CHAPTER VI

COMPLEX FLUOROURANATES(VI). SYNTHESIS, CHARACTERIZATION AND STRUCTURAL ASSESSMENT OF NEW MIXED-FLUORO COMPLEXES OF UO$_2$$^{2+}$ CONTAINING PHOSPHATE, NITRATE OR HYDRAZINE AS THE CO-LIGANDS AND IMPROVED SYNTHESIS OF A$_2$[UO$_2$F$_4$.3H$_2$O (A = K, Na or NH$_4$)*

In continuation to our endeavour in the field of binary fluoro and mixed-fluorouranates(VI) as highlighted in Chapter V of

* A major portion of the work described herein has been accepted for publication in Polyhedron (in press) [Manuscript No. 905478].
the thesis, we decided to embark on the study of hetero-ligand fluoro complexes of $\text{UO}_2^{2+}$ containing inorganic co-ligands as well. Our chief concern here is to develop appropriate synthetic methodologies that would not only be operationally simple but also capable of affording pure products in high yields. The only inorganic co-ligand that was dealt with in our previous studies on mixed-fluorouranates was peroxide ($\text{O}_2^{2-}$), wherein the complex $[\text{UO}_2(\text{O}_2)\text{F}_2]^{2-}$ was synthesized.

The co-ligands chosen for the present work include phosphate, nitrate and hydrazine. These ligands besides being good probes easily amenable to spectroscopic characterization are known to interact with $\text{UO}_2^{2+}$ to form compounds of varying compositions and stability. Moreover, both phosphato and nitrato-uranyl complexes are technologically important. For instance, the formation of insoluble and slightly soluble uranyl phosphates is important in the technology of uranium production especially for low-grade uranium phosphate ores and in fuel reprocessing. However, there appears to be some synthetic problem related to phosphato complexes of $\text{UO}_2^{2+}$ specifically owing to the gelatinous nature of the products, while the uranyl-nitrato complexes are generally very weak. It was expected that the presence of fluoride might assist in bringing about stability to the nitrato complexes and improve upon the crystallinity of the phosphato ones. The complexes of coordinated hydrazine in general find considerable
interest owing to their tendency to act as possible intermediates in the chemistry of coordinated dinitrogen and its reduction to NH\textsubscript{3} catalyzed by nitrogenases. Besides, the coordination chemistry of hydrazine and substituted hydrazines is of special interest because of the variety of ways in which it can be bonded to the metal ion. Interestingly, there have been only a few reports on hydrazine complexes of UO\textsubscript{2}\textsuperscript{2+} and all of them are hetero-ligand complexes\textsuperscript{5c} with SO\textsubscript{4}\textsuperscript{2-}, NCS\textsuperscript{-}, NO\textsubscript{3}\textsuperscript{-}, C\textsubscript{2}O\textsubscript{4}\textsuperscript{2-} or a heavier halide like Cl\textsuperscript{-}, Br\textsuperscript{-} or I\textsuperscript{-} as the co-ligand. Surprisingly, there has been no mention of the corresponding fluoro(hydrazine) complex of UO\textsubscript{2}\textsuperscript{2+} for which we were unable to discern any reason. Hence, we considered it important to include this aspect in our agenda.

Having achieved the syntheses of difluoro, hexafluoro and heptafluorodioxouranates(VI) as described in Chapter V of the thesis, we were interested in the synthesis of dioxotetrafluoro-uranate(VI) complex, [UO\textsubscript{2}F\textsubscript{4}]\textsuperscript{2-}. It may be recalled that a number of salts of the complex species [UO\textsubscript{2}F\textsubscript{4}]\textsuperscript{2-} with the general formulae A\textsubscript{2}[UO\textsubscript{2}F\textsubscript{4}].nH\textsubscript{2}O\textsuperscript{7} (A = K, Na or NH\textsubscript{4}) were prepared from metathesis reactions of [Ni(py)\textsubscript{4}][UO\textsubscript{2}F\textsubscript{4}].H\textsubscript{2}O and NaClO\textsubscript{4} or AI (A = K or NH\textsubscript{4}). Further [Ni(py)\textsubscript{4}][UO\textsubscript{2}F\textsubscript{4}].H\textsubscript{2}O was prepared from UO\textsubscript{2}F\textsubscript{2}, which for itself requires an extra preparation step. In view of these as well as our interest in fluorouranates(VI) in particular, it was incumbent on us to develop a rather simple and direct synthetic route for A\textsubscript{2}[UO\textsubscript{2}F\textsubscript{4}].nH\textsubscript{2}O (A = K, Na or NH\textsubscript{4}).
Accordingly the work that has been identified above was undertaken and a detailed account of the results are incorporated in this Chapter.

Experimental

The reagents used in these studies were reagent-grade or better (E.Merck (India) Ltd., S.d-Fine Chem., Qualigens Fine Chemicals). The details of the instruments/equipment used for characterization of the complexes are given in Chapter II.

Synthesis of $A_2\left[UO_2\left(PO_4\right)F\left(H_2O\right)_3\right]cdot3H_2O \ [A = K, Na or NH_4]$

An amount of 1.0g (2.79 mmol) of $UO_3\cdot4H_2O$ was dissolved in an aqueous solution (5 cm$^3$) of $AHF_2$ (8.37 mmol). This was followed by the addition of $H_3PO_4$ (0.3 cm$^3$, 5.37 mmol). The pH of the resultant clear solution was measured to be ca.2. The reaction solution was then concentrated on a steam-bath while lemon-yellow crystals began to appear. Addition of cold ethanol (7 cm$^3$) at this stage facilitated precipitation of the lemon-yellow crystalline isolate by centrifugation, washed three or four times with ethanol, and finally dried in vacuo over cone. $H_2SO_4$. The yields of $K_2\left[UO_2\left(PO_4\right)F\left(H_2O\right)_3\right]cdot3H_2O$, $Na_2\left[UO_2\left(PO_4\right)F\left(H_2O\right)_3\right]cdot3H_2O$ and $(NH_4)_2\left[UO_2\left(PO_4\right)F\left(H_2O\right)_3\right]cdot3H_2O$ were 1.1g (69%), 1g (67%) and 1g (67.5%), respectively.
Synthesis of $A_2\left[UO_2\left(NO_3\right)_3F\right].3H_2O$ [$A = K$, Na or NH$_4$]

Uranyl nitrate hexahydrate, $UO_2\left(NO_3\right)_2\cdot6H_2O$, (1.0g, 1.99 mmol) was dissolved in water (15 cm$^3$) followed by a slow addition of 20% AOH solution or aqueous ammonia (sp.gr. 0.91) until the precipitation of the yellow product was complete. This was filtered and washed free from alkali and nitrate, and then dissolved in 10 cm$^3$ (20.8 mmol) of 2.08 M HNO$_3$. To the clear solution, 48% HF (3 cm$^3$, 72 mmol) was added and stirred at an ambient temperature for ca. 10 min. The reaction solution was then concentrated on a steam-bath to nearly half of its volume to afford a lemon-yellow solid. The whole was cooled to room temperature. The compound thus obtained was isolated by filtration, washed thrice with acetone, and finally dried in vacuo over conc. H$_2$SO$_4$. The yields of $K_2[UO_2\left(NO_3\right)_3F].3H_2O$, $Na_2[UO_2\left(NO_3\right)_3F].3H_2O$ and $(NH_4)_2[UO_2\left(NO_3\right)_3F].3H_2O$ were 0.98g (74%), 0.8g (69.6%) and 0.8g (70.8%), respectively.

