Dioxouranium(VI) Complexes of Acetone Isonicotinoylhydrazone

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New complexes of acetone isonicotinoylhydrazone (AIH) with uranyl nitrate, acetate and thiocyanate of the types UO₂[AIH]X₂ (X = NO₃, CH₃COO, SCN⁻) and UO₂[AIH]₂X₂ (X = NO₃, SCN⁻) have been isolated and characterized by analytical, melting point, molar conductance and infrared and Raman spectral data. It is shown that in UO₂[AIH]X₂ complexes, the ligand molecule, although a potentially tetradentate ligand, acts in a neutral tridentate manner and coordinates to one uranium atom through carbonyl oxygen and azomethine nitrogen atom and to another uranium atom through pyridine nitrogen atom in a bridging manner. In UO₂[AIH]₂X₂ complexes, one ligand molecule acts as a tridentate bridging ligand and the other ligand molecule acts as a monodentate ligand bonding terminally through pyridine ring nitrogen atom only to the uranyl group. Nitrate, acetato and thiocyanato groups act as terminal monodentate ligands.

Although a good deal of work has been reported on transition metal complexes of acylhydrazines1,2 and acylhydrazones3–5, work on corresponding complexes with actinides is rather scanty. In continuation of our recent study on the synthesis and characterisation of dioxouranium(VI) complexes of some acylhydrazines6,7, we now report preparation and characterisation of dioxouranium(VI) complexes of acetone isonicotinoylhydrazone (AIH)(1).

![Structural formula of AIH](AIH)

Uranyl nitrate hexahydrate, uranyl acetate dihydrate, isonicotinoyl hydrazone, ammonium thiocyanate and acetone were BDH reagents of AR quality. Uranyl thiocyanate was obtained by the interaction of ammonium thiocyanate and uranyl nitrate hexahydrate in methanol. AIH was obtained by condensing acetone with isonicotinoylhydrazone and was recrystallized from ethanol, m.p. 160⁰ (lit. 8, 159–160⁰ C). Uranium in the complexes was estimated6 as U₂O₅. Nitrate and thiocyanate were estimated as nitron nitrate8 and silver thiocyanate8. Hydrazine was estimated volumetrically by KI0₃ after submitting the complexes to acid hydrolysis for ~ 4 hr9. Nitrogen was analyzed by microanalysis. The molar conductances of the complexes at 10⁻³ M dilution in methanol and DMF were measured using an Elco-conductivity bridge model CM-82T with a dip-type conductivity cell. IR spectra of the ligand and its complexes were recorded on a Perkin-Elmer 983 spectrophotometer in KBr in the region 4000-180 cm⁻¹. The laser Raman spectra were recorded at ambient temperatures on a SPEX Ramalog 1403 spectrophotometer using the line at 4880 Å from a Spectra Physics model 165 argon laser as the excitation source. The rotating sample technique was used to avoid the decomposition of the sample which was taken in the form of a pressed KBr pellet.

**Preparation of UO₂[AIH]X₂ (X = NO₃, CH₃COO, SCN) complexes**

The uranyl salt (55 ml, 0.01 M) in hot methanol was added into a solution of the ligand (50 ml, 0.01 M) in hot methanol. The mixture was refluxed for 2 hr on a steam bath. The volume was reduced to 70 ml by evaporation and the contents cooled to room temperature. Then 100 ml of ether was added. The nitrate and acetato complexes precipitated immediately. In the case of thiocyanato complex, a viscous liquid was obtained which was extracted with 100 ml benzene. The solution was kept over anhydrous calcium chloride in a desiccator overnight when the complex precipitated. The complexes were filtered by suction, washed with methanol and finally with ether and isolated as above. The complexes were dried over anhydrous calcium chloride in vacuo.

**Preparation of UO₂[AIH]₂X₂ (X = NO₃, SCN) complexes**

Uranyl salt solution (0.01 M, 50 ml) in methanol was added to a well-stirred hot solution of AIH (0.01 M, 102 ml) in methanol. The mixed solution was heated on a steam bath for 1 hr accompanied by stirring and simultaneous concentration to 100 ml. The solution was cooled to room temperature followed by addition of 100 ml ether. This precipitated the nitrate complex which was filtered by suction, washed with methanol and finally with ether and isolated as above. In the case of thiocyanato complex, a semi-solid was
Table 1—Analytical, Melting Point, and Molar Conductance Data of Dioxouranium(VI) Complexes of Acetone Isonicotinoylhydrazone

