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Polymeric Structure in *N*-Picolinoyl-1,3-propanolaminatocopper(II) Dihydrate

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A number of copper(II) complexes have been synthesized with terdentate ligands. Magnetic measurements have indicated the presence of dimeric molecules in the crystals of these compounds.[1] Subsequently, the binuclear structure of acetylacetonemono(*o*-hydroxyanil)copper(II) has been established by X-ray crystal analysis.[2] The compound presents a typical example of binuclear structure in which copper atoms are bridged by two oxygen atoms. Its magnetic susceptibility conforms to the Bleaney-Bowers equation. On the other hand, the magnetic property of *N*-[2-(2-hydroxyethylthio)phenyl]arenesulfoamidatocopper(II) obeys a theoretical equation for isolated ternuclear rings.[3] Ojima[4] has synthesized *N*-picolinoyl-1,3-propanolaminatocopper(II) dihydrate, which presents a new type of copper (II) complexes having terdentate ligands. Since the complex is prepared in basic solutions as described below, the nitrogen atom of the amide group coordinates to the metal ion as shown in Fig. 1.[5] In order to obtain some information about the structure of the copper(II) complex, we have determined the magnetic susceptibility in a temperature range of 80–300°K, using a Gouy magnetic balance described in previous papers.[3,6]

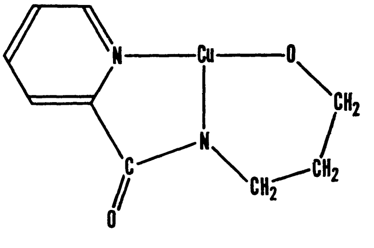

Fig. 1. Coordination of *N*-picolinoyl-1,3-propanolamine to a copper ion.

The material was prepared by a method described in a previous paper.[4] A mixture of methyl picolinate (1 mol) and 1,3-propanolamine (1 mol) was heated at 180—200°C for 8 hr. When the reaction product was diluted with water (1 : 2) and a saturated solution of copper(II) sulfate (1/2 mol) was added to it, the solution turned deep blue with heat evolution. On adding ethanol to the hot solution, blue crystals separated on cooling. When the crystals were left to stand in a desiccator over calcium chloride, $Cu(C_9H_{12}N_2O_2)_2SO_4\cdot2.5H_2O$ was obtained. Found: Cu, 11.45; N, 9.70; H_2O, 7.91%. Calcd for $Cu(C_9H_{12}N_2O_2)_2SO_4\cdot2.5H_2O$: Cu, 11.25; N, 9.92; H_2O, 7.97%. On adding sodium hydroxide solution (2 mol) to a concentrated aqueous solution of $Cu(C_9H_{12}N_2O_2)_2SO_4\cdot2.5H_2O$ (1 mol), *N*-picolinoylpropanolaminatocopper(II) dihydrate was obtained. It was recyrstallized from hot water. Found: Cu, 22.86; C, 38.86; H, 5.20; N, 10.20; H_2O, 12.99%. Calcd for $CuC_9H_{10}N_2O_2\cdot2H_2O$: Cu, 22.87; C, 38.92; H, 5.08; N, 10.09; H_2O, 12.97%.

The dihydrate was dehydrated in a vacuum desiccator over phosphorus pentoxide at about 100°C. Found: Cu, 26.28; C, 44,56; H, 4.22; N, 11.44%. Calcd for $CuC_9H_{10}N_2O_2$: Cu, 26.45; C, 44.72; H, 4.18; N, 11.59%.

The molar magnetic susceptibilities of the dihydrate and the anhydrous complex were determined as $0.77_8\times10^{-3}$ emu/mol (25°C) and 0.254×10^{-3} emu/mol (31°C), respectively. Corrections were made for diamagnetic contributions (in 10^{-6} emu/mol) from *N*-picolinoylpropanolamine (−120), water (−13),[7] and copper(II) ions (−11).[8] The value for the ligand was calculated from Pascal's constants.[7] The corrected molar susceptibilities are shown in Fig. 2 as functions of temperature.

Bleaney and Bowers[9] have proposed a theoretical

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[1] M. Kishita, Y. Muto and M. Kubo, *Aust. J. Chem.*, **10**, 386 (1957); **11**, 309 (1958).

[2] G. A. Barclay, C. M. Harris, B. F. Hoskins and E. Kokot, *Proc. Chem. Soc.*, **1961**, 264.

[3] S. Emori, M. Inoue, M. Kishita, M. Kubo, S. Mizukami and M. Kono, *Inorg. Chem.*, **7**, 2419 (1968).

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[5] K. Yamasaki and M. Sekizaki, This Bulletin, **38**, 2206 (1965).

[6] M. Inoue, M. Kishita and M. Kubo, *Inorg. Chem.*, **6**, 900 (1967); M. Inoue, S. Emori and M. Kubo, *ibid.*, **7**, 1427 (1968).

[7] G. Foëx, " Constantes Sélectionnées, Diamagnétisme et Paramagnétisme," Masson, Paris (1957).

[8] P. W. Selwood, " Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y. (1956).

