Oxovanadium(IV) complexes with tridentate dibasic schiff base ligands and 2-(2'-pyridyl)benzimidazole

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Several tridentate dibasic schiff base ligands with ONO donor set react with VO(OAc)₃ in presence of the neutral bidentate ligand 2-(2'-pyridyl)benzimidazole (PBH) containing NN donor set to form monomeric and six-coordinated complexes of the type [VO(SB)(PBH)] (H₂SB = tridentate schiff bases). These are orange to brown coloured paramagnetic solids with normal magnetic moments. All the complexes exhibit a strong IR band at 960 cm⁻¹ due to ν(V=O). Their EPR spectra are characterised by a single unresolved signal at g = 2.00 ± 0.02.

Electrochemical measurements are characterised by oxidation to vanadium(V) and reduction to vanadium(III) at +0.98 to +1.26 V vs SCE and -1.08 to -1.50 V vs SCE, respectively. The thermogravimetric measurements indicate the stability of the complexes and their stepwise thermal decomposition finally giving V₂O₅ as the end product.

Among the oxometal species, the oxovanadium(IV) ion, VO²⁺, is considered as the most stable oxycation of the first row transition metal ions. It forms stable anionic, catipnic and neutral complexes with various types of ligands. Oxovanadium(IV) forms monomeric and five-coordinated complexes, [VO(SB)₃], with several bidentate schiff bases, but dimeric and six-coordinated complexes [VO(SB)₂] with tridentate schiff bases. On treatment with strong chelating ligands, the dimer is broken forming mononuclear mixed ligand complexes of the type [VO(SB)L] (L = strong bidentate chelating ligand). The present work deals with the monomeric, six-coordinated mixed-ligand complexes of oxovanadium(IV) with dibasic tridentate schiff base ligands (ONO donor set) and the bidentate chelating ligand 2-(2'-pyridyl)benzimidazole (PBH) containing N₂ donor set.

Experimental

All the analyses and physical measurements were carried out as reported earlier. Cyclic voltammograms of the complexes were recorded in MeCN using Pt electrodes with TEAP (tetraethylammonium perchlorate) as the supporting electrolyte on a PAR equipment model 174 A polarographic analyser, a PAR model 175 universal programmer and a Houston RE 0074 XY recorder.

Synthesis of ligands and complexes

The schiff base ligands were obtained by the condensation of hydroxylaldehydes (e.g. salicylaldehyde, 5-bromosalicylaldehyde or 2-hydroxy-1-naphthaldehyde) with o-aminophenol (H₂SAP, H₂5-BrSAP, H₂NAP) or anthranilic acid (H₂SAN, H₂NAN) as per literature methods. 2-(2'-Pyridyl)benzimidazole (PBH) was either prepared from the condensation of α-picolinic acid with o-phenylenediamine or obtained commercially from Ega Chemie, FRG. Oxovanadium(IV) acetate was prepared by a reported procedure.

All the complexes were synthesised by a common synthetic method involving the reaction of the preformed solid schiff base ligand, VO(OAc)₂, and 2-(2'-pyridyl)benzimidazole in EtOH medium. The details for a prototype complex are outlined below. All other complexes were similarly prepared.

Solid oxovanadium(IV) acetate, VO(OAc)₂ (0.185g, 1 mmol) was added gradually to a well-stirred solution of N-(2-hydroxyphenyl)salicyldieneimine, H₂SAP (0.213g, 1 mmol) in EtOH (10 cm³) and then held under reflux for 30 min during which time the colour of the solution changed to brownish black. To this was added 2-(2'-pyridyl)benzimidazole (PBH, 0.195g, 1 mmol) dissolved in EtOH (5 cm³) and the entire mixture was refluxed for 4h in order to ensure completion of the reaction. The orange coloured solid that separated out was collected on a glass sinter, washed with small aliquots of EtOH followed by Et₂O and finally dried in vacuo; yield 0.38 g, 80%.

Results and discussion

The dibasic tridentate schiff bases (H₂SB) obtained by condensing hydroxylaldehydes with o-aminophenol or anthranilic acid possess ONO donor set and interact with VO²⁺ forming dimeric, six-coordinated complexes [VO(SB)₃] which exhibit subnormal magnetic moments. The dimeric structure was reported to be broken on treatment of [VO(SB)₂] with pyridine forming a monomeric, six-coordinated monopyridine adduct with a normal magnetic moment of 1.75 BM at room temperature. With the similar monodentate ligand imidazole (or its derivatives), however, only dimeric complexes could
### Table 1—Analytical and other characterising data of \([\text{VO(SB)}(\text{PBH})]\) complexes

<table>
<thead>
<tr>
<th>[\text{VO(SB)}(\text{PBH})]</th>
<th>Formula</th>
<th>Colour</th>
<th>Found (Calc.), %</th>
<th>(\mu_{\text{eff}}) (B.M.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SB = SAP</td>
<td>VC(<em>{25})H(</em>{18})N(<em>{4})O(</em>{3})</td>
<td>Orange</td>
<td>10.3 (10.7) 63.7 (63.4) 3.7 (3.8) 11.5 (11.8) 1.84</td>
<td></td>
</tr>
<tr>
<td>5-BrSAP</td>
<td>VC(<em>{25})H(</em>{17})N(<em>{4})O(</em>{3})Br</td>
<td>Brick red</td>
<td>9.6 (9.2) 54.1 (54.3) 3.3 (3.1) 10.5 (10.1) 1.79</td>
<td></td>
</tr>
<tr>
<td>NAP</td>
<td>VC(<em>{29})H(</em>{20})N(<em>{4})O(</em>{3})</td>
<td>Chocolate</td>
<td>9.4 (9.7) 66.7 (66.5) 3.6 (3.8) 10.3 (10.7) 1.86</td>
<td></td>
</tr>
<tr>
<td>SAN</td>
<td>VC(<em>{26})H(</em>{18})N(<em>{4})O(</em>{4})</td>
<td>Chocolate</td>
<td>10.5 (10.1) 62.1 (62.2) 3.7 (3.6) 11.4 (11.1) 1.78</td>
<td></td>
</tr>
<tr>
<td>NAN</td>
<td>VC(<em>{30})H(</em>{20})N(<em>{4})O(</em>{4})</td>
<td>Dark brown</td>
<td>9.7 (9.2) 65.4 (65.3) 3.5 (3.6) 10.4 (10.1) 1.82</td>
<td></td>
</tr>
</tbody>
</table>

