

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

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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.

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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 peroxy- and fluoroperoxyphosphates constitute the basis of Chapter 3. Heretofore unreported ammonium and sodium monoperoxyphosphate trihydrates, $A_3 \left[PO_3(O_2) \right] \cdot 3H_2O$ ($A = Na$, 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 $Na_3 \left[PO_3(O_2) \right] \cdot 3H_2O$ and $(NH_4)_3 \left[PO_3(O_2) \right] \cdot 3H_2O$ 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, $Na_3 \left[PO_3(O_2) \right] \cdot 3H_2O$, has been found to oxidise chalcones to chalcone epoxides, salicylaldehyde 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.

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Also included in this Chapter are the first chemical synthesis of a fluorinated peroxophosphate, ammonium mono(fluoro)peroxophosphate dihydrate, $(\text{NH}_4)_2 \left[\text{PO}_2(\text{O}_2)\text{F} \right] \cdot 2\text{H}_2\text{O}$, along with its characterisation, structural assessment, and the results of studies of some reactivity. The compound $(\text{NH}_4)_2 \left[\text{PO}_2(\text{O}_2)\text{F} \right] \cdot 2\text{H}_2\text{O}$ has been synthesised from the reaction of $(\text{NH}_4)_2\text{H}_2\text{PO}_4$ 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 $\text{Na}_3 \left[\text{PO}_3(\text{O}_2) \right] \cdot 3\text{H}_2\text{O}$ and $(\text{NH}_4)_2 \left[\text{PO}_2(\text{O}_2)\text{F} \right] \cdot 2\text{H}_2\text{O}$ 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. $(\text{NH}_4)_2 \left[\text{PO}_3\text{F} \right] \cdot \text{H}_2\text{O}$ and $\text{K}_2 \left[\text{PO}_3\text{F} \right]$. The synthesis is based on the reaction of H_3PO_4 with AHF_2 ($\text{A} = \text{NH}_4$ 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, $\text{A}_2 \left[\text{ZrO}(\text{O}_2)\text{F}_2 \right]$ ($\text{A} = \text{Na}, \text{K}$ or NH_4) and oxodiperoxomonofluorozirconate(IV) compounds, $\text{A}_3 \left[\text{ZrO}(\text{O}_2)_2\text{F} \right] \cdot 2\text{H}_2\text{O}$ ($\text{A} = \text{Na}$ or NH_4), and isolation of decafluoro- μ -oxo-dizirconates(IV), $\text{A}_4 \left[\text{F}_5\text{Zr}-\text{O}-\text{ZrF}_5 \right]$ ($\text{A} = \text{Na}, \text{K}$ or NH_4), en route to oxoperoxofluorozirconates(IV) constitutes the subject matter of this Chapter.

Novel complex oxomonoperoxodifluorozirconates(IV), $\text{A}_2 \left[\text{ZrO}(\text{O}_2)\text{F}_2 \right]$ ($\text{A} = \text{Na}, \text{K}$ or NH_4), and oxodiperoxomonofluorozirconates(IV), $\text{A}_3 \left[\text{ZrO}(\text{O}_2)_2\text{F} \right] \cdot 2\text{H}_2\text{O}$ ($\text{A} = \text{Na}$ or NH_4), the first diperoxozirconates to be obtained in the solid state, have been synthesised from the reaction of hydrated zirconium oxide,

$ZrO_2 \cdot nH_2O$, 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 $[F_5Zr-O-ZrF_5]^{4-}$ 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 $pH \geq 5 < 6$ 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, $A_2 [UO_2(O_2)C_2O_4] \cdot H_2O$

(A = NH_4 , Na or K), and a molecular mixed-ligand peroxo complex $\left[\text{UO}_2(\text{O}_2)\text{EDTA} \right]$ (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 $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ with alkali-metal or ammonium hydroxide, AOH, with 30% H_2O_2 and oxalic acid solution, in the concentration ratio of $\text{U}:\text{H}_2\text{O}_2:\text{C}_2\text{O}_4$ 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, $\left[\text{UO}_2(\text{O}_2)\text{SO}_4(\text{H}_2\text{O}) \right]^{2-}$, 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 $\text{C}_2\text{O}_4^{2-}$ in the respective cases. The IR and Raman spectra suggest that the O_2^{2-} and SO_4^{2-} in $\left[\text{UO}_2(\text{O}_2)\text{SO}_4(\text{H}_2\text{O}) \right]^{2-}$ are bonded to the UO_2^{2+} centre in a bridging and in a monodentate manner, respectively, while both the O_2^{2-} and $\text{C}_2\text{O}_4^{2-}$ ligands in $\left[\text{UO}_2(\text{O}_2)\text{C}_2\text{O}_4 \right]^{2-}$ bind the uranyl centre in a bidentate chelated fashion. The $\text{A}_2 \left[\text{UO}_2(\text{O}_2)\text{C}_2\text{O}_4 \right] \cdot \text{H}_2\text{O}$ compounds are comparatively less stable than the $\text{A}_2 \left[\text{UO}_2(\text{O}_2)\text{SO}_4(\text{H}_2\text{O}) \right]$ species. Whereas H_2O in $\text{A}_2 \left[\text{UO}_2(\text{O}_2)\text{C}_2\text{O}_4 \right] \cdot \text{H}_2\text{O}$ 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 $A_2[UO_2(O_2)C_2O_4] \cdot H_2O$, over that of the previously reported $(NH_4)_2[UO_2(O_2)C_2O_4] \cdot 3H_2O$, 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 $UO_2(NO_3)_2 \cdot 6H_2O$ 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.