Dioxouranium(VI) Complexes with Some N and O Donor Ligands

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Dioxouranium(VI) complexes of 2-furoyl- and 2-thenoylhydrazines and their Schiff bases with acetone and salicylaldehyde have been prepared and characterized by various physicochemical methods. Molar conductance values suggest that nitrato complexes are 1:2 electrolytes while the remaining complexes are nonelectrolytes in 10^{-3} M DMF solution. The IR studies indicate that the acylhydrazines and their Schiff bases with acetone behave as bidentate ligands coordinating through carbonyl oxygen and nitrogen of –NH₂ or –C≡N group. The corresponding Schiff bases derived from salicylaldehyde act as tridentate ligands coordinating through carbonyl oxygen, azomethine nitrogen and phenolic oxygen.

The complexes of 3d metal ions with 2-furoyl- and 2-thenoylhydrazines [R – C(=O) – NH – NH₂, R = C₄H₄O or C₄H₄S] and their Schiff bases derived from acetone and salicylaldehyde are well studied¹⁻⁹. Syamal et al.⁸,⁹ have reported dioxouranium(VI) complexes of the type UO₂L₂.CH₃OH where L² are salicylaldehyde furoyal and thienoyl hydrazones. In the present note we report preparation and characterization of uranyl complexes with 2-furoyl- and 2-thenoylhydrazines and their Schiff bases with acetone and salicylaldehyde (structures I and II).

$$\text{FAH, TAH}$$  
$$\text{H₂FCS, H₂TCS}$$  
$$\text{(I)}$$  
$$\text{(II)}$$

The important infrared frequencies of the ligands and the complexes are recorded in Table 2.

The chemicals used in the present study were BDH reagents or reagents of equivalent quality. 2-Furoylhydrazine (FH) and 2-thienoylhydrazine (TH) obtained from M/s Ega, Chemie (Germany) were used without further purification while acetone 2-furoylhydrazine (AFH), acetone 2-thienoylhydrazine (ATH), N-(furan-2-carboxamido)salicylaldimine (H₂FCS) and N-(thiophene-2-carboxamido)salicylaldimine (H₂TCS) were prepared as reported earlier²⁻⁷.

**Preparation of complexes**

The complexes were prepared by mixing together the ethanolic solutions of uranyl nitrate (1 mmol, 10 ml) and ligand (2 mmol, 20 ml). The complexes of H₂FCS and H₂TCS precipitated on refluxing the reaction mixture while those of the remaining ligands were obtained by concentrating the reaction mixture to about half of its original volume. Microcrystalline compounds thus obtained were filtered, washed with ethanol and ether and dried in vacuo.

Metal contents of the complexes were determined following the literature procedure¹⁰ while nitrogen was estimated microanalytically. Hydrazine was estimated volumetrically by titrating against KIO₃ after subjecting the complexes to acid-catalyzed hydrolysis for 3 h. The analytical data are recorded in Table 1.

The molar conductances of the complexes were measured in 10^{-3} M DMF solution with a WTW conductivity bridge. The values of molar conductances are included in Table 1. IR spectra of the ligands in nujol (4000-200 cm⁻¹) as well as in MeCN (4000-475 cm⁻¹) and those of the complexes in nujol (4000-200 cm⁻¹) were recorded on a Perkin-Elmer spectrophotometer model 621. The X-ray powder photographs of the complexes were obtained on a Philips X-ray generator using nickel filtered CuKα radiation and Guinier FR 552 camera.

The complexes are yellow or orange yellow in colour. They are insoluble in common organic solvents but are soluble in DMF. Analytical data agree well with 1:2 (metal-ligand) stoichiometry of the complexes. Molar conductance values of H₂FCS and H₂TCS complexes indicate their non-electrolytic nature while those of the remaining complexes show their 1:2 electrolytic nature. The insolubility of the complexes in a suitable solvent prevented the determination of their molecular weights.

The important infrared frequencies of the ligands and the complexes are recorded in Table 2.

