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

ABSTRACT

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

DOCTOR OF PHILOSOPHY

To

THE NORTH-EASTERN HILL UNIVERSITY
SHILLONG
INDIA

DECEMBER, 1991

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ABSTRACT

The results of investigations related to the chemistry of peroxo- and heteroligand-peroxo compounds of zirconium, thorium, uranium, and carbon, and alkalimetal acetylacetonates form the basis of the present thesis. The contents of the thesis have been distributed over **Seven Chapters**.

Chapter I presents a brief general introduction pertaining the work embodied in the thesis. The importance of and the interest in the chemistry of dioxygen, in general, and peroxo and heteroligand-peroxo compounds of zirconium, thorium, uranium, and carbon, in particular, have been highlighted. The problems encountered in the synthesis and reactivity of peroxo compounds of the chosen elements are also emphasised therein.

Apart from this, attention has been drawn to the significance of and contemporary interest in the study of metal-acetylacetonato complexes with special reference to alkali-metal acetylacetonates. Some facets of the scope of work on the chosen theme of research has also been enumerated in the **Chapter**.

Chapter II describes the details of the methods of elemental analyses as well as the particulars of the instruments/equipment used for characterisation and structural assessment of the

compounds. Also included in the Chapter is a procedure for obtaining deoxygenated water required for reactivity studies.

The results of reaction of a complex peroxozirconate(IV), $(NH_4)_2[ZrO(O_2)F_2]$, with $SO_2(g)$ in aqueous medium and a rationalisation of the observations constitute the subject matter of Chapter III. The reaction of monoperoxofluorozirconate(IV) complex, $(NH_4)_2[ZrO(O_2)F_2]$ with $SO_2(g)$ in aqueous medium afforded a new ternary complex of the metal, $(NH_4)_2[ZrO(SO_4)F_2].7H_2O$. The compound has been characterised by chemical analyses, magnetic susceptibility measurements, IR and laser Raman (LR) spectroscopic studies. The spectral data (IR and LR) suggest the presence of a zirconyl (ZrO^{2+}) core and the occurrence of chelated sulphato ligand in the complex. An interpretative account of the results has been given and the advantages of such a route to mixed fluorozirconates highlighted.

Chapter IV of the thesis includes the synthesis, characterisation, and structural assessment of new heteroligand peroxo compounds of tetravalent thorium of the types $A_2[Th(O_2)F_2(OH)_2].nH_2O$ ($A=NH_4$, $n=3$; Na or K, $n=1$) and $[Th_2(O_2)_3L(H_2O)_4].5H_2O$ ($L=C_2O_4$ or SO_4). The identity and structural motifs of the compounds have been ascertained from the results of chemical analysis, magnetic susceptibility measurements, IR, and LR spectroscopic studies. While freshly prepared hydrated thorium oxide, $ThO_2.nH_2O$, was used for the synthesis of fluoroperoxothorates(IV), aqueous solutions of $Th(NO_3)_4.6H_2O$ were used for the preparation of the molecular complexes. The fluoroperoxothorates were prepared from the reaction of hydrated ThO_2 with aqueous HF and H_2O_2 at pH 10-11 maintained by the addition of the corresponding alkali-metal hydroxide or aqueous ammonia. The molecular peroxo(oxalato)-, and peroxo(sulphato)-thorium compounds were synthesised by a direct reaction of $Th(NO_3)_4.6H_2O$ with $A_2C_2O_4$ or A_2SO_4 ($A=NH_4$, Na or K), and H_2O_2 at pH 7-8 and 2, respectively. Vibrational spectroscopy has been used to provide evidence for the presence of triangularly (C_{2v}) bonded peroxide and terminal fluoride ligands in the complexes, $A_2[Th(O_2)F_2(OH)_2].nH_2O$ ($A=NH_4$, n=3; Na or K, n=1). The occurrence of both chelated and bridging `peroxo' ligands in the molecular complexes $[Th_2(O_2)_3L(H_2O)_4].5H_2O$ ($L=C_2O_4$ or SO_4) were ascertained from the results of laser Raman spectroscopic studies. An internal comparison of the new results with those of its congeners, Ti and Zr, has been made.

Chapter V of the thesis deals with the results of studies on complex peroxouranates. The salient features of the content of this Chapter are: (i) the synthesis of a new dinuclear peroxouranium complex, $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ and investigation of its reactions with $SO_2(g)$, $CO_2(g)$ and $NO_2(g)$, in aqueous medium, and (ii) a new and easier synthesis of $A_2[UO_2(O_2)F_2].nH_2O$ ($A=NH_4$, n=0; K, n=1), and the reaction of $(NH_4)_2[UO_2(O_2)F_2]$ with $SO_2(g)$. The compounds and their reaction products were characterised by chemical analyses, magnetic susceptibility and molar conductance measurements, IR and LR spectroscopic studies. The synthesis of the complex,

$(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$, was accomplished from the reaction of $UO_3.4H_2O$ with H_2O_2 at a pH value of 8-9 maintained by the addition of aqueous ammonia (sp. gr. 0.9). The $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ is a rare example of a peroxouranium species containing structurally two different types of `peroxo' ligands as ascertained by spectroscopic investigations. In an attempt to explore some aspects of the reactivity of this complex, its reaction with small inorganic molecules viz., SO_2(g), CO_2(g), and NO_2(g) were conducted in aqueous medium. The reaction sequence was rationalised by isolation of products at different stages of the reactions. An internal comparison of the results clearly demonstrate a general reactivity pattern. The reaction with each of the chosen substrates proceeds through a unique, isolable intermediate, $UO_2(O_2).4H_2O$, which ultimately produces a sulphato, a carbonato or presumably a nitrato complex of UO_2^{2+}. Reduction of the metal centre did not take place in any of the reactions.

