# SYNTHESIS AND STRUCTURAL ASSESSMENT OF FLUORO COMPLEXES OF BERYLLIUM AND PEROXO COMPLEXES OF URANIUM AND A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

(ABSTRACT)

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# SYNTHESIS AND STRUCTURAL ASSESSMENT OF FLUORO COMPLEXES OF BERYLLIUM AND PEROXO COMPLEXES OF URANIUM AND A NEW REAGENT FOR THE SPECTROPHOTOMETRIC DETERMINATION OF URANIUM

## ABSTRACT

The present thesis embodies the results of investigations pertaining to the chemistry of fluoroberyllates, especially mixed fluoroberyllates, peroxo and heteroligand peroxo chemistry of uranium as well as development of a spectrophotometric method for the determination of uranium. The content of the thesis has been divided into six Chapters. Each Chapter has been presented as a self contained one including relevant bibliography, while Chapters III to VI also contain sections on a very brief Introduction, Experimental and Results and Discussion. Chapter I provides a brief general introduction covering the importance of and interest in fluoro, especially mixed fluoro chemistry of beryllium and peroxo and hetero-ligand peroxo chemistry of Uranium. Apart from this, the intricacies involved in and the problems encountered with the reported synthetic methodologies as well as the main features of the results of reactivity studies have been highlighted. Besides, attention has been drawn to the significance of and contemporary interest in the newer methodologies for the spectrophotometric determination of uranium in solution. Also clearly figures in this Chapter is the scope of work in the chosen aspects of the present research.

Chapter II describes the details of the methods of elemental analyses as well as the particulars of the instruments/equipment employed in characterising and assessing the structure of the newly synthesised compounds. A procedure for obtaining deoxygenated water required for reactivity studies has been included herein. The synthesis and characterisation of new mixed-fluoro complexes of beryllium constitute the subject matter of Chapter III. Heteroligands were drawn from acid oxalate, $HC_2O_4^-$, glycinate, and acid-phosphate, $H_2PO_4^-$. The complexes were synthesised from the reactions of the products obtained by treating $BeSO_4.4H_2O$ with AOH(A = $NH_4$, Na or K), with AF and the corresponding coligands at pH 2. The compounds have been characterised by elemental analyses, solution electrical conductance measurements, IR and LR spectroscopy. The spectroscopic investigation suggests that the oxalate occurs in the complexes as an acid oxalate, being coordinated through the O-atoms. The phosphate and the glycine in respective complexes have been found to be present as an acid phosphate and glycinate. The following complexes have been obtained from the synthetic study:

(i) $A_2[BeF_3(HC_2O_4].nH_2O$ (A = $NH_4$ or Na, n = 1; A = K, n = 0),

(ii) $A_2[BeF_3(NH_2CH_2COO)].H_2O$(A = $NH_4$ or Na)

and

(iii) $A_2[BeF_2(H_2PO_4)_2]$ (A = $NH_4$ or K).

The compounds are all stable under ordinary conditions. The laser Raman (LR) spectrum of $K_2[BeF_3(HC_2O_4)]$ has been particularly important as it provided a clean evidence for $HC_2O_4^-$ by showing an intense signal at 1630 $cm^{-1}$ in support of the contention. In addition, the IR spectra of ammonium salt of the complexes demonstrated the presence of hydrogen bonding.

Chapter IV of the thesis includes the synthesis, characterisation and structural assessment of new heteroligand monoperoxouranates(VI) of the type,

(i) $A_3[UO_2(O_2)(PO_4)(H_2O)_2].nH_2O$ (A = $NH_4$ or K,n = 4;A = Na,n = 2) and

(ii)$A_2[UO_2(O_2)F_2(H_2O)_2].nH_2O$ (A = $NH_4$, n = 0, A =Na or K,n = 2).

These compounds were synthesised from the reaction of $UO_2(NO_3)_2.6H_2O$ with $H_2O_2$ and the corresponding coligands at pH 7. Also included in this Chapter is the reactivity of $(NH_4)_2[UO_2(O_2)F_2(H_2O)_2]$ with $SO_2.xH_2O$ leading to the isolation of $(NH_4)_2[UO_2(SO_4)F_2].H_2O$. The complexes have been characterised by elemental analysis, solution electrical conductance measurements, and vibrational spectroscopic studies. As a representative case, the $(NH_4)_3[UO_2(PO_4)(H_2O)_2].4H_2O$ was pyrolysed at 710°C. The product obtained was ascertained to be $(UO_2)_2P_2O_7$. In order to probe into the homogeneity of the peroxophosphatouranates(VI), $K_3[UO_2(O_2)(PO_4)(H_2O)_2].4H_2O$, as a representative case, was subjected to Scanning Electron Micrography (SEM). The SE micrograph gave evidence for the presence of cubic crystals as well as the homogeneity of the product.

