CHAPTER - III

DIOXOURANIUM(II) AND THORIUM(IV) COMPLEXES WITH -NNN- AND -NNNO- DONOR LIGANDS
INTRODUCTION

Uranium is known to exhibit a wide range of coordination numbers\(^1\). Quite a good number of hexa-coordinated dioxouranium(II) complexes are documented in the literature\(^2\). In many dioxouranium(II) complexes a considerable amount of data is accumulated on the nature of the O-U-O bonds\(^3\). McGlynn et al.\(^4\) have shown that these O-U-O bonds can be used as sensitive probes to know the change in the coordination number. Now the nature of O-U-O bonds is established to be linear by X-ray data\(^5\). However the linearity is perturbed in certain of the complexes, where local palorisation effects are contributing to the O-U-O bonds. No doubt, quite a large number of dioxouranium(II) complexes with wide range of Schiff bases containing O,N,S donor atoms are reported in literature\(^6\)\textsuperscript{13}, but only a few have given criteria about the nature of O-U-O bonds in the dioxouranium(II) adducts as well as in chelates. Some complexes of uranium(VI) with Schiff bases and aldoximes have been reported from our laboratory\(^14\)\textsuperscript{15}\textsuperscript{16}.

The coordination chemistry of thorium(IV) ion has been less extensively investigated, eventhough it presents an excellent area of research because of it's possibility of formation of compounds with coordination numbers greater than six, a feature sparingly observed in transition metal chemistry. For a metal ion to achieve a higher coordination number, two conditions are to be satisfied (a) effective
size of metal ion and (b) a high positive formal charge of the central metal atom. A high positive formal charge of the central metal atom is necessary, in order to prevent an excess amount of negative charge from accumulating on the metal atom as a result of association with the electrons contributed by large number of bonding atoms (8 or more). The large thorium(IV) ion with the ionic radii of 0.99 Å and its high charge, it is expected to satisfy the optimum requirements for the formation of compounds with a higher coordination number.

Thorium(IV) is an electron acceptor, coordinating strongly to the smaller and more electro-negative atoms like N, O and F. Thorium(IV), is also known to display a variable stoichiometry from ligand to ligand. Keeping in view this large variation in stoichiometry and the possibility of achieving a higher coordination number, it was considered worthwhile to study systematically the formation of complexes of thorium(IV) with Schiff bases as ligands.

Literature survey has shown that a very little work is done on 2,6-diaminopyridine and the Schiff bases, specially the uranium(VI) and thorium(IV) complexes with above Schiff bases. This fact made the author to take up the study of U(VI) and Th(IV) ions with Schiff base ligands.

The ligands used in the study of uranium(VI) and thorium(IV) complexes in this chapter are:
I  Benzilidene-2,6-diaminopyridine

\( \text{C}_{12}\text{H}_{11}\text{N}_{3} \) \( \text{L} \)

(BDP)

II  Salicylidene-2,6-diaminopyridine

\( \text{C}_{12}\text{H}_{11}\text{N}_{3}\text{O} \) \( \text{LH} \)

(SDP)

III  Vanillidene, 2,6-diaminopyridine

\( \text{C}_{13}\text{H}_{13}\text{N}_{3}\text{O}_{2} \) \( \text{LH} \)

(YDP)
Preparation of Schiff bases and complexes

The Schiff bases and complexes were prepared according to the methods detailed in Chapter II.

Elemental analysis

The thorium and uranium contents were determined by the methods mentioned in the Chapter II and weighed as ThO$_2$ and U$_3$O$_8$ respectively.$^{19}$ Nitrogen was estimated microanalytically by Dumas method.

Physical measurements

Conductance measurements were done in DMF on ELICO conductivity bridge CM-82 with a cell constant having 0.51 cm$^{-1}$.

The ir spectrum of all the complexes and ligands in KBr were recorded on Perkin Elmer 983 spectrum in the region 4000-200 cm$^{-1}$.

