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Synthesis, EPR and Optical Properties of Oxovanadium(IV) Complexes with Tris(2-aminoethyl amine) and Substituted Imidazoles

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The synthesis, characterization with EPR and electronic absorption spectra of $[VO(tren)](BPh_4)_2$, $[VO(tren)ImH](BPh_4)_2$, $[VO(tren)M\text{-}ImH](BPh_4)_2$ and $[VO(tren)E\text{-}ImH](BPh_4)_2$ using tris(2-aminoethyl amine), 2-methylimidazole and 2-ethylimidazole as ligands have been reported.

Key Words: Synthesis, EPR, optical properties, Oxovanadium(IV) Complex, Tris(2-aminoethyl amine), Imidazoles.

INTRODUCTION

Vanadium is an important element and widely distributed[1–4] in rocks, soils, plants and to a lesser extent in water. Vanadium has abundance in the earth's crust of about 0.02%. Vanadium has a rich and varied chemistry[5], spread over a large number of oxidation states ranging from –1 to +5. Vanadium is an important trace element for different organisms and essential nutrients for higher animals[6, 7]. VO^{2+} binding investigations have been carried out on a relatively large number of proteins in which EPR spectroscopy was the major investigative tool employed. In solid state, there are only limited mixed ligand oxovanadium(IV) complexes[8–12] isolated and studied.

EXPERIMENTAL

Tris(2-aminoethyl amine), 2-ethylimidazole (Aldrich), vanadyl sulphate, 2-methylimidazole, imidazole, sodium tetraphenyl boron (S.D. Fine Chemicals) were used as supplied. Other chemicals used were of reagent grade.

$[VO(tren)](BPh_4)_2$: Equimolar ratios of vanadyl sulphate (0.326 g, 2 mmol) and tris(2-aminoethyl amine) (tren) (0.299 g, 2 mmol) were dissolved in water-methanol, 50 : 50 (v/v) and stirred well. The reaction mixture was filtered and kept overnight. The light blue product formed isolated and dried in calcium chloride desiccator.

$[VO(tren)ImH/M\text{-}ImH/E\text{-}ImH](BPh_4)_2$: This was synthesized equimolar ratios of vanadyl sulphate (0.326 g, 2 mmol), tris(2-aminoethyl amine) (0.299 g, 2 mmol) and imidazoles (IMH) 2-methylimidazole (M-IMH) 2-ethylimidazole (E-IMH) (0.136 g/0.164 g/0.192 g, 2 mmol) were dissolved in water-methanol, 50 : 50 (v/v) and stirred well. The reaction mixtures were filtered and kept overnight. The light yellow product formed was isolated and dried in calcium chloride desiccator.

Magnetic susceptibility measurements were recorded on a Gouy balance at room temperature. Hg[Co(NCS)$_4$] was used as a calibrant (16.44 × 10^{-6} cgs unit). X-band EPR spectra were recorded with a Varian E-line Century Series EPR spectrometer equipped with a dual cavity and operating at X-band of 100 kHz modulation frequency. Tetracyanoethylene was used as field marker (g = 2.00277). The visible spectra were recorded on a Shimadzu UV-Vis recording spectrometer UV-160 with 1 cm quartz cell.

RESULTS AND DISCUSSION

The present complexes were prepared by addition of a stoichiometric amount of ligands to a solution vanadyl sulphate. The synthesized complexes gave satisfactory elemental analysis (Table-1).

TABLE-1
ANALYTICAL AND PHYSICAL DATA FOR OXOVANADIUM(IV) COMPLEXES

Complex	Colour	m.p. (°C)	Yield (%)	Found/(Calculated) (%)				μ_{eff} (B.M.)
				C	H	N	VO	
[VO(tren)](BPh$_4$)$_2$	Light blue	160	64	76.08	6.81	6.57	7.86	0.98
[VO(tren)ImH](BPh$_4$)$_2$	Light yellow	200	70	74.45	6.64	9.14	7.28	1.20
[VO(tren)M-ImH](BPh$_4$)$_2$	Light yellow	270	65	74.61	6.75	9.00	7.17	1.70
[VO(tren)M-ImH](BPh$_4$)$_2$	Light yellow	280	50	76.04	6.86	8.87	7.07	1.80