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour (m.p.,°C)</th>
<th>Found/Calc. %</th>
<th>Anion</th>
<th>Molar conductance ((\Lambda_m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{UO}_2\text{AIH(No}_3\text{)}_2)</td>
<td>Yellow (240)</td>
<td>42.39</td>
<td>12.75</td>
<td>5.49 21.23</td>
</tr>
<tr>
<td>(\text{UO}_2\text{AIH(CH}_3\text{COO)}_2)</td>
<td>Yellow (250)</td>
<td>42.88</td>
<td>7.49</td>
<td>5.63 -</td>
</tr>
<tr>
<td>(\text{UO}_2\text{AIH(SCN)}_2)</td>
<td>Orange yellow (245)</td>
<td>43.12</td>
<td>12.12</td>
<td>5.79 20.03</td>
</tr>
<tr>
<td>(\text{UO}_2\text{AIH(No}_3\text{)}_2)</td>
<td>Dull yellow (165*)</td>
<td>31.11</td>
<td>14.45</td>
<td>8.32 16.96</td>
</tr>
<tr>
<td>(\text{UO}_2\text{AIH(SCN)}_2)</td>
<td>Orange yellow (162*)</td>
<td>32.78</td>
<td>14.65</td>
<td>8.83 15.90</td>
</tr>
</tbody>
</table>

*Melts with decomposition.

obtained. The thiocyanato complex was isolated in the same way as the \(\text{UO}_2\text{AIH(SCN)}_2\) complex.

The complexes isolated in the present study, their analytical data, decomposition temperatures and molar conductances are presented in Table 1. The analytical data show that the reactions of uranyl salts with AIH in 1:1 and 1:2 molar ratio in methanol give 1:1 and 1:2 (metal:ligand) complexes in the cases of uranyl nitrate and thiocyanate, but only 1:1 complex in the case of uranyl acetate. The 1:2 complexes melt with decomposition slightly above the melting point of the ligand molecule but the 1:1 (metal:ligand) complexes decompose above 200°C. The complexes vary in their colour from dull yellow to yellow to orange yellow. All the complexes are soluble in boiling water to give suspensions. Nitrate and thiocyanato complexes are soluble in ethanol, methanol, DMF, and DMSO; but acetato complex is insoluble in alcohol, being slightly soluble in methanol and completely so in donor solvents like DMF and DMSO; but acetato complex is insoluble in alcohol, being slightly soluble in methanol and completely so in donor solvents like DMF and DMSO. The electrical conductances of nitrate complexes (82.5 and 79.3 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\)) in methanol correspond to 1:1 electrolytic behaviour while acetato and thiocyanato complexes have molar conductance values in the range 28.9 - 15.7 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) indicating their non-electrolytic behaviour. In DMF, all the complexes show molar conductance in the range 70.2 - 58.9 ohm\(^{-1}\) cm\(^2\) mol\(^{-1}\) indicating their 1:1 electrolytic behaviour and suggest that the nitrate complex in methanol and all complexes in DMF undergo dissociation in solution presumably due to their solvolysis.

IR spectrum of the ligand AIH shows a strong band at 3287 and another strong multiplet in the region 3257-2900 cm\(^{-1}\) due to \(\nu\text{NH}\) mode. The positions of these bands indicate that –NH group is involved in intermolecular hydrogen bonding. In metal complexes, the \(\nu\text{NH}\) bands are split up and shift to higher frequency by about 28-274 cm\(^{-1}\). The positive shift in \(\nu\text{NH}\) frequency upon coordination indicates that secondary amine group does not participate in bonding.

The \(\nu\text{C} = \text{O}\) (1666 cm\(^{-1}\)) and \(\nu\text{C} = \text{N}\) (1633 and 1602 cm\(^{-1}\)) bands of the free ligand, AIH, suffer marked negative shifts in the spectra of the complexes and appear in the ranges 1654-1635 and 1624-1592 cm\(^{-1}\), respectively, indicating coordination through carbonyl oxygen and azomethine nitrogen. The occurrence of two bands at 1633 and 1602 cm\(^{-1}\) due to > C = N group in the uncoordinated ligand can be attributed to solid state interactions. Further evidence of the coordinations of nitrogen of > C = N to the uranyl ion is obtained from the loss of doublet character of the \(\nu\text{C} = \text{N}\) band in the IR spectra of the complexes. The coordination of the ligand through its pyridine nitrogen is evident from the splitting and shifting of the free ligand band at 1553 cm\(^{-1}\) (attributed to pyridine ring vibrations and amide II band) to regions 1590-1570 and 1548-1535 cm\(^{-1}\) respectively. The coordination of the ligand through its pyridine nitrogen is also confirmed by the shift of the inplane and out-of-plane ring deformation modes occurring at 661 and 435 cm\(^{-1}\), respectively, in the uncoordinated ligand molecule to the regions 694-674 and 466-455 cm\(^{-1}\), respectively, in the IR spectra of the complexes.

