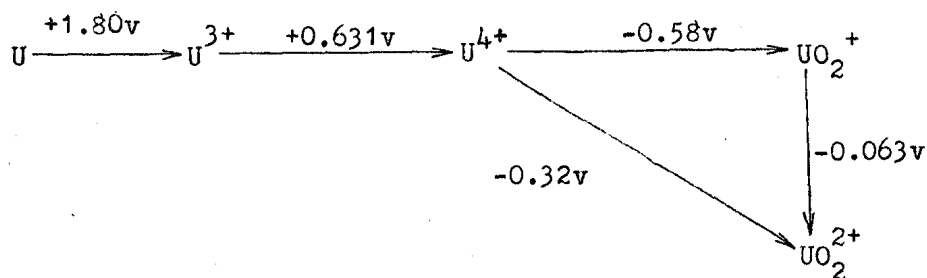


## INTRODUCTION

The element uranium has long been known, but detailed studies of this element was delayed till 1939 when the nuclear fission was discovered. As a nuclear fuel and a source of transuranic elements, particularly of plutonium, uranium is considered as one of the most precious elements having enormous strategic importance. For its use in atomic piles a purity of 99.98%, which is much greater than the usual purity standards set up for other elements, is required. The study of the chemistry and technology of the element is thus of great importance and it is hardly an exaggeration to say that in recent years the chemistry of uranium has been receiving by far the most serious attention to scientists than any other element.

Uranium with an outermost electronic configuration of  $5f^3 6d^1 7s^2$  exhibits variable oxidation states. The closeness of the energy levels of the 5f and 6d orbitals is responsible for such behaviour. Altogether four well-defined oxidation states are known:  $+3(5f^3)$ ,  $+4(5f^2)$ ,  $+5(5f^1)$  and  $+6(5f^0)$ . The hexavalent state is by far the stablest and most well known. Solutions of  $U^{3+}$  ions are rose-purple, those of  $U^{4+}$  ions are deep green and those of uranyl ion,  $UO_2^{2+}$ , bright yellow. These solutions have characteristic absorption spectra which can often be used to identify the valence states of uranium.

in solution<sup>1</sup>. The oxidation/reduction relationships are given by the formal potentials which may be depicted as<sup>2</sup>



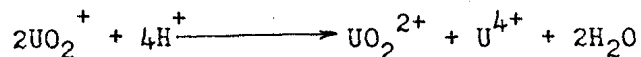
Formal potentials in 1.0N  $\text{HClO}_4$  at 25°

The reducing property of  $\text{U}^{3+}$  ion is so strong that hydrogen is evolved from aqueous solutions. As a consequence the properties of U(III) in aqueous solution are incompletely known. Very powerful reducing conditions are necessary for the formation of U(III) compounds. The compounds isolated are mostly covalent or insoluble. They bear close resemblance to the corresponding lanthanide compounds.

The ion  $\text{U}^{4+}$  is moderately stable in solution and a fairly large number of simple and complex compounds are known for tetrapositive uranium. These are in many cases analogous to and isomorphous with the corresponding compounds of thorium. Due to high charge the U(IV) ion is easily hydrolysed.

The +5 oxidation state of uranium is rather uncommon.

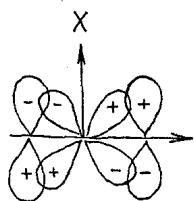
U(V) exists in solution as  $\text{UO}_2^+$  which is much susceptible to oxidation and disproportionation. The equilibrium



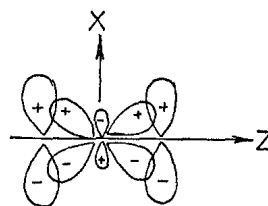
is dependent on pH. Only at low uranium concentration ( $\sim 10^{-3}\text{M}$ ) and between pH of 2 and 2.5 the rate of disproportionation is reported to be negligibly slow. The well characterised compounds of U(V) are the fluoride, chloride, alkoxides, fluoro and oxochloro complexes.

The ion  $\text{U}^{6+}$  is unstable in aqueous solution. Only covalent compounds like  $\text{UF}_6$ ,  $\text{UCl}_6$ ,  $\text{UO}_3$  etc. of U(VI) are known. In aqueous solution  $\text{U}^{6+}$  forms the uranyl ion,  $\text{UO}_2^{2+}$  which remains unchanged in chemical reactions other than reduction. The tendency of uranium to form the uranyl group is so strong that it is the end product of the exposure to moist air of any other type of uranium compounds. Although the uranyl group was originally considered to be an entity of fixed size and geometry, structural studies on a wide variety of compounds have disproved this assumption. The  $\text{UO}_2^{2+}$  group is linear or nearly so. The U-O bond length is susceptible to the number and nature of the coordinating groups which always occur in the equatorial plane. The plane containing O=U=O group is considered as axial. There is probably considerable covalent character present in the U-O bond. The presence of this is supported by the U-O bond

length which varies in the range of 1.6-2.0Å. Simple ionic bonding cannot easily explain why in the vast majority of uranyl compounds there are two short U-O bonds shorter than the sum of the ionic radii of  $U^{6+}$  and  $O^{2-}$  as obtained from the observed uranium-ligand distances other than those in the  $UO_2$  group. It is also probable that apart from  $\sigma$ -covalent character in the  $UO_2^{2+}$  group there is a large  $\pi$  contribution involving oxygen orbitals and a combination of uranium 5f and 6d orbitals. This can be schematically represented as<sup>3</sup>



(a)

$$d_{xz} - p_x$$


(b)

$$f_{xz^2} - p_x$$

Orbital overlaps that may be invoked to explain

$\pi$  bonding in uranyl complexes

Uranyl ion forms a great variety of complexes with negative ions and neutral molecules. Crystallographic data show that four, five or six ligand atoms can lie in the equatorial plane of the O-U-O group. The ligand atoms may or may not be entirely coplanar depending on the circumstances. Planar 5- and 6- coordination in the equatorial plane is commonest and appears to give geometry more stable than the puckered hexagonal configurations.

