Dioxouranium (VI) Complexes of Benzoylhydrazine & Isonicotinoylhydrazine

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Complexes of benzoylhydrazine (BH) and isonicotinoylhydrazine (IH) with uranyl sulphate and oxalate have been isolated and characterized on the basis of analytical, molar conductance, infrared and Raman spectral data. IR spectra indicate that BH and IH act as neutral bi- and tri-dentate ligands coordinating through C=O, –NH₂ and C=O, –NH₂ and pyridine nitrogen respectively. Sulphato and oxalato groups act as bridging and chelating bidentate ligands respectively. IR and Raman spectral data indicate that all ligand atoms are arranged in the equatorial plane around the UO₂⁺ group which maintains its linearity in all the complexes.

Considerable interest has been shown in the study of the complex compounds of acyl- and aroyl-hydrazines with bivalent metal ions of the first transition series. Studies on the complexes with the lanthanides and actinides, are, however, meagre. Previous studies show that benzoylhydrazine coordinates to the transition metal ions in the keto form while isonicotinoylhydrazine coordinates in the keto as well as enol forms. A literature survey has shown the absence of systematic work on the uranyl complexes of the title ligands. The tendency of uranyl ion to coordinate in the equatorial plane with 4 to 8 donor atoms can lead to the formation of unusual geometrical structures. Preparation and characterization of the uranyl sulphate and oxalate complexes with the title ligands is reported in the present study.

Uranyl nitrate hexahydrate, ethyl benzoate, isonicotinic acid hydrazide, hydrazine hydrate, oxalic acid and sulphuric acid were BDH reagents of AR or equivalent quality. Uranyl sulphate was obtained by evaporating a mixture of uranyl nitrate hexahydrate and conc. H₂SO₄ upto dryness and recrystallizing the product from hot water. Benzoylhydrazine (m.p. 111°C, lit. 112.5°C) was prepared by refluxing ethylbenzoate and hydrazine hydrate in 1:1 molar ratio for about 4 hr and recrystallizing the product from hot benzene. The purity of IH was checked by its (m.p. 162°C, lit. 163°C) determination. Uranium was determined by standard literature procedure. Sulphate was estimated as barium sulphate. Hydrazine was estimated volumetrically by KI₀₃ after removing uranium and anions and then subjecting the filtrate to acid hydrolysis for about 4 hr. For estimating oxalate, the corresponding complexes were dissolved in sulphuric acid and uranium precipitated by dilute ammonia solution. From the filtrate, oxalate was precipitated as calcium oxalate and determined by titration with KMnO₄ in hot 2N sulphuric acid medium. Nitrogen was determined by a Coleman nitrogen analyzer. Molar conductances were determined in DMF at 10⁻³ M dilution using an Elanco conductivity bridge model CM-82T with dip-type conductivity cell. IR spectra were recorded on an infrared spectrophotometer (Perkin-Elmer Model No. 621) in nujol mull in the range 4000-200 cm⁻¹. Raman spectra were recorded on a Raman spectrophotometer (Ramanlog 1403) in KBr by employing rotating sample technique to avoid decomposition of the sample.

The sulphato complexes were isolated by mixing together the methanolic solutions of the uranyl salt and ligands in 1:2 molar ratio. The mixed solutions were concentrated by evaporation and complexes crystallized out on cooling. The complexes were filtered, washed with methanol, then with ether, dried at room temperature and finally in an electric oven at 60-70°C.

The oxalato complexes were obtained by treating uranyl nitrate hexahydrate, ligand and oxalic acid in 1:2:2 molar ratio in alcoholic medium and concentrating the solutions by evaporation. The complexes were filtered and isolated as above.

The analytical data (Table 1) of the present complexes are consistent with 1:1 (metal:ligand) stoichiometry except for the UO₂(BH)₂C₂O₄H₂O complex. UO₂(BH)₂C₂O₄H₂O is soluble in ethanol and methanol but not the other complexes. The sulphate complexes are completely soluble in DMSO and partially in DMF, but the oxalate complexes are completely soluble in both the solvents. The low values of the molar conductances (Table 1) of the complexes in DMF suggest that they are non-electrolytes in this solvent.