Based on the molecular model of the ligand, it is suggested that the ligand coordinates in a bridging fashion through pyridine ring nitrogen atom to one uranium atom and through carbonyl oxygen and azomethine nitrogen atoms to the other uranium atom with the formation of a more stable five-mem-
bered chelate ring, leading to the polymeric structures.

The $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{X}\rangle_2$ complexes show bands at 1667, 1635, 1596 and 1694, 1687, 1653, 1627 cm$^{-1}$ in their IR spectra. The bands at 1667, 1694 and 1635, 1687 cm$^{-1}$ may be assigned to stretching vibrations of uncoordinated $\text{C} = \text{O}$ and $\text{C} = \text{N}$ groups respectively while the band at 1635 cm$^{-1}$ (merged with stretching vibrations of uncoordinated $\text{C} = \text{N}$), 1653 cm$^{-1}$ and 1596, 1627 cm$^{-1}$ are due to stretching vibrations of coordinated $\text{C} = \text{O}$ and $\text{C} = \text{N}$ groups respectively. Such a feature of IR spectra of these complexes clearly indicates that $\text{C} = \text{O}$ and $\text{C} = \text{N}$ groups of one ligand molecule are coordinated while those of the other ligand molecule remain unbounded. The single band at 1553 cm$^{-1}$ due to pyridine ring vibration and amide II band is split up in the spectra of these complexes also showing positive and negative shifts by about 5-18 cm$^{-1}$. Further, the IR spectra indicate a significant positive shift of in-plane and out-of-plane ring deformation modes of pyridine ring. These facts clearly suggest that one ligand molecule acts as a tridentate ligand coordinating through pyridine nitrogen, carbonyl oxygen and azomethine nitrogen atoms and the other as a monodentate ligand coordinating through pyridine nitrogen atom only.

All the uranyl complexes show strong absorptions in the range 938-897 cm$^{-1}$ and weak absorptions in the range 857-850 cm$^{-1}$ which may be assigned to $\nu_3$ and $\nu_1$ vibrations of the uranyl group. The doublet character of $\nu_3$ in $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{X}\rangle_2$ ($\text{X} = \text{NO}_3, \text{SCN}$) may be explained in terms of several mechanisms such as Fermi resonance, solid state unit cell coupling and the presence of more than one molecule in the unit cell. The appearance of $\nu_3$ mode of the uranyl group, formally IR-forbidden, in the range 857-850 cm$^{-1}$, can be related to the crystalline perturbation of the local symmetry of the $\text{UO}_2^+$ group rather than to its slight bending mode$^{27}$. The Raman spectra of $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{NO}_3\rangle_2$ and $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{CH}_3\text{COO}\rangle_2$ complexes, recorded as representative samples, in the range 1000-800 cm$^{-1}$ show a strong broad band (864 and 858 cm$^{-1}$) but do not show band corresponding to the $\nu_1$ vibration. These facts suggest that the linearity of the OOO group is maintained in these complexes. The OOO bending vibration occurs as a medium to strong band at 270-247 cm$^{-1}$ in the low frequency IR spectra of these complexes and masks the ligand bands in this region.

The nitrato complexes $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{NO}_3\rangle_2$ and $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{SCN}\rangle_2$ show new bands at 1515 m, 1329 m, 826 which are assigned to $\nu_1$, $\nu_2$, $\nu_3$, $\nu_4$ and $\nu_5$ modes of the coordinated nitrato groups. The unidentate coordination of the nitrato groups to the uranyl ion is evident from the fact that the range 1800-1700 cm$^{-1}$ of the IR spectra of the complexes, which contains combination bands, shows weak absorption bands at ~1780 and ~1766 cm$^{-1}$, assigned to $(\nu_2 + \nu_3)$ and $(\nu_2 + \nu_5)$ modes respectively which are of much stronger intensity than in the other complexes and are separated by ~14 cm$^{-1}$. The $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{CH}_3\text{COO}\rangle_2$ complex shows new bands at 1634 m, 1418 m and 678s (masking the strong band at 678 cm$^{-1}$) which are assigned to $\nu_5$, $\nu_3$, $\nu_2$ COO and $\delta$ COO modes of the coordinated acetato groups. The positions of these bands indicate unidentate coordination of acetato group with the uranyl ion.

The nitrato complexes $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{NO}_3\rangle_2$ and $\text{UO}_2\langle\text{AIH}\rangle_2\langle\text{SCN}\rangle_2$ are as- signed to $\nu_3$, $\nu_3$ and $\nu_5$ respectively which may be assigned to $\nu_3$, $\nu_4$ and $\nu_5$ modes respectively which indicate unidentate coordination of thiocyanato groups through the nitrogen atom to the uranyl ion.

References


