_2(O_2)F_2]$, it is presumably not merely due to the presence of F^- but may also be due to the occurrence of O_2^{2-}. The O_2^{2-} by way of its bonding to uranyl (UO_2^{2+}) centre indirectly enhances the attraction between hydrogen in ammonium and the fluoride (F^-).

Reactivity

(i) *Reactions of* $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ *with* $SO_2(g)$, $CO_2(g)$ *and* $NO_2(g)$. *Isolation of* $UO_2(O_2).4H_2O$ *as a Unique Reaction Intermediate.*

Although peroxometal complexes exhibit a variety of reactions,[22] a lot is yet to be explored. In an earlier work, reported[23] from this laboratory, the reaction of a highly peroxygenated vanadate(V) complex, $K[V(O_2)_3]$, with $SO_2(g)$ was conducted and the results rationalised in terms of the products isolated at

Table 5.2 : Structurally significant IR and LR bands of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$; $UO_2(O_2).4H_2O$; $(NH_4)_2[UO_2(SO_4)_2].2H_2O$; $(NH_4)_2[UO_2(CO_3)_2].5H_2O$; $A_2[UO_2(O_2)F_2].nH_2O$ (A=NH_4, n=0; A=K, n=1) and $(NH_4)_2[UO_2(SO_4)F_2].H_2O$.

Compound	IR (cm^{-1})	LR(cm^{-1})	Assignment
$(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$	900s	905	$\nu_{U=O}$ (trans-linked)
	860m	855	ν_{O-O}
	3445s		ν_{O-H}
	1635		δ_{H-O-H}
	728w		ρ_r(H-OH)
	490	495	$\nu_2(U-O_2)$
	465	460	$\nu_3(U-O_2)$
	795w,br	798	ν_{O-O}(bridging)
$(NH_4)_2[UO_2(O_2)F_2]$.	900s	900	$\nu_{U=O}$
	885s	875	
	855s	850	ν_{O-O}
	355s,br		ν_{U-F}
	1430,1470		ν_{N-H}
	1710		$\nu_4 + \nu_6$
	2845		$2\nu_4$

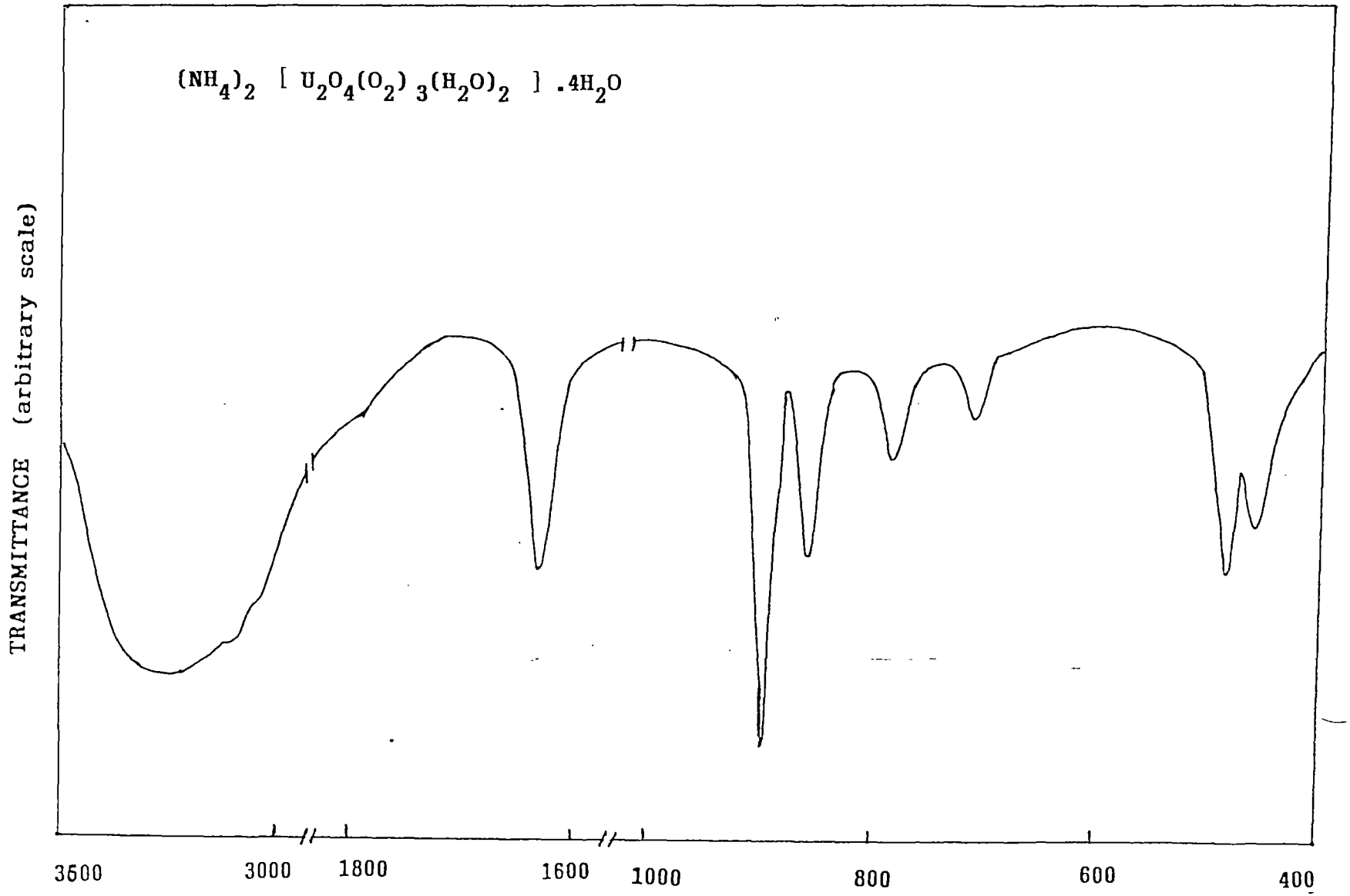
Table 5.2 (Contd.)

$K_2[UO_2(O_2)F_2].H_2O$	900s		$\nu_{U=O}$
	860s		ν_{O-O}
	360s		ν_{U-F}
	3445s,br		ν_{O-H}
	1640m		δ_{H-O-H}
$(NH_4)_2[UO_2(SO_4)_2].2H_2O$	900s	915	$\nu_{U=O}$ (trans-linked)
	1150,1120,	1160, 1115,	ν_3
	1070	1075	
	995		ν_1
	450		ν_2
	677,618,	670,625	ν_4
	597	585	
	3445s,br		ν_{O-H}
	1640m		δ_{H-O-H}
$(NH_4)_2[UO_2(CO_3)_2].5H_2O$	920s	905	$\nu_{U=O}$ (trans-linked)
	1602	1595	ν_1 (C-O)
	1209		ν_5 (C-O)
	3450s, br		ν_{O-H}
	1640m		δ_{H-O-H}

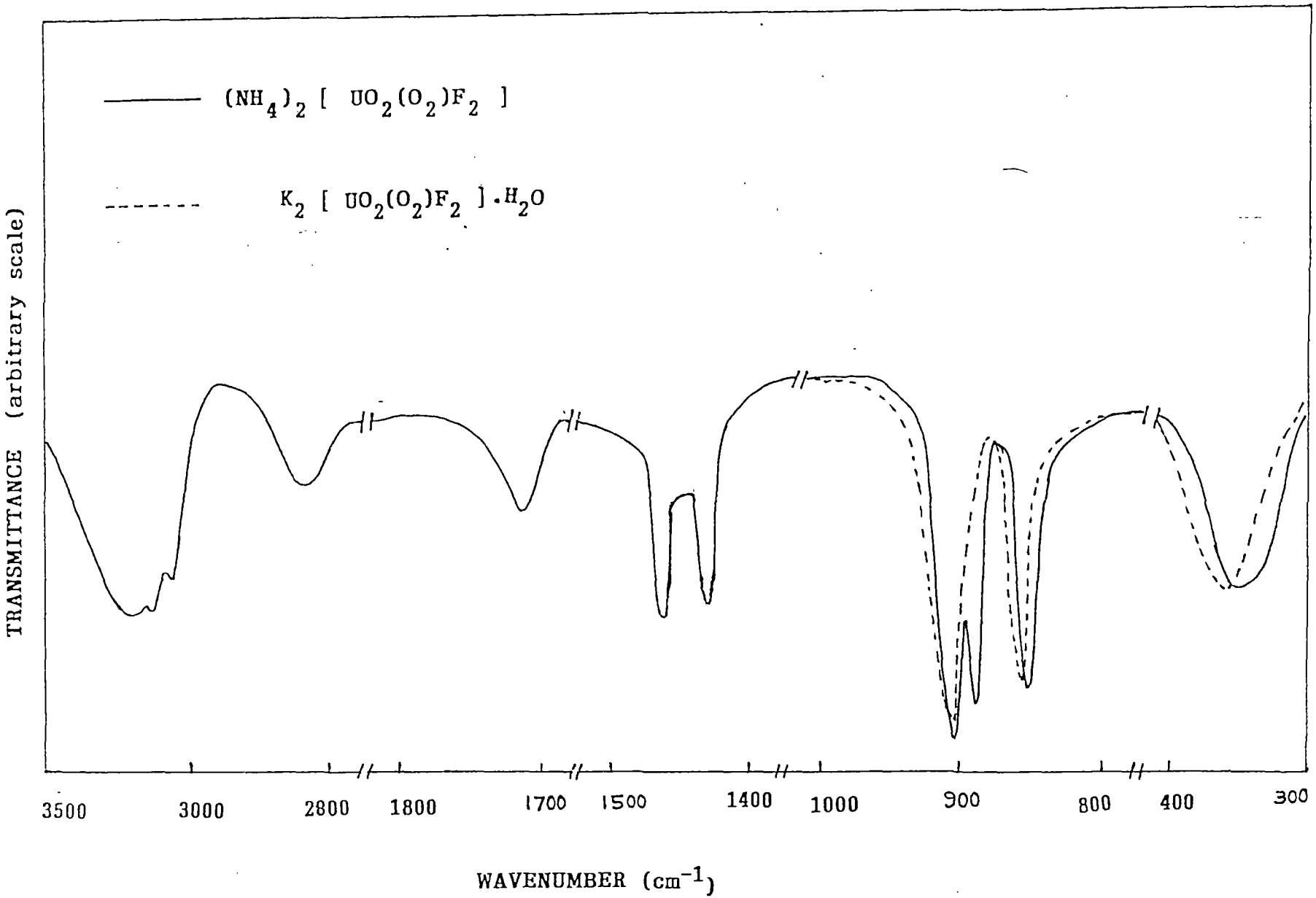
ν_{S-O}

Table 5.2 (Contd.)

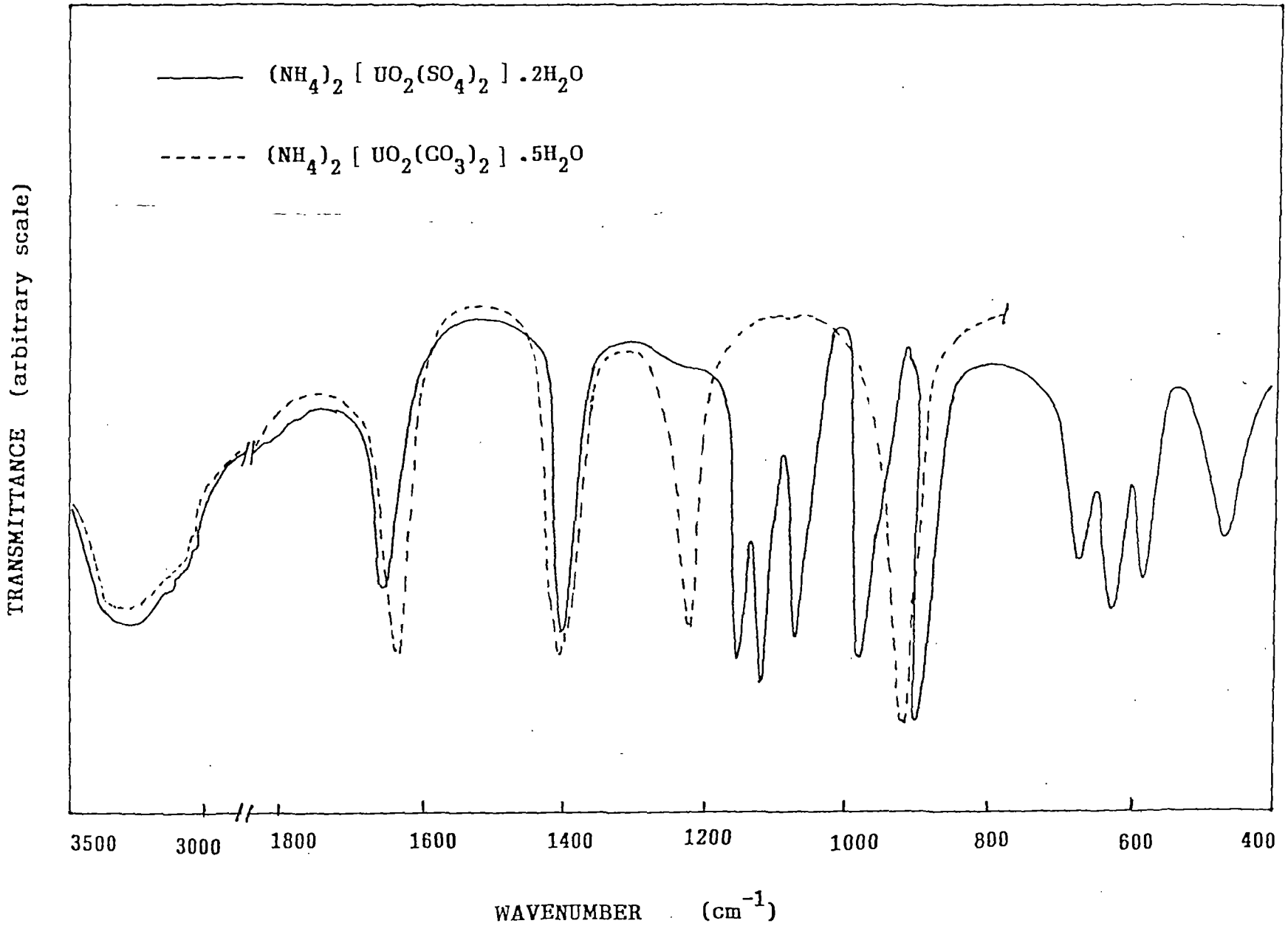
$UO_2(O_2).4H_2O$	905s	900	$\nu_{U=O}$ (trans-linked)
	860	860	ν_{O-O}
	1630m		δ_{H-O-H}
	728w		$\rho_r(H-O-H)$
	615m	620	$\nu_2(U-O_2)$
	597m	600	$\nu_3(U-O_2)$
$(NH_4)_2[UO_2(SO_4)F_2]$	900s		$\nu_{U=O}$ (trans-linked)
	1160,1120,1075		ν_3]
	995		ν_1] ν_{S-O}
	678,625,560		ν_4]
	455		ν_2]
	3450s, br		ν_{O-H}
	1640		δ_{H-O-H}
	370s		ν_{U-F}
	1430		ν_{N-H}
	1790		$\nu_4 + \nu_6$
	2850		$2\nu_4$


$(NH_4)_2$ [$U_2O_4(O_2)_3(H_2O)_2$] .$4H_2O$
TRANSMITTANCE (arbitrary scale)
3500
3000
1800
1600
1000
800
600
400
WAVENUMBER (cm^{-1})

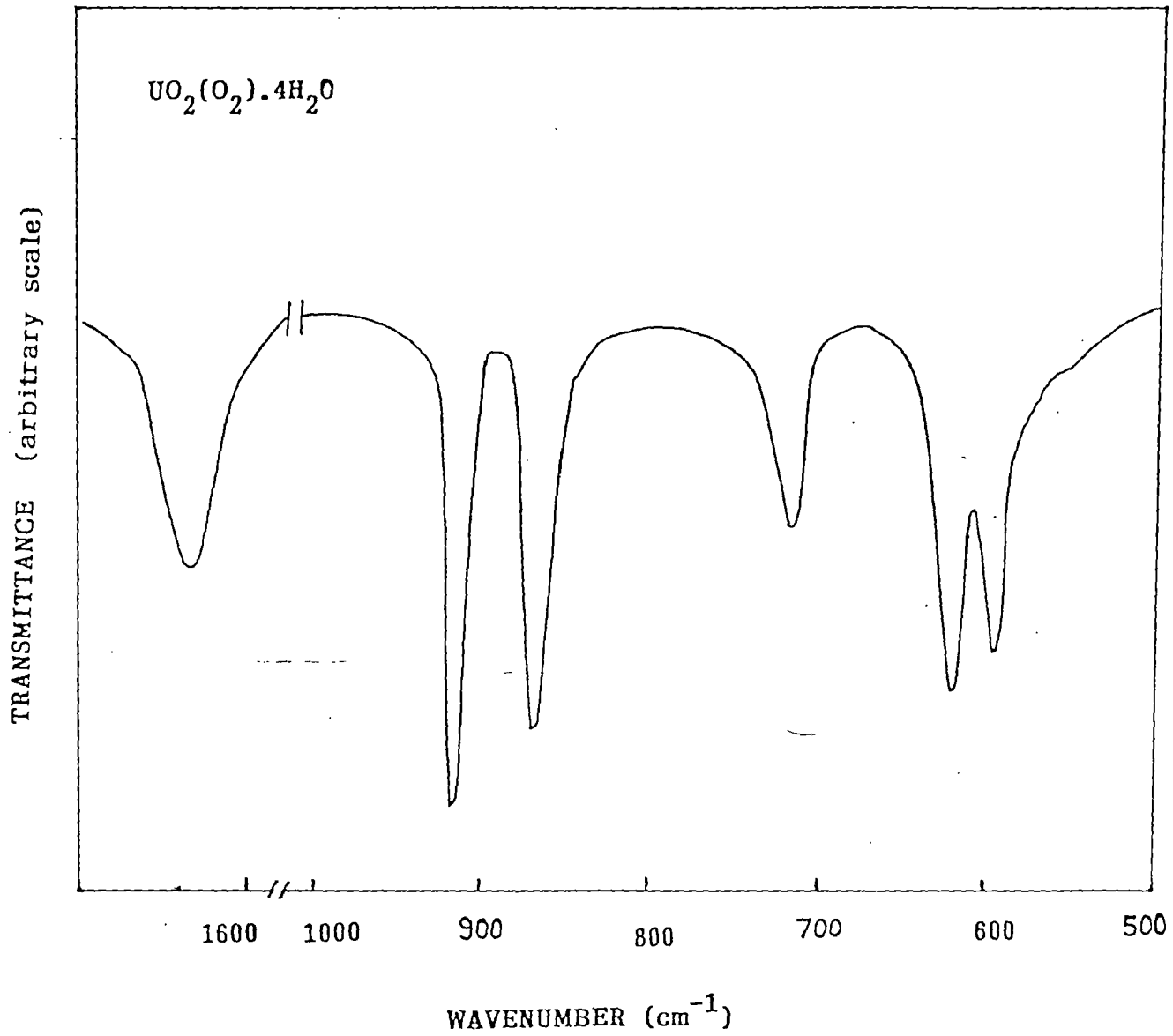
IR SPECTRUM


(NH4)2 [UO2(O2)F2]
K2 [UO2(O2)F2].H2O
TRANSMITTANCE (arbitrary scale)
3500
3000
2800
1800
1700
1500
1400
1000
900
800
400
300
WAVENUMBER (cm-1)

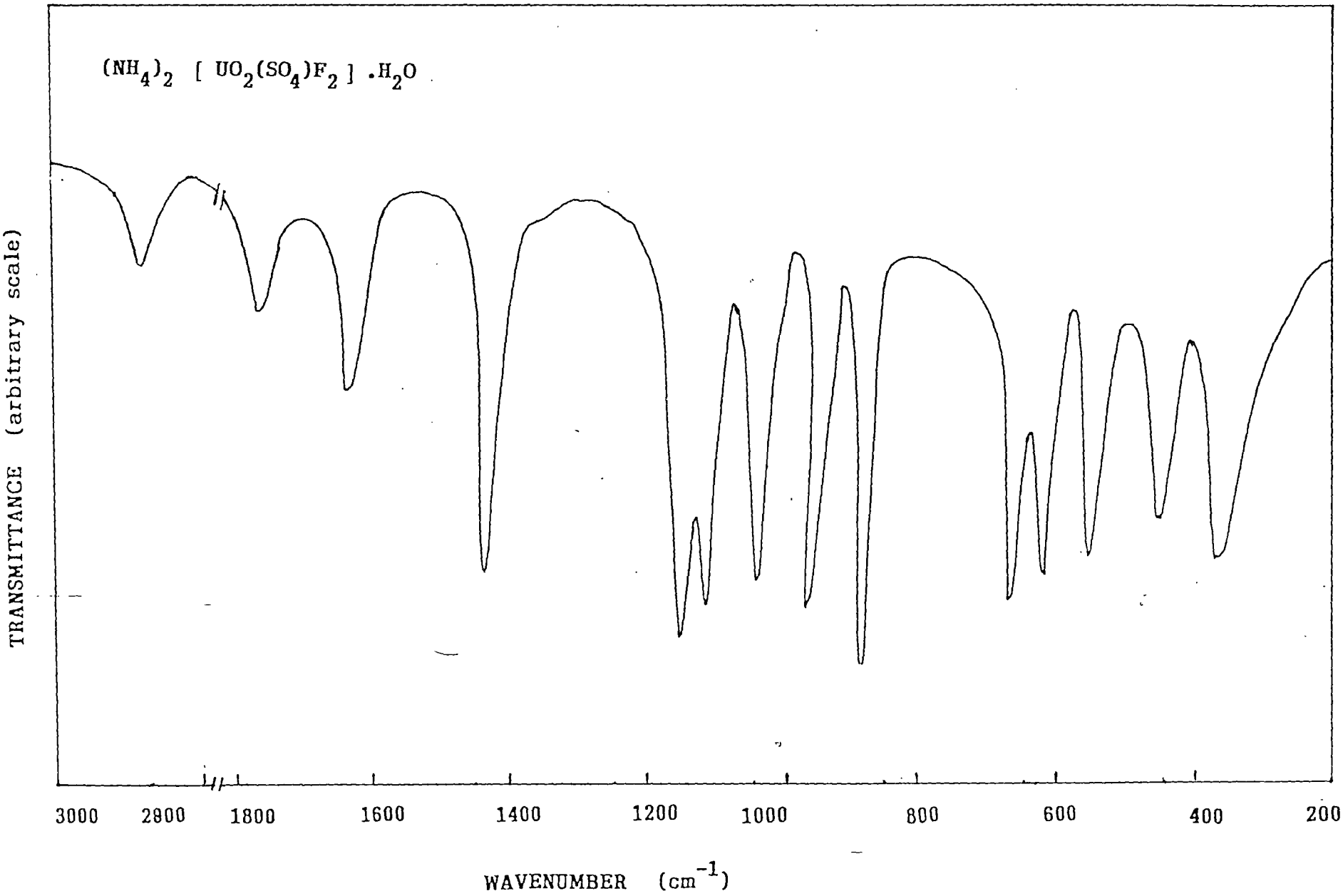
IR SPECTRUM


$(NH_4)_2 [UO_2(SO_4)_2] .2H_2O$
$(NH_4)_2 [UO_2(CO_3)_2] .5H_2O$
TRANSMITTANCE (arbitrary scale)
3500
3000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER (cm^{-1})

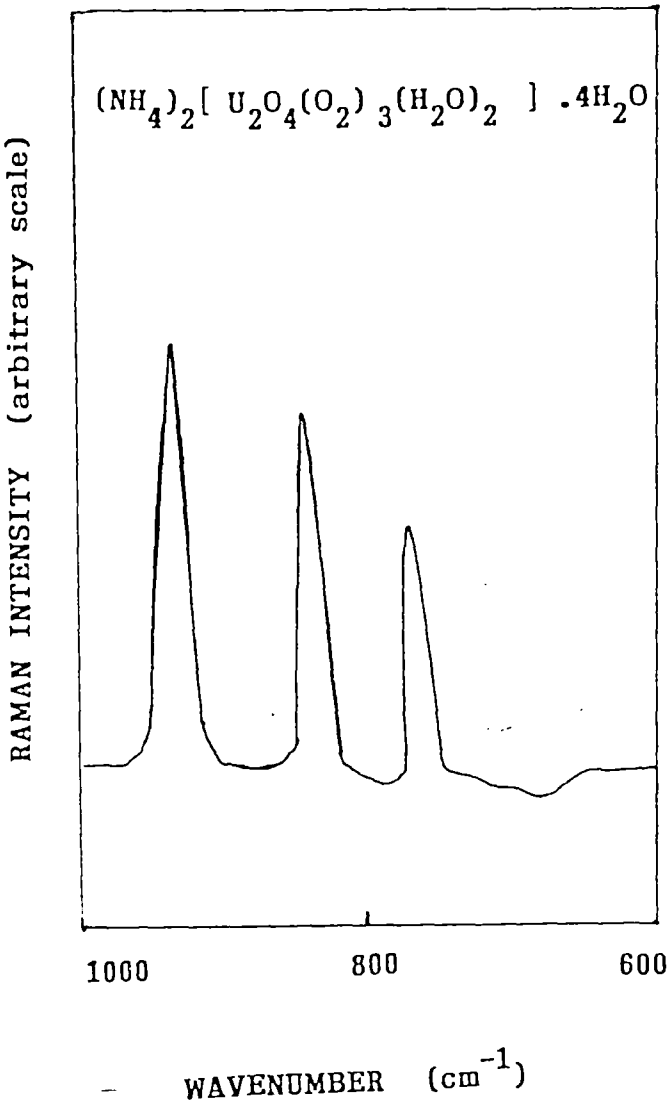
IR SPECTRUM


$UO_2(O_2).4H_2O$
TRANSMITTANCE (arbitrary scale)
1600
1000
900
800
700
600
500
WAVENUMBER (cm^{-1})

