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Crystal Structure and Magnetic Property of Cubane Tetranuclear Copper(II) Complex with Ferromagnetic Coupling

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Synopsis. The magnetic susceptibility measurement down to the liquid helium temperature and the single-crystal X-ray analysis of alkoxo-oxygen bridged tetranuclear copper(II) complex [CuL]$_4$ have been performed, where H_2L is a tridentate ligand derived from condensation of 3-ethoxymethylene-2,4-pentanedione and 2-aminoethanol. The magnetic data demonstrated that the four unpaired electrons of the four copper(II) ions are ferromagnetically coupled, the ground spin state of the cubane molecule being S=2. The structural analysis has confirmed several structural features, i.e., the distorted Cu_4O_4 cubane structure, the square pyramidal coordination geometry, nearly perpendicular arrengement between adjacent basal coordination planes, and inequivalent Cu-O bond distances.

Studies on discrete dinuclear or oligonuclear metal complexes with ferromagnetic spin coupling are fundamental requirement not only for elucidation of the structural and electronic factors governing magnetic interaction between paramagnetic centers but also for developing ferromagnetic materials.[1–4)] However, such complexes are relatively rare, while a large number of polynuclear metal complexes with antiferromagnetic interaction have been known.[5)]

Previously some of the present authors[6)] synthesized copper(II) complex with a tridentate ligand derived from condensation of 3-ethoxymethylidene-2,4-pentanedione and 2-aminoethanol, and measured the magnetic susceptibility in the temperature range 80—300 K. The magnetic susceptibility obeys the Curie-Weiss law ($\chi_A = C/(T-\theta)$) with positive Weiss constants suggesting a ferromagnetic interaction between copper(II) ions. In this study, in order to detect the spin ground state of the molecule and elucidate the structural factors causing ferromagnetic coupling, the complex has been subjected to the magnetic susceptibility measurement down to the liquid helium temperature and the single-crystal X-ray analysis.

Experimental

Synthesis. The complex was prepared according to the method reported previously[6)] and recrystallized twice from dichloromethane/methanol solution. Calcd for [CuL], $CuO_3NC_8H_{11}$: C, 41.29; H, 4.76; N, 6.02%. Found: C, 41.16; H, 4.86; N, 5.99%.

Physical Measurements. Elemental analyses were performed at the Elemental Analysis Center of Kyushu University. Magnetic susceptibilities were obtained at 4.2—100 K by use of a HOXAN HSM-D SQUID magnetometer in the magnetic field 0.5 T and at 80—300 K by a Faraday balance designed in our laboratory. The data were corrected for magnetization of the sample holder and for the diamagnetism of the component atoms by the use of Pascal's constants. The molar effective magnetic moment was calculated by the equation $\mu_{eff}=2.828(\chi_A T)^{1/2}$.

X-Ray Crystallography. Reflection data were measured on a Rigaku Denki AFC-5 automated four-circle diffractometer with graphite-monochromatized Mo $K\alpha$ radiation at room temperature. The details of data collection and crystallographic data are summarized as follows: [CuL]$_4$, formula=$Cu_4O_{12}N_4C_{32}H_{44}$, FW=930.91, triclinic, space group $P\bar{1}$, a=12.330(2) Å, b=13.766(4) Å, c=11.109(3) Å, α=97.44(2)°, β=92.05(2)°, γ=85.09(2)°, V=1862.3(7) Å^3, D_m=1.64 g cm^{-3} (by floatation method in aqueous KI solution), D_x=1.66 g cm^{-3} (Z=2), crystal size 0.3×0.3×0.4 mm, μ(Mo $K\alpha$)=23.23 cm^{-1}, scan mode θ-2θ, scan range 2.5—52°, scan width $(1.2+0.35\tan\theta)°$, octant measured $+h$, $\pm k$, $\pm l$, number of observed reflections with $|F_o|>3\sigma(|F_o|)$ 5516, R=4.20%, R_w=5.01%, highest peak on the final D-Fourier 0.4 e Å^{-3}.

