STUDIES ON
PEROXO, FLUORO(PEROXO), AND FLUORO COMPOUNDS OF PHOSPHOROUS
AND
HETERO-LIGAND PEROXO COMPOUNDS OF ZIRCONIUM AND URANIUM

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Dedicated to my

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Studies On
Peroxo, Fluoro(Peroxo), And Fluoro Compounds of Phosphorous
And
Hetero-Ligand Peroxo Compounds of Zirconium and Uranium

ABSTRACT

The present thesis deals with the results of studies on synthesis, assessment of structure, and reactivity of some peroxo, fluoro-peroxo, and fluoro compounds of phosphorous as well as synthesis and structural assessment of some hetero-ligand peroxo complexes of zirconium and uranium. The content of the thesis has been distributed over six Chapters.

Chapter 1 presents a brief introduction pertaining the work embodied in the thesis. The interest in and the importance of the chemistry of dioxygen, in general, and peroxo and hetero-ligand peroxo compounds of phosphorous, zirconium, and uranium, in particular, are highlighted. Also emphasised in this Chapter is the lack of information concerning non-metal peroxo compounds.

Apart from the importance of studies of peroxo-chemistry, attention has also been drawn to the study of fluorophosphates. In addition, this Chapter projects the scope of work on the chosen aspects of phosphorous, zirconium and uranium chemistry.

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

Synthesis, characterisation and structural assessment, and reactivity of peroxo- and fluoroperoxophosphates constitute the basis of Chapter 3. Heretofore unreported ammonium and sodium monoperoxophosphate trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = Na, or NH_4), have been synthesised from the reaction of A_2HPO_4 (A = Na or NH_4) with 30% H_2O_2 at pH 9.5 held by the addition of the corresponding alkali. The compounds have been characterised from the results of chemical analyses, determination of molar conductances in water, IR and laser Raman (lR) spectroscopic studies. IR and laser Raman spectroscopy suggests that the O_2^{2-} is bonded to the phosphorous centre in an end-on fashion. The compounds are stable for several hours. The pH values of 0.01M solutions of $Na_3[PO_3(O_2)].3H_2O$ and $(NH_4)_3[PO_3(O_2)].3H_2O$ have been found to be 8.9 and 7.9, respectively. The efficacy of the newly synthesised compounds have been explored especially in terms of a viable substitute for the basic-H_2O_2 reagent. As a representative example, the sodium salt, $Na_3[PO_3(O_2)].3H_2O$, has been found to oxidise chalkones to chalkone epoxides, salicyldehyde to catechol, benzonitrile to benzamide, and benzil to benzoic acid in good yields. Further it has been shown that the compound in presence of an acid is capable of oxidising primary and secondary alcohols to the corresponding carbonyl compounds, and anthracene to anthraquinone.

Also included in this Chapter are the first chemical synthesis of a fluorinated peroxophosphate, ammonium mono(fluoro)peroxophosphate dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$, along with its characterisation, structural assessment, and the results of studies of some reactivity. The compound $(NH_4)_2[PO_2(O_2)F].2H_2O$ has been synthesised from the reaction of $(NH_4)H_2PO_4$ with 48% HF and 30% H_2O_2 at pH 10-11, maintained by the addition of aqueous ammonia, at an ice-bath temperature. The compound has been characterised by chemical analyses, IR and laser Raman spectroscopic studies. The IR and Raman spectra of the compounds indicate the presence of peroxide, P-F, and P=O vibrations. Peroxide (O_2^{2-}) has been shown to be bonded in an end-on manner.

Some properties of the compound are also reported herein. It is of interest that this compound, in the presence of an acid, is capable of oxidising hydrocarbon, alcohols, and olefins. Thus, in stoichiometric reactions it oxidises anthracene to anthraquinone, 2-propanol to acetone, n-butanol to butaldehyde, n-propanol to propionaldehyde, cyclohexene to 1,2-cyclo-hexanediol, and styrene to 1-phenylethyleneglycol, generally in ca. 40% yield. Equally interesting is the phosphorous product isolated after working up of the oxidation product in each of the above reactions. This has been identified as the monofluorophosphate, PO_3F^{2-}, a species important because of its use as an additive in dentifrice formulations. In the absence of air, the peroxo compound in water reacts with SO_2 to produce sulphate.

The results hitherto obtained with $Na_3[PO_3(O_2)].3H_2O$ and $(NH_4)_2[PO_2(O_2)F].2H_2O$ are very satisfactory and suggest the new reagents as valuable addition to the existing oxidising agents.

Chapter 4 of the thesis describes a new direct general method for the synthesis of crystalline fluorophosphates, viz. $(NH_4)_2[PO_3F].H_2O$ and $K_2[PO_3F]$. The synthesis is based on the reaction of H_3PO_4 with AHF_2 (A = NH_4 or K) followed by precipitation with ethanol. The identity of the compounds has been established from the results of elemental analyses, molar conductance measurements, IR, and laser Raman spectroscopic studies. Advantages of the new method are also highlighted.

Reported in Chapter 5 are the results of investigation on complex peroxozirconates. Synthesis and structural assessment of oxomonoperoxodifluorozirconate(IV) complexes, $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4) and oxodiperoxomonofluorozirconate(IV) compounds, $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4), and isolation of decafluoro-μ-oxo-dizirconates(IV), $A_4[F_5Zr\text{-}O\text{-}ZrF_5]$ (A = Na, K or NH_4), en route to oxoperoxofluorozirconates(IV) constitutes the subject matter of this Chapter.

Novel complex oxomonoperoxodifluorozirconates(IV), $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4), and oxodiperoxomonofluoro-zirconates(IV), $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4), the first diperoxozirconates to be obtained in the solid state, have been synthesised from the reaction of hydrated zirconium oxide,

$ZrO_2.nH_2O$, with 30% hydrogen peroxide and 48% hydrofluoric acid in the concentration ratio of $Zr:H_2O_2:HF$ as 1:33:6 at pH 6 and 12-14, respectively, held by the addition of the corresponding alkali hydroxide solutions or aqueous ammonia. Under the given experimental conditions, no peroxozirconate could be obtained until pH 6. A μ-oxo-species $[F_5Zr\text{-}O\text{-}ZrF_5]^{4-}$ has been isolated as its alkali-metal or NH_4^+ salt by conducting a similar reaction at pH 5. Isolation of this complex species at $pH \geqslant 5 < 6$ causes us to state that such a complex might be the precursor for the oxomonoperoxozirconates(IV), however, the chances of formation of a peroxozirconate(IV) at pH ca 5, which might have decomposed to the μ-oxo complex either in the solution or in the process of isolation, should not be discounted.

The compounds have been characterised by elemental analyses, magnetic susceptibility and EPR measurements, and IR and laser Raman spectroscopic studies. The results of vibrational spectral studies provide evidence for the presence of triangularly (C_{2v}) bonded peroxide (O_2^{2-}) and terminally bonded fluoride in each of the complexes. An internal comparison of these results with those of titanium have also been made.

Chapter 6, indeed the concluding Chapter of the thesis, deals with the results of studies on complex peroxouranates. The main features of the content of this Chapter are the synthesis and assessment of structures of alkali-metal and ammonium dioxo-peroxo(oxalato)uranate(VI) hydrates, $A_2[UO_2(O_2)C_2O_4].H_2O$

(A = NH_4, Na or K), and a molecular mixed-ligand peroxo complex $[UO_2(O_2)EDTA]$ (EDTA = Ethylenediaminetetra-acetic acid).

The complex peroxo(oxalato)uranates(VI) have been synthesised from the reaction of the product obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with alkali-metal or ammonium hydroxide, AOH, with 30% H_2O_2 and oxalic acid solution, in the concentration ratio of $U:H_2O_2:C_2O_4$ as 1:111:1 at pH 6. The pH value has been maintained by the addition of the corresponding alkali-metal or ammonium hydroxide. Precipitation of the compounds was completed by the addition of ethanol. The compounds have been characterised by elemental analyses, magnetic susceptibility measurements, and IR and laser Raman spectroscopic studies. Reference has been made to the corresponding peroxo-(sulphato)uranate(VI) complex, $[UO_2(O_2)SO_4(H_2O)]^{2-}$, in order to comment, on a comparative basis, on the modes of bonding of peroxide (O_2^{2-}) and the co-ligands SO_4^{2-} and $C_2O_4^{2-}$ in the respective cases. The IR and Raman spectra suggest that the O_2^{2-} and SO_4^{2-} in $[UO_2(O_2)SO_4(H_2O)]^{2-}$ are bonded to the UO_2^{2+} centre in a bridging and in a monodentate manner, respectively, while both the O_2^{2-} and $C_2O_4^{2-}$ ligands in $[UO_2(O_2)C_2O_4]^{2-}$ bind the uranyl centre in a bidentate chelated fashion. The $A_2[UO_2(O_2)C_2O_4].H_2O$ compounds are comparatively less stable than the $A_2[UO_2(O_2)SO_4(H_2O)]$ species. Whereas H_2O in $A_2[UO_2(O_2)C_2O_4].H_2O$ occurs as a water of crystallisation, it is coordinated to the UO_2^{2+} centre in the corresponding peroxo-sulphato compounds. The

advantages of the new method of synthesis of $A_2[UO_2(O_2)C_2O_4].H_2O$, over that of the previously reported $(NH_4)_2[UO_2(O_2)C_2O_4].3H_2O$, have been highlighted.

Also figure in this Chapter is a molecular complex $[UO_2(O_2)EDTA]$ (EDTA = Ethylenediaminetetra-acetic acid). This has been synthesised from the reaction of the product obtained by the addition of aqueous ammonia to an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with solid ethylenediaminetetra-acetic acid and 30% H_2O_2 maintaining the concentration ratio of $U:H_2O_2$:EDTA as 1:66:1. The pH value of the reaction solution was recorded to be 2. Characterisation and structural assessment have been made by elemental analyses, IR and Raman spectroscopic studies. The compound is diamagnetic. IR and Raman spectra suggest the presence of unionised ethylenediaminetetra-acetic acid (EDTA) being bonded through its N-atoms and the presence of triangularly bonded peroxide.

The results of studies described in Chapter 3 and 4 and a part of the results incorporated in Chapter 6 have been published, while the results included in Chapter 5 and the rest of those of Chapter 6 are now under communication.

Chapter 3

J. Chem. Soc., Dalton Trans., 1988, 2005

(On peroxofluorophosphate)

Proceedings of I World Congress II European Workshop Meeting Symposium in New Developments in Selective Oxidation, (Rimini, Italy), 1989.

(On peroxophosphate)

Chapter 4

J. Chem. Soc., Dalton Trans., 1987, 477.

Chapter 6

Inorg. Chem., 1986, 25, 2354.

Chapter 1

INTRODUCTION

Interest in the studies of the chemistry of dioxygen is one of the focal themes of current research.[1,2] This in part is due to the fact that combining dioxygen with hydrocarbons is a rewarding goal, in that it provides a direct access to a number of valuable oxygenated products such as alcohols, ketones, epoxides, glycols, phenols etc. Millions of tons of oxygenated products are now produced annually all over the world by this method.[3] Apart from this dioxygen plays a central role in living cells.[3,4] It can either be transported by respiratory pigments, like hemoglobin, hemocyanin etc and released at the active sites, or activated in enzymatic systems called oxygenases such as cytochrome P450.[4-8] At physiological temparature these oxygenases bring about important selective oxidations such as hydroxylation of hydrocarbons, epoxidation of alkenes, oxidative cleavage etc.

Recent interest in the chemistry of molecular oxygen has involved biochemists interested in biological oxygen transport and oxygen function as well as industrial chemists interested in developing homogeneous analogues to heterogeneously catalysed oxidation reactions. The isolation and characterisation of stable dioxygen complexes and the variety of reactions that they themselves undergo are beginning to yield general information about bonding, structure, and reactivity of co-ordinated dioxygen.[1,9]

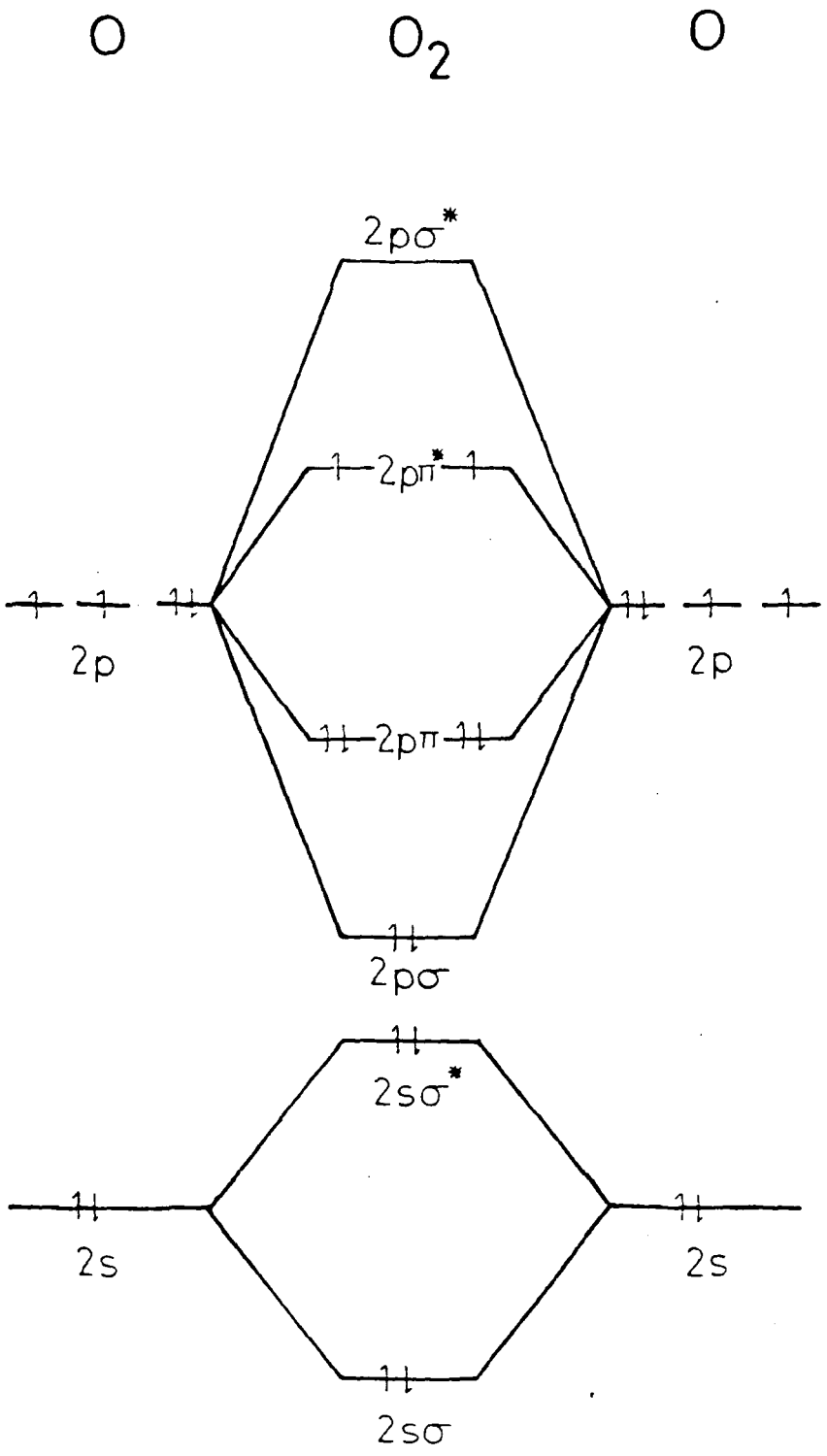


Fig.1 Molecular orbital diagram for O_2

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 understanding the bonding properties of dioxygen and its effect upon the extent to which the O-O bond of co-ordinated O_2 is activated.[9]

The bonding in molecular oxygen is best described by MO theory.[10] This theory describes the bonding as arising out of the combination of the valence orbitals of the two 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 degenarate π^* anti-bonding 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. MO theory also predicts

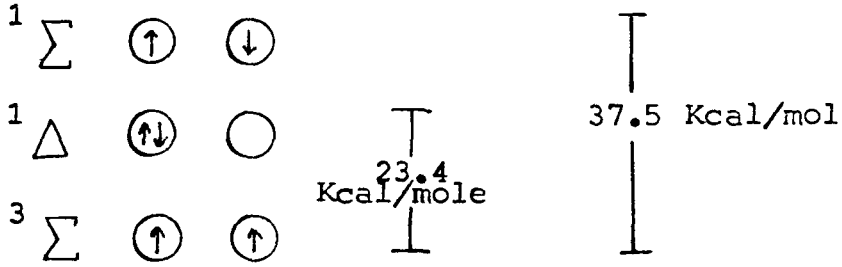


Fig. 2 π^* orbital occupancy and energies of the first two excited states of O_2

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. Some of the salient features for O_2^+, O_2, O_2^- and O_2^{2-} are summarised in Table 1.1.

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

Species	Bond Order	Compound	O-O distance (Å)[11]	Bond Energy (Kcal/mol)[10]	ν(O-O) cm^{-1}
O_2^+	2.5	O_2PtF_6	1.12	-	1905[11]
O_2	2	O_2	1.207	117.2	1554[12]
O_2^-	1.5	KO_2	1.28	-	1145[13]
O_2^{2-}	1	Na_2O_2	1.49	35	842[14]

Although the term molecular oxygen refers only to the free unco-ordinated O_2 molecule with the ground state configuration $^3\Sigma$, 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 a combined state.[15] For use of this term it is essential that a covalent bond has to exist between the oxygen atoms. According to the rationalisation made by Vaska,[15] peroxo compounds involve co-valently bound dioxygen resembling O_2^{2-} in peroxo configuration.

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, rationalised by Vaska[15] can be represented as shown in Fig. 3. The bridging peroxo could vary from cis-planar and trans-planar to trans-nonplanar configuration. An unusual symmetrical double

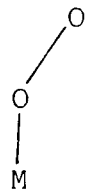
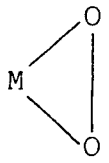
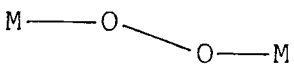
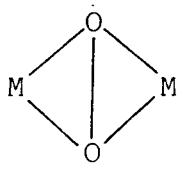
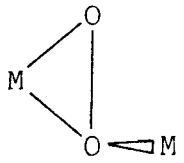
Structural type	Structural designation	Vaska Classification
	η^2 dioxygen	Type a (superoxo)
	η^2 dioxygen	Type IIa (peroxo)
	η^1: η^1 dioxygen	Type Ib (superoxo)
	η^1: η^1 dioxygen	Type IIb (peroxo)
	η^2: η^2 dioxygen	-
	η^1: η^2 dioxygen	-

Fig.3. Structural Classification of dioxygen complexes

bridging was also found,[16,17] however, such examples are very rare. Deviations from the ideal symmetry are also observed very often.

In case of non-metal peroxo compounds, however, peroxo group is found to be bonded mainly in two different fashions, viz. terminal monodentate[18,19] (i.e. end-on) and bridging trans-planar configuration,[18,20-23] although in some cases, for example in peroxoborates, peroxo group has been shown to be bonded in a triangular bidentate manner.[24] In addition peroxo group is also capable of being bonded as a hydroperoxide as observed in the cases of peroxo monocarbonate[18] and peroxo-monosulphate.[19]

Vibrational spectroscopy is essential for the characterisation of complexes containing peroxo groups. For a bidentate peroxide, regarded as a C_{2v} unit, three IR active modes are expected.[25] All the three IR active modes are also Raman active. The three modes are: Peroxo stretching (A_1) and symmetric and assymmetric $M-O_2$ stretching A_1 and B_2. The $\nu(O-O)(A_1)$ band is the most sensitive and intense one, and characteristically occurs between 800 and 950 cm^{-1}, but generally observed below 900 cm^{-1}. The frequency of this band remains fairly independent of the heteroligand environment but is effected by the mass of the central ion, indicating some degree of coupling of the $\nu(O-O)$ with $M-O_2$ vibrations. For the compounds where a peroxo group (O_2^{2-}) is bonded in an end-on fashion, the (O-O) stretching frequency occurs at ca

900 cm^{-1}, however, for complete characterisation labelling studies are generally recommended.[26]

Simple peroxo compounds are those which contain peroxides, hydroperoxides, and water molecules. Whereas hetero ligand peroxo compounds contain one to three co-ordinated peroxo groups and one or more monodentate or polydentate ligands. Hetero ligands may vary from monodentate ions to bulky porphyrins (F^-, Cl^-, NH_3, $C_2O_4^{2-}$, SO_4^{2-}, CO_3^{2-}, PPh_3, EDTA, O-phen, Oxine, Porphyrins, Pyridine-2,6-dicarboxylic acid etc.).[27]

Peroxo compounds can be synthesised either by activation of oxygen or by the interaction of peroxide with the appropriate starting material.[28]

The stability of peroxo complexes is generally enhanced by hetero ligand environment.[27] Many simple peroxides often explode spontaneously, some are sensitive to shock or decompose above 0°C, and several do not exist at all as stoichiometric compounds,[29] but many hetero ligand peroxo complexes, on the other hand, survive recrystallisation from boiling aqueous solutions, heating <u>in vacuo</u>, and remain unchanged for prolong periods in closed containers.[27,30]

Peroxo complexes besides having an intrinsic interest of their own[9,31-53] constitute an important class of reactive intermediates in catalytic oxidations[54-59] and are involved as potential oxygen-donors in the oxygen transfer reactions to organic substrates including hydrocarbons.[54] Moreover, the research leading to gain an insight into the roles of peroxo-

transition metal compounds in the storage and transport of oxygen and oxidase functions in biological systems is of growing interest.[28,56,60-66] The importance of neutral dioxygen complexes in biochemistry is well known,[60] but the biochemical connection of the metal peroxy complexes with biological processes is not very well understood. The metals Sc, Ti, V, Cr, Y, Nb, Mo, La, Hf, Ta, W,[28] and U[67] form stable hetero ligand peroxy complexes and evidences show that some of these metals have significant biological roles.[3,68-72]

It is somewhat surprising, however, that information on the peroxo-chemistry of heavier metals and actinides are rather scanty as opposed to a host of reports on peroxo-complexes of lighter transition metals covering a wide range of studies, namely synthesis, characterisation, reactivity,[1-3] crystal structure determination[73-76] and some biochemical aspects.[77]

A perusal of peroxo-element chemistry further reveals that this particular aspect of non-metals did not receive due attention and comparatively a very little is reported about non-metal peroxo compounds. Some peroxo-compounds of non-metals like peroxodicarbonates,[78] peroxomonocarbonates[78] peroxodisulphates[79,80] peroxomonosulphates,[81,82] peroxodiphosphates[83] and peroxomonophosphoric acid[83] are known and are widely used[84-92] in laboratory as well as in industry, but generally methods of their synthesis are cumbersome.

As a case in point, phosphorus, having the atomic number 15 and the atomic weight 30.97, belongs to group V of the periodic

table. The elements of this group, namely nitrogen, phosphorus, arsenic, antimony and bismuth are sometimes known as pnictides. In a general sense the chemistry of phosphorus resembles that of arsenic much more closely than that of nitrogen. The stable isotope ^{31}P has a nuclear spin of $\frac{1}{2}$ and constitutes 100% of the naturally abundant species. There are six unstable isotopes of the element (^{28}P, ^{29}P, ^{30}P, ^{32}P, ^{33}P, ^{34}P) known which have very short half lives. The electronic structure of phosphorus atom is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^3$ with three unpaired electrons in the outer 3p orbitals which are available for chemical bonding. Phosphorus can thus be formally trivalent or pentavalent, using only three or all the five electrons, respectively, in the outer shell to form covalent linkages to other atoms.

Interestingly phosphorus is a vital element in the composition of all living matters[93] and there is no known organism in which the chemistry of the element is not utilised.[93] The human body contains about 1% by weight of the element with about four-fifth of this being present as hydroxyapatite in bones and teeth.[93] Many of the most essential chemicals in life processes are phosphate esters.[94] These include the nucleic acids like DNA and RNA, as well as adenosine monophosphate (AMP). The transfer of phosphate groups between ATP and ADP is a fundamental process in the energetics of biological systems.[94]

Our interest in the studies of peroxo-element chemistry led us to look into the literature pertaining this aspect of phosphorus chemistry. As mentioned in passing that somewhat like carbon and sulphur, phosphorus is also known to form a few

peroxo compounds. The most well documented among them are peroxomonophosphoric acid[95] in solution and peroxodiphosphates, $A_4P_2O_8$, in addition to a poorly characterised unstable peroxide, P_2O_6,[96] and a diperoxophosphate.[95] Between the two namely peroxomonophosphoric acid and peroxodiphosphates, the latter are rather well characterised. Synthesis of non-metal peroxo compounds in general and peroxophosphates in particular involves either an electrochemical reaction[83] or a complicated chemical method.[83]

Although the importance of peroxomonophosphoric acid has been highlighted in the literature,[97,98] it is not very easy to obtain. Further free peroxomonophosphoric acid does not permit its isolation easily. Accordingly the acid is generated only in solutions for any investigation. The first report of peroxomonophosphoric acid dates back to 1910[99] and since then various techniques for its preparation,[98,100] and results of studies of decomposition mechanism,[101] and dissociation constants[102,103] have been reported. A scrutiny of the reported methods of generating the acid clearly shows that while some of the procedures afford an impure product,[98] the others are capable of producing a pure 2M solution of peroxomonophosphoric acid.[98,100] However, the latter methods require highly concentrated hydrogen peroxide (80-95%) that is not very commonly available thus limiting an accessibility of the acid. It is noteworthy that no salt of the $\left[PO_3(O_2)\right]^{3-}$ ion, but for an acid salt $KH_2\left[PO_3(O_2)\right]$, is reported.[97] The acid salt $KH_2\left[PO_3(O_2)\right]$ has been prepared from the interaction of P_4O_{10} with 84% H_2O_2 in the presence of 43% KOH solution[97] by conducting the reaction in a perhalogenated solvent.[97]

Despite the difficulties in obtaining peroxomonophosphoric acid, it has drawn quite a lot of attention especially because of its versatile oxidising potentialities. Thus, the acid has been shown to oxidise aromatic amines to nitro compounds,[89] and alkenes to epoxides.[86] It is known to cause aromatic hydroxylation[85] and Baeyer-Villiger reaction of acetophenone[88] and biacetals.[104] It has also been demonstrated that the acid is capable of oxidising inorganic species like Mn^{2+} [99] and I^- [99] to permanganate and iodine, respectively.

In addition to all that have been mentioned so far regarding peroxophosphates, there is another important aspect which deserves a due consideration. This addresses to peroxo-(fluoro)phosphates. In addition to a few fluorinated peroxides of carbon and sulphur,[105] which were generally synthesised by fluorination of oxo-compounds of the corresponding elements, one also finds a mention of two peroxo(fluoro)phosphoric acids viz., $H_2PO_2(O_2)F$ and $H_2P_2O_4(O_2)F_2$ in the literature. It was reported over half-a-century ago[106] that anodic oxidations of fluorophosphoric acids produced the peroxo(fluoro)phosphoric acids $H_2PO_2(O_2)F$ and $H_2P_2O_4(O_2)F_2$, only in ca. 2% yields. The compounds are very poorly characterised and to our knowledge neither any salts of the acids nor any chemical syntheses of fluorinated peroxophosphate is reported until date.

In an appreciation of the interesting properties of peroxo-compounds of phosphorous,[84-92] studies of peroxo-

chemistry of the element was considered to be worthwhile and rewarding area of investigation despite the acknowledged difficulties in getting an access to this field. Following selective aspects were identified as a part of the present Ph.D research:

(i) Synthesis, characterisation, and assessment of structure of alkali metal and ammonium peroxomonophosphate, $A_3[PO_3(O_2)]$ (A = alkali metal or ammonium), and studies of reactivities to explore their efficacy as good oxidants; and

(ii) Chemical synthesis, isolation in the solid state, and evaluation of structure and properties including reactivity of fluorinated peroxophosphate.

Accordingly, such studies were undertaken and a good amount of success achieved. Chapter 3 of the thesis presents an account of the first synthesis, characterisation, and assessment of structure and properties of sodium and ammonium peroxomonophosphate trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = Na or NH_4). Sodium peroxomonophosphate trihydrate, $Na_3[PO_3(O_2)].3H_2O$, was chosen as a representative example and a number of oxidation reactions have been conducted with particular emphasis on exploration of its capability as a viable substitute for the basic-H_2O_2 reagent. Also included in the same Chapter are the first chemical synthesis of a fluorinated peroxophosphate, ammonium fluoroperoxomonophosphate dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$, its characterisation, and the results of studies of reactivity as an oxidant for organic substrates.

Quite interesting was the phosphorous product isolated after working up of the oxidation product of the reactions that were conducted involving $(NH_4)_2[PO_2(O_2)F].2H_2O$. This was identified as the monofluorophosphate, PO_3F^{2-}, and the species generated interest in us particularly because of its acknowledged use as an additive in dentifrice formulations for the inhibition of dental caries. Looking back into the relevant literature, it was evident that there did not exist any simple and easily accessible route to alkali metal and ammonium monofluorophosphates, $A_2[PO_3F]$ (A = alkali metal or NH_4), although they have been known for quite sometime.[107-111] The recommended methods[107-111] for their synthesis involve either a high temperature fusion reaction, or fluorophosphoric acid as the starting material which requires extra preparation and purification, in addition to one or more steps to remove unwanted products, inevitably formed in either of the methods, to obtain the pure products. Thus while studying the other aspects of the chemistry of phosphorous, we sought for an easy access to alkali metal and ammonium monofluorophosphate. Chapter 4 of the thesis deals with the direct synthesis of ammonium monofluorophosphate monohydrate, $(NH_4)_2[PO_3F].H_2O$ and potassium monofluorophosphate, $K_2[PO_3F]$, their characterisation and properties, and also highlights the advantages of the new method over those previously reported.