The PMR spectra of the ligands and complexes were recorded on a WH 270 FT NMR spectrometer.
Table III. 1: Showing the elemental analysis and conductance data of dioxouranium(II) and thorium(IV) complexed with tetridentate Schiff bases

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Complex No.</th>
<th>Empirical formula of the complex</th>
<th>Colour</th>
<th>M.P. °C</th>
<th>% Metal</th>
<th>% Nitrogen</th>
<th>Molar cond. ohm^{-1} cm^{-2} mole^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>IV</td>
<td>[(C_{12}H_{11}N_{3})<em>{2}(NO</em>{3})<em>{2}UO</em>{2}]</td>
<td>Light green</td>
<td>226</td>
<td>29.97 (30.20)</td>
<td>14.14 (14.21)</td>
<td>42</td>
</tr>
<tr>
<td>2</td>
<td>V</td>
<td>[(C_{12}H_{10}N_{3}O)<em>{2}UO</em>{2}]</td>
<td>Yellow</td>
<td>222</td>
<td>33.98 (34.29)</td>
<td>11.86 (12.10)</td>
<td>41</td>
</tr>
<tr>
<td>3</td>
<td>VI</td>
<td>[(C_{13}H_{12}N_{3}O_{2})<em>{2}UO</em>{2}]</td>
<td>Violet</td>
<td>228</td>
<td>31.01 (31.56)</td>
<td>10.89 (11.14)</td>
<td>43</td>
</tr>
<tr>
<td>4</td>
<td>VII</td>
<td>[(C_{12}H_{11}N_{3})<em>{2}(NO</em>{3})_{4}Th]</td>
<td>Dark brown</td>
<td>201</td>
<td>26.38 (26.54)</td>
<td>15.8 (16.02)</td>
<td>40</td>
</tr>
<tr>
<td>5</td>
<td>VIII</td>
<td>[(C_{12}H_{10}N_{3}O)<em>{2}(NO</em>{3})_{2}Th]</td>
<td>Brown</td>
<td>215</td>
<td>29.27 (29.74)</td>
<td>14.17 (14.35)</td>
<td>38</td>
</tr>
<tr>
<td>6</td>
<td>IX</td>
<td>[(C_{13}H_{12}N_{3}O_{2})<em>{2}(NO</em>{3})_{2}Th]</td>
<td>Brown</td>
<td>218</td>
<td>27.58 (27.62)</td>
<td>13.14 (13.33)</td>
<td>41</td>
</tr>
</tbody>
</table>
RESULTS AND DISCUSSIONS

Nature and stoichiometry

The complexes investigated are presented in Table III.X along with colour, m.p., conductance and analytical data. All the complexes are intensely coloured, insoluble in most of the organic solvents. These are soluble in DMF and DMSO. The limited solubility of the complexes in organic solvents did not permit the determination of their molecular weights.

Molar conductance

The molar conductance values determined in DMF (Table III.I) at the concentration $10^{-3} \text{M}$, fall in the range of $38-43 \text{ ohm}^{-1} \text{ cm}^{2}/\text{ mole}$. These values are low to account for any dissociation of the complex in that solvent. Hence these can be looked upon as non-electrolytes in that solvent.²⁰

Infrared spectra

The infrared frequencies of the ligands and the complexes are listed in Table III.2. Typical infrared spectra of the ligand and complexes are shown in Fig. III.1 and III.2.
Table III.2: Infrared spectral data of Schiff bases and their complexes

