Synthesis & Spectral Studies of Monomeric Oxovanadium(IV) Complexes of Some N, O-Donor Ligands

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Vanadyl complexes of the type $\text{VO}L_2\text{Cl}_2$ [L = (N-benzoyl)glycinylhydrazide, BzGH ($n = 2$); acetone (N-benzoyl)glycylhydrazone, BzAGH ($n = 2$); o-hydroxyacetophenone (N-benzoyl)glycylhydrazone, o-HABzGH ($n = 1$)] have been synthesised. The complexes have been characterised on the basis of elemental analyses and various physicochemical techniques. The complexes are non-electrolytic in nature and their room temperature magnetic studies indicate presence of one unpaired electron. Electronic spectral studies indicate square-pyramidal geometry around the metal ion. IR spectral studies show neutral monodentate behaviour of BzGH and BzAGH and bidentate chelating behaviour of o-HABzGH.

In continuation of our previous work on 3d-metal complexes of amino acid hydrazides and their derivatives$^{1-4}$, we describe in this note the synthesis and characterisation of oxovanadium(IV) complexes of (N-benzoyl)glycine hydrazide, acetone (N-benzoyl)glycylhydrazone and o-hydroxyacetophenone (N-benzoyl)glycylhydrazone abbreviated as BzGH, BzAGH and o-HABzGH, respectively.

All the chemicals used were BDH reagents of AR grade. BzGH, BzAGH and o-HABzGH were prepared as described previously.$^{2-4}$

The complexes were prepared by mixing together ethanolic solutions of vanadyl chloride and the corresponding ligand in a 1:2 molar ratio. The reaction mixture was heated at $\sim$60°C for $\sim$5 min with stirring; precipitation of the complexes was induced by the addition of a small amount of acetone. The micro-crystalline complex thus obtained in each case was filtered, washed successively with ethanol and ether and dried in vacuo. The C, H and N micro-analyses were done on a Coleman Analyser; the values were found to be in agreement with the proposed compositions (Table 1). The metal and halogen contents were estimated gravimetrically as vanadium pentoxide and silver chloride respectively.$^6$ The details of the physicochemical techniques used were the same as described earlier.$^1, 2$ The analytical, magnetic and ESR spectral data are given in Table 1.

All the complexes are stable at room temperature and are only slightly soluble in water and common organic solvents. However, they are fairly well soluble in coordinating solvents like DMF and DMSO. Molar conductance values of all the complexes in 0.001 $M$ DMSO (3.54-5.26 mho cm$^{-1}$ mol$^{-1}$) indicate the non-electrolytic behaviour of the complexes.$^6$ The room temperature magnetic moments of the complexes are close to the spin-only value for a $d^1$ system and thus indicate the absence of any metal-metal interaction.$^7$

The electronic spectra of the complexes show three bands. The first one is a shoulder centered in the region 12120-12900 cm$^{-1}$; it is assigned to an unresolved band resulting from the $d_{x^2} \rightarrow d_{yz}$, $d_{xz}$ transition. The second and third bands occurring at 14705-15265 and 21050-22000 cm$^{-1}$ may be attributed to $d_{x^2} \rightarrow d_{xy}$ and $d_{y^2} \rightarrow d_{z^2}$ transitions respectively. The number and positions of the bands are consistent with a square-pyramidal arrangement around the metal ion$^8, 9$ (structure I).

In the IR spectra of all the complexes a negative shift is observed in the $\nu(C=O)$ mode of the hydrazide moiety compared with the position of the band in ligand spectra while $\nu(C=N)$ suffers a negative shift

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Table 1—Elemental Analyses†, Magnetic Moments and ESR Spectral Data of Oxovanadium(IV)

<table>
<thead>
<tr>
<th>Complex (colour)</th>
<th>Found (Calc.), %</th>
<th>$\mu_{\text{eff}}$ (B.M.)</th>
<th>$g_\parallel$</th>
<th>$g_\perp$</th>
<th>$&lt;g&gt;$</th>
<th>$A_\parallel$ (G)</th>
<th>$A_\perp$ (G)</th>
<th>$&lt;A&gt;$ (G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{VO(BzGH)}_2\text{Cl}_2$ (Green)</td>
<td>9.61 (9.73)</td>
<td>13.47 (13.53)</td>
<td>1.78</td>
<td>1.948</td>
<td>1.982</td>
<td>1.971</td>
<td>187.9</td>
<td>70.8</td>
</tr>
<tr>
<td>$\text{VO(BzAGH)}_2\text{Cl}_2$ (Blue)</td>
<td>8.51 (8.44)</td>
<td>11.71 (11.74)</td>
<td>1.81</td>
<td>1.941</td>
<td>1.981</td>
<td>1.968</td>
<td>194.2</td>
<td>67.8</td>
</tr>
<tr>
<td>$\text{VO(o-HABzGH)}_2\text{Cl}_2$ (Green)</td>
<td>11.30 (11.35)</td>
<td>15.88 (15.80)</td>
<td>1.73</td>
<td>1.946</td>
<td>1.983</td>
<td>1.970</td>
<td>191.4</td>
<td>67.1</td>
</tr>
</tbody>
</table>

†Satisfactory C, H and N analyses were also obtained.
only in VO(o-HABzGH)Cl₂. This indicates monodentate coordination through hydrazide carbonyl group of BzGH and BzAGH, and a bidentate coordination through the hydrazide carbonyl group and azomethine nitrogen of o-HABzGH. A new peak observed in all the complexes around 980 cm⁻¹ may be assigned to ν(V=O). The non-ligand bands occurring in the region 440-430 cm⁻¹ may be tentatively assigned to ν(V−O).

ESR spectra of the complexes have been recorded in DMF solution at room temperature and as DMF glass at liquid nitrogen temperature (LNT). Room temperature spectra show normal eight line isotropic features revealing hyperfine splitting of the ⁵¹V nucleus (I = 7/2) in each case. The absence of super-hyperfine splitting in these isotropic spectra indicates that the unpaired electron is in the b₂g(dx²-y²) orbital localized on the metal. Frozen DMF glass spectra are, however, anisotropic showing the parallel and perpendicular features separately.

Various molecular orbital coefficients have been evaluated by the use of experimental values of the spin-Hamiltonian parameters, spin-orbital coupling constant and the visible absorption band energies. The values of β₂, β₁ and εₓ² thus obtained are normal and indicate a considerable in-plane σ-bonding and weak in-plane and out-of-plane π-bonding nature of the ligands.

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References