Quite apart from the studies of chemistry of phosphorous, research involving peroxo-chemistry of transition metals has emerged out as one of the most exciting and important areas of investigation in contemporary inorganic chemistry.[1-4,64-75,112]

A number of research groups round the world[1-4,64-75,112] have engaged their attentions on various aspects of peroxo-metal chemistry, and consequently a remarkable amount of significant informations are now available in the literature especially on these aspects of lighter metals. Contrary to a host of reports on different aspects of peroxo-compounds of lighter transition metals, however, reports on the corresponding aspects of their heavier congeners are scanty. As a case in point, for example, although a variety of investigations have been carried out on the peroxo-titanium chemistry,[113-115] peroxo-zirconium chemistry has received far less attention. Success has been achieved by other workers, of the laboratory, where the present research has been carried out, in their endeavours related to synthesis, characterisation, and evaluation of structures of a host of hetero-ligand-peroxo titanates(IV),[116-119] and a good number of new compounds of this type have been prepared and newer synthetic strategies developed.[116-119] The heteroligands were drawn from F^-, Cl^-, SO_4^{2-} etc. It was also possible to synthesise a few molecular hetero ligand peroxo-titanium(IV) compounds like $[Ti(O_2)_2(L\text{-}L)]$ (L-L = 1,10-phenanthroline, 2,2'-bipyridine), and $[Ti(O_2)_2(tu)]$ (tu = thiourea).[119] To our knowledge, information on similar studies on the zirconium chemistry is only very scant.

It may be mentioned in passing the metal zirconium occurs widely on the earth's crust but not in very concentrated deposites. The major minerals are baddeleyite, ZrO_2 and Zircon, $ZrSiO_4$. Because of the effects of lanthanide contraction both the atomic

radii of zirconium and hafnium, the radii of Zr^{4+} and Hf^{4+} ions are virtually identical, and accordingly they tend to display a similar chemistry. The chemical similarity of zirconium and hafnium is well exemplified in the context of their geochemistry. The metal of our interest at this juncture is zirconium which shows a spectrum of oxidation states ranging from zero to +4. One of the most striking difference of the chemistry of zirconium from that of titanium is that the lower oxidation states of zirconium are of minor importance. There are few authenticated compounds of the element except those of its tetravalent ones. Zirconium(IV) oxide, ZrO_2, is more basic than TiO_2 and is virtually insoluble in an excess of base. There is, however, a more extensive aqueous chemistry of the metal because of its lower tendency towards complete hydrolysis. Nevertheless hydrolysis does occur and it is very doubtful indeed if Zr^{4+} aquo ions exist even in strongly acid solutions. The hydrolysed ion is often referred to as the "zirconyl" ion and written ZrO^{2+}. Our specific interest in the peroxo-zirconium chemistry led to a survey of the relevant literature. It is evident from the literature that zirconyl salts are known to form hydrated peroxides $ZrO(O_2)(H_2O)_x$[120] and peroxo-salts $K_4Zr(O_2)_4(H_2O)_6$, $K_4Zr_2O_{11}(H_2O)_9$,[120] which have been isolated. In addition, there are claims for the existence of $[ZrO(O_2)_2]^{2-}$ in strong alkali and species with peroxo: Zr ratios of 1:1 and 0.5:1 in acid (2N HCl)solutions.[120] Moreover a series of products were reported in somewhat older literature[121] to be obtained from zirconium sulphate-hydrogen peroxide solutions at different pH values:

$Zr_2(O_2)_3SO_4(H_2O)_{8-10}$ (pH = 0.1-0.7), $Zr_3O_3(O_2)_2SO_4(H_2O)_{9-12}$ (pH = 2.0) and $Zr_2O_2(O_2)SO_4(H_2O)_{3-6}$ (pH = 2.2), and cyclic structures were proposed involving two or three zirconium atoms bridged by peroxo and sulphate groups.[121] Only a few peroxo compounds of zirconium are reported in the literature.[120] Later on a few peroxo-fluorozirconates(IV),[122-126] peroxo sulphato[127] and peroxo oxalatozirconates(IV),[128] and neutral peroxozirconium(IV) complexes containing organic ligands such as, picolinic acid, amino carboxylic acids etc.[129] have been synthesised, and with these the history of peroxo-zirconium chemistry more or less ended. It is noteworthy that practically very little is known regarding reactivity of peroxo-zirconium compounds.

It is thus evident from an overview presented above that various aspects of peroxo-chemistry of zirconium not only need a great deal of work to be accomplished but also require a rather systematic approach in order to gain a clear and a deeper insight.

In view of the above and as a part of a general programme of the research group, it was imperative to undertake investigations on peroxo-zirconium chemistry. The specific aim was to evaluate conditions appropriate for the synthesis of peroxo-fluorozirconates(IV) containing both one and two peroxo groups per metal centre in addition to one or more coordinated fluoride ligands. It was also our contention to compare the results with

those of titanium,[116,117] a congener of zirconium and to comment on this aspect of chemistry of the two metals.

Accordingly such work was undertaken and an interpretative account of the results of studies involving peroxofluorozirconates(IV) has been presented in Chapter 5 of this thesis.

Like titanium and zirconium, actinides are known to form simple peroxides,[130,131] but because of the highly complicated nature,[130] peroxo-chemistry of actinides has been far less dealt with compared to that of lighter metals. As a case in point, for instance, uranium is known to form a host of simple peroxides, but its hetero-ligand-peroxo-chemistry has been practically overlooked in earlier investigations.[130,131]

Uranium, the fourth element in the actinide series having ground state electronic configuration $[Rn]5f^3 6d^1 7s^2$, is the heaviest element to occur in nature, in recoverable amounts, and its isotopes are all α-emitters, occuring in the proportions ^{238}U 99.28%, ^{235}U 0.71% and ^{234}U 0.005%.[131] The chemistry of the element shows considerable difference from the earlier actinides of the series. Stable oxidation states of the metal range progressively from +3 to +6, with the corresponding f^n configuration ranging from f^3 to f^0. The most stable oxidation state of uranium is its hexavalent state, and the ligands which stabilise this particular oxidation state of the metal include halides, nitrate, carboxylates, sulphate, β-diketonates, and peroxides etc. In simple compounds the hexavalent state occurs only in hexafluoride, UF_6, and hexachloride, UCl_6,[132] and the

principal chemistry of the +6 state in solid as well as in solution is that of the dioxo cation, UO_2^{2+}, which forms stable complexes with neutral or anionic ligands. The +5 oxidation state of the metal is stable only in dilute acidic solution and in the presence of organic complexing agents. The oxo-cation UO_2^{+} as such is normally not stable in an aqueous solution, as it undergoes rapid disproportionation. In the tetravalent state, U^{+4} ion is stable only in the absence of air or any other oxidising agents, whereas in the trivalent state U^{+3} ion is produced in solutions by the action of powerful reducing agents, but is very susceptible to oxidation. The oxo ions are evidently linear in crystalline compounds as well as in solutions. The uranyl ion, UO_2^{2+}, characteristic of its +6 state, forms a great variety of complexes with anionic ligands and neutral molecules. 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, and may be of potential use in photogeneration of oxygen, which is of great importance for the photo cleavage of water.[133,134] Structural information of the uranyl complexes based on crystallographic data shows that four, five or six atoms can lie in the equatorial plane of O-U-O group with the ligand atoms may or may not be entirely coplanar depending on the circumstances. Planar 5 and 6 co-ordination in the equatorial plane are most common and appear to give geometry more stable than the puckered hexagonal configuration. Planar 5-co-ordination best allows ratio-

lisation of a number of hydroxides and other structures, as well as the behaviour of polynuclear uranyl ion in hydrolysed solutions;[135] and the complex ion $[UO_2(CH_3COO)_3]^-$ represents a typical example of the planar 6-co-ordination in the equatorial plane of the O-U-O ion.[136]

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

Thus, it is evident from the foregoing discussion, that the chemistry of hexavalent uranium is mainly that of the uranyl ion. As mentioned earlier, peroxide (O_2^{2-}) acts as a stabilising ligand for uranium and the metal is known to form peroxo compounds in its highest oxidation state. The complexity involved in peroxo-uranium chemistry is an acknowledged problem,[131,137] and the system is exceedingly complicated[138] owing to the formation of a host of different peroxouranate(VI) species with a slight variation of pH of the reaction medium. Peroxouranates containing O_2^{2-}:U as 1:1, 1:2, 2:1, 3:1, 3:2, and 5:2 have been described in the literature[136,139] in addition to a few more which were rationalised only on the basis of peroxide to uranium ratio,[140,141] Among these peroxouranates, however, $UO_2(O_2).nH_2O$ (n = 2 or 4) appears to be the best characterised one. This species has been

known since 1876,[142] and was also a subject of extensive investigations.[143,144] Nevertheless its constitution was not well established for a long period, since different groups described it in different manners, eg. true peroxide hydrate or a peroxide having the composition U_2O_7, a peroxy acid or an addition compound of uranium oxide, $UO_3.H_2O_2.H_2O$.[144,145] Finally Gordon and Taube[146] showed it to be a true peroxide hydrate on the basis of their isotopic tracer studies on thermal decomposition of uranium-peroxide systems.

Albeit formation of simple peroxides[131,137] of uranium as evident from the above discussion, but its heteroligand peroxo chemistry seems to be rather poorly investigated.[131,137] Despite a long history of peroxo-uranium chemistry, earlier reports on heteroligand peroxouranates are rather scanty, except for some carbonato and oxalato peroxouranates,[137] and a few fluoro peroxouranates.[137] In addition to these there are some reports on the studies of uranyl ion-hydrogen peroxide systems in solution containing ligands like ethylenediamintetra-acetic acid (EDTA),[147] citric acid[148] and fluoride[149] etc. Relatively recent reports on heteroligand peroxouranates include a few nonelectrolytic peroxouranates[150] of the type $[UO_2(O_2)L_2]$ (L = Ph_3PO, Ph_3AsO, Py-N oxide or quinoline N-oxide), and a unique μ_2-peroxo bridged complex benzyl-trimethyl ammonium μ_2-peroxo bis [trichlorodioxouranate(VI)].[151] The above mentioned chloroperoxo complex is one of the rare examples of a complex containing a dioxygen molecule being bonded as a μ_2-peroxo group. In addition, subsequently in 1981 a few more novel mono and diperoxo

complexes of UO_2^{2+} containing organic ligands have been reported.[152] Apart from these, there are two more reports on the synthesis and characterisation of peroxofluoro[67,153] and peroxocarbonato[154] uranates(VI) from the laboratory where the present work has been carried out.

In view of the above discussion, and also taking note of some of the recent results on hetero-ligand peroxo complexes of other metals,[2,116-118,154-157] it appeared that suitable chosen hetero-ligands, under appropriate experimental conditions, could impart stability to peroxo metal systems and permit their isolation in the solid state. This led us to carry out synthesis and structural assessment of some hetero-ligand peroxo-complexes of UO_2^{2+} as a part of the present Ph.D. research programme. The chosen hetero-ligands include oxalate ($C_2O_4^{2-}$) and ethylenediamintetra-acetic acid (EDTA).

While another colleague[153] was engaged in the work involving dioxoperoxo(sulphato)uranates(VI) as a part of his assignment, attention of the present worker was directed to the synthesis, characterisation, and structural assessment of a molecular peroxo complex, dioxoperoxo(ethylenediamintetra-acetic acid)Uranium(VI), $[UO_2(O_2)(EDTA)]$, to improvise a direct route to dioxoperoxo(oxalato)uranate(VI), and to rationalise the modes of bonding of O_2^{2-} and $C_2O_4^{2-}$ with the UO_2^{2+} centre, and to make an internal comparison of the results to correlate with that of the previously reported

$(NH_4)_2UO_4C_2O_4 \cdot 3H_2O$.[158,159] Chapter 6, indeed the concluding Chapter of the thesis, deals with the studies made on complex peroxouranates.

While the present Chapter gives a non-exhaustive background information pertaining the kind of work chosen for the present Ph.D. research and highlights the scope of work in the field, Chapter 2 provides details of the methods of elemental analyses and particulars of instruments/equipment used for characterisation and structural assessment. Chapters 3 to 6 incorporate the results of studies on the chosen problems viz: peroxo-, peroxo(fluoro)- and fluorophosphates, and complex peroxozirconates and complex peroxouranates. Chapters 3 to 6 have been so designed as to make each of them a self-contained one with a brief introduction, sections on experimental and results and discussion followed by relevant bibliography. A good part of the new results has been published, while rest is under communication.

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Chapter 2

Methods of Elemental Analyses and Particulars of Instruments/Equipment Used for Characterisation and Structural Assessment of Compounds

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

Elemental Analyses

Phosphorus[1]

Phosphorus was determined as ammonium magnesium phosphate hexahydrate, $MgNH_4PO_4.6H_2O$. An accurately weighed amount of the phosphorus compound was dissolved in water ($\sim$100 cm^3) to the solution was then added 15-20 cm^3 of concentrated hydrochloric acid. The resulting solution was boiled for ca.30 min. to ensure complete decomposition. The solution was then cooled to room temperature and to it was added 3 cm^3 of concentrated hydrochloric acid followed by the addition of a few drops of methyl red indicator. An amount of 25 cm^3 of magnesia mixture introduced into the solution, followed by a slow addition of concentrated aqueous ammonia with vigorous stirring, until the indicator turned

yellow. Stirring was continued for a further period of 5 min. and finally an excess of 5 cm^3 of concentrated aqueous ammonia was added slowly. The resulting mixture was allowed to stand for 4h, when the white precipitate of ammonium magnesium phosphate hexahydrate settled down. The precipitate was separated quantitatively by filtration, using a sintered glass crucible (grade 4) and washed with distilled ethanol 3 to 4 times and finally with small portions of ether. The precipitate was dried in a vaccuum disiccator for ca 20 min, and finally weighed as $MgNH_4PO_4.6H_2O$.

Active Oxygen (Peroxo Oxygen)[2-4]

(i) Permanganometry[2]

An accurately weighed amount of a peroxo compound of phosphorous or zirconium 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.

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

This method is suitable for determination of peroxide contents in peroxo compounds of phosphorous and zirconium.

(ii) Iodometry[3]

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-phosphorous, a peroxo-

zirconium or a peroxo-uranium compound with continuous stirring. The mixture was allowed to stand for ca 15 min in dark under a CO_2 atmosphere. The liberated amount of 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 in peroxo-uranium compounds. This method is also employed in determining active oxygen contents of peroxo compounds of phosphorous or zirconium.

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

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

Fluoride[5]

An accurately weighed amount of a fluoro-phosphorous compound or a fluorozirconate(IV) 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 then heated for ca 20 min. to ensure complete decomposition. In the cases of fluorozirconates(IV), hydrated zirconium oxide formed was separated by filtration and washed

several times with water. For phosphorous compounds, however, no filtration was necessary. The filtrate and washings were collected for fluoride estimation. To the combined washings and filtrate, 2 to 3 drops of bromophenol blue indicator and 3 cm^3 of 10% sodium chloride solution were added and the whole was diluted to ca 250 cm^3. Dilute nitric acid was added to it until colour changed to just yellow followed by the addition of dilute sodium hydroxide solution until the colour ultimately just changed to blue. The mixture was then treated with 1 cm^3 of concentrated hydrochloric acid and 5.0g of lead nitrate, and then heated on a steam bath. After all the lead nitrate had dissolved, 5.0g crystallised sodium acetate was added to the solution and digested on a steam-bath for about half an hour with occassional 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.

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

Zirconium[6]

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 ml) followed by heating for ca 10 min to ensure complete decomposition. The precipitated hydrated zirconyloxide 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.

Uranium[7]

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 turns yellow, and a yellow precipitate was obtained at this stage. A Whatman accelerator was added and the solution was warmed for 1 to 2 min., 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.

Oxalate[8]

An accurately weighed amount of the uranium-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 potassium permanganate solution maintaining the temperature of the solution at ca. 60°C.

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

Sodium and Potassium

Flame photometry was used in determining sodium and potassium. An acidified (hydrochloric acid) solution containing sodium or potassium was used for flame photometry.

Carbon, Hydrogen, and Nitrogen

Carbon, hydrogen, and nitrogen were estimated by micro analytical methods. The results of analyses were obtained from Regional Sophisticated Instrumentation Centre, Central Drug Research Institute, Lucknow, and Regional Sophisticated Instrumentation Centre, NEHU, Shillong.

Particulars of Instruments/Equipment Used

pH Measurement

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

Molar Conductance

Molar conductance measurements were made in conductivity grade water using 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 standard for calibration.

Infrared Spectra

Infrared spectra were recorded in KBr on the following spectrophotometers:

(1) Perkin-Elmer model 297
(2) Perkin-Elmer model 983

Laser Raman Spectra

Laser Raman (lR) spectra were recorded on a SPEX Ramalog model 1403 Raman spectrometer. The 4880 Å laser line from Spectra Physics model 165-09 Argon laser and 5145 Å laser line from the 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.

^{1}H NMR Spectra

^{1}H NMR spectra were recorded using Varian 390, 90 MHz spectrometer in appropriate deuterated solvents or carbon-tetrachloride. Tetramethyl silane (TMS) was used as the internal standard.

EPR Spectra

EPR spectra of the compounds were recorded in the form of polycrystalline solid using a Varian E109, X-band EPR spectrometer.

Atomic Absorption Spectrometry

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

Melting Point

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

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Chapter 3

Synthesis, Characterisation, and Reactivity of Sodium and Ammonium Peroxomonophosphate Trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = Na or NH_4)

and

First Chemical Synthesis of a Fluorinated Peroxophosphate : Ammonium Peroxo(fluoro)monophosphate Dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$*

A perusal of the literature pertaining peroxo-element chemistry reveals that studies on non-metal peroxo compounds has not received due attention, and comparatively a very little is reported about non-metal peroxo species. Some peroxo-compounds of non-metals like peroxodicarbonates,[1] peroxomonocarbonates,[1] peroxodisulphates,[2,3] peroxomonosulphates,[4,5] peroxodiphosphates[6] and peroxomonophosphoric acid[6] are known and are widely used [7-15] in laboratory as well as in industry, but synthetic routes to many of these compounds are not straight forward. For example,

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Another part of the work has been accepted for publication: Proceedings of I World Congress II European Workshop Symposium in "New Developments in Selective Oxidation ," Rimini, Italy, 1989.

phosphorous is known to form compounds with peroxide, but only a little is known regarding this aspect of phosphorous chemistry. The most well documented among peroxo-phosphorous compounds are peroxomonophosphoric acid[6] in solution and peroxodiphosphates, $A_4P_2O_8$ (A = Na, NH_4 or K) in addition to a poorly characterised unstable peroxide, P_2O_6,[16] and a diperoxophosphate.[17] Between the two categories namely peroxomonophosphoric acid and peroxodiphosphates, the latter ones are rather well characterised.

Although the importance of peroxomonophosphoric acid has been highlighted in the literature,[18,19] it is not very easy to obtain. Further, free peroxomonophosphoric acid does not permit an easy isolation.[20] Peroxomonophosphoric acid came into existence with the first report of its synthesis in 1910[21] and since then various techniques for its preparation,[19,22] and results of studies of decomposition mechanism[23] and dissociation constants[24,25] have been reported. A scrutiny of the reported methods for generation of the acid shows that while some of the methods afford an impure product,[19] the others are capable of producing a pure 2M solution of peroxomonophosphoric acid.[19,22] However, the latter methods require highly concentrated hydrogen peroxide (80-95%) that is not very commonly available, thus limiting its accessibility. It is noteworthy that no salt of the $[PO_3(O_2)]^{3-}$ ion, but for an acid salt $KH_2[PO_3(O_2)]$, is reported.[18] The salt, $KH_2[PO_3(O_2)]$ has been prepared from the reaction of P_4O_{10} with 84% H_2O_2 in the presence of 43% KOH solution by conducting the reaction in a perhalogenated solvent.[18]

Despite the difficulties in obtaining permonophosphoric acid, it has drawn quite a lot of attention especially because of its versatile oxidising potentialities.

In view of the above mentioned interesting and very useful properties of peroxomonophosphoric acid, although it is difficult to obtain, it was considered essential to synthesise the salts of the acid and explore their properties particularly in terms of their reactivity. This was also anticipated to be a rewarding area of investigation and might lead to an easy access to the peroxo-phosphorous chemistry.

Over and above what has been stated, hetero-ligand peroxo compounds of non-metals in general, and of phosphorous in particular, is very poorly investigated. It was reported over a half-a-century ago[26] that anodic oxidations of fluorophosphoric acids produced peroxo(fluoro)phosphoric acids, $H_2PO_2(O_2)F$ and $H_2P_2O_4(O_2)F_2$, only in ca. 2% yields. The compounds are poorly characterised and to our knowledge neither any salts of the acid nor any chemical synthesis of fluorinated peroxophosphate is reported until date. In addition to simple peroxophosphates, we also sought to develope a route to chemical synthesis of fluorinated peroxophosphate followed by studies of reactivity of such species.

Accordingly, studies on peroxo- and fluorinated peroxophosphates were undertaken. The present Chapter of the thesis describes a very simple and efficient method of synthesis along with structural assessment of heretofore unreported ammonium

and sodium peroxomonophosphate trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = Na or NH_4), which are as efficacious as the acid with some added advantages. We also report herein the results of our studies of reactivity of the compounds. This Chapter also describes a simple chemical synthesis of hitherto unknown ammonium peroxo-(fluoro)phosphate dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$, the first chemically synthesised peroxo(fluoro)phosphate, alongwith its structural assessment, and some results of our studies of its reactivity with inorganic as well as organic substrates.

Experimental

All chemicals used were reagent grade products (E. Merck, BDH, Sarabhai M. Chemicals, SISCO).

Synthesis of Ammonium and Sodium Peroxomonophosphate Trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = NH_4, Na)

In a typical procedure, disodium or diammonium hydrogen phosphate, A_2HPO_4 (A = NH_4 or Na) (7.57 mmol) was dissolved in 15 cm^3 (132.3 mmol) of 30% H_2O_2. The reaction solution was stirred for ca. 15 min. followed by slow addition of aqueous ammonia (sp. gr. 0.9) or a 20% solution of sodium hydroxide in the cases of ammonium and sodium salts, respectively, until the pH of the reaction mixture was found to be 9.5. An amount of 50 cm^3 of 95% ethanol was added to the reaction solution with contineous stirring. An oily mass separated out at this stage.

The reaction mixture was stirred further for ca 20 min. and allowed to stand for one hour. The supernetant liquid was decanted off and the oily mass was treated repeatedly with ethanol until white crystalline $Na_3[PO_3(O_2)].3H_2O$ or $(NH_4)_3[PO_3(O_2)].3H_2O$ was obtained. The compound was separated by filtration in a suction, washed 4-5 times with ethanol, and finally dried in vacuo over concentrated H_2SO_4.

The amount of reagents used and the yields of the compounds obtained are set out in Table 3.1.

Studies of Reactivity of Sodium Peroxomonophosphate Trihydrate, $Na_3[PO_3(O_2)].3H_2O$

Starting Material

Commercially available pure samples of various alcohols, benzonitrile, salicyldehyde, and anthracene were used. The compounds were purified before use.

Two α, β-unsaturated ketones e.g., benzylidene acetophenone and benzylidene 4'-methoxy acetophenone were prepared by reported procedures[27], and their purity checked by comparing melting points and spectra with those of the reported ones.[27]

All the following oxidation reactions were conducted under pure N_2 atmosphere.

Table 3.1 : Amounts of Reagents Used and the Yields of Ammonium and Sodium Peroxomonophosphate Trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = NH_4 or Na)

Compound	A_2HPO_4 g (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)	Yield g (%)
$(NH_4)_3[PO_3(O_2)].3H_2O$	1 (7.57)	15 (132.3)	1.6 (96)
$Na_3[PO_3(O_2)].3H_2O$	1.1 (7.57)	15 (132.3)	1.6 (90)

(i) Reactions of Chalcones with Sodium Peroxomonophosphate Trihydrate, $Na_3[PO_3(O_2)].3H_2O$

A 4.81 mmol sample of the chalcone was dissolved in 25 cm^3 of THF. To the above solution was added an aqueous solution (25 cm^3) of $Na_3[PO_3(O_2)].3H_2O$ (1.69g; 7.23 mmol) drop by drop, from a droping funnel, over a period of 20-30 min with contineous stirring at room temperature. The stirring was continued for a further period of two hours. The reaction solution was then poured on to 100 cm^3 of water containing crushed ice. The crude chalcone epoxide separates out at this stage. The mixture was stirred for 15 min and then filtered off under suction and washed 4-5 times with cold water, dried, and recrystallised from methanol.

The amount of reagent used and the yields and melting points of the products obtained are given in Table 3.2. The IR and NMR spectra were found to be superimposable with those reported in the literature.[27]

(ii) Reaction of Salicylaldehyde with Sodium Peroxomonophosphate Trihydrate, $Na_3[PO_3(O_2)].3H_2O$

To a 1.0g (8.27 mmol) sample of salicylaldehyde an aqueous solution (25 cm^3) of $Na_3[PO_3(O_2)].3H_2O$ (2.9g; 12.40 mmol) was added with stirring. The solution temperature rose spontaneously to ca. 60°C and a dark colour developed. The reaction solution was stirred for 8h and then allowed to stand overnight. The solution was neutralised with acetic acid,

evaporated to dryness, and the residue was treated with toluene (5 x 10 cm^3). The toluene fraction was dried (Na_2SO_4) and upon evaporation gave catechol. The crude catechol thus obtained was purified by passing through a 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 reported in Table 3.2. The IR and NMR spectra were compared with those of the reported ones[28] and found to be superimposable.

(iii) Reaction of Benzonitrile with $Na_3[PO_3(O_2)].3H_2O$

Benzonitrile (1.0g, 9.71 mmol) was mixed with 15 cm^3 of ethanol and to this was added an aqueous solution (30 cm^3) of $Na_3[PO_3(O_2)].3H_2O$ (6.8g; 29.07 mmol). The reaction solution was stirred for 3h at ca. 50°C on an oil-bath. The reaction solution was cooled to room temperature and treated with chloroform (3 x 15 cm^3). Combined organic layers were washed with water (1 x 50 cm^3), dried (Na_2SO_4), and concentrated to give crude benzamide which was purified by recrystallisation from chloroform.

Amount of reagent used and the yield and melting of the product are set out in Table 3.2. The IR and NMR spectral position are found to be similar to those of an authentic sample.

(iv) Reaction of $Na_3[PO_3(O_2)].3H_2O$ with Benzil

An acetonitrile (15 cm^3) solution of benzil (1.0g, 4.76 mmol) was mixed with an aqueous solution (30 cm^3) of $Na_3[PO_3(O_2)].3H_2O$

(1.67g; 7.14 mmol) and the mixture was refluxed for ca. 1h. The reaction mixture was poured to ice-cold water (50 cm^3) after cooling to room temperature. Unreacted benzil came out as a yellow solid which was filtered and washed with water (2-3 times). The combined filtrate and washings was acidified with hydrochloric acid and then treated with chloroform (4 x 20 cm^3). The combined organic layers were washed with water (1 x 10 cm^3), dried (Na_2SO_4), and concentrated to obtain benzoic acid. The crude product was purified by recrystallisation from chloroform.

The yield and melting point of the oxidised product as well as the amount of reagent used for the oxidation are included in Table 3.2. The IR spectrum was found to be superimposable with that of an authentic sample.

(v) Reaction of $Na_3[PO_3(O_2)].3H_2O$ with Anthracene

Anthracene (1.0g; 5.62 mmol) and acetic acid (30 cm^3) were placed in a flask and the whole was refluxed until the whole amount of anthracene went into solution. An aqueous solution (15 cm^3) of $Na_3[PO_3(O_2)].3H_2O$ (1.97g; 8.42 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

Table 3.2 : Amounts of the Reagent Used and Yields and Melting Points of the Reaction Product [The Reagent Used was $Na_3[PO_3(O_2)].3H_2O$]

Substrate	Amount of Substrate g (mmol)	Amount of $Na_3[PO_3(O_2)].3H_2O$ g (mmol)	Product	Yields g (%)	m.p. (Uncorrected) °C
Benzylidene acetophenone	1.0 (4.81)	1.69 (7.22)	Epoxide	0.8 (74)	90
Benzylidene p-methoxy acetophenone	1.0 (4.20)	1.47 (6.28)	Epoxide	0.9 (84)	79
Salicylaldehyde	1.0 (8.19)	2.9 (12.40)	Catechol	0.8 (88)	103
Benzonitrile	1.0 (9.70)	6.8 (29.06)	Benzamide	0.9 (76)	128
Benzil	1.0 (4.76)	1.67 (7.14)	Benzoic acid	0.5 (43)	122
Anthracene	1.0 (5.61)	1.97 (8.42)	Anthra-quinone	0.70 (60)	284

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 3.2. The NMR and IR spectra compare very well with those of an authentic sample.

(vi) Reaction of $Na_3[PO_3(O_2)].3H_2O$ with Alcohols. A General Procedure

In a typical procedure the alcohol was mixed with ca. 20 cm^3 of water and to it was added 1.5 cm^3 of concentrated H_2SO_4. To the above reaction mixture was added a solid sample of $Na_3[PO_3(O_2)].3H_2O$ maintaining the ratio of alcohol : PO_5^{3-} as 1:1.5. The reaction mixture was refluxed for 1h and then cooled to room temperature followed by neutralisation with $NaHCO_3$. The aldehyde or ketone was isolated as its 2,4-dinitrophenyl hydrazine derivative from which the yields of the carbonyl compounds were calculated. The amount of reagent used and the yields of the products and the melting points of their 2,4-dinitro-phenyl hydrazine derivatives are summerised in Table 3.3.

