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Magnetic Properties of a Binuclear Copper(II) Complex [Cu(terpy)Cl](PF$_6$)

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Terpy (2 2′, 2″ terpyridine) as ligand forms only two types of metallic complex compounds in aqueous or organo-aqueous solutions, corresponding to ratios of metal to terpy of either 1:1 or 1:2. The equilibrium 2 M(terpy)$^{2+}$ $\rightleftarrows$ M(terpy)$_2$$^{2+}$ + 2 M^{2+}(solv.) seems to be strongly shifted in solution towards formation of the bis species [1], especially for the Cu^{2+} complex. Nevertheless, it has been observed that addition of a large excess of halide or pseudohalide ions to a bis complex solution leads to isolation of mono species such as Cu(terpy)X$_2$, (X = Cl$^-$, Br$^-$, I$^-$, SCN$^-$) [2]. This type of compounds always has a five-coordinate distorted square-pyramidal topology [3, 4] and no interaction between paramagnetic centers is observed. The reaction of the [Cu(terpy)$_2$]$^{2+}$ ion with halide ions in solution can be considered to occur in two steps. Hence it seems possible either to obtain monomeric species, or by choosing a suitable antagonist ion to form X-bridged dimeric or chain structures.

Halide and pseudohalide ions have often worthwhile properties as they may show magnetic exchange interactions between paramagnetic transition metal ions. In this way Landee *et al.* [5] have observed that [Cu(terpy)CN]NO$_3$·H$_2$O has an antiferromagnetic one-dimensional magnetic behavior.

We have prepared the [Cu(terpy)Cl](PF$_6$) compound, where the structure gives evidence for the existence of a binuclear copper(II) complex [6] (see Fig. 1). No dimeric [Cu(terpy)X]L compound has been reported so far. This work is a part of a more extensive research concerning the influence of the nature of X and L ligands upon the magnetic properties of [M(terpy)X]L complexes [7].

Divalent copper complexes are particularly suitable to an EPR study. Two types of information can be obtained. On the one hand the pattern of g values for a particular compound indicates the coordination geometry around Cu^{2+} ion, on the other hand for dimeric complexes it may identify the 'half field' $\Delta M_s = 2$ transition which characterizes the presence of a magnetic exchange interaction.

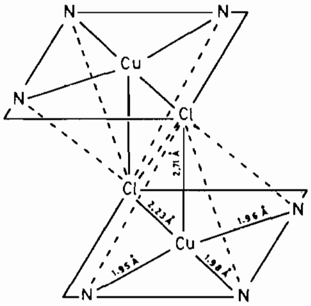

Fig. 1. Schematic representation of the dimeric cation di-μ-chlorobis(copper(II)terpyridine).

The X-band E.P.R. spectrum of [Cu(terpy)Cl](PF$_6$) at 300 K shows an intense quadratic signal with no copper hyperfine structure visible, and g values $g_\perp = 2.052$ and $g_\parallel = 2.213$ which give an average value of 2.106 (at 4.2 K $g_\perp = 2.061$, $g_\parallel = 2.226$ and $g_{aver} = 2.116$) (Fig. 2). These results confirm the existence of a $d_{x^2-y^2}$ orbital ground state, in agreement with our structural results [6].

At 4.2 K a relatively weak signal can also be observed at a half field value of the main signal (Fig. 2). It is not detected above 50 K. This transition is characteristic of a triplet state where the $|0>$ state is no longer degenerate with $|11>$ and $|11>$ in a zero field, and the $\Delta M_s = 2$ transition is no more completely prohibited [8]. This result shows clearly that pairs of Cu^{2+} ions are actually present in the complex.

The magnetic susceptibility variation with temperature is given in Fig. 3. The effective magnetic moment per Cu^{2+} ion drops from 1.85 B.M. at 300 K down to 1.16 B.M. at 4.2 K. The last value is lower than the spin-only value for Cu^{2+} (1.73 B.M.) and provides further conclusive evidence for the presence of an antiferromagnetic exchange between coupled Cu^{2+} ions.

The data have been least-squares fitted using the Bleaney–Bowers equation for isotropic exchange [9] :

$$\chi_M = \frac{Ng^2\beta^2}{kT}\left(\frac{2}{3 + \exp(-2J/kT)}\right) + N\alpha$$

The temperature-independent paramagnetism N α for a Cu^{2+} dimer was taken as 120×10^{-6} c.g.s.u. per mol of dimer. Least-squares fitting of the data for [Cu(terpy)Cl](PF$_6$) gives J = –2.47 cm^{-1} with a g value of 2.116 from E.P.R. results. The dashed curves in Fig. 3 represent the best fits for χ_M and μ_{eff}.

