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PREPARATION AND CRYSTAL STRUCTURE OF A BINUCLEAR COPPER(II) COMPLEX BRIDGED BY AN ALKOXO-OXYGEN ATOM AND AN ACETATE ION

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New binuclear copper(II) complex bridged by an alkoxo-oxygen atom and an acetate ion was prepared, and its crystal structure was determined by X-ray diffraction method.

We have reported the preparation, magnetism, and optical properties of various binuclear copper(II) complexes.$^{1)}$ Furthermore, we have demonstrated a relationship between the structure and reactivity of these complexes in the redox reactions.$^{2)}$ In this report we wish to report the preparation and the crystal structure of a new binuclear copper(II) complex, $[Cu_2(apaca)(CH_3COO)]\cdot H_2O$ having a novel bridging system(for the abbreviation of the ligand, see Fig. 1). Several analogous binuclear copper(II) complexes have also been prepared, and the study on the relationship between the structure and the magnetic property of these complexes is now under progress, and will be reported shortly in a separate paper.

The ligand, $H_3(apaca)$, was obtained by the condensation of 1,3-diamino-2-propanol and acetylacetone. The binuclear complex was obtained as dark blue prisms when the ligand, $Cu(CH_3COO)_2\cdot H_2O$, and triethylamine were mixed in methanol in a 1:2:3 mole ratio. Found: C, 39.50%; H, 5.28%; N, 6.19%. Calcd for $[Cu_2(apaca)(CH_3COO)]\cdot H_2O$: C, 39.56%; H, 5.31%; and N, 6.15%. The unit cell parameters listed in Table 1 were determined from 20 reflections($20° < 2\theta < 30°$) on a Rigaku AFC-5 Automatic Diffractometer. Intensity data were collected by the 2θ-θ scan technique on a Rigaku Automatic Diffractometer at 296 K, using Mo Kα radiation monochromated by the graphite plate. The structure was solved by the conventional heavy-atom method, and refined to $R(=\Sigma(F_o-F_c)/\Sigma F_o)=0.054$ by a block-diagonal least-square method using anisotropic temperature factors

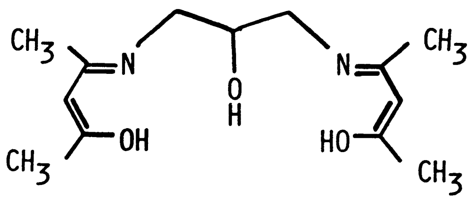

Fig. 1. Chemical structure of $H_3(apaca)$.

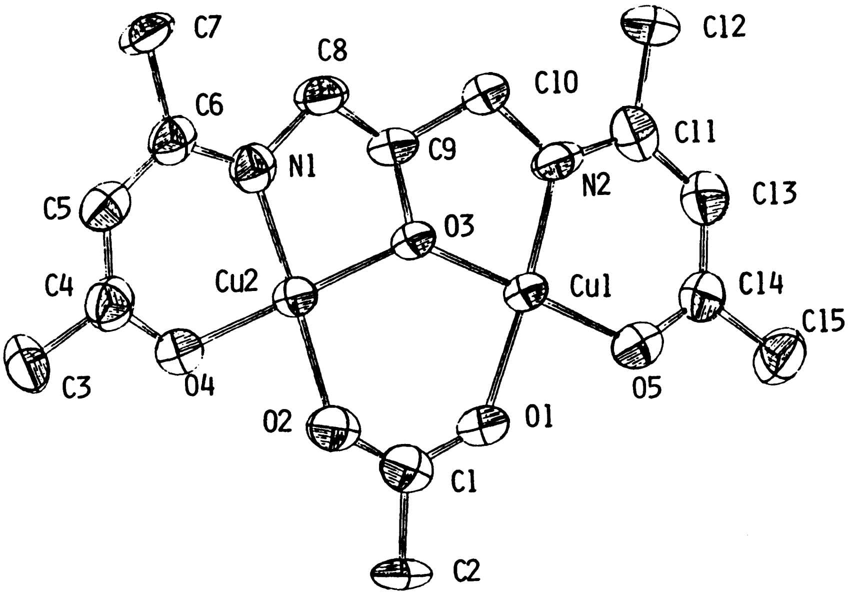

Fig. 2. ORTEP drawing of $[Cu_2(apaca)(CH_3COO)]$ (H_2O was omitted).