Uranyl ion being a hard Lewis acid has a strong tendency to combine with hard Lewis bases like fluorine or oxygen donors. The competition between fluorine and oxygen of forming compounds with uranium, however, tends to favour oxygen<sup>4</sup>. Thus next to oxygen, fluorine acts as the most powerful complexing agent to uranium. The stability of the other halides decreases sharply with increasing size of the halogen. The tendency of uranium to combine with groups containing phosphorus, arsenic or sulphur as donor atoms is very weak.

The fluoro compounds of uranium are of special interest since reactor grade uranium is obtained by the reduction of uranium tetrafluoride and the fissile <sup>235</sup>U is separated from <sup>238</sup>U by the gaseous diffusion of the hexafluoride. The fluoro complexes are directly used in certain stages of the chemical processing of uranium containing materials. Unfortunately, the available information about the nature and chemical properties of the complex uranyl fluoro compounds is still fragmentary.

The problem is complicated due to the ability of fluorine to act as a bridged ligand thus forming polynuclear complexes. As a consequence, the composition of the fluoro complexes isolated from solution depends very much on the concentrations of the different constituents and on the reaction condition.

Various physicochemical studies have been made by many authors to investigate the formation of uranyl fluoro complexes in solution. Ahrland and Larson<sup>5</sup> and Ahrland et.al.<sup>6</sup> have determined potentiometrically the equilibrium constant for the reaction



and have shown that the upper limit of complex formation is  $n=3$  above a  $\text{UO}_2^{2+}$  concentration of 0.1M and  $n=4$  below this concentration respectively. The presence of the complex species  $\text{UO}_2\text{F}^+$ ,  $\text{UO}_2\text{F}_2$  and  $\left[ \text{UO}_2\text{F}_4 \right]^{2-}$  has been confirmed spectrophotometrically by Blake et.al.<sup>7</sup>. However, Day and Powers<sup>8</sup> could not find any evidence for a complex with  $n>1$ . The freezing point data of uranyl fluoride solution (0.1 to 0.5M) indicate no dissociation, but a strong tendency for dimerization<sup>9</sup>. The conductivity measurements by Brown et. al.<sup>10</sup> confirmed this view. The x-ray crystallographic analysis of  $3\text{KF} \cdot \text{UO}_2\text{F}_2$  by Zachariassen<sup>11</sup> indicated the presence of the

ionic species  $\left[ \text{UO}_2\text{F}_5 \right]^{3-}$ . The conductivity of the salt in solution has been interpreted<sup>12</sup> in favour of the existence of  $\left[ \text{UO}_2\text{F}_5 \right]^{3-}$ , whereas spectrophotometric studies by Blake et.al.<sup>7</sup> indicated the presence of  $\left[ \text{UO}_2\text{F}_4 \right]^{2-}$ . The increase in the solubility of  $\text{K}_3\left[ \text{UO}_2\text{F}_5 \right]$  with increasing concentration of free KF has been explained by Baker<sup>13</sup> as due to the formation of  $\text{K}_4\left[ \text{UO}_2\text{F}_6 \right]$  in solution.

Because of the ability of fluoride to occupy one or two coordination positions in its compounds with uranyl ion, Chernyaev<sup>14,15</sup> suggested that fluoride should form a maximum of twelve complex species with uranyl ion having  $\text{F}^- : \text{UO}_2^{2+} = 0.5, 1, 2, 2.5, 3, 3.5, 4, 4.5, 5, 5.5$  and 6. Existence of most of the twelve complex species has been reported. However, contradictory views have been expressed by many authors regarding the actual compositions of these complexes.

The uranyl fluoro complexes isolated in the solid state are shown in Table 1.1.

Table 1.1

Fluoro complexes of  $\text{UO}_2^{2+}$  ion

Type of compound	$\text{UO}_2^{2+} : \text{F}^-$	Known compounds
$\text{[UO}_2\text{F]}^-$	1:1	Pure fluoro complexes are not known; only mixed fluoro complexes with sulphate, acetate, carbonate etc. are known.
$\text{[(UO}_2)_2\text{F}_3]^-$	1:1.5	Only mixed fluoro complexes are known.
$\text{UO}_2\text{F}_2$	1:2	$\text{UO}_2\text{F}_2$ and its hydrates.
$\text{[(UO}_2)_2\text{F}_5]^-$	1:2.5	$\text{LH}[\text{(UO}_2)_2\text{F}_5]^-$ (L = an organic base); $\text{M}[\text{(UO}_2)_2\text{F}_5]^-$ (M = an alkali metal or a quaternary ammonium ion or $\text{[Co(NH}_3)_4\text{F}_2]^+$ ).
$\text{[UO}_2\text{F}_3]^-$	1:3	$\text{M}[\text{UO}_2\text{F}_3]^- \cdot \text{nH}_2\text{O}$ (M = alkali metal, guanidinium or hydrogen ion); $\text{LH}[\text{UO}_2\text{F}_3]^-$ (L = an organic base).

....Contd.



Table 1.1 (Contd.)

Type of compound	$\text{UO}_2^{2+} : \text{F}^-$	Known compounds
$\left[ (\text{UO}_2)_2 \text{F}_7 \right]$	1:3.5	$M_3 \left[ (\text{UO}_2)_2 \text{F}_7 \right] \cdot n\text{H}_2\text{O}$ (M = alkali metal or ammonium ion); $M \left[ (\text{UO}_2)_2 \text{F}_7 \right]$ (M = $\left[ \text{Co}(\text{NH}_3)_6 \right]^{3+}$ or $\left[ \text{Co}(\text{en})_3 \right]^{3+}$ ion); $(\text{LH})_3 \left[ (\text{UO}_2)_2 \text{F}_7 \right]$ (L = an organic base); $M(\text{NH}_4)_2 \left[ (\text{UO}_2)_2 \text{F}_7 \right] \cdot n\text{H}_2\text{O}$ (M = K, Rb and Cs).
$\left[ \text{UO}_2 \text{F}_4 \right]$	1:4	$M \left[ \text{UO}_2 \text{F}_4 \right] \cdot 4\text{H}_2\text{O}$ (M = Zn, Cd, Cu, Mn, Co and Ni); $M_2 \left[ \text{UO}_2 \text{F}_4 \right] \cdot n\text{H}_2\text{O}$ (M = alkali metal or hydrogen ion); $M \left[ \text{UO}_2 \text{F}_4 \right] \cdot n\text{H}_2\text{O}$ (M = $\left[ \text{Nipy}_4 \right]^{2+}$ , $\left[ \text{Ni}(\text{en})_2 \right]^{2+}$ or $\text{Ba}^{2+}$ ion); $\left[ \text{Ni}(\text{NH}_4)_2 \right] \left[ (\text{UO}_2)_2 \text{F}_8 \right] \cdot 6\text{H}_2\text{O}$ ; $(\text{LH})_2 \left[ \text{UO}_2 \text{F}_4 \right] \cdot n\text{H}_2\text{O}$ (L = an organic base); $M_2^{\text{I}} \left[ M^{\text{II}}(\text{H}_2\text{O})_6 \right] \left[ (\text{UO}_2)_2 \text{F}_8 \right]$ (M <sup>I</sup> = K, Rb and Cs; M <sup>II</sup> = Mn, Co, Ni, Cu, Zn, Cd).