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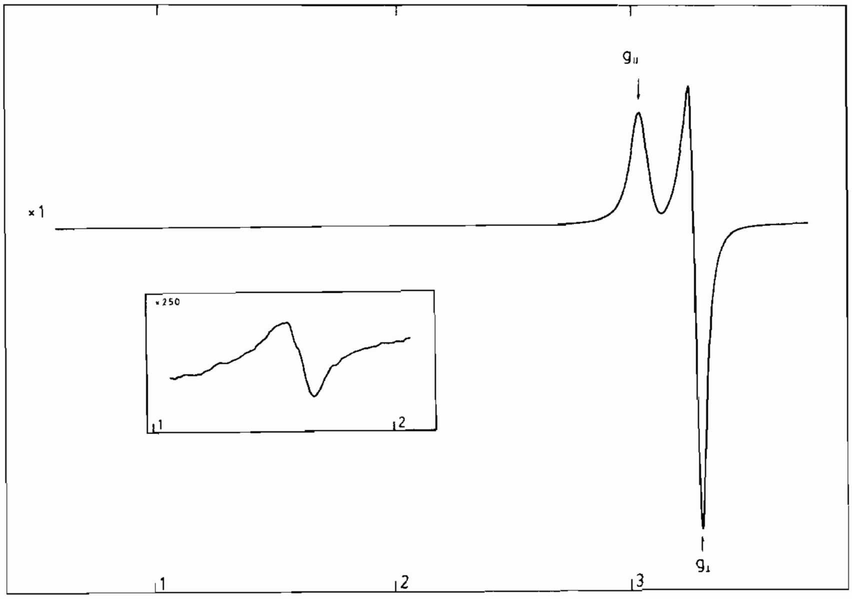

Fig. 2. X-band E.P.R. spectrum of a powdered sample of di-μ-chlorobis(copper(II) terpyridine) hexafluophosphate.

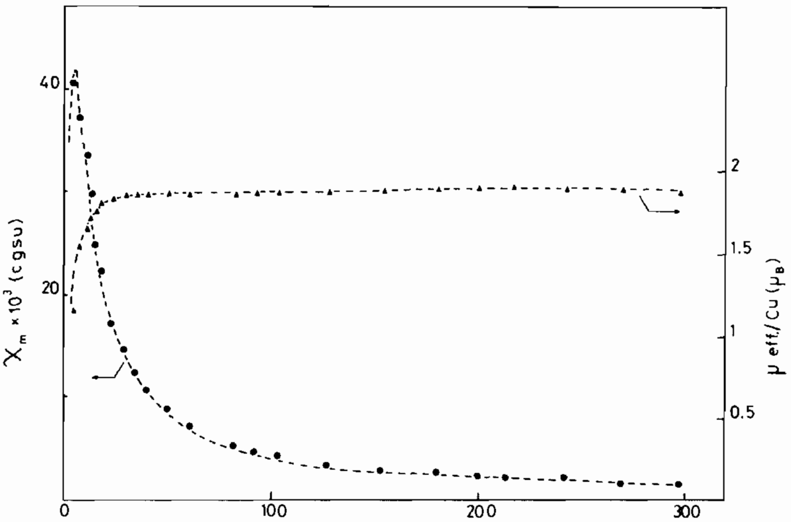

Fig. 3. Experimental molar paramagnetic susceptibility (●) and effective magnetic moment (▲) per Cu^{2+} ion *vs.* temperature for the complex di-μ-chlorobis(copper(II)terpyridine) hexafluophosphate (the dashed lines represent least-squares fits using the Bleaney–Bowers equation).

Experimental

Preparation Method

Samples of [Cu(terpy)Cl](PF_6) where terpy is 2, 2′, 2″ - terpyridine $(C_{15}H_{11}N_3)$ have been prepared from a warm aqueous solution (20 ml) of 0.8 g $(2.07 \times 10^{-3}$ mol) of Cu(terpy)$Cl_2 \cdot H_2O$ which was prepared by us [4]. An excess of a saturated KPF_6 aqueous solution was added. After stirring a blue precipitate was obtained. Crystallization from the saturated aqueous solution of this precipitate gives blue needles of [Cu(terpy)Cl](PF_6). It has been recrystallized after dissolution in a minimum of warm water and dried over P_2O_5 for 24 hr. *Anal.* Calculated for $CuC_{15}H_{11}N_3ClPF_6$: C, 37.34; H, 2.31; N, 8.81; Cu, 13.32; found: C, 37.92; H, 2.36: N, 8.72; Cu, 13.55.

Physical Measurements

Susceptibility measurements were performed with a Faraday type micro-balance between 4.2 and 300 K. E.P.R. spectra were recorded on a Bruker ER

200 tt spectrometer operating at X-band, calibrated by NMR probe for the magnetic field and a HP 5342 A frequency counter. A continuous flow cryostat provided any temperature between 4.2 and 300 K.

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