Synthesis of Ammonium Peroxo(fluoro)monophosphate Dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$

A mixture of 1.0g (8.69 mmol) ammonium dihydrogen-phosphate, $(NH_4)H_2PO_4$, and 1 cm^3 (24 mmol) of 48% HF was allowed to react with 15 cm^3 (132.3 mmol) of 30% hydrogen peroxide in an ice-bath, at pH 10-11 held by a careful addition of aqueous

Table 3.3 : Amounts of the Reagent Used and Yields and Melting Points of 2,4-dinitrophenyl hydrazine Derivatives of Oxidation Products of Alcohols [The Reagent Used was $Na_3[PO_3(O_2)].3H_2O$]

Alcohol	Amount of Alcohol g (mmol)	Amount of $Na_3[PO_3(O_2)].3H_2O$ g (mmol)	Product	Yield %	m.p. of 2,4-dinitro phenyl hydrazone °C
n-Propanol	2.0 (33.27)	11.7 (50.01)	Propional-dehyde	34	153 - 154
n-Butanol	2.0 (26.98)	9.61 (41.08)	Butal-dehyde	36	122 - 123
iso-Butanol	2.0 (26.98)	9.48 (40.52)	isobutal-dehyde	37	187 - 188
iso-Propanol	2.0 (33.27)	11.7 (50.01)	Acetone	40	127 - 128

ammonia (sp. gr. 0.9) with stirring. Stirring was continued for a further period ca.7 min followed by the addition of ca.25 cm^3 of ice-cold ethanol whereupon white crystalline ammonium peroxo-(fluoro)monophosphate dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$ was precipitated. This was separated by filtration, washed 5-6 times with ethanol, and finally dried in vacuo over concentrated H_2SO_4. The yield of $(NH_4)_2[PO_2(O_2)F].2H_2O$ was 1.3g (81%).

Studies of Reactivity of Ammonium Peroxo(fluoro)monophosphate Dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$

Starting Materials

Commercially available pure samples of the various alcohols viz. n-propanol, n-butanol, and isopropanol, styrene and anthracene were used. The compounds were purified before use. Cyclohexene was prepared by the reported method[29] and its identity was confirmed by comparing its IR and NMR spectra with those of the reported ones.[30]

$SO_2(g)$ was generated from the reaction of copper turnings with concentrated sulphuric acid.

(i) Reaction of $(NH_4)_2[PO_2(O_2)F].2H_2O$ with Cyclohexene

A 2.0g (24.39 mmol) sample of cyclohexene and 25 cm^3 of 80% formic acid were placed in a round bottomed flask. To it was added solid $(NH_4)_2[PO_2(O_2)F].2H_2O$ (6.81g; 36.60 mmol). The reaction mixture was stirred magnetically at room temperature for 3h. The mixture was then neutralised with $NaHCO_3$ and

Table 3.4 : Amounts of the Reagent Used and Yields and Melting Points of the Reaction Products [The Reagent Used was $(NH_4)_2[PO_2(O_2)F].2H_2O$]

Substrate	Amount of Substrate g (mmol)	Amount of $(NH_4)_2[PO_2(O_2)F].2H_2O$ g (mmol)	Product	Yield g (%)	m.p. (Uncorrected) °C
Cyclohexene	2.0 (24.39)	6.81 (36.6)	Trans 1,2-cyclohexane-diol	0.7 (49)	102-103
Styrene	2.0 (19.20)	5.37 (28.86)	1-Phenyl ethylene-glycol	0.5 (38)	66 - 68
Anthracene	1.0 (5.62)	1.57 (8.44)	Anthra-quinone	0.8 (68)	284

treated with chloroform (4 x 20 cm^3). The extract was washed with water (1 x 20 cm^3), dried by treating with Na_2SO_4, and then concentrated to afford white crystalline 1,2-cyclohexanediol. The product was purified by passing through a column using hexane/ethylacetate (6:4) as the eluent.

The amount of reagent used for the oxidation and the yield of the product along with its melting point are reported in Table 3.4. The IR and NMR spectra compare very well with those of an authentic sample.

(ii) Reaction of $(NH_4)_2 [PO_2(O_2)F].2H_2O$ with Styrene

The reaction of styrene with ammonium peroxo(fluoro)monophosphate, $(NH_4)_2 [PO_2(O_2)F].2H_2O$, was carried out in a similar manner as described under the reaction of cyclohexene. The end product was found to be 1-phenyl ethyleneglycol.

The yield and melting point of the product, and the amount of reagent used for the oxidation are given in Table 3.4. The IR and NMR spectra were found to be similar to those of a standard sample.

(iii) Reaction of $(NH_4)_2 [PO_2(O_2)F].2H_2O$ with Alcohols. A representative method

In a typical procedure the alcohol was reacted with $(NH_4)_2 [PO_2(O_2)F].2H_2O$ in a manner analogous to that described under the reaction of sodium peroxomonophosphate trihydrate, $Na_3 [PO_3(O_2)].3H_2O$, with alcohols.

Table 3.5 : Amounts of the Reagent Used and Yields and Melting Points of 2,4-dinitrophenylhydrazine Derivatives of the Oxidation Products of Alcohols [The Reagent Used was $(NH_4)_2[PO_2(O_2)F].2H_2O$]

Alcohol	Amount of Alcohol g (mmol)	Amount of $(NH_4)_2[PO_2(O_2)F].2H_2O$ g (mmol)	Product	Yield %	m.p. of 2,4-dinitrophenyl hydrazone °C
n-Propanol	2.0 (33.27)	9.3 (49.99)	Propionaldehyde	38	154 - 155
n-Butanol	2.0 (26.98)	7.54 (40.53)	Butaldehyde	39	122 - 123
iso-Propanol	2.0 (33.27)	9.3 (49.99)	Acetone	41	127 - 128

The amount of reagents used and the yields of the products and melting points of the 2,4-dinitrophenylhydrazine derivatives are incorporated in Table 3.5.

(iv) Reaction of $(NH_4)_2[PO_2(O_2)F].2H_2O$ with Anthracene

The reaction of anthracene with $(NH_4)_2[PO_2(O_2)F].2H_2O$ was carried out in a similar way as that described under the reaction of $Na_3[PO_3(O_2)].3H_2O$ with anthracene. The product anthraquinone was isolated and purified in a similar fashion as already described. The compound was characterised by melting point determination and spectral measurements followed by comparison of the results with those of an authentic sample.

The amount of reagent used and the yield of the product are given in Table 3.4.

(v) Reaction of $(NH_4)_2[PO_2(O_2)F].2H_2O$ with $SO_2(g)$

The water used for the reaction was deoxygenated by the following procedure. The water sample was first boiled for ca. 30 min under N_2 atmosphere and it was cooled to room temperature. This was followed by bubbling of N_2 gas through it for a period of ca. 15 min. The deoxygenated water thus obtained was stored in an air tight container.

Through an aqueous solution (15 cm^3) of 1.0g (5.4 mmol) of ammonium peroxo(fluoro)monophosphate, $(NH_4)_2[PO_2(O_2)F].2H_2O$, $SO_2(g)$ was bubbled for about 15 min with occassional stirring. The bubbling of $SO_2(g)$ was stopped and the reaction solution was

allowed to stand at room temperature. Ethanol (95%) was added to the solution to just initiate precipitation and then left for ca. 2h whereupon white crystalline ammonium sulphate separated. This was filtered, washed 2-3 times with ethanol, and finally dried in vacuo over concentrated H_2SO_4. The product was identified as ammonium sulphate, $(NH_4)_2SO_4$, by chemical analyses and IR spectroscopy.[31]

Elemental Analyses

Quantitative estimation of peroxide, fluoride, phosphorous, nitrogen, and sodium were made by the methods described in Chapter 2. The analytical data and molar conductance values are reported in Table 3.6 and Table 3.8.

Results and Discussion

Ammonium and Sodium Peroxomonophosphate Trihydrate, $A_3[PO_3(O_2)].3H_2O$ (A = NH_4, Na). Synthesis, Characterisation, and an Assessment of Structure

It was reported by Schmidlin and co-workers[21] that an interaction of 30% H_2O_2 solution with P_4O_{10} produced permonophosphoric acid in solution. Subsequently it was shown[19] that the product so obtained was a crude one, and any attempt to prepare the salts of the acid failed. Later on various improvised techniques for its preparation were developed[19,22] but no salt, except an acid salt, KH_2PO_5, could be synthesised. All the improvised routes to permonophosphoric acid referred to above[19,22] required

80-90% H_2O_2. The use of such highly concentrated H_2O_2 solutions need a very careful handling and manipulations causing a restricted accessibility of the desired species.

From the experience gathered in the laboratory, where the present investigation was carried out, in the field of peroxo-element chemistry,[32] it was anticipated that reactions of appropriate salts of phosphoric acid with 30% H_2O_2 under suitable experimental conditions might lead to the synthesis of salts of peroxomonophosphoric acid. It has also been established from a number of experiments[32] that one of the most important parameters in successful synthesis is a conducive pH of the reaction solution.

Accordingly, successful synthesis of the title compounds was achieved from a reaction of the di-ammonium or di-sodium hydrogen phosphate with 30% H_2O_2 at pH 9.5 held by the addition of aqueous ammonia (sp. gr. 0.9) or 20% sodium hydroxide solution.

$$A_2HPO_4 + H_2O_2 + AOH \longrightarrow A_3[PO_3(O_2)] + 2H_2O$$

(A = NH_4 or Na)

the role of alkali was not only to facilitate peroxygenation but also to act as a source of counter cations, while ethanol helped in precipitation of the product.

The compounds have been obtained as white crystalline products and can be stored for a prolonged period in sealed containers at a freezer temperature without decomposition. At room temperature, however, the compounds can be stored undecomposed <u>in vacuo</u> only for a day or so. The stability of the

compounds can be ascertained by quantitative estimation of active oxygen content at a regular interval. The compounds are insoluble in common organic solvents but are highly soluble in water. The molar conductance measurements gave a value of 327-340 $\Omega^{-1}cm^2mol^{-1}$ in conformity with their 3:1 electrolytic nature. The aqueous solutions of the compounds are found to be basic in nature [pH of 0.01M solution of $Na_3[PO_3(O_2)].3H_2O$ = 8.9; pH of 0.01M solution of $(NH_4)_3[PO_3(O_2)].3H_2O$ = 7.9] and this is explained in terms of hydrolysis of the salts in an aqueous medium. This further suggests that peroxomonophosphoric acid is a relatively weak acid and thus an aqueous solution of its salt reacts basic. This property of the compounds is very important particularly in the context of their reactivity (as shown latter in this section). The product decompose in an acidic solution (dil.H_2SO_4) quantitatively liberating H_2O_2 and rendering it easy to estimate the active oxygen contents. The peroxide contents have been determined by redox titrations separately involving a standard $KMnO_4$ solution or a standard Ce^{4+} solution. The results of peroxide estimation, and those of elemental analyses for the counter cation and phosphorous show the stoichiometry of A:P:O_2^{2-} (active oxygen) to be 3:1:1 (Table 3.6) in complete agreement with their formulae, $A_3[PO_3(O_2)].3H_2O$ (A = NH_4 or Na).

The vibrational spectra of the compounds show bands due to the presence of coordinated peroxide (O_2^{2-}),[33] (PO_3),[34] and

Table 3.6 : Analytical Results and Molar Conductance Values of Ammonium and Sodium Peroxomonophosphate Trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = NH_4, Na)

Compound	Molar Conductance $\Omega^{-1}cm^2mol^{-1}$	Found % (Calcd. %)		
		Na or N	P	O_A^a
$(NH_4)_3[PO_3(O_2)].3H_2O$	330	19.1 (19.18)	14.2 (14.13)	14.8 (14.60)
$Na_3[PO_3(O_2)].3H_2O$	340	29.1 (29.49)	13.0 (13.24)	13.5 (13.68)

[a]Active Oxygen

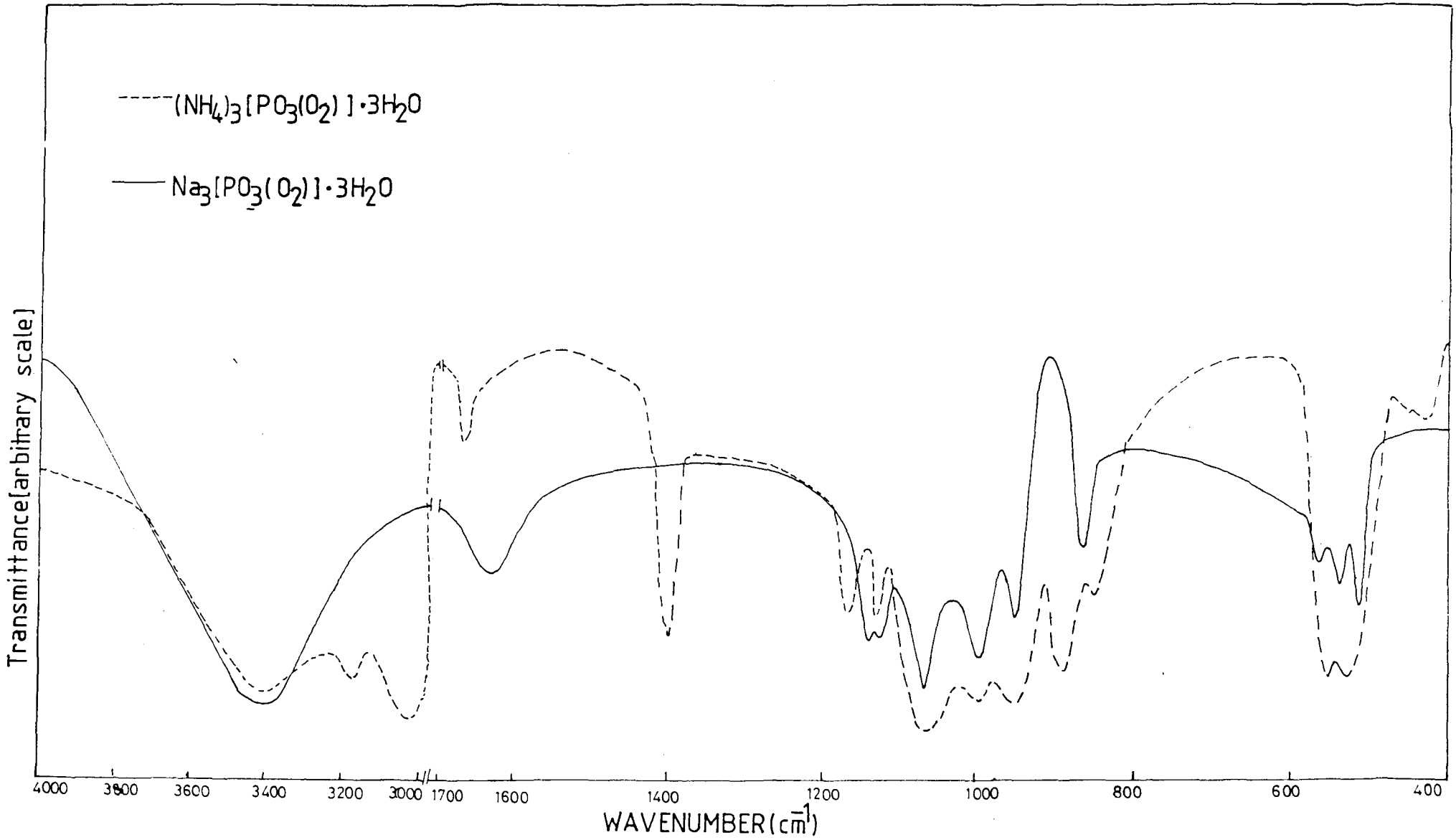
lattice water.[35] The presence of lattice water is clearly evidenced by the IR bands at ca.3400 cm^{-1} due to ν (O-H) and at ca. 1650 cm^{-1} due to δ (H-O-H). There has been no indication for the occurrence of H_2O_2 of crystallisation.[1] The presence of PO_3 moiety is clearly reflected in the IR spectra from the display of wide splitting[1] of the (PO_3) stretching and deformation modes. Thus the bands at ca.1070, 1130, 1140 cm^{-1} have been assigned to $\nu_{as}(PO_3)$[34,36] while those at ca.950s and 1000s cm^{-1} have been attributed to $\nu_s(PO_3)$[34,36] (Table 3.7). The peroxo stretching mode ν (O-O) appears at ca.870 cm^{-1}. The frequencies at ca.510, ca.540, and at ca.570 cm^{-1} have been assigned to $\delta(PO_3)$ modes.[34,36] The laser Raman (lR) spectra of the newly synthesised peroxophosphates show complementary signals at ca.1078, ca.1155, and ca.1189 cm^{-1} due to $\nu_{as}(PO_3)$, at ca.990 and ca.950 cm^{-1} due to $\nu_s(PO_3)$. The laser Raman (lR) signals at ca.872 cm^{-1} complements the corresponding IR signal which owe their origin to ν(O-O) mode of the bonded peroxide. The lR signals at ca.530 and 476 cm^{-1} have been attributed to $\delta(PO_3)$ modes. The IR and laser Raman spectra totally conform to the formulations of the compounds as $A_3[PO_3(O_2)].3H_2O$ with the peroxide (O_2^{2-}) group being presumably bonded in an end-on manner as often encountered in simple monoperoxo derivatives of other elements namely sulphur[2] and carbon.[1]

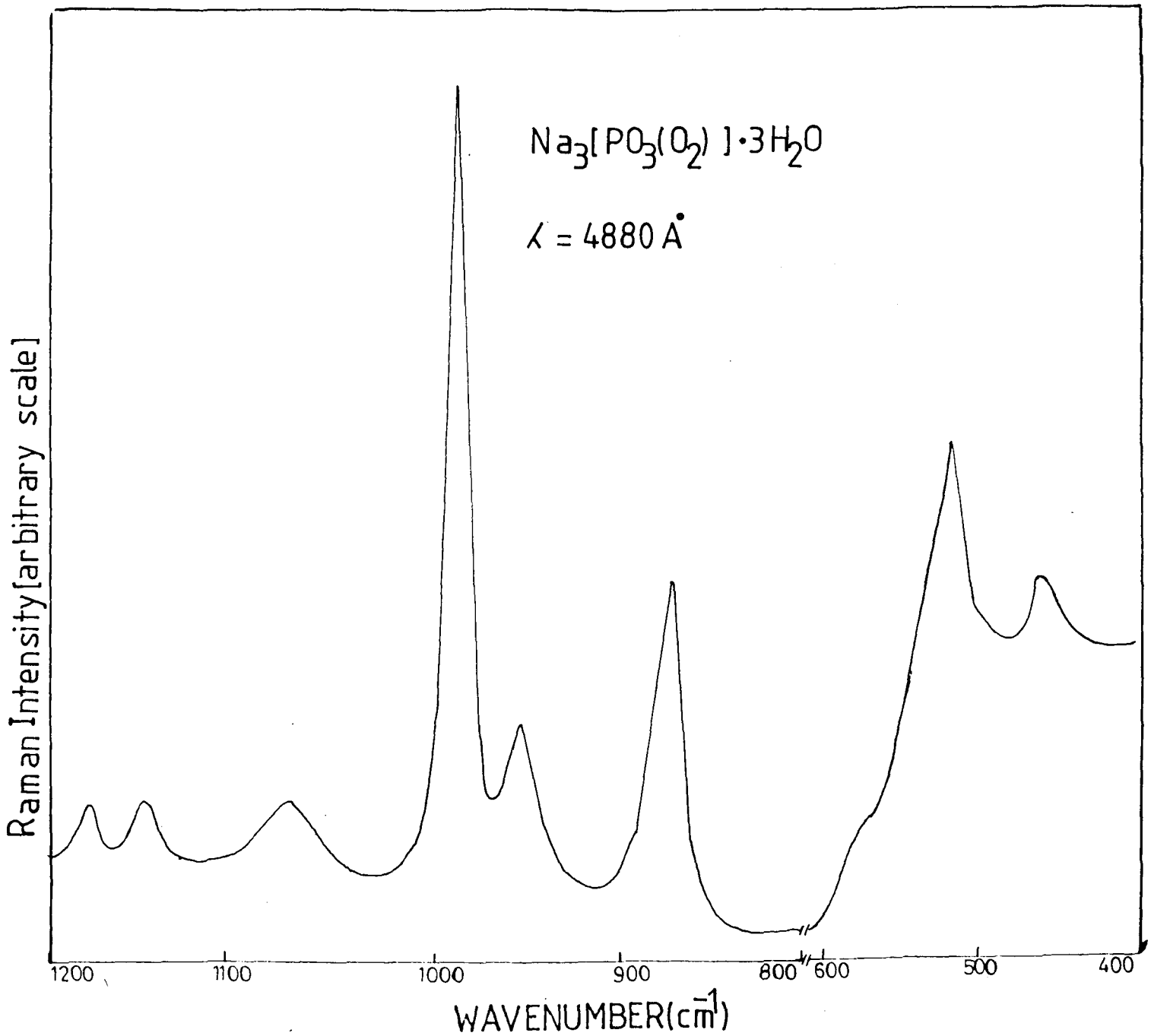
Reactivity of Sodium Peroxomonophosphate Trihydrate, $Na_3[PO_3(O_2)].3H_2O$

As mentioned earlier in this section that aqueous solutions of the peroxomonophosphates react basic with the pH values lying

Table 3.7 : Structurally Significant IR and Raman Bands of Ammonium and Sodium Peroxomonophosphate Trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = NH_4 or Na)

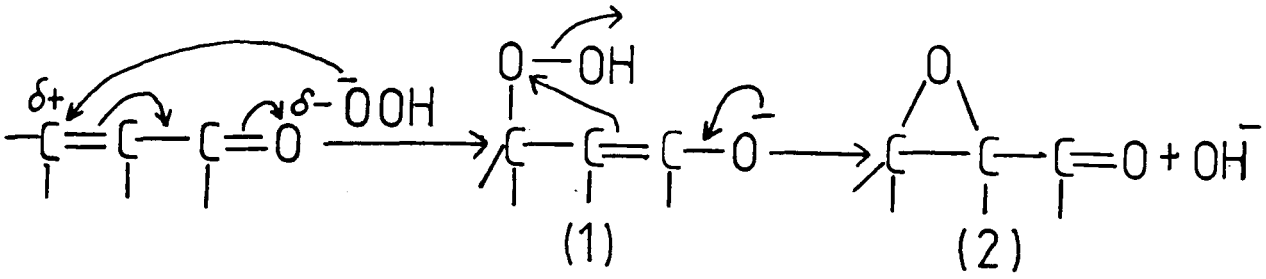
Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$(NH_4)_3[PO_3(O_2)].3H_2O$	1070s, 1110s, 1160s	1070, 1150, 1160	$\nu_{as}(PO_3)$
	950s, 1000s	940, 990	$\nu_s(PO_3)$
	430m, 530s, 560s	470, 530	$\delta(PO_3)$
	890s	880	ν(O-O)
	1660m		δ (H-O-H)
	3400s		ν(O-H)
	1400s, 3050s, 3160m		ν_4, ν_1, ν_3 N-H modes of NH_4^+
$Na_3[PO_3(O_2)].3H_2O$	1070s, 1130s, 1140s	1078, 1155, 1189	$\nu_{as}(PO_3)$
	960s, 990s	952, 986	$\nu_s(PO_3)$
	510s, 540m, 570m	476, 530	$\delta(PO_3)$
	870s	875	ν(O-O)
	1650m		δ (H-O-H)
	3400s		ν(O-H)


(NH4)3[PO3(O2)]·3H2O
Na3[PO3(O2)]·3H2O
Transmittance(arbitrary scale)
4000
3800
3600
3400
3200
3000
1700
1600
1400
1200
1000
800
600
400
WAVENUMBER(cm-1)


$Na_3[PO_3(O_2)]\cdot 3H_2O$
$\lambda = 4880\,\text{Å}$
Raman Intensity[arbitrary scale]
1200
1100
1000
900
800
600
500
400
WAVENUMBER(cm^{-1})

between 8 and 9 (0.01M solutions). This particular property of the compounds was quite intriguing because it led us to anticipate that the compounds might be capable of being used as viable substitutes for the basic-H_2O_2 reagent with some added advantages e.g. easy to handle and to maintain stoichiometry.

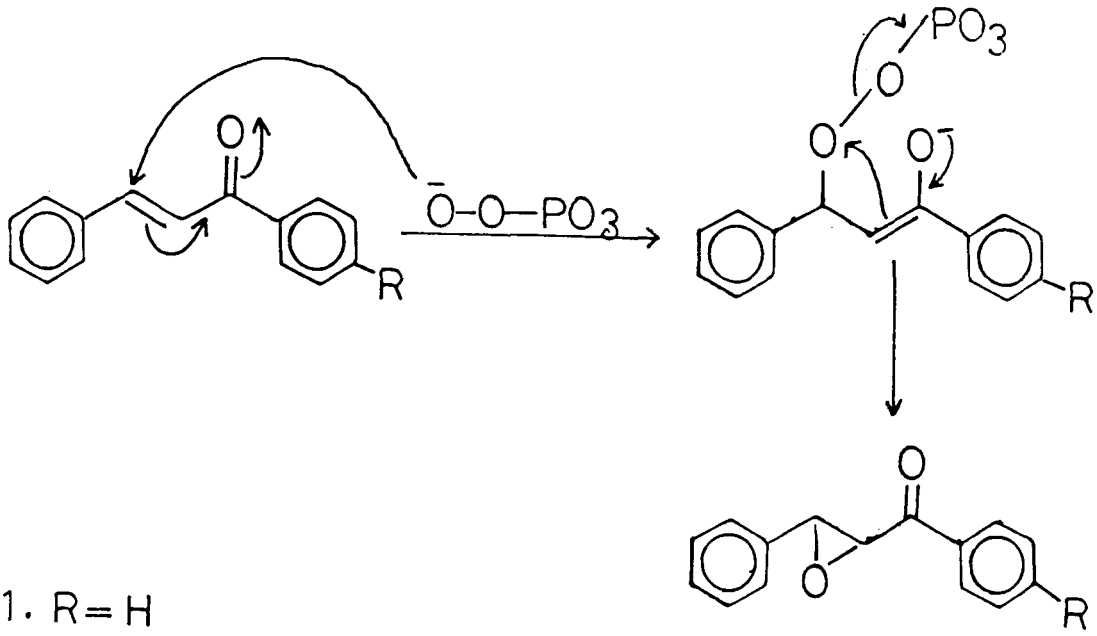
Typically, α , β -unsaturated ketones react with hydrogen peroxide only in a basic medium[37] to give epoxide (2) (Scheme 3.1). The function of the base being probably to generate a nucleophilic hydrogen peroxide anion ($\bar{O}OH$). An 1,4-attack by this species ($\bar{O}OH$) to form (1) followed by the expulsion of hydroxide ion closes the epoxide ring (2). The epoxide function is cleaved by acid but is stable to base.