....Contd.

Table 1.1 (Contd.)

Type of compound	$\text{UO}_2^{2+} : \text{F}^-$	Known compounds
$\text{[(UO}_2)_2\text{F}_9]$	1:4.5	$\text{M}_5\text{[(UO}_2)_2\text{F}_9]$ (M = K and Rb).
$\text{[UO}_2\text{F}_5]$	1:5	$\text{M}_3\text{[UO}_2\text{F}_5] \cdot n\text{H}_2\text{O}$ (M = alkali metal, ammonium or hydroxyl-ammonium ion).
$\text{[(UO}_2)_2\text{F}_{11}]$	1:5.5	Not synthesised
$\text{[UO}_2\text{F}_6]$	1:6	$\text{M}_4^{\text{I}}\text{[UO}_2\text{F}_6] \cdot n\text{H}_2\text{O}$ (M = Li, Na, K and Rb).
$\text{[(UO}_2)_3\text{F}_8]$		$\text{M}_2^{\text{I}}\text{[(UO}_2)_3\text{F}_8] \cdot 4\text{H}_2\text{O}$ (M = K, Rb and $\text{NH}_4$ ).

Uranyl fluoride,  $\text{UO}_2\text{F}_2$  is the most well known oxy-fluoride of hexavalent uranium. The anhydrous compound can be conveniently prepared by the reaction of gaseous hydrogen fluoride on  $\text{UO}_3$  at temperatures of  $300-500^\circ$ . Uranyl fluoride is soluble in water and the hydrated compounds, viz.,  $\text{UO}_2\text{F}_2 \cdot 2\text{H}_2\text{O}$  and  $\text{UO}_2\text{F}_2 \cdot 3\text{H}_2\text{O}$  have been isolated from the system,  $\text{UO}_2\text{F}_2 - \text{H}_2\text{O}$ . Anhydrous uranyl fluoride is a fluoride bridged compound<sup>4,16</sup> with a rhombohedral crystal structure (space group  $R\bar{3}m$ ) in which each uranium atom is bonded to six fluorine atoms. The uranium-oxygen distance is  $1.74\text{\AA}$  and the uranium-fluorine distance is  $2.43\text{\AA}$ . Thermodynamic data of the anhydrous compound are also known<sup>17</sup>.

A large number of complexes of the anion  $[\text{UO}_2\text{F}_3]^-$  are known<sup>18,19</sup>. Olsson<sup>20</sup> isolated a few salts of this series with organic basic cations, e.g., pyridinium, trimethyl p-tolyl ammonium, phenyl diethyl ammonium and propyl ammonium by treating a solution of the bases in dilute hydrofluoric acid with a solution of uranyl nitrate in hydrofluoric acid. Chakravorti and Bandyopadhyay<sup>21</sup> have reported the preparation of many other salts of the type,  $\text{LH}[\text{UO}_2\text{F}_3]^-$  where L =  $\alpha$ -,  $\beta$ -picoline, quinoline, 2,2'-dipyridyl, 1,10-phenanthroline,  $\alpha$ -naphthyl amine,  $\beta$ -naphthyl amine, p-amino phenol, 8-hydroxy-quinoline, anthranilic acid and nicotinic acid. They have also obtained a free acid  $\text{H}[\text{UO}_2\text{F}_3] \cdot \text{H}_2\text{O}$  by dissolving  $\text{UO}_3$  in excess of aqueous hydrofluoric acid, evaporating and drying over caustic soda and sulphuric acid under reduced pressure.

The acid is weaker (pK 4.2 at 32°) than hydrofluoric acid<sup>21</sup>. A dihydrate  $\text{H}[\text{UO}_2\text{F}_3] \cdot 2\text{H}_2\text{O}$  has also been reported<sup>22</sup>. The two salts,  $\text{Rb}[\text{UO}_2\text{F}_3] \cdot \text{H}_2\text{O}$  and  $\text{Cs}[\text{UO}_2\text{F}_3] \cdot \text{H}_2\text{O}$  have been isolated<sup>23</sup> from aqueous solution by treating the alkali fluorides with uranyl fluoride. Both the salts form monoclinic crystals with four molecules per unit cell. Their i.r. data indicate that they are polymeric<sup>23</sup>. The crystal structure analysis of the caesium salt revealed that the compound is  $\text{Cs}_2[\text{(UO}_2)_2\text{F}_6(\text{H}_2\text{O})_2]$  instead of the simple formula given<sup>24</sup>. The anion has two pentagonal bipyramidal  $[\text{UO}_2\text{F}_3(\text{H}_2\text{O})]^-$  units fused along the F-F edge, each bipyramid having almost linear  $\text{UO}_2$  group with O-U-O angle being 175.3°. The guanidinium salt forms<sup>25</sup> monoclinic crystals with space group B2/b or Bb with four molecules per unit cell. The structure of the compound contains polymeric chains of  $[\text{(UO}_2)_2\text{F}_6]_n^{2n-}$ . The chains are formed of pentagonal bipyramids of  $\text{UO}_2\text{F}_5$  groups joined by two common meridional F-F bridges thus each uranium atom has four bridging fluorine and one terminal fluorine atom in the equatorial plane.  $\text{H}_2\text{O}$  and guanidinium ions are joined to the chain by H-bonds. The potassium salt,  $\text{K}_3[\text{(UO}_2)_3\text{F}_9(\text{H}_2\text{O})] \cdot 2\text{H}_2\text{O}$  forms a laminar structure<sup>26</sup> of the complex ions  $[\text{(UO}_2)_3(\text{H}_2\text{O})\text{F}_7\text{F}_{4/2}]_3^-$ .

