SYNTHESIS AND STRUCTURAL ASSESSMENT OF HETERO-LIGAND—PEROXO, ACETATO, AND ACETYLACETONATO COMPLEXES OF URANIUM(VI) AND OXALATO AND MIXED-LIGAND—FLUORO COMPLEXES OF MANGANESE(III)

ABSTRACT

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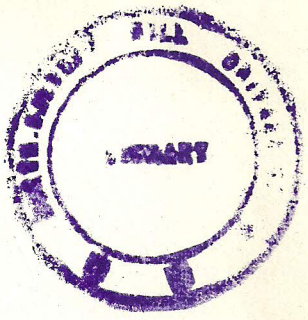

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ABSTRACT

Synthesis and Structural Assessment of Hetero-Ligand-Peroxo, Acetato, and Acetylacetonato Complexes of Uranium(VI) and Oxalato and Mixed-Ligand-Fluoro Complexes of Manganese(III)

Abstract

The present thesis deals with the results of studies involving the syntheses and assessment of structures of some hetero-ligand-peroxo, acetato and acetylacetonato complexes of uranium(VI), and the synthesis and physico-chemical studies of oxalato and mixed-ligand-fluoro complexes of manganese(III). The thesis comprises of a total of eight Chapters. The results described in Chapters 3-8 have been grouped into two, namely, Part A and Part B. While Part A, consisting of Chapters 3-5, deals with the studies on the above-mentioned aspects of uranium chemistry, Part B, which includes Chapters 6-8, contains the results of studies on manganese(III) chemistry.

Chapter 1 presents a brief introduction pertaining to the work embodied in the thesis. The importance of and the interest in the studies of peroxo-metal chemistry in general, and heteroligand peroxouranate(VI) compounds in particular, and the problems associated with the reported methods of syntheses

of acetato, and acetylacetonato complexes of uranium are highlighted in this Chapter. Another piece of a problem, as emphasized in this Chapter, is the lack of evidence regarding the mass spectrometric studies of bis(acetylacetonato)dioxo-uranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$. Apart from uranium, the difficulties encountered in stabilizing manganese(III) in an aqueous medium, and the importance of F^- ligand in stabilizing this particular oxidation state of the metal both in solution as well as in solid state have been accentuated in this Chapter. Peculiarities encountered with structural and magnetic properties of some fluoro and mixed-fluoro complexes of manganese(III) are highlighted. This Chapter also projects the scope of work on the chosen aspects of uranium and manganese chemistry.

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

PART A

Synthesis and structural assessment of alkali-metal and ammonium difluorodioxoperoxouranates(VI), $A_2[UO_2(O_2)F_2]$ ($A = NH_4$ or Cs) and alkali-metal difluorodioxoperoxo-uranate(VI) monohydrates, $A_2[UO_2(O_2)F_2].H_2O$ ($A = K$ or Rb), constitute the subject matter of Chapter 3.

The synthesis of $A_2[UO_2(O_2)F_2]$ (A = NH_4 or Cs) and $A_2[UO_2(O_2)F_2].H_2O$ (A = K or Rb), were achieved from the reaction of the product obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with NH_4OH or KOH, with AF (A = NH_4, Rb or Cs) or KF, 30% H_2O_2, and a very small amount of 40% HF in the mol ratio of $UO_2(NO_3)_2.6H_2O$: AF : H_2O_2 at 1 : 4 : 110.8 at pH 6.5-7. The compounds have been characterized by chemical analyses, magnetic susceptibility measurements, and IR spectroscopic studies. The IR spectra provide evidence for the occurrence of translinked O=U=O, coordinated peroxide, and coordinated fluoride. Further the spectra suggest that the peroxo group is bonded to the UO_2^{2+} center in a triangular bidentate (C_{2v}) manner. The complex $[UO_2(O_2)F_2]^{2-}$ may have a polymeric structure through -U-F-U-F-U- chains.

Chapter 4 of the thesis provides an account of synthesis and physico-chemical studies of alkali-metal dioxoperoxo(carbonato)uranate(VI) monohydrates, $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K), alkali-metal and ammonium dioxoperoxo(sulphato)aquouranates(VI), $A_2[UO_2(O_2)SO_4(H_2O)]$ (A = Na or NH_4), and molecular complex peroxouranates $[UO_2(O_2)L\text{-}L]$ (L-L = ethylenediamine (en), 2,2'-bipyridine (bipy), 1,10-phenanthroline (o-phen), and $[UO_2(O_2)glyH]$ (glyH = glycine). The complexes $A_2[UO_2(O_2)(CO_3)].H_2O$ (A = Na or K) have been synthesised

from the reaction of the product obtained by treating $UO_2(NO_3)_2 \cdot 6H_2O$ with AOH and $AHCO_3$ (ratio $U:CO_3^{2-} = 1:4$) with an excess of 30% H_2O_2 at pH 7-8. The presence of trans O=U=O, triangular bidentate O_2^{2-} and chelated CO_3^{2-} groups in $\left[UO_2(O_2)(CO_3)\right]^{2-}$ has been ascertained from the results of IR and laser Raman (lR) spectroscopic studies. The complex $A_2\left[UO_2(O_2)(CO_3)\right] \cdot H_2O$ can be dehydrated at ca 100 °C.

