

# EPR Spectral Studies of Dimeric and Monomeric Cu(II) Complexes of di-2-pyridyl Ketone N(4)-methyl Thiosemicarbazone

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## ABSTRACT

Four copper(II) complexes,  $[\text{Cu}_2(\text{DpyMeTsc})_2\text{SO}_4] \cdot 3\text{H}_2\text{O}$  (1),  $[\text{Cu}(\text{DpyMeTsc})\text{N}_3] \cdot \text{H}_2\text{O}$  (2),  $[\text{Cu}_2(\text{DpyMeTsc})_2] \cdot (\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (3), and  $[\text{Cu}(\text{DpyMeTsc})(\text{CH}_3\text{COO})] \cdot 2\text{H}_2\text{O}$  (4) of di-2-pyridyl ketone N(4)-methylthiosemicarbazone (HDpyMeTsc) are studied with electron paramagnetic resonance (EPR) spectroscopy. EPR is the most powerful spectroscopic method to discriminate between monomeric and dimeric Cu(II) complexes in solution. EPR studies indicate dimeric nature of (1) and (3) and monomeric nature of (2) and (4).

**Keywords:** Thiosemicarbazone; Cu(II) complex; Di-2-pyridyl ketone; EPR spectra.

## I. INTRODUCTION

The coordination chemistry of transition metal complexes involving nitrogen and sulfur donor ligands has been the cynosure among chemists during recent years due to the application of these chelates in modelling of biomolecules, in the field of chemical and biological reactivity and nuclear medicine. The potential role played by copper ions, being present in the active sites of a large number of metalloproteins having the  $\text{CuN}_2\text{S}_2$  chromophore, has stimulated efforts to design new ligand frames having nitrogen sulfur donor sites and characterize copper complexes as models for providing a better understanding of the biological system<sup>1</sup>. The activity of thiosemicarbazones depends very much on the parent aldehyde or ketone and is affected also by N(4) substitution<sup>2</sup>. Thiosemicarbazones derived from di-2-pyridyl ketone are potentially tetradentate. However in majority of cases they function as tridentate ligands only. Literature survey reveals that the presence of a metal ion increases the activity of or mitigate the side effects of the parent organic compounds<sup>3</sup>.

Copper(II) is a biologically active, essential ion; its chelating ability and positive redox potential allow participation in biological transport reactions. Also, copper(II) forms the active centers of more than a dozen metalloproteins. Further, copper(II) complexes possess a wide range of biological activity and are among the most potent antiviral, antitumor and anti-inflammatory agents<sup>4</sup>. Cu(II) complexes display a wide range of geometric arrangements around the copper ion, from the square planar to deformed tetrahedral geometry. Pseudohalide anions like azides and thiocyanate are found to be versatile ligands in terminal and bridging modes. These phenomena are reflected in their spectral properties. Electron paramagnetic resonance (EPR) is a suitable tool for the study of paramagnetic metal ion complexes and may provide useful information about the oxidation states, modes of coordination, geometry and type of ligand sites<sup>5</sup>.

## II. EXPERIMENTAL

### A. Materials

Di-2-pyridyl ketone, N(4)-methyl thiosemicarbazide, copper(II) acetate monohydrate, copper(II) sulphate pentahydrate, copper(II) perchlorate hexahydrate, sodium azide, ethanol and methanol were used as supplied. Caution: Azide and perchlorate complexes of metals with organic ligands are potentially explosive and should be handled with care.

### B. Synthesis of ligand, HDpyMeTsc

The thiosemicarbazone ligand was synthesized as per the reported procedure <sup>6</sup>.

### C. Syntheses of complexes

#### 1. Syntheses of $[\text{Cu}_2(\text{DpyMeTsc})_2\text{SO}_4]\cdot 3\text{H}_2\text{O}$ (1)

Complex 1 was prepared by refluxing an ethanolic solution of the ligand (0.271 g, 1 mmol) with a solution of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.249 g, 1 mmol) in water for 4 hours. The resulting solution was allowed to stand at room temperature. The complex formed were filtered, washed with ethanol and ether and dried in vacuo over  $\text{P}_4\text{O}_{10}$ .

