EVIDENCE FOR THE OCCURRENCE OF MANGANESE(III) IN $[MnO_4]^-/SO_2$ REDOX REACTION AND SYNTHESIS AND PHYSICO-CHEMICAL STUDIES OF NEWER FLUORO COMPOUNDS OF MANGANESE(III) AND URANIUM(VI) $[UO_2^{2+}]$

ABSTRACT

P. SRINIVAS

DEPARTMENT OF CHEMISTRY
SCHOOL OF PHYSICAL SCIENCES
NEHU

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Evidence for the Occurrence of Manganese(III) in $[MnO_4]^-/SO_2$ Redox Reaction

And

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Abstract

The chemistry of manganese(III) has drawn the attention of a number of research groups around the globe with each group having a specific interest. Somewhat similar is the situation with the chemistry of uranium, in which the interest of chemists never seems to diminish. In cognizance to the contemporary interest, a few selective problems related to the two chemistries were identified for the present Ph.D. research on which the studies were conducted. Thus the results of the investigation on the occurrence of manganese(III) in the $[MnO_4]^-/SO_2$ redox reaction as well as the synthesis and structural evaluation of newer fluoro and mixed-fluoro complexes of manganese(III) and uranium(VI) $[UO_2^{2+}]$ constitute the subject matter of the present thesis. The content of the thesis has been distributed over six Chapters. Attempts have been made to present each Chapter as a self-contained one including bibliography relevant to the text. For Chapters III-VI sections on brief introduction, experimental

description followed by results and discussion have been provided.

Chapter I presents a general introduction pertaining to the type of work undertaken. The relevant background information of the chemistry of the two metals viz., manganese and uranium has been discussed in this Chapter. In addition, the importance of and interest in the chosen aspects of chemistry of the two metals are highlighted. Special emphasis has also been put onto their fluoro chemistry. During this endeavour, a few intriguing problems have been identified to constitute the scope of the present work.

Chapter II describes the details of the methods used for the preparations of starting materials and elemental analyses as well as the particulars of instruments/equipment used for characterization and structural assessment of the newly synthesized compounds.

In Chapter III evidence has been provided for the occurrence of manganese in its tripositive level as an intermediate in the $[MnO_4]^-/SO_2$ redox reaction in an aqueous medium by experimentation involving *in situ* methods as well as by the isolation of manganese(III) products under similar conditions. Fluoride has been used as the intermediate stabilizer. While a combination of EPR and electron absorption spectroscopies was used to provide *in situ* evidence, the results of chemical analyses, chemical determination of oxidation level of manganese, magnetic susceptibility measurements and spectroscopic analyses were used

to ascertain the identity of the isolated products in support of the notion.

The $KMnO_4$ —— SO_2 redox reaction carried out with $Mn:F^-$ atom ratio of 1:4 indicated that the process involved three different stages: (i) formation of a brown product at pH 3-2.5, (ii) formation of a pink solid at pH 2.5-2 and (iii) finally dissolution of the pink product at pH < 2 accompanied by decolourisation of the reaction solution [*cf.* Mn(II)]. However, when an analogous reaction was conducted with $Mn:F^-$ concentration ratio of 1:10, the observations were nearly similar except that at pH 3-2.5 a brown solution instead of a brown product and at pH 2.5-2 a rose-pink product in lieu of a pink species were obtained. While the brown product, isolated from the reaction in which $Mn:F^-$ concentration was held at 1:4, did not adhere to any fixed stoichiometry, the oxidation level of the metal in the product was +3 [as ascertained by redox titrimetry]. The pink and the rose-pink products were identified to be $K_2[MnF_3(SO_4)]$ and $K_2[MnF_5].H_2O$, respectively.

The *in situ* EPR and electron absorption spectroscopic experiments were carried out in solution as a function of pH. While the ESR scan did not show any signal from the point of initiation of the reaction (*cf.* pH 5.5) till pH 2, the electron absorption spectra displayed a pattern characteristic of manganese(III) starting from pH 3.3 which persisted till pH 2. On

the contrary, for the reaction solutions at pH < 2 a typical six line EPR spectrum characteristic of divalent manganese was observed whereas the electronic absorption signals observed above pH 2 disappeared at pH ≤ 2.