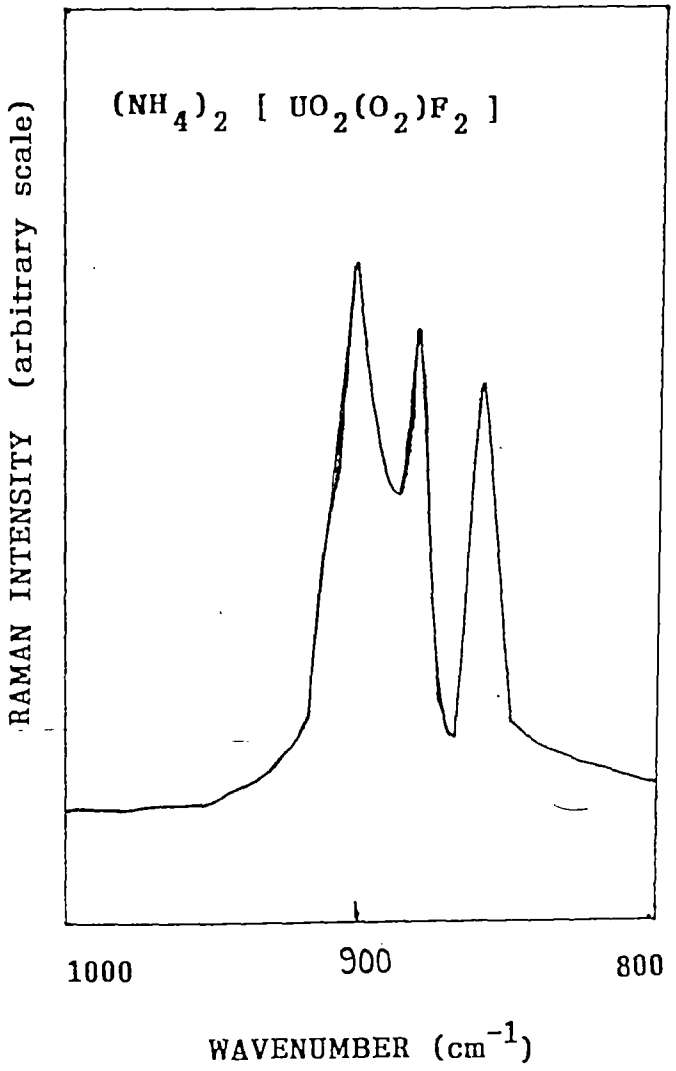
IR SPECTRUM


$(NH_4)_2$ [$UO_2(SO_4)F_2$] .H_2O
TRANSMITTANCE (arbitrary scale)
3000
2800
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER (cm^{-1})

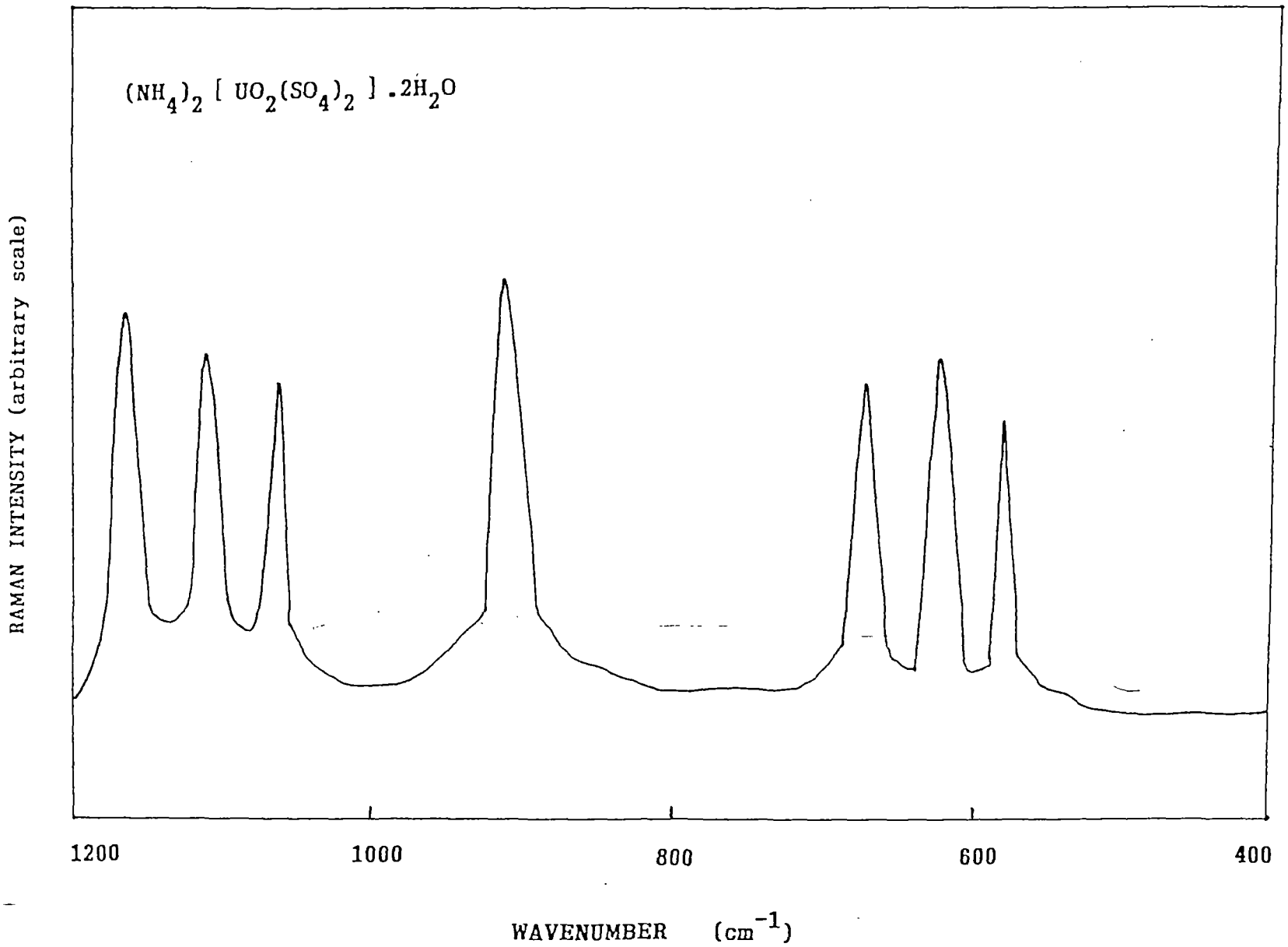
IR SPECTRUM



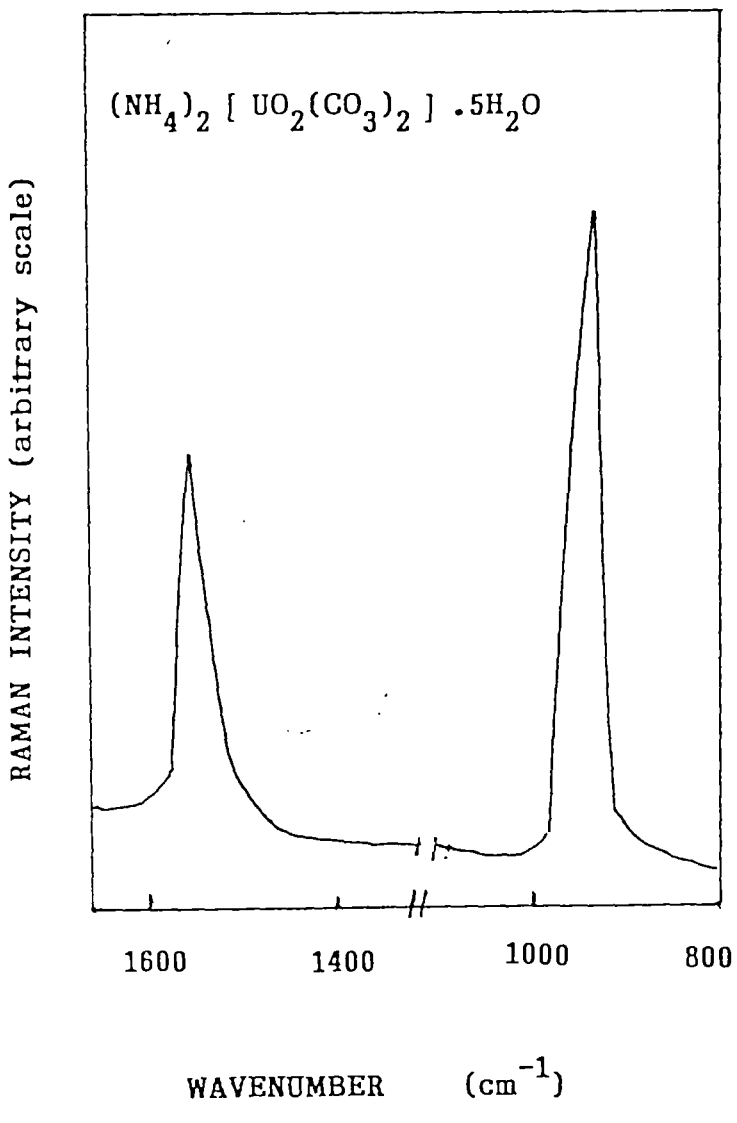
LR SPECTRUM



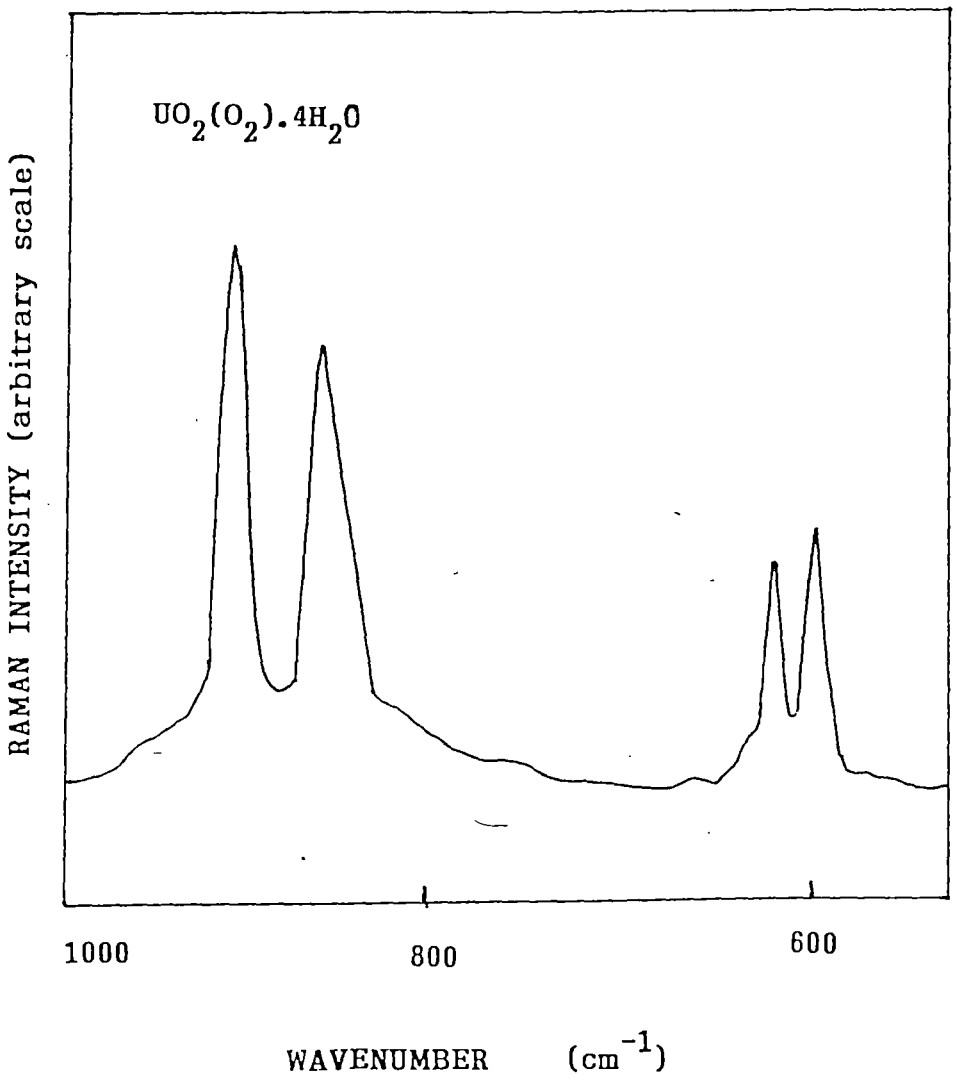
LR SPECTRUM


$(NH_4)_2$ [$UO_2(SO_4)_2$] .$2H_2O$
RAMAN INTENSITY (arbitrary scale)
1200
1000
800
600
400
WAVENUMBER (cm^{-1})

LR SPECTRUM



LR SPECTRUM



LR SPECTRUM

different stages of the reaction. The metal complex had all terminally bonded chelated peroxides and $SO_2(g)$ was the only substrate used. The species $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$, due to the presence of structurally two different types of metal bound peroxides, (namely, chelated and bridged) was expected to provide newer information from its reaction with inorganic polar substrates. The substrates for the present investigations were drawn from $SO_2(g)$, $CO_2(g)$, and NO_2 (g). On allowing $SO_2(g)$ to interact with the chosen complex, $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$, a solid spontaneously separated out of the solution at pH *ca.* 5 which reacted further with the reactant and passed into the solution at the solution pH value of *ca.* 2. Based upon this observation, two separate experiments were carried out. While in the first, the reaction was arrested by discontinuing $SO_2(g)$ flow immediately after the formation of an yellow compound at pH *ca.*5, in the second experiment, however, the bubbling of the gas was continued without halting the reaction at the point of formation of the yellow intermediate until it dissolved completely. The solution at this stage registered a pH value of *ca.* 2 as mentioned above. From this, another yellow product was isolated. Interestingly, the yellow intermediate contained peroxide but the final reaction product had no peroxide in it but contained sulphate as ascertained from a combination of chemical analyses and vibrational spectroscopy. The results of both chemical and physical studies on the intermediate and the final product characterised the compounds to be $UO_2(O_2).4H_2O$ and $(NH_4)_2[UO_2(SO_4)_2].2H_2O$, respectively. Incidentally, $UO_2(O_2).4H_2O$ is one of the best characterised peroxouranium composition, and

different features of the compound compared excellent with those reported in the literature.[6] The final sulphato product was diamagnetic in conformity with the presence of hexavalent uranium. Thus, unlike in the case of peroxovanadate(V),[23] no reduction of the metal centre took place.

The $(NH_4)_2[UO_2(SO_4)_2].2H_2O$ species is soluble in water and stable, as evidenced by both instantaneous and time dependent solution molar conductance (*ca.* 260 $\Omega^{-1}cm^2\ mol^{-1}$) values. The result is also in agreement with a 2:1 electrolytic nature of the compound. The IR spectrum provided clear evidence in support of the formulation of the complex species. While $\nu_{U=O}$ (trans-linked O=U=O)[13] was observed at 920 cm^{-1}, the characteristic ν_3 and ν_4 modes of coordiated sulphate were found to be split into three bands each, namely, 1070, 1120, 1150 cm^{-1}, and at 597, 618, 677 cm^{-1}, respectively. The splitting pattern is in line with the lowering of symmetry of SO_4^{2-} from T_d to C_{2v}. Since all the ν_3 (S-O) frequencies appeared at relatively lower wave numbers (<1200 cm^{-1}) compared to those of a chelated sulphate,[24] it is believed that the SO_4^{2-} ligands in the compound act as bridging groups between the contiguous UO_2^{2+} centres in the crystal lattice. This notion was further augmented when the compound was subjected to laser Raman Spectroscopy. The LR spectrum complimented the IR spectral observations and displayed a strong signal at 915 cm^{-1} due to $\nu_{U=O}$ (trans-linked O=U=O) and three signals each for the ν_3 (at 1075, 1115, 1160 cm^{-1}) and ν_4 (at 585, 625, 670 cm^{-1}) modes. The IR spectrum also exhibited pattern characteristic of lattice water, while the ν_{N-H} mode of

NH_4^+ occurred at 1400 cm^{-1}. It is noteworthy that unlike the $[V(O_2)_3]^-$—— $SO_2(g)$[23] reaction, the present $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$ —— SO_2 (g) reaction did not show any reduction of the metal centre. The observation can be rationalised in terms of standard redox potentials of UO_2^{2+} — U^{4+} ($E°$=-0.32v)[25] or UO_2^{2+} — UO_2^+ ($E°$=-0.063v)[25] and V(V)— V (IV) ($E°$=1.00V)[26] system as compared to SO_2 - SO_4^{2-} ($E°$= -0.17V)[27] system. It is evident therefore from the redox potential values, that V(V) is expected to be reduced to V(IV) and not U(VI) to any of its lower oxidation states.

Having conducted the reactions of the chosen compound with $SO_2(g)$, it was considered important to investigate similar reactions involving a different kind of a substrate,e.g., $CO_2(g)$. Surprisingly, to the best of our knowledge the reaction of $CO_2(g)$ with any peroxometal compound in aqueous medium was not included in previous reports. The reaction of an aqueous solution of $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$ with $CO_2(g)$ was conducted in a similar way as that of the $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$ ——— SO_2 (g) reaction. The reaction went on smooth but at a relatively slow rate. Like in the case of $SO_2(g)$ reaction, the uranium complex reacted with $CO_2(g)$ to thwart a yellow product at pH *ca.* 5 which dissolved on further bubbling of the reactant gas to form a clear solution. The pH value of this solution was *ca.* 3 (somewhat higher than that observed in corresponding SO_2 (g) reaction). In one of the subsequent reaction runs, the yellow product, formed at pH *ca.* 5, was isolated. Interestingly, the product was identified by chemical and spectral analysis to be $UO_2(O_2).4H_2O$ similar to that obtained from the corresponding $SO_2(g)$ reaction. The product

isolated at pH ~3, from the reaction $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$— $CO_2(g)$ did not reveal the presence of peroxide, however, it contained carbonate and was identified to be $(NH_4)_2[UO_2(CO_3)_2].5H_2O$. The IR spectrum of the carbonato compound provided evidence for NH_4^+, lattice water, translinked O=U=O, and bidentate carbonate. Noteworthy is the large separation between the ν_1 (A_1, ν_{C-O}) and ν_5 (B_2, $\nu_{C-O} + \delta_{O-C-O}$) modes appearing at 1602 and 1209 cm^{-1}, respectively. The LR spectrum showed, in addition to the expected $\nu_{U=O}$ (trans-linked O=U=O) band at 910 cm^{-1}, a strong signal at 1595 cm^{-1} due to the ν_{C-O} (ν_1, A_1) mode of coordinated CO_3^{2-}. The large separation between $\nu_1(A_1)$ and ν_5 (B_2) modes in the IR and appearance of $\nu_1(A_1)$ mode in the LR spectra cause us to infer that carbonato ligands in the complex occur as chelated ligands.[27] The features originating from coordinated carbonate matches well with other carbonato complexes dealt with earlier in this laboratory.[3]

The study of reaction profile of $NO_2(g)$ with the chosen substrate was also one of the concerns in the present investigation. Under conditions similar to those maintained in the preceding reactions, $NO_2(g)$ reacted with the uranium complex also to produce the isolable intermediate, $UO_2(O_2).4H_2O$, similar to that obtained in each of the two previous reactions. Like in the earlier cases, $UO_2(O_2).4H_2O$ reacted further with $NO_2(g)$ leading to a clear solution at pH *ca.* 3. Work-up of the solution afforded a yellow microcrystalline product. Although this contained UO_2^{2+} and coordinated nitrate as indicated by vibrational spectroscopic studies, on chemical analysis no well

defined stoichiometry could be worked out. This is not too surprising, since with nitrate (NO_3^-) the actinide complexes are generally very weak and an extensive complex formation occurs normally at a high NO_3^- concentration[28]. In the present reaction the latter condition was not met with, obviously owing to a very low concentration of NO_3^-. The formation of NO_3^- was directly related to the number of available peroxo groups.

In order to understand the formation of the intermediate $UO_2(O_2).4H_2O$ from $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$, two controlled reactions were carried out. As the reactivity studies were conducted in $N_2(g)$ atmosphere it was required to be seen whether N_2 alone would break down the parent uranium-peroxo complex to a simpler monoperoxo compound. Thus, an aqueous solution of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ was allowed to interact with $N_2(g)$ in the absence of any substrate gas. No apparent change was observed and the product isolated by ethanol addition was identified to be the unchanged $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$ complex. This therefore ruled out an involvement of $N_2(g)$ in the reaction. The second reaction was aimed at ascertaining whether an acidic medium alone would conduce the formation of $UO_2(O_2).4H_2O$ from $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$. Accordingly, an aqueous solution of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ was treated separately with dil. H_2SO_4 or dil. HNO_3 or a solution of NH_4HCO_3 at pH 5. This experiment, however, yielded in each case a yellow product identified to be $UO_2(O_2).4H_2O$. If, the yellow product, $UO_2(O_2).4H_2O$ without isolation from the reaction system was treated with an additional amount of dil. H_2SO_4, a clear solution was obtained at pH 2 which ultimately provided

$(NH_4)_2[UO_2(SO_4)_2].2H_2O$ Incidentally, a rather similar reaction involving dil. HNO_3 also produced a clear solution at pH 2. The product isolated from this solution, however, did not analyse to any definite stoichiometry although its IR spectrum indicated the presence of NO_3^-. To test the corresponding acid reaction of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ —— CO_2 (g) reaction, an aqueous solution of $(NH_4)_2$ $[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ was treated with NH_4HCO_3 solution whereupon the intermediate $UO_2(O_2).4H_2O$ spontaneously precipitated out. No change was observed on further addition of more of NH_4HCO_3 solution.

Considering the products $UO_2(O_2).4H_2O$ and $(NH_4)_2[UO_2(SO_4)_2].2H_2O$ isolated at different stages of the reaction and in view of the results of the two controlled reactions just discussed, it seems probable that the formation of $UO_2(O_2).4H_2O$ and the final nonperoxoygenated product were pH-dependent. It may thus be inferred that $UO_2(O_2).4H_2O$, the intermediate, was formed through acid catalysed decomposition of $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$. It may also be commented *inter-alia* that there are two different kind of peroxide one unstable to even weak acid condition while the other kind stable to pH as low as 5. The formation of the end sulphato product can be explained in terms of the formation of UO_2SO_4 through insertion of SO_2 into the terminal peroxide of $UO_2(O_2).4H_2O$. The coordinatively unsaturated species thus formed *insitu* then interacted with SO_4^{2-} available in the reaction solution finally giving rise to $(NH_4)_2[UO_2(SO_4)_2].2H_2O$ compound as obtained.

An internal comparison of the results of reactions of $[U_2O_4(O_2)_3(H_2O)_2]^{2-}$ with $SO_2(g)$, $CO_2(g)$, and NO_2 (g) in aqueous medium clearly demonstrate a general reactivity pattern. The reaction with each of the chosen substrates proceed through a unique, isolable intermediate, $UO_2(O_2).4H_2O$, which ultimately produces a sulphato, a carbonato, or a nitrato complex of UO_2^{2+} in the respective cases. No evidence in support of the reduction of the metal centre was obtained. The facility of the reactions seems to follow the sequence SO_2 (g) > NO_2(g)> CO_2(g). Isolation and identification of the sulphato- and carbonato- products provide *inter-alia* newer routes to technologically important uranyl systems[29a] containing sulphate and carbonate, respectively. It may be mentioned in passing that uranyl carbonato chemistry is of importance in the context of carbonate leaching in the hydrometallurgy of the metal[29a]. Such compounds are also used as intermediates in accessing highly useful uranium and uranium-plutonium ceramics.[29b]

(ii) *Reaction of* $(NH_4)_2[UO_2(O_2)F_2]$ *with* SO_2(g)

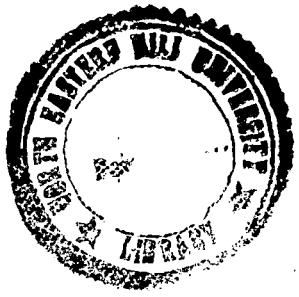
The results of reaction of fluoro(peroxo)metallate with small inorganic polar substrates can provide substantial information concerning the extent of O-O bond activation in a heteroligand coordination sphere. Such reactions are expected to also provide useful methodologies for accessing mixed-fluoro compounds metals. With this in view, the study of reactivity of $(NH_4)_2[UO_2(O_2)F_2]$ with SO_2(g) was undertaken, as a case in point. The reaction, like the fluoro(peroxo)zirconate(IV) complex (vide Chapter III) was typical of monoperoxometal compounds. As expected the

peroxide (O_2^{2-}) bond to UO_2^{2+} interacted with $SO_2(g)$ leading to the formation of a ternary fluorocomplex of uranium, $(NH_4)_2[UO_2(SO_4)F_2].H_2O$, as obtained at pH 2. Interestingly, the compound $(NH_4)_2[UO_2(SO_4)F_2]$ was hitherto unreported although the corresponding $A_2[UO_2(SO_4)F_2]$ with A being Na, K or Rb were prepared from the reaction of $UO_2(SO_4)$ with the corresponding alkali-metal fluorides.

