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Pyrazolate-bridged Bi- and Trinuclear Copper(II) Complexes with Glycylglycine

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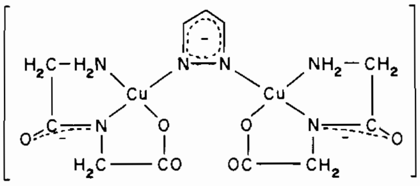
Binuclear metal complexes are of interest in regard to magnetic and redox properties, and as suitable models for understanding the structure-function relationship of the active site of some metalloproteins [1]. A number of studies on polynuclear copper(II) complexes has disclosed that magnetic properties relate to the structure of complexes [2–4]. On the other hand pyrazolate(pz) anion is known to function as a bridging ligand in a number of polynuclear complexes [5–13]. In this letter we report the preparation and the mgnetic properties of pyrazolate-bridged bi- and trinuclear copper(II) complexes with glycylglycinate(Gly·Gly).

Freshly prepared $Cu(OH)_2$ (0.5 g, 5 mmol) was suspended in 20 ml of methanol. To the solution were added glycylglycine (0.53 g, 4 mmol), pyrazole (0.21 g, 1.5 mmol) and calcium hydroxide (0.30 g, 4 mmol) or potassium hydroxide (0.22 g, 4 mmol). The reaction mixture was then stirred at room temperature for 1 h and filtered. The filtrate was then allowed to stand for a day (in the system with calcium ion). Violet-blue crystalline products were deposited and were recrystallized from aqueous methanol. In potassium-containing systems, the filtrate was evaporated to dryness *in vacuo*. The violet blue solid obtained was recrystallized from methanol–ether. *Anal.* Found: C, 24.28; H, 4.21; N, 15.36%. Calcd for $Ca/2[Cu_2(Gly{\cdot}Gly)_2(pz)]\cdot 4H_2O$: C, 24.17; H, 4.25; N, 15.38%. Found: C, 24.87; H, 3.92; N, 15.83%. Calcd for $K_2[Cu_3(Gly{\cdot}Gly)_3(pz)_2]\cdot 5H_2O$: C, 24.47; H, 3.89; N, 15.86%.

The magnetic moments for $Ca/2[Cu_2(Gly{\cdot}Gly)_2(pz)]\cdot 4H_2O$ and $K_2[Cu_3(Gly{\cdot}Gly)_3(pz)_2]\cdot 5H_2O$ gave the same value (μ_{eff} = 1.84 B.M.) at room temperature. Figure 1 shows the temperature-dependence of the magnetic susceptibility for $Ca/2[Cu_2(Gly{\cdot}Gly)_2(pz)]\cdot 4H_2O$. The magnetic parameters can be estimated as $g = 2.21$, $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1}, and $J = -12.3$ cm^{-1} from the best fit of the χ_A values to the Bleaney-Bowers equation [14], indicating the dimeric structure as represented in *1*.



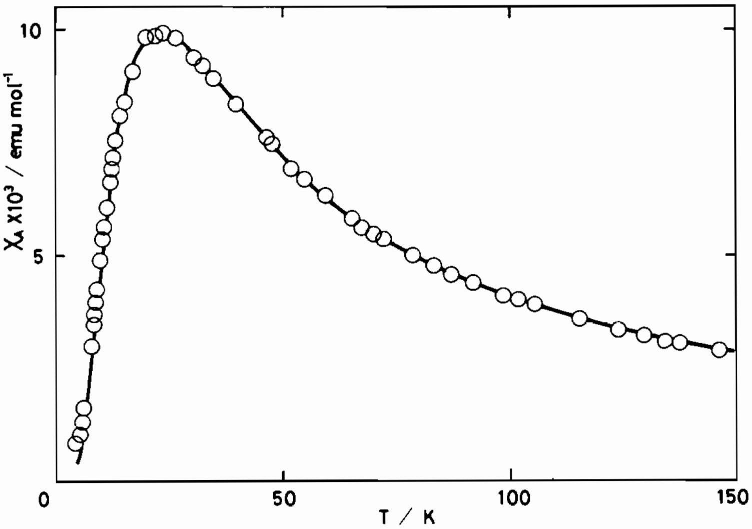


Fig. 1. The temperature-dependence of magnetic susceptibility of $Ca/2[Cu_2(Gly{\cdot}Gly)_2(pz)]\cdot 4H_2O$. The solid line shows theoretical susceptibility, calculated by the Bleaney-Bowers equation, with the parameters described in the text.