[9] B. Bleaney and K. D. Bowers, *Proc. Roy. Soc.*, *Ser. A*, **214**, 451 (1952).

equation for the susceptibility, χ, of copper(II) complexes having a binuclear structure.

$$\chi = \frac{Ng^2\beta^2}{3kT}\left(1+\frac{1}{3}e^{-2J/kT}\right)^{-1} + N\alpha \qquad (1)$$

where apart from obvious notations, J is the exchange integral and $N\alpha$ is the temperature-independent paramagnetism assumed to be equal to 60×10^{-6} emu/mol.[10] As shown in Fig. 2, the observed susceptibility of the anhydrous salt agrees well with the theoretical curve ($J/k=400$°K, $g=2.14$) above about 150°K, indicating the existence of dimer molecules in crystals. Presumably, the paramagnetic behavior below about 100°K is due to the presence of impurities and/or magnetically isolated copper(II) ions in small quantities.

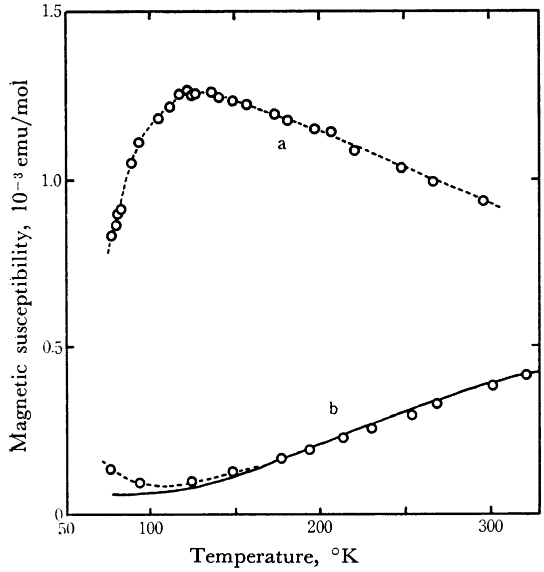

Fig. 2. Magnetic susceptibilities of *N*-picolinoyl-1,3-propanolaminatocopper(II) dihydrate (a) and the anhydrous salt (b). The solid curve represents the Bleaney-Bowers equation.

The magnetic susceptibility of the dihydrate cannot be fitted to the theoretical equation for isolated binuclear clusters. The magnetic susceptibilities for polymeric rings of spins have been calculated numerically by Bonner and Fisher[11] by use of the following Hamiltonian.

$$\mathscr{H} = -2J\sum_{i=1}^{n}\left(S_iS_{i+1}-\frac{1}{4}\right) \qquad (2)$$

where J is the exchange integral and S is the spin angular momentum ($S_{n+1}=S_1$). The theoretical curves are shown in Fig. 3. The observed susceptibility apparently fits the curve for a ring composed of even number of spins, especially that for a four-membered ring. The exchange integral, J, and g value were estimated as $|J|/k=92$°K and $g=2.08$, respectively. However, the observed values do not agree perfectly with the theoretical curve in the whole temperature range investigated. A conceivable reason for the discrepancy is the presence of two kinds of magnetic interaction in the cluster. Alternatively magnetic interaction might exist between clusters. In any case, polymeric structural units mostly containing even number of spins are formed in the crystal. The polymeric molecules in the dihydrate change to the binuclear clusters on dehydration. The important role of water molecules is open to speculation.

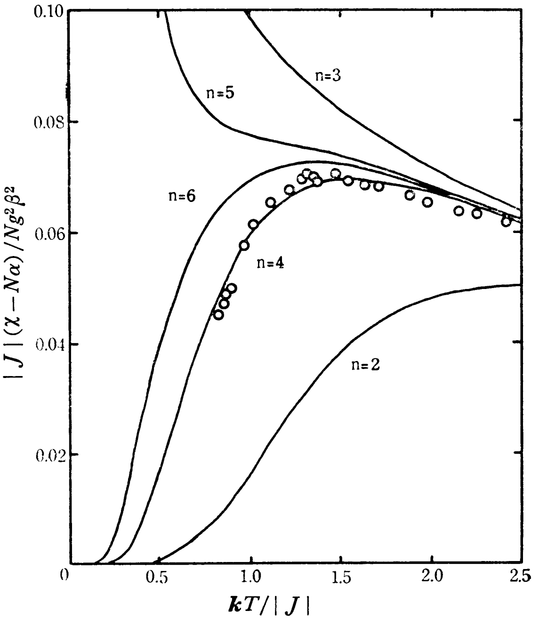

Fig. 3. Observed magnetic susceptibility of *N*-picolinoyl-1,3-propanolaminatocopper(II) dihydrate and theoretical curves calculated by Bonner and Fisher with Eq. (2). For a binuclear cluster ($n=2$), the exchange integral is equal to one fourth of the energy separation between the singlet and triplet states.

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[10] B. N. Figgis and R. L. Martin, *J. Chem. Soc.*, **1956**, 3837.

[11] J. C. Bonner and M. E. Fisher, *Phys. Rev.*, **135A**, 640 (1964).