Vibrational Spectroscopy being the powerful tool in probing the structural motifs of the compounds was used in characterising the compounds. It was inferred from the IR spectra of these complexes that while phosphate occurring as $H_2PO_4^-$, was coordinated to metal centre in a chelated bidentate manner, at least one of the fluorides in peroxofluorouranates(VI) might be acting as a bridging ligand. The mode of peroxide coordination to the $UO_2^{2+}$ centre in both the heteroligand peroxouranates, i.e., peroxo(phosphato) and peroxo(difluoro)uranates, is in a triangular bidentate manner($C_{2v}$ local symmetry) as ascertained by vibrational spectroscopic studies.

Chapter V of the thesis deals with the results of studies on complex diperoxouranates(VI). The salient features of the content of this Chapter are:

(i) the synthesis of newer diperoxouranates(VI), $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = $NH_4$, Na or K) and investigation of their reactions with $SO_2.xH_2O$, $CO_2(g)$ and $HF_2^-$ in aqueous medium and (ii) synthesis of newer heteroligand diperoxouranates(VI) of the type, $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$ and $(NH_4)_3[UO_2(O_2)_2Q].4H_2O$ (Q = 8-quinolinolate).

While the binary diperoxo uranates(VI), $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = $NH_4$, Na or K) were synthesised by the direct reaction of $UO_2(NO_3)_2.6H_2O$ with $H_2O_2$ at pH 10, adjusted by the addition of the corresponding alkali hydroxide solutions or aqueous ammonia, the corresponding heteroligand complexes, $Na_4[UO_2(O_2)_2(CO_3)].2H_2O$

and $(NH_4)_3[UO_2(O_2)_2Q].4H_2O$, were accessed by conducting similar reactions in presence of the respective co-ligands.

In order to explore their reactivity profiles, reactions of the newly synthesised diperoxouranates with inorganic substrates, viz.,$SO_2.xH_2O$,$CO_2(g)$ and $HF_2^-$ were conducted in aqueous medium. Consequently, newer sulphato, $A_2[UO_2(SO_4)_2].nH_2O$ (A = $NH_4$ or K, n = 1 and A = Na, n = 4), peroxocarbonato, $A_2[UO_2(O_2)(CO_3)].2H_2O$ (A = Na or K), and fluoro complexes, $A_6[UO_2F_8].nH_2O$ (A = $NH_4$, n = 0 and A = Na, n = 2), were obtained.

The newly synthesised compounds and their reaction products were all characterised by chemical analyses, molar conductance measurements, IR and LR spectroscopic studies. Vibrational spectroscopy clearly demonstrated that both the peroxides in $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ (A = $NH_4$,Na or K) were coordinated to $UO_2^{2+}$ centre in a triangular bidentate ($C_{2v}$) manner. Evidences for coordinated $H_2O$ were also obtained in support of the formulations, $A_2[UO_2(O_2)_2(H_2O)_2].2H_2O$ ( A = $NH_4$, Na or K). As regards the structural motifs of heteroligand diperoxo complexes of $UO_2^{2+}$, here again, the peroxides were coordinated to the $UO_2^{2+}$ centre in a triangular bidentate manner ($C_{2v}$ local symmetry), while the heteroligands, $CO_3^{2-}$ and 8-quinolinolate, in the respective complexes were bonded to $UO_2^{2+}$ in a chelated bidentate manner.

Chapter VI, indeed the concluding Chapter of the thesis, addresses to the studies on the development of a newer spectrophotometric method for the determination of uranium(VI) using a new reagent, o-hydroxyanisole, commonly known as guaiacol. This reagent reacts rapidly with $UO_2^{2+}$ at pH 6-8, forming a stable yellowish-orange chelate, suitable for spectrophotometric determination of uranium. The presence of methoxy and $OH^-$ groups in 1 and 2 positions, respectively, of the benzene ring facilitates chelate formation. Effects of variables for optimum colour development were studied. Adherence to Beer's law was tested and precision and accuracy were ascertained. The molar absorptivity and Sandell's sensitivity of the new method are $3.72 \times 10^3$ $l.mol^{-1}cm^{-1}$ and 0.063 $\mu g cm^{-2}$, respectively. The selectivity of the method has been improved by the solvent extraction of uranium(VI) in TBP (tributylphosphate) and then developing the colour in solution. The method has been successfully applied to real samples (rock samples of diverse compositions) and the results obtained are found to be favourably comparable with those obtained separately from fluorimetry and radiometry.

The results of studies incorporated in Chapters III and VI have been published and rest is under communication.

Chapter - III

*Bull. Chem. Soc. Jpn.*, 1992, 65, 552.

Chapter-IV

Communicated

Chapter - V

Communicated

Chapter VI

*J.Radioanal. Nucl. Chem.*, 1991,154, 331.