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NOTE

EPR and XRD Spectra of Copper Complexes of 1,4-Phenylene-Bis-Allylthiourea

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The paramagentic character and tetragonal geometrical structure of both complexes of 1,4-phenylene-bis-allylthiourea with Cu(I) and Cu(II) have been confirmed by their EPR and X-ray powder diffraction spectra.

Key Words: Cu(I), Cu(II), 1,4-Phenylene bis-allylthiourea, EPR, XRD.

The complexes of thiourea derivatives, other than 1,4-phenylene bis-allylthiourea (PBATU) have been reported[1–5]. The EPR and X-ray powder diffraction spectral investigations of the complexes of PBATU with Cu(I) and Cu(II), prepared are being presented.

The complexes of PBATU with Cu(I) and Cu(II) were synthesized as reported[6], by using Aldrich make AnalaR grade chemicals and well cleaned pyrex glass wares. The EPR and X-ray powder diffraction spectra of the complexes were carried out subsequently on Varian E-X-4-band (3000–50000 gauss) and ISQ-Debyes-FLEX-2002 German made XRD (source CuK_α, $\lambda = 1{,}5412$ Å) spectrometers at room temperature.

On the basis of quantitative estimations and their mass spectra, the complexes of PBATU with Cu(I) and Cu(II) are assigned by the molecular formulae CuCSN·PBATU and $CuSO_4 \cdot 5H_2O$·PBATU, respectively. Their I.R. and ^1H NMR spectra[7] have predicted the presence of benzene ring, thioureate group and N—H bands alongwith coordination of thioureate group of PBATU through its S and N atoms to metal ions. The electronic spectra of the complexes have inferred their semiconductivity and spin-orbital coupling in them along with charge transfer transition due to Cu^+ and Cu^{2+} ions.

A single broad peak was observed in the EPR spectrum of each complex indicating their paramagnetic character, which is also supported by the values of magnetic moment, μ_{eff}, magnetic susceptibility, χ_Λ and number of unpaired

electrons present (Table-1). The values of $g_x = g_y$ and g_z less than two (02) expound the occurrence of vacant 'd' energy shells in Cu ions, forming coordinate linkage by PBATU through S and N atoms of its thioureate groups. The sp^3 hybridization in both complexes has happened to form tetragonal geometrical structure which is also confirmed by their XRD spectra.

TABLE-1
EPR SPECTRAL DATA OF THE COMPLEXES

Complexes	Magnetic field (G)	$g_x = g_y$	g_z	g_{av}	μ_{eff} (BM)	$\chi_A \times 10^{-4}$	No. of unpaired electrons
Cu(I)PBATU	4850	1.39	1.06	1.72	1.49	9.20	1
Cu(II)PBATU	3990	1.70	1.51	1.63	1.42	8.35	1

From the X-ray powder diffraction pattern of the complexes, the values of $\sin^2\theta$, hkl and interplanar distance 'd' are calculated (Table-2). The values of 'd' observed are in close agreement to the theoretical ones. The gradation in I/I_0 expresses the crystallinity of the complexes. The values of axial ratios along X-axis are determined as:

$$a_0 = \left(\frac{n^2\lambda^2}{4q_{av}}\right)^{1/2}$$

TABLE-2
X-RAY POWDER DIFFRACTION PATTERN OF THE COMPLEXES

Complexes	Cell	Parameters	Geometry
Cu(I)PBATU	2θ (°)	17.14, 19.23, 22.01, 27.29, 36.14, 43.75, 54.69, 56.73, 57.82, 61.21, 76.18, 79.26	
	d (Å) = Exp. (theor.)	5.168, 4.617, 4.036, 3.270 2.483, 2.039, (5.173), (4.616), (4.038), (3.268) (2.485), (2.069), 1.677, 1.621 1.593, 1.513, 1.264, 1.208 (1.678), (1.622) (1.594), (1.514), (1.251), (1.208)	Tetragonal
Cu(II)PBATU	2θ (°)	17.30, 19.91, 24.07, 29.34, 40.64, 42.90, 54.25, 57.21, 64.14, 65.14, 74.63, 75.03	
	d (Å) = Exp. (theor.)	5.127, 4.483, 3.696, 3.043 2.219, 2.108, (5.121), (4.457), (3.609), (3.041) (2.218), (2.160), 1.690, 1.610 1.452, 1.432, 1.272, 1.266 (1.609), (1.611) (1.452), (1.431), (1.270), (1.265)	Tetragonal

After that, values of other axial ratios and axial angles, obtained, are $a_0 = 7.313$ Å, $b_0 = 4.874$ Å, $c_0 = 4.450$ Å, $\alpha = \beta = \gamma = 90°$ and $a_0 = 7.323$ Å, $b_0 = 8.323$ Å, $c_0 = 4.432$ Å, $\alpha = \beta = \gamma = 90°$ for CuCNS·PBATU and $CuSO_4 \cdot 5H_2O$·PBATU complexes, respectively.

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REFERENCES

1. M. Schafer and C. Curram, *Inorg. Chem.*, **5**, 265 (1996).
2. A.C. Fabretti, A. Girusti and W. Malavasi, *J. Chem. Soc. (Dalton Trans)*, 3091 (1990).
3. F.T. Esmadi and A. Al-Hamid, *Transition Met. Chem.*, **19**, 571 (1994).
4. F.T. Esmadi and W. Al-Masry, *Asian J. Chem.*, **13**, 128 (2001).
5. V. Pathak and B.K. Srivastava, *Asian J. Chem.*, **13**, 539 (2001).
6. Pratibha and S.P.S. Jadon, *Asian J. Chem.*, **16**, 1637 (2004).
7. Pratibha, R.C. Dwivedi and S.P.S. Jadon, *Int. J. Chem. Sci.*, **2**, 317 (2004).

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