The syntheses of yellow microcrystalline alkali-metal and ammonium dioxoperoxo(sulphato)aquouranates(VI), $A_2\left[UO_2(O_2)SO_4(H_2O)\right]$ (A = NH_4 or Na) have been achieved 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 sulphuric acid, in mol ratio $UO_2(NO_3)_2 \cdot 6H_2O : H_2O_2 : SO_4^{2-}$ of 1:111:5, at pH 6 maintained by the addition of the corresponding alkali-metal or ammonium hydroxide. Precipitation of the compound was completed by the addition of ethanol. IR and lR spectra suggest that peroxide (O_2^{2-}) and SO_4^{2-} ions in $\left[UO_2(O_2)SO_4(H_2O)\right]^{2-}$ are bonded to the UO_2^{2+} center in a bridging and in a monodentate manner, respectively. The H_2O molecule is also coordinated to the uranyl center. The complex peroxo(sulphato)uranates are diamagnetic in nature and are practically insoluble in water. They are stable upto 110 °C. The complex species $\left[UO_2(O_2)SO_4(H_2O)\right]^{2-}$ very likely has a hexacoordinated polymeric structure through a -U-O-O-U-O-O-U- chain containing peroxide bridges.

The synthesis of molecular peroxouranates $[UO_2(O_2)L\text{-}L]$ (L-L = o-phen or bipy) was accomplished from the reaction of an aqueous solution of $UO_2(CH_3COO)_2 \cdot 2H_2O$, with an ethanolic solution of o-phen or bipy, and an excess of H_2O_2, with the ratio of U:o-phen or bipy being maintained at 1:1, at pH 3.5-4. The infrared spectra provide evidence for the presence of triangular bidentate O_2^{2-} and chelated bidentate o-phen or bipy ligands in the compounds. The compounds are insoluble in water and practically insoluble in organic solvents at room temperature. The compounds $[UO_2(O_2)en]$ and $[UO_2(O_2)glyH]$ were synthesised from the reaction of the product, obtained by treating an aqueous solution of $UO_2(NO_3)_2 \cdot 6H_2O$ with aqueous ammonia, with a small amount of aqueous sulphuric acid, ethylenediamine (en) and glycine (glyH), respectively, and an excess of 30% H_2O_2. The suitable pH for the synthesis of $[UO_2(O_2)glyH]$ was found to be ca 6.5, while that for $[UO_2(O_2)en]$ was ascertained to be ca 9. The IR spectra of $[UO_2(O_2)en]$ and $[UO_2(O_2)glyH]$ exhibit bands characteristic of $\nu(U{=}O)$ (translinked O=U=O), $\nu(O\text{-}O)$, and $\nu(U\text{-}O_2)$ in addition to the absorptions originating from the presence of coordinated en and glyH in the respective cases. While en in the former is bonded to the UO_2^{2+} center in a chelated fashion, glyH in the latter occurs in its Zwitterionic form and coordinates with the metal center through its carboxylic oxygen atom. The spectra also provide strong

evidence for the presence of a triangularly bonded (C_{2v}) peroxide (O_2^{2-}) in each of the complexes. The compounds are all diamagnetic in nature in accord with the presence of hexavalent uranium.

Reported in Chapter 5 are new method of syntheses of alkali-metal and ammonium triacetatodioxouranates(VI), A$[UO_2(CH_3COO)_3]$ (A = Na, K, or NH_4), diacetatodioxouranate(VI) dihydrate $[UO_2(CH_3COO)_2].2H_2O$, and bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2.2H_2O$. Also reported in this Chapter is an interpretative account of the results of electron ionization mass spectrometric studies of $UO_2(C_5H_7O_2)_2$.

The A$[UO_2(CH_3COO)_3]$ (A = Na, K or NH_4) compounds have been synthesised from the reaction of the product, obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with NaOH or KOH or aqueous ammonia, with ACH_3COO (A = Na, K or NH_4) and a small amount of 10% acetic acid in the mol ratio of $UO_2(NO_3)_2.6H_2O$:ACH_3COO as 1:3. The synthetic reactions were conducted at pH 5. The synthesis of $[UO_2(CH_3COO)_2].2H_2O$ has been achieved from the reaction of the product, obtained by treating an aqueous solution of $UO_2(NO_3)_2.6H_2O$ with aqueous ammonia, with an excess of glacial acetic acid. Characterization of the compounds were made by elemental analyses and IR spectroscopic studies.

A direct method for the synthesis of bis(acetylacetonato)-dioxouranium(VI) dihydrate, $UO_2(C_5H_7O_2)_2 \cdot 2H_2O$, has been developed. The new method does not require any buffer. The electron ionization (EI) mass spectra of $UO_2(C_5H_7O_2)_2$ showed a molecular ion signal at m/z 468 without indication of any association in the gaseous state. The molecular ion $[UO_2(C_5H_7O_2)_2]^{+\bullet}$ loses either $CH_3^{\bullet}$ and $C_4H_4O_2$, or $OCCH_2$ and undergoes internal reduction to give $[UO_2(C_5H_7O_2)]^{+\bullet}$. The radical ion $[UO_2(C_5H_7O_2)]^{+\bullet}$ suffers a sequential loss of $CH_3^{\bullet}$ and $C_4H_4O_2$ to produce ultimately the bare species $[UO_2]^{+}$.