#### 2. Synthesis of $[\text{Cu}(\text{DpyMeTsc})\text{N}_3]\cdot \text{H}_2\text{O}$ (2)

To a solution of the ligand (0.271 g, 1 mmol) in hot ethanol, was added a solution of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.199 g, 1 mmol) in water. To this a solution of  $\text{NaN}_3$  (0.065 g, 1 mmol) in water was added and stirred for 3 hours and allowed to stand at room temperature. The complex formed were filtered, washed with ethanol and ether and dried in vacuo over  $\text{P}_4\text{O}_{10}$ .

#### 3. Syntheses of $[\text{Cu}_2(\text{DpyMeTsc})_2][\text{ClO}_4]_2 \cdot 2\text{H}_2\text{O}$ (3)

To a solution of the ligand (0.271 g, 1 mmol) in hot ethanol, was added a solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.370 g, 1 mmol) in methanol. The mixture was refluxed for 4 hours and allowed to stand at room temperature. The complex formed were filtered, washed with ethanol and ether and dried in vacuo over  $\text{P}_4\text{O}_{10}$ .

#### 4. Synthesis of $[\text{Cu}(\text{DpyMeTsc})(\text{CH}_3\text{COO})]\cdot 2\text{H}_2\text{O}$ (4)

To a solution of HDpyMeTsc (0.271 g, 1 mmol) in hot ethanol, was added a solution of  $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$  (0.199 g, 1 mmol) in water. The mixture was refluxed for 4 hours, and kept at room temperature. The complex formed were filtered, washed with ethanol and ether and dried in vacuo over  $\text{P}_4\text{O}_{10}$ .

### D. Physical measurements

The EPR spectra of the complexes were recorded on a Varian E-112 spectrometer using TCNE as the standard at SAIF, IIT, Bombay, India. The EPR spectra of the complexes in the polycrystalline state at 298 K and in solution at 77 K were recorded in the X-band, using 100-kHz field modulation and the g factors were quoted relative to the standard marker TCNE ( $g = 2.00277$ ).

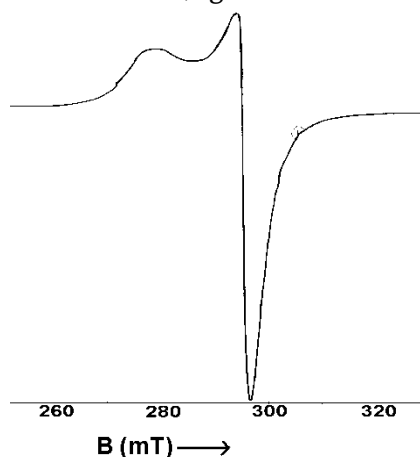
## III. RESULTS AND DISCUSSION

The copper (II) ion, with a  $d^9$  configuration, has an effective spin of  $S = 1/2$  and is associated with a spin angular momentum,  $m_s = \pm 1/2$ , leading to a doubly degenerate spin state in the absence of a magnetic field. In a magnetic field the degeneracy is lifted between these states and the energy difference between them is given by  $E = h\nu = g\beta H$ , where  $h$  is Planck's constant,  $\nu$  is the frequency,  $g$  is the Lande splitting factor (equal to 2.0023 for a free electron),  $\beta$  is the Bohr magneton and  $H$  is the magnetic field. For the case of a  $3d^9$  copper(II) ion, the appropriate spin Hamiltonian assuming a  $B_{1g}$  ground state is given by<sup>7</sup>:

$$\hat{H} = \beta [g_{\parallel} H_z S_z + g_{\perp} (H_x S_x + H_y S_y)] + A_{\parallel} I_z S_z + A_{\perp} (I_x S_x + I_y S_y)$$

The EPR spectra of compounds 2 and 3 in the polycrystalline state at 298 K show only one broad signal at 2.086 and 2.106 respectively. Such isotropic spectra, consisting of a broad signal and hence only one g value, arise from extensive exchange coupling through misalignment of the local molecular axes between different molecules in the unit cell (dipolar broadening) and enhanced spin lattice relaxation.

