



## ELECTRONIC PARAMAGNETIC RESONANCE STUDIES ON BINUCLEAR COPPER(II) COMPLEXES WITH DIFFERENT EXOGENOUS BRIDGES

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**Abstract**—The X-band powder samples and DMF solution EPR spectra of a series of binuclear copper(II) complexes with binucleating ligand 2,6-diformyl-4-methylphenol di(benzoylhydrazone) ( $H_3L$ ) were recorded at both room temperature and 140 K. These complexes incorporate different exogenous ions ( $X^-$ ) into a bridging position to form copper(II) binuclear complexes of formula  $[Cu_2(H_2L)X]Y_2$ , where  $X^- = Br^-$  (**1**),  $Cl^-$  (**2**),  $N_3^-$  (**3**),  $OC_2H_5^-$  (**4**),  $OH^-$  (**5**) and pyrazolyl ( $C_3H_3N_2^-$ ) (**6**) and  $Y$  is  $Br^-$ ,  $Cl^-$  or  $ClO_4^-$ . The coupled and uncoupled copper(II) EPR parameters of complexes **3–6** were obtained from DMF solution spectra. The metal–ligand bonding parameters evaluated showed substantial in-plane  $\pi$ -bonding covalency and a small amount of in-plane as well as out-of-plane  $\pi$ -bonding.

Binuclear copper(II) complexes with pentadentate binucleating ligands derived from condensation of 2,6-diformyl-4-methylphenol with various aromatic mono- and diamines are currently under investigation.<sup>1</sup> The detailed EPR studies on copper(II) complexes of this type are limited. We have synthesized and characterized a series of binuclear copper(II) complexes with 2,6-diformyl-4-methylphenol di(benzoylhydrazone) ( $H_3L$ ).<sup>2</sup> In these complexes, the exogenous bridge ligands are  $Br^-$  (**1**),  $Cl^-$  (**2**),  $N_3^-$  (**3**),  $OC_2H_5^-$  (**4**),  $OH^-$  (**5**) and  $C_3H_3N_2^-$  (**6**), respectively. Based on the elemental analyses, molar conductivities, IR spectra and thermogravimetric analyses, these complexes were proposed to have an empirical formula  $[Cu_2(H_2L)X]Y_2$ . The coordination geometry of copper(II) ions are essentially square pyramidal for **1** and **2** and planar for **3–6**. Magnetic data showed that an anti-ferromagnetic interaction occurred between the  $Cu^{II}$  ions with singlet–triplet separations  $2J = -6.2$  for (**1**),  $-76.4$  for (**2**),  $-86.8$  for (**3**),  $-231.1$  for (**4**),  $-241.9$  for (**5**) and  $-343.8$   $cm^{-1}$  for (**6**).<sup>2</sup> In

this paper, the X-band powder samples and DMF solution EPR spectra of these copper(II) complexes are reported.

### EXPERIMENTAL

The complexes were obtained as described earlier.<sup>2</sup> Electronic spectra of the complexes were recorded on a UV-240 spectrometer. EPR spectra were recorded on an X-band JES-FE1XG EPR spectrometer equipped with 100 kHz field modulation unit and  $g$  values relative to  $Mn(MgO)$  were measured.

### RESULTS AND DISCUSSION

The X-band EPR spectra of powdered samples of complexes **1–6** at both room temperature and 140 K have been recorded. All of the room temperature spectra show a rather atypical pattern with a central signal at *ca* 3500 G and a relatively weak half-field absorption at *ca* 1800 G. The central signals can be tentatively assigned to the overlap of the  $M_s = 1$  transition of coupled copper(II) ions and uncoupled copper(II) signals, and the half-field signals should

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be assigned to the  $M_s = 2$  transition, respectively. The apparent half-field signals are expected for magnetically coupled dinuclear copper(II) complexes. The intensities of coupled copper(II) signals of complexes decreases and the signals of uncoupled copper(II) ions increase relatively upon cooling to 140 K, indicating that an antiferromagnetic coupling operates in the complexes, which is in agreement with the results of magnetic investigation as discussed earlier.<sup>2</sup>