Synthesis of $[UO\left(NH_4\right)_4\cdot2F_2].2H_2O$

To an aqueous solution (10 cm$^3$) of an intimate mixture of 1.0g (2.37 mmol) of $UO_3\cdot4H_2O$ and 8.37 mmol of AHF$_2$ ($A = K$ or NH$_4$) was added an excess (0.6 cm$^3$, 12 mmol) of hydrazine hydrate, $N_2H_4\cdotH_2O$. At this stage, a yellow solid appeared. This reaction mixture was heated on a steam-bath for ca. 30 min. whereupon the
colour of the solid changed from yellow to brown. The brown solid thus formed was isolated by filtration. The compound was purified by washing two or three times with acetone and finally dried in vacuo over conc. $\text{H}_2\text{SO}_4$. The yield of $\text{[UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2]\cdot 2\text{H}_2\text{O}$ was 0.9g (79%). Anal. Calcd. for $\text{[UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2]\cdot 2\text{H}_2\text{O}$: U, 58.31; F, 9.31; N, 13.73; H, 2.97. Found: U, 59.11; F, 9.56; N, 13.32; H, 2.72.

**Synthesis of $\text{A}_2[\text{UO}_2\text{F}_4]\cdot 3\text{H}_2\text{O}$ (A = K, Na or NH$_4$)**

(a) Uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, (1.0g, 1.99 mmol) was dissolved in water (15 cm$^3$) followed by a slow addition of 20% AOH solution or aqueous ammonia (sp.gr. 0.91) until the precipitation of the yellow product was complete. This was filtered and washed free from alkali and nitrate. The product thus obtained was dissolved in 48% HF (1 cm$^3$, 24 mmol). To the resultant solution 3.96 mmol of $\text{A}_2\text{CO}_3$ (A = K, Na or NH$_4$) was added. The whole was then concentrated on a steam-bath to afford a lemon-yellow crystalline solid. This was then isolated by filtration and dried in vacuo over conc. $\text{H}_2\text{SO}_4$. The compound was identified to be $\text{A}_2[\text{UO}_2\text{F}_4]\cdot 3\text{H}_2\text{O}$. The yields of $\text{K}_2[\text{UO}_2\text{F}_4]\cdot 3\text{H}_2\text{O}$, $\text{Na}_2[\text{UO}_2\text{F}_4]\cdot 3\text{H}_2\text{O}$ and (NH$_4$)$_2[\text{UO}_2\text{F}_4]\cdot 3\text{H}_2\text{O}$ were 0.57g (60%), 0.55g (62%) and 0.54g (62%), respectively.

(b) Alternatively, an amount of (1.0g, 1.99 mmol) of uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ was dissolved in 15 cm$^3$ of water and 0.1 cm$^3$ of conc. $\text{HNO}_3$ was added to it. After heating the
resulting solution to about 70°C, 0.5 cm³ of 30% H₂O₂ was added washed thoroughly with water. This was then dissolved in 48% HF (1 cm³, 24 mmol). To the resulting solution 12 mmol of AF (A = K, Na or NH₄) was added. The whole upon concentration over a steam-bath afforded a lemon-yellow crystalline solid which was isolated by filtration and dried in vacuo over conc. H₂SO₄. The compound was analysed as A₂[UO₂F₄].3H₂O (A = K, Na or NH₄). The yields of K₂[UO₂F₄].3H₂O, Na₂[UO₂F₄].3H₂O and (NH₄)₂[UO₂F₄].3H₂O were 0.53g (56%), 0.48g (54%) and 0.5g (57.5%), respectively.

Elemental Analyses

Quantitative determinations of uranium, fluoride, nitrogen, hydrogen, phosphate, sodium and potassium were made by the methods described in Chapter II.

The analytical and characterization data (except the analytical data of [UO₂(N₂H₄)F₂].2H₂O) are summarised in Tables 6.1-6.8.

Results and Discussion

From the experience gathered by our group in dealing with uranyl systems, especially fluoro complexes of UO₂²⁺ as described in Chapter V, it was conjectured that complexation of PO₄³⁻, NO₃⁻ or N₂H₄ with UO₂²⁺ in the presence of fluoride would be feasible.
Table 6.1: Analytical Data of the Complexes

