Synthesis and characterization of uranium(IV) complexes with 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases

P B Maravalli, K B Gudasi & T R Goudar
Department of Chemistry, Karnataka University, Dharwad, 580 003, India
Received 15 June 1999; revised 25 October 1999

The metal complexes of uranium(IV) with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacyl/benzil have been synthesized in dry benzene under nitrogen atmosphere. These complexes have been characterized by elemental analyses, molar conductance, electronic, infrared and thermal studies. On the basis of these observations it is suggested that uranium(IV) complexes exhibit coordination number six.

Biologically significant triazole derivatives are well documented in the literature. The biocidal activities of these compounds together with similar heterocycles have already been correlated with their complexing ability with the metal ions. In continuation of our earlier work on uranium(IV) complexes with 2-aminobenzoyl hydrazone and furic acid hydrazones, we report herein the isolation and characterization of uranium(IV) complexes with Schiff bases derived from 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacyl/benzil.

Preparation of ligand

The Schiff bases L₁-L₁₂ were synthesized by reacting 3-substituted-4-amino-5-mercapto-1,2,4-triazole and glyoxal/biacyl/benzil in 2:1 molar proportion in ethanol containing two drops of conc. HCl. The reaction mixture was heated under reflux for 3-4h. The product separated on evaporation of ethanol from resulting yellow solution was filtered, washed with ethanol and recrystallised from ethanol.

Synthesis of uranium(IV) complexes

Uranium(IV) acetate was prepared as reported earlier. Uranium(IV) acetate 4.74g (0.01 mol) was refluxed with (0.01 mol) of the ligand in dry benzene (100 ml) under nitrogen atmosphere for 3h. The precipitated complex was filtered at suction and washed with dry benzene (50 ml). The complexes were then dried and stored in vacuo over fused calcium chloride (Yield 70%).

Results and discussion

The uranium(IV) complexes are orange to cream in colour. These are soluble in ethanol and methanol. The elemental analyses (Table 1) show that, the complexes analyzed for 1:1 stoichiometry are of the type U.L. (CH₃COO)₄. The molar conductance measurements in methanol at 10⁻³ M for these complexes fall in the range 10.25-30.27 ohm⁻¹ cm² mol⁻¹ indicating their non-electrolyte behaviour. The magnetic moments (μₚ) for the uranium(IV) complexes as measured on a Gouy balance at room
Table I—Characterization data of uranium(IV) complexes with 3-substituted-4-amino-5-mercapto-1,2,4-triazole Schiff bases

<table>
<thead>
<tr>
<th>Complex code</th>
<th>Complex</th>
<th>Found (Calcd.), %</th>
<th>Molar conductance $i_\text{M}$ ohm$^{-1}$ cm$^2$ mol$^{-1}$</th>
<th>$\mu_{\text{eff}}$ (BM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$B_1$</td>
<td>[U(GAMT)(OAc)$_4$]</td>
<td>23.09 (23.19)</td>
<td>15.35 (15.33)</td>
<td>8.67 (8.79)</td>
</tr>
<tr>
<td>$B_2$</td>
<td>[U(GMAMT)(OAc)$_4$]</td>
<td>25.39 (25.42)</td>
<td>14.82 (14.81)</td>
<td>8.50 (8.46)</td>
</tr>
<tr>
<td>$B_3$</td>
<td>[U(GEAMT)(OAc)$_4$]</td>
<td>27.55 (27.47)</td>
<td>14.26 (14.28)</td>
<td>8.18 (8.16)</td>
</tr>
<tr>
<td>$B_4$</td>
<td>[U(GPAMT)(OAc)$_4$]</td>
<td>29.55 (29.63)</td>
<td>13.75 (13.79)</td>
<td>7.86 (7.88)</td>
</tr>
<tr>
<td>$B_5$</td>
<td>[U(BIAMT)(OAc)$_4$]</td>
<td>25.39 (25.47)</td>
<td>14.84 (14.86)</td>
<td>8.44 (8.46)</td>
</tr>
<tr>
<td>$B_6$</td>
<td>[U(BIMAMT)(OAc)$_4$]</td>
<td>27.55 (27.60)</td>
<td>14.25 (14.28)</td>
<td>8.15 (8.16)</td>
</tr>
<tr>
<td>$B_7$</td>
<td>[U(BIEAMT)(OAc)$_4$]</td>
<td>29.55 (29.53)</td>
<td>15.20 (15.46)</td>
<td>15.26 (15.46)</td>
</tr>
<tr>
<td>$B_8$</td>
<td>[U(BIPAMT)(OAc)$_4$]</td>
<td>31.45 (31.40)</td>
<td>13.86 (13.97)</td>
<td>7.84 (7.75)</td>
</tr>
<tr>
<td>$B_9$</td>
<td>[U(BEAMT)(OAc)$_4$]</td>
<td>35.43 (35.35)</td>
<td>14.50 (14.45)</td>
<td>8.35 (8.44)</td>
</tr>
<tr>
<td>$B_{10}$</td>
<td>[U(BEMAMT)(OAc)$_4$]</td>
<td>37.00 (37.08)</td>
<td>14.15 (14.13)</td>
<td>7.92 (8.19)</td>
</tr>
<tr>
<td>$B_{11}$</td>
<td>[U(BEAMT)(OAc)$_4$]</td>
<td>38.48 (38.56)</td>
<td>13.65 (13.69)</td>
<td>7.75 (7.86)</td>
</tr>
<tr>
<td>$B_{12}$</td>
<td>[U(BEPAMT)(OAc)$_4$]</td>
<td>39.83 (39.82)</td>
<td>13.10 (13.25)</td>
<td>7.45 (7.56)</td>
</tr>
</tbody>
</table>

