CHAPTER VI

ALDOXIME COMPLEXES OF DIOXOURANIUM(VI)
The transition metal complexes with aldoximes are well documented in the literature.\textsuperscript{1} In most of the instances, the structural information is obtained through the spectral and magnetic data.\textsuperscript{2} However, the information on dioxouranium(VI) complexes with aldoximes is limited. There have been some isolated examples of spectrophotometric studies of dioxouranium(VI) aldoximates.\textsuperscript{3} Kumar et al.,\textsuperscript{4} have used pyridine-2-aldoxime and 6-methyl-pyridine-2-aldoxime for the gravimetric estimations of dioxouranium(VI). Buscarons and Izquierdo\textsuperscript{5} have used N-ethyl-β-isatoxime to estimate uranium gravimetrically. There appears no information on the synthesis of dioxouranium(VI) complexes with aldoximes. The object of present series of investigations is to synthesise dioxouranium(VI) complexes with aldoximes shown below (I-VI), and obtain structural information through the spectral data.

\begin{align*}
\text{I.} & \quad \text{H} \\
\text{II.} & \quad 3\text{-Me} \\
\text{III.} & \quad 4\text{-Me} \\
\text{IV.} & \quad 5\text{-Me} \\
\text{V.} & \quad 5\text{-Cl} \\
\text{VI.} & \quad R
\end{align*}

\begin{align*}
\text{R} & \quad \text{H} \\
\text{I.} & \quad \text{H} \\
\text{II.} & \quad 3\text{-Me} \\
\text{III.} & \quad 4\text{-Me} \\
\text{IV.} & \quad 5\text{-Me} \\
\text{V.} & \quad 5\text{-Cl}
\end{align*}
EXPERIMENTAL

Materials and Method:

Hydroxylamine hydrochloride was of Reagent Grade and uranyl nitrate hexahydrate was of BDH make.

All the substituted aldehydes were prepared by Duff method.\(^6\)

The aldoximes were prepared according to the method reported elsewhere.\(^7\)

General Method for Preparing the Complexes:

Uranyl nitrate hexahydrate (10 m. mole) dissolved in minimum quantity of aqueous alcohol was treated with an aldoxime solution (22 m. mole) and the resulting deep red solution was stirred thoroughly. The pH of the reaction solution was then raised to about 8 by adding dilute aqueous ammonia. The precipitated complex was stirred and allowed to stand for a while. The complex was filtered washed with aqueous alcohol till it was free from the reagent and dried in vacuum over fused calcium chloride.
Analysis:

Uranium in the complexes was estimated gravimetrically as $U_2O_8$ and nitrogen by kjeldahl method.

The results of the elemental analysis are shown in Table 1.

Physicochemical Measurements:

Conductance measurements were done in DMF on an ELICO conductivity bridge CM-82 with a cell having cell constant 0.829 cm$^{-1}$.

The infrared spectra of the complexes and ligands in Nujol mull were recorded on a Perkin Elmer spectrometer-337, in the region 4000-400 cm$^{-1}$.

RESULTS AND DISCUSSION

Physical Properties and Stoichiometry:

The complexes are orange-yellow to yellowish-brown coloured, amorphous substances. These are not soluble in benzene, chloroform and nitrobenzene but are soluble in pyridine, DMF and DMSO, to a limited extent. This limited
**TABLE 1**

Elemental analysis of uranyl aldoxime complexes

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>VII</td>
<td>$\text{UO}_2(\text{Saldox})_2$</td>
<td>$\text{UO}_2(\text{C}_7\text{H}_6\text{O}_2\text{N})_2$</td>
<td>43.98</td>
<td>43.68</td>
<td>5.17</td>
<td>4.95</td>
</tr>
<tr>
<td>VIII</td>
<td>$\text{UO}_2(3-\text{Me-Saldox})_2$</td>
<td>$\text{UO}_2(\text{C}_8\text{H}_5\text{NO}_2)_2$</td>
<td>41.76</td>
<td>42.34</td>
<td>4.91</td>
<td>4.90</td>
</tr>
<tr>
<td>IX</td>
<td>$\text{UO}_2(4-\text{Me-Saldox})_2$</td>
<td>$\text{UO}_2(\text{C}_8\text{H}_6\text{NO}_2)_2$</td>
<td>41.76</td>
<td>42.12</td>
<td>4.91</td>
<td>4.84</td>
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<tr>
<td>X</td>
<td>$\text{UO}_2(5-\text{Me-Saldox})_2$</td>
<td>$\text{UO}_2(\text{C}_8\text{H}_6\text{NO}_2)_2$</td>
<td>41.76</td>
<td>41.56</td>
<td>4.91</td>
<td>4.85</td>
</tr>
<tr>
<td>XI</td>
<td>$\text{UO}_2(5-\text{O1-Saldox})_2$</td>
<td>$\text{UO}_2(\text{C}_7\text{H}_5\text{NO}_1)_2$</td>
<td>39.08</td>
<td>39.26</td>
<td>4.6</td>
<td>4.71</td>
</tr>
<tr>
<td>XII</td>
<td>$\text{UO}_2(2-\text{OH-Naphthaldox})_2$</td>
<td>$\text{UO}<em>2(\text{C}</em>{11}\text{H}_8\text{NO}_2)_2$</td>
<td>37.16</td>
<td>37.35</td>
<td>4.39</td>
<td>4.43</td>
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</table>
solubility of the complexes has excluded the possibility of determining the molecular weights.

