BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 3717—3718 (1972)

Binuclear Structure of Copper(II) 2-Pyridinolate Complex

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(Received June 1, 1972)

Copper(II) acetate monohydrate has a typical isolated binuclear structure.[1] The temperature dependence of its magnetic susceptibility was clearly interpreted by a simple singlet-triplet equilibrium.[2,3] However, there has been controversy over the coupling mechanism in the crystal; direct interaction by a metal-metal δ-bond or superexchange interaction *via* the acetate bridges. Dubicki and Martin[4] pointed out that the δ-bond in the crystals of copper(II) acetate monohydrate is virtually nonbonding and that the configuration of the binuclear clusters is maintained by four bridging acetate groups. Their view has been supported by the following experimental results. The Cu–Cu separation, 3.02 Å in dichlorobis(6-hydroxypurine)copper(II) monohydrate[5] is much greater than 2.66 Å in copper(II) acetate monohydrate, although their exchange integrals are nearly equal.[6] The exchange integral $-305\ \mathrm{cm}^{-1}$ of $(CH_3)_4NCu(CH_3COO)_2(NCS)$ is much higher than $-485\ \mathrm{cm}^{-1}$ of of $(CH_3)_4NCu(HCOO)_2(NCS)$, although their Cu–Cu distances are nearly equal.[7] Thus we see that the cause of the formation of binuclear clusters of the type of copper(II) acetate monohydrate is the relative position of two active sites in the bidentate ligand and the direction of lone pairs of the active sites. We have attempted a synthesis of the copper(II) complex with 2-pyridinol whose ligand has the same site-structure and directionality as acetic acid.

Copper(II) 2-pyridinolate mono(2-pyridinol) was prepared by adding freshly prepared copper(II) hydroxide to a solution of excess 2-pyridinol. The reactants were agitated vigorously for 15 min to ensure maximum contact between the reactants. From the resulting suspension, crystals of $Cu(pyO)_2\cdot pyOH$ (py denotes 2-pyridyl radical) were formed in a week. The remaining non-reacted copper(II) hydroxide was removed by decantation and the crystals of pyridinolate were washed by ethanol and dried over silica gel in a desiccator. The salt was also prepared by adding dropwise a solution of sodium hydroxide to a mixture of copper(II) chloride and 2-pyridinol solution. Crystals of $Cu(pyO)_2\cdot pyOH$ were obtained overnight from the dark green suspension. No difference was observed between the two samples in analytical and magnetic data. Found: C, 51.10; N, 11.86; H, 3.74; Cu, 18.29%. Calcd for $CuC_{15}N_3O_3H_{13}$: C, 51.95; N, 12.12; H, 3.78; Cu, 18.32%.

The molar magnetic susceptibility of the complex was determined to be 565 μemu/mol (18°C) by the Gouy method, the magnetic field strength amounting to about 8000 Oe. Corrections were made for diamagnetic contributions (in μemu/mol) from 2-pyridinol (−54) and copper(II) ion (−11).[8] The value for the ligand was calculated from Pascal's constants.[9] Bleaney and Bowers[2] proposed a theoretical equation for the susceptibility χ of copper(II) compounds having a binuclear structure.

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

where J is the exchange integral and $N\alpha$ the temperature independent paramagnetism assumed to be equal to 60 μemu/mol,[3] the other quantities having their usual meanings. The observed susceptibility of the compound agrees well with the theoretical curve (Fig. 1), indicating the existence of dimer molecule in crystals. We realized that the structure of bidentate ligand is a factor in the formation of the dimeric structure of the type of copper(II) acetate mono-

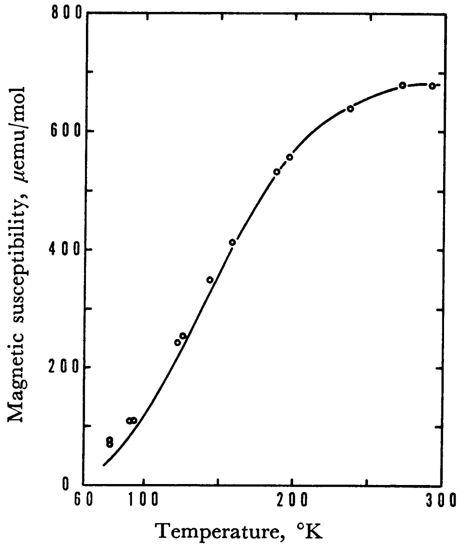

Fig. 1. Magnetic susceptibility of copper(II) 2-pyridinolate mono(2-pyridinol). The solid curve represents the Bleaney-Bowers equation.

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hydrate. This indicates that the spin interactions between copper atoms occur by superexchange *via* pyridinol groups. The exchange integral and g-value of $Cu(pyO)_2 \cdot pyOH$ are evaluated as $J/k=-245°K$, $g=2.10$. The magnitude of superexchange interaction depends to a great extent on the electronic structure of bridging ligands. This was proved by the fact that magnetic interaction operates more strongly in bis(6-aminopurinato)copper(II) tetrahydrate.⁶⁾ Our result where the antiferromagnetic interaction operates more strongly in the complex of $Cu(pyO)_2 \cdot pyOH$ than in $Cu(CH_3COO)_2 \cdot H_2O$ can be explained by considering that 2-pyridinol promotes the migration of positive holes to a greater extent than acetate groups.