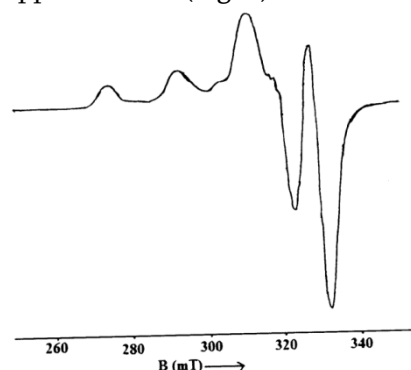
This type of spectra unfortunately give no information on the electronic ground state of the Cu(II) ion present in the complexes. However the spectra of compounds **1** and **4** show typical axial behavior (Fig. 1) with well defined  $g_{\parallel}$  and  $g_{\perp}$  features. The variation in the  $g$  values indicates that the geometry of the compound is affected by the nature of the coordinating anions. The geometric parameter  $G$ , which is a measure of the exchange interaction between the copper centers in the polycrystalline compound, is calculated using the equation<sup>8</sup>:  $G = (g_{\parallel} - 2.0023)/(g_{\perp} - 2.0023)$ . If  $G > 4$ , exchange interaction is negligible and if it is less than 4, considerable exchange interaction is indicated in the solid complex. In all the complexes  $g_{\parallel} > g_{\perp} > 2.0023$  and  $G$  values within the range 2.14–2.91 are consistent with a  $d_{x^2-y^2}$  ground state<sup>9</sup>.



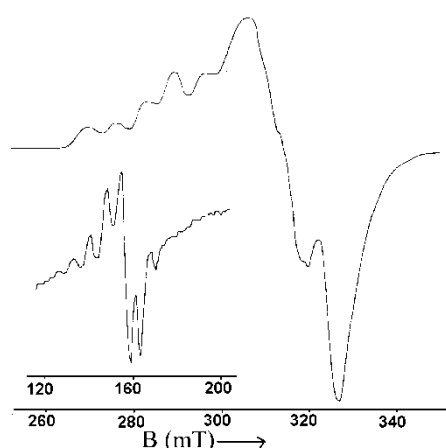
**Figure 1.** EPR spectrum of  $[\text{Cu}_2(\text{DpyMeTsc})_2\text{SO}_4] \cdot 3\text{H}_2\text{O}$  (**1**) in polycrystalline state at 298 K

For the complexes **2** and **4**, we obtain well-resolved four hyperfine lines in the parallel region (Fig.2). But for complexes **1** and **3**, axial spectra with seven hyperfine lines are obtained, suggesting a dimeric state with two copper centres. The splitting in the perpendicular region of the spectra can be attributed to interaction of an unpaired electron spin with the copper nuclear spin and two  $^{14}\text{N}$  ( $I = 1$ ) donor nuclei. The most important aspect found in the spectra of complexes **1** and **3** were the presence of half field signal with seven hyperfine splitting due to the

coupling of the electron spin with the nuclear spin of the two copper centers (Fig. 3).