Salts of the type  $\text{M}_2[\text{UO}_2\text{F}_4]$  have been characterised only in recent years. The ethylene diamine, biguanide and phenyl biguanide salts,  $\text{LH}_2[\text{UO}_2\text{F}_4] \cdot n\text{H}_2\text{O}$  have been isolated

by mixing solutions of uranyl nitrate or uranyl fluoride and the base fluorides<sup>15,27</sup>. The compounds  $M[UO_2F_4] \cdot 4H_2O$  where  $M = Zn, Cd, Cu, Mn, Co$  and  $Ni$  have been prepared by evaporating solutions containing uranyl fluoride and the metal fluorides<sup>28</sup>. These complexes are isostructural and can be recrystallised from water. The potassium, rubidium and caesium salts have also been isolated by the same method<sup>29,14</sup>. A few salts with complex cations, viz.,  $[Nipy_4][UO_2F_4] \cdot H_2O$  and  $[Nien_2][UO_2F_4] \cdot 3H_2O$  have also been prepared. Metathesis of these compounds with sodium perchlorate, potassium iodide and ammonium iodide gives the corresponding alkali metal or ammonium salts<sup>27</sup>. The barium salt  $Ba[UO_2F_4] \cdot H_2O$  was obtained by the metathesis between the potassium salt and barium chloride in the presence of boric acid<sup>27</sup>. IR spectral studies on the rubidium and caesium compounds  $M_2[UO_2F_4] \cdot H_2O$  have indicated that the anion has a distorted pentagonal bipyramidal structure with four fluorine and one oxygen of water in the equatorial plane<sup>30</sup>. Crystal structure analysis on these salts is very much lacking. X-ray powder diffraction data of the rubidium and caesium salts have been reported<sup>33</sup>.

A number of mixed salts of the type  $M_2^I[M^{II}(H_2O)_6][UO_2)_2F_8]$  ( $M^I = K, Rb$  and  $Cs$ ;  $M^{II} = Mn, Co, Ni, Cu, Zn, Cd$ ) have been isolated<sup>31</sup> by evaporation of solutions containing  $M^{II}F_2, M^IF, UO_2F_2$  and  $HF$ . However, no structural investigation has been carried out on them. The mixed salt  $Ni(NH_4)_2[UO_2)_2F_8] \cdot 6H_2O$  is known to form monoclinic crystals of space group

$P_{b/b}$  in which the O-U-O bond was found to be almost linear<sup>32</sup> with the angle being  $178^\circ$ .

The free acid,  $H_2[UO_2F_4]$  isolated from the HF- $UO_2F_2$ - $H_2O$  system has been reported to contain varying amounts of water molecules<sup>22</sup>.

Dioxopentafluorouranate(VI),  $[UO_2F_5]^{3-}$  is the most thoroughly studied uranyl fluoro complex ion. Sodium, potassium, ammonium and guanidinium salts of the series  $[UO_2F_5]^{3-}$  have been isolated by mixing the corresponding fluorides with uranyl nitrate or uranyl fluoride solution<sup>29,35</sup>. The barium salt was prepared by the double decomposition between the potassium salt and barium chloride<sup>36</sup>. Thermogravimetric analysis of the ammonium salt,  $(NH_4)_3[UO_2F_5]$  has been reported by two groups of workers<sup>37,38</sup> to give different products, viz.,  $NH_4[UO_2F_3]$  and  $NH_4[(UO_2)_2F_5]$ . The infrared<sup>39-46</sup>, Raman<sup>42,47</sup> and polarised luminescence<sup>48</sup> spectroscopic studies on the potassium, rubidium and caesium salts indicate that the ion  $[UO_2F_5]^{3-}$  has pentagonal bipyramidal structure. This arrangement is slightly distorted in the ammonium salt which is attributed to the presence of H.....F and H.....O bonding<sup>49</sup>. The unit cell dimensions of a few complex salts are listed in Table 1.2.

Table 1.2

X-ray crystallographic data of the complexes

Compound	Symmetry	Space group	a(Å)	b(Å)	c(Å)	Ref.
$K_3[UO_2F_5]$	tetragonal	$C_{4h}^6 - I4_1/a$	9.160		18.167	50
$Rb_3[UO_2F_5]$	tetragonal	$I4_1/a$	9.578		19.898	51
$Cs_3[UO_2F_5]$	cubic		9.869			52
$(NH_4)_3[UO_2F_5]$	monoclinic	$C_s^3 - C_m$	29.22	9.48	13.51	53

Salts of the ion  $\left[ \text{UO}_2\text{F}_6 \right]^{4-}$  have not been studied in detail. Alkali metal salts (Li, Na, K and Rb) of this ion have been obtained by the fusion of uranium oxide with the corresponding metal fluorides<sup>54,15</sup>. An ethylenediamine salt was isolated by crystallisation of a solution containing uranyl nitrate and the base fluoride. No structural investigation has been done on these complexes.