The results of the elemental analysis (Table 1) show that dioxouranium(VI) forms complexes of 1:2 stoichiometry with the ligands I–VI, losing two NO$_3^-$ ions.

**Molar Conductance:**

The molar conductance values in DMF at the concentration $10^{-3}$M fall in the range 0–5 ohm$^{-1}$ cm$^2$/mole. This value is too small to account for any dissociation of the complexes in DMF. Hence, these can be regarded as non-electrolytes in that solvent.

**Infrared Spectra:**

The infrared frequencies along with their assignments are shown in (Table 2).

The infrared spectra of the aldoximes (Fig. 1) exhibit two bands, one around 3340 cm$^{-1}$ and the other around 3200 cm$^{-1}$. The first one is broad with medium intensity and the second one is broad and weak. These bands are respectively assigned to the intermolecular and
<table>
<thead>
<tr>
<th>VII</th>
<th>VIII</th>
<th>IX</th>
<th>X</th>
<th>XII</th>
<th>Assignments</th>
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<tbody>
<tr>
<td>3205 br.m.</td>
<td>3180 br.m.</td>
<td>3200 br.m.</td>
<td>3200 br.m.</td>
<td>3200 br.m.</td>
<td>Intermolecular H-bonded -OH- stretch.</td>
</tr>
<tr>
<td>1525 s</td>
<td>1525 s</td>
<td>1525 s</td>
<td>1535 s</td>
<td>1535 s</td>
<td>C=N stretching.</td>
</tr>
<tr>
<td>1283 s</td>
<td>1283 s</td>
<td>1283 s</td>
<td>1283 s</td>
<td>1284 s</td>
<td>≱ (C=O) + ≱ (C-H) + ≱ (N=O) vibrations</td>
</tr>
<tr>
<td>1202 s</td>
<td>1224 m</td>
<td>1203 s</td>
<td>1233 m</td>
<td>1213 m</td>
<td>N-O stretch.</td>
</tr>
<tr>
<td>955 w</td>
<td>950 w</td>
<td>958 s</td>
<td>952 w</td>
<td>950 s</td>
<td>N-O stretch.</td>
</tr>
<tr>
<td>995 w</td>
<td>1000 w</td>
<td>990 w</td>
<td>990 w</td>
<td>997 w</td>
<td>C-O stretch of the hydrogen bonded ring system.</td>
</tr>
<tr>
<td>870 br.s.</td>
<td>868 br.s.</td>
<td>870 br.s.</td>
<td>870 br.s.</td>
<td>878 br.s.</td>
<td>O=U=O antisymmetric stretch.</td>
</tr>
<tr>
<td>580 s</td>
<td>595 m</td>
<td>599 m</td>
<td>555 m</td>
<td>562 m</td>
<td>U-N stretch</td>
</tr>
<tr>
<td>500 br.m.</td>
<td>515 br.m.</td>
<td>490 br.m.</td>
<td>490 br.m.</td>
<td>522 br.m.</td>
<td>≱ (U-O) stretch.</td>
</tr>
</tbody>
</table>

s=Strong; m=Medium; w=Weak; br=Broad.
1. Saldoxime
2. 5-Me-saldoxime
3. o-Naphthaldoxime
intramolecular hydrogen bondings of the following type.

In salicylideneanilines the intramolecular hydrogen bonded –OH is reported to occur in the 2800-2600 cm⁻¹ region. This suggests that the hydrogen bonding in aldoximes is weaker than that in salicylideneanilines. In the complexes of dioxouranium(VI), (Figs. II-VII), we observe a broad band of medium intensity around 3200 cm⁻¹ and this has been attributed to the intermolecular hydrogen bond. The broad weak band in the region 3200-3150 cm⁻¹ is not at all observed in the spectra of the complexes. In the copper(II) and nickel(II) complexes of salicylaldoxime, the moderate intensity band around 3300 cm⁻¹ is due to the intermolecular hydrogen bonded –OH stretch.
This type of bonding is not present in lead(II) salicylaldoximate because the complex does not contain any hydrogen bonding nor does it contain any water of hydration in it. In this complex both $\omega$-OH and $\omega$-N-OH groups take part in the reaction. The observed shift of 3300 cm$^{-1}$ band to the lower frequency in these dioxouranium (VI) aldoximates may be interpreted as a consequence of strong intermolecular hydrogen bonding.