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>υ(C-O)</th>
<th>υ(NH)</th>
<th>υ(O=U=O)</th>
<th>υ(OH)</th>
<th>υ(C=N)</th>
<th>υ(C=C)</th>
<th>Pyridine ring vibration</th>
<th>υ(M-O)</th>
<th>υ(M-N)</th>
<th>υ(M-NO₃)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>[C₇H₁₇N₃]₂</td>
<td>-</td>
<td>3470</td>
<td>-</td>
<td>1660</td>
<td>1550</td>
<td>1490</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>II</td>
<td>[C₁₂H₁₀N₃O₂]</td>
<td>1250</td>
<td>3340</td>
<td>-</td>
<td>1280</td>
<td>1658</td>
<td>1555</td>
<td>1500</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III</td>
<td>[C₁₃H₁₂N₃O₂]</td>
<td>1270</td>
<td>3320</td>
<td>-</td>
<td>1265</td>
<td>1660</td>
<td>1545</td>
<td>1560</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IV</td>
<td>[(C₁₂H₁₁N₃)₂(NO₃)₂]UO₂</td>
<td>-</td>
<td>3465</td>
<td>1</td>
<td>830w</td>
<td>-</td>
<td>1620</td>
<td>1550</td>
<td>1495</td>
<td>-</td>
<td>510</td>
</tr>
<tr>
<td>V</td>
<td>[(C₁₂H₁₀N₃O)₂]UO₂</td>
<td>1310</td>
<td>3345</td>
<td>1</td>
<td>830w</td>
<td>-</td>
<td>1650</td>
<td>1560</td>
<td>1500</td>
<td>440</td>
<td>530</td>
</tr>
<tr>
<td>VI</td>
<td>[(C₁₃H₁₂N₃O₂)₂]UO₂</td>
<td>1315</td>
<td>3380</td>
<td>1</td>
<td>885w</td>
<td>-</td>
<td>1630</td>
<td>1560</td>
<td>1555</td>
<td>460</td>
<td>520</td>
</tr>
<tr>
<td>VII</td>
<td>[(C₁₂H₁₁N₃)₂(NO₃)₄]Th</td>
<td>-</td>
<td>3460</td>
<td>-</td>
<td>1635</td>
<td>1545</td>
<td>1495</td>
<td></td>
<td>-</td>
<td>560</td>
<td>1260</td>
</tr>
<tr>
<td>VIII</td>
<td>[(C₁₂H₁₀N₃O)₂(NO₃)₂]Th</td>
<td>1320</td>
<td>3335</td>
<td>-</td>
<td>1646</td>
<td>1545</td>
<td>1510</td>
<td></td>
<td>450</td>
<td>570</td>
<td>1240</td>
</tr>
<tr>
<td>IX</td>
<td>[(C₁₃H₁₂N₃O₂)₂(NO₃)₂]Th</td>
<td>1310</td>
<td>3315</td>
<td>-</td>
<td>1635</td>
<td>1545</td>
<td>1565</td>
<td></td>
<td>445</td>
<td>580</td>
<td>1245</td>
</tr>
</tbody>
</table>
Fig. 1: SALICYLIDENE-2,6-DIAMINOPYRIDINE

TRANSMITTANCE (%)
Fig. III. 2: UO$_2$(II) complex of salicylidene-2,6-diminoypyridine
C=N band

The non conjugated $\text{C=N}$ is reported\textsuperscript{21} to appear in the 1690-1650 cm\textsuperscript{-1} region, and conjugation lowers it to the region around 1630 cm\textsuperscript{-1}. In benzelidene-anilines Clougherty et al.\textsuperscript{21b} have reported the $\text{C=N}$ in the region 1630-1620 cm\textsuperscript{-1}, and in salicylidene-aniline, it normally occurs in the region 1620-1600 cm\textsuperscript{-1}. The hydrogen bonding further lowers the $\text{C=N}$ stretch.

The infrared frequencies of the ligands reported here have been shown to exhibit a fairly intense band around 1600-1610 cm\textsuperscript{-1} region, is assigned to $\text{C=N}$ stretch. In the complexes the $\text{C=N}$ appears in the region 1630-1650 cm\textsuperscript{-1}. The shift of these frequencies is observed in all complexes (Table III-2) and it may be interpreted as a consequence of coordination of azomethine nitrogen to the metal ion\textsuperscript{21-23}. This results in an increase in the bond order of carbon to nitrogen link.