$A_2[\text{UO}_2(\text{PO}_4)\text{F(H}_2\text{O})_3].3\text{H}_2\text{O}$ ($A = \text{K, Na or NH}_4$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Element</th>
<th>Found (%)</th>
<th>Calcd (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2[\text{UO}_2(\text{PO}_4)\text{F(H}_2\text{O})_3].3\text{H}_2\text{O}$</td>
<td>U</td>
<td>40.88</td>
<td>41.75</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>3.23</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td>$\text{PO}_4^{3-}$</td>
<td>15.95</td>
<td>16.66</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>2.24</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>K</td>
<td>12.95</td>
<td>13.68</td>
</tr>
<tr>
<td>$\text{Na}_2[\text{UO}_2(\text{PO}_4)\text{F(H}_2\text{O})_3].3\text{H}_2\text{O}$</td>
<td>U</td>
<td>44.11</td>
<td>44.24</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>3.33</td>
<td>3.53</td>
</tr>
<tr>
<td></td>
<td>$\text{PO}_4^{3-}$</td>
<td>17.42</td>
<td>17.65</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>2.28</td>
<td>2.25</td>
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<tr>
<td></td>
<td>Na</td>
<td>8.87</td>
<td>8.54</td>
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<tr>
<td>$(\text{NH}_4)_2[\text{UO}_2(\text{PO}_4)\text{F(H}_2\text{O})_3].3\text{H}_2\text{O}$</td>
<td>U</td>
<td>44.25</td>
<td>45.06</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>3.48</td>
<td>3.60</td>
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<tr>
<td></td>
<td>$\text{PO}_4^{3-}$</td>
<td>17.85</td>
<td>17.98</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>3.48</td>
<td>3.82</td>
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<tr>
<td></td>
<td>N</td>
<td>5.22</td>
<td>5.30</td>
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### Table 6.2: Analytical Data and Solution Electrical Conductance Values of $A_2\left[UO_2\left(NO_3\right)_3F\right].3H_2O$ (A = K, Na or NH$_4$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conductance (Ω$^{-1}$ cm$^2$ mol$^{-1}$)</th>
<th>Element</th>
<th>Found (%)</th>
<th>Calcd. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2\left[UO_2\left(NO_3\right)_3F\right].3H_2O$</td>
<td>244</td>
<td>U</td>
<td>39.42</td>
<td>39.21</td>
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<tr>
<td></td>
<td></td>
<td>F</td>
<td>3.24</td>
<td>3.13</td>
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<tr>
<td></td>
<td></td>
<td>N</td>
<td>6.78</td>
<td>6.92</td>
</tr>
<tr>
<td></td>
<td></td>
<td>K</td>
<td>13.11</td>
<td>12.85</td>
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<tr>
<td>$Na_2\left[UO_2\left(NO_3\right)_3F\right].3H_2O$</td>
<td>242</td>
<td>U</td>
<td>40.31</td>
<td>41.39</td>
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<td></td>
<td></td>
<td>F</td>
<td>3.36</td>
<td>3.30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>N</td>
<td>7.52</td>
<td>7.31</td>
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<tr>
<td></td>
<td></td>
<td>Na</td>
<td>7.89</td>
<td>7.99</td>
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<tr>
<td>$\left(NH_4\right)_2\left[UO_2\left(NO_3\right)_3F\right].3H_2O$</td>
<td>244</td>
<td>U</td>
<td>42.32</td>
<td>42.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>F</td>
<td>3.24</td>
<td>3.36</td>
</tr>
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<td></td>
<td>N</td>
<td>12.41</td>
<td>12.39</td>
</tr>
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<td></td>
<td>H</td>
<td>2.55</td>
<td>2.50</td>
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Table 6.3: Analytical Data and Solution Electrical Conductance Values of $A_2[\text{UO}_2\text{F}_4].3\text{H}_2\text{O}$ ($A = K$, Na or $\text{NH}_4$)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conductance ($\Omega^{-1} \text{cm}^2 \text{mol}^{-1}$)</th>
<th>Element</th>
<th>Found (%)</th>
<th>Calcd. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2[\text{UO}_2\text{F}_4].3\text{H}_2\text{O}$</td>
<td>245</td>
<td>U</td>
<td>50.12</td>
<td>49.77</td>
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<td>16.23</td>
<td>15.89</td>
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<td>H</td>
<td>1.33</td>
<td>1.27</td>
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<tr>
<td></td>
<td></td>
<td>K</td>
<td>15.96</td>
<td>16.35</td>
</tr>
<tr>
<td>$Na_2[\text{UO}_2\text{F}_4].3\text{H}_2\text{O}$</td>
<td>238</td>
<td>U</td>
<td>53.21</td>
<td>53.26</td>
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<tr>
<td></td>
<td></td>
<td>F</td>
<td>16.85</td>
<td>17.04</td>
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<td></td>
<td></td>
<td>H</td>
<td>1.52</td>
<td>1.30</td>
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<td></td>
<td></td>
<td>Na</td>
<td>10.43</td>
<td>10.31</td>
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<tr>
<td>$(\text{NH}_4)_2[\text{UO}_2\text{F}_4].3\text{H}_2\text{O}$</td>
<td>242</td>
<td>U</td>
<td>54.84</td>
<td>54.57</td>
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<td>F</td>
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<td></td>
<td>H</td>
<td>3.36</td>
<td>3.24</td>
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<td>N</td>
<td>6.63</td>
<td>6.42</td>
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</table>
Table 6.4: IR and LR Spectral Data of the Complexes $A_2[U_2(PO_4)_3F(H_2O)_3].3H_2O$ (A = K, Na or NH$_4$) with their Assignments

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (cm$^{-1}$)</th>
<th>LR (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_2[U_2(PO_4)_3F(H_2O)_3].3H_2O$</td>
<td>920s</td>
<td>903s</td>
<td>$\nu$(U=O)</td>
</tr>
<tr>
<td></td>
<td>382m</td>
<td></td>
<td>$\nu$(U-F)</td>
</tr>
<tr>
<td></td>
<td>903m</td>
<td></td>
<td>$\nu_1$(PO$_4$)</td>
</tr>
<tr>
<td></td>
<td>1002s</td>
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<td>$\nu_3$(PO$_4$)</td>
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<tr>
<td></td>
<td>1069s</td>
<td></td>
<td>$\rho_r$(H$_2$O)</td>
</tr>
<tr>
<td></td>
<td>1130s</td>
<td></td>
<td>$\delta$(H-O-H)</td>
</tr>
<tr>
<td></td>
<td>742m</td>
<td></td>
<td>$\nu$(O-H)</td>
</tr>
<tr>
<td></td>
<td>1657m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3477m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| $Na_2[U_2(PO_4)_3F(H_2O)_3].3H_2O$ | 926s | 900s | $\nu$(U=O) |
| | 415m | | $\nu$(U-F) |
| | 908m | | $\nu_1$(PO$_4$) |
| | 1004s | | $\nu_3$(PO$_4$) |
| | 1085s | | |
| | 1120s | | |
| | 737m | | $\rho_r$(H$_2$O) |
| | 1654m | | $\delta$(H-O-H) |
| | 3418m | | $\nu$(O-H) |
Table 6.4 contd.

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (cm$^{-1}$)</th>
<th>LR (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(NH_4)_2[\text{UO}_2(\text{PO}_4)\text{F(H}_2\text{O})_3].3\text{H}_2\text{O}$</td>
<td>925s 408m 905m 1008s 1068s 1120s 735m 1630m 3467m</td>
<td>905s</td>
<td>$\nu$(U=O) $\nu$(U-F) $\nu_1(\text{PO}_4^3-) \nu_3(\text{PO}_4^3-) \rho_r(\text{H}_2\text{O}) \delta(\text{H-O-H}) \nu(\text{O-H})$ $\nu$(N-H)$_4$ $\nu$(N-H)$_1$ $\nu$(N-H)$_3$</td>
</tr>
</tbody>
</table>
Table 6.5: IR and LR Spectral Data of the Complexes $\text{A}_2[\text{UO}_2(\text{NO}_3)_3]\text{F}.3\text{H}_2\text{O}$ ($\text{A} = \text{K, Na or NH}_4$) with their Assignments