Scheme 3.1

In order to explore the efficacy of the newly synthesised peroxomonophosphates, reactions between chalcones and $Na_3[PO_3(O_2)].3H_2O$ (chosen as a representative) were conducted in THF. The reactions

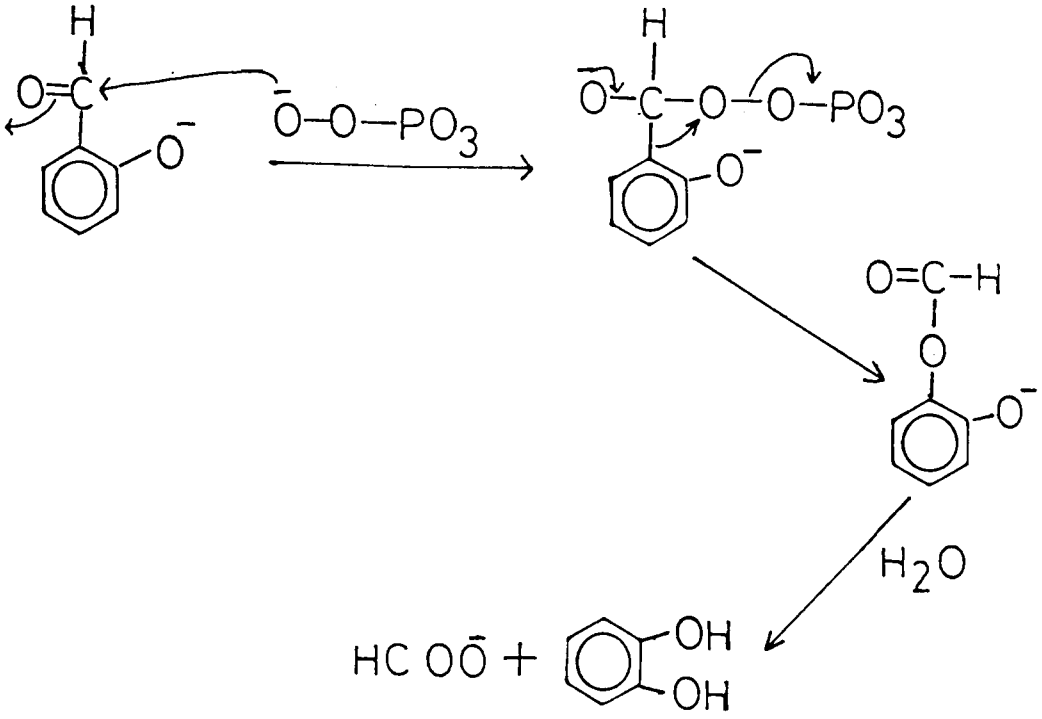
went on quite smoothly to afford the corresponding epoxides (Scheme 3.2) in high yields (vide Experimental)



1. R = H
2. R = OMe

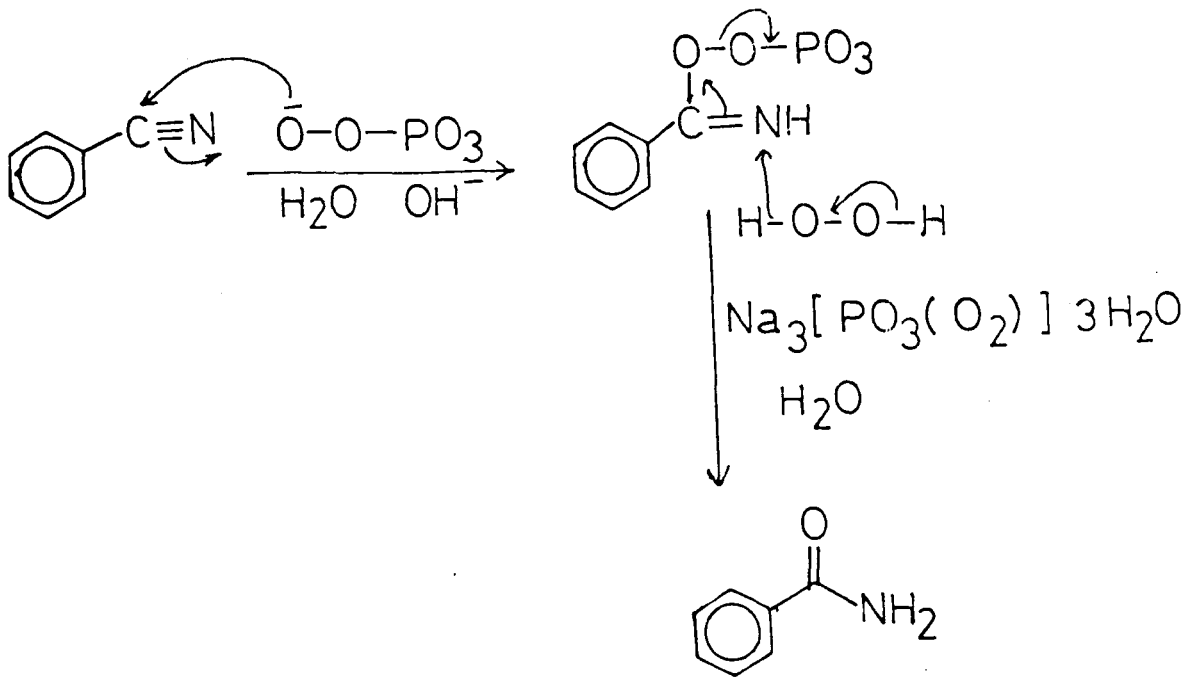
Scheme 3.2

The Dakin reaction[37] is another very characteristic reaction in which hydrogen peroxide in a basic medium is used to convert an aldehydic or a ketonic group ortho to a hydroxylic group to the corresponding dihydroxy compounds. It has been now possible for us to demonstrate that salicylaldehyde readily reacts with the chosen peroxomonophosphate to produce catechol (Scheme 3.3)



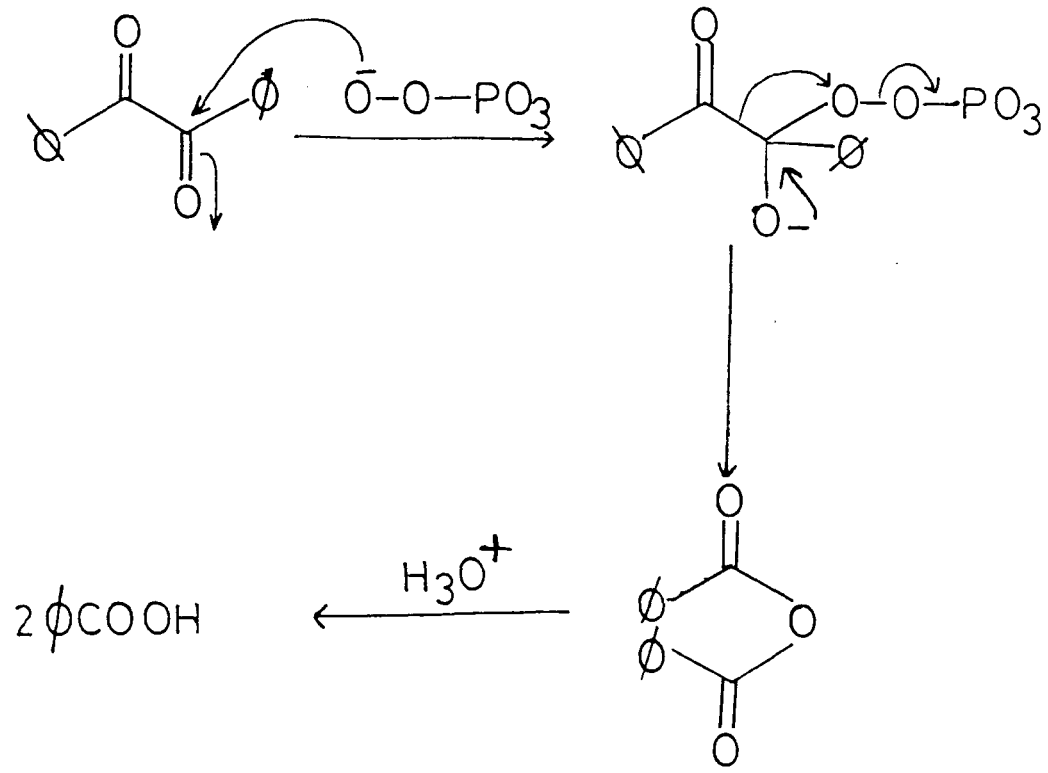
Scheme 3.3

Similarly, benzonitrile has been shown to react with $Na_3[PO_3(O_2)].3H_2O$ in an aqueous medium to yield the corresponding amide (Scheme 3.4). This is an interesting reaction, again characteristic of an oxidation otherwise achieved by basic hydrogen peroxide[37] oxidation.



Scheme 3.4

Further, it is important to note that the new reagent is also capable of bringing about Baeyer-Villiger type of an oxidation.[38] Thus when the substrate benzil was reacted with $Na_3[PO_3(O_2)].3H_2O$ in acetonitrile gave benzoic acid as the end product (Scheme 3.5). A probable mechanism of the reaction is shown in Scheme 3.5.

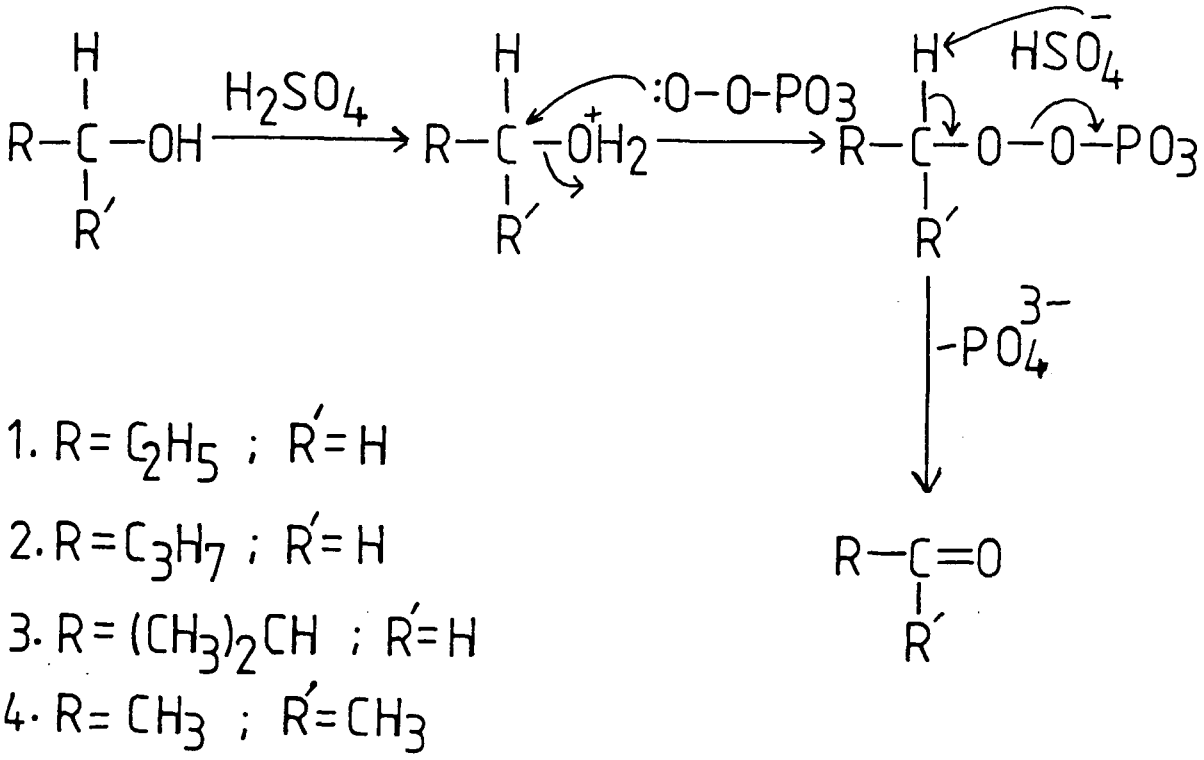


Scheme 3.5

The results of the reactions described above are very convincing and suggest beyond doubt that sodium peroxomonophosphate trihydrate, $Na_3[PO_3(O_2)].3H_2O$, is a viable substitute for a basic hydrogen peroxide reagent with the additional advantages being that the reagent is a solid one and easy to handle, and maintenance of stoichiometry involving the reagent is also very easy.

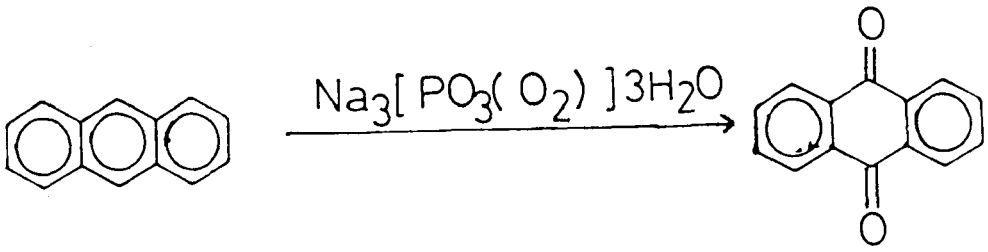
This property alone causes us to state that $Na_3[PO_3(O_2)].3H_2O$ is a potential reagent for specific oxidations and in turn is a valuable addition to the wealth of oxidising agents for oxidation of organic substrates.

In our attempt to further explore the properties of sodium peroxomonophosphate, it has been observed that $Na_3[PO_3(O_2)].3H_2O$ is also capable of oxidising alcohols and anthracene. For instance, in stoichiometric reactions with the reagent n-propanol, n-butanol and iso-butanol were oxidised to the corresponding aldehydes (Scheme 3.6) while 2-proponal was found to be oxidized to acetone.



Scheme 3.6

The reagent in acetic acid oxidised anthracene to anthraquinone in a high yield (Scheme 3.7)



Scheme 3.7

Ammonium Peroxo(fluoro)monophosphate Dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$

While investigating some other aspects of phosphorous chemistry (vide Chapter 4), it was observed that a direct interaction of phosphoric acid with alkali hydrogenfluoride, AHF_2, afforded PO_3F^{2-}. A similar reaction conducted in the presence of hydrogen peroxide, however, did not give an access to a peroxo-(fluoro)phosphate. Subsequently it was noticed that a raise of pH of the reaction medium and thence isolation of a solid product indicated the formation of a kind of product looked for. Accordingly, the first chemical synthesis of a peroxo(fluoro)phosphate, $(NH_4)_2[PO_2(O_2)F].2H_2O$, was achieved from the reaction of ammonium dihydrogenphosphate with 48% HF and hydrogen peroxide at pH 10-11 maintained by the addition of aqueous ammonia (sp. gr. 0.9)

$$NH_4H_2PO_4 + HF + H_2O_2 + NH_4OH \longrightarrow (NH_4)_2[PO_2(O_2)F].2H_2O + 3H_2O$$

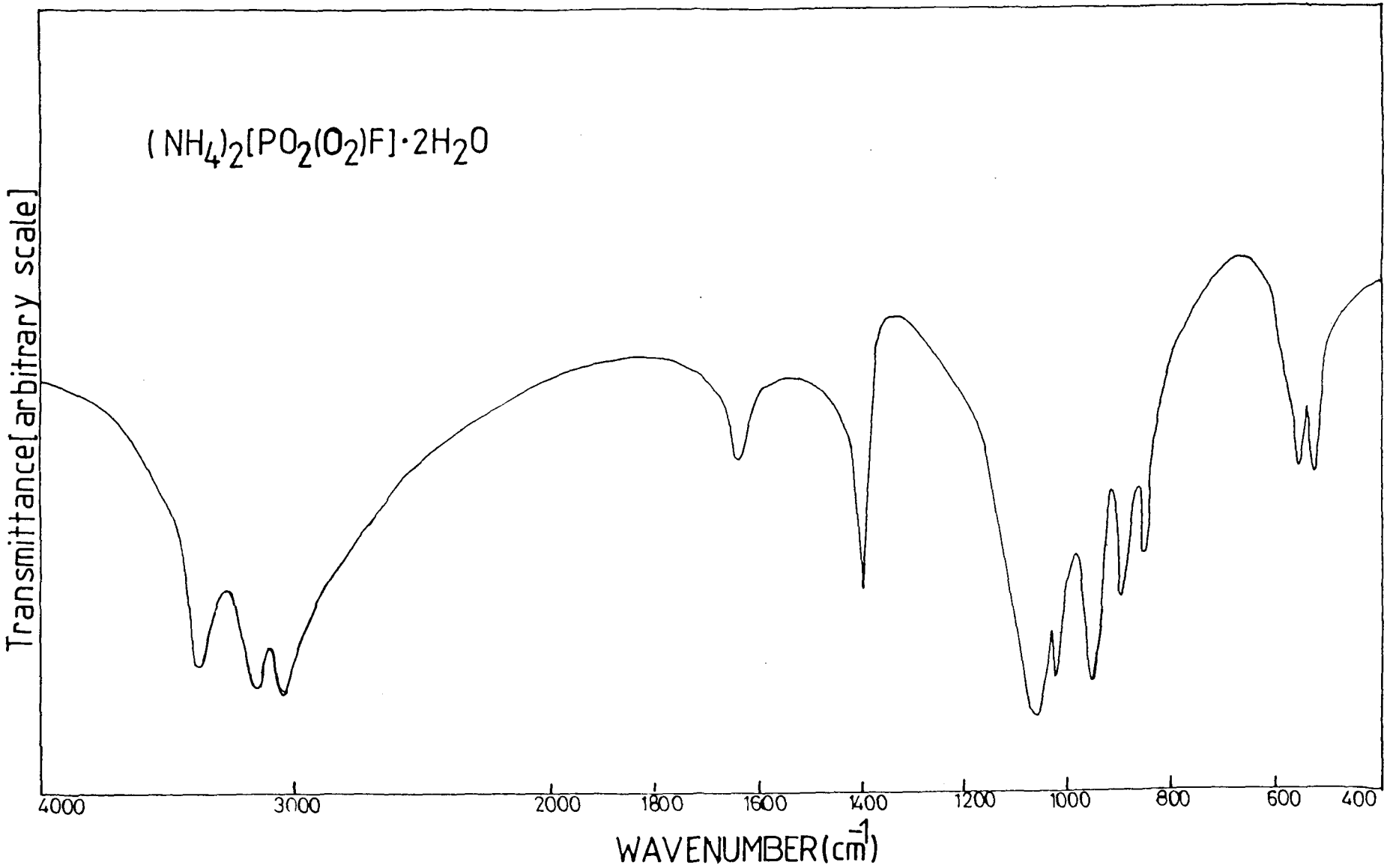
The role of ammonia was not only to raise the pH to facilitate formation of peroxo(fluoro)phosphate but also to act as the source of counter cations, while ethanol helped in precipitating the product. The compound is capable of being stored for a prolonged period in a sealed polyethylene envelope at a freezer temperature, and is insoluble in common organic solvents. It decomposes in water, and thus precludes molar conductance measurement. It liberates H_2O_2 quantitatively in the presence of sulphuric acid rendering it easy to determine the active oxygen content. The results of peroxide estimation and elemental analyses are in complete agreement with the formula $(NH_4)_2[PO_2(O_2)F].2H_2O$.

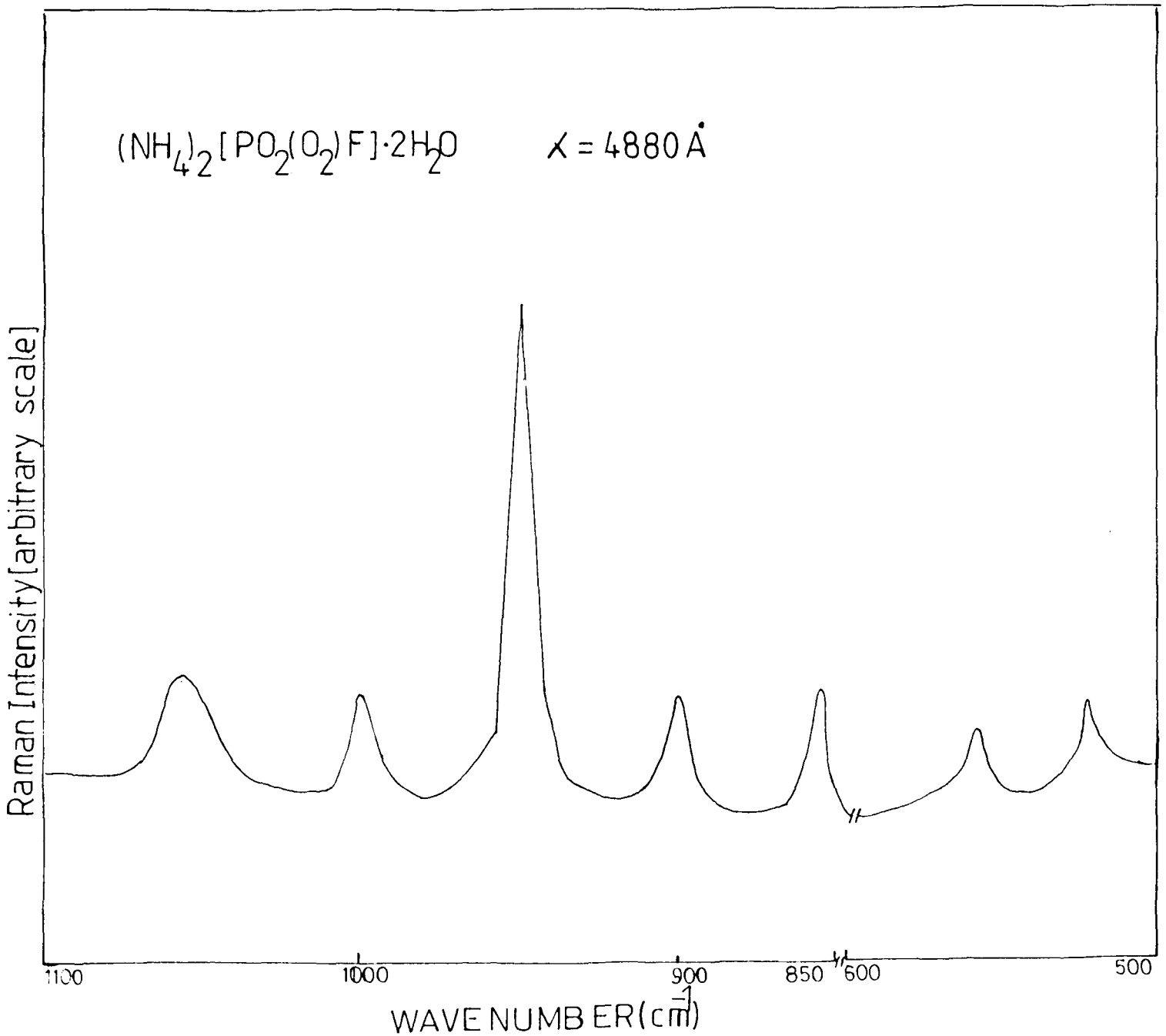
The IR spectrum of the compound evidences for the presence of PO, PF and peroxide vibrations. Bands at 1020s and 1070s cm^{-1} are similar in position to those of the asymmetric stretching[34,36] of (PO) vibrations, while the absorptions at 950, 550 and 530 cm^{-1} have been assigned to symmetric (PO) vibrations and δ (OPO) modes, respectively.[34,36] The sharp band at 900 cm^{-1} is similar in shape and position to that of ν (P-F) mode.[39] The band at 855 cm^{-1} has been assigned to ν (O-O) mode of bonded peroxide. The IR spectrum also provides evidence for NH_4^+ and lattice water.[35,40] The bands at 1400s, 3040s, and at 3165m cm^{-1} have been assigned to ν_4, ν_1, and ν_3 modes of NH_4^+. Appearance of ν (O-H) at 3400s cm^{-1} and δ (H-O-H) at 1660m cm^{-1} conforms well with those one finds for lattice type of water.[35] The laser Raman (lR) spectrum of the solid is in close agreement with its

Table 3.8 : Analytical Results and Structurally Significant IR and Raman Bands of Ammonium Peroxo(fluoro)monophosphate Dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$

Compound	Found % (Calcd. %)				IR	Raman	Assignment
	N	P	O_A^a	F	cm^{-1}	cm^{-1}	
$(NH_4)_2[PO_2(O_2)F].2H_2O$	14.7 (15.06)	16.8 (16.64)	16.9 (17.2)	9.9 (10.21)	1020s 1070s	1000 1055	ν_{as} (PO)
					950s	950	ν_s (PO)
					530s 550s	530 555	δ (OPO)
					900s	900	ν (P-F)
					855m	860	ν (O-O)
					1660m		δ (H-O-H)
					3400s		ν (O-H)
					1400s 3040s 3165m		ν_4 ν_1 ν_3 } N-H modes of NH_4^+

[a]Active Oxygen

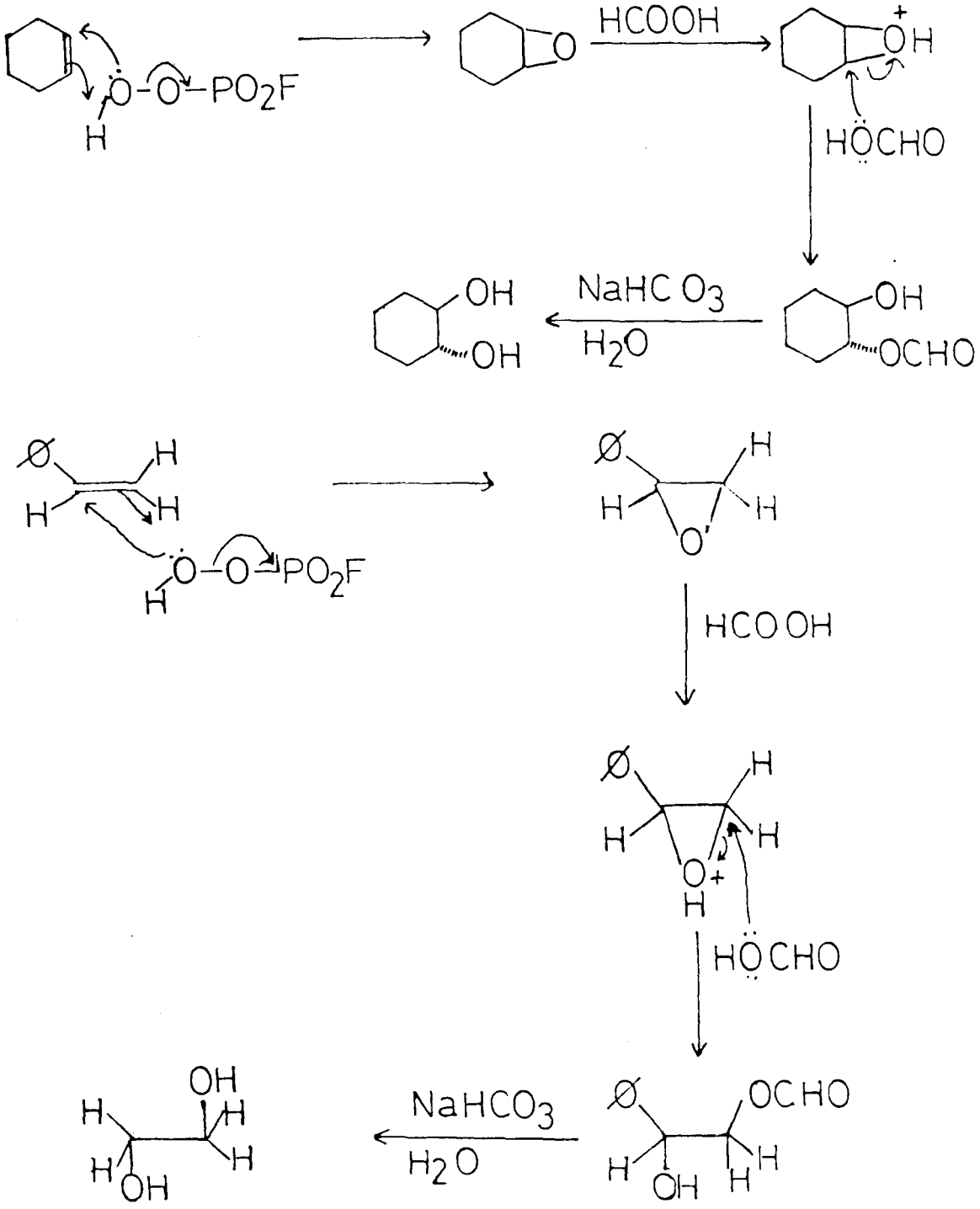

$(NH_4)_2[PO_2(O_2)F]\cdot 2H_2O$
Transmittance[arbitrary scale]
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER(cm^{-1})


$(NH_4)_2[PO_2(O_2)F]\cdot 2H_2O$
$\lambda = 4880\,\text{Å}$
Raman Intensity [arbitrary scale]
1100
1000
900
850
600
500
WAVE NUMBER (cm^{-1})

i.r. spectrum, and shows signals at 1055 and 1000 cm^{-1} due to $\nu_{as}(PO)$ and at 950 cm^{-1} due to $\nu_{s}(PO)$. The bands at 555 and 530 cm^{-1} have been assigned to $\delta(OPO)$ modes.[41] The peroxo stretching, $\nu(O-O)$, appears at 860 cm^{-1}. The IR and laser Raman results conform to the formulation of the compound as $(NH_4)_2[PO_2(O_2)F].2H_2O$ with the peroxide being bonded in an end-on manner as encountered in simple monoperoxo derivatives of sulphur[2] and carbon.[1]

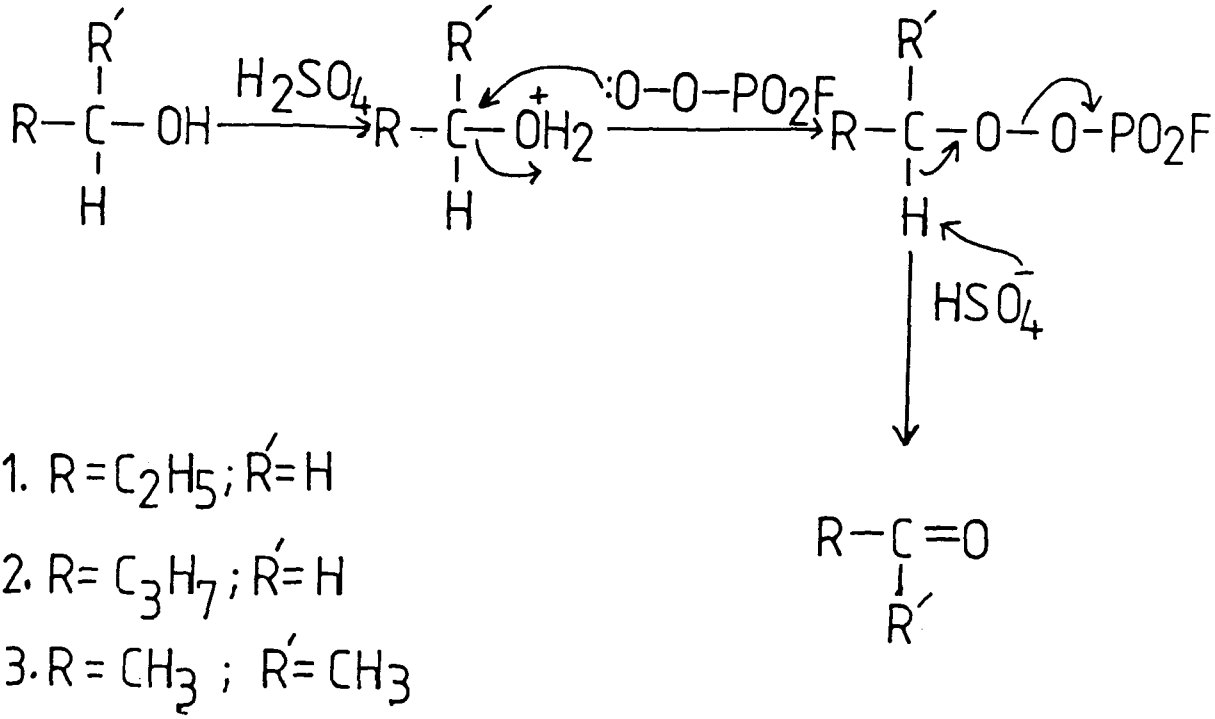
Reactivity of $(NH_4)_2[PO_2(O_2)F].2H_2O$

Having achieved the first chemical synthesis of a peroxo-(fluoro)phosphate, $(NH_4)_2[PO_2(O_2)F].2H_2O$, it was incumbent on us to also study its reactivity. Strategically it was planned to conduct the oxidation reactions under acidic conditions. It is known that hydrogen peroxide in formic acid is capable of hydroxylating alkenes.[42] The reaction is believed to proceed via epoxide formation. We anticipated that the peroxo(fluoro)phosphate might show a similar reactivity. Accordingly, stoichiometric reactions were carried out involving alkenes like 1,2-cyclohexene and styrene in formic acid media with the chosen reagent. The reactions took place smoothly, and the products obtained have been identified to be trans 1,2-cyclohexanediol and 1-phenyl ethyleneglycol (Scheme 3.8). The results of physical studies evidenced that the compounds are exactly similar to those reported in the literature.[43,44] The most probable mechanisms are depicted in Scheme 3.8.