It is observed that the free amine group exhibits two infrared absorption bands in the region 3500-3300 cm\textsuperscript{-1}, due to asymmetric and symmetric stretching vibration of $\text{NH}_2$ group. The band present, in the region around 3470-3320 cm\textsuperscript{-1} is assigned to $\text{NH}_2$ stretching frequencies and a band around 1260 cm\textsuperscript{-1} is assigned to C-N stretching frequencies in the ligands. This also indicates that one of the $\text{-NH}_2$ of the diamine has not condensed with aldehyde in ligands $L$, $LH$ and $LH$. The splitting and shifting of the band in complexes makes it
imperative that free -NH₂ has taken part in the coordination bond formation.

\[ \text{O}=\text{U}=\text{O} \text{ bands} \]

Uranyl ion reported to possess three characteristic frequencies \(^3\).

1. Symmetric stretching \((\gamma_1)\) 860 cm\(^{-1}\).

2. Asymmetric stretching \((\gamma_3)\) 930 cm\(^{-1}\).

3. Bending vibration \((\gamma_2)\) 210 cm\(^{-1}\).

If \(\text{UO}_2\) is not linear all the three frequencies should become Raman as well as infrared active. \(\gamma_1\) should be Raman active and \(\gamma_2, \gamma_3\) should be infrared active if \(\text{UO}_2\) is linear. The theoretical calculations show that \(\gamma_3\) is greater than \(\gamma_1\). Patel and Savant\(^{26}\) have assigned an antisymmetric stretch i.e. \(\gamma_3\) of O=U=O band at 915 cm\(^{-1}\) in aceto-complexes. The previous authors have attributed the lowering of the \(\gamma_3\) to the perturbation due to the stray chelate ring in the complexes.

The Schiff base complexes of dioxyuranium(II) reported by Biradar and Goudar\(^{10}\) have found \(\gamma_3\) band around 925 cm\(^{-1}\). A stray bands observed invariably in the region 830-950 cm\(^{-1}\) in uranyl complexes have been assigned to \(\gamma_1\) sym and \(\gamma_3\) asym O=U=O stretching vibration.
for complexes IV, V and VI, \( \gamma_1 \) band observed in these complexes is weak. This is in close agreement with theoretical predictions that intensity of \( \gamma_3 \) should be more than \( \gamma_1 \). These observations agree well with the concept of almost linear uranyl group disturbed by strong local field.

**C-O band**

A strong and sharp band in region 1280-1265 cm\(^{-1}\) found in the Schiff bases LH and LH\(_2\) are attributed to the phenolic C-O stretch. But in the complexes V, VI, VIII and IX, C-O stretch is found in the region 1310-1320 cm\(^{-1}\) which shows that phenolic oxygen has taken part in the coordination.

**600-200 cm\(^{-1}\) region**

The high intensity ligand bands appearing in the 600-200 cm\(^{-1}\) region often interfere with the metal ligand bands. Thus the assignments of the bands to the various \( \gamma \) M-N, \( \gamma \) M-O, vibrations in this region become much complicated. However the assignment of the bands to various modes has been made, by comparing the spectra of the complexes with that of ligands. It is observed that the skeleton vibration appearing in the ligands as a medium to high intensity bands remain almost unchanged in the complexes.
M-O stretch

The data available on pure M-O vibrations prescribes the region between 400-500 cm\(^{-1}\) for M-O stretching\(^{27}\). The band found in the region of 440-460 cm\(^{-1}\) in complexes V, VI, VIII and IX was assigned to the M-O stretching mode\(^{28a}\). This is indicative of metal-oxygen bond formation, with the oxygen of the -OH group of the ligands L\(_2\)H and LH.

M-N stretch

The intense broad band formed in the region of 510-530 cm\(^{-1}\) in UO\(_2^+\) complexes is ascribed to the U-N and the band at 560-580 cm\(^{-1}\) assigned to Th-N vibration in Th(IV) complexes\(^{28b}\).