The modes of coordination of the ligands to the metal ion were investigated by comparing the IR spectra of the complexes with those of the free ligands. The amide-I band occurring at 1650 cm⁻¹ in the IR spectra of the ligands indicates that a strong intramolecular hydrogen bonding exists between the >C=O and –NHNH₂ groups of the ligand in the solid state. This band shows a negative shift of 20-40 cm⁻¹ in the spectra of the complexes. Since amide-I band suffers a significant negative shift upon coordination, the effect of coordination is more than...
Table 1—Analytical Decomposition Temperature and Molar Conductance Data of Dioxouranium (VI) Complexes with Benzoyl and Isonicotinoyl Hydrazines

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>(m.p.,°C)</th>
<th>Found (Calc.)%</th>
<th>(\Lambda_m) (ohm(^{-1}) cm(^2) mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>U</td>
<td>N</td>
</tr>
<tr>
<td>(UO_2(BH)SO_4)</td>
<td>Light yellow</td>
<td>(220)*</td>
<td>46.7</td>
<td>5.3</td>
</tr>
<tr>
<td>(UO_2(BH)C_2O_4)</td>
<td>Red brown</td>
<td>(&gt; 250)</td>
<td>36.9</td>
<td>9.0</td>
</tr>
<tr>
<td>(H_2O)</td>
<td></td>
<td></td>
<td>(36.7)</td>
<td>(8.6)</td>
</tr>
<tr>
<td>(UO_2(IH)SO_4)</td>
<td>Yellow brown</td>
<td>(250)</td>
<td>48.0</td>
<td>8.6</td>
</tr>
<tr>
<td>(H_2O)</td>
<td></td>
<td></td>
<td>(47.3)</td>
<td>(8.3)</td>
</tr>
<tr>
<td>(UO_2(IH)C_2O_4)</td>
<td>Yellow</td>
<td>(&gt; 250)</td>
<td>45.9</td>
<td>7.9</td>
</tr>
<tr>
<td>(H_2O)</td>
<td></td>
<td></td>
<td>(46.4)</td>
<td>(8.2)</td>
</tr>
</tbody>
</table>

*Melts with decomposition.

the effect of hydrogen bonding. This suggests that the oxygen atom of the \(> \text{C} = \text{O}\) group and nitrogen atom of \(- \text{NH}_2\) group are involved in coordination. The involvement of \(> \text{C} = \text{O}\) and \(- \text{NH}_2\) groups in coordination is also supported by the fact that amide-II and \(- \text{NH}_2\) bands occurring at 1550 and 1605 cm\(^{-1}\) in BH and at 1535 and 1610 cm\(^{-1}\) in IH suffer negative shifts of about 15-30 and 20-40 cm\(^{-1}\) respectively, in the IR spectra of the complexes. The spectrum of free IR shows bands at 660 and 425 cm\(^{-1}\) due to in-plane and out-of-plane deformation modes of the pyridine ring respectively. The corresponding bands appear in the regions 680-670 and 454-445 cm\(^{-1}\) respectively in the spectra of the complexes suggesting the coordination of the pyridine nitrogen to the uranyl group. The arrangement of the donor groups, viz., ring nitrogen atom and hydrazide unit at para position in IH favours coordination of IH through pyridine nitrogen to one uranium atom and through oxygen and nitrogen atom of hydrazide unit to another uranium atom resulting in the formation of polymeric structures.

In addition to the ligand bands, the IR spectra of all the uranyl complexes studied here show weak absorption at 890-850 cm\(^{-1}\) and strong absorptions at 925-905 cm\(^{-1}\). The strong absorption at 925-905 cm\(^{-1}\) in assigned to \(v_3\) mode but the absorption at 890-850 cm\(^{-1}\) cannot be assigned to \(v_1\) band because absorption bands of medium to weak intensity also occur at 875 and 870 cm\(^{-1}\) in BH and IH respectively. Moreover, the Raman spectrum of \(UO_2(BH)SO_4\), recorded as a representative sample, shows a very strong band at about 852 cm\(^{-1}\), a fact which suggests that the linearity of the OUO group is maintained in these complexes. The absorption band of medium intensity at 910 cm\(^{-1}\) in BH is masked by strong absorption at 925-905 cm\(^{-1}\) due to \(v_3\) vibration. The doubly degenerate \(\text{OUO}\) bending mode, \(v_2\), is observed between 255 and 235 cm\(^{-1}\) in the low frequency IR spectra of these complexes.