The oxovanadium(IV) ions belong to the S = 1/2 system; the magnetically dilute oxovanadium(IV) complexes usually exhibit magnetic moments close to their spin-only value, *i.e.*, 1.73 BM. At room temperature magnetic moments in the solid states are in 0.98 BM for [VO(tren)](BPh$_4$)$_2$. As the values are significantly lower than the spin-only value, so dimeric structure must be supposed in order to reach penta coordination of the vanadium atom; such a dimeric structure is in the plane of the tridentate ligand thus creating a favourable geometry for an antiferromagnetic exchange interaction[13]. There are reports[14, 15] for subnormal magnetic moments for oxovandium(IV) complexes with tridentate ligands. The magnetic moment value for [VO(tren)ImH](BPh$_4$)$_2$ compound are 1.20 BM. Similarly, magneitc moment values for [VO(tren)(M-ImH/E-ImH](BPh$_4$)$_2$ compounds are 1.70 and 1.80 BM, respectively. For these compounds five coordinated type geometry is suggested in which a molecule of imidazole/2-methylimidazole/2-ethylimidazole occupies one of the coordination sites.

EPR spectra of these complexes were recorded polycrystalline (RT) and in LNT. The derived EPR parameters are given in Table-2. The X-band EPR spectra for the powdered samples gave broad signals centred at g_{iso} = 1.97, typical of a solid oxovanadium(IV) complex. The EPR spectra of [VO(tren)ImH](BPh$_4$)$_2$

reveals eight lines attributable to a single S = 1/2 species in which the unpaired electron in a d_{xy} orbital is coupled to the nuclear spin of the vanadium nucleus[16–18] (^{51}V, 99.76 atom %, I = 7/2, $\mu = 5.149$ BM). These results are consistent with the magnetic moments and show that ligand dissociation has not occurred during preparation of EPR samples. In frozen solution, the spectra are anisotropic and two sets of resonance components, one each due to parallel and perpendicular features, are observed for these complexes. The frozen solution EPR spectra of these present compounds gave the spin Hamiltonian parameters[16, 17]. $A_{\parallel} = 135$ G, $A_{\perp} = 39$ G, $g_{\parallel} = 1.921$ G and $g_{\perp} = 1.961$ for the complex $[VO(tren)](BPh_4)_2$ and $A_{\parallel} = 131$ G, $A_{\perp} = 31$ G, $g_{\parallel} = 1.931$ G and $g_{\perp} = 1.940$ for the complex $[VO(tren)ImH](BPh_4)_2$. Spectra of $[VO(tren)M\text{-}ImH](BPh_4)_2$ and $[VO(tren)E\text{-}ImH](BPh_4)_2$ were not resolved at LNT.

TABLE-2
X-BAND EPR PARAMETERS OF SOME OXOVANADIUM(IV) COMPLEXES

Complex	$g_{\parallel}$	g_{iso}	$A_{\parallel}$	$A_{\perp}$	$g_{\perp}$	Peak to peak width (G)
$[VO(tren)](BPh_4)_2$	—	1.971	—	—	—	147
$[VO(tren)ImH](BPh_4)_2$	2.229	—	146.25	116	2.030	—
$[VO(tren)M\text{-}ImH](BPh_4)_2$	—	—	—	—	—	—
$[VO(tren)E\text{-}ImH](BPh_4)_2$	—	—	—	—	—	—

The visible absorption spectra of these complexes were recorded in acetonitrile and the band positions are given in Table-3. These oxovanadium(IV) complexes are soluble enough for solution studies in CH_3CN. The electronic spectra of the oxovanadium(IV) complexes having square pyramidal geometry are characterized by the presence of three absorption bands corresponding to $d_{xy} \rightarrow d_{xz}, d_{yz}$ (band I), $d_{xy} \rightarrow d_{x^2-y^2}$ (band II), $d_{xy} \rightarrow d_{z^2}$ (band III). The band observed at 750 and 747 nm in $[VO(tren)M\text{-}ImH](BPh_4)_2$ and $[VO(tren)E\text{-}Imh](BPh_4)_2$ complexes, respectively. Other two complexes did not give the resolved electronic spectra.

TABLE-3
ELECTRONIC SPECTRAL BANDS (nm)

Transitions	$[VO(tren)M\text{-}ImH](BPh_4)_2$	$[VO(tren)E\text{-}ImH](BPh_4)_2$
Band I ($d_{xy} \rightarrow d_{xz}, d_{yz}$)	750	747
Band II ($d_{xy} \rightarrow d_{x^2-y^2}$)	560	562
Band III ($d_{xy} \rightarrow d_{z^2}$)	—	—

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