Pyrazolate-bridged Binuclear Copper(II) Complex with Diethylenetriamine

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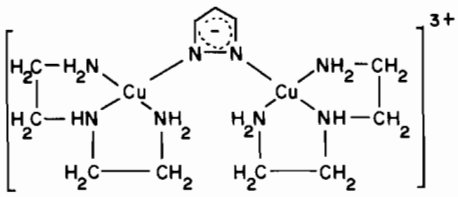
A number of papers have been published [1] reporting preparations and characterizations of binuclear metal complexes bridged by imidazolate anion (im), in view of their importance as structural models for the active site of bovine erythrocyte superoxide dismutase [2]. For these complexes, we have already pointed out that both the Cu–N(imidazolate)–C(imidazolate) angle (α) and the angle (θ) between the Cu–N(imidazolate) vectors are important factors in determining J values (*i.e.*, parameter in spin Hamiltonian $-2JS_1 \cdot S_2$) [1n]. On the other hand, there has been continuing interest in the synthesis of metal complexes bridged by pyrazolate anion ($C_3H_3N_2^-$), abbreviated pz) [3–7]. However, binuclear copper(II) complex bridged by only one pyrazolate ion has not been reported so far. In this paper, we report the preparation and magnetic properties of the pyrazolate-bridged binuclear copper(II) complex, $[Cu_2(dien)_2(pz)]Br_3 \cdot H_2O$, *1*.

To a mixture of 0.89 g (4 mmol) of $CuBr_2$ and 0.41 g (4 mmol) of diethylenetriamine in 20 ml of methanol were added a methanol solution containing 0.41 g (2 mmol) of pyrazole and 0.08 g (2 mmol) of sodium hydroxide. The reaction mixture was then stirred at room temperature for half an hour, being allowed to stand for several hours in a refrigerator. Blue crystals were deposited, which were filtered and recrystallized from methanol. *Anal.* Found: C, 20.13; H, 4.63; N, 16.90%. Calcd. for $[Cu_2(C_{11}H_{29}N_8)]Br_3 \cdot H_2O$: C, 20.07; H, 4.75; N, 17.02%.



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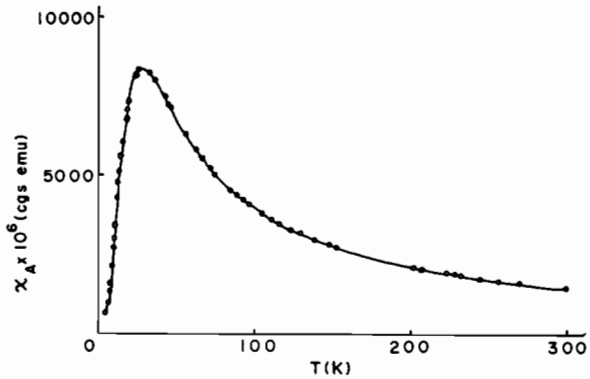

Fig. 1. The temperature-dependence of magnetic susceptibility of copper(II) complex *1*. The solid line shows theoretical susceptibility calculated by Bleaney-Bowers equation

$$\chi_A = \frac{Ng^2\beta^2}{kT} \times \frac{1}{3 + \exp(-2J/kT)} + N\alpha$$

with g = 2.18, 2J = −43 cm^{-1}, $N\alpha = 60 \times 10^{-6}$ cgs emu.

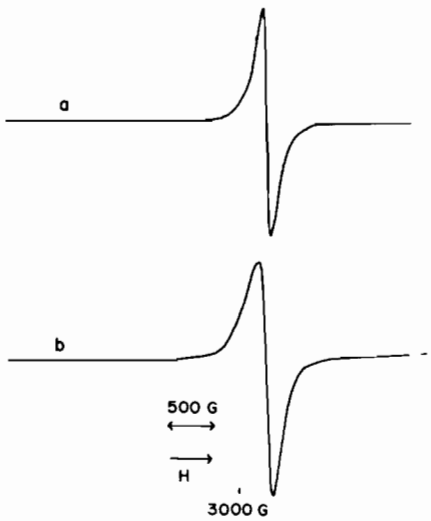

Fig. 2. X-band ESR spectra of powdered samples of $[Cu_2(dien)_2(pz)]Br_3 \cdot H_2O$ (a) and $[Cu_2(dien)_2(im)](ClO_4)_3$ (b).

The magnetic moment, μ_{eff} value, which was determined at 25 °C by using a Gouy magnetic apparatus, was found to be 1.84 B.M. Figure 1 represents the temperature-dependence of the magnetic susceptibility. The values of magnetic susceptibility agree well with the theoretical ones calculated by Bleaney-Bowers equation, supporting the dimer-structure as represented in *1*. This complex exhibits antiferromagnetic interaction (J = −21.5 cm^{-1})

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that is somewhat weaker than that observed ($J = -30$ cm^{-1}) for the corresponding imidazolate-bridged copper(II) complex, $[Cu_2(dien)_2(im)](ClO_4)_3$ [1e]. The powder X-band ESR spectra of these complexes at room temperature were recorded and the reproductions are shown in Fig. 2. As is clear from Fig. 2, the spectrum for $[Cu_2(dien)_2(im)](ClO_4)_3$ exhibits a broader line shape than that of the complex *1*. In addition, the half-field absorption in the $\Delta M_s = 2$ region was not observed for both the pyrazolate- and imidazolate-bridged complexes.

Spectral data in the visible region for solid samples of the complex *1* and $[Cu_2(dien)_2(im)](ClO_4)_3$ are listed in Table I, which shows that the d–d band of *1* is observed at a longer wavelength than that of $[Cu_2(dien)_2(im)](ClO_4)_3$.

TABLE I. Electronic Spectra of Copper(II) Complexes.[a]

Complex	λ_{max}, nm
$[Cu_2(dien)_2(pz)]Br_3 \cdot H_2O$	610
$[Cu_2(dien)_2(im)](ClO_4)_3$	560

[a]Measured in nujol mull.

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