The complexes other than **2** were dissolved in DMF and five room-temperature spectra were obtained (**2** dissolves poorly in DMF). The room temperature spectrum of **1** is reported in Fig. 1. It shows four typical hyperfine lines of uncoupled copper(II) ( $I = 3/2$ ) with  $A_o(\text{Cu}) = 74.6$  G. Each copper in **1** is in a  $\text{NO}_2\text{Br}_2$  environment and the extrahyperfine structure, which is probably due to splitting by a nitrogen atom ( $I = 1$ ), is seen on the strongest copper hyperfine line. The absence of evidence of coupled copper(II) signals at room temperature is puzzling. We have shown that the magnitude of the antiferromagnetic coupling in **1** is significantly less than that in other complexes of this series.<sup>2</sup> However, the chemical evidence favours the existence of a dimer at room temperature. Thus, it may be that rotations and vibrations, for example, within the complexes, as well as tumbling in the solvent perhaps, could increase the width of the spectrum of coupled copper(II) beyond detection. In some complexes, the definite dimer signal could appear just below the freezing temperature of the solution.<sup>3</sup>

The DMF solution spectra of complexes **3–6** are

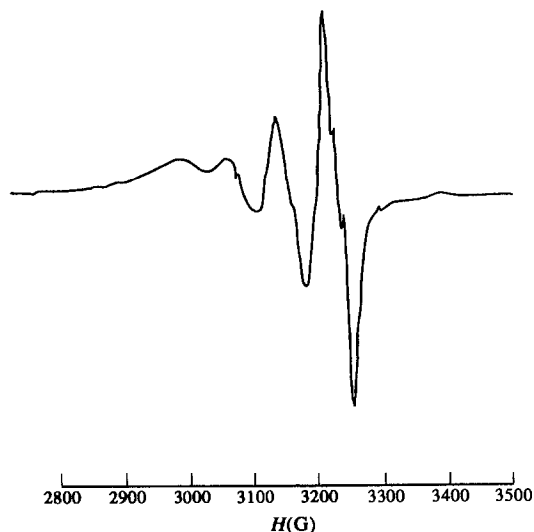


Fig. 1. The DMF solution EPR spectrum of complex **1** at room temperature.

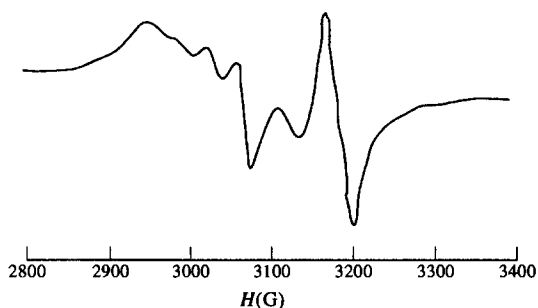


Fig. 2. The DMF solution EPR spectrum of complex **5** at room temperature.

very similar. As an example the spectrum of **5** is shown in Fig. 2. We observed two groups of EPR signals from the spectra. Those at higher field can be assigned to uncoupled copper(II) signals, in spite of the fact that some peaks were concealed by the one at lower field. If we assume that the signals at lower field are due to coupled copper(II) signals, then the observed splitting constant ( $A'_o$ ) will be approximately half the value of that observed for the uncoupled copper(II) ( $A_o$ ).<sup>4</sup> From an analysis of the spectra of complexes **3–6**,  $A_o$  and  $A'_o$  were obtained and are listed in Table 1. These results rationalize our assumption.

With a reasonably good characterization of the magnetic parameters, the frozen DMF solution spectra of complexes **1** and **3–6** were investigated. All the spectra are similar to each other. Figure 3 shows the DMF solution spectra of **5** at 140 K. The EPR signals of uncoupled copper(II) are relatively strong and the magnetic parameters were obtained from the spectra, and are listed in Table 1. However, the parallel region signals of spectra of coupled copper(II) are observed at lower field relative to uncoupled copper(II) signals, which correspond to the spectra at room temperature. Whereas the perpendicular region signals of the spectra of coupled copper(II) are covered by the signals of uncoupled copper(II). There is a strong EPR band at higher field relative to the strongest line of uncoupled copper(II). At first glance, this is the additional