NO\(_3^-\) - stretch

A strong and sharp band for complexes IV, VII, VIII and IX appears in the region 1260-1240 cm\(^{-1}\), has been assigned to covalent NO\(_3^-\) group\(^{29}\). This is however not observed in case of remaining complexes.

Pyridine ring vibrations

It is known that pyridine exhibits the ring stretching vibrations as sharp bands at 1590 cm\(^{-1}\) and 1482 cm\(^{-1}\), CH in plane deformation
vibrations at 1030 cm\(^{-1}\) and 993 cm\(^{-1}\). The investigations of Adam's and Cornell\(^{30}\) and P.K.Mondal\(^{31,32}\) have observed the band at 1600 cm\(^{-1}\) (pyridine ring vibrations) which is shifted to higher frequencies by about 20-25 cm\(^{-1}\), which is characteristic of coordinated ring.

In the present investigation the band around 1490 cm\(^{-1}\) and 1560 cm\(^{-1}\) has been assigned to pyridine ring vibrations in the Schiff base ligands. But in complexes there is no shifting of these bands. Thus non-shifting of bands clearly indicates that pyridine nitrogen has not taken part in the coordination in the complexes.

Proton magnetic resonance spectra

The PMR signals of tri and tetradeinate Schiff bases and their complexes are listed in Table III 'C'.

The typical PMR spectra of the ligand III and respective uranium complex(VI) are presented in Fig. III Fig 'C'. The PMR spectra of ligand III is characterised by five signals at 12.18, 3.7, 7.5, 7.2 and 7 to 9.4 ppm and they are attributed to the -OH proton, -OCH\(_3\) protons, methine proton, NH\(_2\) protons and due to phenyl and pyridine ring protons respectively. It has been established by previous workers\(^{33,34}\) that hydroxy group in case of Schiff bases appear in the range of 10-13 ppm as a sharp signal. The resonance due to NH is concentration dependent, and span over wide range from 5-11 ppm;
Table III. 3: Showing proton magnetic resonance chemical shifts of triand tetradentate Schiff bases and their dioxouranium(II) and thorium(IV) complexes $\delta$(ppm)

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Compounds</th>
<th>Aldehydic hydroxy proton</th>
<th>$-\text{OCH}_3$ protons</th>
<th>Methine proton</th>
<th>$-\text{NH}_2$ protons</th>
<th>Phenyl and pyridine ring protons</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>$(C_{12}H_{11}N_3)_2$</td>
<td>-</td>
<td>-</td>
<td>7.5</td>
<td>7.3</td>
<td>7.2 - 9.4</td>
</tr>
<tr>
<td>II</td>
<td>$(C_{12}H_{11}N_3O)_2$</td>
<td>12.65</td>
<td>-</td>
<td>7.45</td>
<td>7.3</td>
<td>7.2 - 9.3</td>
</tr>
<tr>
<td>III</td>
<td>$(C_{13}H_{13}N_3O_2)_2$</td>
<td>12.18</td>
<td>3.7</td>
<td>7.5</td>
<td>7.2</td>
<td>7.1 - 9.4</td>
</tr>
<tr>
<td>IV</td>
<td>$[(C_{12}H_{11}N_3)_2(NO_3)_2UO_2]$</td>
<td>-</td>
<td>-</td>
<td>7.8</td>
<td>7.4</td>
<td>7.0 - 9.2</td>
</tr>
<tr>
<td>V</td>
<td>$[(C_{12}H_{10}N_3O)_2UO_2]$</td>
<td>-</td>
<td>-</td>
<td>7.7</td>
<td>7.3</td>
<td>7.4 - 9.3</td>
</tr>
<tr>
<td>VI</td>
<td>$[(C_{13}H_{12}N_3O_2)_2UO_2]$</td>
<td>-</td>
<td>3.7</td>
<td>7.8</td>
<td>7.4</td>
<td>7.0 - 9.4</td>
</tr>
<tr>
<td>VII</td>
<td>$[(C_{12}H_{11}N_3)_2(NO_3)_4Th]$</td>
<td>-</td>
<td>-</td>
<td>7.9</td>
<td>7.2</td>
<td>6.8 - 9.3</td>
</tr>
<tr>
<td>VIII</td>
<td>$[(C_{12}H_{10}N_3O)_2(NO_3)_2Th]$</td>
<td>-</td>
<td>-</td>
<td>7.8</td>
<td>7.4</td>
<td>7.1 - 9.4</td>
</tr>
<tr>
<td>IX</td>
<td>$[(C_{13}H_{12}N_3O_2)_2(NO_3)_2Th]$</td>
<td>-</td>
<td>3.6</td>
<td>7.7</td>
<td>7.3</td>
<td>7.0 - 9.1</td>
</tr>
</tbody>
</table>
Fig. III.3: O-Vanilidene-2,6-Diamopyridine
Fig. III: 4:

