CHAPTER-V

DIOXOURANIUM (VI) AND THORIUM (IV) COMPLEXES WITH 2,6-BIS (BENZOXAZOL-2’-YL) PYRIDINE
5.1. Introduction

Among the metal oxocations, the species with a metal-oxygen bond of order higher than unity are particularly interesting. Indeed, the metal-oxygen multiple bonds have generated considerable theoretical and experimental interest. Dioxouranium(VI) is itself a strong complex of uranium and oxygen in which oxygen is strongly bonded to the metal. Although the metal-oxocations are widely known for the lighter transition elements of groups IV, V and VI, the theoretical treatment of bonding and electronic structure in oxocation complexes have been made for UO$_2^{2+}$ [217-222] and VO$_2^{2+}$ [223,224].

Both the dioxouranium(VI) and thorium(IV), because of their high charge and large size, are expected to form compounds with high coordination number. The dioxouranium(VI) ion is interesting, since it can coordinate from 2 to 10 ligand atoms about its equator with a strong tendency to make these atoms coplanar [225].

The dioxouranium(VI) and uranium(IV) are known to gain access to the body by a variety of routes and are toxic to the enzymes located in the kidney cells [226]. Since metal ion toxicity is associated with a chelation mechanism, a study of uranium chelates of actinide elements finds a possible use as a tool for selective separation. The coordination chemistry of tetravalent thorium ion has been relatively less extensive [227], even though it presents an exciting area of investigation, because of its
possibility to form compounds with coordination number greater than six, a feature which has aroused considerable interest [228].

As far as the ligand is concerned, the chelating ligand has been chosen, since such ligands dominate the area of higher coordination polyhedra in scope, numbers and in kinetic and thermodynamic stability. The tridentate ligand 2,6-bis(benzoxazol-2-yl) pyridine (bzopxy) is an analogue of 2,2':6',2''-terpyridine in which the pyridine nitrogen and nitrogens of the benzoxazole rings coordinate to the metal ions. Survey of literature depicts that number of complexes of transition metal and lanthanide ions with this and its nitrogen analogue 2,6-bis(benzimidazol-2-yl) pyridine have been reported [100, 101]. But no work has been done with uranium(VI) and thorium(IV). So in the present investigation, we report here some uranium(VI) and thorium(IV) complexes with non-fused biheterocycle 2,6-bis(benzoxazol-2-yl) pyridine.

5.2 Experimental

The ligand bzopxy was prepared as described in Chapter-II.
Synthesis of complexes

The complexes $\text{UO}_2 (\text{bzopxy})_n \text{X}_2$ ($X = \text{Cl, I, NCS, OAc, n = 1; X - NO}_3, 0.5 \text{SO}_4$, $n = 2$) and $\text{Th(bzopxy)}_2 \text{X}_4$ ($X = \text{NCS, I, NO}_3$) were synthesized by a common procedure. The metal salt solution in methanol was mixed with requisite stoichiometric amount of ligand solution in chloroform. This solution mixture was refluxed for about 2h, after which period the solution was concentrated. On cooling desired metal complexes were obtained. These were collected by filtration, followed by washing with small aliquot of methanol, finally with diethylether and dried in vacuo.

5.3. Results and Discussion

The ligand 2,6-bis(benzoxazol-2'-yl) pyridine has three potential sites for coordination. The ligand forms well defined complexes with the metal ions that are presented in Table 5.1, alongwith relevant characterizing data. The high melting point and poor solubility of the complexes in suitable organic solvents did not allow molecular mass determination by cryoscopic methods.
Table - 5.1 : Analytical data of dioxouranium(VI) and thorium(IV) complexes with bzopxy.

