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Characterisation and Electron Paramagnetic Resonance Spectra of Two Octahedral Complexes of Copper(II) Vanadate Derived from 1,2-Diaminoethane and 1,2-Diaminopropane

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Two complexes of copper(II) vanadate with 1,2-diaminoethane and 1,3-diaminopropane have been prepared. Their analytical and molar conductance data suggest molecular formulae to be $[Cu(C_2H_8N_2)_3](VO_3)_2{\cdot}2H_2O$ and $[Cu(C_3H_{10}N_2)_3](VO_3)_2{\cdot}2H_2O$. The magnetic and spectroscopic data indicate octahedral structure. The EPR data suggest monomeric nature of the complexes.

INTRODUCTION

In the last few years a large number of complexes derived from nitrogen donors have been prepared and characterised[1–6]. The anion is found to exert a profound effect on the coordination number of copper(II). In the present investigation the authors have been able to isolate two octahedral complexes of copper(II).

EXPERIMENTAL

The complexes were prepared by treating excess amount of diamine with copper(II) vanadate suspended in acetone-ethanol (1 : 1) mixture and refluxing the reactants for about 30–40 hrs or till the dissolution is complete. The complexes were crystallised by distilling off 50% solvent and cooling the concentrated solution. The complexes were redissolved in a suitable solvent and recrystallised and dried in vacuo over $CaCl_2$.

The physical measurements were performed as reported earlier.[1–6] The electron paramagnetic resonance spectra were obtained on a Varian V_3 spectrometer at room temperature on polycrystalline samples. The settings used are: RF power, 2 mW; Frequency 9.47 GHz; Scan range 1000 gauss; DPPH standard at 3401 gauss.

The data obtained are as follows:

1. $[Cu(C_2H_8N_2)_3](VO_3)_2{\cdot}2H_2O$, violet.

Found (%):	Cu, 13.02;	C, 15.60;	H, 6.31;	N, 17.08.
Calc.(%):	Cu, 13.30;	C, 15.08;	H, 5.90;	N, 17.60
Molar conductance:	33.00 mhos.			

Magnetic susceptibility: χ_g, 2.82 × 10^{-6}; χ_M, 1347 × 10^{-6}.
Pascal constant: 266.34 × 10^{-6}; χ'_M ,1613.34 × 10^{-6}; T, 298 K; μ_{eff}, 1.97 BM
Electronic spectrum: λ_{max}, 550 nm; energy, 18.18 kK; Dq, 1818 cm^{-1}.
EPR data: $g_{\perp}$, 2.15; g_{11}, 205; g_{ave}, 2.11; G, 0.33, μ_{eff}, 1.82.

2. $[Cu(C_3H_{10}N_2)_3](VO_3)_2 \cdot 2H_2O$, violet.
Found (%): Cu, 11.89; C, 21.20; H, 7.00; N, 15.75
Calc. (%): Cu, 12.22;‘ C, 20.77; H, 6.59; N, 16.17
Molar conductance: 35.00 mhos.
Magnetic susceptibility: χ_g, 2.65 × 10^{-6}; χ_M, 1378 × 10^{-6}.
Pascal constant: 301.92 × 10^{-6}; χ'_M, 1679.92 × 10^{-6}; T, 298. K; μ_{eff}, 2.01 BM
Electronic spectrum: λ_{max}, 550 nm; energy, 18.18 kK; Dq, 1818 cm^{-1}.
EPR data: $g_{\perp}$, 2.16; g_{11}, 2.11; g_{ave}, 2.12; G, 0.68; μ_{eff}, 1.83.

RESULTS AND DISCUSSION

The evidence for the cordination of 1,2-diaminoethane and 1,3-diaminopropane is obtained by a negative shift of ν_{NH} which appears in the form of asymmetric and symmetric stretches at 3135 cm^{-1}, 3220 cm^{-1} and 3025 cm^{-1}, 3130 cm^{-1} respectively. The asymmetric and symmetric stretching vibrations of free NH_2 group are observed in the region 3400–3300 cm^{-1}.

The lowering in the stretching frequencies is a clear indication of the formation of M–V bond. The ν(CN) also undergoes a negative shift and is observed near 1010 ± 5 cm^{-1} in both the complexes[7,8]. In both the complexes, the asymmetric and symmetric ν_{OH} of lattice water are observed in the vicinity of 3500 cm^{-1}. This is also confirmed by TGA; the loss in weight between 60° and 80°C corresponds to the number of lattice water molecules present in the complexes. The free vanadate ion has C_{3v} symmetry and has four fundamentals, out of which ν_1 and ν_3 are usually observed. The ν_1 and ν_3 bands are seen at 724 ± 2 cm^{-1} and 733 ± 3 cm^{-1} confirming the presence of free vanadate ion in complexes[9].

The complexes are violet in colour and paramagnetic with μ_{eff}, 1.97 B.M. and 2.01 B.M. respectively. These are hexacoordinated and assigned octahedral structure with sp^3d^2 hybridisation[10,11]. The complexes show only one band at 18.18 kK. The splitting of this band in three components is not seen and the band is probably due to simple $d_{z^2} \rightarrow d_{x^2-y^2}$ transition[12].

In the EPR spectra the two g factors have been obtained. The $g_{\perp}$ is obtained at low field strength and g_{11} at high fields. These values have been used to calculate g_{ave}, μ_{eff}. and G. The observed g values lie in the range 2.05–2.16 with no other absorption at either high or low fields. The values indicate magnetically dilute copper(II) environment and rule out the possibility of any copper-copper interaction[13,14]. The values of μ_{eff} which have been calculated using these values show good agreement with gram susceptibility measurements.

The low G values suggest very little exchange coupling[15]. This may be due to the symmetric alignment of the coordinate axes of different copper(II) ions present in the crystal lattice. The lowest g values are all above 2.04; a $d_{x^2-y^2}$ or d_{xy} location of ground state electron is suggested.[16]

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