URANIUM(VI) COMPLEX O-VANILIDENE-2,6-DIMINO-PYRIDINE
depending upon concentration of the solution. This proton always appears as a broad signal. In the ligand III the broad signal appearing at 7.5 ppm is attributed to the resonance due to the methine proton.

In uranyl complex(VI), the signals appeared at £3.7, 7.8, 7.4 and 7 to 9.4 ppm attributed to -OCH₃ protons, methine proton, -NH₂ protons and phenyl and pyridine ring protons respectively. Non appearance of -OH resonance in complex shows the deprotonation and the complexation of the ligand with dioxouranium(II) through the oxygen of -OH group. A comparison of azomethine proton signal in the ligand with that of the complex shows down field shift, and this is due to deshielding, caused by coordination through the nitrogen of the azomethine with the metal in the complex. Similarly a shift in the case of -NH₂ proton signal in the complex indicate that N of the -NH₂ has undergone coordination with the metal. Similar assignments are made for ligands I and II and complexes IV, V, VI, VIII and IX.

**Pharmacology**

**Antibacterial and antifungal activity**

The antibacterial and antifungal activity of Schiff bases and their complexes are listed in Table III. These compounds were screened for their antibacterial activity against two micro-organisms viz. *Bacillus cirrofluglosces* (gram-positive) and *E. coli* (gram-negative).
and against two fungi viz. Candida albicans and Aspergillus niger by cup plate method as mentioned in Chapter II. The test compounds were dissolved in DMF and added a nutrient agar for bacteria to give concentration range of 10 mg/ml. The extent of inhibition was measured by the zone of inhibition produced in mm after 48 hours. The bacteriostatic and antifungal property of Schiff base complexes of dioxouranium(II) and thorium(IV) were compared against parent compounds and the zone of inhibition recorded under identical conditions. The results are summarised in Table III. 5% aqueous solution of phenol was tested as positive control.

Result and Discussion

Among the Schiff base compounds I is weakly active against bacteria fungi AN whereas it is moderately active against fungi CA. Compound II is moderately active against BC and whereas in-active towards both the fungi. Compound III is moderately active against both the fungi and bacteria. Among the complexes of uranium compound IV is moderately active against E. coli, but inactive towards fungi whereas compound V is in-active against bacteria but moderately active against CA. Uranium complex VI is highly active against bacteria BC but moderately active towards remaining microorganisms. Among the thorium complexes, complex VII is moderately active against bacteria BC and fungi AN whereas in-active and weakly active against E. coli and CA respectively. Complex VIII is highly active against
Table III. 4: Antibacterial and antifungal results of tri and tetradentate Schiff bases and their dioxouranium(IV) complexes.