<table>
<thead>
<tr>
<th>Compounds</th>
<th>IR (cm$^{-1}$)</th>
<th>LR (cm$^{-1}$)</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{K}_2[\text{UO}_2(\text{NO}_3)_3]\text{F}.3\text{H}_2\text{O}$</td>
<td>950s</td>
<td>890s</td>
<td>$\nu(\text{U}=\text{O})$</td>
</tr>
<tr>
<td></td>
<td>403m</td>
<td></td>
<td>$\nu(\text{U-F})$</td>
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<td>1503s</td>
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<td>$\nu_1(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>1026m</td>
<td></td>
<td>$\nu_2(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>744m</td>
<td></td>
<td>$\nu_3(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>1283s</td>
<td></td>
<td>$\nu_4(\text{NO}_3)$</td>
</tr>
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<td>705w</td>
<td></td>
<td>$\nu_5(\text{NO}_3)$</td>
</tr>
<tr>
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<td>808m</td>
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<td>$\nu_6(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>1657m</td>
<td></td>
<td>$\delta(\text{H-O-H})$</td>
</tr>
<tr>
<td></td>
<td>3442m</td>
<td></td>
<td>$\nu(\text{O-H})$</td>
</tr>
<tr>
<td>$\text{Na}_2[\text{UO}_2(\text{NO}_3)_3]\text{F}.3\text{H}_2\text{O}$</td>
<td>948s</td>
<td>894s</td>
<td>$\nu(\text{U}=\text{O})$</td>
</tr>
<tr>
<td></td>
<td>396m</td>
<td></td>
<td>$\nu(\text{U-F})$</td>
</tr>
<tr>
<td></td>
<td>1503s</td>
<td></td>
<td>$\nu_1(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>1026m</td>
<td></td>
<td>$\nu_2(\text{NO}_3)$</td>
</tr>
<tr>
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<tr>
<td></td>
<td>708w</td>
<td></td>
<td>$\nu_5(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>805m</td>
<td></td>
<td>$\nu_6(\text{NO}_3)$</td>
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<tr>
<td></td>
<td>1621m</td>
<td></td>
<td>$\delta(\text{H-O-H})$</td>
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<tr>
<td></td>
<td>3440m</td>
<td></td>
<td>$\nu(\text{O-H})$</td>
</tr>
<tr>
<td>Compounds</td>
<td>IR</td>
<td>LR</td>
<td>Assignment</td>
</tr>
<tr>
<td>------------------------------------------------</td>
<td>-----</td>
<td>-----</td>
<td>------------------</td>
</tr>
<tr>
<td>$(\text{NH}_4)_2[\text{UO}_2(\text{NO}_3)_3\text{F}] \cdot 3\text{H}_2\text{O}$</td>
<td>939s</td>
<td>900s</td>
<td>$\nu(\text{U}=\text{O})$</td>
</tr>
<tr>
<td></td>
<td>401m</td>
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<td>$\nu(\text{U}-\text{F})$</td>
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<tr>
<td></td>
<td>1505s</td>
<td></td>
<td>$\nu_1(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>1024m</td>
<td></td>
<td>$\nu_2(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>741m</td>
<td></td>
<td>$\nu_3(\text{NO}_3)$</td>
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<tr>
<td></td>
<td>1296s</td>
<td></td>
<td>$\nu_4(\text{NO}_3)$</td>
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<tr>
<td></td>
<td>707w</td>
<td></td>
<td>$\nu_5(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>811m</td>
<td></td>
<td>$\nu_6(\text{NO}_3)$</td>
</tr>
<tr>
<td></td>
<td>1657m</td>
<td></td>
<td>$\delta(\text{H-O-H})$</td>
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<tr>
<td></td>
<td>3446m</td>
<td></td>
<td>$\nu(\text{O-H})$</td>
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<tr>
<td></td>
<td>1427s</td>
<td></td>
<td>$\nu(\text{N-H})\nu_4$</td>
</tr>
<tr>
<td></td>
<td>3094s</td>
<td></td>
<td>$\nu(\text{N-H})\nu_1$</td>
</tr>
<tr>
<td></td>
<td>3182m</td>
<td></td>
<td>$\nu(\text{N-H})\nu_3$</td>
</tr>
<tr>
<td>Compound</td>
<td>UV-VIS</td>
<td>( \lambda_{\text{nm}} )</td>
<td>( \varepsilon ) (Lmol(^{-1})cm(^{-1}))</td>
</tr>
<tr>
<td>---------------------------</td>
<td>--------</td>
<td>----------------------------</td>
<td>-----------------------------------------------</td>
</tr>
<tr>
<td>( \text{K}_2[\text{UO}_2(\text{NO}_3)_3]\text{F}.3\text{H}_2\text{O} )</td>
<td></td>
<td>415</td>
<td>52</td>
</tr>
<tr>
<td></td>
<td></td>
<td>425</td>
<td>105</td>
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<td>435</td>
<td>102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>465</td>
<td>48</td>
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<tr>
<td>( \text{Na}_2[\text{UO}_2(\text{NO}_3)_3]\text{F}.3\text{H}_2\text{O} )</td>
<td></td>
<td>415</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td></td>
<td>425</td>
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<td>435</td>
<td>108</td>
</tr>
<tr>
<td></td>
<td></td>
<td>465</td>
<td>45</td>
</tr>
<tr>
<td>( \text{(NH}_4)_2[\text{UO}_2(\text{NO}_3)_3]\text{F}.3\text{H}_2\text{O} )</td>
<td></td>
<td>410</td>
<td>55</td>
</tr>
<tr>
<td></td>
<td></td>
<td>420</td>
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<tr>
<td></td>
<td></td>
<td>460</td>
<td>50</td>
</tr>
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Table 6.7: IR and LR Spectral Data of \([UO_2(N_2H_4)_2F_2].2H_2O\) with their Assignments

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR</th>
<th>LR</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>([UO_2(N_2H_4)_2F_2].2H_2O)</td>
<td>924s</td>
<td>907s</td>
<td>(\nu(U=O))</td>
</tr>
<tr>
<td></td>
<td>415m</td>
<td></td>
<td>(\nu(U-F))</td>
</tr>
<tr>
<td></td>
<td>307m</td>
<td></td>
<td>(\nu(U-N))</td>
</tr>
<tr>
<td></td>
<td>3265s</td>
<td></td>
<td>(\nu(N-H))</td>
</tr>
<tr>
<td></td>
<td>3207m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>3131w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1607m</td>
<td></td>
<td>NH(_2) bending</td>
</tr>
<tr>
<td></td>
<td>1555m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1384w</td>
<td></td>
<td>NH(_2) wagging</td>
</tr>
<tr>
<td></td>
<td>1336w</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1228w</td>
<td></td>
<td>NH(_2) twisting</td>
</tr>
<tr>
<td></td>
<td>1196m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>955m</td>
<td></td>
<td>(\nu(N-N))</td>
</tr>
<tr>
<td></td>
<td>1657m</td>
<td></td>
<td>(\delta(H-O-H))</td>
</tr>
<tr>
<td></td>
<td>3438m</td>
<td></td>
<td>(\nu(O-H))</td>
</tr>
</tbody>
</table>
Table 6.8: IR and LR Spectral Data of A₂[\(\text{UO}_2\text{F}_4\)].3\(\text{H}_2\text{O}\) (A = K, Na or NH₄) with their Assignments