Table 1. Crystal data of $[Cu_2(apaca)(CH_3COO)]\cdot H_2O$

Space group	$P2_1/n$
a(Å)	17.716(3)
b(Å)	13.147(3)
c(Å)	7.716(1)
β(°)	92.91(1)
V(Å^3)	1794

Table 2. Selected bond lengths and angles

(i) Bond length(Å)					
Cu1-Cu2	3.502(2)	Cu1-O1	1.946(1)	Cu1-O3	1.902(6)
Cu1-O5	1.903(6)	Cu2-O2	1.930(6)	Cu2-O4	1.893(6)
Cu2-O3	1.913(6)	Cu2-N1	1.896(7)	Cu1-N2	1.936(7)
(ii) Bond angle(°)					
Cu1-O3-Cu2	133.3(3)	O1-Cu1-O5	85.5(2)		
O1-Cu1-O3	94.2(3)	O1-Cu1-N2	169.5(3)		
O3-Cu1-N2	86.1(3)	O3-Cu1-O5	179.3(3)		
O2-Cu2-O4	85.6(3)	O4-Cu2-N1	94.5(3)		
O3-Cu2-O4	178.3(3)	O3-Cu2-N1	84.8(3)		
O2-Cu2-N1	174.2(3)	O2-Cu2-O3	95.1(3)		

for non-hydrogen atoms.3)

In Fig. 2, the ORTEP drawing and the atomic numbering system are shown. The figure shows that the complex is binuclear and the two copper(II) ions are bridged by an alkoxo-oxygen atom and an acetate ion. So far we know, no copper(II) complex with such a bridging system has ever been demonstrated by the X-ray analysis. Selected bond lengths and the angles are listed in Table 2, and the least-square plane consisting of Cu1, Cu2, O1, O2, and O3, and the deviations of the atoms from the plane are given in Table 3. It should be noted that the Cu-Cu distance is 3.50 Å, which is longer than those observed for the binuclear copper(II) complexes bridged by two alkoxo-oxygen atoms.5) The shortest Cu-Cu distance between the binuclear complex and the nearest neighboring one is 3.47 Å.

Table 3. Least-square plane(Cu1, Cu2, O1, O2, and O3) and the deviations(Å) from the plane

$$-0.16570\,X - 0.39155\,Y + 0.91236\,Z = -2.05960$$

	Deviation(Å)		Deviation(Å)
Cu1	-0.017	O4	0.019
Cu2	-0.007	O5	-0.072
O1	0.011	N1	-0.201
O2	-0.004	N2	-0.398
O3	0.017		

The magnetic moment of this complex is 1.64 BM(295 K). The temperature dependence of magnetic susceptibility can be interpreted in terms of the modified Bleaney-Bowers equation,

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

where $2J=-165$ cm^{-1}, $\theta=10$ K, $g=2.10$ and $N\alpha=50\times10^{-6}$ cgs emu mol^{-1}. The non-zero value of θ may be due to the intermolecular interaction between the binuclear complexes. Hodgson and his-coworkers investigated the relationship between the 2J-value and the angle(Cu-O-Cu) for di-μ-hydroxo binuclear copper(II) complexes. According to their conclusion -2J value increases with the increase of the Cu-O-Cu angle in the range 90-110°.6) If their discussion is extraporated to a range of larger Cu-O-Cu angle like the angle of the present complex(133°, cf. Table 2), very large -2J value($\gg$ 1000 cm^{-1}) would emerge. In practice, however, -2J value observed was 165 cm^{-1}, which is very small even though the fact that the present complex has only one alkoxo-oxygen bridge is taken into consideration. Thus, the present result can not be interpreted by the conventional superexchange model. For the comprehensive elucidation of the mechanism of magnetic interaction, more refined or completely novel model seems to be necessary.

References

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3) All the calculations were performed at the Computer Center of Kyushu University using UNICS system.4)

4) "Universal Crystallographic Computer Program System(UNICS)," ed by T. Sakurai, The Crystallographic Society of Japan,Tokyo(1967).

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