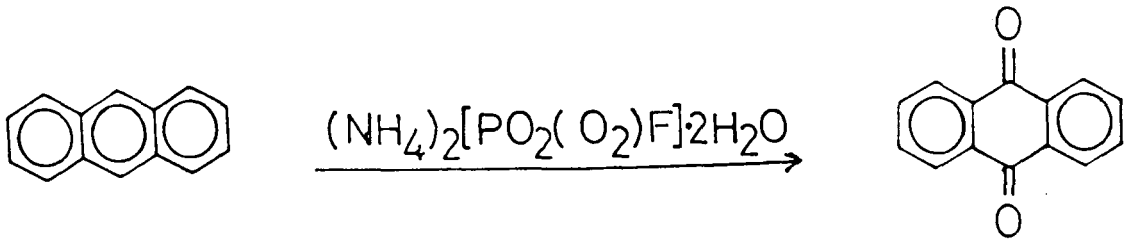
Scheme 3.8

Further, in stoichiometric reactions $(NH_4)_2[PO_2(O_2)F].2H_2O$ has been found to oxidise n-propanol and n-butanol, in the presence of an acid (dil.H_2SO_4), to the corresponding aldehyde in good yields (Scheme 3.9). Similarly, 2-propanol, a secondary alcohol, has been readily oxidised to acetone by the peroxo-(fluoro)phosphate.



Scheme 3.9

Ammonium peroxo(fluoro)monophosphate was also found to oxidise anthracene to anthraquinone in an acetic acid medium (Scheme 3.10).



Scheme 3.10

The phosphorous product, isolated after working up of the oxidation product in each of the reactions has been identified to be monofluorophosphate, PO_3F^{2-}, a species important because of its use as an additive[45] in dentifrice formulations. The results obtained so far, on oxidation reactions involving the newly synthesised peroxo(fluoro)phosphate are quite encouraging. It is expected that the compound will be also very useful as an oxidant. Further, studies of reactivity of this reagent, especially under a different set of reaction conditions will be reported elsewhere.

To conclude this Chapter following points may be emphasized. Sodium and ammonium peroxomonophosphate trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = Na or NH_4), can be synthesised under suitable experimental conditions. The compounds are white solids and crystalline in nature. Fluorinated peroxophosphate is also capable of being synthesised chemically. First chemical synthesis of such a compound ammonium peroxo(fluoro)phosphate dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$, has been achieved under an appropriate condition. While both types of compounds are highly soluble in

water, but not in common organic solvents, the former ones are comparatively more stable than the latter one.

Both non-fluorinated and fluorinated peroxophosphates have exhibited very interesting oxidation chemistry. Based on the results obtained so far, it is anticipated that these compounds are potential new reagents and they will be significant additions to the wealth of existing oxidising agents.

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Chapter 4

Direct Synthesis of Ammonium Monofluorophosphate Monohydrate, $(NH_4)_2[PO_3F].H_2O$ and Potassium Monofluorophosphate, $K_2[PO_3F]$*

As mentioned in the general introduction (Chapter 1) monofluorophosphate, $[PO_3F]^{2-}$, is important particularly because of its use as an additive in dentifrice formulations for the inhibition of dental caries. Tests have also shown that when Na_2PO_3F is added at a level of 40 ppm F equivalent to the drinking water of Syrian hamsters, a reduction of dental caries[1] in these animals is observed. Since the $[PO_3F]^{2-}$ ion apparently is not hydrolysed appreciably in the animal body, the fluorine therefore does not have to be in the free ionic form to be active as dental caries inhibitor. Alkali monofluorophosphates have been known for quite some time,[2-6] however, there is no simple and easily accessible route to such compounds. The recommended methods[2-6] for their synthesis involve either a high temperature fusion reaction, or fluorophosphoric acid as the starting material which requires extra preparation and purification, in addition to one or more steps to remove unwanted products, inevitably formed in either of the methods to obtain the pure products.

*This piece of work has been published :
J. Chem. Soc., Dalton Trans., 1987, 477.

In view of difficulties involved in the preparation of these extremely useful compounds, search for a new and easily accessible route to the synthesis of the title compounds was warranted. In the light of the past experience gained in the laboratory in which the present research was carried out, it was anticipated that a much simpler synthesis of such compounds might be possible. In accord with the expectation, a systematic investigation in search of a new route to salts of $[PO_3F]^{2-}$ was undertaken. This Chapter of the thesis deals with the direct synthesis of ammonium monofluorophosphate monohydrate, $(NH_4)_2[PO_3F].H_2O$ and potassium monofluorophosphate, $K_2[PO_3F]$, and also highlights the advantages of the new method over those previously reported.

Experimental

All chemicals used were reagent grade products. (SISCO, E, Merck, B.D.H., Sarabhai M. Chemicals).

Synthesis of $(NH_4)_2[PO_3F].H_2O$ and $K_2[PO_3F]$

Since the method of synthesis is a general one only a representative procedure is described.

In a typical procedure 88% phosphoric acid (1.0 cm^3, 17.9 mmol; density 1.75g cm^3) was thoroughly mixed with AHF_2 (72 mmol; A = NH_4 or K), followed by the addition of water (ca 10 cm^3). The solution thus obtained was stirred for 15 min.

An amount of 95% ethanol (ca 20 cm^3) was added with stirring, whereupon white crystalline $(NH_4)_2[PO_3F].H_2O$ or $K_2[PO_3F]$ was precipitated. Stirring was continued for a further period of 15-20 min and the mixture was then allowed to stand for ca 10 min. The compound was then separated by centrifugation, washed 3-4 times with ethanol, and finally dried in vacuo over P_4O_{10}. The amounts of reagents used and the yields of the product are set out in Table 4.1.

Elemental Analyses

Quantitative estimation of phosphorous, fluoride, nitrogen, and potassium were made by the methods described in Chapter 2. The analytical data and molar conductance values are reported in Table 4.2.

Results and Discussion

Reaction of phosphoric acid, H_3PO_4, with hydrofluoric acid, under the appropriate conditions, gives rise to the formation of monofluorophosphoric acid, $H_2[PO_3F]$.[7] Substitution of ionisable protons by ammonium or alkali-metal ions (A^+) then provides the corresponding $A_2[PO_3F]$, if the wet methods of synthesis are chosen. A simple and general method for the preparations of alkali-metal and ammonium bifluorides, AHF_2 (A = alkali-metal or NH_4), was developed in this laboratory a decade ago.[8] It has been shown since then that alkali hydrogenfluorides, sources of HF,

Table 4.1 : Amounts of Reagents Used and Yields of $(NH_4)_2[PO_3F].H_2O$ and $K_2[PO_3F]$

Compound	Yield g (%)	Amount of 88% H_3PO_4 cm^3 (mmol)	Amount of AHF_2 (A = NH_4 or K g (mmol)
$(NH_4)_2[PO_3F].H_2O$	1.8 (66)	1 (17.9)	4.1 (72)
$K_2[PO_3F]$	1.9 (60)	1 (17.9)	5.6 (72)

possess some special qualities as reagents, as they can not only act as fluorinating agents,[9,10] but also maintain an acidic environment in a polar medium thereby providing conditions conducive to some syntheses which are otherwise difficult.[9,10] Thus for a solution to the present problem it was expected that interaction of an alkali hydrogenfluoride with phosphoric acid might lead directly to the title compounds. Accordingly, in line with the synthetic strategy, AHF_2 (A = NH_4 or K) were treated with H_3PO_4 which underwent a very facile fluorination and led to the direct synthesis of $A_2[PO_3F]$ as searched for. The alkali hydrogenfluoride acted here not only as a fluorinating agent but also as the source of counter cation. The role of ethanol in the present synthesis was to bring about precipitation of the desired compounds. It may be mentioned that while the ammonium salt was obtained as a monohydrate the corresponding potassium salt was anhydrous. The new method, which can be scaled up, if desired, is a straight one, and it neither involves any extra preparation step nor the use of hydrofluoric acid, rendering it easy to handle.

The results of elemental analyses are satisfactory and no recrystallisation is necessary. The compounds are stable for a prolonged period and are soluble in water. They permit molar conductance measurements, and the values were found to lie in the range 220-235 $\Omega^{-1}cm^2mol^{-1}$, in complete agreement with a 2:1 electrolyte. Further, these results suggest that the compounds are also stable in solution and do not undergo decomposition or

Table 4.2 : Analytical Data and Molar Conductance Values of $(NH_4)_2[PO_3F].H_2O$ and $K_2[PO_3F]$

Compound	Molar Conductance $\Omega^{-1}cm^2mol^{-1}$ (25°C)	Found% (Calcd.%)		
		K or N	P	F
$(NH_4)_2[PO_3F].H_2O$	230	18.6 (18.4)	20.6 (20.35)	12.7 (12.5)
$K_2[PO_3F]$	225	44.6 (44.4)	17.8 (17.6)	11.1 (10.8)

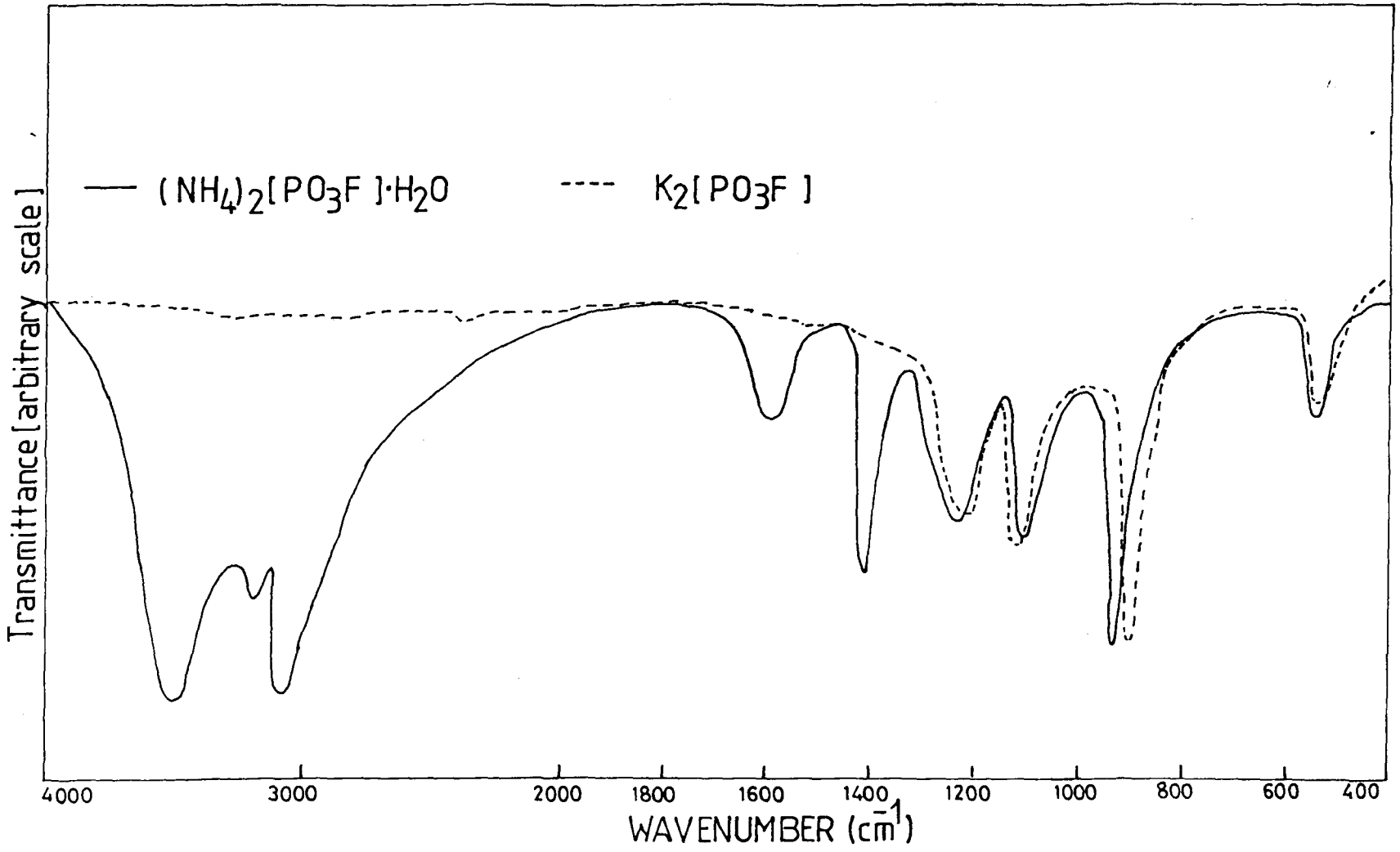
hydrolysis at least under the experimental conditions employed. This property of $A_2[PO_3F]$ is very important and relevant particularly in the context of its use in the dentifrice formulations.

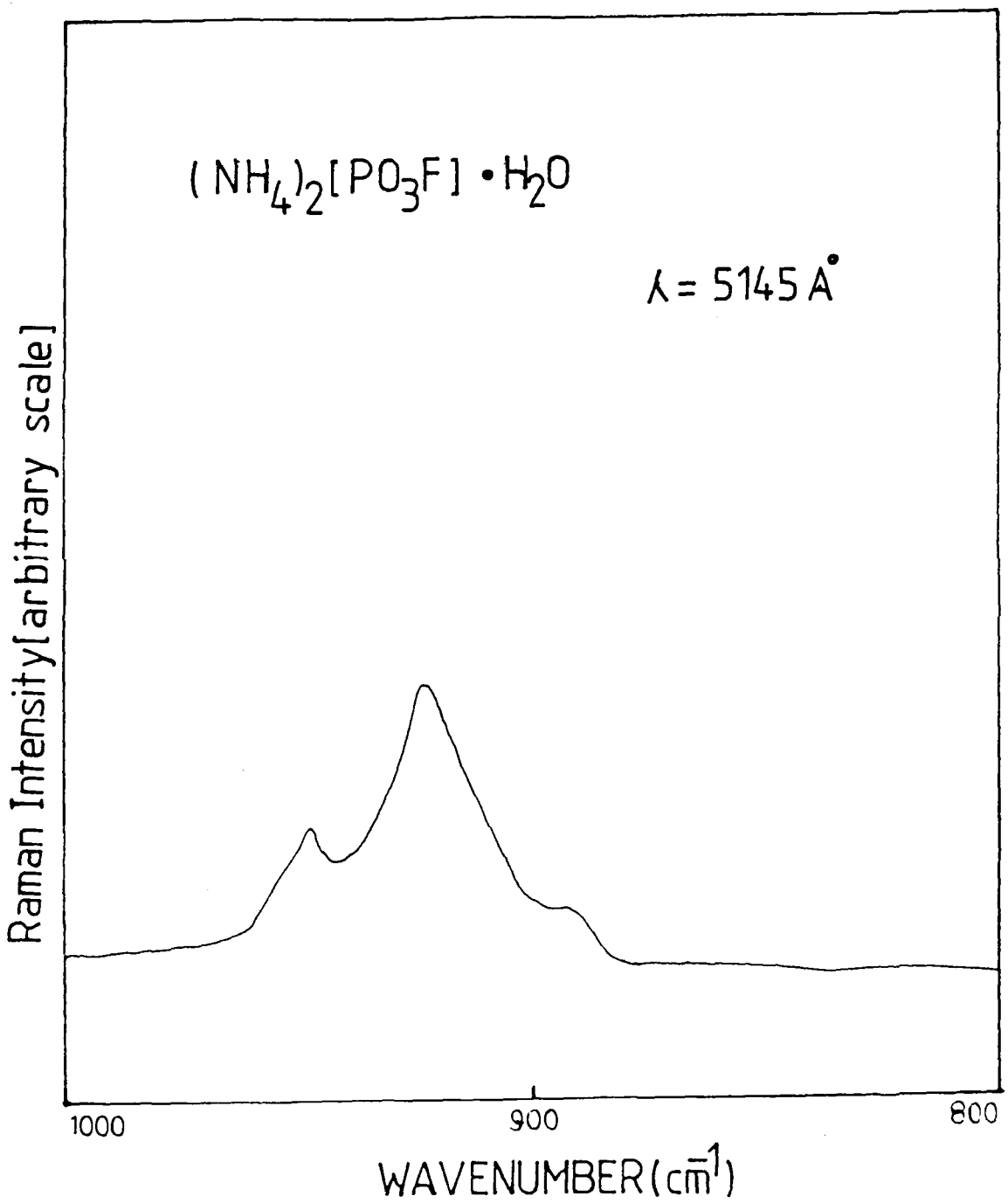
IR spectra of the compounds synthesised by the new method are in order[11] and are similar to that reported earlier.[11] Thus, the broad band at ca. 1100s cm^{-1} has been assigned to $\nu_s(PO)$,[12] while the absorption at ca 1295s has been attributed to the $\nu_{as}(PO)$[12] mode of the $[PO_3]$[12] moiety. The appearance of a band at ca. 920s cm^{-1} is significant, and it was quite rational[13] to assign this band to $\nu(P-F)$ mode. In order to adduce further support to their identity, the compounds were also investigated by Raman spectroscopy. The laser Raman spectra, recorded on solids between 1200 and 600 cm^{-1}, show signals at ca. 922 and ca. 950 cm^{-1} which have been assigned[13] to $\nu(P-F)$ and $\nu(P=O)$ vibrations, respectively, lending credence to the contention. Thus the results of our chemical as well as physical studies suggest that the compounds reported herein are the same as those described earlier.[2-6]

In conclusion it may be mentioned that the present method of synthesis of fluorophosphate, $[PO_3F]^{2-}$, is comparatively easier than the literature reported procedures. The new method has also some additional advantages, e.g., redundency of the use of hydrofluoric acid and the simplicity of the method. It is also pertinent to mention here that the new method straight away gives pure products in high yields.

Table 4.3 : Structurally Significant IR and Raman Bands of Potassium Monofluorophosphate and Ammonium Monofluorophosphate Monohydrate, $K_2[PO_3F]$ and $(NH_4)_2[PO_3F].H_2O$

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$(NH_4)_2[PO_3F].H_2O$	1295br,s		ν_{as}(PO)
	1100s		ν_s(PO)
	-	950	ν(P=O)
	920s	922	ν(PF)
	540s		δ(OPO)
	1400s		ν_4 } N-H modes of NH_4^+
	3050s		ν_1 } N-H modes of NH_4^+
	3150m		ν_3 } N-H modes of NH_4^+
	1640m		δ(H-O-H)
	3400s,br		ν(O-H)
$K_2[PO_3F]$	1290br,s		ν_{as}(PO)
	1110s		ν_s(PO)
	-	955	ν(P=O)
	910s	915	(P=F)
	540s		δ(OPO)


— $(NH_4)_2[PO_3F]\cdot H_2O$
---- $K_2[PO_3F]$
Transmittance [arbitrary scale]
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
WAVENUMBER (cm^{-1})


$(NH_4)_2[PO_3F] \cdot H_2O$
λ = 5145 Å
Raman Intensity[arbitrary scale]
1000
900
800
WAVENUMBER (cm^{-1})

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Chapter 5

Complex Peroxozirconates. Synthesis and Assessment of Structure of Oxomonoperoxodifluorozirconate(IV) Complexes, $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4), and Oxodiperoxomonofluorozirconate(IV) Complexes, $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4), and Isolation of Decafluoro- μ-oxo-dizirconates(IV), $A_4[F_5Zr\text{-}O\text{-}ZrF_5]$ (A = Na, K or NH_4), en route to Oxoperoxofluorozirconates(IV)

The importance of peroxo-metal compounds has been emphasised in the introductory remarks (Chapter 1) of the thesis. Interest in the studies of peroxo-metal chemistry, an active area of research[1-11] in contemporary inorganic chemistry, stems mainly from an intrinsic biochemical relevance,[9,11-14] fascinating coordination chemistry as well as the role and use of peroxometal compounds in the oxidation chemistry,[1-8,10] and the extent of activation of coordinated peroxide (O_2^{2-}) in such compounds. Synthesis followed by characterisation of peroxo complexes of metals is undisputedly the prerequisite for a systematic approach to this field. Knowledge derived thereof is expected to contribute to the understanding of interaction, binding, and reactivity of peroxide (O_2^{2-}) at metal centres. This in turn would be useful for

synthetic modelling as well as for developing of viable systems for practical use in the oxidation of organic substrates.[1-8]

Based on the above rationale a programme aimed at synthesis and assessment of structure of peroxo-metal compounds[1,2,15-18] was taken up as the first step in accessing the chosen field. Some of the earlier workers of the laboratory, where the present work was done, dealt with titanium[15] in some details and it became necessary to conduct similar investigations involving its congener zirconium in order to obtain heretofore unreported results and to provide a comparative account of this aspect of chemistry of the two metals. It was also of our concern to explore the possibility of obtaining diperoxozirconates(IV) in the solid state. Moreover, we were also very keen in isolating and characterising the precursor of peroxozirconate(IV) just before peroxygenation of the metal initiated so that a reasonable insight into the course of the whole process could be gained. Pertinent here is to mention that information on peroxozirconates is rather scanty.[19-22] To the best of our knowledge there has been no report on the existence of diperoxozirconates(IV) in the solid state except probably the one in which diperoxo species were claimed[23] but not isolated. It may be relevant to note in the present context that a few peroxofluorozirconates(IV) for instance, $\left[Zr(O_2)F_5\right]^{3-}$ (Ref. 20,24) and $\left[Zr_2(O_2)_2F_7\right]^{3-}$ (Ref. 25) are known, and the structure of $(NH_4)_3\left[Zr(O_2)F_5\right]$ has been confirmed very recently[24] by x-ray crystallography. An account of

the results of our endeavour is presented herein. Thus, this Chapter of the thesis describes the synthesis and structural assessment of alkali-metal and ammonium oxomonoperoxodifluorozirconates(IV), $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4), and sodium or ammonium oxodiperoxomonofluorozirconate(IV) dihydrates, $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4). Further a clear evidence has been provided for the formation of a μ-oxo-dizirconate(IV) species $[F_5Zr\text{-}O\text{-}ZrF_5]^{4-}$ just before peroxygenation of the metal begins, under the chosen reaction conditions, by isolating the complex species as its alkali-metal and ammonium salts in the solid state followed by their characterisation.

Experimental

Reagent grade chemicals were used throughout. (B.D.H, E. Merck, Loba Chemie, Sarabhai M. Chemicals, SISCO, S.D.'s).

Synthesis of Alkali-Metal and Ammonium Oxomonoperoxodifluorozirconates(IV), $A_2[ZrO(O_2)F_2]$

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 zirconyloxide precipitate ceased to appear. The product was filtered off and washed free from ammonia and nitrate. To the water suspension of hydrated zirconyloxide 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 alkali-metal hydroxide solution (20%) or aqueous ammonia (sp.gr. 0.9). At this pH value a small amount of white product appeared. To ensure complete precipitation, ca. 50 cm^3 of precooled ethanol was added with constant stirring. The compound thus obtained was filtered and washed 4-5 times with ethanol, and finally dried in vacuo over P_4O_{10}. The amounts of reagents used and yields of the products are given in Table 5.1.

Synthesis of Sodium and Ammonium Oxodiperoxomonofluorozirconate(IV) Dihydrates, $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4)

Hydrated zirconyloxide was prepared in a manner analogous to that described above for the synthesis of oxomonoperoxodifluorozirconate(IV) compounds. To the water suspension of hydrated zirconyloxide 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 to obtain a clear solution. The solution was stirred further for ca. 15 min and filtered to remove any undissolved residue. The pH of the reaction solution was raised to 12-14 by careful addition of sodium hydroxide solution (20%) or aqueous ammonia (sp.gr. 0.9). A white product appeared. To ensure complete precipitation, ca. 50 cm^3 of precooled ethanol was added with

Table 5.1 : Amounts of Reagents Used for the Synthesis of and the Yields Obtained for $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4), $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4), and $A_4[F_5Zr\text{-}O\text{-}ZrF_5]$ (A = Na, K or NH_4)

Compound	Yield g (%)	Amount of $ZrO(NO_3)_2.H_2O$ g (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)	Amount of 48% HF cm^3 (mmol)
$(NH_4)_2[ZrO(O_2)F_2]$	0.75 (87)	1 (4)	15 (132.36)	1 (24)
$Na_2[ZrO(O_2)F_2]$	0.73 (82)	1 (4)	15 (132.36)	1 (24)
$K_2[ZrO(O_2)F_2]$	0.81 (79)	1 (4)	15 (132.36)	1 (24)
$(NH_4)_3[ZrO(O_2)_2F].2H_2O$	0.78 (75)	1 (4)	15 (132.36)	1 (24)
$Na_3[ZrO(O_2)_2F].2H_2O$	0.87 (71)	1 (4)	15 (132.36)	1 (24)
$(NH_4)_4[F_5Zr\text{-}O\text{-}ZrF_5]$	1.38 (74)	1 (4)	15 (132.36)	1 (24)
$Na_4[F_5Zr\text{-}O\text{-}ZrF_5]$	1.37 (72)	1 (4)	15 (132.36)	1 (24)
$K_4[F_5Zr\text{-}O\text{-}ZrF_5]$	1.73 (80)	1 (4)	15 (132.36)	1 (24)

constant stirring. The compound thus obtained was filtered and washed 4-5 times with ethanol, and finally dried *in vacuo* over P_4O_{10}.

The amounts of reagents used and the yields of the products are shown in Table 5.1.

Isolation of Alkali-Metal and Ammonium μ-oxodecafluorodizirconates(IV), $A_4[F_5Zr\text{-}O\text{-}ZrF_5]$ (A = Na, K or NH_4)

To a water suspension of hydrated zirconyloxide, obtained in a similar way to that described under the synthesis of $A_2[ZrO(O_2)F_2]$ compounds, 15 cm^3 (132.36 mmol) of 30% H_2O_2 was added with stirring followed by a slow addition of 1 cm^3 (24 mmol) of 48% HF. The resultant clear solution was filtered to remove any undissolved material. The pH of the reaction medium was raised to 5 by the addition of alkali-metal hydroxide solution (20%) or aqueous ammonia (sp.gr. 0.9). Addition of *ca* 50 cm^3 of cold ethanol resulted into the precipitation of a white compound. The compound was filtered, washed 4-5 times with ethanol, and finally dried *in vacuo* over P_4O_{10}.

The amounts of reagents used and the yields of the compounds are set out in Table 5.1.

Elemental Analyses

Quantitative determination of zirconium, fluoride, peroxide, nitrogen, and alkali-metal contents were made by the methods described in Chapter 2.

The analytical data and structurally significant IR and Raman bands along with their assignments are summarised in Table 5.2.

Results and Discussion

Our experience[15-17] with peroxo-metal compounds permitted us to envisage that such complexes can be stabilised under appropriate hetero-ligand environments. Fluoride was chosen as a co-ligand in the present investigation because it helps to stabilise zirconium(IV) and it is rather easy to ascertain its presence and to determine its content. It is also known from the literature[20,22] that both fluoride and peroxide (O_2^{2-}) can, under the appropriate conditions, coordinate to zirconium. From the previous experience[15] it was possible to anticipate that fluoride can get along well with O_2^{2-} as a co-ligand to form hetero-ligand complexes. Moreover, IR spectroscopic detection of $\nu(O-O)$ in the presence of co-ordinated fluoride is not affected enabling a clean characterisation. Freshly prepared hydrated zirconium oxide, $ZrO_2.nH_2O$, was used as the source of zirconium. The strategy for achieving the goal was to allow zirconium(IV) to interact with peroxide and fluoride in the presence of each other, rather than dissolving the metal oxide in aqueous HF prior to the addition of hydrogen peroxide. The latter was apprehended to be detrimental as that route might lead to binary fluoro complexes of zirconium in lieu of the desired hetero-ligand ones in view of a greater

tendency of F^- to form stable compounds with the metal. It was also of concern to evaluate the appropriate pH value of the reaction medium for the successful synthesis of the complexes looked for.