Temperature are found to be 2.81 to 3.05 B.M. corresponding to two unpaired electrons and a triplet ground state ($^3H_6$).

The spectra of the ligands $L^1$ to $L^{12}$ exist both in thiol and thione form. A medium band in the region 3280-3130 cm$^{-1}$ due to $\nu$(NH) indicates the thione form whereas a weak intensity broad band 2400 cm$^{-1}$ due to $\nu$(SH)$^{11-14}$ represents the thiol form. All these ligands exhibit high intensity bands 1618-1640 cm$^{-1}$ region which may be assigned to $\nu$(C=N) group. The thioamide band which is mainly due to stretching vibration is observed at 750 cm$^{-1}$. The IR spectra of uranium(IV) complexes exhibit broad medium bands in the region 3275-3180 cm$^{-1}$ followed by weak broad bands 2400 cm$^{-1}$ assignable due to $\nu$(NH) and $\nu$(SH). The position of the ligand band at 750 cm$^{-1}$ due to $\nu$(C=S) is unaffected in the complexes. This indicates non-involvement of sulphur in the coordination$^{16}$. The new bands in the spectra of complexes in the region 633-645 cm$^{-1}$ are assigned to $\nu$(U-N) modes. The non-ligand bands at 1580 and 1215 cm$^{-1}$ are assigned to $\nu_8$ and $\nu_3$ modes of acetate moieties and their extent of separation indicates unidentate nature of the acetate group attached to the central uranium(IV) ion$^{17}$.

The electronic spectra of the ligands in methanol exhibit intense band maxima in the region 300-375 nm and these involve changes of vibrational energy state of hydrogen bonding chelate rings and also indicates thiol-thione tautomerism.

The electronic spectra of uranium(IV) complexes with these ligands display modified broad bands having very high intensity in the regions 279-352 and...
380-469 nm. The observed shift in the ligand band and appearance of new bands in the region 380-469 nm in the spectra of the complexes may be contemplated for the complex formation. In these uranium(IV) complexes, the strong bands appearing at 400 and 430 nm may be attributed to charge-transfer transitions from equatorial ligands (p-orbitals of ligands to 'f' orbital of uranium).

The TG curves of uranium(IV) complexes do not show the presence of water molecules either in or out of the coordination sphere. In the complexes (B_2) and (B_10), the first step of decomposition occurs between 100-245 and 105-299 °C with weight loss of 32.41 and 25.99% respectively. This loss corresponds to the loss of four acetate molecules. In the second step, decomposition occurs between 246-560 and 236-685 °C and this decomposition accounts for the loss of another acetate and ligand molecules. Beyond 685 °C, a plateau is obtained, which indicates the formation of stable U_3O_8. The weight of U_3O_8 agrees well with the analytical results. The complexes are stable in vacuum for four weeks. The complexes undergo air oxidation and the rate is more in the presence of moist air.

References