The mixed-fluoro complex $(NH_4)_2[UO_2(SO_4)F_2].H_2O$ was obtained as a yellow microcrystalline product. This is readily soluble in water and conductance measurement on a 10^{-3}M solution gave a value of 260 $\Omega^{-1}cm^2mole^{-1}$ in good agreement with its 2:1 electrolytic nature. The IR spectral signatures of $(NH_4)_2[UO_2(SO_4)F_2].H_2O$ showed a broad band at 1430 cm^{-1} owing to ν_4 mode of NH_4^+ ion. However, there was neither lowering nor any broadening of the ν_{U-F} mode which appeared as a sharp band at 370 cm^{-1}. A weak and broad band at 1785 cm^{-1}, like in the case of $(NH_4)_2[UO_2(O_2)F_2]$, indicated the possibility of a rather strong hydrogen bonding in the complex. The S-O modes due to SO_4^{2-}, albeit typical of bidentate sulphate, showed noticeable shift (below 1200 cm^{-1}) of ν_3 to lower frequencies and occurred at 1198, 1130, 1075 cm^{-1} causing us to state that sulphato ligand is involved in intermolecular bridging. Now if both SO_4^{2-} and F^- were to be excluded from the involvement in H-bonding, evidence for the same had to be sought from the modes due to water. Interestingly, the δ_{H-O-H} mode in the present case located at 1657 cm^{-1} (*ca.* 20 cm^{-1} higher than is usually found for δ_{H-O-H} of lattice water) and the lowering of ν_{O-H} to 3300 cm^{-1} provides

ample evidence in favour of H-bonding involving H-O-H and NH_4^+ ion. That the shift in band positions owing to water are not due to its coordination is revealed by absence of any band near 700 cm^{-1}. The LR spectra could not be recorded owing to excessive fluorescence.

Thus, it is evident from what preceeds that the presence of acceptors and donors alone do not suffice to direct the course of H-bonding but the role of other ancilliary ligands are also important as exemplified by the present cases.



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CHAPTER VI

PERCARBONATES. SYNTHESIS, CHARACTERISATION AND REACTIVITY OF A NEW AMMONIUM HYDROGENMONO-PEROXOCARBONATE TRIHYDRATE, $NH_4[HCO_4].3H_2O$, AND A REINVESTIGATION OF THE SYNTHESIS OF $(NH_4)_2[CO_3].H_2O_2$

As opposed to a host of reports[1] on the synthesis and reactivity studies of metal-peroxo complexes, parallel information on non-metals is scanty presumably owing to their limited accessibility. Although some peroxononmetallates like peroxocarbonates,[2] peroxosulphates,[3,4] peroxophosphates,[5] and peroxoborates[6] are known and widely used[7-15] in laboratory and industry, synthetic routes to many of these compounds are not simple as they involve manipulation under delicate reaction conditions. For instance,

carbon has long been known[16] to form compounds with peroxides called `percarbonates', and their role in industry[17] and biochemical processes[18] recognised from an early date, yet no simple routes to their synthesis exist.

Percarbonates are classed into two groups[2] viz. `perhydrates' containing hydrogen peroxide of crystallisation made from $H_2O_2$ and parent carbonate, and `peroxocarbonate' containing C-O-O linkage as in organic peroxides and are prepared from the reaction of alkali-metal hydroxides with H_2O_2 and carbon dioxide[2] or by anodic oxidation of carbonates[2]. Thus, $Na_2[CO_3].1.5H_2O_2$[2], $K_2[CO_3].3H_2O_2$[2], $Rb_2[CO_3].3H_2O_2$[2] belong to the perhydrate class while $AHCO_4$[2] (A = Na, K and Rb) and $A_2[C_2O_6]$[2] (A = K, Rb, Cs) are the well known examples of `peroxocarbonates'. Recently evidence[19] has been provided for the existence of peroxocarbonate species likely to be HCO_4^- or CO_4^{2-} at higher pH in an aqueous solution of bicarbonate and H_2O_2. This led us to conjecture that it might as well be possible to obtain peroxocarbonate in solid state under similar conditions. Literature survey also reveals that there exists no ammonium salt of peroxocarbonate. Prompted by this and in view of the difficult accessibility of peroxocarbonate, it was considered worthwhile to synthesise the ammonium salt of HCO_4^- following an easier route and explore the properties of such compounds in terms of their reactivity. Moreover, in order to demonstrate that a slightly varying synthetic methodology leads to a different compound, the case of $(NH_4)_2[CO_3].H_2O_2$ has been reinvestigated. An additional interest was also to involve this species in the proposed reactivity experiments.

Accordingly, studies on peroxocarbonate and perhydrate were addressed. The present Chapter of the thesis describes a very simple and efficient method for the synthesis of heretofore unreported ammonium hydrogen peroxomonocarbonate trihydrate, $NH_4[HCO_4].3H_2O$, followed by its characterisation. Also included herein are the results of a few typical reactions with some chosen organic substrates. The synthesis of $(NH_4)_2[CO_3].H_2O_2$ has been revisited and the results of reactivity studies involving it towards the typically chosen organic substrates are also incorporated in this Chapter.

EXPERIMENTAL

Reagent grade chemicals have been used throughout the present work.

(i) Synthesis of Ammonium Hydrogenperoxomonocarbonate,trihydrate, $NH_4[HCO_4].3H_2O$

Ammonium hydrogen carbonate (1.0g, 12.66 mmol) was dissolved in aqueous ammonia (sp.gr. 0.9g cm, 10 cm^3) in a 250 cm^3 beaker. The reaction container was placed in an ice-bath containing crushed ice mixed with common salt, and the temperature inside the beaker was maintained below -5°C. To the clear solution was then added 15 cm^3 of 30% H_2O_2 (132.35 mmol) while stirring for 5 min. An amount of 20 cm^3 of ethanol was added to the reaction solution to completely precipitate out the white crystalline ammonium hydrogenmonoperoxocarbonate trihydrate, $NH_4[HCO_4].3H_2O$. The compound was separated by filtration, washed 3-4 times with

ethanol, and finally dried by pressing between folds of a filter paper. The yield of $NH_4[HCO_4].3H_2O$ was 1.35g (72%).

(ii) Synthesis of Ammonium Carbonate Perhydrate $(NH_4)_2[CO_3].H_2O_2$

Ammonium hydrogen carbonate (1.0g, 12.66 mmol) was dissolved in 10 cm^3 of water in a 250 cm^3 beaker and placed in an ice-bath. The temperature was maintained below -5°C in a manner analogous to that described under (i). To the resultant clear solution was added 15 cm^3 of 30% H_2O_2 (132.35 mmol) and the mixture was stirred for *ca.* 10 min. The reaction solution was then kept in a freezer for *ca.* 30 min. Addition of 20 cm^3 of ethanol precipitated out the white crystalline product. The compound was isolated by filtration and washed several times with ethanol. The yield of $(NH_4)_2[CO_3].H_2O_2$ was 1.28g (78%).

Studies of Reactivity of $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$ with organic substrates

Starting Materials

Commercially available samples of benzonitrile, salicylaldehyde, anthracene, and n-butanol were used and purified before use. The purity was checked by comparing melting points and spectra with those of the reported ones.[20] All the reactions were conducted in daerated water (vide Chapter II) under N_2 atmosphere.

(i) Reaction of salicylaldehyde with $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$

To 1.0g (8.19 mmol) of salicylaldehyde, an aqueous solution (25 cm^3) of either $NH_4[HCO_4].3H_2O$ (1.83g, 12.29 mmol) or

$(NH_4)_2[CO_3].H_2O_2$ (1.59g, 12.23 mmol) was added with constant stirring. On addition of the peroxocarbon compounds, the solution temperature spontaneously rose to *ca.* 50°C and a dark colour developed. It was stirred for *ca.* 6h and then allowed to stand overnight. The solution was neutralised with acetic acid and evaporated to dryness, and the residue was treated with toluene (5x10 cm^3). The toluene fraction was dried with Na_2SO_4 and upon evaporation gave catechol. The crude catechol thus obtained was purified by passing through silica-gel column using hexane-ethylacetate (6:4) as the eluent.

The amount of reagent used and the yield of the product obtained and its melting point are displayed in Table 6.2. The IR and NMR spectral data compared well with those of the reported ones[2b] and are set out in Table 6.2.

(ii) Reaction of benzonitrile with $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$

Benzonitrile (1g, 9.71 mmol) was mixed with 15 cm^3 of ethanol and to this was added an aqueous solution (30 cm^3) of either $NH_4[HCO_4].3H_2O$ (2.16g, 14.50 mmol), or $(NH_4)_2[CO_3].H_2O_2$ (1.89g, 14.54 mmol). The reaction solution was stirred for 3h at *ca.* 50°C on an oil-bath. It was then cooled to room temperature and treated with chloroform (3x15 cm^3). The combined organic layers were washed with water, dried (Na_2SO_4), and concentrated to give crude benzamide, which was purified by recrystallisation from chloroform.

The amount of reagent used and the yield of the product obtained and its melting point are set out in Table 6.2. The IR and NMR spectral feature compared well with those reported[2c] and are shown in Table 6.2.

(iii) Reaction of anthracene with $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$

Anthracene (1.0g; 5.62 mmol) and acetic acid (30 cm^3) were placed in a flask and refluxed until the whole amount of anthracene went into solution. An aqueous solution (15 cm^3) of either $NH_4[HCO_4].3H_2O$ (1.25g, 8.43 mmol) or $(NH_4)_2[CO_3].H_2O_2$ (1.11g, 8.43 mmol) was added to it and the reaction mixture was refluxed for *ca.* 2h. The reaction solution was cooled and poured into cold water (150 cm^3) with stirring. The crude anthraquinone separated out as a solid. The product was isolated by filtration under suction, washed 4-5 times with hot water and then with a dilute solution of sodium hydroxide, and finally with cold water. The product thus obtained was purified by passing through a silica gel column using hexane/ethylacetate (9:1) as the eluent. The yield and melting point of the product, and amount of reagent used are presented in Table 6.2. The IR and NMR spectral characteristics compared well with those of reported[2c] one and are given in Table 6.2.

(iv) Reaction of n-butanol with $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$

To a mixture of 2g (26.98 mmol) of n-butanol and 1.5 cm^3 of concentrated H_2SO_4, was added a solid sample of either

$NH_4[HCO_4].3H_2O$ (6.03g, 40.47 mmol) or $(NH_4)_2[CO_3].H_2O_2$ g, (5.34g, 40.47 mmol). The reaction mixture was refluxed for 1 h and then cooled to room temperature followed by neutralisation with $NaHCO_3$. The aldehyde was isolated as its 2,4-dinitrophenyl hydrazone derivative from which the yield of the carbonyl compound was calculated. The amount of reagents used, the yield of the product, and the melting point of the 2,4-dinitrophenyl hydrazone derivative along with its IR and NMR data[2e] are summarised in **Table 6.2.**

Elemental Analyses

Quantitative estimation of peroxide, carbon, hydrogen, and nitrogen were done by the methods described in **Chapter II.** The analytical and spectral data of the peroxocarbon compounds are set out in **Table 6.1.**

RESULTS AND DISCUSSION

Synthesis

Two principal methods of synthesis of peroxocarbonate are documented in the literature;[2] one method uses alkali-metal hydroperoxides as precursors, and the other uses H_2O_2. Both the methods, however, involve $CO_2(g)$. Besides these, no direct and easy route to the synthesis of peroxocarbonate from aqueous solution existed. In a rather recent report Griffith et al.[19] provided Raman and ^{13}C spectroscopic evidence for the likely existence of CO_4^{2-} or HCO_4^- in solutions of HCO_3^- in an excess of H_2O_2 at a high pH and a low temperature. Based upon this, it was anticipated that under suitable experimental conditions it might

be possible to achieve synthesis of peroxocarbonate species from an aqueous solution. An evaluation of appropriate pH and reaction temperature was considered to be the important prerequisites. Strategically, reaction of an ammoniacal solution of ammonium bicarbonate, NH_4HCO_3 with H_2O_2 at -5 to -10°C led to the synthesis of $NH_4[HCO_4].3H_2O$. The use of ammonia solution served at least two purposes, namely maintaining an alkaline pH and supplying cations, thus conducing the formation of peroxocarbonates. The role of ethanol was to bring about precipitation of the product. A pH value of *ca.* 10.5 and a temperature of -5 to -10°C have been ascertained to be ideal for the synthesis of the compound looked for.

At this stage it became necessary to reinvestigate the synthesis of the perhydrate, $(NH_4)_2[CO_3].H_2O_2$, in order to make a clear distinction from $NH_4[HCO_4].3H_2O$. The documented[2] method of synthesis of the perhydrate required 3-4 days. In the course of reinvestigation of the synthesis of the perhydrate, however, we found that it could be prepared rather easily within 30 min. if a small excess of H_2O_2 was used and the temperature was maintained below -5°C.

Properties

The compounds $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$ are white crystalline solid. In water, both the compounds decompose fast with the loss of active oxygen thereby precluding measurements of molar conductance. Though neither of the compound is hygroscopic, they are not very stable at ambient temperatures if left exposed to air for more than 5 h or so. A loss of 4-5%

active oxygen content in a span of 24h has been noticed. However, they can be stored in sealed ampules in the absence of air for several days. Significantly, the pH value of a 10^{-3}M aqueous solution of each of the compounds has been found to be 8-9.5.

Characterisation and Structural Assessment

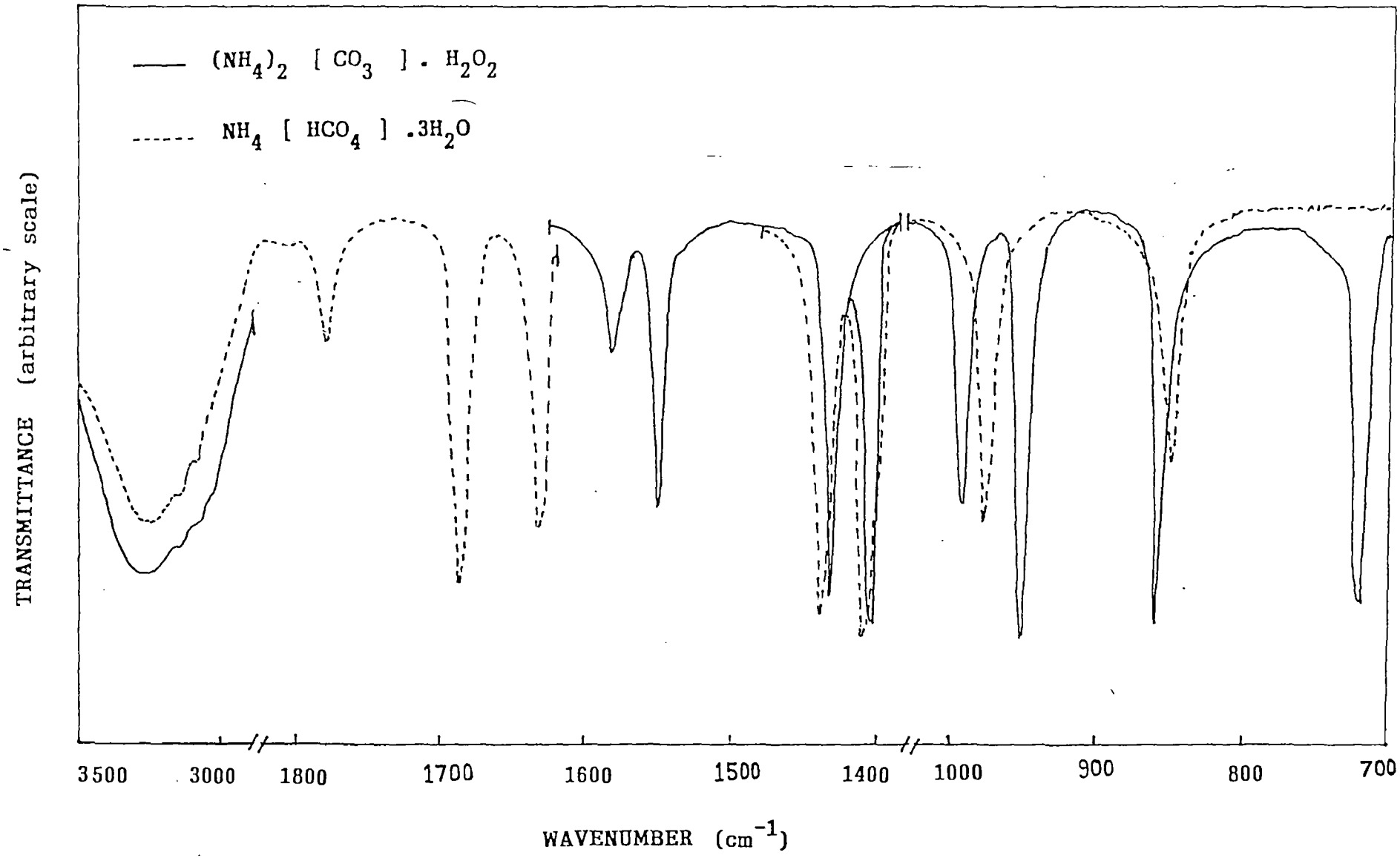
Both $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$ decompose in the presence of sulphuric acid, liberating H_2O_2 quantitatively, thereby rendering it easy to determine active oxygen content of the compounds. The chemical determination of active oxygen in such compounds are considered to be of crucial importance. The active oxygen content was determined by titrimetric analysis with $KMnO_4$. Boric acid was used to prevent any loss of active oxygen. The results of chemical determination of active oxygen and the other elements present suggested the occurrence of carbon and peroxide (O_2^{2-}) in 1:1 stoichiometry in each of the compounds.

Each of the compounds, $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$, displayed characteristic spectral feature in the infrared region. The significant features (Table 6.1) of the IR spectrum of $NH_4[HCO_4].3H_2O$ involve absorptions at 1780w, 1690s and 975 cm^{-1} owing C-O stretches, 840 m cm^{-1} due to O-O stretching and 1440s cm^{-1} due to ^-OOH deformation mode.[2] The observed band positions and the assignments appear to be in order and agree well with those of $NaHCO_4$.[2] The bands at 3150s,br and at 1640 cm^{-1} have been assigned, respectively, to ν_{O-H} and δ_{H-O-H} in line with the occurrence of lattice water. The absence of any bands

Table 6.1 : Analytical and structurally significant IR data of $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$

Compound	Analysis[a] (%)				IR (cm^{-1})	Assignment
	N	C	O_2^{2-}	H		
$NH_4[HCO_4].3H_2O$	9.45	8.11	22.31	7.23	840m	ν_{O-O}
	(9.39)	(8.06)	(21.47)	(7.38)	1440s	$^-$OOH def.
					975	
					1690s	ν_{C-O}
					1780w	
					3150s.br	$\nu_{O-H}(H_2O)$
					1640	$\delta_{H-O-H}(H_2O)$
$(NH_4)_2[CO_3].H_2O_2$	21.58	9.35	24.4	7.62	990m	$\nu_4(H_2O_2)$
	(21.54)	(9.24)	(24.6)	(7.69)	950s	
					1570w	ν_2 (H_2O_2)
					1550	
					1430s	ν_3(C-O)
					855s	ν_2(C-O)
					720s	ν_4(C-O)
					3005	$\nu_1(H_2O_2)$

[a] Calculated values are in parenthesis


—— $(NH_4)_2$ [CO_3] . H_2O_2
------ NH_4 [HCO_4] .$3H_2O$
TRANSMITTANCE (arbitrary scale)
3500
3000
1800
1700
1600
1500
1400
1000
900
800
700
WAVENUMBER (cm^{-1})

IR SPECTRUM

Table 6.2 : Amounts of the Reagent used, yields, Melting points, and IR, NMR spectral data of the Reaction Products

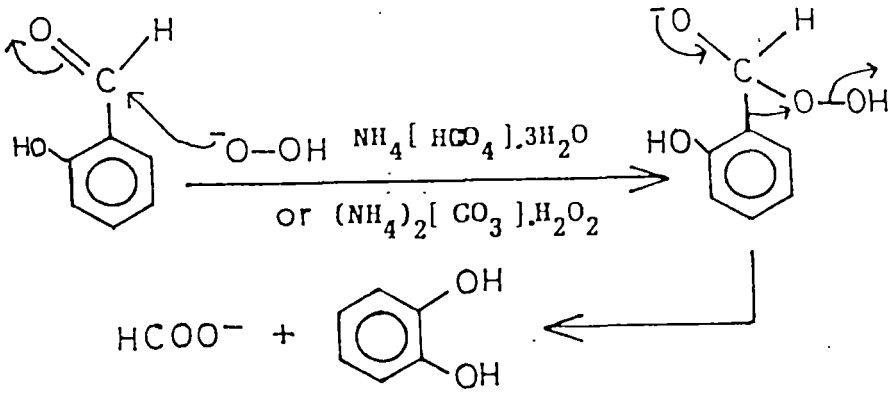
Substrate g (mmol)	Amount of Reagent, $NH_4[HCO_4].3H_2O$	Amount of Reagent $(NH_4)_2[CO_3].H_2O_2$	Product (Yields,** g %)	m.p. (uncorrected) °C	IR (cm^{-1})	NMR δ(ppm)
Salicyl-aldehyde 1.0 (8.19)	1.83 (12.29)	1.60 (12.29)	Catechol (0.36, 40%)	103	3450,3320,3050,1620, 1590,1510,1460,1360, 1270,1250,1230,1180, 1160,1090,1030,930, 910,840,760,750,730, 630,560,490,360.	5.4,6.8 $CDCl_3$
Benzonitrile 1.0 (9.71)	2.16 (14.56)	1.90 (14.56)	benzamide (0.47, 38%)	128	3448,3220,1665,1640, 1585,1445,1370,1125, 782,692.	7.5-8.1
Anthracene 1.0 (5.62)	1.25 (8.43)	1.11 (8.43)	Anthraquinone (0.47, 40%)	284	1675,1590,1580,1330, 1285,1170,940,810, 690,630,390.	-
n-butanol 2.0 (26.98)	6.03 (40.47)	5.34 (40.47)	n-butanaldehyde (0.81, 43%)	122*	2940,2860,2780,2700, 1720,1470,1370,1140, 1110,1000,960,780	1.0,1.7, 2.4,9.9, $CDCl_3$

* 2,4-dinitrophenylhydrazone derivative; ** average yield.

assignable to H_2O_2 of crystallisation[2] or to CO_3^{2-} in the IR spectrum of $NH_4[HCO_4]3H_2O$ as against those observed for $(NH_4)_2[CO_3]H_2O_2$, clearly revealed the distinction between the two compounds. The vibrational spectrum of the perhydrate, $(NH_4)_2[CO_3].H_2O_2$ comprised of features (Table 6.1) which matched well with that previously reported.[2]

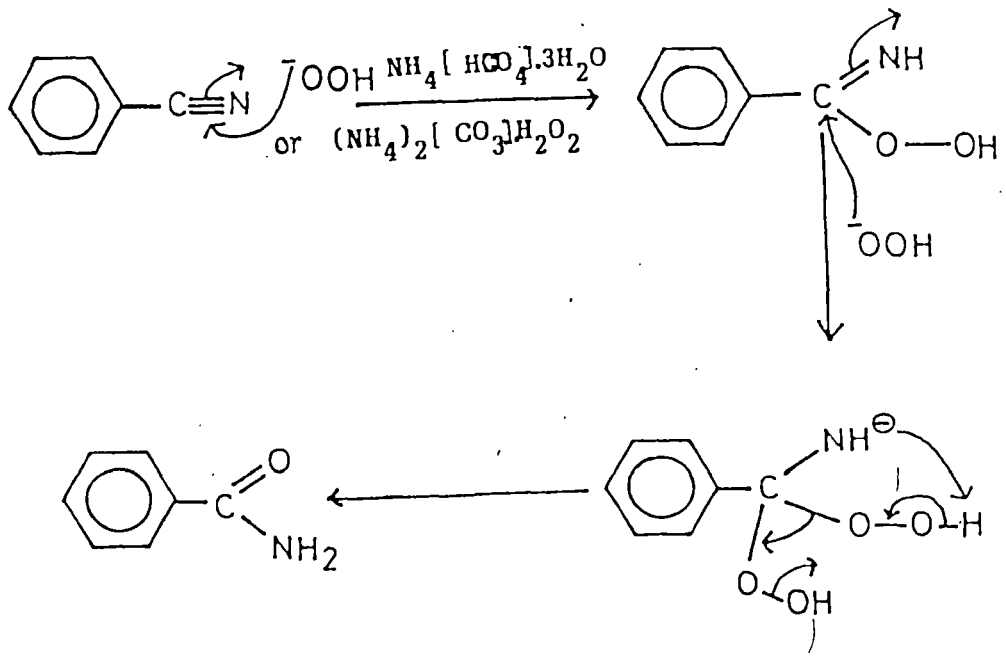
Reactivity

The observed pH values (8-9.5) of the compounds in aqueous solution led us to anticipate that these, like alkaline —— H_2O_2 reagent,[21] might serve as viable reagents to effect transformation of several organic substrates. Thus, Dakin reaction,[21] which employs alkaline ——— H_2O_2 reagent to convert salicylaldehyde to catechol, has been carried out with each of the two compounds. As anticipated, the reactions (Scheme I) took place successfully with an average yield of the product as *ca.* 40%.



Scheme I

Another characteristic reaction of base-catalysed H_2O_2 oxidation is the conversion of a nitrile functionality to the corresponding amide.[21] Benzonitrile was chosen for the present study to demonstrate the efficacy of the reagent, and the substrate was found to readily undergo conversion to benzamide.



Scheme II

The mechanism (Scheme II) involved in such a reaction has been the subject of intense study. It has been shown by Wiberg[22] that the reaction is initiated by the attack of hydroperoxide on the nitrile function and the oxygen introduced into it comes from the hydroperoxide and not from water or a hydroxyl anion. It has also been suggested that the reaction involves the formation of an unisolable peroxocarboximidic acid as an intermediate.

Epoxidation of chalcones is yet another characteristic reaction of basic-H_2O_2 reagent.[21] However, this reaction involving the newly synthesised compounds yielded the epoxidised product only to an extent of *ca.* 10%.

The compounds in acidic media have been also found to effect transformation of n-butanol to n-butanaldehyde and oxidation of anthracene to anthraquinone.

The results of reactivity studies involving $NH_4[HCO_4].3H_2O$ and $(NH_4)_2[CO_3].H_2O_2$ hitherto obtained are very satisfactory and suggest the new reagents as valuable additions to the existing wealth of reagents especially as viable substitutes for basic-H_2O_2 reagent.