Hydrated zirconium oxide was dissolved in the presence of hydrogen peroxide by a judicial addition of aqueous HF. This was followed by a slow raise of pH value of the reaction solution by a careful addition of alkali hydroxide solution or aqueous ammonia until a stoichiometric peroxozirconate(IV) of definite composition, $[ZrO(O_2)F_2]^{2-}$, was obtained at pH 6. The complex was isolated as its alkali-metal and ammonium salts by the addition of ethanol which facilitated precipitation. That the pH 6 is appropriate for the synthesis of $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4) was ascertained by isolating the product at pH $<$ 6, which did not show any occurrence of active oxygen in them. In order to get an insight into the course of reaction, it was necessary to isolate and identify the product that formed at pH 5. The compound obtained (vide Experimental) at this pH, with other experimental conditions being similar, was identified as a μ-oxo fluoro complex of zirconium, namely, $[F_5Zr\text{-}O\text{-}ZrF_5]^{4-}$. It is believed that even at pH 5, a peroxozirconate might have formed but decomposed either in the solution itself or in the process of isolation leading to the formation of the afore mentioned dimer. This sort of a problem is often encountered in peroxo-metal chemistry.[26]

One of the main concerns was to synthesise the heretofore unreported diperoxozirconates(IV) in the solid state. This, we anticipated, in view of the recent experience,[15] would be possible at a pH higher than that required for the synthesis of the monoperoxo species. The appropriate pH value conducive to the synthesis of a stoichiometric diperoxozirconate(IV), $[ZrO(O_2)_2F]^{3-}$, complex was evaluated to be 12-14. Here again, the complex was isolated by precipitating out with ethanol as sodium or ammonium oxodiperoxomonofluorozirconate(IV) dihydrates, $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4). The reaction was monitored by isolating the reaction products at different stages of pH values of the reaction solution followed by estimation of the active oxygen content until a $Zr:O_2^{2-}$ ratio of 1:2 was achieved at pH 12-14. In this way the goal of synthesis of mono- and diperoxozirconates(IV) complexes, $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$, respectively, was reached.

The compounds are all white and stable for days. They are diamagnetic, as evidenced by the results of magnetic susceptibility measurements. They are also EPR silent in full agreement with the presence of zirconium(IV). The complexes are sparingly soluble in water. While the zirconate(IV) products isolated at pH 6 and pH 12-14 contain both peroxide and fluoride, those isolated at pH 5 contain only fluoride. The peroxozirconates(IV) described herein dissolve completely in acidified (dil. H_2SO_4) aqueous solutions with the quantitative liberation of active oxygen and thereby rendering it easy to determine the peroxide

(O_2^{2-}) contents. The quantitative estimation of peroxide was accomplished by redox titrations separately involving standard $KMnO_4$ and Ce^{4+} solutions. The results of elemental analyses of the compounds obtained at pH 6 and at pH 12-14 are consistent with their formulae $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4) and $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4), respectively. Similar experiments on the products isolated at pH 5, however, did not show any presence of peroxide, while the fluoride contents were quite high. The results of chemical analyses gave A:Zr:F ratio of 2:1:5 and accordingly the compounds were formulated as $A_4[Zr_2OF_{10}]$ (A = Na, K or NH_4). The chemical determination of oxidation state of the metal confirmed the presence of zirconium(IV) in conformity with the results of magnetic susceptibility and EPR measurements. The IR spectra of $A_4[Zr_2OF_{10}]$ is rather simple but very informative. For example, the absorptions at 490s and 440s cm^{-1} owe their origin to ν(Zr-F) modes[22,27] while that at 280m cm^{-1} is assignable to Zr-F deformation modes.[22,27] The clear absence of any terminal Zr=O fragment. In contrast, the consistent appearance of a band at ca 740m,br cm^{-1} is significant as this attests to the occurrence of Zr-O-Zr vibrations.[28] This in conjunction with our results of magnetic susceptibility and EPR measurements, chemical determination of oxidation state of zirconium, and elemental analyses, causes us to state that the complex ion is a μ-oxo-dimer, $[F_5Zr\text{-}O\text{-}ZrF_5]^{4-}$.

Unfortunately owing to extensive fluorescence the laser Raman spectrum of the complex could not be recorded.

The IR and laser Raman (lR) spectra of $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4) and $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4) were recorded on solids. The diagnostic IR signatures for the mono and diperoxozirconates comprise of ν(Zr=O), ν(O-O) (ν_1), ν(Zr-O_2) (ν_2 and ν_3), and ν(Zr-F) modes at ca.980s, ca.850s, ca.640s, and ca.585m (ν_2 and ν_3), and ca.460s cm^{-1}, respectively. The complementary lR signals were observed at ca.1020 cm^{-1} owing to ν(Zr=O), at ca.847, ca.650 and ca.590 cm^{-1}, respectively, due to ν_1, ν_2, ν_3 modes originating from the presence of co-ordinated peroxide (O_2^{2-}), and at ca.480 cm^{-1} assigned to ν(Zr-F) which owes its origin to the occurrence of coordinated fluoride.[22,27] The appearance of ν_1, ν_2 and ν_3 modes of co-ordinated peroxide in both IR and Raman spectra suggests that the peroxo group is bonded to the metal centre in a triangular bidentate (C_{2v}) manner.[15-17,29] The lR results are in conformity with those of IR. The consistent appearance of a medium intensity band at ca.250m cm^{-1} in the IR spectra of both mono and diperoxozirconates(IV) is interpreted in terms of Zr-F deformation modes.[22,27] Two additional IR bands at ca.1640s and ca.3455s cm^{-1} observed only in the case of diperoxozirconates(IV) are unambiguous in their shapes and positions arising from lattice water.[30,31] The appearance of metal fluoride vibration in the range 460-480 cm^{-1} and deformation mode at ca.250 cm^{-1} in all the compounds

Table 5.2 : Analytical Data and Structurally Significant IR and Raman Bands of $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4), $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4), and $A_4[F_5Zr\text{-}O\text{-}ZrF_5]$ (A = Na, K or NH_4)

Compound	Found % (Calcd. %)				IR cm^{-1}	Raman cm^{-1}	Assignment
	A or N	Zr	O_A[a]	F			
$(NH_4)_2[ZrO(O_2)F_2]$	13.0 (13.14)	42.1 (42.76)	15.3 (15.0)	18.1 (17.81)	981s	1020	ν(Zr=O)
					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)
					249m		(Zr-F) def.
$Na_2[ZrO(O_2)F_2]$	20.2 (20.61)	41.1 (40.87)	14.5 (14.34)	17.3 (17.02)	980s	1015	ν(Zr=O)
					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)
					250m		(Zr-F) def.

Table 5.2 continued...

Table 5.2 continued

Compound	Found % (Calcd. %)				IR	Raman	Assignment
	A or N	Zr	O_A [a]	F	cm^{-1}	cm^{-1}	
$K_2[ZrO(O_2)F]$	30.2 (30.62)	36.2 (35.71)	12.8 (12.53)	15.2 (14.88)	985s	1017	ν(Zr=O)
					850s	850	ν(O-O) ν_1
					640s	650	ν(Zr-O_2) ν_2
					585m	590	ν(Zr-O_2) ν_3
					460s	475	ν(Zr-F)
					250m		(Zr-F) def.
$(NH_4)_3[ZrO(O_2)_2F].2H_2O$	15.1 (14.99)	32.2 (32.53)	23.1 (22.82)	7.1 (6.78)	990s	1025	ν(Zr=O)
					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)
					250m		(Zr-F) def.
					3455s		ν(O-H)
					1640s		δ(H-O-H)

Table 5.2 continued...

Table 5.2 continued

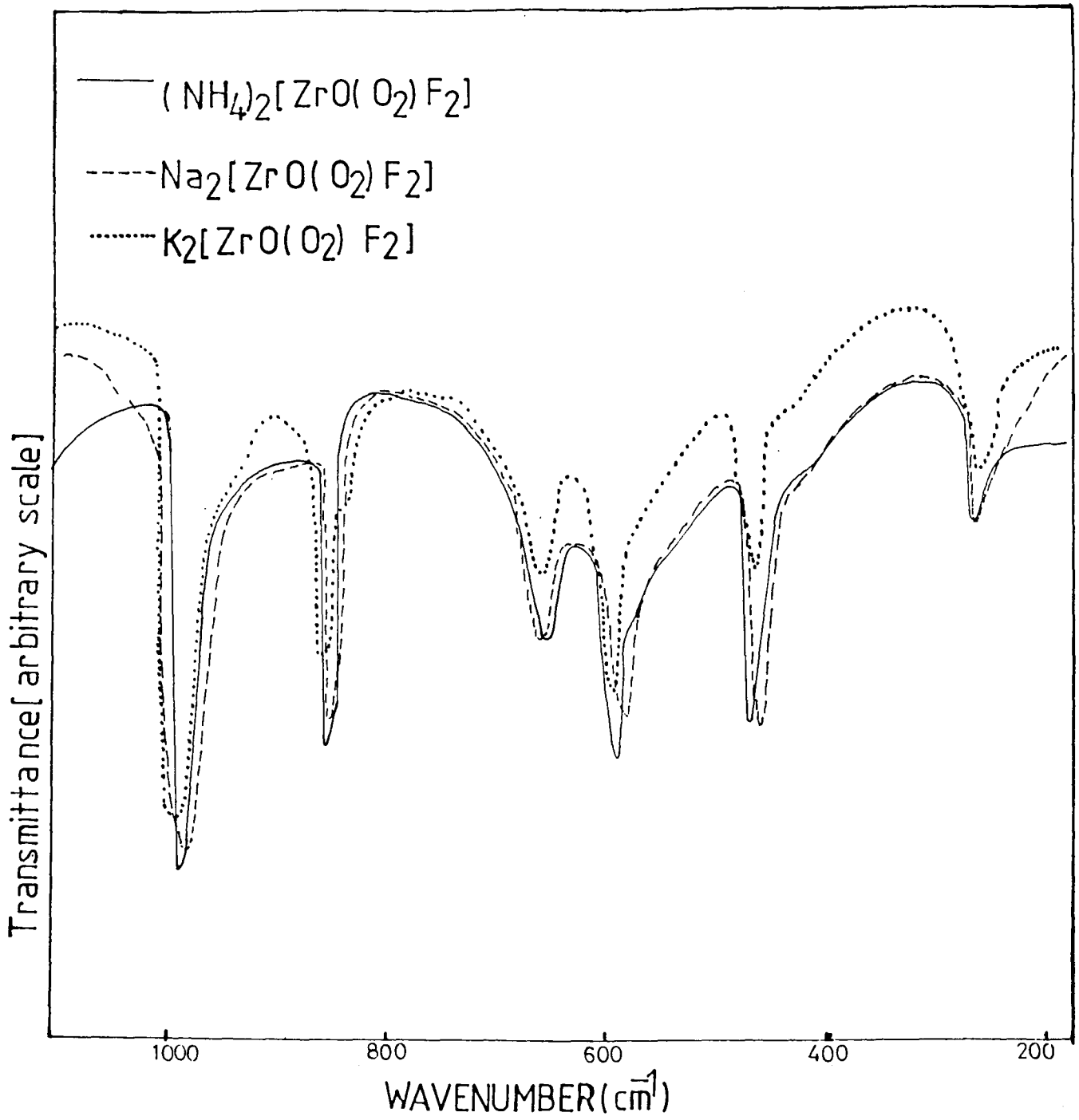
Compound	Found % (Calcd. %)				IR	Raman	Assignment
	A or N	Zr	O_A[a]	F	cm^{-1}	cm^{-1}	
$Na_3[ZrO(O_2)_2F].2H_2O$	23.6 (23.36)	31.3 (30.9)	22.1 (21.68)	6.8 (6.44)	985s	1020	ν(Zr=O)
					860s	860	ν(O-O) ν_1
					650s	650	ν(Zr-O_2) ν_2
					578m	590	ν(Zr-O_2) ν_3
					450s	460	ν(Zr-F)
					250m		(Zr-F) def.
					3460s		ν(O-H)
					1640s		δ(H-O-H)
$(NH_4)_4[F_5Zr-O-ZrF_5]$	12.3 (12.17)	40.1 (39.61)		41.6 (41.25)	741s		ν(Zr-O-Zr)
					490s		ν(Zr-F)
					246m		(Zr-F) def.
$Na_4[F_5Zr-O-ZrF_5]$	19.5 (19.15)	38.0 (38.24)		40.3 (39.55)	749s		ν(Zr-O-Zr)
					468s		ν(Zr-F)
					248m		(Zr-F) def.

Table 5.2 continued...

Table 5.2 continued

Compound	Found % (Calcd. %)				IR cm^{-1}	Raman cm^{-1}	Assignment
	A or N	Zr	O_A[a]	F			
$K_4[F_5Zr\text{-}O\text{-}ZrF_5]$	29.1 (28.71)	34.0 (33.49)		35.2 (34.87)	735s 460s 240m		ν(Zr-O-Zr) ν(Zr-F) (Zr-F) def.

[a]Active Oxygen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Na2[ZrO(O2)F2]
K2[ZrO(O2)F2]
Transmittance[arbitrary scale]
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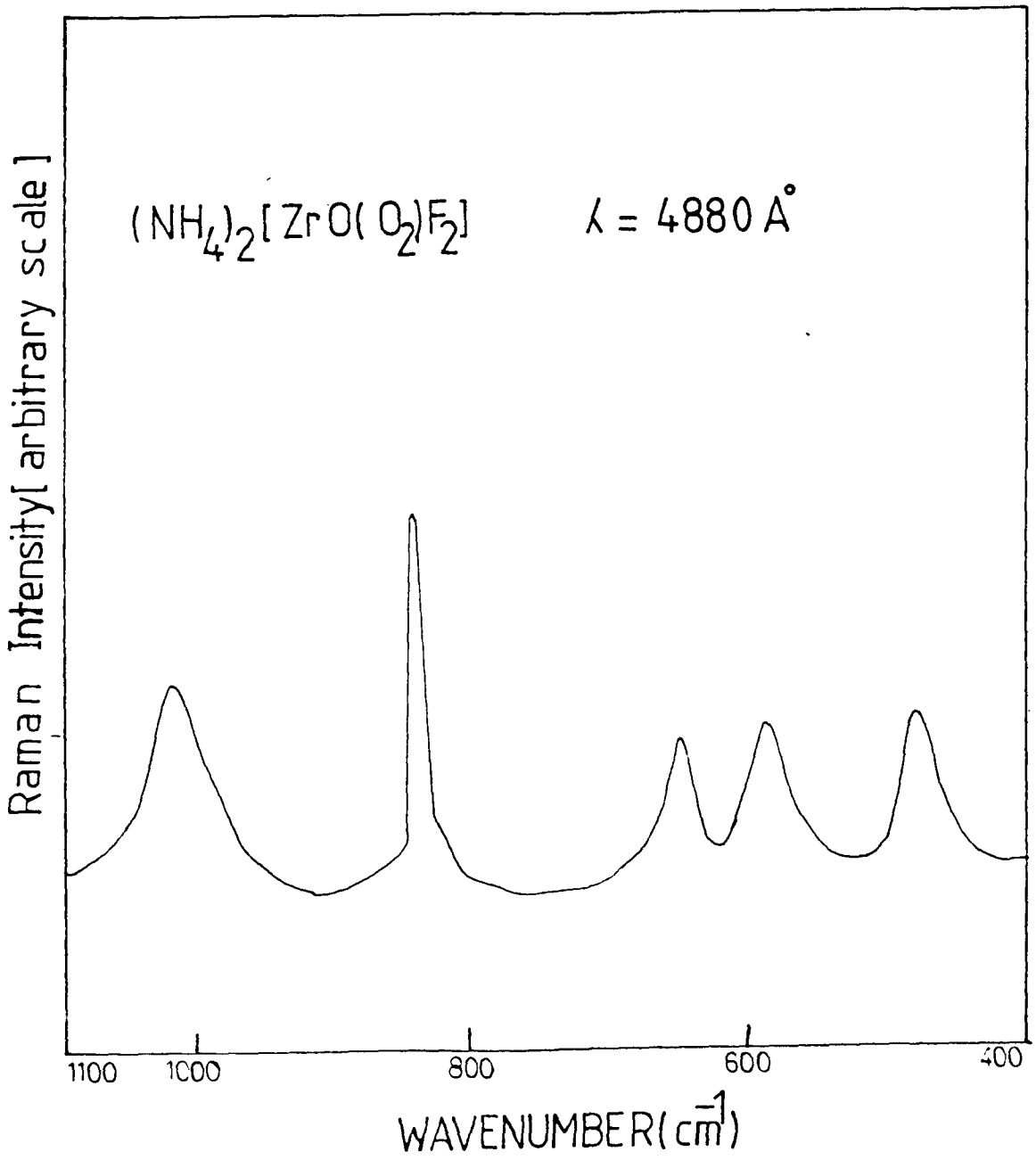
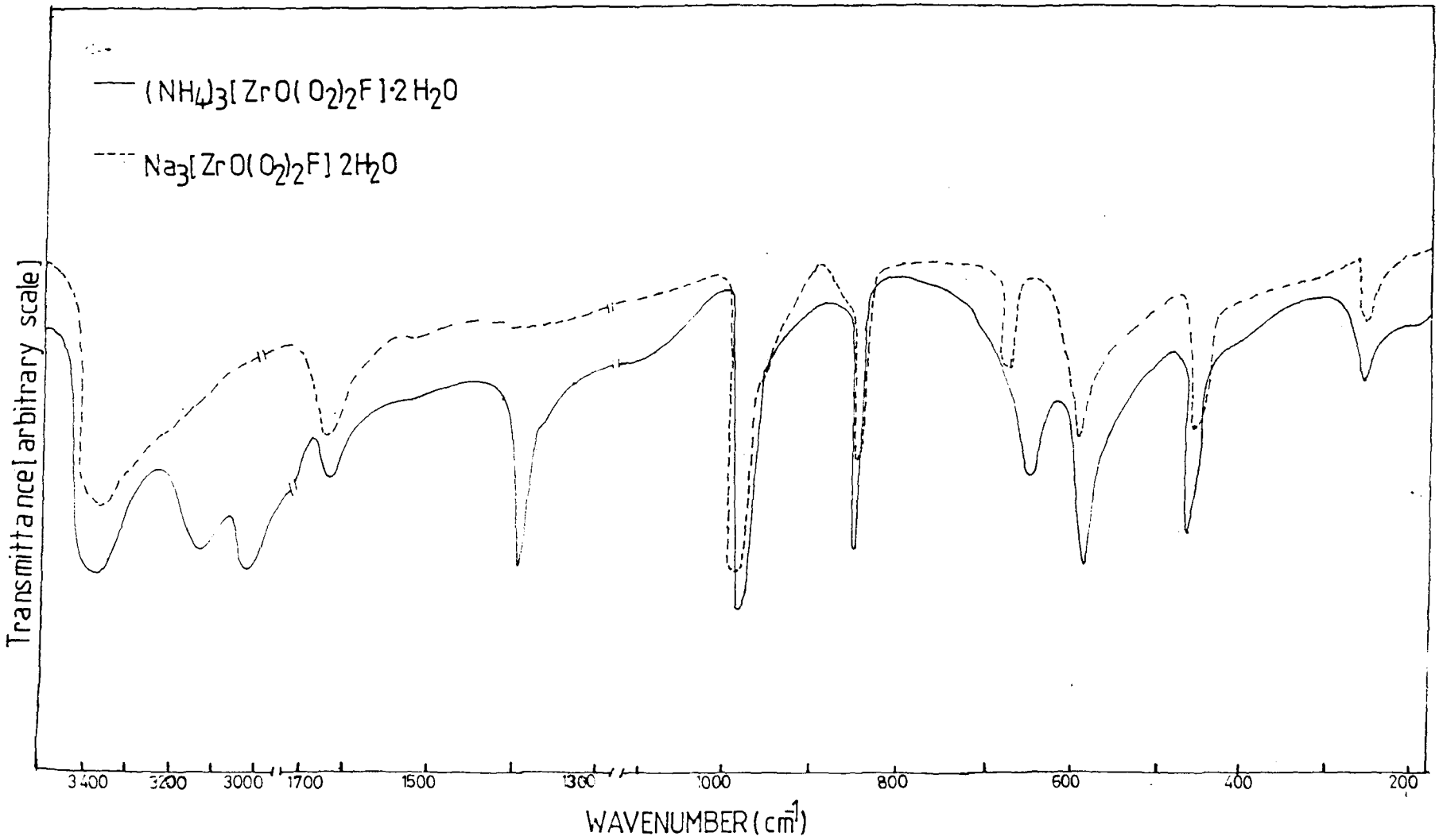
800
600
400
200
WAVENUMBER(cm-1)


$(NH_4)_2[ZrO(O_2)F_2]$
λ = 4880 Å°
Raman Intensity[arbitrary scale]
1100
1000
800
600
400
WAVENUMBER(cm^{-1})


(NH4)3[ZrO(O2)2F]·2H2O
Na3[ZrO(O2)2F]·2H2O
Transmittance[arbitrary scale]
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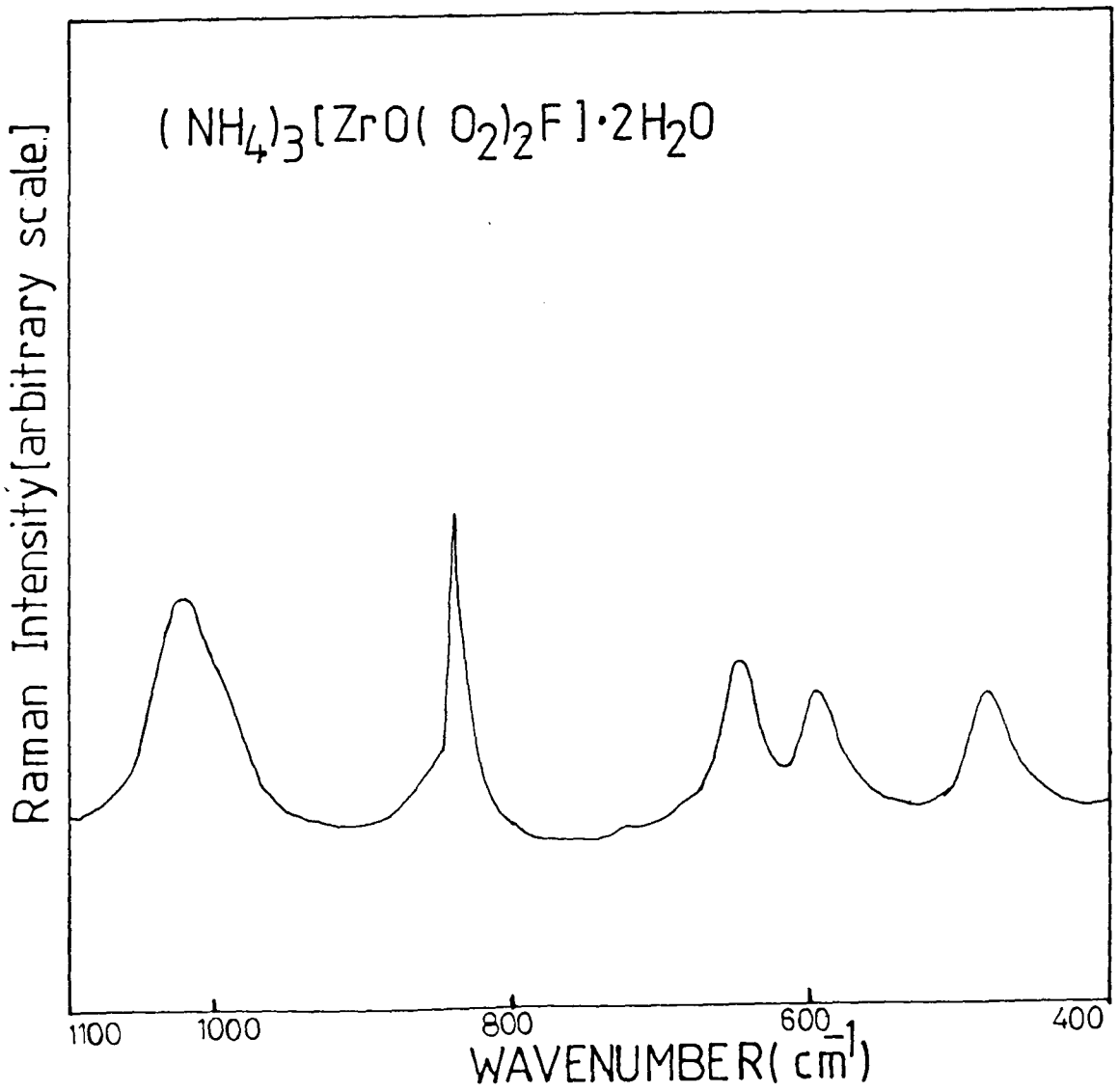
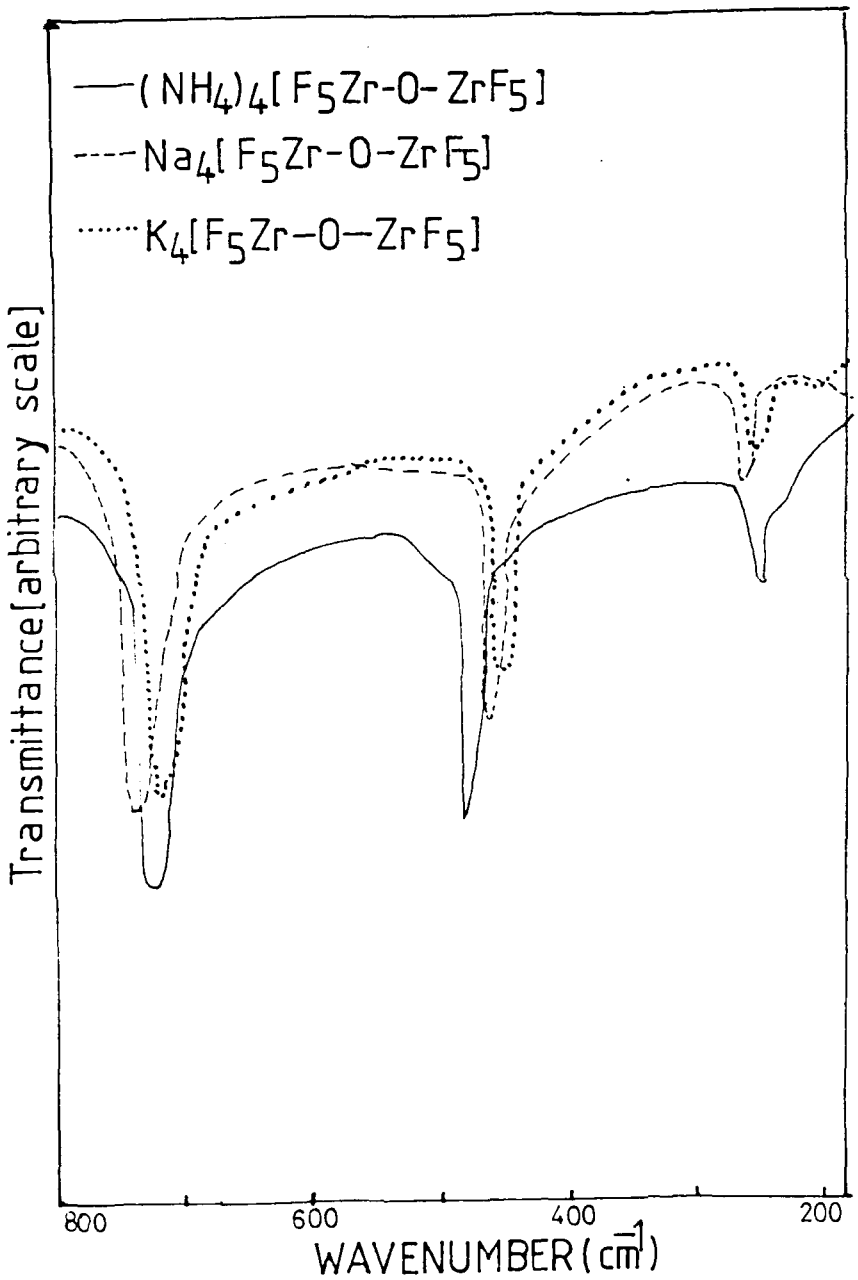
3200
3000
1700
1500
1300
1000
800
600
400
200
WAVENUMBER (cm-1)


$(NH_4)_3[ZrO(O_2)_2F]\cdot 2H_2O$
Raman Intensity(arbitrary scale)
1100
1000
800
600
400
WAVENUMBER(cm^{-1})


—(NH4)4[F5Zr-O-ZrF5]
----Na4[F5Zr-O-ZrF5]
·····K4[F5Zr-O-ZrF5]
Transmittance[arbitrary scale]
800
600
400
200
WAVENUMBER(cm⁻¹)

conform to the presence of terminally bonded fluoride.[22,27] The results of chemical analyses, magnetic susceptibility, and EPR measurements, IR and 1R spectroscopy are consistent with the formulations of the compounds as alkali-metal and ammonium oxomonoperoxodifluorozirconates(IV), $A_2[ZrO(O_2)F_2]$ (A = Na, K or NH_4), and sodium and ammonium oxodiperoxomonofluorozirconate(IV) dihydrates, $A_3[ZrO(O_2)_2F].2H_2O$ (A = Na or NH_4).

Having achieved the synthesis of both mono and diperoxozirconates(IV), it was incumbent on us to make an internal comparison of the present results with those of the earlier investigations on peroxofluorotitanates(IV).[15] It may be necessary to recall that the mono- and diperoxotitanates(IV) were of the types $[Ti(O_2)F_5]^{3-}$ and $[Ti(O_2)_2F_2]^{2-}$ obtained at pH 6 and 9, respectively. A comparison of the results of studies on Ti[15] and Zr (present work) reveals that (i) while the heteroligand monoperoxo complexes can be obtained at pH 6, synthesis of diperoxo complexes requires a higher pH, and (ii) whereas the peroxo complexes of titanium(IV) do not have a "titanyl (TiO^{2+})" core instead they have titanate(IV) centres, the corresponding complexes of zirconium(IV) are zirconyl (ZrO^{2+}) complexes.