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>M.P. (°C)</th>
<th>Found (calc) (%)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>M</td>
<td>C</td>
</tr>
<tr>
<td>UO$_2$(bzopxy)Cl$_2$</td>
<td>Light yellow</td>
<td>&gt; 300</td>
<td>36.2 (36.4)</td>
<td>34.3 (34.9)</td>
</tr>
<tr>
<td>UO$_2$(bzopxy)I$_2$</td>
<td>Yellow</td>
<td>298d</td>
<td>28.2 (28.4)</td>
<td>27.0 (27.2)</td>
</tr>
<tr>
<td>UO$_2$(bzopxy)(NCS)$_2$</td>
<td>Yellow</td>
<td>&gt; 300</td>
<td>33.9 (34.0)</td>
<td>36.3 (36.1)</td>
</tr>
<tr>
<td>UO$_2$(bzopxy)(OAc)$_2$</td>
<td>Pale yellow</td>
<td>&gt; 300</td>
<td>33.7 (33.9)</td>
<td>39.2 (39.4)</td>
</tr>
<tr>
<td>UO$_2$(bzopxy)$_2$(NO$_3$)$_2$</td>
<td>Yellow</td>
<td>285d</td>
<td>23.2 (23.3)</td>
<td>44.6 (44.7)</td>
</tr>
<tr>
<td>UO$_2$(bzopxy)$_2$SO$_4$</td>
<td>Yellow</td>
<td>296d</td>
<td>23.8 (23.9)</td>
<td>46.0 (46.0)</td>
</tr>
<tr>
<td>Th(bzopxy)$_2$I$_4$</td>
<td>Dull white</td>
<td>&gt; 300</td>
<td>16.8 (17.1)</td>
<td>33.4 (33.4)</td>
</tr>
<tr>
<td>Th(bzopxy)$_2$(NCS)$_4$</td>
<td>White</td>
<td>285d</td>
<td>20.8 (21.3)</td>
<td>46.1 (46.2)</td>
</tr>
<tr>
<td>Th(bzopxy)$_2$(NO$_3$)$_4$</td>
<td>Off white</td>
<td>&gt; 300</td>
<td>20.5 (20.9)</td>
<td>41.1 (41.2)</td>
</tr>
</tbody>
</table>
Conductance measurement

Molar conductance values of the complexes were determined in dilute solutions (\( \sim 10^{-3} \) - \( 10^{-4} \) M) in various solvents at room temperature and are presented in Table 5.2. A comparison of all these values indicate that the complexes are essentially non-electrolytes. The molar conductivity of the halocomplexes increase in the order : Cl < I and is in very good agreement with the reported stability of the uranium halogen bond [229]. Higher molar conductivity values were observed in methanol and dimethyl formamide solutions indicating a greater solvolysis in these solvents. As will be shown later, the IR spectra of these complexes provide no evidence for ionic nitrate, thiocyanate, acetate or sulphate. In all the cases, the molar conductivities were measured by adding extra amount of tri-n-octyl phosphine oxide and the results were found unaltered indicating clearly the covalent bonding of all anions.

Among the thorium complexes, NCS and I complexes were non-electrolyte, whereas the nitrate complex is 1:2 electrolyte. However, the IR spectra of these complexes showed the presence of two different types of nitrate group. Similar results were reported for thorium nitrate complexes by Mohanta et al. [230].

Electronic spectra

The electronic spectra of uranyl complexes in methanol showed no bands in the 350-750 nm region. However, in DMSO a broad
Table - 5.2 : Molar conductivity of U(VI) and Th(IV) complexes with 2,6-bis(benzoxazol-2'-yl) pyridine (L).

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductivity (Ω⁻¹ mol⁻¹ cm²)</th>
<th>Ion type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MeOH</td>
<td>DMF</td>
</tr>
<tr>
<td>UO₂LCl₂</td>
<td>65.53</td>
<td>35.02</td>
</tr>
<tr>
<td>UO₂L(NCS)₂</td>
<td>62.69</td>
<td>134.7</td>
</tr>
<tr>
<td>UO₂LI₂</td>
<td>146.3</td>
<td>70.25</td>
</tr>
<tr>
<td>UO₂L₂SO₄</td>
<td>-</td>
<td>4.9</td>
</tr>
<tr>
<td>UO₂L(OAc)₂</td>
<td>27.29</td>
<td>91.6</td>
</tr>
<tr>
<td>UO₂L₂(NO₃)₂</td>
<td>126.0</td>
<td>86.5</td>
</tr>
<tr>
<td>ThL₂I₄</td>
<td>282.3</td>
<td>251.9</td>
</tr>
<tr>
<td>ThL₂(NCS)₄</td>
<td>102.9</td>
<td>109.3</td>
</tr>
<tr>
<td>ThL₂(NO₃)₄</td>
<td>169.25</td>
<td>143.9</td>
</tr>
</tbody>
</table>
band is observed at 428 nm which is due to the excitation of electron from highest filled π-molecular orbital to a non-bonding orbital of uranium [218]. The band observed below 338 nm is due to ligand π - π* transition. The band at 444-459 nm is due to the UO$_{2}^{2+}$ group. The band at 285 nm is due to π - π* transition of phenyl ring.