<table>
<thead>
<tr>
<th>Compound</th>
<th>IR (\text{cm}^{-1})</th>
<th>LR (\text{cm}^{-1})</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{K}_2[\text{UO}_2\text{F}_4]).3(\text{H}_2\text{O})</td>
<td>930s</td>
<td>-</td>
<td>(\nu(\text{U}=\text{O}))</td>
</tr>
<tr>
<td></td>
<td>373m</td>
<td></td>
<td>(\nu(\text{U}-%E2%80%93\text{F}))</td>
</tr>
<tr>
<td></td>
<td>1630m</td>
<td></td>
<td>(\delta(\text{H}-%E2%80%93\text{O}-%E2%80%93\text{H}))</td>
</tr>
<tr>
<td></td>
<td>3468m</td>
<td></td>
<td>(\nu(\text{O}-%E2%80%93\text{H}))</td>
</tr>
<tr>
<td>(\text{Na}_2[\text{UO}_2\text{F}_4]).3(\text{H}_2\text{O})</td>
<td>926s</td>
<td>-</td>
<td>(\nu(\text{U}=\text{O}))</td>
</tr>
<tr>
<td></td>
<td>372m</td>
<td></td>
<td>(\nu(\text{U}-%E2%80%93\text{F}))</td>
</tr>
<tr>
<td></td>
<td>1624m</td>
<td></td>
<td>(\delta(\text{H}-%E2%80%93\text{O}-%E2%80%93\text{H}))</td>
</tr>
<tr>
<td></td>
<td>3450m</td>
<td></td>
<td>(\nu(\text{O}-%E2%80%93\text{H}))</td>
</tr>
<tr>
<td>((\text{NH}_4)_2[\text{UO}_2\text{F}_4]).3(\text{H}_2\text{O})</td>
<td>927s</td>
<td>910s</td>
<td>(\nu(\text{U}=\text{O}))</td>
</tr>
<tr>
<td></td>
<td>376m</td>
<td>425m</td>
<td>(\nu(\text{U}-%E2%80%93\text{F}))</td>
</tr>
<tr>
<td></td>
<td>1626m</td>
<td></td>
<td>(\delta(\text{H}-%E2%80%93\text{O}-%E2%80%93\text{H}))</td>
</tr>
<tr>
<td></td>
<td>3460m</td>
<td></td>
<td>(\nu(\text{O}-%E2%80%93\text{H}))</td>
</tr>
<tr>
<td></td>
<td>1433s</td>
<td></td>
<td>(\nu(\text{N}-%E2%80%93\text{H}))_4</td>
</tr>
<tr>
<td></td>
<td>3074s</td>
<td></td>
<td>(\nu(\text{N}-%E2%80%93\text{H}))_1</td>
</tr>
<tr>
<td></td>
<td>3198m</td>
<td></td>
<td>(\nu(\text{N}-%E2%80%93\text{H}))_3</td>
</tr>
</tbody>
</table>
under appropriate experimental conditions. Thus, it was necessary to first ascertain the suitable experimental conditions and then work out the appropriate methodologies.

Fluoro(phosphato)uranates(VI)

It is known that the interaction of phosphate with $\text{UO}_2^{2+}$ is dependent on a number of parameters like concentrations of reactants, uranyl:phosphate concentration ratios, pH values of the reaction solutions and reaction temperatures. For instance, a ratio of $\text{UO}_3$ to $\text{P}_2\text{O}_5 < 1$ seems to favour the precipitation of $\left(\text{UO}_2\right)_3(\text{PO}_4)_2$ from a concentrated solution of $\text{UO}_2(\text{NO}_3)_2$ and $\text{H}_3\text{PO}_4$ in the pH range 0.9-1.1, whereas a pH of 1.75-2.1 is required for the precipitation of a similar compound from dilute solutions. It was hence conjectured that the optimum conditions for the successful synthesis of fluoro(phosphato)uranates(VI) would be the $\text{UO}_2^{2+}$:phosphate:F$^-\text{ concentration ratio of 1:2:6 in the pH range 1-2.}$ The reaction of $\text{UO}_3.4\text{H}_2\text{O}$ with alkali hydrofluoride, $\text{AHF}_2$ and $\text{H}_3\text{PO}_4$ at a steam-bath temperature gave rise to a natural pH of ca. 2 thereby providing a condition conducive to the synthesis of lemon-yellow crystalline $A_2[\text{UO}_2(\text{PO}_4)_2\text{F}(\text{H}_2\text{O})_3].3\text{H}_2\text{O}$ ($A = \text{K}, \text{Na}$ or $\text{NH}_4$) as obtained. The alkali hydrofluoride is believed to have played two major roles. For instance it has not only functioned as a fluorinating agent but also acted as a buffer to provide the appropriate pH of the reaction medium.
The compounds were insoluble in the commonly available polar or non-polar solvents and hence the question of solution electrical conductance measurement did not arise.

The IR spectra (Figs.6.1-6.3) of the complexes $A_2[UO_2(PO_4)F(H_2O)]_3H_2O$ ($A = K, Na$ or $NH_4$) exhibited bands due to uranyl centre, coordinated fluoride, coordinated phosphate, coordinated and lattice water. The bands in the region of ca. 920-930 cm$^{-1}$ and ca. 380-415 cm$^{-1}$ have been assigned to the asymmetric stretch $\nu_{as}(UO_2)$ of the trans.$O=U=O$ group$^9,10$ and $\nu(U-F)$,$^11$ respectively. Phosphate is an important IR spectral probe for the determination of its mode of coordination to the metal centre. The range 850-1200 cm$^{-1}$ involving the $\nu_1$ and $\nu_3$ fundamentals of coordinated phosphate is the most sensitive IR spectral region for ascertaining the local symmetry of a coordinated phosphato ligand. The observance of a medium intensity band at ca.900 cm$^{-1}$ [$\nu_1(PO_4)$] and the splitting of the $\nu_3$ mode of $PO_4$ into three strong bands at ca.1000, ca.1070 and ca.1120 cm$^{-1}$ clearly shows the $C_{2v}$ symmetry of phosphate ligand. Of particular significance was the absence of an absorption at ca.2700 cm$^{-1}$ discernable to $\nu(P-O-H)$,$^12$ excluding the possibility of formation of hydrophosphate. The observed IR spectral pattern thus lends support to the presence of phosphate as $PO_4^{3-}$ coordinated to the uranyl centre in a bidentate$^{13}$ fashion. In addition, the bands at ca.740 [$\rho_r(H_2O)$], ca.1645 [$\delta(H-O-H)$] and ca.3450 [$\nu(O-H)$] provide evidence for the presence
K$_2$[UO$_2$(PO$_4$)F(H$_2$O)$_3$].3H$_2$O

FIG. 6.1: IR SPECTRUM
Na$_2$[UO$_2$(PO$_4$)$_2$F(H$_2$O)$_3$].3H$_2$O

FIG. 6.2: IR SPECTRUM
FIG. 6.3: IR SPECTRUM

$\text{NH}_4\text{[UO}_2\text{PO}_4\text{F(H}_2\text{O)}_3\text{]}\cdot3\text{H}_2\text{O}$
of both coordinated as well as lattice water molecules in the complexes.