The peroxo ligand in each of the complexes $[ZrO(O_2)F_2]^{2-}$ and $[ZrO(O_2)_2F]^{3-}$ binds the zirconyl centre in a triangular bidentate manner. The complex $[ZrO(O_2)F_2]^{2-}$ ion may have a hexa-coordinated polymeric structure through weak ...Zr.....O... Zr.....O.... interactions, while the $[ZrO(O_2)_2F]^{3-}$ species may

be either a hexa-coordinated monomer although, here again, the possibility of a polymeric structure through ....Zr...O....Zr...O.. or ....Zr——F....Zr——F interactions cannot be totally discounted.

It may be inferred from our studies that, like in the case of titanium, monoperoxo- and diperoxofluoro complexes of zirconium(IV) are capable of being synthesised under appropriate experimental conditions. The pH value of the reaction medium plays a very important role in the synthesis of such compounds. A pH >7 is required for a 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 which contain Ti(IV) centres. It is also evident from the results of the present studies that under experimental conditions described herein oxomonoperoxofluorozirconate(IV) complexes, $[ZrO(O_2)F_2]^{2-}$, can be obtained at pH 6 of the reaction solution, while oxodiperoxofluorozirconate(IV) complexes, $[ZrO(O_2)_2F]^{3-}$, the first diperoxo complexes of the metal to be obtained in the solid state, may be synthesised only at pH 12-14. Isolation of a μ-oxo-dizirconate(IV) species, $[F_5Zr\text{-}O\text{-}ZrF_5]^{4-}$ at pH $\geqslant 5 <6$ renders us to state that such a complex might be the precursor for the oxomonoperoxozirconates(IV), however, the chances of formation of a peroxozirconate(IV) at pH ca 5 which might 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,[26] should not be discounted.

References

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Chapter 6

Complex Peroxouranates. Synthesis and Assessment of Structures of Alkali-Metal and Ammonium Dioxoperoxo(oxalato)uranates(VI) Hydrates, $A_2[UO_2(O_2)(C_2O_4)].H_2O$ (A = NH_4, Na or K), and a Molecular Mixed-Ligand Peroxo Complex, $[UO_2(O_2)(EDTA)]$ (EDTA = Ethylenediaminetetra-acetic acid)*

One of the active areas of research in contemporary inorganic chemistry addresses to studies on compounds that contain peroxo ligands. As mentioned in Chapter 1, this is mainly owing to an intrinsic interest[1-5] on peroxometal compounds as well as their use in practice.[6-8] Although a commendable progress has been made on this aspect of lighter transition metals in recent years,[1-7] however, the peroxo-chemistry of heavier metals has not received due attention. For instance, despite actinide peroxo complexes have been known for a long time,[9-12] their hetero-ligand-peroxo chemistry seems to have been practically overlooked in earlier investigations.[9,10] Uranium, the most important of the actinides, forms peroxo complexes[9-12] of which $UO_2(O_2).nH_2O$ (n = 2 or 4) appears to be the best characterised one. The molecular complex $UO_2(O_2).4H_2O$ was shown to oxidise olefins mainly to epoxides and oxidative cleavage products.[8]

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Peroxo-chemistry of the metal is very complex[9] and reports on hetero-ligand peroxouranate compounds are rather scanty, except for the ones on (carbonato)-,[9,12] (oxalato)-,[9] and (fluoro)-peroxouranates.[11] The only molecular complexes of it known in the literature[13] include $UO_2(O_2).nH_2O$ (n = 2 or 4) and $UO_2(O_2)L$ (L = Ph_3PO, Ph_3AsO or pyridine-N-oxide)[13] in addition to a few dioxo(peroxo)uranium(VI) containing Schiff base as co-ligands.[14] A colleague[15] of our laboratory has very recently synthesised some molecular peroxo complexes of the metal with 1,10-phenanthrolene, 2,2-bipyridyl, ethylenediamine, and glycine being the chosen hetero-ligands. It was observed while investigating some other aspects of peroxo-uranium chemistry[11,12] that '$UO_2(O_2)$', the common frame work for such compounds, was generated <u>in situ</u> from the reaction of UO_2^{2+} with H_2O_2 in aqueous solutions. This caused us to anticipate that under suitable experimental conditions hetero-ligands, for example, oxalate and EDTA (EDTA = ethylenediaminetetra-acetic acid) could be made to co-ordinate with the coordinatively unsaturated uranium centre to afford peroxo-oxalato uranate(VI) and peroxo-EDTA uranium(VI) compounds, respectively.

Based on the afore-mentioned information, it was considered worthwhile to study at least some aspects of peroxo-chemistry of the metal. Accordingly, the present work was undertaken to synthesise hitherto unreported molecular complex of the type $\overline{\langle UO_2(O_2)EDTA \rangle}$ followed by its characterisation and structural assessment as well as to improvise a direct route to peroxo-

(oxalato)uranates(VI), to make an assessment of their structure and to rationalise the IR and laser Raman (lR) spectra in terms of the modes of binding of peroxide (O_2^{2-}) and $C_2O_4^{2-}$ ligands with the UO_2^{2+} centre, to make an internal comparison of the results with those of the peroxo(sulphato)uranates(VI) recently synthesised in this laboratory,[15] and also to correlate with that of the previously reported $(NH_4)_2UO_4C_2O_4.3H_2O$.[16,17] This Chapter, indeed the concluding Chapter of the thesis, has been devoted to the results of the afore-said studies.

Experimental

The chemicals used were all reagent grade products. (Loba Chemie, E. Merck, BDH, Sarabhai M. Chemicals).

Synthesis of Alkali-Metal and Ammonium Dioxoperoxo-(sulphato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4 or Na)[15]

A 1.0g (1.99 mmol) sample of $UO_2(NO_3)_2.6H_2O$ was dissolved in water (10-15 cm^3) followed by addition of 25% aqueous ammonia (sp. gr. 0.9) or a concentrated solution of sodium hydroxide or potassium hydroxide in case of Na^+ or K^+ salt, respectively, with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off and washed free of alkali and nitrate. To an aqueous suspension of the product was added 4 cm^3 (10 mmol) of 2.5M H_2SO_4 solution to obtain a clear solution, which was stirred for ca. 5 min. A 25 cm^3 (220.5 mmol) sample of 30% H_2O_2

was added, while the $U:SO_4^{2-}:H_2O_2$ ratio was maintained at 1:5:111, and the solution was stirred for ca 15 min. followed by careful addition of the corresponding alkali-metal or ammonium hydroxide solution, AOH (A = NH_4, Na), until the pH was raised to 6, whereupon a yellow product just began to appear. An equal volume of ethanol was added with occassional stirring to obtain yellow microcrystalline alkali-metal or ammonium dioxoperoxo(sulphato)-aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4 or Na), in high yields. Each compound was allowed to settle for ca. 20 min, separated by centrifugation, purified by washing with ethanol (3-5 times), and finally dried in vacuo over concentrated H_2SO_4.

These compounds were synthesised for comparative studies.

Synthesis of Alkali-Metal and Ammonium Dioxoperoxo-(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = NH_4, Na or K)

A 1.0g (1.99 mmol) sample of $UO_2(NO_3)_2.6H_2O$ was dissolved in water (10-15 cm^3) followed by addition of 25% aqueous ammonia (sp.gr. 0.9) or a concentrated alkali-metal hydroxide solution, AOH (A = Na or K), with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off and washed free of alkali and nitrate. To an aqueous suspension of the product was added a concentrated solution of oxalic acid (0.25g, 1.98 mmol) to obtain a clear solution, which was stirred for ca. 5 min. A 25 cm^3 (220.5 mmol) sample of 30% H_2O_2 was added,

maintaining the $U:C_2O_4^{2-}:H_2O_2$ ratio at 1:1:111 and the solution was stirred for ca. 15 min followed by careful addition of aqueous ammonia (sp.gr. 0.9) or 20% solution of alkali-metal hydroxide, AOH (A = Na or K), until the pH of the solution was raised to 6. A yellow product just began to appear at this stage. An equal volume of ethanol was added with occassional stirring to obtain yellow microcrystalline alkali-metal or ammonium dioxoperoxo-(oxalato)uranate(VI) hydrates, $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = NH_4, Na or K), in high yields. The compound was allowed to settle for ca. 20 min, separated by centrifugation, purified by washing with ethanol (4-5 times), and finally dried in vacuo over concentrated H_2SO_4.

The amounts of reagents used for the syntheses and the yields of $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = NH_4, Na or K) compounds are summarised in Table 6.1.

Synthesis of (Ethylenediaminetetra-acetic acid)dioxo-peroxouranium(VI)

An amount of 1.0g (1.99 mmol) of $UO_2(NO_3)_2.6H_2O$ was dissolved in 10-15 cm^3 of water followed by addition of an aqueous ammonia solution (sp.gr. 0.9) with stirring until an yellow precipitate ceased to appear. The yellow product was filtered off and washed free from alkali and nitrate. To an aqueous suspension of the yellow product was added 0.58g (1.98 mmol) of solid ethylenediaminetetra-acetic acid (EDTA) with slow stirring. The mixture was then warmed over steam-bath for ca. 15 min, and a

lemon yellow solution was obtained. This was filtered to remove any undissolved residue and then cooled to room temperature. To the clear cold solution was added 15 cm^3 (132.3 mmol) of 30% H_2O_2, and stirred for ca. 15 min, whereupon an yellow microcrystalline product thwarted out. The pH of the reaction solution was recorded to be 2. The product was filtered, washed 4-5 times with ethanol, and finally dried in vacuo over concentrated H_2SO_4.

The amounts of reagents used and the yield of the compound are given in Table 6.1.

Elemental Analyses

Quantitative determination of uranium, peroxide, oxalate, carbon, hydrogen, nitrogen, and alkali-metals were made by the methods already described in Chapter 2.

While the analytical data are reported in Table 6.2, the structurally significant IR and Raman bands along with their assignments are set out in Table 6.3.

Results and Discussion

Complex Peroxo(oxalato)uranates(VI)

The reaction of hydrogen peroxide with UO_2^{2+} leading to a complex peroxouranate(VI) of a definite composition is highly dependent on the pH value of the reaction medium. Thus evaluation of an appropriate pH for successful synthesis of a peroxouranate species is emphasised to be an important prerequisite. In the

Table 6.1 : Amounts of Reagents Used for the Synthesis of and the Yields Obtained for $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = NH_4, Na or K) and $[UO_2(O_2)EDTA]$ (EDTA = Ethylenediaminetetra-acetic acid)

Compound	Yield g (%)	Amount of $UO_2(NO_3)_2.6H_2O$ g (mmol)	Amount of 30% H_2O_2 cm^3 (mmol)	Amount of $H_2C_2O_4.2H_2O$ g (mmol)	Amount of EDTA g (mmol)
$(NH_4)_2[UO_2(O_2)C_2O_4].H_2O$	0.8 (91)	1 (1.99)	25 (220.5)	0.25 (1.98)	-
$Na_2[UO_2(O_2)C_2O_4].H_2O$	0.8 (89)	1 (1.99)	25 (220.5)	0.25 (1.98)	-
$K_2[UO_2(O_2)C_2O_4].H_2O$	0.9 (87)	1 (1.99)	25 (220.5)	0.25 (1.98)	-
$[UO_2(O_2)EDTA]$	1.0 (84)	1 (1.99)	15 (132.3)	-	0.58 (1.98)

present case the suitable pH for bringing about co-ordination of both peroxide and oxalate in the presence of each other with the uranyl centre was ascertained to be 6. The products isolated at a relatively lower pH value (e.g. ca. 4) on being analysed did not show the occurrence of peroxide to the desired level (i.e., $U:O_2^{2-}$ as 1:1), indicating therefore that the O_2^{2-} uptake process was in progress but did not reach the $U:O_2^{2-}$ ratio of 1:1. Based on the knowledge gathered from the afore-mentioned reaction runs, the suitable conditions for successful synthesis of the desired compounds were evaluated. Accordingly, the peroxo(oxalato)-uranates(VI) of the type $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = alkali-metal or ammonium) have been synthesised by carrying out reactions among UO_2^{2+}, H_2O_2, and $C_2O_4^{2-}$ at pH 6 of the reaction solution maintained by addition of the corresponding alkali-metal or ammonium hydroxide, AOH. While ammonium hydroxide was used as a 25% solution (sp.gr. 0.9), sodium and potassium hydroxides were used as 20% solutions. The peroxide uptake process was monitored through chemical determination of active oxygen (O_2^{2-}) in the products isolated from the reaction solution at different pH values. The method of obtaining peroxo(oxalato)uranates(VI) described in the present work is straightforward, does not involve any extra preparation step unlike in the method previously reported for the synthesis of peroxo(oxalato)uranates(VI)[16,17] (which required ammonium uranyl oxalate), and may serve as a paradigm for an access to other hetero-ligand peroxouranates(VI). It is

Table 6.2 : Analytical Data of $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = NH_4, Na or K) and $[UO_2(O_2)EDTA]$ (EDTA = Ethylenediaminetetra-acetic acid)

Compound	Found % (Calcd. %)					
	A or N	U	O_A^a	C_2O_4	C	H
$(NH_4)_2[UO_2(O_2)C_2O_4].H_2O$	6.3 (6.3)	53.8 (53.59)	7.5 (7.2)	20.1 (19.82)	-	-
$Na_2[UO_2(O_2)C_2O_4].H_2O$	10.4 (10.13)	52.7 (52.42)	7.3 (7.05)	19.6 (19.39)	-	-
$K_2[UO_2(O_2)C_2O_4].H_2O$	16.3 (16.08)	48.7 (48.95)	6.8 (6.58)	18.4 (18.1)	-	-
$[UO_2(O_2)EDTA]$	5.3 (5.21)	44.0 (44.23)	6.2 (5.95)	-	13.4 (13.39)	1.5 (1.5)

[a]Active Oxygen

imperative to mention, that according to the present method the complex peroxouranates(VI) start appearing as soon as the solution attains pH 6; however, the addition of ethanol is required to achieve quick and nearly quantitative precipitation of the products. It must also be mentioned that similar compounds were obtained in low yields by allowing the reaction solutions, after adjusting their pH to 6, to stand for several hours at an ice-water temperature.

The $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = NH_4, Na or K) compounds are all yellow microcrystalline products, practically insoluble in water. Their insolubility precludes molar conductance measurements. They do not seem to be hygroscopic, and start losing active oxygen with time (in days), unlike the corresponding sulphato compounds, $A_2[UO_2(O_2)SO_4(H_2O)]$,[15] which are stable for a prolonged period. Pyrolysis studies showed that, while $A_2[UO_2(O_2)C_2O_4].H_2O$ begins to expel water at ca.110°C, leading us to state that the H_2O molecule is rather losely held in the peroxo(oxalato) compounds, the sulphato compounds do not suffer any loss of water at or around this temperature. Both types of complex peroxouranates(VI) readily decompose in dilute sulphuric acid, liberating hydrogen peroxide quantitatively, and thus facilitating determination of active oxygen contents of the compounds. Chemical determination of active oxygen, considered to be very crucial to ascertain the number of O_2^{2-} groups coordinated to the UO_2^{2+} centre, was accomplished by redox titrations involving a standard Ce^{4+} solution, and

also separately with a standard $KMnO_4$ solution. The estimation was conducted in the presence of boric acid in order to prevent any loss of active oxygen. The results suggested the occurrance of one O_2^{2-} group per UO_2^{2+} centre in each of the newly synthesised compounds. The compounds are all diamagnetic in nature, in conformity with the presence of hexavalent uranium.

Albeit complex peroxo(oxalato)uranates(VI) have been reported,[16,17] we became interested in them not only to explore the feasibility of their being obtained by a method analogous to that improvised for the hitherto unknown peroxo(sulphato)-uranates(VI)[15] but also to spectroscopically evaluate the mode of bonding of O_2^{2-} and $C_2O_4^{2-}$ with UO_2^{2+} in the compounds. The IR and laser Raman spectra of the complex peroxo(oxalato)uranates(VI), $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = NH_4, Na or K), were studied particularly to ascertain the mode of bonding of O_2^{2-} with UO_2^{2+} centre in the complex. It is pertinent to mention here that the earlier reports on peroxo(oxalato)uranates(VI)[16,17] suggested the presence of a bridging peroxide. The IR and Raman spectra of the newly synthesised peroxo(oxalato)uranates(VI) showed distinctly strong and sharp bands at ca.890s, ca.860s, and ca.600s cm^{-1}, in each of the compounds, which have been assigned to the $\nu(U{=}O)$ (trans-linked $O{=}U{=}O$)[18] and peroxo modes[19-21] $\nu(O\text{-}O)$ and $\nu(U\text{-}O_2)$, respectively. The definite presence, shapes, and positions of ν (O-O) and the complimentary $\nu(U\text{-}O_2)$ modes in the regions stipulated for the presence of traingularly bonded bidentate peroxide led us to draw an inference that the O_2^{2-} group is

bonded to the UO_2^{2+} centre, in each of the $A_2[UO_2(O_2)C_2O_4].H_2O$ compounds, in a triangular bidentate (C_{2v}) manner. The IR modes due to the co-ordinated $C_2O_4^{2-}$ ligands are quite straight forward and unequivocal, showing the presence of a chelated oxalato group.[22,23] Ionic oxalate has a planar, symmetrical structure with all the C-O bonds of an equal length. For a chelated oxalate all the C-O vibrations become infrared active, with asymmetric (O-C-O) stretchings shifting to higher frequencies and the symmetric (O-C-O) stretchings to lower.[23] The oxalato-modes in the regions 1680-1770s cm^{-1} and at ca 1440m cm^{-1} occur in the positions assigned for the chelated $C_2O_4^{2-}$ group,[23] and accordingly we infer that oxalato-ligand in the present series of complexes are chelated. The ν(O-H) and δ(H-O-H) bands in the IR spectra of the compounds resemble in their shapes and positions those generally observed for unco-ordinated water.[11,23] This result, as well as the facile loss of water as evident from the pyrolysis studies, suggest that the H_2O molecule in $A_2[UO_2(O_2)C_2O_4].H_2O$ occurs as a lattice water and probably is not co-ordinated to the uranyl centre. The solubility property of the compounds suggests a fair possibility of a polymeric structure of the complex species $[UO_2(O_2)C_2O_4]^{2-}$ through a -U=O....U=O... interaction.

A comparison between the peroxo(oxalato)- and peroxo(sulphato)[15]uranates(VI) show that (i) the peroxo(oxalato)uranates(VI), $A_2[UO_2(O_2)C_2O_4].H_2O$, are comparatively less stable than the corresponding peroxo(sulphato)uranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$,

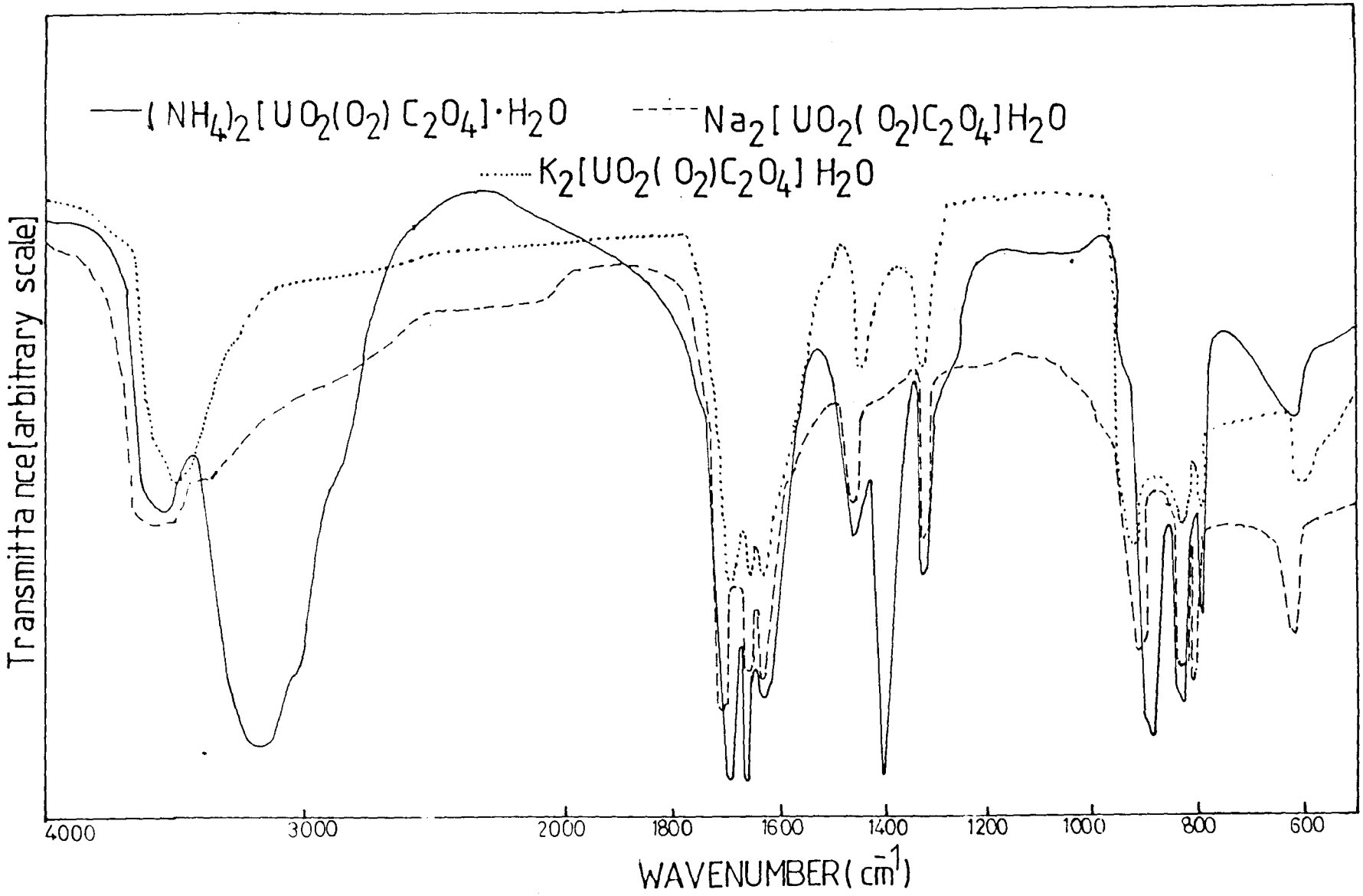
Table 6.3 : Structurally Significant IR and Raman Bands of $A_2[UO_2(O_2)C_2O_4].H_2O$ (A = NH_4, Na or K) and $[UO_2(O_2)EDTA]$ (EDTA = Ethylenediaminetetra-acetic acid)

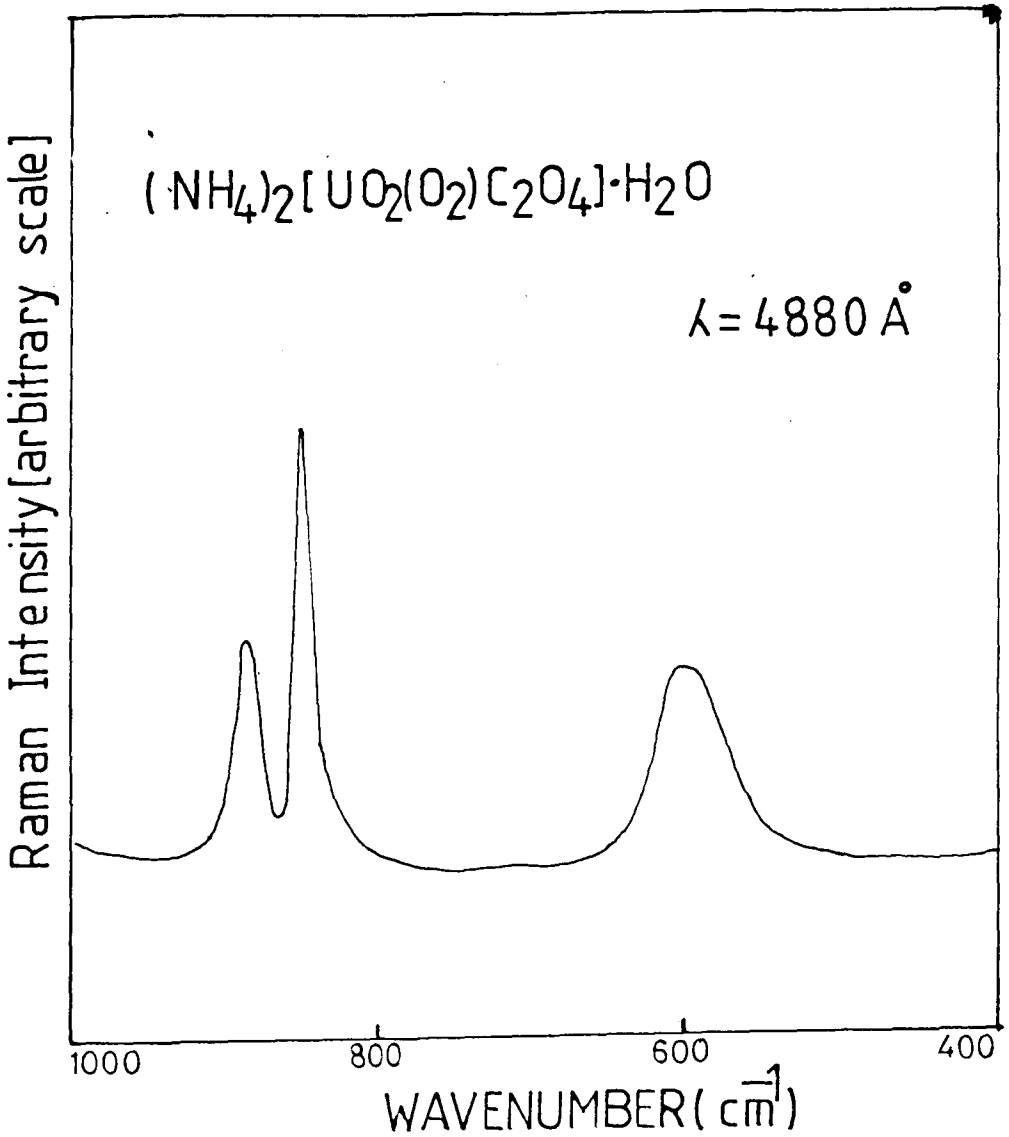
Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$(NH_4)_2[UO_2(O_2)C_2O_4].H_2O$	880s	890	ν(U=O) (trans-linked O=U=O)
	860s	850	ν(O-O)
	610s	600	ν(U-O_2)
	1694s		ν_{as}(C=O)
	1674s		ν_{as}(C=O)
	1430m		ν(C-O + C-C)
	1325s		ν(C-O) + δ(O-C-O)
	790s		δ(O-C-O)
	3455m		ν(O-H)
	1640s		δ(H-O-H)
$Na_2[UO_2(O_2)C_2O_4].H_2O$	890s	890	ν(U=O) (trans-linked O=U=O)
	860s	860	ν(O-O)
	600s	600	ν(U-O_2)
	1694s		ν_{as}(C=O)
	1674s		ν_{as}(C=O)
	1440m		ν(C-O + C-C)
	1325s		ν(C-O) + δ(O-C-O)
	800s		δ(O-C-O)
	3460m		ν(O-H)
	1640s		δ(H-O-H)

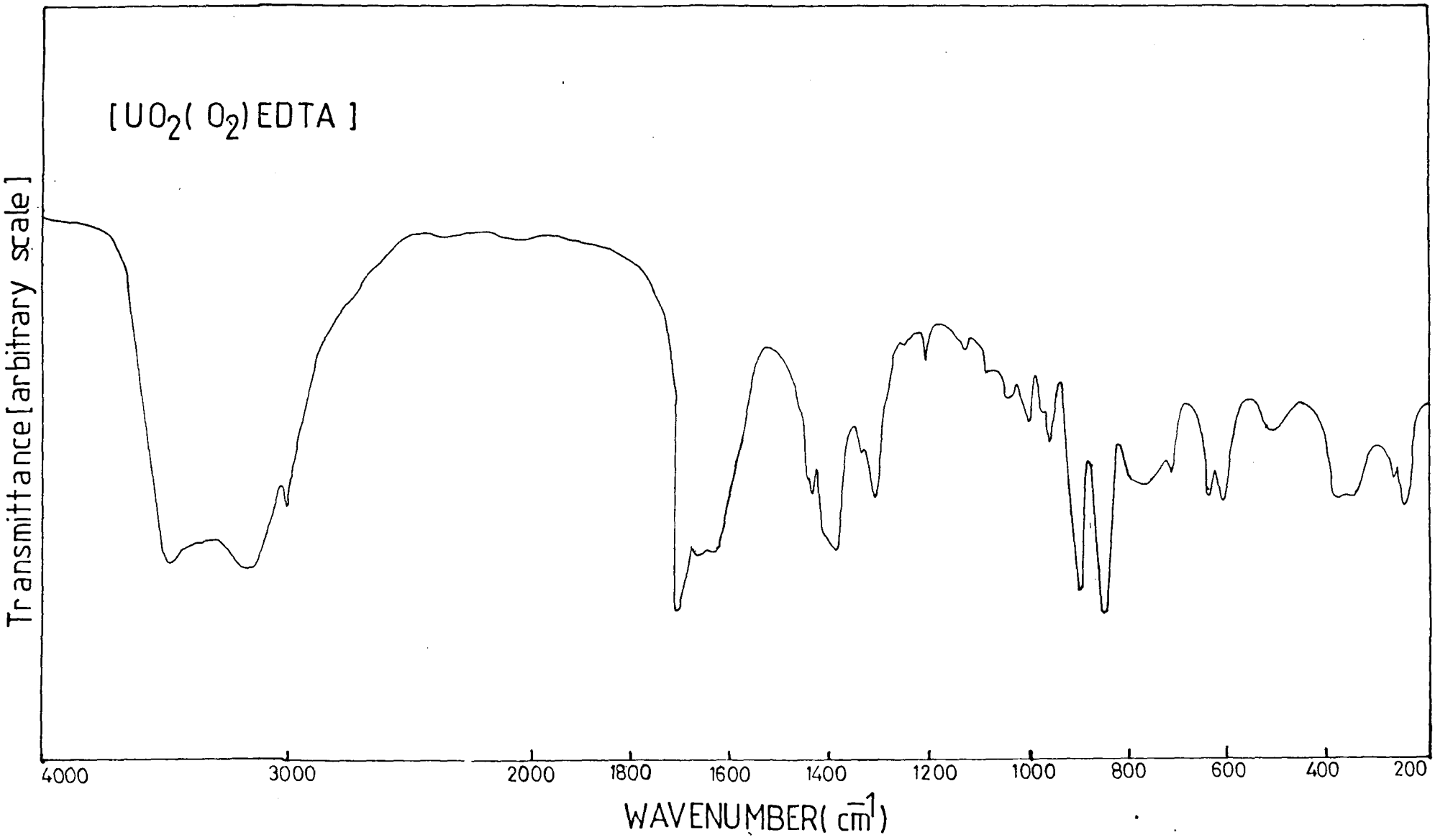
Table 6.3 continued...