*All compounds have m.p. higher than 290°C.

**Abbreviations:** H\(_{2}\)SAP = N-(2-hydroxyphenyl)salicylideneimine; H\(_{2}\)(5-Br-SAP) = 5-Bromo N(2-hydroxyphenyl)salicylideneimine; H\(_{2}\)NAP = N-(2-hydroxyphenyl)2-hydroxynaphthylideneimine; H\(_{2}\)SAN = N-(2-carboxyphenyl)salicylideneimine; H\(_{2}\)NAN = N(2-carboxyphenyl)2-hydroxynaphthylideneimine; PBH = 2-(2'-pyridyl)-benzimidazole.

...be isolated which were antiferromagnetic possessing magnetic moments of 1.4 BM at room temperature. Splitting of the dimeric structure of \([\text{VO(SB)}]_2\) is also reported on treatment with chelating ligands like 2-2'bipyridyl or 1,10-phenanthroline resulting in the formation of mononuclear, hexacoordinated complexes with magnetic moments close to the spin-only value of 1.73 BM for vanadium(IV).

The bidentate chelating ligand, 2-(2'-pyridyl)-benzimidazole (PBH) is a powerful chelating ligand similar to 2-2'bipyridyl and 1,10-phenanthroline. It is known to be important biochemically and finds use as a biochemical, anticancer and analytical reagent. The interaction of the chelating agent, PBH, with VO(OAc)\(_2\) in presence of the ligands, H\(_{2}\)SB (SB = dianion of tridentate Schiff base) results in the formation of mononuclear hexacoordinated complexes of the type \([\text{VO(SB)}(\text{PBH})]\). The relevant analytical and other characterising data of the complexes are presented in Table 1. These complexes are only sparingly soluble in common organic solvents. The molar conductance values (1.41-8.81 mho cm\(^{2}\) mol\(^{-1}\)) in DMSO indicate their non-electrolytic behaviour.

The IR spectral and analytical data and the valency requirement of the metal ion suggest the tridentate, dibasic behaviour of the Schiff base ligands. The prominent IR bands due to the Schiff base ligands in the complexes are \(v(C-H)\) at 3050 cm\(^{-1}\), coupled \((C=N)\) and \(v(C\cdots C)\) modes at 1600 cm\(^{-1}\), \(\nu_{ad}(\textrm{COO})\) at 1580 and 1530 cm\(^{-1}\), \(\nu_{ct}(\textrm{COO})\) at 1450 and 1430 cm\(^{-1}\), and \(v(C-O)\) at 1540 cm\(^{-1}\). The broad hydrogen-bonded OH stretch near 2700 cm\(^{-1}\) present in the free ligands is absent in the complexes suggesting the coordination of the deprotonated phenolic oxygen. The prominent bands of PBH are either split or shifted due to coordination and show the bidentate coordination of PBH through the unsaturated N atom and the N atom of the pyridine ring.

In general, the \(\nu(V=O)\) of monomeric complexes are observed in the 950-1000 cm\(^{-1}\) range, whereas in the oligomeric complexes this is lowered to 850 cm\(^{-1}\) due to reduction of \(V=O\) bond order. All the present complexes exhibit a clear sharp band at 960-970 cm\(^{-1}\) corresponding to \(\nu(V=O)\) indicating a monomeric structure.

The T.I.P. corrected room temperature magnetic moments of these complexes are in the range 1.78 to 1.86 BM, in close agreement with the spin-only value of a \(d^1\) system with no orbital contribution. The EPR spectra of polycrystalline compounds at X-band frequencies at room temperature (300K) and also at liquid nitrogen temperature (77K) exhibit a single unresolved EPR signals at \(g = 2.00 \pm 0.02\), very close to the free electron value of 2.0023. The EPR linewidths of these complexes are in the range 80-170 G and are independent of the temperature. The complexes exhibit a broad \(d-d\) band in the region 14-16 kK and another intense band at 17-18 kK for which the probability of ligand to metal charge transfer could not be ruled out.

The electrochemical investigation of the complexes \([\text{VO(SB)}(\text{PBH})]\) in acetonitrile revealed one-electron oxidation to vanadium(V) at +0.98 to +1.26 V vs SCE and irreversible one-electron reduction to vanadium(III) at -1.08 to -1.50 V vs SCE. The thermogravimetric measurements showed that the complexes do not melt or decompose...
to about 325°C. With increase in temperature, these complexes decompose in several stages corresponding to the loss of ligands in varying proportions ultimately yielding $\text{V}_2\text{O}_5$ as the end product at around 500°C. Further heating to about 900°C results in considerable volatilisation of the residue leaving only 15-20% residue, a fact which is substantiated by heating the compounds at the same temperature in a furnace and estimating the mass loss on heating.

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References