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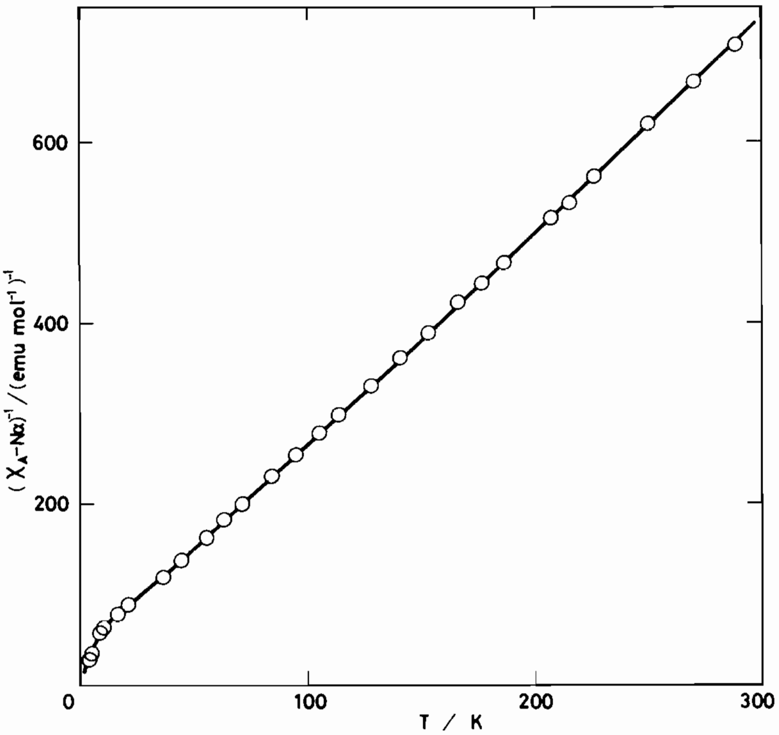


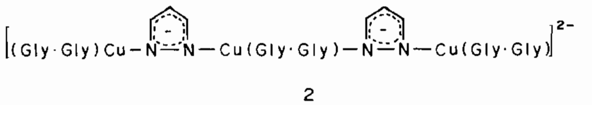
Fig. 2. The temperature-dependence of magnetic susceptibility of $K_2[Cu_3(Gly{\cdot}Gly)_3(pz)_2]\cdot 5H_2O$. The solid line shows theoretical susceptibility calculated by eqn. (1) with the parameters described in the text.

The temperature-dependence of the magnetic susceptibility for $K_2[Cu_3(Gly{\cdot}Gly)_3(pz)_2]\cdot 5H_2O$ is represented in Fig. 2. The observed susceptibility obeyed the Curie-Weiss law in the temperature ranges $T \gtrsim 15$ K and $T \lesssim 7$ K: the Curie and Weiss constants were determined as $C_h = 0.421$ emu K mol^{-1} and $\theta_h = -13.4$ K for the high temperature range, and $C_l = 0.153$ emu K mol^{-1} and $\theta_l = -0.8$ K for the low temperature range.

In addition, the ratio C_h/C_l is 2.8. These data suggest that the potassium salt is the compound containing three copper(II) ions magnetically interacted. The theoretical susceptibility, χ_A, for linear-chain trinuclear complexes is depicted by a solid line in Fig. 2. The calculation of these χ_A values was carried out according to the eqn. (1) [15]

$$\chi_A = \frac{Ng^2\beta^2}{12kT} \times \frac{1 + \exp(-2J/kT) + 10\exp(J/kT)}{1 + \exp(-2J/kT) + 2\exp(J/kT)} + N\alpha \qquad (1)$$

Magnetic parameters were as follows: $g = 2.12$, $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1}, $J = -9.4$ cm^{-1}. Thus the present complex is estimated to have the trimeric structure indicated in *2*.



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Of particular interest here is that an alteration of counter ions of a complex salt leads to an isolation of a complex with an entirely different structure.

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