As noted above some of the uranyl fluoro complexes containing two, three or four fluorine atoms per uranium are in fact polynuclear. Besides these, a few other polynuclear complexes have been prepared. A large number of complexes of the type  $\text{LH} \left[ (\text{UO}_2)_2\text{F}_5 \right]^-$  (where L is an organic base, e.g., pyridine, quinoline, dimethylphenyl amine etc.) have been prepared by treating uranyl nitrate or fluoride with the bases in dilute hydrofluoric acid medium<sup>55</sup>. Similar compounds with a number of quaternary ammonium salts have been prepared by the same method<sup>20</sup>. Chakravorti and Bandyopadhyay<sup>21</sup> have prepared the 2-picoline, quinoline, 2,2'-dipyridyl and anthranilic acid salts of this series by the pyrolysis of the corresponding salts of the ion  $\left[ \text{UO}_2\text{F}_3 \right]^-$ . They have also isolated the cis- and trans-  $\left[ \text{Co}(\text{NH}_3)_4\text{F}_2 \right]^+$  salts of the ion  $\left[ (\text{UO}_2)_2\text{F}_5 \right]^-$  by adding solutions of cis- and trans-  $\left[ \text{Co}(\text{NH}_3)_4\text{Cl}_2 \right]^+$  in dilute hydrofluoric acid to a solution of uranyl fluoride containing hydrofluoric acid<sup>21</sup>.



Complexes of the type  $M\left[ \text{UO}_2 \right]_2 \text{F}_5^-$  (where  $M = \text{K}, \text{Rb}$  and  $\text{Cs}$ ) have been prepared from concentrated aqueous solutions of  $\text{UO}_2\text{F}_2$  and alkali metal fluoride in 0.5:1 mole ratio<sup>56</sup>.

A large number of salts of the ion  $\left[ \text{UO}_2 \right]_2 \text{F}_7^{3-}$  have been reported in recent years. Alkali metal and ammonium salts have been prepared by treating alkali metal or ammonium fluoride with uranyl nitrate in aqueous media<sup>13,15</sup>. Chernyaev and coworkers<sup>14</sup> have also prepared the potassium salt  $\text{K}_3\left[ \text{UO}_2 \right]_2 \text{F}_7 \cdot 2\text{H}_2\text{O}$  by recrystallising a solution of  $\text{K}_3\left[ \text{UO}_2 \right]_2 \text{F}_5^-$  in the presence of a small amount of  $\text{UO}_2(\text{NO}_3)_2$ . Chakravorti and coworkers<sup>57</sup> have prepared a large number of salts having the formulae  $(\text{LH})_3\left[ \text{UO}_2 \right]_2 \text{F}_7^-$  and  $\text{M}^{\text{III}}\left[ \text{UO}_2 \right]_2 \text{F}_7^-$  (where  $\text{L} = \text{p-toluidine}, \text{p-anisidine}$  and  $\text{m-chloroaniline}$  and  $\text{M}^{\text{III}}$  is  $\left[ \text{Co}(\text{NH}_3)_6 \right]^{3+}$  and  $\left[ \text{Co}(\text{en})_3 \right]^{3+}$ ). These have been prepared by adding the bases or  $\left[ \text{Co}(\text{NH}_3)_6 \right] \text{Cl}_3$  or  $\left[ \text{Co}(\text{en})_3 \right] \text{Cl}_3$  to a solution of uranyl fluoride in dilute hydrofluoric acid medium<sup>57</sup>. Addition of  $\left[ \text{Co}(\text{NH}_3)_6 \right] \text{Cl}_3$  to solutions of  $\text{LH}\left[ \text{UO}_2 \right]_2 \text{F}_3^-$  (where  $\text{L}$  is  $\alpha$ -picoline, anthranilic acid and  $\text{p-aminophenyl}$ ) also gave precipitates of  $\left[ \text{Co}(\text{NH}_3)_6 \right] \left[ \text{UO}_2 \right]_2 \text{F}_7^-$ . A sodium salt,  $\text{Na}_3\left[ \text{UO}_2 \right]_2 \text{F}_7^- \cdot 2\text{H}_2\text{O}$  was obtained by these workers by the metathesis or ion exchange of the above salts of the ion  $\left[ \text{UO}_2 \right]_2 \text{F}_3^-$ . These studies indicate the high stability of the ion  $\left[ \text{UO}_2 \right]_2 \text{F}_7^{3-}$ . The salts of the type  $\text{M}(\text{NH}_4)_2\left[ \text{UO}_2 \right]_2 \text{F}_7^- \cdot n\text{H}_2\text{O}$  ( $M = \text{K}, \text{Rb}$  and  $\text{Cs}$ )

have been prepared by treating MF,  $\text{UO}_2\text{F}_2$  and  $\text{NH}_4\text{F}$  in 1:1:1 molar ratio<sup>58</sup>. The potassium and rubidium salts lose two molecules of  $\text{NH}_4\text{F}$  at 220-320° to form  $\text{M}[\text{UO}_2)_2\text{F}_5]$ . The sodium and potassium salts,  $\text{Na}_3[\text{UO}_2)_2\text{F}_7] \cdot 6\text{H}_2\text{O}$  and  $\text{K}_3[\text{UO}_2)_2\text{F}_7] \cdot 2\text{H}_2\text{O}$  have also been synthesised<sup>59</sup>. The structure of the sodium salt has been found to consist of linear chains of  $[\text{UO}_2)_2\text{F}_6\text{-F}_{2/2}\text{-}]_n^{3-}$  ions. The links display nearly perfect  $\text{D}_{2h}$  symmetry.

Only two compounds with  $\text{UO}_2^{2+} : \text{F} = 1:4.5$  viz.,  $\text{K}_5[\text{UO}_2)_2\text{F}_9]$  and  $\text{Rb}_5[\text{UO}_2)_2\text{F}_9]$  have been reported<sup>56</sup>. They were prepared from a solution containing MF and  $\text{UO}_2\text{F}_2$  in 2.5:1 mole ratio. The potassium salt was also obtained by recrystallising  $\text{K}_3[\text{UO}_2)_2\text{F}_5]$  from water<sup>13,15</sup> and as a product<sup>52</sup> in the phase study of the system  $\text{KF-UO}_2\text{F}_2\text{-H}_2\text{O}$ . It forms monoclinic crystals with space group  $\text{C}_{2/c}$ . Crystal structure analysis<sup>60</sup> shows that the anion  $[\text{UO}_2)_2\text{F}_9]^{5-}$  is formed by two  $[\text{UO}_2)_2\text{F}_5]^{3-}$  pentagonal bipyramids sharing one common fluorine atom. The U-O and U-F bond distances are equal to 1.79(8) and 2.29(6) Å respectively, same as in the ion  $[\text{UO}_2)_2\text{F}_5]^{3-}$ . IR absorption and Raman diffusion spectra of the compound showed that condensation of two  $[\text{UO}_2)_2\text{F}_5]^{3-}$  ions to form a  $[\text{UO}_2)_2\text{F}_9]^{5-}$  ion had little effect on the spectra<sup>61</sup>.