The non-conjugated C=N normally appears in the 1690-1650 cm$^{-1}$ region. The conjugation shifts it to the lower frequency and is found around 1630 cm$^{-1}$ for the Schiff bases. In all these aldoximes (I-VI), we observe an intense band around 1623 cm$^{-1}$ and this does not show much variation in the complexes. This absence of shifting of the band means that it should not be assigned to the C=N stretch. This band has been assigned to the OH-deformation vibration. Similar observations have been made by Ramaswamy et al. and Biradar et al. The high intensity band observed around 1570 cm$^{-1}$ shows considerable variation in the complexes and appears around 1525 cm$^{-1}$. This band is considered to be the band due to the C=N stretch in view of the previous assignments. The observed low frequency shift of C=N(1525 cm$^{-1}$)stretch
not only indicates the coordination of the C=N group
to the dioxouranium(VI) through nitrogen but also the
decrease in the bond order of carbon to nitrogen link.
The large shift of the C=N from the normal value 1650 cm$^{-1}$
to 1570 cm$^{-1}$ appears to be due to such factors as
resonance, conjugation or coupling with C=O and hydrogen
bonding.

The medium intensity band of the ligands around
1280 cm$^{-1}$ shows an unusual increase in the intensity and
becomes broad. Hence, this may be considered to be mixture
of $\nu$(C=O) + $\delta$(C-H) + $\nu$(N-O) vibrations. The bands in
the regions 1235-1150 cm$^{-1}$ and 970-910 cm$^{-1}$ in the complexes
are attributed to the N-O stretching vibrations. An intense
band around 990 cm$^{-1}$, in the ligands due to the C-O stretch
of the hydrogen bonded ring system is broadened, inten-
sified and appears in the region 1020-990 cm$^{-1}$ in the
complexes.

Uranyl ion is reported to exhibit three characteri-

ëstic bands, $\gamma^\prime$, Sym. 860 cm$^{-1}$, $\gamma^\prime\prime$, asy. 930 cm$^{-1}$ and
$\gamma^\prime$, bend. 210 cm$^{-1}$. If UO$_2$ is not linear, all the three
frequencies should be i.r. and Raman active. If UO$_2$ is
linear $\gamma_4$ should be Raman active and $\gamma_2$, $\gamma_3$ should be i.r. active. Patel and Savant\textsuperscript{14} have assigned an antisymmetric stretch i.e. $\gamma_3$ of O-U-O to the band at 915 cm\textsuperscript{-1} in acetato complex. In Schiff base complexes of dioxouranium(VI), Biradar et al.\textsuperscript{15} have found $\gamma_3$ band around 925 cm\textsuperscript{-1}. In these complexes, peculiarly enough, we observe an intense and broad band around 870 cm\textsuperscript{-1}. This band is ascribed to the $\gamma_3$ antisymmetric stretch of O-U-O. The observed exceptionally low frequency for this vibration may be due to the greater perturbations caused by the strong chelation of the aldoxide groups and hydrogen bonding.

The metal-nitrogen bands are reported to occur in the 600-500 cm\textsuperscript{-1} region for a number of metal complexes.\textsuperscript{16} In glycine complexes,\textsuperscript{17} this band is assigned near 540 cm\textsuperscript{-1}. Patel et al.\textsuperscript{18} have located $\gamma$(M-N) band in the region 590-500 cm\textsuperscript{-1} for Mn(III) Schiff base complexes. Whereas Biradar et al.\textsuperscript{19} have attributed a strong band in the region 540-490 cm\textsuperscript{-1} in lead(IV) Schiff base complexes to $\gamma$(Pb-N) vibration. In view of all these observations, the intense band found in the region 580-580 cm\textsuperscript{-1} is ascribed to the $\gamma$(U-N) vibration. The presence of only
one band in this region for these complexes suggests that they exist in the trans form.

The data available on the pure $\gamma$(M-O) vibrations prescribe the region between 500 and 400 cm$^{-1}$ for M-O stretching.$^{20}$ A few authors$^{21}$ have reported metal sensitive M-O bands below 400 cm$^{-1}$. The authors$^{19,22}$ have reported $\gamma$(M-O) almost in the same region for lead (IV) and thorium(IV) complexes. In the light of these observations a medium intensity band found in the region 590-490 cm$^{-1}$ is assigned to $\gamma$(U-O) vibration. The $\gamma$(M-O) bands are shown to be sensitive to the coordination number and oxidation state of the metal ion.$^{23}$ The observed little variance in the $\gamma$(U-O) band suggests that the same coordination number is prevailing in all the complexes.

All these observations suggest that these dioxouranium(VI) complexes have six coordinated octahedral structure with two aldoxime units lying in the same plane perpendicular to the O=U=O group.
Oxouranium(VI) complexes with various substituted aldoximes have been prepared by reacting uranyl nitrate hexahydrate with aldoximes. They have been characterised by elemental analysis, molar conductivity and spectroscopic data. With the help of these data, six coordinated octahedral configuration with nitrogen atoms occupying the trans positions, have been proposed.
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