**Infra red spectra**

The IR spectra of the ligand and complexes Table 5.3 are identical and ligand bands in the complexes are clearly identified. The comparison of IR data of the complexes with those of ligand revealed the most diagnostic feature to be the red shifts of v (C=N) indicating the coordination of ligand to the metal through the heterocyclic nitrogen atoms. The pyridine ring vibration of bzopxy is shifted to higher energy which is also a good indication of the coordination of the heterocyclic nitrogen atom. The spectra of the complexes exhibit two high energy pyridine ring vibrations in the range 1590-1565 and 1498-1465 cm$^{-1}$ as expected [206].

The uranyl ion exhibits three vibrational frequencies, a symmetric $\nu_1$, asymmetric $\nu_3$ and stretching and bending $\nu_2$. In the normal IR spectrum the moderate to strong absorption band observed at 900-945 cm$^{-1}$ and weak bands at 800-860 cm$^{-1}$ are assigned to $\nu_3$ or $\nu_{as}$ and $\nu_1$ or $\nu_{s}$, respectively of the UO$_{2}^{2+}$ group [231].
Polyatomic anion vibrations also indicate the mode of their coordination. The thiocyanate complexes exhibit bands at 2068 and 810 cm\(^{-1}\) for the dioxouranium(VI) and at 2078 and 820 cm\(^{-1}\) for the thorium(IV) complexes corresponding to the \(\nu(C=N)\) and \(\nu(C-S)\) vibrations of a N-coordinated terminally bonded iso-thiocyanate [232-234]. For the free nitrate ion, of the four fundamentals, only three (\(\nu_2, \nu_3\) and \(\nu_4\)) are IR active. On coordination in unidentate or bidentate fashion, the effective symmetry of the nitrate ion gets lowered to \(C_{2v}\) from \(D_{3h}\). This causes the degeneracies to split and fundamentals of all the six normal mode of vibrations to be IR active. The uranyl complexes exhibited bands at 1530, 1280, 1020, 790 and 755 cm\(^{-1}\) corresponding to the unidentate coordination of the nitrate group exemplifying 10-coordinate complex of uranium. For the thorium nitrate complex, however, it is clear that there are two different types of nitrate anions present as was reported earlier by Manhas et al. [235] and also by Curtius [236] and Alvey et al. [257]. A set of \(2\) NO\(_3\)\(^-\) ions are coordinated in a bidentate manner and the other set of \(2\) NO\(_3\)\(^-\) ions are present as ionic nitrate. Bands at 1500, 1285, 825, 790 and 745 cm\(^{-1}\) correspond to bidentate nitrate group [238]. Ionic nitrate vibrations were observed at 1370, 1275, 1058 and 830 cm\(^{-1}\). The presence of bi-coordinated sulphate [239] group is evident from the splitting of \(\nu_3\) and \(\nu_4\) modes and the appearance of the IR forbidden \(\nu_1\) band in uncoordinated sulphate group. The IR spectrum of the acetate complex exhibits two bands at 1560 and 1410 cm\(^{-1}\) assigned to \(\nu_{as}\) (COO) and \(\nu_s\) (COO) respectively, which indicate that acetate groups are
<table>
<thead>
<tr>
<th>Complex</th>
<th>Anion vibrations</th>
<th>Uranyl vibrations $\nu_{as}$</th>
<th>$\nu_{s}$</th>
<th>-C=N-str</th>
<th>Py breathing</th>
<th>Py ring vibrations</th>
</tr>
</thead>
<tbody>
<tr>
<td>L</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1610</td>
<td>945</td>
<td>1540, 1490</td>
</tr>
<tr>
<td>UO$_2$LCl$_2$</td>
<td>-</td>
<td>921</td>
<td>850</td>
<td>1622</td>
<td>980</td>
<td>1545, 1490</td>
</tr>
<tr>
<td>UO$_2$L(NCS)$_2$</td>
<td>2062, 810</td>
<td>928</td>
<td>815</td>
<td>1625</td>
<td>980</td>
<td>1560, 1440</td>
</tr>
<tr>
<td>UO$_2$LI$_2$</td>
<td>-</td>
<td>918</td>
<td>817</td>
<td>1621</td>
<td>958</td>
<td>1575, 1480</td>
</tr>
<tr>
<td>UO$_2$L$_2$SO$_4$</td>
<td>1137, 1025</td>
<td>921</td>
<td>791</td>
<td>1637</td>
<td>968</td>
<td>1545, 1452</td>
</tr>
<tr>
<td>UO$_2$L(OAc)$_2$</td>
<td>1615, 1440</td>
<td>918</td>
<td>790</td>
<td>1630</td>
<td>950</td>
<td>1540, 1440</td>
</tr>
<tr>
<td>UO$_2$L$_2$(NO$_3$)$_2$</td>
<td>1480, 1280, 1030, 745</td>
<td>912</td>
<td>783</td>
<td>1625</td>
<td>980</td>
<td>1590, 1453</td>
</tr>
<tr>
<td>ThL$_2$I$_4$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1610</td>
<td>985</td>
<td>1568, 1456</td>
</tr>
<tr>
<td>ThL$_2$(NCS)$_4$</td>
<td>2098, 810</td>
<td>-</td>
<td>-</td>
<td>1625</td>
<td>956</td>
<td>1547, 1445</td>
</tr>
<tr>
<td>ThL$_2$(NO$_3$)$_4$</td>
<td>152.5, 1280, 1022, 743</td>
<td>-</td>
<td>-</td>
<td>1612</td>
<td>985</td>
<td>1540, 1451</td>
</tr>
</tbody>
</table>