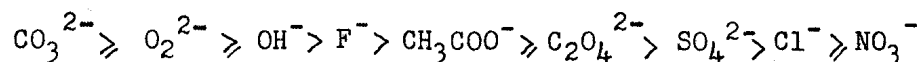
The potassium, rubidium and ammonium salts of the type  $\text{M}_2[\text{UO}_2)_3\text{F}_8] \cdot 4\text{H}_2\text{O}$  have been prepared by treating MF

and  $\text{UO}_2\text{F}_2$  in aqueous media<sup>62</sup>. The thermal decomposition of the ammonium salt<sup>63</sup> has been studied. The structure<sup>64</sup> of the rubidium compound,  $\text{Rb}_2\left[\left(\text{UO}_2\right)_3\text{F}_8\left(\text{H}_2\text{O}\right)\right]\cdot 3\text{H}_2\text{O}$  consists of infinite layers of  $\left[\left(\text{UO}_2\right)_3\text{F}_8\left(\text{H}_2\text{O}\right)\right]_n^{2n-}$  formed by a collectivization of apexes on the equatorial surfaces of neighbouring uranium polyhedra.

Thus it is found that although a large number of uranyl fluoro complexes have been isolated, authenticity of many of them is still in doubt. Thorough study by physical and physicochemical means is necessary to characterise the compounds fully. Recent trend in this field includes the structural investigation by x-ray diffraction, photoelectron spectroscopy, polarized luminescence spectroscopy, IR and Raman spectroscopy etc.

Complexes of uranyl ion with oxo anions

The investigation of oxygen donor ligands in the complex formation reactions with uranyl ( $\text{UO}_2^{2+}$ ) group is very important from two aspects. Firstly, oxygen forms the strongest bond with uranium. Secondly, there is a wide variation in the complex forming ability of different oxygen donor ligands. Thus, nitrate, sulphate, carbonate, acetate, oxalate, peroxy, hydroxyl groups behave differently towards  $\text{UO}_2^{2+}$  with respect to the formation of complexes. Chernyaev suggested<sup>65</sup> the ligand displacement series as:



which reflects the difference in behaviour of the ligands in complex formation with the uranyl ion. In the present review of the oxo anion complexes of the uranyl group only the sulphato and oxalato complexes will be discussed.

The uranyl sulphato complexes have long received much attention because they play an important role in the processing of uranium from its ores. Crystallisation of  $\text{UO}_2^{2+}$  solution from aqueous sulphuric acid results in the formation of the trihydrate,  $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$  as orthorhombic crystals<sup>66</sup> with space group  $P_{nma}$ . Thermal decomposition of the compound has been studied by various workers<sup>67</sup> although the results are incoherent. Thermodynamic data of the compound are also avail-

able.<sup>67</sup> A considerable number of papers<sup>68</sup> have dealt with the hydrolysis of uranyl sulphate but without agreement as to the mechanism of the process.

Physicochemical studies<sup>68</sup> have revealed the existence of three uranyl sulphato complexes with the  $\text{UO}_2^{2+}:\text{SO}_4^{2-} = 1:1$ ,  $1:2$  and  $1:3$ . The formation constants of the complexes  $\text{UO}_2\text{SO}_4$ ,  $[\text{UO}_2(\text{SO}_4)_2]^{2-}$  and  $[\text{UO}_2(\text{SO}_4)_3]^{4-}$  have been determined.

Compounds with the ratio of  $\text{UO}_2^{2+}:\text{SO}_4^{2-}=1:2$  have been thoroughly studied. The ammonium salt,  $(\text{NH}_4)_2[\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2]$  was isolated by the evaporation of a mixture of uranyl and ammonium sulphate solution<sup>68</sup>. The greenish crystals are stable in air and exhibit a strong fluorescence. Effect of heating on this compound has been studied by different workers<sup>68</sup> although their results do not agree with each other. The alkali metal salts of this ion have been isolated from the system: uranyl sulphate-alkali sulphate-water. Molar conductance data<sup>68</sup> show that all of them are dissociated in dilute solutions. Other known salts of the anion  $[\text{UO}_2(\text{SO}_4)_2]^{2-}$  are the thallium, magnesium and the guanidinium salts<sup>69,70,71</sup>. A few quaternary ammonium salts have also been prepared<sup>72,73</sup>. The free acid,  $\text{H}_2[\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2]$  has been isolated<sup>74</sup> in the solid state from the system:  $\text{UO}_2\text{SO}_4\text{-H}_2\text{SO}_4\text{-H}_2\text{O}$ . The i.r. spectra<sup>75</sup> of the potassium salt,  $\text{K}_2[\text{UO}_2(\text{SO}_4)_2]\cdot 2\text{H}_2\text{O}$  has been studied. Absorption and fluorescence spectral data are discussed in the review of Rabinowitch

and Belford<sup>76</sup> and in a more recent publication by Pant and Pande<sup>77</sup>.

The compounds of the ion  $\left[ \text{UO}_2(\text{SO}_4)_3 \right]^{4-}$  appear to be maximally saturated with sulphate substituents. Complexes of this type are, however, very unstable in aqueous solution and are readily converted into the ion  $\left[ \text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2 \right]^{2-}$ . Nevertheless, the sodium, potassium, rubidium and ammonium salts have been isolated from aqueous media<sup>74,78</sup>.