Phosphato complexes of $\text{UO}_2^{2+}$ generally obtained from precipitation reactions are gelatinous in nature. Thus in the present case it was imperative to make use of Scanning Electron Microscopy to get an idea of the homogeneity and crystallinity of the newly synthesized fluoro(phosphato)complexes. As a typical case, micrographs of $\text{Na}_2\left[\text{UO}_2\left(\text{PO}_4\right)\text{F}(\text{H}_2\text{O})_3\right]\cdot3\text{H}_2\text{O}$ were recorded to expose two different stereo-views in Figs. 6.4 and 6.5. Fig.6.4 shows the symmetric hexagonal crystal morphology of the complex, whilst Fig.6.5 evidences for its cylindrical shape.

**Fluoro(nitrato) complexes of $\text{UO}_2^{2+}$**

Nitrate, one of the common inorganic anions is known to form binary complexes with uranyl ion. However, the complexes formed are very weak, the strength, in fact, comparable to the complexes formed by heavier halide ions. Moreover extensive complex formation appears to occur only at high nitrate ion concentration as observed by our group in an earlier occasion and by others. Significant in this context is that while 1-4 M nitric acid was shown to favour tri- or tetranitrato complex formation, an acid concentration of < 1M facilitates the hydrolysis of $\text{UO}_2^{2+}$. It was hence anticipated that a concentration range of 1-4 M $\text{HNO}_3$ would be conducive to the complexation of $\text{NO}_3^-$.
**FIG. 6.4:** SE MICROGRAPH OF

\[ \text{Na}_2\text{[UO}_2\text{(PO}_4\text{)}\text{F(H}_2\text{O)}_3].3\text{H}_2\text{O} } \]

**FIG. 6.5:** SE MICROGRAPH OF

\[ \text{Na}_2\text{[UO}_2\text{(PO}_4\text{)}\text{F(H}_2\text{O)}_3].3\text{H}_2\text{O} \]
to UO$_2^{2+}$ in the presence of F$^-$. Owing to the high concentrations of nitrate required for the syntheses as well as our goal being to access mixed-fluoro(nitrato) complexes of UO$_2^{2+}$, we were to also maintain an appreciably high F$^-$ concentration. Accordingly, the reaction of A$_2$UO$_2$O$_7$ (A = K, Na or NH$_4$) with 2.08 M HNO$_3$ and aqueous HF maintaining the concentration of UO$_2^{2+}$:NO$_3^-$:F$^-$ as 1:ca.11:ca.36 afforded the complexes A$_2$[UO$_2$(NO$_3$)$_3$F].3H$_2$O (A = K, Na or NH$_4$).

The fluoro(nitrato) complexes are lemon-yellow in colour and highly soluble in water. They are hygroscopic in nature and absorb moisture rather rapidly on exposure to air.

The IR spectral features (Figs.6.6-6.8) of all the three salts of the mixed-fluoro(nitrato) complexes were essentially similar bearing a close internal resemblance in respect of their patterns. The strong bands in the region ca.930-950 cm$^{-1}$ and ca. 390-405 cm$^{-1}$ owe their origins to the $\nu$(U=O) [trans.linked O=U=O] and coordinated fluoride, respectively. The 700-1550 cm$^{-1}$ region is important for coordinated nitrate group$^{16}$ and for the complexes under discussion, barring the absorption from $\nu$(U=O) at 930-950 cm$^{-1}$, there is no interference from any other ligands. Incidentally, the coordinated nitrate does not exhibit any vibration in the $\nu$(U=O) region. The symmetry of the free nitrate ion upon coordination changes from D$_{3h}$ to C$_{2v}$ and thereby six normal modes of vibration become IR active$^{10b,16}$ irrespective of
Fig. 6.6: IR Spectrum

$K_2[\text{UO}_2(\text{NO}_3)_3\text{F}].3\text{H}_2\text{O}$
\[
Na_2[\text{UO}_2(\text{NO}_3)_3\text{F}].3\text{H}_2\text{O}
\]

**FIG. 6.7: IR SPECTRUM.**
(NH₄)₂[UO₂(NO₃)₃F].3H₂O

FIG. 6.8: IR SPECTRUM
its mono- or bidentate type of coordination. The complexes A₂[\text{UO}_2(\text{NO}_3)_3\text{F}].3\text{H}_2\text{O} (A = \text{K}, \text{Na} \text{ or NH}_4) displayed all the six modes with the \( \nu_1 \) to \( \nu_6 \) occurring at ca.1504s, ca.1025m, ca.742m, ca.1290s, ca.707w and ca.805m cm\(^{-1}\), respectively, thereby making it certain that the nitrates are coordinated to the metal centre.

In order to distinguish between mono- and bidentate coordination from IR data, a large separation of \( \nu_1 \) and \( \nu_4 \) (ca.200 cm\(^{-1}\)) is used as an important criterion for bidentate coordination of the ligand. This view is strongly supported by IR studies on crystallographically confirmed bidentate nitrates. The \((\nu_1-\nu_4)\) values in the present complexes was found to be ca.215 cm\(^{-1}\), thereby making it logical to assume that the nitrates in the present complexes are coordinated to the metal centre in a bidentate fashion.

A high solubility of the fluoro(nitrato) complexes in water enabled us to carry out solution electrical conductivity measurements in order to know the mode of ionization of the complexes. Indeed, the recorded values of 244, 242 and 245 \( \Omega^{-1} \text{cm}^2 \text{mol}^{-1} \) respectively for the K, Na and NH\(_4\) salts of the complex \([\text{UO}_2(\text{NO}_3)_3\text{F}]^{2-}\) ion conform to the 1:2 electrolytic nature befitting to their formulae. Moreover, the unaltered solution electrical conductivity values over a period of three or four days is a clean reflection of their stability in aqueous solution under the present experimental conditions.
The stability of the complexes in aqueous solution (as evidenced by solution electrical conductance experiments) prompted us to record their electron absorption spectra as well. The electronic absorptions were observed at ca.415, ca.425, ca.435 and ca.465 nm (Figs.6.9-6.11). These have been attributed to be the electron transfer bands of uranyl ion. The bathochromic shift observed as compared to that for the free uranyl ion can be explained in terms of coordination of the UO$_2$$^{2+}$ ion. The nitrate ion that has got a high tendency to transfer electrons upon coordination must have most probably caused the electron-transfer bands to shift further into the visible region. The spectral pattern compares very well with those observed by others for uranyl-nitrato complexes. This therefore provides credence to the contention that nitrates are coordinated to the metal centre in the respective complexes.