A negative shift in amide I band in the spectra of all the complexes compared to its position in the spectra of the parent ligands indicates coordination through carbonyl oxygen. The shifts of β(NH₂) mod in FH and TH complexes and that

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Table 1—Characterisation Data of Dioxouranium(VI) Complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>Found (Calc.), %</th>
<th>( \lambda_m ) (ohm cm(^{-1}) cm(^2) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{UO}_2(\text{FH})_2</a>_2)</td>
<td>Yellow</td>
<td>36.90 (36.84)</td>
<td>12.92 (13.00) 10.00 (9.90) 127.0</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{UO}_2(\text{TH})_2</a>_2)</td>
<td>Yellow</td>
<td>35.20 (35.10)</td>
<td>12.40 (12.39) 9.34 (9.44) 123.3</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{UO}_2(\text{AFH})_2</a>_2)</td>
<td>Yellow</td>
<td>32.82 (32.78)</td>
<td>11.56 (11.57) 8.80 (8.81) 129.1</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{UO}_2(\text{ATH})_2</a>_2)</td>
<td>Yellow</td>
<td>31.20 (31.40)</td>
<td>11.15 (11.08) 8.34 (8.44) 124.5</td>
</tr>
<tr>
<td>([\text{UO}_2(\text{HFC})_2])</td>
<td>Brown</td>
<td>32.70 (32.69)</td>
<td>7.68 (7.69) 8.85 (8.80) 6.5</td>
</tr>
<tr>
<td>([\text{UO}_2(\text{HTCS})_2])</td>
<td>Brown</td>
<td>31.34 (31.31)</td>
<td>7.40 (7.36) 8.40 (8.42) 3.3</td>
</tr>
</tbody>
</table>

Table 2—Diagnostic IR Bands (cm\(^{-1}\)) of Ligands and their Dioxouranium(VI) Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Amide I</th>
<th>( \beta(\text{NH}_2) )</th>
<th>( v(\text{C}=\text{N}) )</th>
<th>( v(\text{N} = \text{N}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{UO}_2(\text{FH})_2</a>_2)</td>
<td>1690s</td>
<td>1640s</td>
<td>–</td>
<td>950m</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{UO}_2(\text{TH})_2</a>_2)</td>
<td>1645m</td>
<td>1605s</td>
<td>–</td>
<td>980m</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{UO}_2(\text{AFH})_2</a>_2)</td>
<td>1665s</td>
<td>1630s</td>
<td>–</td>
<td>940m</td>
</tr>
<tr>
<td>(<a href="%5Ctext%7BNO%7D_3">\text{UO}_2(\text{ATH})_2</a>_2)</td>
<td>1630s</td>
<td>1620s</td>
<td>–</td>
<td>980m</td>
</tr>
<tr>
<td>([\text{UO}_2(\text{HFC})_2])</td>
<td>1655s</td>
<td>1640s</td>
<td>–</td>
<td>1010m</td>
</tr>
<tr>
<td>([\text{UO}_2(\text{HTCS})_2])</td>
<td>1620s</td>
<td>1590s</td>
<td>–</td>
<td>1025m</td>
</tr>
</tbody>
</table>

The appearance of bands\(^{19}\) at \(-1380\) and \(-820\) cm\(^{-1}\) in the spectra of all the nitrate complexes indicates the ionic nature of nitrate ion. This observation is in agreement with the molar conductance values of the complexes as discussed above. These bands remain practically unchanged in the spectra of all the complexes indicating thereby that thiophene ring sulphur and furan ring oxygen are not involved in bonding with the metal ion. The inability of coordination of thiophene sulphur and furan ring oxygen has been attributed to the involvement of the lone pair of electrons on sulphur and oxygen in the aromatic sextet and lower capacity of \(\pi\)-orbitals to accept the electron pair from the metal.

The X-ray powder diffraction patterns of all the complexes indicate that the complexes are crystalline and that the \(\text{H}_2\text{FCS}\) and \(\text{H}_2\text{TCS}\) complexes are isomorphous.

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References