Sulphate group can act as a unidentate or bidentate group. It can also act as a bidentate bridging group in polynuclear complexes. It is quite likely that in many of the complexes described above the sulphate ion acts as a bidentate group. A few salts of the ions  $\left[ (\text{UO}_2)_2(\text{SO}_4)_3 \right]^{2-}$  and  $\left[ (\text{UO}_2)_2(\text{SO}_4)_5 \right]^{6-}$  have been reported in which the sulphate ion may act as a bridging group. The ammonium salt  $(\text{NH}_4)_2 \left[ (\text{UO}_2)_2(\text{SO}_4)_3 \right] \cdot 5\text{H}_2\text{O}$  was detected<sup>74</sup> in the solid phase of the system  $\text{UO}_2\text{SO}_4 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$  at 25°. The caesium salt  $\text{Cs}_2 \left[ (\text{UO}_2)_2(\text{SO}_4)_3 \right]$  was prepared by evaporation of solutions containing stoichiometric amounts of the two sulphates at room temperature<sup>79</sup>. The free acid  $\text{H}_2 \left[ (\text{UO}_2)_2(\text{SO}_4)_3 \right] \cdot 5\text{H}_2\text{O}$  has been obtained as deliquescent crystals<sup>74</sup>. The lattice parameters of these compounds have been reported. The ammonium and the potassium salts of the ion  $\left[ (\text{UO}_2)_2(\text{SO}_4)_5 \right]^{6-}$  have been prepared by Ellert<sup>80</sup>. Such compounds were not, however,

detected during the investigation of systems containing uranyl sulphate and alkali metal sulphate. Little is known about the properties of the two synthesised salts, except that they are very unstable in solution and are rapidly converted to the corresponding diaquodisulphato complex.

A few sulphato complexes of uranyl ion containing hydroxide ion have been reported<sup>81,82</sup>. These are  $\text{Cu}\left[\text{UO}_2(\text{OH})(\text{SO}_4)(\text{H}_2\text{O})_3\right]_2$  and  $(\text{NH}_4)_4\left[\text{UO}_2(\text{OH})_2(\text{SO}_4)_2\right] \cdot 3\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\left[\text{(UO}_2)_2(\text{OH})_4(\text{SO}_4)(\text{H}_2\text{O})_n\right]$ . The existence of the two ammonium salts, however, does not appear to be fully confirmed. X-ray powder data of a few of the complexes are known (vide Table 1.3), but full structural details<sup>79,82</sup> are available only for  $\text{Cs}_2\left[\text{(UO}_2)_2(\text{SO}_4)_3\right]$  and  $\text{Cu}\left[\text{(UO}_2)_2(\text{SO}_4)_2(\text{OH})_2\right] \cdot 6\text{H}_2\text{O}$ .

Like the sulphato complexes a very large number of oxalato complexes of uranyl ion have been prepared. But the structures of the compounds have not been studied.

Uranyl oxalate trihydrate separates out as monoclinic crystals on the addition of oxalic acid to  $\text{UO}_2^{2+}$  solution<sup>84</sup>. The crystal parameters have been reported<sup>84</sup>. On heating the compound loses water in three stages. The oxalato complexes of uranyl ion are similar to the corresponding sulphato complexes in composition. The known types are  $\left[\text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2\right]^{2-}$ ,  $\left[\text{UO}_2(\text{C}_2\text{O}_4)_3\right]^{4-}$ ,  $\left[\text{(UO}_2)_2(\text{C}_2\text{O}_4)_3\right]^{2-}$  and  $\left[\text{(UO}_2)_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_2\right]^{6-}$ . The dioxalato complexes have

Table 1.0

X-ray crystallographic data of the complexes

Compound	Symmetry	Space group	a(Å)	b(Å)	c(Å)	Ref.No.
$\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$	rhombic	$P_{bmm}$	12.58	17.00	6.73	83
$\text{H}_2\left[\text{UO}_2\right)_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$	rhombic	$P_{mnn}$	12.86	12.99	11.57	65
$\text{Cs}_2\left[\text{UO}_2\right)_2(\text{SO}_4)_3$	tetragonal	$P4_21_m(D_{2d}^3)$ or $P4_21_2(D_d^3)$	9.62		8.13	79
$(\text{NH}_4)_2\left[\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2\right]$	monoclinic	$P2_1/n$	20.53	7.30	7.74	83
$\text{K}_2\left[\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2\right]$	rhombic	$P_{mnb}$	11.55	13.78	7.28	83
$\text{Rb}_2\left[\text{UO}_2(\text{SO}_4)_2(\text{H}_2\text{O})_2\right]$	rhombic	$P_{bmm}$ or $P_{bn}2_1$	11.50	13.48	7.42	79



been most comprehensively studied.

A large number of salts of the ion  $\left[ \text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2 \right]^{2-}$  with cations like lithium, sodium, potassium, ammonium, rubidium, caesium, thallium, barium, strontium, guanidinium etc. have been prepared by crystallising solutions of uranyl oxalate and the corresponding oxalate<sup>85-88</sup>. These generally contain additional water molecules.

Very few salts of the trioxalato type, viz.,  $\left[ \text{UO}_2(\text{C}_2\text{O}_4)_3 \right]^{4-}$  have been prepared. The ammonium compound crystallises out<sup>89</sup> from a solution containing stoichiometric amounts of the two oxalates at 65-75°. It decomposes in water to give the dioxalato compound  $(\text{NH}_4)_2 \left[ \text{UO}_2(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2 \right]$ . The thallium compound  $\text{Tl}_4 \left[ \text{UO}_2(\text{C}_2\text{O}_4)_3 \right]$  which is isomorphous with the ammonium compound is precipitated from a solution of uranyl oxalate and an excess of thallium oxalate<sup>87</sup>.

Oxalate ion like sulphate may act as a bridging group in polynuclear complexes. The ions  $\left[ (\text{UO}_2)_2(\text{C}_2\text{O}_4)_3 \right]^{2-}$  and  $\left[ (\text{UO}_2)_2(\text{C}_2\text{O}_4)_5(\text{H}_2\text{O})_2 \right]^{6-}$  most probably contain oxalate group bridging two uranium atoms. Potassium, ammonium, caesium and guanidinium salts of both the ions have been reported<sup>86-88</sup>. The compounds are moderately stable in solution.