*Hetero-ligand Fluoro(hydrazine) complex of UO$_2$$^{2+}$*

Owing to the success in using alkali hydrofluoride as the fluorinating agent for the synthesis of a number of mixed-ligand fluorodioxouranates(VI) with a variety of co-ligands like amino acids (Chapter V), phosphate (present work), it was anticipated that a mixed-ligand fluoro complex of UO$_2$$^{2+}$ with hydrazine as the co-ligand could be synthesized by adopting a similar methodology. In accordance with this, UO$_3$.4H$_2$O on reaction with AHF$_2$ (A = K or...
**FIG. 6.9: ELECTRON ABSORPTION SPECTRUM**

K$_2$[UO$_2$(NO$_3$)$_3$]F$_3$H$_2$O in water

ABSORPTION (ARBITRARY SCALE)
$\text{Na}_2\text{[UO}_2\text{(NO}_3\text{)}_3\text{F}\text{].3H}_2\text{O in water}}$

**FIG. 6.10: ELECTRON ABSORPTION SPECTRUM**
(NH₄)₂[UO₂(NO₃)₃F].3H₂O in water

FIG. 6.11: ELECTRON ABSORPTION SPECTRUM
and hydrazine hydrate, $\text{NH}_4$-$\text{H}_2\text{O}$ at steam-bath temperature afforded the hitherto unreported complex $[\text{UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2].2\text{H}_2\text{O}$. The pH value of the reaction solution measured at the stage of precipitation of the compound was found to be ca.8.5 which has facilitated the coordination of $\text{N}_2\text{H}_4$ to the metal centre since in a basic medium the possibility of hydrazonium ion ($\text{N}_2\text{H}_5^+$) formation does not exist.

The compound is brownish in colour and insoluble in most of the commonly available polar and non-polar solvents. The scanning electron micrograph (Fig.6.12) is a reflection of the crystalline and homogenous nature of the complex $[\text{UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2].2\text{H}_2\text{O}$. However, no definitive shape of the crystals could be discerned from the micrograph.

The IR spectrum (Fig.6.13) of $[\text{UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2].2\text{H}_2\text{O}$ showed a few bands at 924s [υ(U=O), trans.linked O=U=O], 415m, [υ(U-F)] and bands typical of coordinated hydrazine. However, the absorptions of particular significance for coordinated hydrazine are those arising from N-N stretching vibrations. In complexes containing unidentate hydrazine ligands υ(N-N) occurs around 930 cm$^{-1}$ while in complexes containing bidentate hydrazine υ(N-N) appears at ca. 970 cm$^{-1}$. In the present case a medium intensity band was observed at 955 cm$^{-1}$. Further the appearance of $\text{NH}_2$ stretches at 3265s, 3207m and 3131w cm$^{-1}$ and the similarity in spectral pattern with hydrazine and mixed-ligand hydrazine complexes of different metals.
FIG. 6.12: SE MICROGRAPH OF

$[\text{UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2].2\text{H}_2\text{O}$
synthesized earlier by others and our group cause us to state that the complex \([\text{UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2].2\text{H}_2\text{O}\) contains only bidentate hydrazine ligands. Though the hydrazines in \([\text{UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2].2\text{H}_2\text{O}\) might act as chelated ligands, the possibility of hydrazine bridges leading to a polymeric network in the crystal lattice cannot be ruled out. The insolubility of \([\text{UO}_2(\text{N}_2\text{H}_4)_2\text{F}_2].2\text{H}_2\text{O}\) might as well be an indication of polymeric nature of the complex. The metal-nitrogen stretching was observed at 307 cm\(^{-1}\) as a consequence of hydrazine coordination.

Pyrolysis studies were conducted on each of the mixed-fluoro (phosphato), fluoro(nitrato) and fluoro(hydrazine) complexes in order to ascertain the nature of water molecules present in the complexes. Pyrolyses of the compounds at ca.150°C for nearly 2h gave products with weight losses corresponding to the loss of three molecules of water for each of the fluoro(phosphato) and fluoro(nitrato) complexes and product corresponding to the loss of two molecules of water in the case of fluoro(hydrazine) complex. This therefore enables us to state that each of the fluoro(phosphato) and fluoro(nitrato) complexes contains three molecules of lattice water whereas the fluoro(hydrazine) complex contains two such water molecules. Significant to note here is that each of the pyrolysed product of fluoro(hydrazine) and fluoro (nitrato) complexes did not show the characteristics of any kind of water in its IR spectra, but those of fluoro(phosphato)
complexes displayed the features of bonded water at \( \text{ca.} 740 \text{ cm}^{-1} \) attributed to the rocking mode of coordinated water \([\rho_r(H_2O)]\).

In this way a number of mixed-ligand fluoro complexes of \( \text{UO}_2^{2+} \) containing inorganic co-ligands could be obtained in high isolated yields. A notable general point in the context of the present synthetic study is the avoidance of an excess of fluoride ion concentration to inhibit preponderance of binary fluoro complex formation.

**Raman Spectroscopic Studies on Hetero-Ligand Fluoro(phosphato), Fluoro(nitrato) and Fluoro(hydrazine) complexes of UO\(_2^{2+}\)**

One of the most important and powerful techniques useful for the characterization of coordination compounds of uranyl ion is Raman spectroscopy. The \( \nu_s(U=O) \) is believed to be an important laser Raman (LR) probe. In the Raman, only the symmetric stretching mode, \( \nu_s(\text{UO}_2)(\nu_1) \) is active \([\nu_{as}(\text{UO}_2)(\nu_3) \text{ is not active}\) and this has generally been observed at \( \text{ca.} 900 \text{ cm}^{-1} \) in the solids.\(^{1,23}\) In solutions, however, \( \nu_s(\text{UO}_2)(\nu_1) \) of \( \text{UO}_2^{2+} \) ions appears at 870 cm\(^{-1}\). This generally decreases on complex formation with a variety of inorganic and organic ligands. A good correlation between the shift in the \( \nu_1 \) frequency and the number of ligands coordinated to the metal centre has been discussed in a recent paper.\(^24\)
In the present study, the laser Raman spectra (Figs. 6.14–6.19) of the reaction solutions were recorded in the following manner. A small amount of the solution was drawn out from the reaction vessel and the spectra were recorded in each of the cases of fluoro(phosphato) and fluoro(nitrato) complexes before precipitating out the compounds. In each case the $\nu_1$ frequency was observed to occur at ca. 840 cm$^{-1}$. The observed shift in frequency by 30 cm$^{-1}$ (cf. 870 cm$^{-1}$ for aqueous uranyl ion) is a clear reflection of complex formation by uranyl ion and most probably also of the increase in stability upon complexation as compared to that of hydrated uranyl ion. Significant to note here is that though the $\nu_s$(UO$_2$)($\nu_1$) mode of UO$_2^{2+}$ is insensitive to the coordination of NO$_3^-$ (Refs. 24,25) to the uranyl centre, the observed lowering in frequency of fluoro(nitrato) complexes indicates that the presence of fluoride ligands must have been responsible for the increase in stability of mixed-fluoro(nitrato) complexes of the metal. Such an exercise could not be conducted for the complex [UO$_2$(N$_2$H$_4$)$_2$F$_2$].2H$_2$O since a solid product precipitated out of the solution instantaneously on the addition of hydrazine.