The results therefore suggest that in the presence of F^- ion manganese(VII) is directly reduced to manganese(III) and thence to manganese(II).

Chapter IV of the thesis presents the results of studies on the effect of fluoride on the interaction of manganese(III) with some biochemically relevant ligands, viz., salicylic acid ($salH_2$), 1,2-bis(salicylideneiminato)ethane ($salenH_2$) and N,N'-(acetylacetonato)ethylenediamine ($acacenH_2$) in an aqueous medium. The investigation was monitored by isolation of a variety of binary as well as mixed-fluoromanganates(III) under different conditions.

The complexes $A_2[MnF_4(salH)]$ (A = K, Na or NH_4) were obtained from the reactions of MnO(OH) with alkali hydrofluoride, AHF_2, and salicylic acid at a molar stoichiometry of Mn:F:$salH_2$ of 1:4:6. The mixed-fluoro(salicylato)manganates(III) were green in colour, stable in the solid form and moderately soluble in methanol. The compounds have been characterized by a combination of elemental analyses, chemical determination of the oxidation state of manganese, solution electrical conductivity measurements, IR, LR and electron absorption spectroscopies and Scanning Electron

Microscopy. The room temperature (300 K) magnetic moment values of the complexes were found to lie in the range 4.5-4.6 BM. The values are somewhat lower than that expected for an ideal d^4 system. This has been attributed to weak antiferromagnetic exchange interactions between the contiguous manganese atoms through -Mn-F-Mn-F- chains in the crystal lattice. The notable features of the IR spectra of the complexes were the bands at *ca.* 1604, *ca.*1385 and *ca.*1230 cm^{-1} owing their origins to $\nu_{as}(COO^-)$, $\nu_s(COO^-)$ and δ(O-H) modes, respectively, of the coordinated salicylate ligand. The observed decrease and increase of $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively, as compared to free carboxylic acids, provide evidence for the salicylate being coordinated through its carboxyl oxygens in a monodentate fashion. Further, the lowering in frequency of δ(O-H) (*cf.* free alcohols) also provides an indication for the presence of a protonated hydroxyl functionality in the complexes with the OH group being coordinated to the metal centre through its oxygen lone pair electrons. Complimentary Raman signals at *ca.*1597, *ca.*1315 and *ca.*1237 cm^{-1} as well as the adopted synthetic methodology, wherein the natural pH of the reaction medium was 4, lend support to our contention. It is therefore logical to assume that salicylate is coordinated in a bidentate fashion through its protonated phenolic and deprotonated carboxyl groups. The presence of salicylate as $Hsal^-$ and the manner in which it is coordinated are very important

structural features of the complexes. This type of a situation is rather unusual though not unprecedented.

Also highlighted in this Chapter are the antagonistic effects of F^- on the formation of mixed-ligand fluoromanganates(III). Reactions conducted at similar concentrations of manganese and salicylic acid but higher concentrations of F^-, for instance at the molar stoichiometry of $Mn:salH_2:F$ as 1:6:12, afforded $A[MnF_4(H_2O)_2].H_2O$ (A = K, Na or NH_4). Incidentally, this enables us also to make the first report on the K and NH_4 salts of the diaquotetrafluoromanganates(III). However, the reactions carried out in the presence of a still larger excess of F^- (eg., $Mn:salH_2:F$ = 1:6:24) afforded the very well known binary pentafluoromanganates(III). Control reactions carried out in the absence of salicylic acid required lesser amount of F^- to produce $A[MnF_4(H_2O)_2]$ (A = K, Na or NH_4). But if similar reactions are conducted with comparable concentrations of F^- (*cf.* that of $A[MnF_4(H_2O)_2].H_2O$ the pentafluoromanganates(III) are obtained instead of the corresponding aquatetrafluoromanganates(III). It is thus evident from the above investigation that a large excess of F^- prevents the coordination of different co-ligands present in the reaction medium to manganese(III), thereby leading to the formation of binary fluoromanganates(III) only. This therefore implies that F^- is certainly a better ligand to stabilize and trap manganese(III).