In sulphato complexes, the \(v_3\) and \(v_4\) modes of uncoordinated sulphate group expected in the ranges 1120-1080 cm\(^{-1}\) and ~610 cm\(^{-1}\) are split up. Moreover, the \(v_1\) mode (IR forbidden in the uncoordinated sulphate) appears at 970 and 1030 cm\(^{-1}\) respectively. Besides the \(v_1\), \(v_3\) and \(v_4\) modes, the \(v_2\) mode is observed as a strong band at 470 and 415 cm\(^{-1}\) in these complexes. The positions of the absorptions bands due to sulphato group suggest its bidentate bridging nature in the complexes.

IR spectra of the oxalato complexes show bands at 1700 m, 1645ssh; 1470 msh, 1365 s, 1300 m cm\(^{-1}\) (complex with BH) and 1695 s, 1640 s; 1480 ssh, 1455 s, 1300 cm\(^{-1}\) (complex with IH). These bands are observed neither in the spectra of the ligands nor in the spectra of their sulphato complexes and are, therefore, identified as \(v_4\) = \(\text{C}=\text{O}\) (1700 m, 1645ssh for BH complex and 1695 s, 1640 s cm\(^{-1}\) for IH complex) and \(v_2\) = \(\text{C}=\text{O}\) (1470 msh, 1365 s, 1300 cm\(^{-1}\) for BH complex and 1480 ssh, 1455 s, 1300 cm\(^{-1}\) for IH complex) modes respectively of the coordinated oxalate group. The free oxalate group belongs to \(D_{2h}\) symmetry and shows \(v_{as}\) = \(\text{C}=\text{O}\) and \(v_{e}\) = \(\text{C}=\text{O}\) modes at 1640 and 1335, 1316 cm\(^{-1}\) respectively. In compounds where the oxalato group is covalently bonded through four (bridging) oxygen atoms, the symmetry remains unchanged but when the oxalato group is covalently bonded through two oxygen atoms (chelating or bridging), the symmetry is changed to \(C_2\) (chelation) or to \(C_{2h}\) (bridging) respectively. In chelated oxalato complexes, the
antisymmetric and symmetric C=O vibrations become IR-active. From the number of C=O stretching vibrations, it is, in principle, possible to make a distinction between the different modes of coordination of oxalato group although only a full X-ray structural analysis can solve the problem unambiguously. IR frequencies associated with oxalato group in these complexes are in good agreement with those normally associated with the bidentate chelating oxalato group. The spectra of all the oxalato complexes show bands around 3600 cm⁻¹ which may be due to the presence of adsorbed water. When the complexes are heated at ~110°C, the loss in weight corresponds to one molecule of water.

Keeping in view the fact that BH acts as a bidentate ligand coordinating through carbonyl oxygen and primary nitrogen atom, and sulphato and oxalato groups act as bidentate bridging and chelating ligands respectively, the complex UO₂(BH)SO₄ may be assigned a linear polymeric structure (I) involving six coordinated uranium. The complex UO₂(BH)₂C₂O₄H₂O may be postulated to have monomeric structure (II) involving eight coordinated uranium atom. Further, considering that IH acts as a bridging tridentate ligand coordinating through carbonyl oxygen and primary nitrogen to one uranium atom and pyridine ring nitrogen to another uranium atom, and sulphato and oxalato groups act as bidentate bridging and chelating ligands respectively, the complexes UO₂(IH)SO₄ and UO₂(IH)C₂O₄H₂O may be postulated to have polymeric structures (III & IV) with seven coordinated uranium atoms.

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