PART B

Chapter 6 of the thesis deals with a direct synthesis of potassium tris(oxalato)manganate(III) trihydrate, $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$. The new method of synthesis involves a reaction among MnO(OH), $H_2C_2O_4$, and $K_2C_2O_4$, in the ratio of 1:1.5:1.5, at ca 0°C directly giving $K_3[Mn(C_2O_4)_3] \cdot 3H_2O$ in a high yield. The identity of the compound has been ascertained on the basis of the results of elemental analyses, magnetic susceptibility measurements, electronic and IR spectroscopic studies. Evidence for the existence of the complex $[Mn(C_2O_4)_3]^{3-}$ ion in solutions in the presence of countercations like Na^+, Rb^+, Cs^+ or NH_4^+ has also been provided in this Chapter. Isolation of the corresponding $[UO_2]^{+}$ salts in the solid state was not possible owing to their instability.

Synthesis and assessment of structures of a number of new mixed ligand fluoro complexes of manganese(III) of the types $A_3[MnF_2L_2].3H_2O$ ($L = C_2O_4^{2-}$, A = K; $L = HPO_4^{2-}$, A = Na, K or NH_4), and $A[MnF_4L_n].3H_2O$ (L = EDTA, n = 1, A = K; L = glyH, n = 2, A = Na, K or NH_4), form the subject matter of Chapter 7.

Synthesis of the compounds were accomplished by the following methods:

(i) $K_3[Mn(C_2O_4)_2F_2].3H_2O$ was obtained from the reaction of $KMnO_4$ with $H_2C_2O_4$, and KF in the ratio of 1:4:2 at ca 0°C in the absence of light;

(ii) $A_3[Mn(HPO_4)_2F_2].3H_2O$ (A = Na, K or NH_4) was prepared from the reaction of MnO(OH) with H_3PO_4 and AF;

(iii) $K[Mn(EDTA)F_4].3H_2O$ was synthesised from the reaction of MnO(OH), 48% HF, KF, and ethylenediaminetetra-acetic acid (EDTA); and

(iv) $A[Mn(glyH)_2F_4].3H_2O$ (A = Na, K or NH_4) was obtained from the reaction of MnO(OH), 40% HF, glycine (glyH), and A_2CO_3.

The compounds are cherry-red to pink-brown in colour. While $K_3[Mn(C_2O_4)_2F_2].3H_2O$ is unstable, the other compounds are generally stable. The compounds have been characterized by chemical analysis, chemical determination of oxidation

state of manganese, magnetic susceptibility measurements, and IR and electronic spectroscopic studies. The results suggest that complex species in each case has a distorted octahedral structure. The compounds have normal magnetic moments in conformity with the occurrence of a high spin d^4 manganese(III) in each of them.

Chapter 8 indeed the last Chapter of the thesis describes synthesis and physico-chemical studies of molecular mixed-ligand fluoro complexes of manganese(III), viz., $[Mn(o\text{-phen})F_3(H_2O)].2H_2O$, $[Mn(bipy)F_3(H_2O)].2H_2O$, and $[Mn(urea)_2F_3].3H_2O$. The compounds were synthesised from the reaction of a solution of MnO(OH) in 48% HF with an ethanolic solution of 1,10-phenanthroline (o-phen), an ethanolic solution of 2,2'-bipyridine (bipy), and solid urea, respectively. They are stable in the solid state. Characterization of the compounds were made from the results of elemental analyses, chemical determination of oxidation state of the metal, magnetic susceptibility measurements, infrared and electronic spectroscopic studies. While o-phen and bipy occur as bidentate ligands in the respective compounds, urea in $[Mn(urea)_2F_3].3H_2O$ acts as a monodentate ligand. The compounds $[Mn(o\text{-phen})F_3(H_2O)].2H_2O$ and $[Mn(bipy)F_3(H_2O)].2H_2O$ exhibit normal magnetic moments (ca $5\ \mu_B$) at room temperature, whereas $[Mn(urea)_2F_3].3H_2O$

has a magnetic moment of 4.3 μ_B. The complexes have distorted octahedral structures.

The results of studies described in Chapters 3,4,5 and 6 have been published, and those described in Chapters 7 and 8 are under communication.

Chapter 3

J. Chem. Soc., Dalton Trans., 1985, 409.

Chapter 4

J. Chem. Soc., Dalton Trans., 1986, 709; Inorg. Chem., 1986, 25, 2354.

Chapter 5

Ind. J. Chem., 1986, 25A, 1048;

Int. J. Mass Spectrom. Ion Processes, 1986, 71, 109.

Chapter 6

Inorg. Chem., 1985, 24, 447.