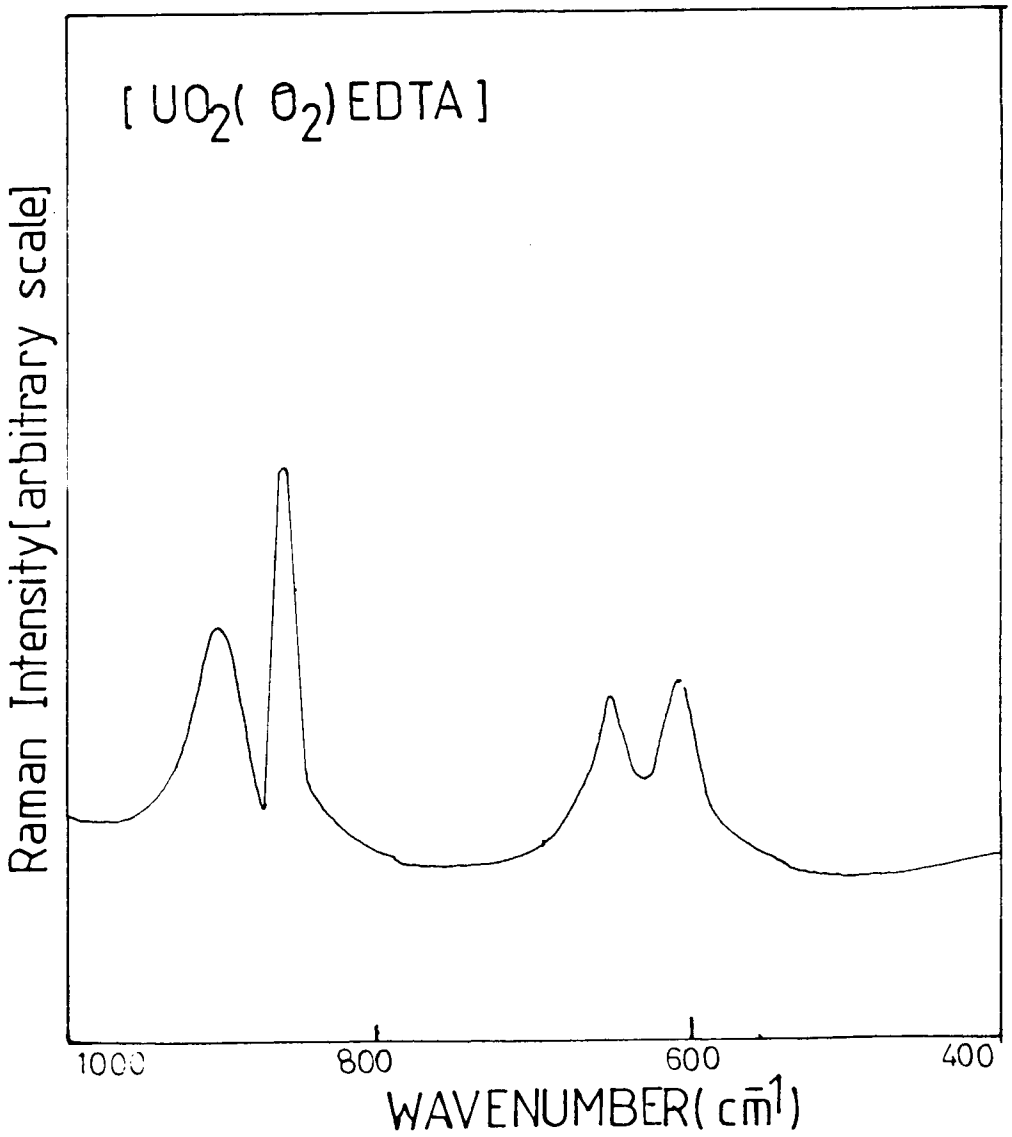
Table 6.3 continued

Compound	IR cm^{-1}	Raman cm^{-1}	Assignment
$K_2[UO_2(O_2)C_2O_4].H_2O$	890s	880	ν(U=O) (trans-linked O=U=O)
	850s	860	ν(O-O)
	600s	600	ν(U-O_2)
	1690s		ν_{as}(C=O)
	1650s		ν_{as}(C=O)
	1428m		ν(C-O + C-C)
	1325s		ν(C-O) + δ(O-C-O)
	3455m		ν(O-H)
	1640s		δ(H-O-H)
$[UO_2(O_2)EDTA]$	910s	900	ν(U=O) (trans-linked O=U=O)
	870s	870	ν(O-O) (ν_1)
	615m	610	ν(U-O_2) (ν_2)
	635w	625	ν(U-O_2) (ν_3)
	1710s		ν(COOH)
	260m		ν(U-N)


—(NH4)2[UO2(O2)C2O4]·H2O
----Na2[UO2(O2)C2O4]H2O
.....K2[UO2(O2)C2O4]H2O
Transmittance[arbitrary scale]
4000
3000
2000
1800
1600
1400
1200
1000
800
600
WAVENUMBER(cm-1)


$(NH_4)_2[UO_2(O_2)C_2O_4]\cdot H_2O$
λ = 4880 Å
Raman Intensity (arbitrary scale)
1000
800
600
400
WAVENUMBER (cm⁻¹)


[UO2(O2) EDTA]
Transmittance [arbitrary scale]
4000
3000
2000
1800
1600
1400
1200
1000
800
600
400
200
WAVENUMBER(cm-1)


[UO2(O2)EDTA]
Raman Intensity[arbitrary scale]
1000
800
600
400
WAVENUMBER(cm-1)

(ii) the former undergoes dehydration at 110°C, a temperature at which the latter does not, (iii) both types of compounds decompose in dilute sulphuric acid, quantitatively liberating H_2O_2, (iv) while the peroxide group in $[UO_2(O_2)C_2O_4]^{2-}$ is bonded to the UO_2^{2+} centre in a triangular bidentate (C_{2v}) manner, the O_2^{2-} in $[UO_2(O_2)SO_4(H_2O)]^{2-}$ is bound to the UO_2^{2+} in a bridging bidentate fashion, and (v) whereas the $C_2O_4^{2-}$ in the peroxo(oxalato)-uranate(VI) acts as bidentate chelating ligand, the SO_4^{2-} in the corresponding peroxo(sulphato)uranates(VI) occurs as a monodentate ligand.

Complex(Ethylenediaminetetra-acetic acid)uranium(VI)

The formation of '$UO_2(O_2)$' in solution provides a good scope of its use as a precursor, so that based on this as the core framework and allowing suitable ligands to co-ordinate with the metal an access to molecular-peroxo-complexes of uranyl ion UO_2^{2+} could be achieved.

Important in this context were to ascertain the right pH and select an appropriate ligand that would be capable of acting as a neutral ligand under the chosen reaction conditions. The co-ligand chosen for the present study was ethylenediaminetetra-acetic acid (EDTA). An appropriate pH for the co-ordination of neutral ethylenediaminetetra-acetic acid (EDTA) was evaluated by isolating a small amount of product from the reaction solution followed by quantitative determination of active oxygen content chemically. A pH value of 2 of the reaction solution was found to

be appropriate for the synthesis of $\lceil UO_2(O_2)EDTA \rfloor$. The co-ligand EDTA was added as such to dissolve the yellow product obtained by the addition of alkali to an aqueous solution of $UO_2(NO_3)_2.6H_2O$. This was followed by the addition of 30% H_2O_2. It is important to stress on a point at this juncture that the reverse order of addition of the reactants is detrimental owing to a pronounced tendency of formation of sparingly soluble $UO_2(O_2).nH_2O$ (n = 2-4). The compound is yellow, microcrystalline in nature and is practically insoluble in water and common organic solvents. It is diamagnetic and e.s.r. silent in conformity with the occurrence of UO_2^{2+}.

The most significant features of vibrational spectrum of the compound are the IR signatures for $\nu(O-O)(\nu_1)$, $\nu(U-O_2)(\nu_2)$, $\nu(U-O_2)(\nu_3)$, and $\nu(U=O)$ (trans linked O=U=O) modes at 870s, 615m, 625w, and 910s, respectively. The laser Raman (lR) spectrum, recorded on a solid sample owing to its insolubility, exhibited the corresponding complimentary signals at 870, 610, 625, and at 900 cm^{-1} providing strong credence to the contention that the central framework of the compound, $\lceil UO_2(O_2)EDTA \rfloor$ is '$UO_2(O_2)$' containing a trans-linked O=U=O and a chelated (C_{2v}) peroxide ligand. The IR spectra of the compound, $\lceil UO_2(O_2)EDTA \rfloor$ shows bands at 1710s and at 260m cm^{-1} assigned to unionised, uncoordinated (COOH) stretching[24a] and $\nu(U-N)$,[14] respectively. This observation and the absence of any band in the region 1590-1650 cm^{-1} cause[24b] us to state that the hetero-ligand EDTA

occurs as a neutral ligand and binds the metal centre through its N-atoms[24b,25] and the O-atoms are not involved in coordination[24b,25] with the metal. In other words it may be stated that the co-ligand EDTA did not ionise, under the chosen experimental conditions, but co-ordinated with the UO_2^{2+} centre involving the two nitrogen atoms as expected. The complex $\overline{\angle UO_2(O_2)EDTA\rangle}$ may have a polymeric structure through ...O = U = O....U = O.... interactions in the crystal lattice. This is in agreement with its insoluble nature.

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APPENDIX

LIST OF PUBLICATIONS

1. Complex Peroxyuranates. Synthesis and Structural Assessment of Alkali-Metal and Ammonium Dioxoperoxy-(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4 or Na), and Alkali-Metal and Ammonium Dioxoperoxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4].H_2O$
M. Bhattacharjee, M.K. Chaudhuri, and R.N. Dutta Purkayastha.
Inorg. Chem., 1986, 25, 2354.

2. Direct Synthesis of Ammonium Monofluorophosphate Monohydrate, $(NH_4)_2[PO_3F].H_2O$ and Potassium Monofluorophosphate, $K_2[PO_3F]$
M. Bhattacharjee and M.K. Chaudhuri
J. Chem. Soc., Dalton Trans., 1987, 477.

3. Ammonium Fluoroperoxomonophosphate Dihydrate, $(NH_4)_2[PO_2(O_2)F].2H_2O$. First Chemical Synthesis of a Fluorinated Peroxophosphate
M. Bhattacharjee and M.K. Chaudhuri
J. Chem. Soc., Dalton Trans., 1988, 2005.

4. Sodium and Ammonium Peroxomonophosphate Trihydrates, $A_3[PO_3(O_2)].3H_2O$ (A = Na or NH_4), as Efficient Oxidants and Viable Substitute for the Basic-H_2O_2 Reagent

M. Bhattacharjee and M.K. Chaudhuri

I World Congress II European Workshop Proceedings of the Symposium on "New Developments in Selective Oxidation," Rimini, Italy, 1989, Elsevier Publication.

Reprinted from Inorganic Chemistry, 1986, 25, 2354

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

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Received September 4, 1985

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

Introduction

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

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

Experimental Section

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

Synthesis of Alkali-Metal and Ammonium Dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na). A 1.0-g (1.99-mmol) sample of $UO_2(NO_3)_2\cdot 6H_2O$ was dissolved in water (10–15 cm^3) followed by addition of 25% ammonium hydroxide solution or a concentrated solution of sodium hydroxide in the case of the Na^+ salt with stirring until the yellow precipitate ceased to appear. The yellow precipitate was filtered off and washed free of alkali-metal ion or ammonium ion and nitrate. To an aqueous suspension of the product was added 4 cm^3 (10 mmol) of 2.5 M H_2SO_4 solution to obtain a clear solution, which was stirred for ca. 5 min. A 25-cm^3 (220.5-mmol) sample of 30% H_2O_2 was added, while the U:SO_4^{2-}:H_2O_2 ratio was maintained at 1:5:111, and the solution was stirred for ca. 15 min followed by careful addition of the corresponding alkali-metal or ammonium hydroxide solution, AOH (A = NH_4, Na), until the pH was raised to 6, whereupon a yellow product just began to appear. An equal volume of ethanol was added with occassional stirring to obtain yellow microcrystalline alkali-metal or ammonium dioxoperoxy(sulfato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na), in high yields. Each compound was allowed to settle for ca. 20 min, separated by centrifugation, purified by washing with ethanol (3–5 times), and finally dried in vacuo over concentrated H_2SO_4.

Synthesis of Alkali-Metal and Ammonium Dioxoperoxy(oxalato)uranate(VI) Hydrates, $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ (A = NH_4, Na, K). The $A_2[UO_2(O_2)C_2O_4]\cdot H_2O$ compounds were prepared in a manner analogous to that described above for the synthesis of the peroxy(sulfato)uranate compounds. The two points of differences are that (i) a concentrated solution of oxalic acid ($H_2C_2O_4\cdot 2H_2O$) was used in lieu of the 2.5 M H_2SO_4 solution and (ii) a U:$C_2O_4^{2-}$:H_2O_2 ratio of 1:1:111 was maintained for the synthesis.

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

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

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

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

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

Results and Discussion

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

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

Albeit complex peroxy(oxalato)uranates(VI) have been reported,[7] we became interested in them not only to explore the feasibility of their being obtained by a method analogous to that improvised for the hitherto unknown peroxy(sulfato)uranates(VI) but also to spectroscopically evaluate the mode of bonding of O_2^{2-} with UO_2^{2+} in the compounds. The infrared and laser Raman spectra of all the compounds were recorded in the range 4000–200 and 2000–150 cm^{-1}, respectively. The significant features of the IR spectra of the $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) compounds involve absorptions of coordinated sulfate, coordinated water, and the U=O stretch. The appearance of medium-intensity ν_1 and ν_2 modes of S–O stretchings at ca. 980 and ca. 450 cm^{-1}, respectively, and the splitting of ν_3 and ν_4 into two bands each (Table II), as opposed to the absence of ν_1 and ν_2 and the presence of unsplit ν_3 and ν_4 modes in the ionic sulfate, provide strong evidences for the lowering of the symmetry of SO_4^{2-} from T_d to C_{3v} and also for its occurrence as a coordinated unidentate ligand in the complex peroxy(sulfato)uranates(VI). A very strong absorption, in addition to the sulfate ligand bands, was observed at ca. 895 cm^{-1} and assigned to the $\nu_{U=O}$ stretching (trans-linked O=U=O group).[11] The LR spectra of $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = NH_4, Na) complement the IR spectra by exhibiting SO peaks at ca. 970 and ca. 440 cm^{-1} owing to ν_1 and ν_2 and at ca. 1040, ca. 1140, ca. 600, and ca. 650 cm^{-1} due to the ν_3 and ν_4 modes of a coordinated SO_4^{2-} (C_{3v}) ligand. A very strong peak observed at ca. 900 cm^{-1}, because of large polarizability changes involved in the U–O bond, is attributed to the $\nu_{U=O}$ (trans-linked O=U=O) mode. The presence of coordinated water causes the distinct appearance of ν_{O-H} and δ_{H-O-H} modes, which occur in the IR spectra as medium-intensity bands at 3160 and 1630 cm^{-1}. The lowering of ν_{O-H} frequencies and broadening of δ_{H-O-H} bands relative to those of free water suggest a clear possibility of intramolecular hydrogen bonding[12,13] involving uranyl oxygens. This might be a reason for lowering of $\nu_{U=O}$ as well. Especially noteworthy, over and above the patterns just discussed, is the absence of any band in the IR or LR spectra of the peroxy(sulfato)uranates(VI) in the range 890–800 cm^{-1}, a position where ν_{O-O} would appear if peroxide ligand were coordinated in the triangular bidentate (C_{2v}) manner commonly encountered in peroxy compounds of V(V)[3,5,14] and Ti(IV),[6,14,15] for example. This causes us to infer that the O_2^{2-} ligand is present as a bridging group

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

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

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

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

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

Conclusions

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

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

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

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

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

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

Direct Synthesis of Ammonium Monofluorophosphate Monohydrate, $[NH_4]_2[PO_3F]\cdot H_2O$, and Potassium Monofluorophosphate, $K_2[PO_3F]$

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A new direct general method for the synthesis of crystalline $[NH_4]_2[PO_3F]\cdot H_2O$ and $K_2[PO_3F]$, based on the reaction of H_3PO_4 and AHF_2 (A = NH_4 or K) followed by precipitation with ethanol, is described. The identity of the compounds has been established from the results of elemental analyses, molar conductance measurements, i.r. and laser Raman spectroscopic studies. Advantages of the new method are highlighted.

Monofluorophosphate, $[PO_3F]^{2-}$, is important particularly because of its use as an additive in dentifrice formulations for the inhibition of dental caries. Alkali monofluorophosphates have been known for quite some time,[1-5] however, there is no simple and easily accessible route to such compounds. The recommended methods[1-5] for their synthesis involve either a high-temperature fusion reaction, or fluorophosphoric acid as the starting material which requires extra preparation and purification, in addition to one or more steps to remove unwanted products, inevitably formed in either of the methods, to obtain the pure products. While studying the chemistry of fluoro compounds of some other elements,[6] it became necessary to synthesise alkali monofluorophosphates. The present work deals with the direct synthesis of ammonium monofluorophosphate monohydrate, $[NH_4]_2[PO_3F]\cdot H_2O$, and potassium monofluorophosphate, $K_2[PO_3F]$, and also highlights the advantages of the new method over those previously reported.

Experimental

Concentrated phosphoric acid (88%, 1.75 g cm^{-3}) used was of reagent-grade quality. The difluorides AHF_2 (A = NH_4 or K) were synthesised by the method developed in this laboratory.[7] Freshly distilled ethanol was used as a precipitant. Molar conductance was measured in conductivity-grade water using a Systronic type 304 digital direct reading conductivity bridge. I.r. spectra were recorded on a Perkin-Elmer model 983 spectrophotometer. The laser Raman spectra were recorded on a SPEX Ramalog model 1403 spectrophotometer. The 5 154-Å laser line from a Spectra-Physics model 165 argon laser was used as the excitation source. The scattered light at 90° was detected with the help of a cooled RCA 31034 photomultiplier tube followed by a photon count processing system. The spectra were recorded at ambient temperatures by making pressed pellets of the compounds.

Synthesis of $[NH_4]_2[PO_3F]\cdot H_2O$ *and* $K_2[PO_3F]$.—Since the method of synthesis is a general one only a representative procedure is described.

In a typical procedure 88% phosphoric acid (1.0 cm^3, 17.9 mmol; density 1.75 g cm^{-3}) was thoroughly mixed with AHF_2 (72 mmol; A = NH_4 or K), followed by the addition of water (*ca.* 10 cm^3). The solution thus obtained was stirred for 15 min. An amount of ~95% ethanol (*ca.* 20 cm^3) was added with stirring, whereupon white crystalline $[NH_4]_2[PO_3F]\cdot H_2O$ or $K_2[PO_3F]$ was precipitated. Stirring was continued for a further 15—20 min and the mixture was then allowed to stand for *ca.* 10 min. The compound was separated by centrifugation, washed 3—4 times with ethanol, and finally dried *in vacuo* over P_4O_{10}. The yields of $[NH_4]_2[PO_3F]\cdot H_2O$ and $K_2[PO_3F]$ were 1.8 g (66%) and 1.9 g (60%) respectively {Found: F, 12.7; N, 18.55; P, 20.6. Calc. for $[NH_4]_2[PO_3F]\cdot H_2O$: F, 12.5; N, 18.4; P, 20.35%. Molar conductance (Λ_M): 230 Ω^{-1} cm^2 mol^{-1}. Found: F, 11.1; K, 44.55; P, 17.8. Calc. for $K_2[PO_3F]$: F, 10.80; K, 44.40; P, 17.60%. Molar conductance (Λ_M): 225 Ω^{-1} cm^2 mol^{-1}}.

Elemental Analyses.—Phosphorus was estimated gravimetrically as $Mg_2[P_2O_7]$.[8] Fluoride was precipitated as PbClF and chloride was estimated by Volhard's method, from which the fluoride content was calculated.[9] Nitrogen and potassium were determined by the methods described earlier.[10]

Results and Discussion

Reaction of phosphoric acid, H_3PO_4, with hydrofluoric acid, under the appropriate conditions, gives rise to the formation of monofluorophosphoric acid, H_2PO_3F.[11] Substitution of ionisable protons by ammonium or alkali-metal ions (A) then provides the corresponding $A_2[PO_3F]$, if the wet methods are chosen. Alkali hydrogenfluorides, sources of HF, possess some special qualities as reagents, as they can not only act as fluorinating agents[6] but also maintain an acidic environment in a polar medium thus providing conditions conducive to some syntheses which are otherwise difficult.[6] Thus it was expected that interaction of an alkali hydrogenfluoride with phosphoric acid might lead directly to the title compounds. Accordingly, in line with the synthetic strategy, AHF_2 (A = NH_4 or K) were treated with H_3PO_4 which underwent a very facile fluorination and led to the direct synthesis of $A_2[PO_3F]$. The alkali hydrogenfluoride acted here not only as a fluorinating agent but also as the source of counter cation. The role of ethanol in the present synthesis was to bring about precipitation of the desired compounds. It may be mentioned that while the ammonium salt was obtained as a monohydrate the corresponding potassium salt was anhydrous. The new method, which can be scaled up if desired, is a straight one, and it neither involves any extra preparation step nor the use of hydrofluoric acid, rendering it easy to handle.

The results of elemental analyses are satisfactory (see Experimental section) and no recrystallisation is necessary. The compounds are stable for a prolonged period and are soluble in water. They permit molar conductance measurements, and the values were found to lie in the range 220—235 Ω^{-1} cm^2 mol^{-1}, in complete agreement with a 2:1 electrolye. Further, these results suggest that the compounds are also stable in solution and do not undergo decomposition, at least under the experimental conditions employed. I.r. spectra of the compounds synthesised

by the new method are in order.[12] Laser Raman spectra, recorded on the solids between 1 200 and 600 cm^{-1}, show signals at *ca.* 922 and *ca.* 950 cm^{-1} which have been assigned[13] to ν(P–F) and ν(P=O) vibrations, respectively. Thus the results suggest that the compounds are the same as those described earlier.[2,3,5]

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Ammonium Fluoroperoxomonophosphate Dihydrate, $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$. First Chemical Synthesis of a Fluorinated Peroxophosphate

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The salt $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$ has been synthesised from the reaction of $[NH_4][H_2PO_4]$ with 48% HF and 30% H_2O_2 at pH 10—11, maintained by the addition of aqueous ammonia, at an ice-bath temperature. The compound has been characterised by chemical analysis, i.r., and laser-Raman spectroscopic studies. Some properties of the compound are also reported.

In contrast to a host of reports concerning the synthesis, characterisation, and reactivity of peroxometal compounds, information on the corresponding aspects of non-metals is scanty, probably because of a limited access to such compounds. Some peroxo compounds of carbon, sulphur, and phosphorus, for example, are known[1,2] in addition to a few fluorinated peroxides of carbon and sulphur[3] which were generally synthesised by fluorination of oxo-compounds of the corresponding elements, a method which requires a very careful manipulation. It was reported over half a century ago[4] that anodic oxidations of fluorophosphoric acids produced fluoroperoxophosphoric acids $H_2PO_2(O_2)F$ and $H_2P_2O_4(O_2)F_2$, only in *ca.* 2% yields. The compounds are poorly characterised and to our knowledge neither salts of the acids nor chemical syntheses of fluorinated peroxophosphates, have been reported. We report herein a simple and efficient synthesis for the heretofore unknown ammonium fluoroperoxomonophosphate dihydrate, $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$, the first chemically synthesised fluoroperoxophosphate, along with its structural assessment and some results of our studies of its chemistry.

Experimental

Reagent-grade chemicals were used throughout. I.r. and laser-Raman spectra were recorded on instruments and under conditions already described.[5,6] The pH measurements were accomplished with a Systronics type 335 digital pH meter as well as with pH indicator (BDH) paper.

Synthesis of Ammonium Fluoroperoxomonophosphate Dihydrate, $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$.—A mixture of ammonium dihydrogenphosphate, $[NH_4][H_2PO_4]$ (1 g, 8.69 mmol), and 48% HF (1 cm^3, 24 mmol) was allowed to react with 30% hydrogen peroxide (15 cm^3 132.3 mmol) in an ice-bath, at pH 10—11 maintained by careful addition of aqueous ammonia (sp. gr. 0.9) with stirring. Stirring was continued for *ca.* 7 min followed by the addition of ice-cold ethanol (*ca.* 25 cm^3), whereupon white crystals were precipitated. These were filtered off, washed five to six times with ethanol, and dried *in vacuo* over concentrated H_2SO_4. Yield 1.3 g (81%) {Found: H, 6.6; F, 9.9; N, 14.7; O_2^{2-} (active oxygen), 16.9; P, 16.8. Calc. for $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$: H, 6.5; F, 10.2; N, 15.05; O_2^{2-} (active oxygen), 17.2; P, 16.65%}.

Elemental Analyses.—The fluoride and phosphorus[6] and peroxide, nitrogen, and hydrogen[7] contents were determined by methods described earlier.

Results and Discussion

It was shown recently[6] that a direct interaction of phosphoric acid with alkali hydrogenfluoride, AHF_2, afforded monofluorophosphate, PO_3F^{2-}. A similar reaction conducted in the presence of hydrogen peroxide, however, did not give access to a fluoroperoxophosphate. Subsequently it was noticed that a rise in pH of the reaction medium and thence isolation of a solid indicated the formation of the kind of product looked for. Accordingly, the first chemical synthesis of a fluoroperoxophosphate, $[NH_4]_2[PO_2(O_2)F]\cdot 2H_2O$, was achieved by the reaction of ammonium dihydrogenphosphate with 48% HF and hydrogen peroxide at pH 10—11 maintained by the addition of aqueous ammonia [equation (1)]. The role of ammonia was not

$$[NH_4][H_2PO_4] + HF + H_2O_2 + NH_4OH \longrightarrow [NH_4]_2[PO_2(O_2)F] + 3H_2O \quad (1)$$

only to raise the pH to facilitate formation of fluoroperoxophosphate but also to act as the source of counter cations, while ethanol helped in precipitating the product. The compound can be stored for a prolonged period in a sealed polyethylene envelope in a freezer, and is insoluble in common organic solvents. It decomposes in water, and quantitatively liberates H_2O_2 in the presence of sulphuric acid, rendering it easy to determine the active oxygen content. The results of peroxide estimation and elemental analyses are in complete agreement with the formula given.

The i.r. spectrum of the compound indicates the presence of peroxide, P–F, and P=O vibrations. Features at 960—1 060s and 900s cm^{-1} are similar in shape and position to those expected for the stretching modes of P=O and P–F, respectively.[8] Quite significant is the medium-intensity absorption at 853 cm^{-1} which has been assigned to ν(O–O) originating from a peroxide group bonded to the phosphorus centre. The doublet at 550s and 530s cm^{-1} is believed to arise from δ(OPO) modes. The i.r. spectrum also provides evidence for NH_4^+ and lattice water.

The laser-Raman spectrum of the solid is in close agreement with its i.r. spectrum and shows signals at 950 and 900 cm^{-1} due[9] to ν(P=O) and ν(P–F), respectively, at 858 cm^{-1} assigned to ν(O–O), and 556 and 528 cm^{-1} attributed to δ(OPO) modes. These results confirm the formulation of the compound, with the peroxide (O_2^{2-}) group being presumably bonded in an end-on manner as encountered in simple monoperoxo derivatives of sulphur and phosphorus.

It was of interest that this compound, in the presence of an acid, was capable of oxidising an hydrocarbon, alcohols, and olefins. Thus in stoicheiometric reactions it oxidised anthracene

to anthraquinone, 2-propanol to acetone, n-butanol to butanal, cyclohexene to 1,2-cyclohexanediol, and styrene to 1-phenylethylene glycol, generally in *ca.* 40% yield. Equally interesting is the phosphorus product isolated after working up of the oxidation product in each of the above reactions. This has been identified as the monofluorophosphate, PO_3F^{2-}, a species important because of its use as an additive in dentifrice formulations. In the absence of air, the peroxo compound in water reacts with SO_2 to produce sulphate.

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