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CHAPTER VII

ALKALI-METAL ACETYLACETONATES. FIRST SYNTHESIS OF (ACETYLACETONATO)RUBIDIUM(I), Rb(acac), A DIRECT ROUTE TO (ACETYLACETONATO)CAESIUM(I), Cs(acac), AND EVIDENCE FOR STRONG ION ASSOCIATION/ION PAIR FORMATION IN A(acac) (A=Li, Na, K, Rb or Cs)*

The importance of metal-acetylacetonato compounds has been duly emphasised in Chapter I. Owing to their manifold uses, there has been an upsurge of interest in the studies of various aspects of such compounds. Quite exciting in this context is to draw attention to to a recent report on the semiconducting behaviour of Na(acac).[1]

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* The work described herein has been published :
J. Chem. Research (S), 1991, 250.

Developing direct synthetic routes to a large number of acetylacetonato-metals, with metal : acac ($C_5H_7O_2^-$) as 1:2,[2] 1:3,[3] 1:4[4], and an extensive investigation of their EI induced mass spectra have been pursued for a decade in the laboratory wherein the present work was carried out. Despite such progress, the 1:1 type acetylacetonato-alkali metal complexes do not appear to have received similar attention. For instance, while acetylacetonato-metals are known for almost all the metals in the periodic table, Rb(acac) did not seem to have any reported existence, although a corresponding fluorinated acetylacetonate, $Rb(C_5HO_2F_6)$, was documented.[5] Besides this, the method of preparation of Cs(acac) is rather cumbersome.[6]

As a part of an ongoing programme of the laboratory, attention of the present worker was drawn to acetylacetonato-alkali metals and it was considered rather imperative to make a systematic investigation.

The principal concerns were to synthesise the missing member of the A(acac) [A=Li-Cs] series, to provide an easy access to Cs(acac), and also to comment on the possible existence of strong ion-association/ion-pair formation of A(acac) in solution, based upon the results of conductance measurements and ^1H NMR experiments.

Accordingly, the present Chapter, indeed the concluding Chapter of the thesis, deals with the first synthesis of Rb(acac) and a direct route to Cs(acac), and comment on the covalent-like character of A(acac) compounds.

EXPERIMENTAL

Chemicals of reagent-grade quality were used. Acetylacetone (acacH, $C_5H_8O_2$) was used after purifying by distillation. The compounds Li(acac),[7] Na(acac)[8], and K(acac)[8] were prepared following reported methods.

Synthesis of (Acetylacetonato)rubidium(I), Rb(acac)

To 1.0g (0.43 mmol) of Rb_2CO_3 was added 20 cm^3 (200 mmol) of acetylacetone and the mixture was refluxed for *ca.* 15 min. until a clear solution was obtained. The solution was filtered hot. The filtrate, which registered a pH value of *ca.* 6, on cooling to room temperature afforded a white shiny crystalline solid. The compound was filtered off and dried by pressing between the folds of a filter paper. The yield of Rb(acac) was 1.1g (69%).

Synthesis of (Acetylacetonato)caesium(I), Cs(acac)

This compound was synthesised in an analogous manner as described for Rb(acac). Starting from 1.0g (0.30 mmol) of Cs_2CO_3, the yield of Cs(acac) was 0.9g (63%).

Elemental Analyses

The methods of estimation of the elements are described in Chapter II and the results of elemental analyses are summarised in Table 7.1. Details of the instruments/equipment used for physical studies have been given in Chapter II.

Table 7.1 : Analytical data of A(acac) (A=Li, Na, K, Rb and Cs)

Compound	Analysis [a] (%)		
	A	C	H
Li(acac)	6.48	56.01	6.72
	(6.54)	(56.66)	(6.6)
Na(acac)	18.65	48.97	5.81
	(18.83)	49.21)	(5.73)
K(acac)	28.72	43.43	5.5
	(28.25)	(43.49)	(5.07)
Rb(acac)	45.92	33.01	4.04
	(46.32)	(32.54)	(3.79)
Cs(acac)	56.88	26.10	2.87
	(57.29)	(25.89)	(3.01)

[a] Calculated values are in parenthesis.

RESULTS AND DISCUSSION

Synthesis

The hitherto unknown Rb(acac) has now been synthesised from a direct reaction of Rb_2CO_3 and acetylacetone. A pH value of *ca.*6, considered suitable for synthesis of such compounds, was spontaneously attained in the reaction. The strategy for the synthesis was based on an acid-base type reaction and can be expressed as follows:

$$Rb_2CO_3 + 2C_5H_8O_2 \longrightarrow 2Rb(C_5H_7O_2) + H_2O + CO_2$$

The reaction is quite facile and clean, without contamination by side products, and the yield of the white crystalline, Rb(acac), was high. The successful synthesis of Rb(acac) led to the adoption of a similar strategy to improvise an easy and direct route to Cs(acac). The plan worked well to provide an easy access to Cs(acac). Pertinent here is to mention that the literature method[6] requires a prior preparation of caesium ethoxide from the reaction of Cs-amalgam, obtained in a low yield by electrolysis, with ethanol and then reacting with acetylacetone.

While both Rb(acac) and Cs(acac) readily absorbs moisture, the latter appears to be relatively more hygroscopic. The results of chemical analyses are consistent with the formulae $Rb(C_5H_7O_2)$, and $Cs(C_5H_7O_2)$. Neither Rb(acac) nor its Cs-analogue has a sharp melting point. Whereas the former begins to decompose at *ca.* 185°C, the latter decomposes above 200°C. As with their lighter congeners, both Rb(acac) and Cs(acac) are soluble in water, but insoluble in nonpolar organic solvents. The acetylacetonato-

alkalimetals, A(acac) [A=Li-Cs] have, however, varying degree of solubility in polar organic solvents showing a decreasing trend with increasing atomic mass of the metal.

Physico-chemical Studies

The alleged 'salt-like' properties and water-soluble nature of univalent metal-acac compounds render the analytical chemistry of the metals rather complicated.[5] Despite that the question of nature of the bonding in acetylacetonato-alkali metals were addressed in some investigations by previous workers.[6,9,10] The bidentate chelate geometry of the $acac^-$ ($C_5H_7O_2^-$) ligand (Fig.1) was expected to impart strong ion-association or ion-pair formation with alkali-metal ions. The notion was further augmented in view of a strong possibility of U-shaped configuration of $acac^-$ in such complexes.[10] Indeed the

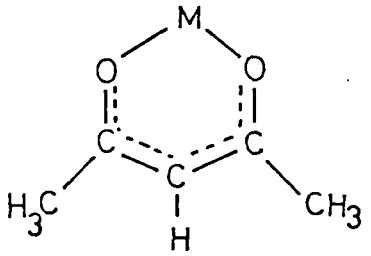


Fig. 1 Metal-acetylacetonate.

results of UV-spectral studies of Zaugg and Schaefer[10] provided some concrete evidence with regard to strong ion-association or ion-pair formation in dilute solutions of acetylacetonato-alkali metals in aprotic solvents as well as in water. It was also noted[10] that the spectral behaviour did not reveal significant

cation sensitivities on the change of solvents. Further, from the results of molecular conductivity measurements on mixtures of an ethanolic solution of sodium and potassium ethoxide and acetylacetone, it was inferred that complete dissociation was not achieved even at the maximum dilution.[11]

Since the A(acac) [A=Li-Cs] are readily soluble in water, experiments on molar conductance measurements were performed on an aqueous solution of each of acetylacetonato-alkali metals at ambient temperature. The values (Table 7.2) recorded (an average of five measurements with a deviation of ± 1-2 units) for 10^{-3}M solutions of Li(acac), Na(acac), K(acac), Rb(acac), and Cs(acac) were 70, 72, 107, 106, and 110 $ohm^{-1}cm^{2}mol^{-1}$, respectively. A perusal of the results reveals that the molar conductance values of A(acac) compounds are generally lower than those expected for an ideal 1:1 electrolyte,[12] with Li(acac) and Na(acac) having the lowest conductance. It is evident that the relative degree of dissociation of Li(acac) or Na(acac) is far less than K(acac), Rb(acac) or Cs(acac). It may be commented *inter-alia* that conductance experiments provide a good evidence for ion-association or ion-pair formation by A(acac) in aqueous solution with an enhanced association for A=Li or Na than for A=K, Rb or Cs. Further, in order to comment on their stability in aqueous solution, conductance measurements were carried out as a function of time and the values were found to be practically unaltered over a period of 5-7 days which again conforms to the ion-association as suggested and attest to their stability in water. This calls for a set of large number of newer experiments to be

conducted by changing both the parameters such as concentration of A(acac) solution and temperature of the experiments. The designed experiments have already been initiated involving a coworker in the laboratory and the results will be presented elsewhere. The infrared spectra of acetylacetonato-alkali-metals, A(acac), except Rb(acac), were investigated earlier[6] and the generalisation made thereof are now well accepted. The IR spectrum of Rb(acac) has been found to compare well with those of its congeners. The spectrum also bears a close resemblance to that of Tl(acac)[6] containing a chelated $acac^-$ group. The IR result is in line with the prediction made earlier by West and Riley[6] in the context of geometrical arrangement of the ligand both in acetylacetonato-alkali metals and polyvalent metal-acetylacetonates.

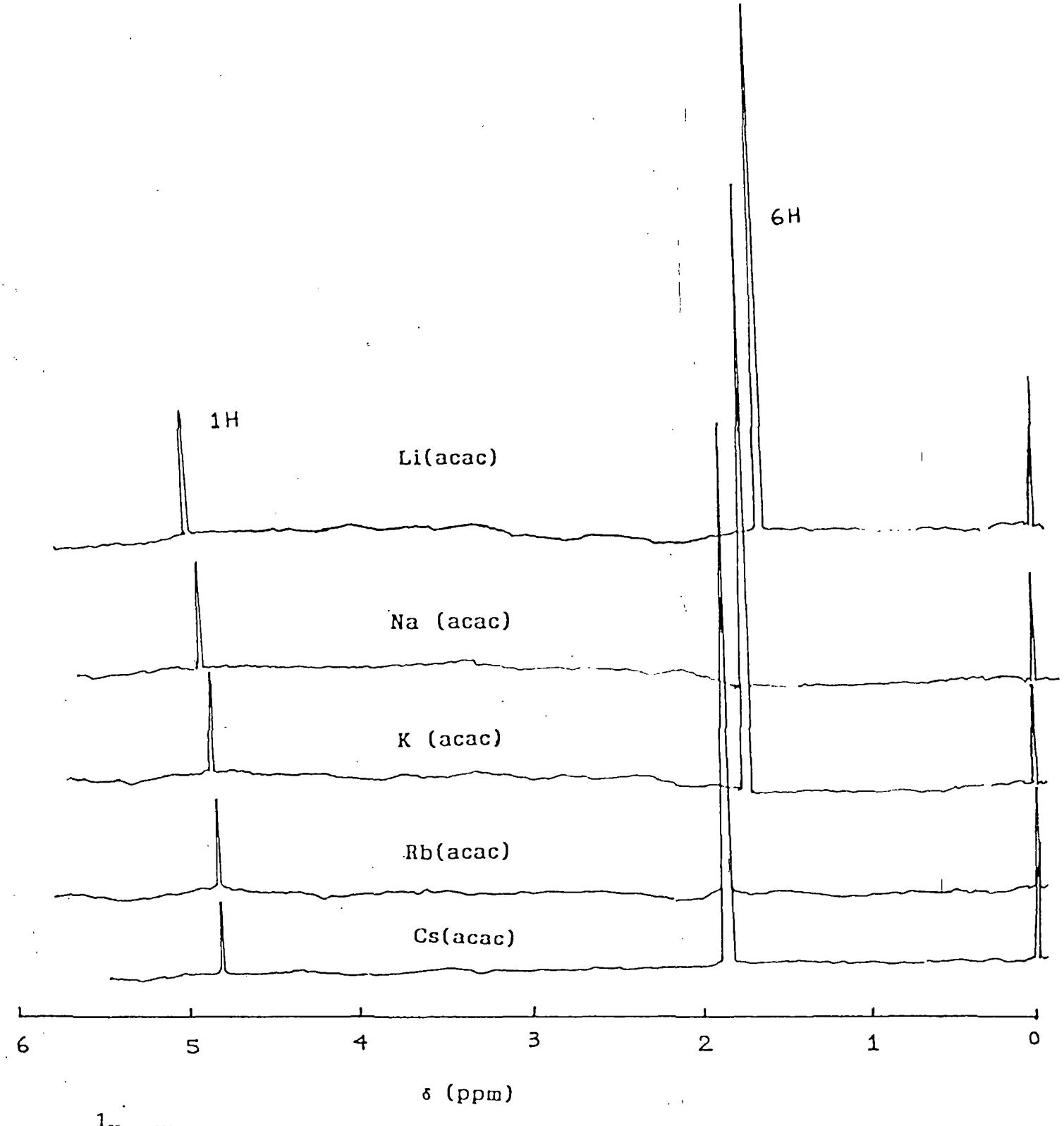
In an attempt to detect the differences in electronic distribution in the chelate ring of acetylacetonate as a function of metal ion completing the chelate ring, the nuclear magnetic resonance of ring proton (γ-H) was recorded earlier for a number of acetylacetonato-metals, with containing metal : $acac^-$ stoichiometry being 1:2, 1:3, and 1:4.[9] Significantly, the chemical shift values were found to be nearly independent of the nature of the metal ion completing the chelate ring, its charge, size, and ability to Π- bond with the ligand system. This implies the occurrence of a similar electronic environment in the compounds investigated. To the best of our knowledge, such studies, however, were not made on acetylacetonato-alkali metals presumably owing to the problem of solubility in organic solvents usually chosen for the purpose. However, the acetylacetonates of

Li, Na, and K are fairly soluble in a polar solvent like dimethylsulphoxide (DMSO) at ambient temperature, while those of Rb and Cs dissolve on slight warming. This observation and the availability of ^1H NMR data of a covalent compound namely $Zn(acac)_2$[13] recorded in DMSO-d_6 prompted us to record the ^1H NMR spectra of A(acac) compounds and compare the results with those of $Zn(acac)_2$. The spectra of the A(acac) compounds exhibit a general pattern with two signals at values *ca.* 1.7 ppm (6H, CH_3 protons) and *ca.* 4.8 ppm (1H, CH proton) [Table 7.2].

Table 7.2 : Molar Conductance and ^1H NMR data.

Compound	Molar conductance ($\Omega^{-1}cm^2mole^{-1}$)	^1H NMR in DMSO-d_6 δ(ppm)	
		-CH protons	$-CH_3$ protons
Li(acac)	70	5	1.66
Na(acac)	72	4.9	1.72
K(acac)	107	4.7	1.72
Rb(acac)	106	4.7	1.80
Cs(acac)	110	4.7	1.80

Although there are several parameters expected to contribute to these small chemical shift differences through for condense, space electric field, molecular shape, and electron density changes, it is notable that the present chemical shift values are similar to those of the covalent bis(acetylacetonato)zinc(II)



^{1}H NMR SPECTRUM

recorded in DMSO-d_6 (1.8 ppm, 6H; 5.2 ppm, 1H).[13] Further, the results (Table 7.2) clearly demonstrate that the values owing to the vinylic proton register a upfield shift whereas that for the methyl protons moves downfield, though not very appreciably, in descending the group (i.e. Li(acac) to Cs(acac)). This observation is in keeping with the replacement of a smaller cation with a larger one which in turn can be correlated to the suggested (cf. molar conductance values) increase in the relative ionic character from Li(acac) to Cs(acac). It is very rational to expect that probably additional and more direct information can be derived through C-13 NMR studies but unfortunately owing to the lack of such locally available facilities, the experiments could not be undertaken in the limited time. Such experiments will surely constitute part of the work of other collaborators as and when facility is available, and the results will be reported elsewhere.

Thus, both Rb(acac) and Cs(açac) can be synthesised from the direct interaction of respective metal carbonate and acetylacetone. The heretofore unreported molar conductance and proton NMR studies on acetylacetonato-alkali metal are highly informative and imply strong ion-association or ion-pair formation even in an ionising solvent, with a relative weakening of the association as a function of increased atomic number of alkali metal.

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1. New Developments in the Chemistry of Metal-Acetylacetonates
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2. New Heteroligand Peroxothorates(IV) of the Type $A_2[Th(O_2)F_2(OH)_2].nH_2O$ (A=NH_4, n=3; A=Na or K, n=1) and Molecular Peroxothorium(IV) Complexes of the Type $[Th(O_2)_3L(H_2O)_4].5H_2O$ (L=C_2O_4 or SO_4).
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NEW DEVELOPMENTS IN THE CHEMISTRY OF METAL-ACETYLACETONATE COMPLEXES

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New, direct and convenient, methods of synthesizing acetylacetonato metal complexes are described and their advantages highlighted. Two general methods of synthesis have been devised, (*i*) Acid-base and (*ii*) Electron-Transfer (REDOX) reactions enabling a large number of metal-acetylacetonate complexes, for example, $M(acac)_2$ (M = Mn, Fe, Co, Ni, Cu, MoO_2^{2+} or UO_2^{2+}; $(acac) = C_5H_7O_2$), Mo_2O_3 $(acac)_4$, $M(acac)_3$ (M = Cr, Mn, Fe or Ru) and $M(acac)_4$ (M = Ce or Th), to be synthesized. REDOX reaction between acetylacetone and a higher-valent transition metal ion also enabled the isolation of α, α, β, β-tetra-acetylethane as the oxidation product of acetylacetone, for the first time, from such a reaction. Newer reactions involving some of these compounds are described and the scope of such reactions in the context of research in synthetic inorganic chemistry has been emphasised. Salient features of electron-ionization mass spectra of acetylacetonatometal compounds, in terms of molecular association and structure-fragmentation correlation are also highlighted.

Key Words : New General Routes to Acetylacetonatometals; Oxidation Product of Acetylacetone; Newer Reactions; Mass Spectrometry

INTRODUCTION

ACETYLACETONE is the simplest of the β-diketones. The presence of β-carbonyl groups with at least a proton on the intermediate carbon, allows a keto ⇌ enol tautomerism to be operative in β-diketones (Fig. 1). The enolic proton (Fig. 1) can be replaced from the β-diketo-enols, with various ligands, under appropriate

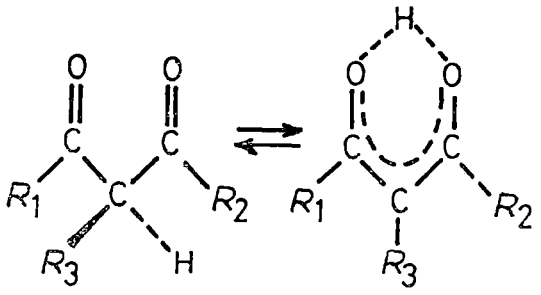


FIG 1 Keto-enol tautomerism with β-diketone

conditions. Although a variety of substituents can appear at R_1, R_2, R_3 of the β-diketones (Fig. 1), however, acetylacetone (H*acac* : R_1, R_2, = CH_3; R_3 = H) and compounds that are formed when the enolic proton is replaced by metals in several of their oxidation states from acetylacetone (Fig. 2) constitute the subject matter of the present report.

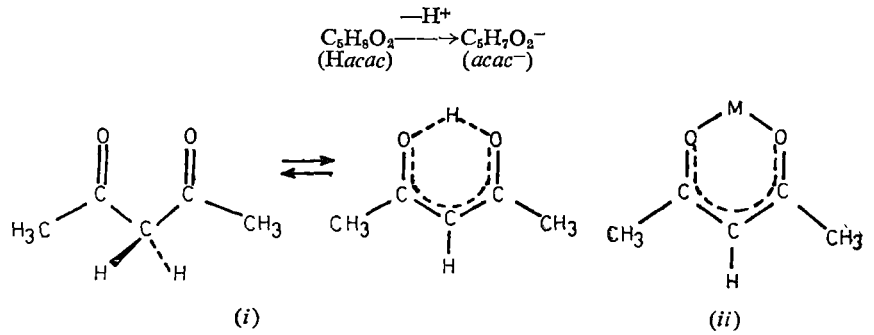


FIG 2· (*i*) Keto-enol tautomerism with acetylacetone (*ii*) Metal-acetylacetonate

Metal-acetylacetonato complexes, as they are called, have been known and studied for almost a century yet much remains to be understood.[1] Complexes with acetylacetone are known for all nonradioactive metals and metalloids and can broadly be grouped into two viz., the molecular and the ionic complexes. However, the present report is exclusively restricted to the ones which are molecular in nature. The types of molecular complexes and the corresponding metals for which they are known have been enlisted in Table I.

TABLE I

Metals for which different types of molecular complexes are known

M (*acac*)	: Li, Na, K, Cs, Cu, Ag, Tl
M $(acac)_2$	: Be, Ca, Ba, Zn, Hg, Cr, Mn, Fe, Co, Ni, Cu, Mg, Sr, Pd, Pt, Pb, UO_2^{2+}, VO^{2+}
M $(acac)_3$	: Sc, Y, Ce, Ln's, V, Cr, Mo, Mn, Re, Fe, Ru, Co, Rh, Ir, Al, Ga, In, Ce, Os
M $(acac)_4$	: Zr, Hf, Th, U, Pu, Ce

Metal acetylacetonate complexes are known for quite a long time so also their synthesis known for long. Evidently there exists more than one route to such complexes. But those synthetic routes had some limitations in scope owing to the involvement of several complications. Improvising newer and convenient synthetic routes in order to have a rather easy access to the chemistry of metal-acetylacetonates, therefore had been one of the primary concerns. Our interest in the synthetic inorganic chemistry have eventually led us to devise two new, direct and general methods—one based on (*i*) *ACID-BASE* and the other on (*ii*) *ELECTRON-TRANSFER* (redox) concepts. The essential features of the

newly devised methods, their advantages over the earlier ones alongwith a brief summary of various acetylacetonato-metals that have been successfully synthesized in our laboratory following the new routes are reported in this work. Also summarised herein are some newer reactions of acetylacetonato-metals and their scope, and the salient aspects of electron-impact induced positive ion mass spectrometry of a variety of the title compounds. No attempt, however, is made here to give an exhaustive coverage to every 'acetylacetonato-metal prepared, rather the contention is to approach their studies with special reference to their synthesis, newer reactions and EI-induced positive ion mass spectrometric investigations that will complement the work of various other groups reported earlier in this field.

But before we enter into a discussion on the problems encountered in the synthesis of acetylacetonato-metals and the new methods developed to circumvent such problems, it is appropriate to briefly enumerate the vast potential and immense importance that such complexes hold. The role of metal-acetylacetonates as catalysts in important organic reactions such as oligomerisation, polymerisation, hydrogenation, isomerisation of olefins, hydrosilylation of alkynes and coupling of organic halides,[2] is well recognised. Metal-acetylacetonato complexes have also found applications in various industrial processes, for example, in rubber technology for vulcanisation,[3] in polymer[4,5] plastic, and paints industries as additives and for metal planting from organic solvents[3] and for extraction, separation of metals[6,7,8] and also as semiconductors,[9] antioxidants[10] etc. Their ability, to function as probes in NMR spectroscopic studies, has rendered them a useful class of NMR shift reagents.[11,12] Two important properties namely volatility and solubility in organic solvents are significant. While the former renders this class of compounds as suitable probes amenable to mass spectrometric studies, the latter causes them to be useful synthetic precursors for organometallic synthesis. In addition, it has been conclusively proved that metal-chelates of β-ketoenolate under certain specific conditions are capable of laser emission.[13,14] Work[15] in this regard has confirmed the fact that metal chelate anion is responsible for laser action in a number of such complexes. Metal acetylacetonates or for that matter β-ketonates have been also found to exhibit quenching effect of triplet state.[16] It is believed that the effect is due to the presence of unsaturated ligands.[16] Consequent upon the applied needs as well as the interests in academic research metal-β-diketonates, in general, and metal-acetylacetonates, in particular have thus always engaged the attention of various groups of workers over the years.

SYNTHESIS

As already mentioned in the introduction of this article, an easy access to pure metal-acetylacetonato compounds have always been a major difficulty owing to problems elaborated below.

Earlier methods,[17,18,19] reported in the literature for the synthesis of metal acetylacetonato complexes may be discussed under the following heads :-

1. Metal-Acetate

2. Metal Salt
3. Metal Carbonyl

Certain amount of caution, which we outline below, must be exercised in using any of the above-mentioned techniques. The metal-acetate method uses acetates in order to control the *p*H. Chances of end-product contamination by acetates, owing to the use of large excess of buffer, cannot be ruled out. The metal salt technique which is a modification of aqueous solution synthesis[17] from metal salts, on the other hand, appeared to have some general usefulness and products in many cases could be obtained free from base contamination. But, since this procedure requires a metal salt to be soluble in strongly basic or amomniacal solution, formation of basic compounds[18] on many occasions were unavoidable. While it is essential to exercise some caution in both of these procedure, the metal-carbonyl route was proved to be free from the afore-mentioned limitations and purity of the end product could thus be ensured. However, this technique has some other kinds of limitations viz., involvement of extra preparation steps in addition to the difficulties encountered in the handling of air-sensitive toxic metal carbonyl.[20] Taking note of the limitations and problems highlighted above, a search for easier general synthetic routes to acetylacetonato-metals was therefore warranted. With this background we embarked on a research programme aimed at improvising easily accessible routes to pure acetylacetonato-metals. Fortunately it has been possible for us to improvise two direct general methods (*vide supra*) for the purpose, the theme and scope of which will be developed in some details below.

Acid-Base

Acetylacetone, because of the presence of active methylenic hydrogen, shows weak acidity and it was thought that an interaction of acetylacetone (H*acac*) with metal hydroxides or hydrated basic metal oxides would lead to an acid-base type of reaction thereby bringing about co-ordination of acetylacetone with metal (Eqn. 1). Accordingly, based on this philosophy we were successful in obtaining a good number

$$M(OH)_x + x\ Hacac \longrightarrow M(acac)_x + x\ H_2O \qquad ...(1)$$

of acetylacetonato-metals. The advantage of this method, unlike the earlier ones, are that it neither requires any extra preparation steps nor any external buffering agent for the maintenance of a requisite *p*H. The *p*H of the reaction medium was found to be controlled spontaneously at *ca* 5, a condition conducive to the successful synthesis of the desired compounds. The method, therefore, not only resulted in pure products but also ensured shorter reaction time. Further the method is direct, simple and easy to manipulate. Outlined below are the syntheses of several acetylacetonato-metals which were successfully achieved in our laboratory following this procedure.

