Mixed Ligand Complexes of Bis(Acetylacetonato)oxovanadium (IV) & Imidazole Derivatives

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Five-coordinate, square-pyramidal bis(acetylacetonato)oxovanadium (IV) reacts with imidazole and substituted imidazoles (L) in ether medium forming six-coordinate, distorted octahedral bis(acetylacetonato)(imidazole)oxovanadium(IV), [VO(acac)₂L] having an expanded coordination shell around vanadium (IV). These complexes are characterised by IR and electronic spectral, magnetic susceptibility and conductivity measurements.

The chemistry of oxovanadium (IV) is of interest from chemical, structural and biological point of view\(^1\)\(^-\)\(^5\). We report herein the synthesis and characterisation of several mixed ligand complexes of oxovanadium (IV) containing acetylacetonate and imidazole or its derivatives.

Infrared and electronic spectra, conductivities and magnetic susceptibilities of the mixed ligand complexes were measured as reported earlier\(^6\). Bis (acetylacetonato)oxovanadium (IV), [VO(acac)₂] was prepared from V₂O₅ and acetylacetone (Hacac) in EtOH medium following the literature method\(^7\).

Bis (acetylacetonato) (imidazole) oxovanadium (IV), [VO(acac)₂(Im)] was synthesised by adding, with stirring, solid VO(acac)₂ (1 mmol, 0.26 g) to a solution of imidazole (1.2 mmol, 0.08 g) in diethyl ether (50 ml). Initially a clear solution was formed from which a yellow-green solid separated out in about 5 min. The stirring was continued for 1 hr to ensure completion of the reaction.

The compounds similarly prepared and reported in this work are [VO(acac)₂(L)], where L = 1 - MeIm, 1 - EtIm, 1 - ViIm, 1 - AlIm, 2 - MeIm, 1 - Vi-2-MeIm and BzIm (Im = imidazole, Me = methyl, Et = ethyl, Vi = vinyl, Al = allyl and BzIm = benzimidazole).

The compounds reported here (Table 1) do not have a sharp melting point and the decomposition temperatures vary widely depending on the imidazole base. All compounds are reasonably stable under ordinary conditions and could be stored in a desiccator. They have the general stoichiometry [VO(acac)₂L] and are nonelectrolytes in organic solvents\(^9\).

The observed magnetic moments of these six-coordinated oxovanadium (IV) complexes lie in the range 1.6-1.8 B.M., close to the spin-only value of a \(d^1\)-system\(^10\). The electronic spectra of majority of the complexes in solution are not well-resolved and two low-intensity bands are observed and assigned according to the semi-empirical molecular orbital model of Ballhausen and Gray\(^11\). The band-I, corresponding to \(b_2(d_{xy})+e_g^*(d_{zz}, d_{yz})\) transition appears as a broad band centred at 13,000 cm\(^-1\) with a molar extinction coefficient of 13-18 dm\(^3\)cm\(^-1\)mol\(^{-1}\).

### Table 1—Analytical and Other Characterising Data of Mixed Ligand Complexes of Oxovanadium (IV)

<table>
<thead>
<tr>
<th>Compound*</th>
<th>Colour</th>
<th>Decomp. temp. (°C)</th>
<th>Found (calc), %</th>
<th>(\mu_{eff.}) (B.M.)</th>
<th>(\lambda_M) in MeOH (mhcm(^2)mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A(Im)]</td>
<td>Yellow green</td>
<td>130</td>
<td>14.8 (15.3)</td>
<td>46.6 (46.8)</td>
<td>4.9 (5.4)</td>
</tr>
<tr>
<td>[A(1-MeIm)]</td>
<td>Dirty green</td>
<td>150</td>
<td>14.8 (14.7)</td>
<td>48.8 (48.4)</td>
<td>5.9 (5.8)</td>
</tr>
<tr>
<td>[A(1-EtIm)]</td>
<td>Light green</td>
<td>140</td>
<td>14.0 (14.1)</td>
<td>49.7 (49.8)</td>
<td>6.0 (6.1)</td>
</tr>
<tr>
<td>[A(1-ViIm)]</td>
<td>Yellow green</td>
<td>205</td>
<td>13.5 (13.3)</td>
<td>50.2 (50.1)</td>
<td>5.4 (5.5)</td>
</tr>
<tr>
<td>[A(1-AlIm)]</td>
<td>Dark green</td>
<td>140</td>
<td>14.0 (13.7)</td>
<td>51.1 (51.4)</td>
<td>5.7 (5.9)</td>
</tr>
<tr>
<td>[A(2-MeIm)]</td>
<td>Light yellow</td>
<td>150</td>
<td>15.6 (15.3)</td>
<td>48.6 (48.4)</td>
<td>5.5 (5.8)</td>
</tr>
<tr>
<td>[A(1-Vi-2-MeIm)]</td>
<td>Green</td>
<td>210</td>
<td>13.5 (13.6)</td>
<td>51.7 (51.4)</td>
<td>5.7 (5.9)</td>
</tr>
<tr>
<td>[A(BzIm)]</td>
<td>Grey</td>
<td>190</td>
<td>14.0 (13.7)</td>
<td>53.2 (53.3)</td>
<td>5.3 (5.2)</td>
</tr>
</tbody>
</table>

*\(A = \text{VO(acac)}_2\)  
†Estimated either as \(\text{V}_2\text{O}_3\) or \(\text{AgVO}_3\) (see ref. 8)
It is not unlikely that this band covers the transitions $d_{xy} \rightarrow d_{xz}$ and $d_{xz} \rightarrow d_{yz}$. The second band seen at 19,000 cm$^{-1}$ (e, 14-21) is not assigned unequivocally and may be due both to the $b_2(d_{xy}) \rightarrow b_1 \ast(d_{x^2-y^2})$ and the $b_3(d_{xy}) \rightarrow a_1 \ast(d_{z^2})$ transitions. These complexes exhibit an intense band around 40,000 cm$^{-1}$ most likely due to the charge transfer or intraligand transitions.

The infrared spectra of VO(acac)$_2$ and its mixed ligand complexes with imidazole and its derivatives, recorded as nujol mulls in the region 4,000-650 cm$^{-1}$, indicate that the IR spectrum of each adduct is a combination of the spectra of the starting material and the base (L), although the ligand bands are either split or shifted to higher or lower frequencies suggesting bonding of the base to the metal$^6$. The $\nu(C=O)$ and $\nu(C \equiv C)$ of the acetylacetonate ring appear at 1570 and 1520 cm$^{-1}$ in VO(acac)$_2$, respectively, which are shifted to 1580 and 1525 cm$^{-1}$ in the imidazole adducts. The methine CH-bending vibration appearing as a weak band at 1190 cm$^{-1}$ in VO(acac)$_2$ virtually remains unchanged in the adducts. The most characteristic feature of the IR spectrum of the parent VO(acac)$_2$ is the appearance of a sharp, strong band at 995 cm$^{-1}$ assignable to $\nu V=O$ mode$^{12,13}$. The coordination of imidazole or its derivatives in the sixth coordination position lowers ($\Delta \nu = 40-50$ cm$^{-1}$) $\nu V=O$ from 995 cm$^{-1}$ in VO(acac)$_2$ to 950-955 cm$^{-1}$ in the [VO(acac)$_2$L] complexes. While some authors assign this large shift to the trans-structure of [VO(acac)$_2$L]$^{14}$, others suggest a cis-structure$^{12}$. The X-ray crystal structure of [VO(acac)$_2$(4-phenylpyridine)], however, substantiates that the large shift is due to the cis-structure$^{12}$. The complexes reported here are, therefore proposed to have a cis-structure.

References