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Compounds</th>
<th>B. cirroflu-glosces</th>
<th>Activity against E. coli</th>
<th>Fungi C. albican</th>
<th>A. niger</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>((C_{12}H_{11}N_3))</td>
<td>+</td>
<td>+</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>II</td>
<td>((C_{12}H_{10}N_3O))</td>
<td>++</td>
<td>+</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>III</td>
<td>((C_{13}H_{12}N_3O_2))</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>IV</td>
<td>(((C_{12}H_{11}N_3)_2(NO_3)_2UO_2)</td>
<td>+</td>
<td>++</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>V</td>
<td>(((C_{12}H_{10}N_3O)_2UO_2)</td>
<td>-</td>
<td>-</td>
<td>++</td>
<td>+</td>
</tr>
<tr>
<td>VI</td>
<td>(((C_{13}H_{12}N_3O_2)_2UO_2)</td>
<td>+++</td>
<td>++</td>
<td>++</td>
<td>++</td>
</tr>
<tr>
<td>VII</td>
<td>(((C_{12}H_{11}N_3)_2(NO_3)_4Th)</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>VIII</td>
<td>(((C_{12}H_{10}N_3O)_2(NO_3)_2Th)</td>
<td>+</td>
<td>+</td>
<td>+++</td>
<td>+</td>
</tr>
<tr>
<td>IX</td>
<td>(((C_{13}H_{12}N_3O_2)_2(NO_3)_2Th)</td>
<td>+++</td>
<td>++</td>
<td>+</td>
<td>+</td>
</tr>
<tr>
<td>DMF</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Key to interpretation:

Zone of inhibition in mm

- (In-active) Less than 10 mm
+ (Weakly active) 11-13
++ (Moderately active) 14-16
+++ (Highly active) 17-19
fungi whereas weakly active against remaining organisms. But complex IX is highly active against bacteria and moderately active against other bacteria and fungi. Some compounds are found to be more potent than the parent compounds which could be explained due to their lipid solubility and subsequent cellular penetrations according to Jain et al.37

Preliminary studies on the effect of salicylidene-2,6-diaminopyridine and its uranium and thorium complexes, on the liver of Indian Skipper frog Rana cyanophlyctis

Metal exposures from many exposure routes (inhalation, ingestion, skin transfer, transplantal pareral) do occur and health effects in humans have been reported for all metals (Kjellstrom et al38). Fowle et al.39 have reported that the metal in excess or lack of the metals constitutes a health hazard.

The present study was thus undertaken to investigate the effect of ligand and their complexes on the physiology of the animals.

In this chapter we are reporting the effect of salicylidene-2,6-diaminopyridine and its uranium and thorium complexes on the liver weight and total protein of an Indian Skipper frog Rana cyanophlyctis.
Table III.5: Showing the results of toxicity of Schiff base and its Uranium and Thorium complexes on weight and protein content of liver of frog *Rana cyanophlyctis*.

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Group</th>
<th>Body weight (g)</th>
<th>Liver weight per 100 g body weight</th>
<th>Protein per 10 g liver weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Control</td>
<td>9.6 ± 0.4</td>
<td>4736.38 ± 458.18</td>
<td>0.40 ± 0.13</td>
</tr>
<tr>
<td>II</td>
<td>26 dap sal</td>
<td>10.83 ± 0.91</td>
<td>2350.87 ± 249.17</td>
<td>0.92 ± 0.17</td>
</tr>
<tr>
<td>III</td>
<td>26 dap sal UO₂</td>
<td>6.66 ± 0.92</td>
<td>2484.99 ± 171.15</td>
<td>1.19 ± 0.22</td>
</tr>
<tr>
<td>IV</td>
<td>26 dap sal Th</td>
<td>9.17 ± 0.65</td>
<td>2892.03 ± 94.01</td>
<td>0.82 ± 0.03</td>
</tr>
</tbody>
</table>

Liver weight

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>I vs II</td>
<td>P &lt; 0.001</td>
</tr>
<tr>
<td>I vs III</td>
<td>P &lt; 0.001</td>
</tr>
<tr>
<td>I vs IV</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>III vs IV</td>
<td>P &lt; NS</td>
</tr>
</tbody>
</table>