(i) *Synthesis of Bis(acetylacetonato) metal(II)-Hydrates*[21]

(*a*) $M(acac)_2.nH_2O$(M = Co, Ni or Cu, $n = 2$; UO_2^{2+}, $n = 0$)—Freshly prepared alkali-free metal hydroxide $M(OH)_2$ (M = Co, Ni or Cu) (20mmol) or a yellow precipitate (1.99mmol) resulting from addition of aqueous ammonia to a solution of uranyl nitrate (eqn. 2) was made to react with *ca* 10cm³ of over a steam-bath for *ca* 30min (1hr for $M = UO_2^{2+}$), A clear coloured solution or, in the case of nickel

$$UO_2(NO_3)_2.6H_2O \xrightarrow{Aq.NH_3} Y \xrightarrow{Hacac} UO_2(acac)_2 \qquad ...(2)$$

green-blue microcrystalline product, was obtained. The *p*H of the solutions recorded at this stage was found to be 5–6, a *p*H range conductive for metal-acetylacetonate formation. The solutions as obtained above were cooled to ice-bath temperature and the product was separated by filtration. Yields of the compounds are 90–95 per cent.

(*b*) $M(acac)_2.2H_2O$(M=Mn(II) or Fe(II)[21]—Bis(acetylacetonato) manganese(II) dihydrate, [Mn (*acac*)$_2$].$2H_2O$, and *bis* (acetylacetonato) iron(II) dihydrate, [Fe(*acac*)$_2$].$2H_2O$, have been synthesized following the general procedure described for those of other $[M(acac)_2].2H_2O$ complexes described under (*i*) (*a*). The only difference was that the syntheses were carried out in the presence of 2.5–3.0cm³ 38 per cent formaldehyde solution to prevent undesirable oxidation of manganese(II) and iron(II).

(*c*) *Tetrakis* (*acetylacetonato*) *dioxo-μ-oxomolybdenum*(V)[22], $[Mo_2O_3(C_5H_7O_2)_4]$—Tetrakis (acetylacetonato) dioxo-μ-oxodimolybdenum (V), $Mo_2O_3(C_5H_7O_2)_4$, has been synthesized directly from the reaction of $MoO(OH)_3$ (6.1mmol) and acetylacetone (60.0mmol) by refluxing in a round-bottomed flask for *ca* 3hr. The deep brown solution thus obtained was filtered and the filtrate was cooled in an ice-bath for *ca* 2.5hr to obtain brown microcrystalline $[Mo_2O_3(C_5H_7O_2)_4]$. The compound was washed with ethanol and dried *in vacuo*.

(ii) *Synthesis of Tris* (*acetylacetonato*) *Metal(III)* $M(acac)_3$ (M = Fe[20], Co[20], Mn[23] or Ru[24])

Novel synthesis of tris(acetylacetonato) iron(III) has been achieved in high yield directly from the reaction of iron(III) hydroxide with acetylacetone under gentle warming over a steam-bath for 30min (eqn. 3)

$$Fe(OH)_3 + 3\ Hacac \longrightarrow [Fe(acac)_3] + 3\ H_2O \qquad ...(3)$$

Analogous methods have been used with success for the synthesis of [Co(*acac*)$_3$] from CoO(OH), [Mn (*acac*)$_3$] from MnO(OH) and [Ru(*acac*)$_3$] from hydrated ruthenium oxide. The *p*H of the solution recorded immediately after the formation of the compound, was found to be *ca* 5 which concurs with that maintained by using a large amount of sodium acetate in the earlier methods of Synthesis of such compounds.

(iii) *Synthesis of Tetrakis(acetylacetonato) metals(IV)*, $M(acac)_4$ (M = Ce[25] or Th)

The $Ce(acac)_4$ and Th $(acac)_4$ were synthesized directly from the reactions of hydrated Ce (IV) oxide and Th(IV) oxide, respectively, with acetylacetone and finally concentrating the reaction solution over a steam-bath. The solutions so obtained were cooled to 0 °C in the case of Ce and to room-temperature in the case of Th to obtain crystalline $M(acac)_4$ (M = Ce or Th) in very high yields.

ELECTRON-TRANSFER (REDOX)

The chelating ability of acetylacetone has long been recognised and, based on some very recent studies[23,26] on the synthesis of fluoro-metallates of Mn(III) from $KMnO_4$, its potential as a suitable reducing agent has also been proved beyond doubt. In view of this it was expected that the synthesis of acetylacetonato-metals might as well be possible from the reactions of higher-valent transition metals with acetylacetone. As anticipated, the strategy worked in line with the contention enabling us to devise another direct general route to acetylacetonato-metals based on the concept of redox reaction. The reduction of higher valent metal ions by acetylacetone and subsequent formation of the chelates owing to the presence of an excess acetylacetone appear to be the driving forces for the reactions.[27] It is imperative to mention that an excess of acetylacetone should be used so that, after the electron-transfer reaction between a metal ion and H*acac* is over, an appreciable amount of H*acac* is still available in the medium to act as ligands. The course of the reaction is observed to be such that it spontaneously maintains the *p*H conductive to the synthesis. Thus, here again like our acid-base method (*vide supra*) no additional buffer is required. The Redox method has been very successful for the synthesis of a number of acetylacetonatometals, as outlined below :

(i) *Synthesis of Tris (acetylacetonato) Metal(III)*, $M(acac)_3$ (M = Mn(III)[26] or Cr(III)[28]

Tris (acetylacetonato) manganese(III), $[Mn(acac)_3]$ has been prepared starting from a hot aqueous solution of $KMnO_4$ and an excess of H*acac* with vigorous stirring over steam-bath for *ca* 5min and then cooling to room temperature. The dark brown-black shiny crystals of $[Mn(acac)_3]$ so obtained were filtered off and washed several times with small amounts of H*acac* : water mixture and finally dried *in vacuo*.

The synthesis of $[Cr(acac)_3$ required a somewhat vigorous reaction condition. A quantity of 2.0g powdered CrO_3 was added to 2.0g distilled acetylacetone with constant stirring whereupon an exothermic reaction set in and the colour of the solution became dark violet. Stirring was continued for another 5–10 min after the addition was complete. The solution was heated over a steam-bath for *ca* 4hr in an open beaker and then allowed to cool for *ca* 1hr in a freezer. The dark

pink-violet shiny crystals of [Cr(*acac*)$_3$] were filtered off and washed several times with water and finally dried *in vacuo.*

(ii) *Synthesis of Bis (acetylacetonato) Nickel(II) Dihydrate,* [Ni(*acac*)$_2$].2H$_2$O[29]

Synthesis of [Ni(*acac*)$_3$].2H$_2$O was achieved from the reaction of NiO(OH). The NiO (OH) was prepared by oxidation of an alkaline suspension by bromine. The reaction of NiO (OH) with H*acac* is an exothermic one and proceeds almost mmediately. The reaction-mixture needs to be stirred continuously until the black NiO(OH) is converted completely to a blue-green product.

Isolation of α, α, β, β-Tetraacetylethane as the Oxidation Product of Acetylacetone from Redox Reaction

Having achieved success[26,28,29] in the synthesis of acetylacetonato-metals through the redox method, as demonstrated above, it was our concern to identify the oxidation product of H*acac* in such a reaction. Incidentally there exists no firm evidence regarding the oxidation product of H*acac* when it acted as a reducing agent until we published[29] our results first in 1983. Interest in ascertaining the identity of the oxidation product of H*acac,* was not only to provide a concrete evidence for its identity but also to have an insight into the redox mechanism of such reactions. Our first success in this context came through the synthesis of [Ni(*acac*)$_2$].2H$_2$O from NiO(OH) wherein work-up of the mother liquor, after separating [Ni(*acac*)$_2$].2H$_2$O, afforded colourless crystals. The compound was obtained in a very high yield and found to melt at 190 °C. The product was very sparingly soluble in water, benzene and ether. Its various physical and chemical properties (colur, m.p., solubility, reaction with FeCl$_3$, and mass and NMR spectra) compare very well with those of a specimen prepared by the action of iodine upon sodium acetylacetonate.[30] Accordingly the identity of the compound has been established as α, α, β, β-tetra-acetylethane, (CH$_3$CO)$_2$ CH-CH(CH$_3$CO)$_2$.

In an attempt to generalise the contention that electron-transfer reactions between higher-valent transition metal ions and acetylacetone leading to the corresponding acetylacetonates, give (CH$_3$CO)$_2$CH-CH (CH$_3$CO)$_2$ as the oxidation product, we performed the reactions of H*acac* with Mn^{7+} and Cr^{6+} following the procedures described in our previous paper[26,28] Isolation of (CH$_3$CO)$_2$CH-CH-(CH$_3$CO)$_2$ from each of the reactions, after separation of the corresponding [*M*(*acac*)$_3$] complex, was successful again owing to the oxidation of acetylacetone. We therefore conclude that in the electron-transfer reactions of the types discussed above, acetylacetone is oxidised to α, α, β, β-tetraacetylethane, (CH$_3$CO)$_2$CH-CH-(CH$_3$CO)$_2$. In view of the products isolated from the reactions of Ni^{3+} (eqn 4), Mn^{7+} or Cr^{6+} with acetylacetone, and the observed *p*H of the reaction medium, it is

$$[Ni(III)\,O(OH)] + 3\,Hacac \rightarrow [Ni(acac)_2] + \tfrac{1}{2}\,acac + 2H_2O \qquad ...(4)$$

felt that acetylacetone first undergoes ionization giving (CH$_3$CO)$_2$CH$^-$(*acac*$^-$) and H^+ (cf. the observed *p*H) followed by the oxidation of (CH$_3$CO)$_2$CH$^-$ ion to (CH$_3$CO)$_3$$^{\cdot}$ CH radical (with corresponding reductions of the metals) which dimerises

to yield $(CH_3CO)_2$ CH-CH$(CH_3CO)_2$.[29] It may be mentioned in passing that this route to α, α, β, β-tetraacetylethane is relatively simpler than the method described in the literature.[31]

Newer Reactions

The synthetic potentiality of acetylacetonato-metal compounds as precursor in organometallic synthesis is well documented[32,33] in the literature. Having achieved an easy access to such compounds by the methods reviewed in this article, the authors got interested in exploring a newer facet of application of acetylacetonato-metals as synthetic precursors for the synthesis of inorganic compounds which are otherwise very difficult to get an access to. As a part of one of our general programmes dealing with the fluoro-chemistry of metals and non-metals, it was anticipated that the reactions of such compounds with F^- in acidic medium would lead to the cleavage of metal-oxygen bond of β-ketoenolate complexes ultimately leading to newer synthetic routes to fluoro-metallates.[34] The strategy worked in line with the contention enabling us to obtain a good number of fluoro compounds of metals as highlighted below, in an unprecedented easy manner. It is believed that the success of the strategy largely depends on the presence of both H^+ as well as the stabilising ligand (F^-, in these cases) in the solution phase.[23]

Thus the complexes $A_2[NiF_4]$ (A = NH_4, K or Rb) and $A_2[ZnF_4]$ (A = NH_4, K, Rb or Cs) have been synthesised,[27] from $[Ni(acac)_2].2H_2O$ and $[Zn(acac)_2]$ H_2O, respectively, with 40 per cent HF and AF, in a very high yields. Literature methods[35,36,37] for the synthesis of $[NiF_4]^{-2-}$ or $[ZnF_4]^{2-}$ complexes employ fusion of NiF_2 or ZnF_2 with stoichiometric amounts of alkali-metal or alkaline-earth metal fluorides *in vacuo* or in an atmosphere of dry HF. Such methods require not only MF_2(M = Ni or Zn) but also anhydrous HF which is difficult to handle, consequently limiting their accessibility.

The alkali-metal trifluoronicklete(II) monohydrates, $ANiF_3.H_2O$(A = NH_4, Na or K), are simple, yet show interesting properties. For example, the mere change of the counter cation in $ANiF_3.H_2O$ brings about very drastic and significant changes of magnetic properties. Although Machin and Nyholm reported[38] the analytical data and magnetic properties of $ANiF_3.H_2O$ about 25 years ago, there was no report on their synthesis until we published[34] a general procedure in 1985, as outlined below. In a typical procedure, $[Ni(acac)_2.2H_2O$ was reacted with AF(A = NH_4, Na or K) and an excess of 40 per cent HF on a steam-bath. The light-green crystalline product obtained thereof on treatment with water was shown to be alkali-metal trifluoronickelate(II) monohydrate, $ANiF_3.H_2O$. In an attempt to explore the scope of the new synthetic procedure, similar reactions involving $[VO(acac)_2]$,[39] $[Cr(acac)_3]^-$[28] or $[Mn(acac)_3]$[26] with NH_4F and 40 per cent HF were carried out and the products obtained were identified as $(NH_4)_4$ $[VOF_4]$, $(NH_4)_2$ $[CrF_5(H_2O)]$, and $(NH_4)_2$ $[MnF_5]$, respectively, thereby supporting our notion that the method can be used as a paradigm for other such syntheses.

Mass Spectrometry

Since β-ketoenol-metal complexes have been such a commonly used commodity around the chemistry laboratories for half a century or more, it is but natural to expect that various physico-chemical[40] studies involving them were carried out. Low and sharp melting points of acetylacetonato-metals, however, rendered this class of coordination compounds suitable probes for mass spectrometric studies. Accordingly, a good amount of mass spectrometry of such compounds, mainly involving bis- and tris-chelates of higher metals,[20,28,41,42,43] were carried out. In contrast, the corresponding heavy metal analogues, and tetrakis-chelates, the examples of which are only a few in number, have not received due attention. Although a hike in current interest in this area has been accentuated in some of the recent reports dealing with mass spectra of fluorinated β-diketonato complexes of Eu,[44] Pd,[44] UO_2^{2+} (Ref. 45), and Ce,[46] we are unable to discern any obvious reasons for taking no notice of the corresponding nonfluorinated acetylacetonato complexes in the previous mass spectrometric investigations. As a case in point, the mass spectrum of $UO_2(C_5H_7O_2)_2$, an important compound of uranium has been reported[21] only in 1986, while that of $Ce(C_5H_7O_2)_4$ is yet to be seen in print. Further it was commented[41,43] that attempts to obtain good mass spectrum of acetylacetonato-metals were not always successful. In view of this and in a continuation of our work[20,26,28] in this field, the mass spectrometric studies of several acetylacetonato-metals were undertaken. We present in this section of the article, the salient features of Electron-Impact induced positive ion mass spectrometric studies of acetylacetonato-metals of the types $M(acac)_2^{2+}$ (M = Mn, Fe, Co, Ni or Cu), $M(acac)_3$ M = Mn,[26] Fe[20] or Cr[28] and $M(acac)_4$ (M = Ce[25] or Th). Also highlighted herein are the results of mass spectrometric studies of bis(acetylacetonato) dioxouranium(VI), $[UO_2(acac)_2]$[21], bis(acetylacetonato) dioxomolybdenum) (VI),[22] $MoO_2(acac)_2$, and tetrakis(acetylacetonato) dioxo-μ-oxomolybdenum(V), $Mo_2O_3(acac)_4$,[22] which were reported for the first time in 1986. Moreover, an attempt has also been made to internally compare the results of mass spectrometry of the related systems.

Mass spectrometrically, bis(acetylacetonato) metal, $M(C_5H_7O_2)_2$ (M = Mn, Fe, Co, Ni or Cu) compounds may be classified into two groups with M = Mn, Fe, Co forming one, and M = Ni or Cu the other. The molecular ion in each case loses CH_3 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 (Scheme 1) is distinctly different from that with M being Ni or Cu (Scheme 2). 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 H 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 reaction.[21]

$$[M(C_5H_7O_2)_2]^+ \xrightarrow[*]{-CH_3} [M(C_5H_7O_2)(C_4H_4O_2)]^+ \xrightarrow[*]{-C_4H_4O_2} [M(C_5H_7O_2)]^+$$

$$*\downarrow -CH_3$$

$$[M]^+ \xleftarrow[*]{-C_4H_4O_2} [M(C_4H_4O_2)]^+$$

(M = *Mn, Fe or Co*)

SCHEME 1

We believe hydrogen transfer to the metal, rather than to any oxygen atom of the other ligand as proposed by others,[47] as a 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.

$$[M(C_5H_7O_2)_2]^+ \xrightarrow[*]{-CH_3} [M(C_5H_7O_2)(C_4H_4O_2)]^+ \xrightarrow[*]{-C_4H_4O_2} [M(C_5H_7O_2)H]^+$$

$$*\downarrow -H$$

$$[M(OCCH_2)]^+ \xleftarrow[*]{-OCCH_2} [M(C_4H_4O_2)]^+ \xleftarrow[*]{-CH_3} [M(C_5H_7O_2)]^+$$

$$-OCCH_2 \downarrow *$$

$$[M]^+$$

(M = Ni *or* Cu)

SCHEME 2

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, $OCCH_2$, and again another $OCCH_2$ ultimately to give the $[M]^+$ ion (as shown in Scheme 2). While for M = Mn, Fe or Co, the ion $[M(C_5H_7O_2)]^+$ sequentially loses CH_3 and $C_4H_4O_2$ to produce the $[M]^+$.

A comparison of the Schemes 1 and 2 shows that the mode of fragmentation of the $[M(C_5H_7O_2)]^+$ ion is different in two cases. Thus, for M = Mn, Fe or Co, the $[M(C_5H_7O_2)]^+$ first expels CH_3 and then $C_4H_4O_2$ moiety to produce the bare $[M]^+$ ion however, for M = Ni or Cu three steps are involved as depicted in the Scheme 2. Another point of difference lies in the appearance of the base peaks. Whereas the $[M(C_5H_7O_2)]^+$ 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 of the corresponding complexes of Ni or Cu. Enough metastable peaks have been observed in support of Schemes 1 and 2 to lend credence to the suggested mode of fragmentation. Mass spectra of bis(acetylacetonato) metal(II), with M being Mn, Fe, Co, Ni or Cu, were reported by earlier workers. It is in order to collate the mass spectrometric results of these compounds with those of the heavier metal analogues that we re-investigated the mass spectra of such compounds under analogous experimental conditions. The selective

*indicates metastable supported transitions.

acetylacetonates of heavy metals incorporated for the purpose mentioned above include $[MoO_2(C_5H_7O_2)_2]$, $[Mo_2O_3(C_5H_7O_2)_4]$, $[UO_2(C_5H_7O_2)_2]$, and $[Ce(C_5H_7O_2)_4]$.

The mass spectrum of $MoO_2(C_5H_7O_2)_2$ (structure shown in Fig. 3) showed a parent ion signal at m/z 328, due to $[MoO_2(C_5H_7O_2)_2]^+$, followed by the signals at m/z 286 and 229 assigned to $[MoO_2(C_5H_7O_2)(C_3H_5O)]^+$ and $[MoO_2(C_5H_7O_2)]^+$, respectively, suggesting that the parent ion first loses CH_2CO and then C_3H_5O to produce the ion $[MoO_2(C_5H_7O_2)]^+$. It is important to note that, unlike the *bis* (acetylacetonato) complexes of first-row transition metals,[21] the molecular ion of $[MoO_2(C_5H_7O_2)_2]$ undergoes a loss of a ketene (CH_2CO) instead of a CH_3 radical.[22] This difference may, in part, arise as a consequence of the fact that the former usually have d electrons so that valency changes become important, whereas in $[MoO_2(C_5H_7O_2)_2]$. Mo atom has d^0 configuration. The $[MoO_2(C_5H_7O_2)]^+$ ion, however, undergoes further fragmentation in two different ways, as evident from the appearence of signals of almost equal intensities owing to $[MoO_2(C_5H_5O)]^+$ and $[MoO_2(C_3H_5O)]^+$, respectively. Both of these fragments ultimately crack down to the bare ion $[MoO_2]^+$. The most probable fragmentation pattern, in line with the experimental observations, is shown in Scheme 3. The observation of a metastable ion peak at m^*/z 99.6 is consistent with the fragmentation $[MoO(C_3H_5O)]^+$ (m/z 211) $\rightarrow$ $[MoO_2CH_3]^+$ (m/z 145), and suggests the occurrence of a methyl transfer reaction from the ligand, presumably to one of the oxygen atoms already bound to the metal or to form a new Mo-CH_3 band. A somewhat similar methyl shift has been observed[20] in the case of Fe $(C_5H_7O_2)_3$ (*vide infra*).

The mass spectrum of $Mo_2O_3(C_5H_7O_2)_4$ appears to be more complicated than that of $MoO_2(C_5H_7O_2)_2$. The compound $Mo_2O_3(C_5H_7O_2)_4$ (structure shown in Fig. 4) showed the molecular ion signal at m/z 636 due to $[Mo_2O_3(C_5H_7O_2)_4]^+$ suggesting that it did not undergo any association in the vapourstate.

The molecular ion fragments in two distinctly different ways as shown in Scheme 4. While path I involves fragments containing bimetallic ions, path involves only monometallic fragments.

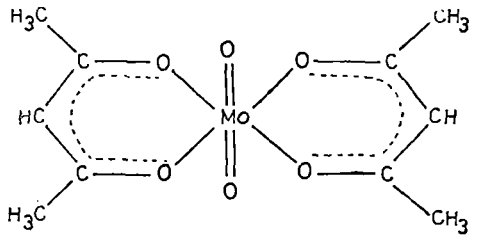


FIG 3 Structure of $MoO_2(C_5H_7O_2)_2$

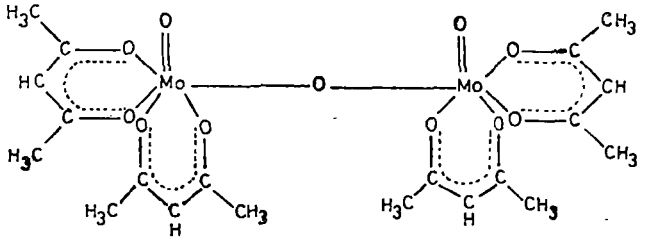
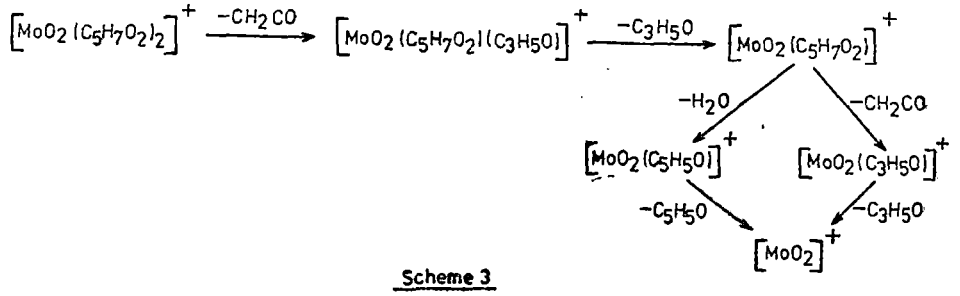
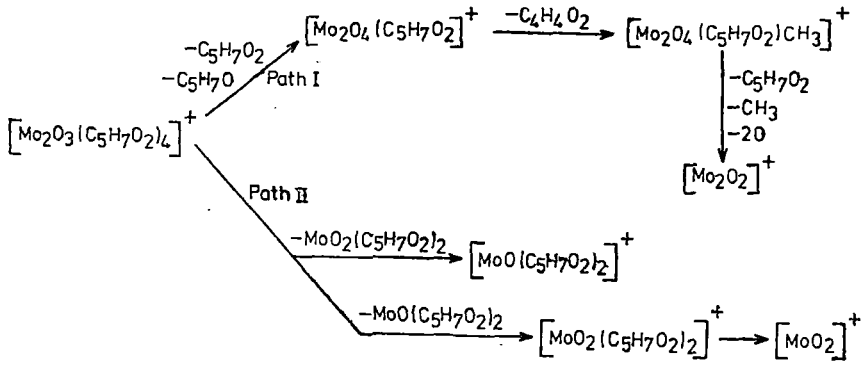


FIG 4 Structure of $Mo_2O_3(C_5H_7O_2)_4$



Scheme 3



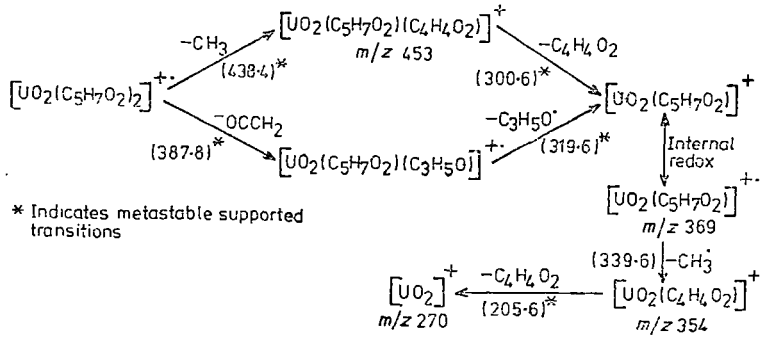
Scheme 4

Natural molybdenum contains a mixture of isotopes forming a characteristic pattern diagnostic for the presence of Mo in a given ion. The isotope pattern for ions containing two Mo atoms can be predicted by well-established methods,[45,46,47] from the isotope distribution of the metal. The reported relative abundance data for the monometallic fragment ions are based on the heights of signals of the ions containing the isotope ^{98}Mo (23.8 per cent natural abundance), while the bimetallic fragment ions of compound Mo_2O_3 (*acac*)$_4$ are based on the ions where Mo_2 contributed 192 (13.1 per cent natural abundance by calculation) to the total mass of the fragment ion. Typical patterns for the bimetallic and monometallic fragment ions were observed in the respective cases. The parent ion, in accord with the path *I*, loses one $C_5H_7O_2$ moiety and C_5H_7O moiety in

steps to produce $[Mo_2O_4(C_5H_7O_2)_2]^+$ ion. Whereas the loss of $C_5H_7O_2$ has been observed in the spectra of many acetylacetonatometals, the loss of C_5H_7O from such compounds is rather rare though not unprecedented.[51] It is believed that the strong tendency of Mo^{5+} to form Mo = O causes fragmentation of the coordinated $C_5H_7O_2^-$ ligand leading to the expulsion of C_5H_7O with the retention of one oxygen atom (as Mo = O). The fragment thus formed, then loses $C_4H_4O_2$ to yield $[Mo_2O_4(C_5H_7O_2)\ CH_3]^+$ which again, as observed for $[MoO_2(C_5H_7O_2)_2]$, is a case of methyl shift from ligand to the oxo-oxygen already bound to the metal or directly to the metal itself. The ion $[Mo_2O_4(C_5H_7O_2)\ CH_3]^+$ ultimately breaks down to $[Mo_2O_2]^+$.