Table 1. EPR parameters for the complexes

Complex	$A_o(\text{G})$	$A_{  }(\text{G})$	$A_{\perp}(\text{G})$	$g_o$	$g_{  }$	$g_{\perp}$	$A'_o(\text{G})$
<b>1</b>	74.6	161.8	31.0	2.119	2.277	2.040	
<b>3</b>	66.6	165.4	17.2	2.128	2.260	2.062	35.0
<b>4</b>	68.6	181.8	12.0	2.134	2.275	2.064	36.7
<b>5</b>	71.2	167.8	22.9	2.134	2.265	2.068	39.5
<b>6</b>	65.5	149.2	23.6	2.129	2.268	2.060	33.8

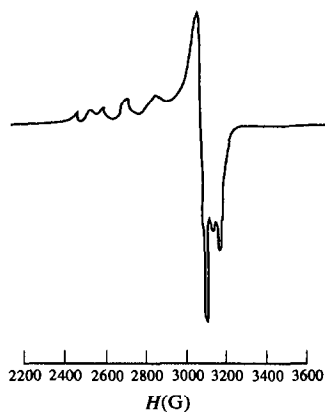


Fig. 3. The DMF solution EPR spectrum of complex **5** at 140 K.

Table 2. Bond parameters for the complexes

Complex	$\Delta E$ (cm <sup>-1</sup> )	$\alpha^2$	$\beta_1^2$	$\beta^2$
<b>3</b>	15,152	0.752	0.784	0.726
<b>4</b>	14,514	0.811	0.737	0.667
<b>5</b>	14,493	0.766	0.750	0.751
<b>6</b>	15,873	0.718	0.887	0.770

peak of uncoupled copper(II) signals. However, the results of computer simulation of uncoupled copper (II) show that the additional peak is not at such a high field. Maybe it is the overlap of the perpendicular region signals of the coupled copper(II) and the additional peak of uncoupled copper(II).

Besides DMF, we tried to use methanol, acetonitrile, acetone, trichloromethane and DMSO as solvents. Unfortunately, the EPR signals were not observed in all solvents other than DMSO because of poor solubility. The DMSO solution EPR spectra of complexes **1–6** at room temperature show two groups of EPR signals, which are similar to the DMF solution spectra. Therefore, dissociation occurs, perhaps due to the coordinating nature of the solvent.

These complexes are proposed to have an endogenous bridge (phenoxide) and an exogenous bridge (X).<sup>2</sup> The coordination geometry of copper (II) ions is essentially square planar and in  $D_{4h}$  sym-

metry for **3–6**. The metal–ligand bonding parameters can be evaluated approximately by the energies of electronic transitions and EPR parameters of uncoupled copper(II) species using Kivelson and Neiman's method.<sup>5</sup> The magnitude of  $\alpha^2$ ,  $\beta_1^2$  and  $\beta^2$  can be estimated using the following approximate formula<sup>6–9</sup>

$$\alpha^2 = \frac{A_{\parallel}}{P} + (g_{\parallel} - 2.0023) + \frac{3}{7}(g_{\perp} - 2.0023) + 0.04 \quad (1)$$

$$g_{\parallel} = g_e - 8K_{\parallel}^2 \lambda_o / \Delta E, \quad K_{\parallel} = \alpha \beta_1 \quad (2)$$

$$g_{\perp} = g_e - 2K_{\perp}^2 \lambda_o / \Delta E, \quad K_{\perp} = \alpha \beta, \quad (3)$$

where  $P = 0.036$  cm<sup>-1</sup> and  $\lambda_o = -828$  cm<sup>-1</sup> for Cu<sup>2+</sup> free ions, and  $A$  is expressed in cm<sup>-1</sup>.  $\alpha^2$  measures the covalency of the in-plane  $\sigma$ -bonds,  $\beta_1^2$  of the in-plane  $\pi$ -bonds and  $\beta^2$  of the out-of-plane  $\pi$ -bonds. These parameters are close to 1.0 for ionic bonds and become smaller with increasing covalent bonding.

The  $\alpha^2$ ,  $\beta_1^2$  and  $\beta^2$  values obtained by eq. (1)–(3) for complexes **3–6** are listed in Table 2. The results show substantial in-plane bonding covalency and a medium amount of in-plane as well as out-of-plane  $\pi$ -bonding.

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