Total protein

<table>
<thead>
<tr>
<th>Comparison</th>
<th>Significance</th>
</tr>
</thead>
<tbody>
<tr>
<td>I vs II</td>
<td>P &lt; 0.05</td>
</tr>
<tr>
<td>I vs III</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>I vs IV</td>
<td>P &lt; 0.01</td>
</tr>
<tr>
<td>III vs IV</td>
<td>NS</td>
</tr>
</tbody>
</table>
Material and methods

Detailed procedure and materials used in this experiment is detailed in Chapter II. The results were analysed following the method of Steel and Torrie (students 't' test) and the results were considered significant only where the computed values are more than the tabulated (Table III.5 ) values at P. £ 0.05.

Results and Discussion

Results

The results obtained in this experiment have been summarised in the table.

It has been seen that there was a significant reduction in the weight of the liver of the frogs treated with the ligand II, salicylidene - 2,6-diaminopyridine and the complex of uranium and thorium, when compared to the weight of the liver in the control frogs (group I). On the other hand there was a significant increase in the protein of the liver in the frogs treated with the ligand (group II) and complex of uranium (group III) and thorium (group IV) to that of the liver protein in the control frogs (group I). However, there was no significant difference between the weight of the liver of the frogs treated with the complexes of uranium and thorium respectively. Further, there was also no significant difference between the liver protein of the frogs treated with complex V and VIII and ligand II.
Discussion

Uranium is an industrial hazard both chemically and radiologically, the chief hazard is in mining from radiation. Uranium can enter the body fluids through processes of anionic and cationic substitution.

The symptoms of chronic chemical toxicity of uranium compounds are growth retardation, renal dysfunctions and abnormal hepatic function (Venugopal and Luckey\textsuperscript{41}). In dogs, rats and rabbits hepatic damage and high minary proteins have been observed following uranium intoxication\textsuperscript{42,43}. In the present investigations, it is found that a complex of uranium has caused a significant decrease in the weight of the liver and a significant increase in the liver proteins of the frogs. This decrease in the liver weight and increase in the liver protein of the frogs might be due to the hepatic damage caused by the complex of uranium, similar to that reported by Bencosome et al.\textsuperscript{42} and Nomiyama and Foulkes\textsuperscript{43}.

Thorium and its isotopes are toxic radiologically, but the chemical toxicity of the thorium is low and depends on the nature of the salt. Reports about the chemical toxicity of the thorium compounds and their involvement in any physiological and biochemical functions in living tissue are scarce. In this study a significant decrease in the liver weight and a significant increase in the liver proteins of the frogs found after they were treated with the complex of thorium,
might be due to toxicity of the metal thorium and its coordinating ligand II damaging the liver of the animals.

The ligand II has caused a significant reduction in the liver weight and a significant increase in the liver protein of the frogs exhibiting its toxic nature, similar to the toxicity brought about by its complexes with uranium and thorium.

Summary

A few complexes of dioxouranium(II) and thorium(IV) with 2,6-diaminopyridine Schiff bases obtained by condensation of benzaldehyde, salicylaldehyde, and o-vanillin were prepared. The elemental analysis shows that these complexes have 1:2 stoichiometry. The conductance data of these complexes indicate that these are non-electrolytes. The conclusion about the coordination to the uranyl and thorium atoms through the azomethine nitrogen and -o- of hydroxy group by deprotonation and non-involvement of -OCH$_3$ group in case of o-vanilline complexes is drawn from the infrared spectral data, well supported by PMR results. These results also confirm that nitrogen of the free NH$_2$ group is involved in the coordination.

Antibacterial and antifungal activities of ligands and complexes were carried out, the results have shown that thorium complex of o-vanillidene-2,6-diaminopyridine is very active against microorganisms.
Similarly preliminary study of effect of these compounds on the liver weight and protein content of the liver has shown significant toxicity of some compounds when they were compared with the standards.

On the basis of the analytical and spectrochemical data, the dioxouranium(II) and thorium(VI) complexes under investigation exhibit coordination number eight.
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