A perusal of the signals arising from the monometallic fragments reveals that the signal at *m/z* 312 assigned to the $[MoO(C_5H_7O_2)_2]^+$ ion forms the base peak of the spectrum of $[Mo_2O_3(C_5H_7O_2)_4]$. Unfortunately, no metastable peak for the transition $[Mo_2O_3(C_5H_7O_2)_4]^+ \rightarrow [MoO_2(C_5H_7O_2)_2]^+$ could be observed. The other signals due to monometallic fragments correspond to those observed in the spectrum of $MoO_2(C_5H_7O_2)_2$, but generally of much lower intensities, suggesting that the formation and subsequent fragmentation of the ion $[MoO_2(C_5H_7O_2)]^+$ can not be totally ruled out. Metastable transition studies lend strong support to the proposed fragmentation pattern.

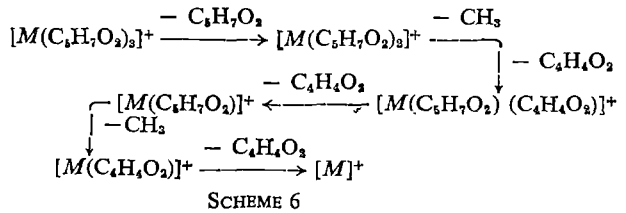
The EI-induced positive ion mass spectrum of $[UO_2(C_5H_7O_2)_2]$ exhibited parent ion signal at *m/z* 468 due to $[UO_2(C_5H_7O_2)_2]^+$ and no signal beyond *m/z* 468 thereby showing the obsence of any molecular association in the gaseous state. The molecular ion, $[UO_2(C_5H_7O_2)_2]^+$; so obtained fragments (Scheme 5) to $[UO_2(C_5H_7O_2)\ (C_4H_4O_2)]^+$ and $[UO_2(C_5H_7O_2)]^+$ with an equal probability via a methyl radical (CH_3) or a ketene ($OCCH_2$) loss, respectively. While CH_3· radical loss from the molecular ion $[UO_2(C_5H_7O_2)_2]^+$ involves simply the cleavage of 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 $[UO_2(C_2H_5O_7)^{2+}$ must involve a rearrangement in the ligand to give the odd-electron ion $[UO_2(C_5H_7O_2)\ (C_3H_5O)]^{+\cdot}$ The ions $[UO_2(C_5H_7O_2)\ (C_4H_4O_2)]^+$ and $[UO_2(C_5H_7O_2)]^{+\cdot}$ lose $C_4H_4O_2$ and C_3H_5O· species, respectively, to form the most dominant ion $[UO_2(C_5H_7O_2)]^+$, which



Scheme 5

again fragments in two different ways by the loss of H_2O and CH_3·, respectively, to give $[UO_2(C_5H_5O)]^+$ and $[UO_2(C_4H_4O_2)]^+$ ions. The weak nature of the signal at *m/z* 351 owing to the loss of H_2O 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· radical. The loss of a CH_3· 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 $[U(V)\ O_2(C_5H_7O_2)]^+$ which then expels a CH_3· radical to produce $[UO_2(C_4H_4O_2)]^+$. This even electron ion ultimately cracks down to bare $[UO_2]^+$. The last two steps of fragmentation involving loss of CH_3· and $C_4H_4O_2$ from the $[UO_2(C_5H_7O_2)]^+$ fragment resemble those generally observed for the corresponding $[M(C_5H_7O_2)]^+$ where M = Mn, Fe or Co, as discussed earlier. Methyl transfer from ligand to the uranyl (UO_2) centre, like in the case of $MoO_2(C_5H_7O)_2$ or hydrogen transfer from ligand to the uranyl centre, like in the case $M(C_5H_7O_2)_2$ (M = Ni or Cu), could not be observed in $[UO_2(C_5H_7O_2)_2]$. Like the *bis* (acetylacetonato) metals of first row transition metals, $UO_2(C_5H_7O_2)_2$ exists as a monomer in the gaseous state without undergoing any association. As pointed out in the case of $MoO_2(C_5H_7O_2)_2$, the difference between $[UO_2(C_5H_7O_2)_2]$ and $M(acac)_2$ (M = Mn, Fe, Co Ni or Cu) may, in part, owe its origin to the $5f^0\ 6d^0$ configuration of U in $UO_2(C_5H_7O_2)_2$ as opposed to a d^n configuration in the latter. The unique feature of EI-mass spectrum of bis(acetylacetonato) dioxouranium(VI) $UO_2(C_5H_7O_2)_2$, as against other $M(acac)_2$ (M = Mn, Fe, Co, Ni or Cu), $MoO_2(C_5H_7O_2)_2$, and $Mo_2O_3(C_5H_7O_2)_4$ compounds is that it provides evidence for the simultaneous loss of CH_3· and ketene ($OCCH_2$) from the molecular ion. The most probable fragmentation pathway, in conformity with the experimental observations, $[UO_2(C_5H_7O_2)_2]$ is as depicted in Scheme 5.

In going from *bis* (acetylacetonato) metals to the corresponding tris (acetylacetonato) metals one finds some notable differences as emphasised in the following discussion. Mass spectrometrically the three compounds, namely $[Mn(C_5H_7O_2)_3]$, $[Cr(C_5H_7O_2)_3]$ and $[Fe(C_5H_7O_2)_3]$, included herein behave generally in an analogous manner. Their typical fragmentation pathway can be displayed as shown in Scheme 6. As evident from the fragmentation pattern, the $M(acac)_2$ compound, like $M(acac)_2$, show their respective molecular ion signals indicating an absence of any association in the vapour state.



SCHEME 6

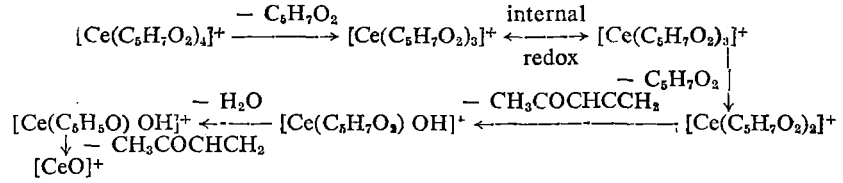
The molecular ion in each case, unlike those of $M(acac)_2$ compounds, expels $C_5H_7O_2$ ligand. It may be recalled that the molecular ions of bis(acetylacetonato) metals generally lose a CH_3 group from one of the ligands. The fragment ion

$[M(C_5H_7O_2)]^+$ originated from the process $[M(C_5H_7O_2)_3]^+ \xrightarrow{-C_5H_7O_2} [M(C_5H_7O_2)_2]^+$, constitutes the base peak of the spectrum in each case. The fragment ion $[M(C_5H_7O_2)_2]^+$ then undergoes loss of CH_3 and $C_4H_4O_2$ in successive steps to produce the $[M(C_5H_7O_2)]^+$ ion which again repeats a similar sequence of fragmentation ultimately to produce the bare $[M]^+$ ion (*vide* Scheme 6). It may be mentioned in passing that the fragmentation of $[M(C_5H_7O_2)_2]^+$, irrespective of its origin either from the process $[M(C_5H_7O_2)_3]^+ \xrightarrow{-C_5H_7O_2} [M(C_5H_7O_2)_2]^+$, or from that of $[M(C_5H_7O_2)_2] \underset{-2e}{\overset{+2e}{\rightleftharpoons}} [M(C_5H_7O_2)_2]^+$, until the bare $[M]^+$ ion follows a similar pattern (cf. Schemes 1, 2 and 6). Experiments on metastable transition studies showed enough metastable peaks adducing strong support to the suggested mode of fragmentation of the compounds (Scheme 6). This general mode of fragmentation agrees well with those of similar compounds reported by some other workers. A significant point in this context, which needs a special mention here, is the observance of two metastable supported signals at *m/z* 170 and 71 assigned to $[Fe(CH_3)(C_5H_7O_2)]^+$ and $[Fe(CH_3)]^+$, respectively, in the case of $[Fe(C_5H_7O_2)_3]$ providing evidence for easy methyl migration (cf. $[MoO_2(acac)_2]$) from carbon to metal presumably favoured by the formation of a new bond between metal atom and CH_3.

The tetrakis (acetylacetonato) metals, $M(acac)_4$, are very few in number (See Table) as opposed to a host of complexes of the types $M(acac)$ and $M(acac)_2$. Comparatively very little is therefore known on the mass spectrometry of the spectrometry of the $M(acac)_4$ class of compounds. As a case in point, for instance, *tetrakis* (acetylacetonato) cerium(IV), $Ce(C_5H_7O_2)_4$ has been known in the literature, however there is no reported existence of its mass spectrum until date.

The electron-impact induced positive ion mass spectrum of $Ce(C_5H_7O_2)_4$, recorded under conditions similar to those maintained for other compounds already described in this section, showed weak molecular signal at *m/z* 536 due to the formation of the odd-electron ion $Ce(C_5H_7O_2)_4^+$ in which Ce maintains + 4 state. Absence of any signal beyond *m/z* 536 in the mass range covered, indicates the monomeric nature of the molecule in the gaseous state. The weak nature of molecular ion appears to be the common features of *tetrakis* (β-diketonato) complexes of metals irrespective of whether the β-diketonate is either $C_5H_7N_2^-$ (e.g. present work) or a fluorinated β-diketonate[46] with the metal being Ce[46] Zr or Th.[52] This may at least, in part be due to the rapid decomposition of $[Ce(C_5H_7O_2)_4]^+$ to the even-electron ion $[Ce(C_5H_7O_2)_3]^+$ with the expulsion of $C_5H_7O_2$ radical. The signal due to $[Cel(C_5H_7O_2)_3]^+$ constitutes the most dominant peak, and in this respect there exists a very strong resemblance between $Ce(C_5H_7O_2)_4$ and $M(C_5H_7O_2)_4$, (M = Zr or Th)[41] or CeL_4[46] (L = fluorinated β-diketone). The *tris*-chelate fragment ion generally like CeL_3^+ as well as like those of tris-chelates of trivalent transition metals,[41,42,43] but unlike that of

$[M(C_5H_7O_2)_2]^+$, suffers loss of an intact ligand radical $C_5H_7O_2$ to give $[Ce(C_5H_7O_2)^2]^+$. The corresponding $[M(C_5H_7O_2)_3]^+$ (M = Zr or Th), in contrast, fragments to $M[C_5H_7O_2)(OH)]^+$ expelling an even-electron neutral $CH_3COCHCCH_2$ which can be understood in terms of a loss familiar +3 state of Zr or Th thus the metal valency change becomes unimportant and leads to the loss of an even-electron neutral instead of a neutral radical. Further fragmentation starting from the ion $[Ce(C_5H_7O_2)_2]^+$



SCHEME 7

involves stepwise loss of three even-electron neutrals in the sequence $CH_3COCHCCH_2$, H_2O and $CH_3COCHCCH_2$, as shown in Scheme 7, until the bare $[CeO]^+$ ion is reached without invoking any internal reduction. The events starting from the fragmentation of $[Ce(C_5H_7C_2)_3]^+$ are just parallel to those observed[41] in the case of $[La(C_5H_7O_2)_3]^+$ and enable us to state that this feature may be regarded as a typical one for tris-acetylacetonato-chelates of lanthanides. No methyl migration from ligand has been observed in the present case unlike in those of some other heavy metal cases viz. $[MoO_2(C_5H_7O_2)_2]$ and $[Mo_2O_3(C_5H_7O_2)_4]$. The cracking pattern beyond $[Ce(C_5H_7O_2)_3]^+$ till $[CeO]^+$ resembles only that of $[La(C_5H_7O_2)_3]^+$ but not those of the zirconium and thorium analogue. The step of fragmentation $[Ce(C_5H_7O_2)_3]^+ \rightarrow [Ce(C_5H_7O_2)_2]^+$ also resembles that of tris-chelates of the first row transition metals, however, the fragmentation beyond $[Ce(C_5H_7O_2)_2]^+$ does not do so.

CONCLUDING REMARKS

Following are the important points that emerge out of our research in the field of (acetylacetonato) metal chemistry :

(*i*) Acetylacetonato-metal complexes of the types $M(acac)_2$ (M = Mn, Fe, Co, Ni or Cu), $[Mo_2O_3(C_5H_7O_2)_4]$, $[UO_2(C_5H_7O_2)_2]$; $M(acac)_3$ (M = Cr, Mn, Fe or Ru) and $M(C_5H_7O_2)_4$ (M = Ce or Th) are capable of being synthesized, without involving any buffer, exploiting either the ACID-BASE or the Electron-Transfer (REDOX) concept. Successful synthesis of a large number of the afore-mentioned compounds clearly demonstrates the scope of the newly developed methods.

(*ii*) α, α, β, β-Tetraacetylethane, $(CH_3CO)_2$ CH-CH$(CH_3CO)_2$, has been shown to be the oxidation product of acetylacetone in the REDOX reactions of higher-valent metal ions with acetylacetone leading to acetylacetonato-metals.

(*iii*) Newer reactions based on the interaction of (acetylacetonato)-metal with HF and alkali-metal fluorides leading to the synthesis and of fluorometallates, which are otherwise difficult to have an access to, have been described. Important in the context of research in synthetic inorganic chemistry, this novel route to fluoro-metallates can be regarded as a paradigm to the synthesis of such compounds.

(*iv*) Electron-impact induced positive ion mass spectra of a large number of acetylacetonato-metal compounds, with varying stoichiometry between metal and acetylacetonate, have been investigated enabling an internal comparison of their fragmentation behaviours. Comments have also been on molecular association of such compounds in the vapour state. The results cause us to recommend the direct insertion technique to be suitable for mass spectrometry of coordination compounds.

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PREPARATION AND REACTION OF SALTS OF $[ZrO(O_2)F_2]^{2-}$ AND $[ZrO(O_2)_2F]^{3-}$

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Abstract—Salts of oxoperoxofluorozirconates(IV), $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$, have been prepared from the reaction of $ZrO_2 \cdot nH_2O$ with H_2O_2 and hydrofluoric acid at pH 6 and 12, respectively. No peroxozirconate could be obtained below pH 6. A μ-oxo species $[F_5Zr—O—ZrF_5]^{4-}$ has been isolated from a similar reaction at pH 5. The compounds have been characterized by chemical analyses, magnetic susceptibility and EPR measurements, IR and laser Raman spectroscopic studies. $(NH_4)_2[ZrO(O_2)F_2]$ in water reacts with SO_2(g) to produce a ternary complex $(NH_4)_2[ZrO(SO_4)F_2] \cdot 7H_2O$.

Investigation of various aspects of peroxo–metal systems[1–4] is of current interest. Synthesis and characterization, followed by studies of reactivity provide a systematic approach to this field. Some of our earlier papers dealt with this aspect of a few lighter transition metals[1,4,5] and as a sequel such studies have now been extended to zirconium. Information on peroxozirconates is scanty.[6] Complexes $[Zr(O_2)F_5]^{3-}$ and $[Zr_2(O_2)_2F_7]^{3-}$ are known and the structure of $(NH_4)_3[Zr(O_2)F_5]$ has been determined by X-ray crystallography.[8] There has been no report of solid diperoxozirconates(IV) except one in which diperoxo species were claimed[9] but not isolated. Our aim was to prepare newer peroxozirconates including diperoxozirconates(IV) from the reaction of ZrO_2 with H_2O_2 and F^-, and to rationalize the course of reactions through isolation of compounds at different stages of the reaction. It was also of interest to study the reaction of peroxozirconates with SO_2(g) in aqueous medium. This was important since the earlier reports[10] involved group VIII metal–peroxo species and the reactions were conducted in non-aqueous medium. This report presents an account of the preparation, characterization and reaction of salts of $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$.

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EXPERIMENTAL

The chemicals used were all reagent grade products. IR and laser Raman (LR) spectra were recorded on the instruments described earlier.[11–13] LR spectra were recorded only on solids. Magnetic susceptibilities were measured by the Gouy method; $Hg[Co(NCS)_4]$ was the calibrant. The pH values were measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper. The reactions and other manipulations were conducted in polyethylene apparatus. The water used for reactivity studies was deoxygenated by first boiling for 30 min under N_2 atmosphere and then cooling to room temperature, followed by bubbling of N_2(g) for 15 min. The water was stored in an airtight container. A suspension of $(NH_4)_2[ZrO(O_2)F_2]$ was prepared under N_2.

Synthesis of alkali metal or ammonium oxomonoperoxodifluorozirconates(IV), $A_2[ZrO(O_2)F_2]$ (A = Na, K *or* NH_4)

An aqueous solution (20 cm^3) of $ZrO(NO_3)_2 \cdot H_2O$ (1.0 g, 4 mmol) was treated with aqueous ammonia (sp.gr. 0.9) until $ZrO_2 \cdot nH_2O$ was completely precipitated. This was filtered off and washed thoroughly. To a water suspension of $ZrO_2 \cdot nH_2O$ was added 15 cm^3 (132.36 mmol) of

30% H_2O_2 with stirring followed by 1 cm^3 (24 mmol) of 48% HF, when a clear solution resulted. The pH of the solution was increased to 6 by adding AOH solution (20%) or aqueous ammonia (sp. gr. 0.9), whereupon a small amount of white product appeared. To ensure complete precipitation, 50 cm^3 of ethanol was added. The compound was filtered, washed 4–5 times with ethanol, and finally dried *in vacuo* over P_4O_{10}. Yields of $Na_2[ZrO(O_2)F_2]$, $K_2[ZrO(O_2)F_2]$ and $(NH_4)_2[ZrO(O_2)F_2]$ were 0.73 g(82%), 0.81 g (79%) and 0.75 g (87%), respectively.

Synthesis of sodium or ammonium oxodiperoxomonofluorozirconate(IV) *dihydrates*, $A_3[ZrO(O_2)_2F]\cdot 2H_2O$ (A = Na *or* NH_4)

The $A_3[ZrO(O_2)_2F]\cdot 2H_2O$ compounds were prepared in a manner analogous to that described above for the synthesis of $A_2[ZrO(O_2)F_2]$ except that the pH of the reaction solution was increased to 12. Yields of $Na_3[ZrO(O_2)_2F]\cdot 2H_2O$ and $(NH_4)_3[ZrO(O_2)_2F]\cdot 2H_2O$ were 0.87 g (71%) and 0.78 g (75%), respectively.

Isolation of alkali metal or ammonium μ-oxodecafluorodizirconates(IV), $A_4[F_5Zr—O—ZrF_5]$ (A = Na, K *or* NH_4)

The $A_4[F_5Zr—O—ZrF_5]$ complexes were isolated from reaction solutions obtained in a similar way to those described under the synthesis of $A_2[ZrO(O_2)F_2]$. However, the pH of the reaction solution was held at 5 instead of increasing it to 6. The compound was precipitated out by the addition of ethanol. Yields of $Na_4[Zr_2OF_{10}]$, $K_4[Zr_2OF_{10}]$ and $(NH_4)_4[Zr_2OF_{10}]$ were 1.37 g (72%), 1.73 g (80%) and 1.38 g (74%), respectively.

Reaction of $(NH_4)_2[ZrO(O_2)F_2]$ *with* SO_2(g). *Isolation of* $(NH_4)_2[ZrO(SO_4)F_2]\cdot 7H_2O$

Through an aqueous (25 cm^3) suspension of $(NH_4)_2[ZrO(O_2)F_2]$ (1 g, 4.69 mmol), SO_2(g) was slowly bubbled until the solution registered a pH value of 2–1. This was filtered and ethanol was added to initiate precipitation. It was allowed to stand for 2 h and then filtered to isolate the white crystalline product. The compound was washed with water and ethanol, and finally dried *in vacuo* over conc. H_2SO_4. The yield of $(NH_4)_2[ZrO(SO_4)F_2]\cdot 7H_2O$ was 0.97 g (47%).

Elemental analyses

Zirconium was estimated gravimetrically as ZrO_2.[14a] The peroxide content was determined by redox titration with standard solutions of $KMnO_4$[14b] or Ce^{4+}.[14c] Fluoride was precipitated as PbClF and chloride estimated by Volhard's method, from which the fluoride content was calculated.[14d] Nitrogen, potassium, sodium and sulphate were estimated by methods described previously.[11,15] The analytical results are given in Table 1.

RESULTS AND DISCUSSION

Synthesis

Peroxo–metal systems can be stabilized in the presence of an appropriate heteroligand at a suitable pH.[1,5,11–13] The present strategy was to react ZrO_2 with H_2O_2 and F^- in the presence of each other and also to evaluate the appropriate pH for the desired synthesis. The pH values conducive to the preparation of $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$ were ascertained to be 6 and 12, respectively. While the salts of the monoperoxo complex were anhydrous, those of the diperoxo species were dihydrates. $A_3[ZrO(O_2)_2F]\cdot 2H_2O$ (A = Na or NH_4) were obtained, for the first time, in the solid state. In order to gain an insight into the course of the reaction, the product at pH 5 was isolated and characterized as a μ-oxo species, $[F_5Zr—O—ZrF_5]^{4-}$. It is possible that a peroxozirconate might have formed at this pH but decomposed leading to the μ-oxo complex as obtained. Such a problem is encountered in peroxo–metal chemistry.[16]

Characterization

The compounds are diamagnetic, EPR silent and sparingly soluble. They dissolve in an acidified (dil. H_2SO_4) solution in which the peroxozirconates(IV) quantitatively liberate active oxygen. The results of chemical analyses are consistent with the formulae, $A_2[ZrO(O_2)F_2]$, $A_3[ZrO(O_2)_2F]$ and $A_4[Zr_2OF_{10}]$. LR spectra of $A_4[Zr_2OF_{10}]$ could not be recorded owing to extensive fluoroescence, however, the IR spectra (Table 1) provide clear evidence for the ν(Zr—F) and Zr—F deformation modes.[7] Absence of any absorption at *ca* 950 cm^{-1} and the consistent appearance of a band at *ca* 740m,br cm^{-1} attest to the occurrence of Zr—O—Zr vibrations[17] in accord with a μ-oxo dimer. The diagnostic IR and LR signatures for $A_2[ZrO(O_2)F_2]$ and $A_3[ZrO(O)_2F]\cdot 2H_2O$ comprise ν(Zr=O), ν(O—O) (ν_1), ν(Zr—O_2) (ν_2,ν_3), and ν(Zr—F) modes (Table 1). The peroxide ligand binds the metal centre, in each case, in a triangular bidentate manner. Two additional IR bands at *ca* 1640s and *ca* 3455s cm^{-1} for the

Table 1. Analytical data and structurally significant IR and Raman bands of $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4), $A_3[ZrO(O_2)_2F]\cdot 2H_2O$ (A = Na or NH_4) and $A_4[F_5Zr—O—ZrF_5]$ (A = Na, K or NH_4)

Compound	Analysis[a] (%)				IR (cm^{-1})	Raman (cm^{-1})	Assignment
	A or N	Zr	O_A[b] or SO_4[c]	F			
$(NH_4)_2[ZrO(O_2)F_2]$	13.0	42.1	15.3	18.1	981s	1020	ν(Zr=O)
	(13.1)	(42.8)	(15.0)	(17.8)	850s	847	ν(O—O) ν_1
					640s	650	ν(Zr—O_2) ν_2
					585m	590	ν(Zr—O_2) ν_3
					460s	480	ν(Zr—F)
					249		(Zr—F) def.
$Na_2[ZrO(O_2)F_2]$	20.2	41.1	14.5	17.3	980s	1015	ν(Zr=O)
	(20.6)	(40.9)	(14.3)	(17.0)	850s	850	ν(O—O) ν_1
					645s	650	ν(Zr—O_2) ν_2
					580m	595	ν(Zr—O_2) ν_3
					455s	480	ν(Zr—F)
					250		(Zr—F) def.
$K_2[ZrO(O_2)F_2]$	30.1	36.2	12.8	15.2	985s	1017	ν(Zr=O)
	(30.6)	(35.7)	(12.5)	(14.9)	850s	850	ν(O—O) ν_1
					640s	650	ν(Zr—O_2) ν_2
					585m	590	ν(Zr—O_2) ν_3
					440s	475	ν(Zr—F)
					250		(Zr—F) def.
$(NH_4)_3[ZrO(O_2)_2F]\cdot 2H_2O$	15.1	32.2	23.1	7.1	990s	1025	ν(Zr=O)
	(15.0)	(32.5)	(22.8)	(6.8)	860s	858	ν(O—O) ν_1
					640s	650	ν(Zr—O_2) ν_2
					580m	590	ν(Zr—O_2) ν_3
					455s	470	ν(Zr—F)
					250		(Zr—F) def.
					3455s		ν(O—H)
					1640s		δ(H—O—H)
$Na_3[ZrO(O_2)_2F]\cdot 2H_2O$	23.6	31.3	22.1	6.8	985s	1020	ν(Zr=O)
	(23.4)	(30.9)	(21.7)	(6.4)	860s	860	ν(O—O) ν_1
					650s	650	ν(Zr—O_2) ν_2
					578m	590	ν(Zr—O_2) ν_3
					450s	460	ν(Zr—F)
					250		(Zr—F) def.
					3460s		ν(O—H)
					1640s		δ(H—O—H)
$(NH_4)_4[F_5Zr—O—ZrF_5]$	12.3	40.1		41.6	741		ν(Zr—O—Zr)
	(12.2)	(39.6)		(41.2)	490		ν(Zr—F)
					246		(Zr—F) def.
$Na_4[F_5Zr—O—ZrF_5]$	19.5	38.0		40.3	749		ν(Zr—O—Zr)
	(19.1)	(38.2)		(39.5)	468		ν(Zr—F)
					248		(Zr—F) def.
$K_4[F_5Zr—O—ZrF_5]$	29.1	34.0		35.2	735		ν(Zr—O—Zr)
	(28.7)	(33.5)		(34.9)	460		ν(Zr—F)
					240		(Zr—F) def.
$(NH_4)_2[ZrO(SO_4)F_2]\cdot 7H_2O$	6.9	22.3	24.2[c]	9.2	980s	1010	ν(Zr=O)
	(6.9)	(22.6)	(23.8)	(9.4)	970m	990	ν_1 } SO_4 modes
					470m	470	ν_2
					1220s	1215	
					1145s	1145	ν_3
					1030s	1020	
					685s	680	
					635s	640	ν_4
					605s	610	
					460m	460	ν(Zr—F)

[a] Calculated values are given in parentheses. [b] Active oxygen. [c] Sulphate.

diperoxo complexes are in agreement with the presence of lattice water.[18,19]

Reaction of SO_2(g) *with* $(NH_4)_2[ZrO(O_2)F_2]$

The oxoperoxodifluorozirconate(IV) readily reacted with SO_2(g) in an aqueous medium as evident from a near quantitative solubility of the complex species during the bubbling of SO_2(g) (*vide* Experimental). The reaction solution registered a pH value of 2–1 at that stage and the product isolated was characterized to be $(NH_4)_2[ZrO(SO_4)F_2]\cdot 7H_2O$.