Another objective of the study was to probe the effect of F^- on the interaction of manganese(III) with Schiff bases. Thus, the reactions of MnO(OH) with acacenH_2 or salenH_2 and aqueous HF led to the isolation of heretofore unreported tetrafluoromanganate(III), enH[MnF_4],instead of a mixed-fluoromanganate(III). The room temperature magnetic moment of the complex was recorded to be 4.2 BM. The relatively low value, as compared to that of 4.9 BM normally expected for ideal d^4 systems, is indicative of antiferromagnetic exchange interaction being operative in the system between the contiguous manganese atoms through the formation of -Mn-F-Mn-F- chains in the crystal lattice. This has been interpreted in terms of the effect of the specific counter ion (ie., enH^+) in bringing about a polymeric structure of the complex through enhanced hydrogen bonding. The observance of two strong bands at 578 and 625 cm^{-1} in the IR spectrum of the complex renders it reasonable to assume that the manganese(III) ion in the complex finds itself in a distorted octahedral environment probably with a D_{4h} symmetry (*cf.* MF_6^{n-}). Metatheses reactions of the complex enH[MnF_4] with Rb_2CO_3 and $CsNO_3$ afforded Rb[$MnF_4(H_2O)$] and Cs[$MnF_4(H_2O)$], respectively.

Chapter V of the thesis addresses to a simple synthesis of bis(acetylacetonato)dioxouranium(VI) dihydrate, $UO_2(acac)_2.2H_2O$, investigation of its nucleophilic substitution reactions with F^- as the nucleophile thereby gaining an access to the hitherto

unreported $[UO_2F_6]^{4-}$ and $[UO_2F_7]^{5-}$ and newer mixed-fluorouranates(VI) with organic co-ligands viz., amino acids, acetylacetonate and acetate.

$UO_3.4H_2O$ reacted with acetylacetone ($C_5H_8O_2$) to produce $UO_2(C_5H_7O_2)_2.2H_2O$ in a nearly quantitative yield. $UO_2(acac)_2.2H_2O$ underwent nucleophilic substitution reactions separately with NH_4F and aqueous HF. While the reaction of $UO_2(acac)_2.2H_2O$ with NH_4F in acetylacetone at pH 4 led to the first synthesis of $(NH_4)_4[UO_2F_6]$, the reaction of $UO_2(acac)_2$ generated *in situ*, with a controlled amount of aqueous HF at pH 3.5 afforded the molecular $[UO_2(acac)F(H_2O)_2].3H_2O$ complex. However, on lowering the pH value to *ca.*2 by the addition of aqueous HF only $[UO_2F_2].3H_2O$ was produced. The molecular $[UO_2(acac)F(H_2O)_2].3H_2O$ complex can therefore be considered to be an isolable intermediate in the process $UO_2(acac)_2.2H_2O$ to $[UO_2F_2].3H_2O$. The knowledge obtained from the above reactions as well as the reaction of $K_2U_2O_7$ with KF and acacH at pH 3.5 leading to $K_2[UO_2(acac)F_3]$ suggests that a pH of *ca.* 3.5 is conducive to the synthesis of the mixed-ligand fluoro(acetylacetonato) complexes of UO_2^{2+}.

The mixed-fluoro(acetato) complexes, $A[UO_2(CH_3COO)_2F].3H_2O$ (A = K, Na or NH_4), were obtained from the reactions of $A_2U_2O_7$ with glacial acetic acid and aqueous HF enabling us to provide the missing K and Na salts in addition to providing a general synthetic methodology for the salts of the $[UO_2(CH_3COO)_2F]^-$

complex ion. By adapting a synthetic methodology comparable to that of $[UO_2(acac)F(H_2O)_2].3H_2O$, a molecular mixed-ligand fluoro(acetato) complex $[UO_2(CH_3COO)F(H_2O)_2]$ was obtained from the reaction of $UO_3.4H_2O$ with glacial acetic acid and aqueous HF.