On the contrary, each of the mixed-fluoro(phosphato), fluoro(nitrato) and fluoro(hydrazine) complexes of UO$_2^{2+}$ displayed a strong Raman signal at ca. 900 cm$^{-1}$ in the solid state and this has been attributed to the $\nu_s$(UO$_2$)($\nu_1$) mode of UO$_2^{2+}$ ion. The
FIG. 6.14: Raman spectrum of

\[ K_2[UO_2(PO_4)F(H_2O)_3].3H_2O \]
FIG. 6.15: RAMAN SPECTRUM OF

\[ \text{Na}_2\text{[UO}_2\text{(PO}_4\text{)F(H}_2\text{O)}_3\text{].3H}_2\text{O}} \]

\( \Delta_s (O=U=O) \)

--- solid

--- solution

\( \lambda = 6471 \text{ Å} \)
Fig. 6.16: Raman spectrum of

\[(\text{NH}_4)_2[\text{UO}_2(\text{PO}_4)\text{F}(\text{H}_2\text{O})_3].3\text{H}_2\text{O}\]
FIG. 6.17: RAMAN SPECTRUM OF

\[ \text{K}_2\text{[UO}_2\text{(NO}_3\text{)}_3\text{F}]\cdot3\text{H}_2\text{O} \]
\( \lambda = 6471 \, \text{Å} \)

FIG. 6.18: RAMAN SPECTRUM OF

\[ \text{Na}_2\text{[UO}_2\text{(NO}_3\text{)}_3\text{F]} \cdot 3\text{H}_2\text{O} \]
\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{raman_spectrum.png}
\caption{Raman Spectrum of $(\text{NII}_4)_2[\text{UO}_2(\text{NO}_3)_3\text{F}].3\text{H}_2\text{O}$}
\end{figure}
observed increase in $\nu_1$ frequency in going from the solution to
the solid state is most probably due to the decrease in number of
aqua ligands in the $\text{UO}_2^{2+}$ coordination shell of the solid
complexes. A similar trend is occasionally encountered in highly
ligand concentrated solutions of $\text{UO}_2^{2+}$.26

$\text{Alkali tetrafluorodioxouranates(VI) trihydrates } \text{A}_2[\text{UO}_2\text{F}_4].3\text{H}_2\text{O}$
($\text{A} = \text{K, Na or NH}_4$)

Having been encouraged by the successful synthesis of a
number of binary and mixed-ligand oxofluorouranates(VI) as
described in Chapter V of the thesis as well as those set out in
the present Chapter, our attention was drawn to the
dioxotetrafluorouranate, $[\text{UO}_2\text{F}_4]^{2-}$ species as well. The complex
species has been known and there is more than one method available
for its preparation but the procedures are all circuitous. This
point has been emphasized in the introduction section. Our goal in
this context was to improvise direct synthetic routes to the
complex $[\text{UO}_2\text{F}_4]^{2-}$ species. To this end we have been able to
improvise two methodologies the strategies of which are
highlighted below.

One of the methodologies is based upon the reaction of a
yellow product, obtained by treating uranyl nitrate,
$\text{UO}_2(\text{NO}_3)_2.6\text{H}_2\text{O}$, solution with an aqueous alkali, AOH ($\text{A} = \text{K or}
Na), or aqueous ammonia (sp.gr.0.91), with 48% aqueous hydrofluoric acid and $A_2\text{CO}_3$ ($A = K$, Na or NH$_4$). The presence of alkali carbonate was apparently essential for it not only provided an appropriate concentration of the counter cation, $A^+$, but also presumably controlled the reaction pH ($4H^+ + \text{CO}_3^{2-} \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$) to a level required for the success.

The basis of the other method has been a sort of nucleophilic substitution reaction. What was done in this case was that a well known$^{27}$ peroxouranium(VI) species, $\text{UO}_2(\text{O}_2).2\text{H}_2\text{O}$, was reacted with aqueous HF (48%) in the presence of alkali fluoride, AF ($A = K$, Na or NH$_4$) to afford $A_2[\text{UO}_2\text{F}_4].3\text{H}_2\text{O}$ in very high yields. The mechanism of the reaction presumably involved a concerted process wherein the hydrofluoric acid interacted with the bonded peroxide to liberate $\text{H}_2\text{O}_2$ quantitatively and $\text{F}^-$ ions present in the reaction medium occupied the sites made available to provide the complex as obtained. Although one might tend to presume the formation of an aquated uranyl viz., $[\text{UO}_2(\text{H}_2\text{O})_n]^{2+}$ ion resulting from the reaction of $\text{UO}_2(\text{O}_2)$ with aq. HF followed by its interaction with $\text{F}^-$ ions already available in the solution. We wish to subscribe to the former pathway preferred to the latter because of the presence of a good amount of fluoride at a stage when $\text{UO}_2(\text{O}_2)$—HF reaction was to take place. Since fluoride is certainly a superior ligand as compared to aqua ligands ($\text{H}_2\text{O}$) our proposition seems to be rather rational.
The alkali dioxotetrafluorouranates(VI), $A_2[UO_2F_4].3H_2O$ ($A = K, Na$ or $NH_4$) are lemon-yellow crystalline solids highly soluble in water. The solution electrical conductances of the compounds in water were found to lie in the range $230-240 \Omega^{-1}cm^2mol^{-1}$ which conform to their 2:1 electrolytic nature. The favourable experimental result attests to their stability in aqueous solution.

The significant features of IR spectra (Figs.6.20-6.22) of the complexes $A_2[UO_2F_4].3H_2O$ ($A = K, Na$ or $NH_4$) were the bands at ca.928, ca.374, ca.1627 and ca.3460 cm$^{-1}$, which have been attributed to the absorptions originating from $\nu$(U=O) [trans. linked O=U=O], $\nu$(U-F), $\delta$(H-O-H) and $\nu$(O-H) modes, respectively.

In order to obtain further support to the structural motifs of the complexes $A_2[UO_2F_4].3H_2O$ ($A = K, Na$ or $NH_4$), $(NH_4)_2[UO_2F_4].3H_2O$, as a typical example, was subjected to laser Raman (LR) spectroscopy. The Raman signals (Fig.6.23) observed at 425 and 910 cm$^{-1}$ have been assigned as the $\nu$(U-F) and $\nu$(U=O) [trans. linked O=U=O) modes, respectively. Importantly the LR spectral features also complement the IR spectral results obtained on the complexes.

The results of the Infrared and laser Raman spectroscopic studies are thus in full agreement with the formulae $A_2[UO_2F_4].3H_2O$. 
FIG. 6.20: IR SPECTRUM

$K_2[\text{UO}_2\text{F}_4].\text{H}_2\text{O}$
$\text{Na}_2[\text{UO}_2\text{F}_4].3\text{H}_2\text{O}$

**FIG. 6.21: IR SPECTRUM**
(NH₄)₂[UO₂F₄].3H₂O

**FIG. 6.22: IR SPECTRUM**
FIG. 6.23: RAMAN SPECTRUM

\[ \text{\(\left(\text{NH}_4\right)_2\left[\text{UO}_2\text{F}_4\right].3\text{H}_2\text{O}\)} \]

\[ \lambda = 4880 \, \text{\AA} \]

\[ \text{WAVE-NUMBER (cm}^{-1}) \]

\[ \text{INTENSITY (ARBITRARY SCALE)} \]
References