Facility of the reactions seem to follow the sequence $SO_2(g) > NO_2(g) > CO_2(g)$. In order to understand the nature of the reactions several control experiments were conducted involving $(NH_4)_2[U_2O_4(O_2)_3(H_2O)_2].4H_2O$ and N_2(g) only and bubbling N_2(g) through aqueous solutions of the complex separately in presence of H_2SO_4, $(NH_4)_2SO_4$, NH_4HCO_3, $(NH_4)_2CO_3$, HNO_3, and NH_4NO_3 and the results rationalised. An internal comparison of the results of various reactions has been made.

Also incorporated in this Chapter is a new synthesis of $A_2[UO_2(O_2)F_2].nH_2O$ ($A=NH_4$, n=0, K, n=1). One of the most significant points about the new synthesis is the redundancy of the use of hydrofluoric acid. The strategy of the new synthesis was based on a direct interaction of $UO_3.4H_2O$ with H_2O_2 in the presence of the corresponding bifluorides, AHF_2. The complex $(NH_4)_2[UO_2(O_2)F_2]$, has been shown to undergo SO_2 insertion into the O-O bond of coordinated peroxide leading to the formation of a mixed fluoro(sulphato)uranate(VI), $(NH_4)_2[UO_2(SO_4)F_2].H_2O$. The mode of coordination of the sulphato ligand has been ascertained. The ligand occurs as a bridging bidentate sulphate. This Chapter also embodies an account of interesting H-bonding phenomena exhibited by $(NH_4)_2[UO_2(O_2)F_2]$ and $(NH_4)_2[UO_2(SO_4)F_2].H_2O$ as ascertained from IR studies.

Reported in **Chapter VI** of the thesis are the synthesis and reactivity of a new peroxocarbonate, $NH_4[HCO_4].3H_2O$, and a rapid synthesis of $(NH_4)_2[CO_3].H_2O_2$. The white crystalline, $NH_4[HCO_4].3H_2O$, has been synthesised from the reaction of an ammoniacal solution of NH_4HCO_3 with 30% H_2O_2 (pH. 10.5) at -5°C to -10°C, while the perhydrate, $(NH_4)_2[CO_3].H_2O_2$, has been prepared from the reaction of NH_4HCO_3 with 30% H_2O_2 below -5°C. Both the compounds have been characterised by chemical analyses and physicochemical studies. The compounds lose active oxygen contents when left exposed to air. The pH values of $10^{-3}M$ aqueous solutions of the compounds have been found to be 8-9.5. Based upon this efficacy of the compounds as viable substitutes for alkaline-H_2O_2 reagent has been tested. Each of the compounds has been shown to bring about transformation of salicylaldehyde to catechol, and benzonitrile to benzamide in *ca.* 40% yields. In addition, in the presence of an acid, the compounds are capable of oxidising anthracene to anthraquinone, and n-butanol to n-butanaldehyde. The identity of the products of reactions were ascertained by chemical and physicochemical studies, and comparing with those of the authentic samples.

Chapter VII, indeed the concluding Chapter of the thesis, addresses to studies on alkalimetal acetylacetonates. The principal features of the subject matter are the first synthesis of heretofore unreported rubidium acetylacetonate, Rb(acac), and a direct synthesis of caesium acetylacetonates, Cs(acac), and evidence for strong ion-association/ion-pair formation in alkali-metal acetylacetonates. The synthesis of both Rb(acac) and Cs(acac) was achieved from the reactions of acetylacetone with the corresponding alkali-metal carbonates. In order to investigate the ion-pair formation in alkali-metal acetylacetonates, the compounds A(acac) (A=Li, Na or K) were also synthesised following literature methods. The results of molar conductance measurements of A(acac) (A=Li-Cs) compounds provide evidence for strong ion-association/ion-pair formation in such compounds. The ^{1}H-NMR (recorded in DMSO-d_6) spectral pattern of A(acac) (A=Li-Cs) compounds further augments the view. The extent of ion-association is found to decrease steadily from

Li(acac) to Cs(acac). A rationalisation of the results has been presented.

A short review on the current status of metal-acetylacetonate chemistry (described towards the later part of the Chapter I) has been published.

The results of studies described in Chapters III, IV and VII have been published, while a part of the work described in Chapter V is now under revision, and those incorporated in Chapter VI are under communication.

Chapter I

Proc. Ind. natn. Sci. Acad., 1989, 55, 194.

Chapter III

Polyhedron, 1990, 9, 1653.

Chapter IV

Inorg. Chim.Acta., 1989, 160, 147.

Chapter VII

J. Chem.Res.(S), 1991, 251.

Chapter V

J. Chem. Soc., Dalton Trans. (under revision).