The compound is diamagnetic in nature and sparingly soluble. The IR and LR spectra of the compound produced evidence for the complete absence of peroxide, which was also ascertained by chemical analysis. The spectra provide clear evidence for the ν(Zr=O) and ν(Zr—F) vibrations in similar regions to those of the other compounds reported herein and the expected bands for the presence of NH_4^+ and lattice water. For sulphate, the appearance of medium intensity ν_1 and ν_2 modes and the splitting of ν_3 and ν_4 vibrations into three bands each (Table 1), in contrast to the absence of ν_1 and ν_2 and occurrence of unsplit ν_3 and ν_4, suggest the lowering of the symmetry of SO_4^{2-} from T_d to C_{2v},[20] and its presence as a chelated ligand in the complex. The formation of the sulphato complex is explained in terms of an insertion of SO_2 into the O—O bond of the coordinated peroxide, without causing any reduction of the metal centre. This is an interesting reaction because it not only provides access to a new ternary complex of zirconium(IV), but also this route prevents the formation of a binary fluorozirconate(IV) which is normally a problem in the synthesis of mixed-ligand fluorozirconates(IV).

Concluding remarks

As in the case of titanium, monoperoxo and diperoxofluoro complexes of zirconium(IV) are capable of being synthesized under the appropriate experimental conditions. The pH of the reaction medium plays a very important role; a pH > 7 is required for the successful synthesis of diperoxo complexes of both titanium and zirconium. The peroxo compounds of zirconium are obtained as oxoperoxozirconate(IV) species containing a zirconyl (ZrO^{2+}) centre, unlike those of titanium[5] which contain titanium(IV) centres. Isolation of a μ-oxo-dizirconate(IV) species, $[F_5Zr—O—ZrF_5]^{4-}$, at pH $\geqslant 5 < 6$ suggests that such a complex might be the precursor for the oxomonoperoxozirconate(IV), however, the chances of peroxozirconate(IV) formation at a pH of *ca* 5 which may have decomposed to the μ-oxo complex either in the solution or in the process of its isolation, so often encountered in peroxo–metal chemistry,[16] should not be discounted. The complex $[ZrO(O_2)F_2]^{2-}$ ion reacts with SO_2(g) in aqueous medium to afford the ternary $[ZrO(SO_4)F_2]^{2-}$ complex through insertion of SO_2 into the O—O bond.

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PREPARATION AND REACTION OF SALTS OF $[ZrO(O_2)F_2]^{2-}$ AND $[ZrO(O_2)_2F]^{3-}$

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Abstract—Salts of oxoperoxofluorozirconates(IV), $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$, have been prepared from the reaction of $ZrO_2 \cdot nH_2O$ with H_2O_2 and hydrofluoric acid at pH 6 and 12, respectively. No peroxozirconate could be obtained below pH 6. A μ-oxo species $[F_5Zr—O—ZrF_5]^{4-}$ has been isolated from a similar reaction at pH 5. The compounds have been characterized by chemical analyses, magnetic susceptibility and EPR measurements, IR and laser Raman spectroscopic studies. $(NH_4)_2[ZrO(O_2)F_2]$ in water reacts with SO_2(g) to produce a ternary complex $(NH_4)_2[ZrO(SO_4)F_2] \cdot 7H_2O$.

Investigation of various aspects of peroxo–metal systems[1–4] is of current interest. Synthesis and characterization, followed by studies of reactivity provide a systematic approach to this field. Some of our earlier papers dealt with this aspect of a few lighter transition metals[1,4,5] and as a sequel such studies have now been extended to zirconium. Information on peroxozirconates is scanty.[6] Complexes $[Zr(O_2)F_5]^{3-}$ and $[Zr_2(O_2)_2F_7]^{3-}$ are known and the structure of $(NH_4)_3[Zr(O_2)F_5]$ has been determined by X-ray crystallography.[8] There has been no report of solid diperoxozirconates(IV) except one in which diperoxo species were claimed[9] but not isolated. Our aim was to prepare newer peroxozirconates including diperoxozirconates(IV) from the reaction of ZrO_2 with H_2O_2 and F^-, and to rationalize the course of reactions through isolation of compounds at different stages of the reaction. It was also of interest to study the reaction of peroxozirconates with SO_2(g) in aqueous medium. This was important since the earlier reports[10] involved group VIII metal–peroxo species and the reactions were conducted in non-aqueous medium. This report presents an account of the preparation, characterization and reaction of salts of $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$.

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EXPERIMENTAL

The chemicals used were all reagent grade products. IR and laser Raman (LR) spectra were recorded on the instruments described earlier.[11–13] LR spectra were recorded only on solids. Magnetic susceptibilities were measured by the Gouy method; $Hg[Co(NCS)_4]$ was the calibrant. The pH values were measured with a Systronics type 335 digital pH meter and also with pH indicator (BDH) paper. The reactions and other manipulations were conducted in polyethylene apparatus. The water used for reactivity studies was deoxygenated by first boiling for 30 min under N_2 atmosphere and then cooling to room temperature, followed by bubbling of N_2(g) for 15 min. The water was stored in an airtight container. A suspension of $(NH_4)_2[ZrO(O_2)F_2]$ was prepared under N_2.

Synthesis of alkali metal or ammonium oxomonoperoxodifluorozirconates(IV), $A_2[ZrO(O_2)F_2]$ (A = Na, K *or* NH_4)

An aqueous solution (20 cm^3) of $ZrO(NO_3)_2 \cdot H_2O$ (1.0 g, 4 mmol) was treated with aqueous ammonia (sp.gr. 0.9) until $ZrO_2 \cdot nH_2O$ was completely precipitated. This was filtered off and washed thoroughly. To a water suspension of $ZrO_2 \cdot nH_2O$ was added 15 cm^3 (132.36 mmol) of

30% H_2O_2 with stirring followed by 1 cm^3 (24 mmol) of 48% HF, when a clear solution resulted. The pH of the solution was increased to 6 by adding AOH solution (20%) or aqueous ammonia (sp. gr. 0.9), whereupon a small amount of white product appeared. To ensure complete precipitation, 50 cm^3 of ethanol was added. The compound was filtered, washed 4–5 times with ethanol, and finally dried *in vacuo* over P_4O_{10}. Yields of $Na_2[ZrO(O_2)F_2]$, $K_2[ZrO(O_2)F_2]$ and $(NH_4)_2[ZrO(O_2)F_2]$ were 0.73 g(82%), 0.81 g (79%) and 0.75 g (87%), respectively.

Synthesis of sodium or ammonium oxodiperoxomonofluorozirconate(IV) *dihydrates*, $A_3[ZrO(O_2)_2F]\cdot 2H_2O$ (A = Na *or* NH_4)

The $A_3[ZrO(O_2)_2F]\cdot 2H_2O$ compounds were prepared in a manner analogous to that described above for the synthesis of $A_2[ZrO(O_2)F_2]$ except that the pH of the reaction solution was increased to 12. Yields of $Na_3[ZrO(O_2)_2F]\cdot 2H_2O$ and $(NH_4)_3[ZrO(O_2)_2F]\cdot 2H_2O$ were 0.87 g (71%) and 0.78 g (75%), respectively.

Isolation of alkali metal or ammonium μ-oxodecafluorodizirconates(IV), $A_4[F_5Zr—O—ZrF_5]$ (A = Na, K *or* NH_4)

The $A_4[F_5Zr—O—ZrF_5]$ complexes were isolated from reaction solutions obtained in a similar way to those described under the synthesis of $A_2[ZrO(O_2)F_2]$. However, the pH of the reaction solution was held at 5 instead of increasing it to 6. The compound was precipitated out by the addition of ethanol. Yields of $Na_4[Zr_2OF_{10}]$, $K_4[Zr_2OF_{10}]$ and $(NH_4)_4[Zr_2OF_{10}]$ were 1.37 g (72%), 1.73 g (80%) and 1.38 g (74%), respectively.

Reaction of $(NH_4)_2[ZrO(O_2)F_2]$ *with* SO_2(g). *Isolation of* $(NH_4)_2[ZrO(SO_4)F_2]\cdot 7H_2O$

Through an aqueous (25 cm^3) suspension of $(NH_4)_2[ZrO(O_2)F_2]$ (1 g, 4.69 mmol), SO_2(g) was slowly bubbled until the solution registered a pH value of 2–1. This was filtered and ethanol was added to initiate precipitation. It was allowed to stand for 2 h and then filtered to isolate the white crystalline product. The compound was washed with water and ethanol, and finally dried *in vacuo* over conc. H_2SO_4. The yield of $(NH_4)_2[ZrO(SO_4)F_2]\cdot 7H_2O$ was 0.97 g (47%).

Elemental analyses

Zirconium was estimated gravimetrically as ZrO_2.[14a] The peroxide content was determined by redox titration with standard solutions of $KMnO_4$[14b] or Ce^{4+}.[14c] Fluoride was precipitated as PbClF and chloride estimated by Volhard's method, from which the fluoride content was calculated.[14d] Nitrogen, potassium, sodium and sulphate were estimated by methods described previously.[11,15] The analytical results are given in Table 1.

RESULTS AND DISCUSSION

Synthesis

Peroxo–metal systems can be stabilized in the presence of an appropriate heteroligand at a suitable pH.[1,5,11–13] The present strategy was to react ZrO_2 with H_2O_2 and F^- in the presence of each other and also to evaluate the appropriate pH for the desired synthesis. The pH values conducive to the preparation of $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$ were ascertained to be 6 and 12, respectively. While the salts of the monoperoxo complex were anhydrous, those of the diperoxo species were dihydrates. $A_3[ZrO(O_2)_2F]\cdot 2H_2O$ (A = Na or NH_4) were obtained, for the first time, in the solid state. In order to gain an insight into the course of the reaction, the product at pH 5 was isolated and characterized as a μ-oxo species, $[F_5Zr—O—ZrF_5]^{4-}$. It is possible that a peroxozirconate might have formed at this pH but decomposed leading to the μ-oxo complex as obtained. Such a problem is encountered in peroxo–metal chemistry.[16]

Characterization

The compounds are diamagnetic, EPR silent and sparingly soluble. They dissolve in an acidified (dil. H_2SO_4) solution in which the peroxozirconates(IV) quantitatively liberate active oxygen. The results of chemical analyses are consistent with the formulae, $A_2[ZrO(O_2)F_2]$, $A_3[ZrO(O_2)_2F]$ and $A_4[Zr_2OF_{10}]$. LR spectra of $A_4[Zr_2OF_{10}]$ could not be recorded owing to extensive fluoroescence, however, the IR spectra (Table 1) provide clear evidence for the ν(Zr—F) and Zr—F deformation modes.[7] Absence of any absorption at *ca* 950 cm^{-1} and the consistent appearance of a band at *ca* 740m,br cm^{-1} attest to the occurrence of Zr—O—Zr vibrations[17] in accord with a μ-oxo dimer. The diagnostic IR and LR signatures for $A_2[ZrO(O_2)F_2]$ and $A_3[ZrO(O)_2F]\cdot 2H_2O$ comprise ν(Zr=O), ν(O—O) (ν_1), ν(Zr—O_2) (ν_2,ν_3), and ν(Zr—F) modes (Table 1). The peroxide ligand binds the metal centre, in each case, in a triangular bidentate manner. Two additional IR bands at *ca* 1640s and *ca* 3455s cm^{-1} for the

Table 1. Analytical data and structurally significant IR and Raman bands of $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4), $A_3[ZrO(O_2)_2F]\cdot 2H_2O$ (A = Na or NH_4) and $A_4[F_5Zr{-}O{-}ZrF_5]$ (A = Na, K or NH_4)

Compound	Analysis[a] (%) A or N	Zr	O_A[b] or SO_4[c]	F	IR (cm^{-1})	Raman (cm^{-1})	Assignment
$(NH_4)_2[ZrO(O_2)F_2]$	13.0	42.1	15.3	18.1	981s	1020	ν(Zr=O)
	(13.1)	(42.8)	(15.0)	(17.8)	850s	847	ν(O—O) ν_1
					640s	650	ν(Zr—O_2) ν_2
					585m	590	ν(Zr—O_2) ν_3
					460s	480	ν(Zr—F)
					249		(Zr—F) def.
$Na_2[ZrO(O_2)F_2]$	20.2	41.1	14.5	17.3	980s	1015	ν(Zr=O)
	(20.6)	(40.9)	(14.3)	(17.0)	850s	850	ν(O—O) ν_1
					645s	650	ν(Zr—O_2) ν_2
					580m	595	ν(Zr—O_2) ν_3
					455s	480	ν(Zr—F)
					250		(Zr—F) def.
$K_2[ZrO(O_2)F_2]$	30.1	36.2	12.8	15.2	985s	1017	ν(Zr=O)
	(30.6)	(35.7)	(12.5)	(14.9)	850s	850	ν(O—O) ν_1
					640s	650	ν(Zr—O_2) ν_2
					585m	590	ν(Zr—O_2) ν_3
					440s	475	ν(Zr—F)
					250		(Zr—F) def.
$(NH_4)_3[ZrO(O_2)_2F]\cdot 2H_2O$	15.1	32.2	23.1	7.1	990s	1025	ν(Zr=O)
	(15.0)	(32.5)	(22.8)	(6.8)	860s	858	ν(O—O) ν_1
					640s	650	ν(Zr—O_2) ν_2
					580m	590	ν(Zr—O_2) ν_3
					455s	470	ν(Zr—F)
					250		(Zr—F) def.
					3455s		ν(O—H)
					1640s		δ(H—O—H)
$Na_3[ZrO(O_2)_2F]\cdot 2H_2O$	23.6	31.3	22.1	6.8	985s	1020	ν(Zr=O)
	(23.4)	(30.9)	(21.7)	(6.4)	860s	860	ν(O—O) ν_1
					650s	650	ν(Zr—O_2) ν_2
					578m	590	ν(Zr—O_2) ν_3
					450s	460	ν(Zr—F)
					250		(Zr—F) def.
					3460s		ν(O—H)
					1640s		δ(H—O—H)
$(NH_4)_4[F_5Zr{-}O{-}ZrF_5]$	12.3	40.1		41.6	741		ν(Zr—O—Zr)
	(12.2)	(39.6)		(41.2)	490		ν(Zr—F)
					246		(Zr—F) def.
$Na_4[F_5Zr{-}O{-}ZrF_5]$	19.5	38.0		40.3	749		ν(Zr—O—Zr)
	(19.1)	(38.2)		(39.5)	468		ν(Zr—F)
					248		(Zr—F) def.
$K_4[F_5Zr{-}O{-}ZrF_5]$	29.1	34.0		35.2	735		ν(Zr—O—Zr)
	(28.7)	(33.5)		(34.9)	460		ν(Zr—F)
					240		(Zr—F) def.
$(NH_4)_2[ZrO(SO_4)F_2]\cdot 7H_2O$	6.9	22.3	24.2[c]	9.2	980s	1010	ν(Zr=O)
	(6.9)	(22.6)	(23.8)	(9.4)	970m	990	ν_1 (SO_4 modes)
					470m	470	ν_2 (SO_4 modes)
					1220s	1215	ν_3 (SO_4 modes)
					1145s	1145	ν_3 (SO_4 modes)
					1030s	1020	ν_3 (SO_4 modes)
					685s	680	ν_4 (SO_4 modes)
					635s	640	ν_4 (SO_4 modes)
					605s	610	ν_4 (SO_4 modes)
					460m	460	ν(Zr—F)

[a] Calculated values are given in parentheses. [b] Active oxygen. [c] Sulphate.

diperoxo complexes are in agreement with the presence of lattice water.[18,19]

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Concluding remarks

As in the case of titanium, monoperoxo and diperoxofluoro complexes of zirconium(IV) are capable of being synthesized under the appropriate experimental conditions. The pH of the reaction medium plays a very important role; a pH > 7 is required for the successful synthesis of diperoxo complexes of both titanium and zirconium. The peroxo compounds of zirconium are obtained as oxoperoxozirconate(IV) species containing a zirconyl (ZrO^{2+}) centre, unlike those of titanium[5] which contain titanium(IV) centres. Isolation of a μ-oxo-dizirconate(IV) species, $[F_5Zr—O—ZrF_5]^{4-}$, at pH $\geqslant 5 < 6$ suggests that such a complex might be the precursor for the oxomonoperoxozirconate(IV), however, the chances of peroxozirconate(IV) formation at a pH of *ca* 5 which may have decomposed to the μ-oxo complex either in the solution or in the process of its isolation, so often encountered in peroxo–metal chemistry,[16] should not be discounted. The complex $[ZrO(O_2)F_2]^{2-}$ ion reacts with SO_2(g) in aqueous medium to afford the ternary $[ZrO(SO_4)F_2]^{2-}$ complex through insertion of SO_2 into the O—O bond.

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New Heteroligand Peroxothorates(IV) of the Type $A_2[Th(O_2)F_2(OH)_2]\cdot nH_2O$ ($A = NH_4$, $n = 3$; A = Na or K, $n = 1$) and Molecular Peroxothorium(IV) Complexes of the Type $[Th_2(O_2)_3L(H_2O)_4]\cdot 5H_2O$ ($L = C_2O_4$ or SO_4)

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Abstract

Synthesis of complex difluorodihydroxomonoperoxothorates(IV), $A_2[Th(O_2)F_2(OH)_2]\cdot nH_2O$ ($A = NH_4$, $n = 3$; A = Na or K, $n = 1$) have been achieved from the reaction of hydrated thorium oxide, $ThO_2\cdot nH_2O$, with 30% H_2O_2 and 48% hydrofluoric acid in the concentration ratio of $Th:H_2O_2:HF$ as 1:77.6:56.5 at a pH range 10–11 maintained by the addition of aqueous ammonia or alkali metal hydroxides. Novel dimeric molecular complexes diperoxotetra-aquo-μ-peroxo-μ-oxalatodithorium(IV) pentahydrate, $[Th_2(O_2)_3(C_2O_4)(H_2O)_4]\cdot 5H_2O$ and diperoxotetra-aquo-μ-peroxo-μ-sulphatodithorium(IV) pentahydrate, $[Th_2(O_2)_3SO_4(H_2O)_4]\cdot 5H_2O$ have been synthesised directly from the reaction of an aqueous solution of thorium nitrate, with ammonium oxalate or ammonium sulphate and 30% hydrogen peroxide in the respective cases, at pH 7–8 and at pH 2, respectively. Characterisation and structural assessment of the compounds have been made from the results of chemical analysis, pyrolysis studies, magnetic susceptibility measurements and ESR, IR and laser Raman spectroscopic studies. An internal comparison of the results so obtained with those of titanium and zirconium analogues has been made.

Introduction

The chemistry of heteroligand peroxo-metallates embraces a fascinating and worthwhile area of investigation in its own right [1–3]. The synthesis of well defined heteroligand peroxo–metal complexes therefore is an important prerequisite for a heuristic approach in this field of chemistry. It is imperative to note that in recent years a commendable progress [4–7] has been made in this aspect of lighter metals and a good amount of newer informations as well as materials has emerged thereof. However, similar studies involving heavy metal especially the actinides have not received due attention. This could, in part, be due to the very complicated nature of peroxo-actinide chemistry [8, 9]. The syntheses and characterisations of heteroligand peroxo complexes of titanium and zirconium have been dealt with in our earlier reports [10–12]. However, as one moves down in the group from titanium to thorium, a significant difference in their familiar chemistry becomes evident particularly because of a much higher tendency of hydrolysis of the latter [8]. Reports on peroxothorium complex are rather scanty [8, 13]. Recent reports [2] still describe that molecular complexes of actinide are only a few although actinides have long been known to form peroxo compounds. As a sequel to our endeavour [4, 10, 12, 14–16] in the field of peroxo–metal chemistry, it was of interest to us to evaluate appropriate reaction conditions in order to have an access to the hitherto unreported heteroligand peroxothorium(IV) complexes. It was expected that the new results would enable an internal comparison to be made with those of titanium [10, 11] and zirconium [12]. The present paper describes synthesis, characterisation and structural assessment of alkali-metal and ammonium difluorodihydroxomonoperoxothorate(IV) hydrates, $A_2[Th(O_2)F_2(OH)_2]\cdot nH_2O$ ($A = NH_4$, $n = 3$; A = Na or K, $n = 1$) and molecular complexes diperoxotetra-aquo-μ-peroxo-μ-oxalatodithorium(IV) pentahydrate, $[Th_2(O_2)_3C_2O_4(H_2O)_4]\cdot 5H_2O$ and diperoxotetra-aquo-μ-peroxo-μ-sulphatodithorium(IV) pentahydrate, $[Th_2(O_2)_3SO_4(H_2O)_4]\cdot 5H_2O$ along with a set of internally consistent information as emerged out of the comparative studies on some facets of heteroligand peroxo chemistry of Ti, Zr and Th (present work).

Experimental

Reagent grade chemicals were used. Infrared (IR) and laser Raman (l-R) spectra were recorded on the instruments and by the methods described in our

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previous papers [11, 14–18]. Laser Raman spectra were recorded on solids due to the insolubility of the compounds. Measurements of magnetic susceptibility were accomplished by the Gouy method using $Hg[Co(NCS)_4]$ as the standard. A systronics type 335 digital pH meter and pH indicator paper (BDH) were used to measure the pH of the reaction solutions. All reactions pertaining to the synthesis of $A_2[Th(O_2)F_2(OH)_2]\cdot nH_2O$ were carried out in polyethylene apparatus.

(i) Synthesis of Alkali-metal and Ammonium Difluorodihydroxomonoperoxothorate(IV) Hydrates, $A_2[Th(O_2)F_2(OH)_2]\cdot nH_2O$ ($A = NH_4$, $n = 3$; $A = Na$ or K, $n = 1$)

Following a typical procedure, representative of the general method, to a solution of 1 g (1.70 mmol) $Th(NO_3)_4\cdot 6H_2O$ in 15 cm^3 of water was added 25% aqueous solution of ammonia (sp. gr. 0.9) or a 15% aqueous solution of AOH (A = Na or K) until the white gelatinous precipitate of hydrated thorium oxide ceased to appear. The hydrated oxide was then washed free from ammonia or alkali or nitrate. To a water suspension of hydrated oxide was added 15 cm^3 (132.25 mmol) of 30% H_2O_2 solution and the mixture was stirred for *c.* 15 min followed by the addition of 4 ml (96.0 mmol) of 48% HF drop by drop with continuous stirring to obtain a clear solution. The pH of the reaction solution at this stage was found to be *c.* 2 which was slowly raised to 10–11 by the addition of corresponding alkali-metal hydroxide or aqueous ammonia. Stirring was continued for a further period of 10 min. A small volume of ethanol was added to facilitate precipitation of alkali-metal or ammonium difluorodihydroxomonoperoxothorate(IV) hydrates. The compound was isolated by filtration and dried *in vacuo* over conc. H_2SO_4. Starting from 1 g of $Th(NO_3)_4\cdot 6H_2O$, in each case the yields were recorded as: $(NH_4)_2[Th(O_2)F_2(OH)_2]\cdot 3H_2O$, 0.58 g (74%); $Na_2[Th(O_2)F_2(OH)_2]\cdot H_2O$, 0.51 g (75%); $K_2[Th(O_2)F_2(OH)_2]\cdot H_2O$, 0.6 g (80%).

(ii) Synthesis of Diperoxotetra-aquo-μ-peroxo-μ-oxalatodithorium(IV) Pentahydrates, $[Th_2(O_2)_3C_2O_4(H_2O)_4]\cdot 5H_2O$

To a solution of 1 g (1.70 mmol) $Th(NO_3)_4\cdot 6H_2O$, in 20 cm^3 of water was added a solution of 0.20 g (1.70 mmol) oxalic acid in 15 cm^3 (132.35 mmol) of 30% H_2O_2. The white gelatinous mass that appeared was stirred for *c.* 10 min followed by a rise in pH to 7–8 by the addition of aqueous ammonia (sp.gr. 0.9) or 15% AOH (A = Na or K) solution. The whole was again stirred for *c.* 5 min and then the product was isolated by filtration, washed with water and portions of ethyl alcohol and finally dried *in vacuo* over conc. H_2SO_4. The yield of the compound was ~1 g (73%).