For the hetero-ligand fluorodioxouranates(VI) with amino acids, the co-ligands were drawn from glycine, L-alanine and L-cysteine. While the mixed-fluoro(glycine) complexes, $A_3[UO_2(GlyH)_2F_5].3H_2O$ (A = K or NH_4), were synthesized from the reactions of $UO_3.4H_2O$ with glycine and a combination of AF and HF, the fluoro(alanine) and fluoro(cysteinate) complexes, $K_3[UO_2(AlanH)_2F_5].2H_2O$ and $(NH_4)_5[UO_2(CysH)_2F_5].2H_2O$, were prepared by a method similar to that employed for the fluoro(glycine) complexes except that AHF_2 was used as the fluorinating agent. Each of the mixed-ligand fluoro(amino acid)-dioxouranates(VI), except $K_3[UO_2(GlyH)_2F_5].3H_2O$, was unstable in aqueous solution undergoing decomposition to form intractable products. Significantly, $K_3[UO_2(GlyH)_2F_5].3H_2O$ underwent hydrolysis in an aqueous medium to afford a well-defined but hitherto unknown binary fluoro complex, $K_5[UO_2F_7].2H_2O$, enabling us to make the first report on the heptafluorodioxouranate(VI) species.

The complexes have been characterized by a combination of chemical analyses, solution electrical conductance measurements, infrared (IR) and laser Raman (LR) spectroscopic studies and

Scanning Electron Microscopy. The common features of IR spectra of the complexes were the bands at *ca.*910 and *ca.*375 cm^{-1} assigned to ν(U=O) [trans-linked O=U=O] and ν(U-F) modes, respectively. In addition, bands due to the coordinated co-ligands were observed in the anticipated positions. The IR spectral features adduced support to the chelated bidentate character of the acetylacetonate and acetate ligands in the corresponding mixed-ligand fluoro complexes. Each of the three amino acid co-ligands acted in a unidentate manner being coordinated to UO_2^{2+} through the carboxylate oxygen atom in the respective complexes. While glycine and alanine occur in the zwitterionic form, cysteine is present as a uninegative ligand ($CysH^-$). The laser Raman (LR) spectra could be recorded only for $(NH_4)_4[UO_2F_6]$, $K_5[UO_2F_7].2H_2O$, $[UO_2F_2].3H_2O$, and $K_2[UO_2(acac)F_3]$, while an extensive fluoroscence foiled such attempts on the others. The Raman signals at *ca.*880 and *ca.*380 cm^{-1} complement the IR spectral results. The Scanning Electron Micrographs of the hitherto unreported binary fluoro complexes $(NH_4)_4[UO_2F_6]$ and $K_5[UO_2F_7].2H_2O$ attest to the homogeneity of the products as well as to their crystalline character.

Chapter VI, indeed the concluding Chapter, deals with the synthesis and structural evaluation of new mixed-fluoro complexes of UO_2^{2+} containing inorganic co-ligands as well as developing of two direct synthetic routes to the dioxotetrafluorouranate(VI), $[UO_2F_4]^{2-}$, complex species. The inorganic co-ligands have been

drawn from phosphate, nitrate and hydrazine.

While the reactions of $UO_3.4H_2O$ with H_3PO_4 and alkali hydrofluorides, AHF_2 (A = K, Na or NH_4), [pH *ca.*2] at a steam-bath temperature led to the isolation of new mixed-fluoro(phosphato) complexes of the type $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ (A = K, Na or NH_4), the mixed-fluoro(nitrato) complexes $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4) were obtained from the reactions of $A_2U_2O_7$ with conc.HNO_3 and aqueous HF (48%) maintaining the $UO_2^{2+}:NO_3^-:F^-$ concentration ratio at 1:*ca.*11:*ca.*36. Synthesis of the mixed-fluoro(hydrazine) complex, $[UO_2(N_2H_4)_2F_2].2H_2O$, was rather straight forward. The reaction of $UO_3.4H_2O$ with AHF_2 (A = K or NH_4) and hydrazine hydrate at a natural pH of 8.5 helped hydrazine coordination to UO_2^{2+} in the presence of F^-, since in a basic medium the possibility of formation of hydrazonium ($N_2H_5^+$) ion did not exist.