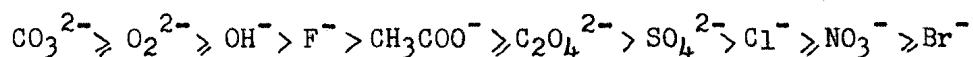
A few uranyl oxalato complexes<sup>89</sup> containing hydroxide ion have been reported, e.g.,  $\text{NH}_4 \left[ \text{UO}_2(\text{OH})(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_3 \right]$ ,

$K_3[UO_2(OH)(C_2O_4)_2(H_2O)] \cdot H_2O$  etc. These, however, have not been well characterised.

Mixed ligand complexes of uranyl containing  
fluoride as one ligand

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Uranyl ion has very strong tendency to form complexes with fluoride. It has also a strong affinity towards various oxoanions like carbonate, sulphate, nitrate and carboxylates. It has very weak affinity for bromide or iodide. Stability of the complex uranyl compounds varies widely with the nature of the ligand. Thus, while the complex  $[UO_2(CO_3)_3]^{4-}$  has a stability constant of the order of  $10^{23}$ , the corresponding value of  $[UO_2(SO_4)_3]^{4-}$  is only about  $10^3$ . Chernyaev has carried out extensive investigations on the mutual replacement of one ligand by another in the uranyl compounds and has given the following displacement series<sup>65</sup>



This series predicts the direction in which a substitution reaction in  $UO_2^{2+}$  complexes takes place. It can be used as a guide to devise the synthetic methods that may be employed for the preparation of mixed complexes.

From the review given above it is evident that considerable attention has been paid till now to the preparative aspect of fluoro and acido (e.g., sulphato and oxalato) complexes of uranyl ion. Mixed complexes containing fluoride as one ligand have not been thoroughly studied. Preparations of a few fluorocarbonato<sup>90</sup>, e.g.,  $\text{Cs}[\text{UO}_2\text{F}(\text{CO}_3)(\text{H}_2\text{O})]$ ,  $\text{Ba}[\text{UO}_2\text{F}_2(\text{CO}_3)(\text{H}_2\text{O})_2]$ ,  $\text{K}_3[\text{UO}_2\text{F}_3(\text{CO}_3)]$ ,  $\text{K}_4[\text{UO}_2\text{F}_4(\text{CO}_3)]$ ; fluorosulphato<sup>91</sup> e.g.,  $\text{K}[\text{UO}_2\text{F}(\text{SO}_4)]$ ,  $\text{K}_3[\text{UO}_2\text{F}(\text{SO}_4)_2]$ ,  $(\text{NH}_4)_3[\text{UO}_2\text{F}_3(\text{SO}_4)_2(\text{H}_2\text{O})]$ ,  $\text{K}_2[\text{UO}_2\text{F}_2(\text{SO}_4)(\text{H}_2\text{O})]$ ,  $\text{K}_4[\text{UO}_2\text{F}_2(\text{SO}_4)_2]$ ,  $\text{K}_3[\text{UO}_2\text{F}_3(\text{SO}_4)]$ ,  $\text{Na}_5[\text{UO}_2\text{F}_3(\text{SO}_4)_2]$ ; fluoroacetato<sup>91</sup>, e.g.,  $\text{K}[\text{UO}_2\text{F}(\text{CH}_3\text{COO})_2]$ ,  $(\text{guanH})_2[\text{UO}_2\text{F}_3(\text{CH}_3\text{COO})(\text{H}_2\text{O})]$  and fluorooxalato<sup>90</sup>, e.g.  $\text{K}_3[\text{UO}_2\text{F}(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})] \cdot \text{H}_2\text{O}$ ,  $\text{K}_3[\text{UO}_2\text{F}_3(\text{C}_2\text{O}_4)(\text{H}_2\text{O})]$  complexes have been reported. Besides preparation, practically nothing is known about the properties or structure of the compounds. These mixed complexes have been prepared by using methods devised from the above displacement series. The series must not, however, be considered infallible, since reactions may proceed in the reverse direction depending on the experimental conditions such as concentration of the reactants and the size of the cation. Thus, the isolation of many other types of mixed complexes may be expected by varying the experimental conditions.

No mixed complex of uranyl ion with fluoride and other halide has been prepared till now. Some mixed halide complexes containing chloride, bromide or iodide, e.g.,  $[\text{UO}_2\text{Cl}_2\text{Br}]^-$ ,

$\left[ \text{UO}_2\text{Cl}_2\text{Br}_2 \right]^{2-}$ ,  $\left[ \text{UO}_2\text{Cl}_3\text{Br} \right]^{2-}$ ,  $\left[ \text{UO}_2\text{ClBr}_3 \right]^{2-}$ ,  $\left[ \text{UO}_2\text{Cl}_3\text{I} \right]^{2-}$ ,  $\left[ \text{UO}_2\text{Br}_3\text{I} \right]^{2-}$  and  $\left[ \text{UO}_2\text{Cl}_2\text{BrI} \right]^{2-}$  have been synthesised and studied by visible and i.r. spectroscopy<sup>92-96</sup>.

Uranyl ion has very weak affinity for ligands with nitrogen, phosphorus or sulphur. Numerous adducts of  $\text{UO}_2\text{Cl}_2$  with oxygen and nitrogen donor ligands have been reported<sup>97</sup>. Such compounds with  $\text{UO}_2\text{F}_2$  are very scanty. A few polymeric compounds of the empirical formula  $\text{UO}_2\text{F}_2 \cdot \text{L}$  are formed with dimethyl sulphoxide<sup>98</sup>, tetramethyl urea, antipyrine, acetamide and dimethyl formamide<sup>99</sup>. With urea, the mononuclear compound,  $\left[ \text{UO}_2\text{F}_2(\text{urea})_3 \right]$  has been isolated<sup>99</sup>. The only known adduct of  $\text{UO}_2\text{F}_2$  with a nitrogen donor is the complex  $\left[ \text{UO}_2\text{F}_2(\text{phen}) \right]$ , where phen is 1,10-phenanthroline<sup>21</sup>.

The present investigation is aimed at the isolation and elucidation of structures of mixed complexes of uranyl ion containing fluoride as one ligand.