(iii) Synthesis of Diperoxotetra-aquo-μ-peroxo-μ-sulphatodithorium(IV) Pentahydrates, $[Th_2(O_2)_3SO_4(H_2O)_4]\cdot 5H_2O$

To a solution of 1 g (1.70 mmol) $Th(NO_3)_4\cdot 6H_2O$ in 20 cm^3 of water was added 1.70 mmol of A_2SO_4 ($A = NH_4$ or Na or K) and the whole was stirred for *c.* 10 min until a clear solution was obtained. To this was added 15 cm^3 (132.35 mmol) of 30% H_2O_2 whereupon a white product appeared. Stirring was continued for a further period of 10 min. Isolation, purification, and drying of the compound were accomplished in a manner similar to those mentioned under (ii). The yield was recorded as 0.9 g (65%).

Elemental Analyses

The results of the elemental analyses are given in Table 1. Thorium was estimated gravimetrically as thoria, ThO_2 [19a]. The peroxide content was determined by redox titrations with standard solution of $KMnO_4$ [19b] or Ce^{4+} solution [19c]. Fluoride was precipitated as PbClF, and chloride was estimated by Volhard's method, from which the fluoride content was calculated [19d]. Carbon, nitrogen, potassium and sodium were estimated by the methods described in our earlier papers [17b]. Oxalate content was determined by microanalysis on carbon as well as by the volumetric method [19c]. In order to determine oxalate volumetrically, it was necessary to remove O_2^{2-}. The removal of O_2^{2-} was achieved by decomposing the compound in an ammoniacal medium by heating for *c.* 30 min. The hydrated thorium oxide was separated by filtration and the filtrate was collected quantitatively, acidified with dilute H_2SO_4 and then titrated with standard $KMnO_4$ solution. The peroxide content in the peroxo-oxalato complex of thorium was, however, determined indirectly by first titrating the total peroxide and oxalate content and then subtracting the contribution due to oxalate from the whole. Sulphate content was estimated as $BaSO_4$ by gravimetric method [19f].

Results and Discussion

Synthesis

That the peroxo–metal compounds can be stabilised under a suitably chosen heteroligand environment has been earlier [4, 20] emphasised by us. In order to have an access to the synthesis of heteroligand peroxothorates(IV) simple heteroligands viz. F^-, $C_2O_4^{2-}$ and SO_4^{2-} were chosen in the first instance for the present work as these ligands are not only known to stabilise the Th(IV) state individually but also make their detection and determination rather easy. Since each of the aforementioned heteroligands and peroxide (O_2^{2-}), independent of each other, forms stable compounds with the chosen metal, it was anticipated that under appropriate

TABLE 1. Analytical data and structurally significant IR and lR bands of $A_2[Th(O_2)F_2(OH)_2]\cdot nH_2O$ (A = NH_4, n = 3; Na or K, n = 1) and $[Th_2(O_2)_3L(H_2O)_4]\cdot 5H_2O$ (L = C_2O_4 or SO_4)

Compound	Found (calc.) (%)				IR (cm^{-1})	lR (cm^{-1})	Assignment
	A or N	Th	O[a]	C_2O_4[b] or SO_4 or F			
$(NH_4)_2[Th(O_2)F_2(OH)_2]\cdot 3H_2O$	6.58	54.9	7.3	8.65	850(w)	850	ν(O–O)
	(6.62)	(54.83)	(7.56)	(8.98)	355(m)		ν(Th–F)
					3560(s)		ν(O–H)(OH^-)
					3420(s)		ν(O–H)(H_2O)
					1640(s)		δ(H–O–H)
$Na_2[Th(O_2)F_2(OH)_2]\cdot H_2O$	11.7	58.32	7.8	9.48	845(w)	845	ν(O–O)
	(11.52)	(58.14)	(8.02)	(9.52)	355(m)		ν(Th–F)
					3555(s)		ν(O–H)(OH^-)
					3415(s)		ν(O–H)(H_2O)
					1638(s)		δ(H–O–H)
$K_2[Th(O_2)F_2(OH)_2]\cdot H_2O$	17.83	53.3	7.1	8.67	850(w)	845	ν(O–O)
	(18.13)	(53.80)	(7.42)	(8.81)	360(m)		ν(Th–F)
					3565(s)		ν(O–H)(OH^-)
					3425(s)		ν(O–H)(H_2O)
					1635(s)		δ(H–O–H)
$[Th_2(O_2)_3C_2O_4(H_2O)_4]\cdot 5H_2O$		58.22	11.68	10.62[c]	835(w)	835 845	ν(O–O)
		(57.92)	(11.98)	(10.98)[c]	725(m)		$\rho_r(H_2O)$
					1640(s)		δ(H–O–H)
					3455(s)		ν(O–H)
					1670(s)		ν_{as}(O–C–O)
					1360(w) 1320(m)		ν_s(O–C–O)
					780(m) 750(w)		δ(O–C–O)
$[Th_2(O_2)_3SO_4(H_2O)_4]\cdot 5H_2O$		57.81	11.65	12.07[d]	830(w)	835 845	ν(O–O)
		(57.34)	(11.86)	(11.87)[d]	728(m)		$\rho_r(H_2O)$
					1635(s)		δ(H–O–H)
					3460(s)		ν(O–H)
					1155(s) 1115(s) 1060(s)	1150 1120 1050	ν_3
					990(m)	975	ν_1
					677(s) 618(s) 520(s)	660 610 550	ν_4
					460(s,br)	460	ν_2
							ν(S–O)

[a]Peroxy oxygen. [b]Microanalysis on C: found 3.15% (calc. 3%). [c]C_2O_4. [d]SO_4.

experimental conditions both the selected heteroligands and peroxide could be made to simultaneously coordinate with the metal centre. While freshly prepared hydrated thorium oxide, $ThO_2\cdot nH_2O$, was used in the synthesis of fluoroperoxothorates(IV), aqueous solutions of thorium nitrate hexahydrate, $Th(NO_3)_4\cdot 6H_2O$, were used for the preparation of the molecular complexes described herein. An important criterion for the successful synthesis of peroxometallate is the evaluation of appropriate pH of the reaction medium [1, 4]. Accordingly it was found that the reaction of hydrated thorium oxide, hydrogen peroxide and hydrofluoric acid leading to the synthesis of the fluoroperoxo complex of thorium, was successful at pH 10–11. The conducive pH for the synthesis of peroxo-oxalato complex of thorium was found to be 7–8 while for the peroxo-sulphato complex it

was found to be 2. The strategy for the reaction leading to fluoroperoxothorates(IV) was that hydrated thorium oxide would first react with H_2O_2 to form a thorium peroxo compound which in turn would interact with F^- to afford the desired compound. The order of addition of the two reagents H_2O_2 and hydrofluoric acid is important since a reverse order of addition of the reagents is detrimental to the successful synthesis of fluoroperoxothorates(IV) owing to the formation of a sparingly soluble binary fluoro complex of thorium(IV).

The white gelatinous mass, resulting from the addition of hydrogen peroxide to hydrated thorium oxide, was dissolved by careful addition of aqueous HF. The pH of the reaction solution was then raised to *c.* 10–11 by slow dropwise addition of aqueous ammonia or alkali-metal hydroxides until the $Th:O_2^{2-}$ ratio reached 1:1. Products isolated at a pH relatively lower than 10–11, on being analysed, were found to contain both O_2^{2-} and F^- but in a nonstoichiometric manner. It is therefore evident that although the O_2^{2-} uptake process might have been in progress at a lower pH, a compound of definite stoichiometry could only be synthesised at pH 10–11. However, apart from O_2^{2-} and F^- getting coordinated to the Th(IV) centre, two hydroxyl (OH^-) groups were also found to enter into the coordination sphere of thorium at this pH. This therefore suggests that although a high concentration of alkaline media is essential for the synthesis of peroxofluorothorates(IV), at a higher pH OH^- groups compete with O_2^{2-} and F^- for getting coordinated to the metal centre resulting in the formation of hydroxofluoroperoxothorates(IV), as obtained. Incorporation of OH^- groups is explained in terms of extensive hydrolysis of the Th^{4+} ion in aqueous solution at a higher pH [8, 21].

The diperoxotetra-aquo-μ-peroxo-μ-oxalatodithorium(IV) pentahydrate, $[Th_2(O_2)_3C_2O_4(H_2O)_4]\cdot 5H_2O$ and diperoxotetra-aquo-μ-peroxo-μ-sulphatodithorium(IV) pentahydrate, $[Th_2(O_2)_3SO_4(H_2O)_4]\cdot 5H_2O$ were synthesised directly from the reaction of an aqueous solution of $Th(NO_3)_4\cdot 6H_2O$ with $A_2C_2O_4$ or A_2SO_4 (A = Na, K or NH_4), respectively, and H_2O_2. The appropriate pH required for the synthesis of $[Th_2(O_2)_3C_2O_4(H_2O)_4]\cdot 5H_2O$ was ascertained to be 7–8, maintained by the addition of aqueous ammonia or 15% solution of AOH (A = Na or K). The reaction leading to the corresponding sulphato complex was, however, found to be complete at pH 2 maintained automatically. In order to ascertain the effect of pH similar reactions were conducted between pH 2 and 9, however, the products isolated were found to be similar to the one obtained at pH 2. This causes us to state that the dimeric $[Th_2(O_2)_3SO_4(H_2O)_4]\cdot 5H_2O$ compound formed at pH 2 does not undergo any change in its composition within the aforesaid pH range.

A point worth commenting on at this stage is that while the fluoroperoxothorates(IV) contain hydroxo ligands, the molecular heteroperoxo complexes containing either 'oxalato' or 'sulphato' involve aquo ligands. Evidently this difference must be owing to the fact that the latter compounds were synthesised at a considerably lower pH than the fluoroperoxothorates(IV). It is believed that at pH lower than that mentioned for the synthesis of fluoroperoxothorates(IV), Th(IV) exists as aquated species and partial substitution of H_2O molecules by O_2^{2-} and SO_4^{2-} or $C_2O_4^{2-}$ leads to the kind of compounds obtained herein. In this way, the synthesis of heteroligand peroxothorium(IV) complexes of the types $A_2[Th(O_2)F_2(OH)_2]\cdot nH_2O$ (A = NH_4, n = 3; A = Na or K, n = 1) and $[Th_2(O_2)_3L(H_2O)_4]\cdot 5H_2O$ (L = C_2O_4 or SO_4) has been achieved.

Characterisation and Structural Assessment

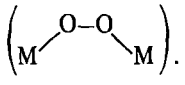
All the compounds were obtained as white microcrystalline products and were found to be stable for a prolonged period. The stability of the compounds was checked by the analysis of O_2^{2-} content from time to time. Recording of ESR spectra on solids at room temperature and results of magnetic susceptibility measurements provide evidence for the diamagnetic nature of the products concurrent with the occurrence of Th(IV) in each of the compounds. The compounds are practically insoluble in water thus precluding their molar conductance measurements. Unlike the fluoroperoxothorates(IV) the peroxooxalato and peroxosulphato compounds were obtained as molecular complexes. All the peroxothorium compounds mentioned herein slowly decompose in dilute sulphuric acid, liberating hydrogen peroxide quantitatively, and thus facilitate determination of active oxygen content. The importance of the chemical determination of active oxygen content has been emphasised earlier [18, 22]. In the present work, this was accomplished by redox titration separately involving standard Ce^{4+} solution as well as standard $KMnO_4$ solution. The redox titrations were performed in the presence of boric acid in order to prevent any loss of active oxygen. The results of chemical analyses of fluoroperoxothorates gave $Th:F:O_2^{2-}$ as 1:2:1 while those for molecular complexes $Th:L(C_2O_4^{2-}$ or $SO_4^{2-}):O_2^{2-}$ were found to be 2:1:3 in accord with their formulae.

Infrared and laser Raman spectroscopic studies were carried out on all the compounds and the results (Table 1) were found to be in order with the assigned formulae. The significant features of the IR spectra of $A_2[Th(O_2)F_2(OH)_2]\cdot nH_2O$ (A = NH_4, n = 3; A = Na or K, n = 1) involve absorption of coordinated fluoride, coordinated peroxide, coordinated OH^- and those of uncoordinated water. The band at *c.* 850 cm^{-1}, though weak in intensity, is typical of the ν(O–O) mode of O_2^{2-} and is indicative of triangu-

larly bonded bidentate chelating $O_2^{2-}(C_{2v})$ group, commonly encountered in peroxo-metallates [17, 18, 20, 22]. This is complemented by a band at *c.* 850 cm^{-1} in the IR spectra. The IR absorption at *c.* 360 cm^{-1} is attributed to the ν_3(Th–F) mode arising from the terminally coordinated F^- ligand [23]. The consistent appearance of a broad band at *c.* 3560 cm^{-1} led us to assign it to the O–H stretching mode of coordinated OH^- groups [24a]. The Th–O stretching modes assignments associated with $Th(O_2)$, however, were not attempted. The presence of several modes owing to Th–OH, Th–O_2 and Th–F in the low energy region makes this task a difficult one. Over and above the band due to coordinated OH^- groups two other bands at *c.* 3420 (ν(O–H)) and *c.* 1640 (δ(H–O–H)) cm^{-1} were observed in the IR spectra of fluoroperoxothorium complexes which are typical of the ones expected for uncoordinated water molecules [24b]. In the ammonium salt, however, one additional sharp band appears at 1400 cm^{-1} which is clearly due to the N–H deformation mode of NH_4^+ ion. The ν(N–H) modes arising from NH_4^+ could not be identified clearly owing to their overlap with the ν(O–H) modes originating from the lattice water. Thus leaving aside the modes due to the NH_4^+ ion in $(NH_4)_2[Th(O_2)F_2(OH)_2]\cdot 3H_2O$, the IR spectrum of all the compounds display a common feature.

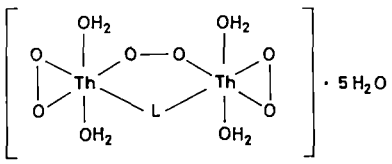
The common features of the IR spectra of $[Th_2(O_2)_3C_2O_4(H_2O)_4]\cdot 5H_2O$ and $[Th_2(O_2)_3SO_4(H_2O)_4]\cdot 5H_2O$ are the bands at *c.* 835w, *c.* 725m, *c.* 1640s and *c.* 3455 cm^{-1} which owe their origins to ν(O–O) (O_2^{2-}), ρ_r (coordinated water), δ(H–O–H) and ν(O–H), respectively. Although from the appearance and observed positions for the δ(H–O–H) and ν(O–H) modes of water no clear inference can be made regarding the nature of the water molecules, the consistent appearance of a distinct band at *c.* 725 cm^{-1} provides evidence for the notion that at least some water molecules are coordinated [25] to the metal centres, in line with the formula assigned. Appearance of signals at *c.* 830 and 845 cm^{-1} in the laser Raman (lR) spectra of both the compounds are indicative of presence of two types of peroxo groups [26] viz. triangularly bidentate type

and bridging type



The IR spectrum of $[Th_2(O_2)_3C_2O_4(H_2O)_4]\cdot 5H_2O$, in addition to the common features enumerated above, also exhibits patterns at ~1670s (ν_{as}(O–C–O)), ~1630w and ~1320m (ν_s(O–C–O)), 780m and ~750w (δ(O–C–O)) cm^{-1} which are in conformity with the occurrence of a bridging oxalato group. These assignments are in good agreement with those described in the literature [27, 28]. That the oxalato group occurs as a bridging ligand is further augmented by the absence of any band at 1680–1750 cm^{-1} which is expected of a chelated oxalato group. Like for $[Th_2(O_2)_3C_2O_4(H_2O)_4]\cdot 5H_2O$, the IR spectrum of the $[Th_2(O_2)_3SO_4(H_2O)_4]\cdot 5H_2O$ complex also shows characteristic patterns for the occurrence of a bridging sulphato ligand. The bands arising from SO_4^{2-} are observed at 1155s, 1115s, 1060s cm^{-1} due to ν_3, at 990m cm^{-1} due to ν_1, at 677s, 618s and 520s cm^{-1} due to ν_4, and at 460s br due to ν_2 of the coordinated sulphate [26, 29–31]. The lR spectrum recorded on solids exhibited signals at 1150, ~1120, ~1050 cm^{-1} due to ν_3, at ~975 cm^{-1} due to ν_1, at 660, ~610 and ~550 cm^{-1} due to ν_4 and 460 due to ν_2 of the sulphato ligand. The IR and lR spectral patterns particularly the appearance of ν_1 and ν_2 vibrations, the splitting of ν_3 and ν_4 into three bands each and the observation of ν_3 bands at a lower energy than generally observed for a chelated SO_4^{2-} ligand, supports the contention that SO_4^{2-} occurs as a bridging ligand in the compound under study.

Pyrolysis studies yielded similar results for both the molecular complexes. The results show that near 100 °C the compound starts losing weight and between 125–130 °C almost all the peroxy oxygen is lost along with 4.5–5 water molecules. The remaining water molecules were lost above 150 °C. The thermal studies therefore clearly suggest the presence of four coordinated water molecules and five uncoordinated water molecules in each of the compounds. Thus on the basis of chemical analyses in conjunction with IR, lR, ESR and pyrolysis studies the following molecular structure can be put forth for the complexes.



A similar structural representation was proposed [26] for $[Zr_2(O_2)_3SO_4(H_2O)_4]\cdot 6H_2O$, an analogue of the thorium peroxosulphato complex reported herein. The number of water molecules associated with such complexes needs to be characterised carefully as vibrational spectroscopy alone makes it very difficult to distinguish between lattice and coordinated water [32].

The successful synthesis of peroxothorates(IV) calls for an internal comparison to be made with

those of our earlier work on peroxotitanates(IV) [10, 11] and peroxozirconates(IV) [12], particularly in view of the fact that Ti, Zr and Th all belong to group IVB of the periodic table. The points that emerge out of the comparative studies are listed below.

(i) While both mono- and di-peroxofluoro complexes can be obtained with Ti [10, 11] and Zr [12] no diperoxofluorothorates could be obtained within the present experimental conditions.

(ii) All three elements Ti, Zr and Th permit synthesis of fluoroperoxo compounds of the corresponding metal, the fluoroperoxotitanates(IV) [10, 11] contain a Ti(IV) centre and fluoroperoxozirconates(IV) [12] contain a zirconyl (Zr=O) centre, whereas the fluoroperoxothorates(IV) (present work) have been shown to contain hydroxo (OH^-) groups bonded to the metal centre.

Concluding Remarks

Thus from the results of the present investigation, it is evident that under the appropriate reaction conditions, it is not only possible to accomplish the synthesis of both heteroligand peroxothorates as well as molecular peroxothorium complexes but such reaction strategies may also serve as a paradigm for the synthesis of new heteroligand peroxothorium(IV) compounds which in turn is expected to throw more light on the complicated peroxothorium chemistry.

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First Synthesis of (Acetylacetonato)rubidium(I), a Direct Route to (Acetylacetonato)caesium(I) and Evidence for Strong Ion Association/Ion-pair Formation in M(acac) (M = Li, Na, K, Rb or Cs)†‡

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First Synthesis of (Acetylacetonato)rubidium(I), a Direct Route to (Acetylacetonato)caesium(I) and Evidence for Strong Ion Association/Ion-pair Formation in M(acac) (M = Li, Na, K, Rb or Cs)†‡

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The first synthesis of Rb(acac) and a direct route to Cs(acac) are described; evidence for strong ion association/ion-pair formation is provided based upon molar conductance and ^{1}H NMR experiments on M(acac) (M = Li,Na,K,Rb or Cs).

The importance of (acetylacetonato)metals in many industrial processes (*e.g.* the extraction and separation of metals) and as semiconductors, antioxidants, catalysts in organic reactions and NMR shift reagents is well recognised.[1] Despite such progress, 1:1-type acetylacetonato-alkali-metal complexes have received far less attention.[1,2] Accordingly, this report deals with the first synthesis of Rb(acac), a direct route to Cs(acac) and comments on the covalent-like character of M(acac) (M = Li–Cs) based on molar conductance and ^{1}H NMR experiments.

Experimental

Elemental analyses were performed by Microanalysis Lab, NEHU, Shillong 793003. Rubidium and caesium were estimated with a Perkin-Elmer 2380 AAS spectrometer. IR spectra and pH measurements were recorded as earlier.[3] NMR spectra were recorded in [$^2H_6$]DMSO ([$^2H_6$]dimethyl sulphoxide) on a 90 MHz Varian EM 390 instrument. Conductances were measured using a Wayne Kerr automatic Precision Bridge B 905 conductometer. Li(acac),[4] Na(acac)[5] and K(acac)[5] were prepared by reported methods.

Synthesis of (Acetylacetonato)rubidium(I).—To Rb_2CO_3 (1.0 g, 0.43 mmol) was added acetylacetone (20 cm^3, 200 mmol) and the mixture was refluxed for *ca.* 15 min until a clear solution was obtained. The solution was filtered whilst hot. The filtrate, which registered a pH value of *ca.* 6, when cooled to room temperature afforded Rb($C_5H_7O_2$) as a white shiny *crystalline solid*, which was filtered off and dried (1.1 g, 69%) (Found: C, 32.7; H, 3.9; Rb, 45.8. $C_5H_7O_2Rb$ requires C, 32.53; H, 3.83; Rb, 46.30%).

Synthesis of (Acetylacetonato)caesium(I).—This was synthesised in an analogous manner as described for Rb(acac). Starting from 1.0 g (0.30 mmol) of Cs_2CO_3, the yield of Cs(acac) was 0.9 g (63%) (Found: C, 26.2; H, 2.9; Cs, 57.8. $C_5H_7CsO_2$ requires C, 25.88; H, 3.05; Cs, 57.28%).

Results and Discussion

The hitherto unknown Rb(acac) has thus now been synthesised. The strategy of the synthesis was as follows:

$$Rb_2CO_3 + 2Hacac \longrightarrow 2\,Rb(acac) + H_2O + CO_2$$

The reaction was facile and clean. A similar strategy was adopted as a direct route to Cs(acac) since the literature[6] method involved several extra preparation steps. Both Rb(acac) and Cs(acac) are hygroscopic and have no sharp melting points; however, they decompose at *ca.* 185 and > 200 °C, respectively. The solubility of M(acac) (M = Li–Cs) in polar organic solvents shows a decreasing trend with increasing mass of the metal.

The nature of the bonding in alkali-metal acetylacetonates has been investigated by previous workers.[6–8] From our experience on such complexes of di-and poly-valent metals,[1,9] it was anticipated that the bidentate chelate geometry of the $acac^-$ ligand would enable a strong ion association or ion-pair formation with M^+ ions. Indeed the strong possibility of the ligand adopting a U-shaped configuration[8] augmented this notion. A UV-spectral investigation[8] on M(acac) has provided good evidence with regard to ion association/ion-pair formation in dilute solutions and the spectral behaviour did not show any cation sensitivity on change of solvent.[7] Moreover, complete dissociation was not approached at the maximum dilution used in molecular conductivity measurements[10] on mixtures of an ethanolic solution of sodium or potassium ethoxide and acetylacetone. Our experiments on molar conductance measurements involved 10^{-3} M solutions of each of the M(acac) complexes at ambient temperatures. The values (an average of five measurements with a deviation of ± 1–2 units), as set out in Table 1, clearly demonstrate that the conductance is lower than that expected for an ideal 1:1 electrolyte[11] with Li(acac) and Na(acac) registering the lowest conductance. An internal comparison of these results suggests that the relative degree of dissociation of Li(acac) or Na(acac) is far less than that of K(acac), Rb(acac) or Cs(acac). The present conductance experiments provide strong evidence for ion association/ion-pair formation by M(acac) in water with a greater association when M = Li and Na than when M = K, Rb or Cs.

Table 1 Molar conductance and ^{1}H NMR data

Compound	Λ/S m^2 mol^{-1}	δ_H[a] CH	δ_H[a] CH_3
Li(acac)	0.70	5.0	1.66
Na(acac)	0.72	4.9	1.72
K(acac)	1.07	4.7	1.72
Rb(acac)	1.06	4.7	1.80
Cs(acac)	1.10	4.7	1.80

[a] In [$^2H_6$]DMSO; values in ppm.

Further conductance measurements, carried out as a function of time, showed that the values remain practically unaltered over a period of 5–7 days. This conforms with the suggested ion-association and attests to the stability of the ion pairs in aqueous solution.

The IR spectra of the M(acac) species, except that of Rb(acac), were investigated earlier.[6] The spectrum of Rb(acac) compares very well not only with those of its congeners but also with that of Tl(acac)[6] which contains a chelated $acac^-$ ligand. The present result is in line with the predicted[6] geometrical arrangement of the ligand in such complexes.

In an attempt to detect the differences in electronic distribution in the $acac^-$ chelate ring as a function of the metal ion, the NMR shifts of ring protons (γ-H) were recorded

*To receive any correspondence.

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‡acac = acetylacetonato (propane-2,4-dionato).

earlier[7] for a variety of metal acetylacetonates. Significantly, the shifts were found to be nearly independent of the metal ion completing the chelate ring, in respect of its charge, size, and ability to π-bond with the ligand. This implies a similar electronic environment in all the compounds studied. To our knowledge, no NMR investigation was conducted on M(acac). The solubility of such species in DMSO and the accessibility of NMR data of $Zn(acac)_2$[12] recorded in [$^2H_6$]DMSO prompted us to record the NMR spectra of M(acac) and compare the results. The spectra of alkali-metal acetylacetonates exhibit a general pattern (Table 1) with signals at δ *ca.* 1.7 (6 H, CH_3 protons) and *ca.* 4.8 (1 H, γ-CH proton). The chemical shifts were comparable with those of $Zn(acac)_2$ [δ_H 1.8 (6 H) and 5.2 (1 H)].[12] Noteworthy are the upfield shift of the δ values of the γ-CH protons and the downfield location of those of the CH_3 protons in descending the series. The trend is in keeping with an increase in the cation size in the complexes as well as an enhanced ionic character in going from Li(acac) to Cs(acac). The similarity of the ^1H NMR patterns of M(acac) and $Zn(acac)_2$, recorded under analogous conditions, provides a strong indication of ion association/ion-pair formation in the former.

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