The characterization of the compounds has been made by a combination of chemical analyses, solution electrical conductance measurements, electron absorption, IR and laser Raman (LR) spectroscopic studies. The occurrence of trans-linked O=U=O, coordinated fluoride and bidentate co-ligands are the common features of the complexes. The appearance of the ν_1 mode at *ca.*905 cm^{-1} and the splitting of the ν_3 mode into three intense bands at *ca.*1000, *ca.*1070 and *ca.*1120 cm^{-1} in the IR spectra of the fluoro(phosphato) complexes clearly indicate the presence of phosphate as PO_4^{3-} and occurring as a chelated ligand. In the IR

spectra of the mixed-fluoro(nitrato) complexes the observance of all the six fundamental modes of vibrations, ν_1 to ν_6 of coordinated nitrate, as well as a large separation of ν_1 and ν_4 modes (*ca.*215 cm^{-1}) makes it rational to suppose that the nitrate in each of the complexes, $A_2[UO_2(NO_3)_3F].3H_2O$ (A = K, Na or NH_4), is present as a bidentate ligand. The IR spectrum of $[UO_2(N_2H_4)_2F_2].2H_2O$ showed a medium intensity sharp band at 955 cm^{-1} which has been assigned to the ν(N-N) stretching vibration. This as well as the similarity of IR spectral features with those of the hydrazine and mixed-ligand hydrazine complexes of different metals enables us to state that the complex contains bidentate hydrazine ligands.

With the afore mentioned success, it has become possible to overcome the synthetic problems related to phosphato- and nitrato-uranyl complexes. The newly synthesized $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ were highly crystalline solids. This has been evidenced by the Scanning Electron Microscopy (SEM). Two different stereo-views of $Na_2[UO_2(PO_4)F(H_2O)_3].3H_2O$, chosen as a representative example, exposed the hexagonal crystal morphology and cylindrical shape of the complex. Though nitrato complexes of uranyl are generally believed to be very weak, the incorporation of fluoride gave additional stability to the uranyl-nitrato system.leading to the synthesis of $A_2[UO_2(NO_3)_3F].3H_2O$. The unaltered solution electrical

conductance values as well as electron absorption spectroscopic studies lend support to the contention.

The laser Raman (LR) spectra of aqueous solutions of the fluoro(phosphato) and fluoro(nitrato)uranates(VI) as well as the corresponding solid complexes, $A_2[UO_2(PO_4)F(H_2O)_3].3H_2O$ and $A_2[UO_2(NO_3)_3F].3H_2O$, were recorded separately. While for the reaction solutions the symmetric stretching frequencies $\nu_s(U=O)$ [of O=U=O] were observed at *ca.*840 cm^{-1}, the band was found to occur at *ca.*900 cm^{-1} for the solids. This has been interpreted in terms of the decrease in the hydration number of the coordination shell of UO_2^{2+} of the solid complexes. Such an experiment could not be conducted for $[UO_2(N_2H_4)_2F_2].2H_2O$ owing to the precipitation of the compound instantaneously on addition of hydrazine.

Two improved synthetic methodologies developed for the dioxotetrafluorouranate(VI), $[UO_2F_4]^{2-}$, species have also been included in this Chapter. While one of the methodologies involved the interaction of a yellow product, obtained by treating a solution of uranyl nitrate with AOH (A = K, Na or NH_4), with aqueous HF (48%) and A_2CO_3, the other was based upon a nucleophilic substitution reaction. In the latter reaction $UO_2(O_2).2H_2O$ was allowed to react with 48% HF in the presence of alkali fluoride, AF (A = K, Na or NH_4), leading to the isolation of $A_2[UO_2F_4].3H_2O$ (A = K, Na or NH_4). The compounds have been

characterized by the techniques mentioned already in the contexts of other complexes.

A large portion of the work described in various Chapters of the thesis has been published in parts:

Chapter III

J.Chem.Soc.,Dalton Trans., 1993 (in press) [Paper No. 3/03328G/DAP].

Chapter V

Proc.Indian Acad.Sci., 1992, 104, 479.

J.Fluorine Chem., 1992, 56, 305.

Polyhedron, 1993, 12, 227.

Chapter VI

Polyhedron (in press) [Paper No. 905478].

A manuscript based upon the results incorporated in Chapter IV is now under preparation for communication.