**Figure 2.** EPR spectrum of  $[\text{Cu}(\text{DpyMeTsc})(\text{CH}_3\text{COO})] \cdot 2\text{H}_2\text{O}$  (**4**) in DMF at 77 K



**Figure 3.** EPR spectrum of  $[\text{Cu}_2(\text{DpyMeTsc})_2](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$  (**3**) in DMF at 77 K

The EPR parameters  $g_{\parallel}$ ,  $g_{\perp}$ ,  $g_{\text{av}}$ ,  $A_{\parallel}$  (Cu) and  $A_{\perp}$  (Cu) and the energies of d–d transition were used to evaluate the bonding parameters  $\alpha^2$ ,  $\beta^2$  and  $\gamma^2$ , which may be regarded as measures of the covalency of the in-plane  $\sigma$  bonds, in-plane  $\pi$  bonds, and out-of-plane  $\pi$  bonds respectively<sup>10</sup>. The value of in-plane sigma bonding parameter  $\alpha^2$  was estimated from the following expression<sup>11,12</sup>:

$$\alpha^2 = -A_{\parallel}/0.036 + (g_{\parallel} - 2.0023) + 3/7(g_{\perp} - 2.0023) + 0.04$$

The orbital reduction factors  $K_{\parallel} = \alpha^2 \beta^2$  and  $K_{\perp} = \alpha^2 \gamma^2$  were calculated using the following expressions<sup>13,14</sup>.

$$K_{\parallel}^2 = (g_{\parallel} - 2.0023)\Delta E(d_{xy} - d_{x^2-y^2})/8\lambda_0$$

$$K_{\perp}^2 = (g_{\perp} - 2.0023)\Delta E(d_{xz,yz} - d_{x^2-y^2})/2\lambda_0$$

Where  $\lambda_0$  is the spin orbit coupling constant and has the value  $-828 \text{ cm}^{-1}$  for a copper(II)  $d^9$  system.

According to Hathaway<sup>15</sup>,  $K_{\parallel} = K_{\perp} = 0.77$  for pure  $\sigma$  bonding and  $K_{\parallel} < K_{\perp}$  for in-plane  $\pi$  bonding, while for out-of-plane  $\pi$  bonding  $K_{\parallel} > K_{\perp}$ . In all the copper (II) complexes, it is observed that  $K_{\parallel} < K_{\perp}$  which indicates the presence of significant in-plane  $\pi$  bonding. Furthermore,  $\alpha^2$ ,  $\beta^2$  and  $\gamma^2$  have values less than 1 which is expected for 100% ionic character of the bonds and become smaller with increasing covalent bonding. The evaluated values of  $\alpha^2$ ,  $\beta^2$  and  $\gamma^2$  of the complexes are consistent with both strong in

plane  $\sigma$  and in plane  $\pi$  bonding. The  $g_{\parallel}$  values are nearly the same for all the complexes indicating that the bonding is dominated by the thiosemicarbazone moiety but are different from that in the solid state Kivelson and Neiman have reported that  $g_{\parallel}$  values less than 2.3 indicate considerable covalent character to M-L bonds and greater than 2.3 indicate ionic character. The  $g_{\parallel}$  values of the complexes are found to be less than 2.3, which indicate considerable covalent character to the M-L bond<sup>12</sup>. EPR spectral assignments of the copper(II) complexes along with the spin Hamiltonian and orbital reduction parameters are given in the Table 1.

**Table 1.** EPR Spectral parameters of the copper(II) complexes

	1	2	3	4
Polycrystalline (298 K)				
$g_{\parallel}$	2.186	---	---	2.191
$g_{\perp}$	2.067	---	---	2.060
$g_{\text{iso}}$ or $g_{\text{av}}$	2.106	2.086	2.106	2.104
DMF(77K)				
$g_{\parallel}$	2.177	2.160	2.177	2.165
$g_{\perp}$	2.065	2.049	2.066	2.046
$A_{\parallel}$	195.00	184.66	193.33	196.66
$\alpha^2$	0.765	0.694	0.786	0.773
$\beta^2$	0.888	0.916	0.822	0.843
$\gamma^2$	1.108	0.996	0.993	0.877
$K_{\parallel}$	0.679	0.636	0.646	0.651
$K_{\perp}$	0.848	0.692	0.781	0.678

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