$L = 2,6$-bis(benzoxazol-2'-yl)
coordinated to the dioxyuranium(VI) centre as bidentate ligand [240].

**NMR spectra**

The NMR studies provide conclusive evidence in favour of the mode of bonding. The $^1H$ NMR spectrum of the free ligand bzopxy in DMSO-$d_6$-CDCl$_3$ medium consists of a doublet at $\delta$ 8.53 for H(3) protons and a triplet at $\delta$ 8.18 ppm for H(4) protons, and two equivalent benzoazoles giving two multiplets at 7.44-7.56 and 7.73-7.78 ppm for protons H(4'-7'). The signals of the pyridine and benzoazole protons of the complexes are all shifted downfield compared with that of free ligand suggesting the coordination of the ligand (fig. 5.2). A difference observed is that the signals for the benzoazole protons broaden, which may be attributed to an exchange of a benzoazole side arm with the solvent on the NMR time-scale [101].

Due to poor solubility of the complexes, the $^{13}C$ NMR spectra of only a few complexes could be recorded. The spectra of the ligand in DMSO-$d_6$-CDCl$_3$ medium exhibits peaks at 139.36, 140.25, 126.56, 125.58 ppm corresponding to C(2'), C(7'), C(6'), C(4',5') of the benzoazole moiety whereas the signals observed at $\delta$ 146.6, 125.26, 120.46, and 110.56 ppm correspond to the C(2,6), C(4), C(3), C(5) of the pyridine moiety of bzopxy. In the complexes the intensity of the $^{13}C$ signals for the carbon C(2,6), C(7'), C(2') and C(6') are very low and are suppressed or even absent.
Fig. 5.2: $^1$H NMR spectra of (a) 2,6-bis(benzoazol-2'-yl)pyridine (bzopxy) (b) UO$_2$Cl$_2$(bzopxy).
Thermal decomposition studies

The thermal decomposition of the complexes were carried out in air in the temperature range 30-900 °C. The thermogram of a typical complex $UO_2(bzopxy)_2(NO_3)_2$ is presented in Fig. 5.3. The thermal decomposition of all the complexes indicate the absence of water molecules. The complexes are found to be fairly stable at room temperature where they can be stored for a long time. Except nitrate containing complexes a general pattern of decomposition is observed. In the first step the biheterocyclic ligand molecule is lost. Then the residue undergoes further decomposition to form the stable oxides $U_3O_8$ or $ThO_2$ at higher temperature. It is generally observed that the decomposition is complete at nearly 540 °C and 600 °C for the thorium and uranium complexes, respectively. In case of nitrate containing complexes the decomposition occurs at one stage forming the respective stable oxide (Fig. 5.3).

Mass spectra

The mass spectra of the ligand was obtained in the El mode and the graphical fragmentation pattern of the ligand bzopxy is presented in Fig. 5.4. The mass peak of the ligand displays a prominent peak at m/z 313 as the base peak which undergoes fragmentation in two different pathways. Firstly, it loses $2C_7H_4NO$ molecules resulting in the formation of an ion at m/z 77, which on subsequent loss of $-C_2H_2$ molecule gives peak at m/z 51.
Fig. 5.3: Thermogram of $\text{UO}_2(\text{NO}_3)_2(\text{bopxy})_2$.

Fig. 5.4: Fragmentation pattern of bopxy.
The second mode of fragmentation consists of a loss of \( \text{C}_7\text{H}_4\text{NO} \) molecule from parent molecule, which resulted in the formation of a peak at m/z 195. Loss of pyridium cation gives peak at m/z 118, which subsequently loses CO and HCN molecule to explain the peak at m/z 63.
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