The intensity data were corrected for Lorentz and polarization effects but not for absorption and extinction effects. The structure was solved by the standard heavy-atom method and refined by the block-diagonal least-squares method, in which the function minimized is $\sum w(|F_o|-|F_c|)^2$ and the equal weight w=1 was adopted for all the reflections. The atomic scattering factors were taken from Ref. 7. All computations were performed on a FACOM M 780 computer at the Computer Center of Kyushu University using the UNICS III program system.[8)] The final atomic coordinates are given in Table 1. Tables of observed and calculated structure factors, listings of atomic positional and anisotropic thermal parameters, and complete lists of bond distances and angles with their estimated standard deviations have been deposited as Document No. 8905 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Results and Discussion

Magnetic Property. The magnetic susceptibilities have been measured in the 4.2—300 K temperature range. Figure 1 shows the result of [CuL]$_4$, in the forms of the χ_A vs. T, the $1/\chi_A$ vs. T, and the μ_{eff} vs. T plots, where χ_A is the magnetic susceptibility per copper atom, μ_{eff} the effective magnetic moment per copper atom, and T the absolute temperature. The numerical values of the magnetic susceptibilities are given as supplementary materials.

The $1/\chi_A$ vs. T plot follows the Curie-Weiss law ($\chi_A = C(T-\theta)$) above 50 K with a Weiss constant 20 K, suggesting a ferromagnetic interaction. The effective magnetic moment at room temperature is 1.84 μ_B/Cu, which is close to the spin-only value (1.72 μ_B). As the temperature is lowered, the magnetic moment increases from 1.84 μ_B at 297.8 K, reaches a maximum value of 2.49 μ_B at 13 K, and finally decreases to 2.41 μ_B at 4.5 K. The maximum value (2.49 μ_B/Cu=4.98 μ_B/4Cu) agrees well with the spin-only value (4.90 μ_B expected for S=2 spin state effected by a ferromagnetic spin coupling of four unpaired electrons. The decrease of μ_{eff} below 13 K is attributable to either the intermolecular effect or the zero-field splitting of the S=2 ground state. The result clearly demonstrates that a ferromagnetic spin-exchange coupling is operating within a molecule and the spin ground state of the cubane molecule is $S=2$ and is fully populated below 13 K.

Structural Description. The ORTEP drawing of $[\mathrm{CuL}]_4$ with the atom numbering scheme is shown in Fig. 2. The selected bond distances and angles with their estimated standard deviations are available in Table 2. The complex has a cubane-type alkoxo-oxygen bridged tetranuclear structure. The distances of Cu1-Cu3 and Cu2-Cu4 are 3.337(1) Å and 3.316(1) Å, respectively, which are longer than the other four Cu-Cu distances (3.092(1)—3.126(1) Å), indicating a distortion from the ideal cubane struc-

Table 1. Positional Parameters of Non-Hydrogen Atoms ($\times 10^4$)

Atom	x	y	z	B_{eqv}
Cu1	2301(1)	3048(0)	4214(1)	2.8
Cu2	622(1)	1528(1)	3427(1)	2.7
Cu3	2712(1)	1293(0)	1869(1)	2.6
Cu4	1203(1)	3184(1)	1680(1)	2.7
O1	2109(3)	1634(3)	3996(3)	2.8
O2	1144(3)	1467(3)	1749(3)	2.8
O3	2691(3)	2731(3)	2119(3)	2.6
O4	890(5)	3243(3)	3402(3)	2.9
O5	2608(4)	4400(3)	4446(4)	4.0
O6	3701(6)	5865(4)	7674(6)	8.3
O7	62(3)	1397(3)	4980(4)	3.8
O8	−3643(4)	1169(3)	3996(4)	5.6
O9	2794(3)	−109(3)	1418(4)	3.6
O10	5549(4)	−2062(3)	1337(5)	5.4
O11	1409(4)	3134(3)	−33(4)	3.9
O12	−927(6)	3610(5)	−2718(5)	9.1
N1	3391(4)	2744(3)	5393(4)	2.7
N2	−741(4)	1305(3)	2640(4)	2.9
N3	4243(4)	1325(3)	1884(4)	2.9
N4	−233(4)	3810(4)	1524(4)	3.4
C1	2588(5)	1215(4)	5010(6)	3.4
C2	3619(5)	1676(4)	5382(5)	3.1
C3	3744(5)	3359(4)	6240(5)	3.0
C4	3583(5)	4405(4)	6321(5)	3.3
C5	3933(7)	4981(5)	7430(7)	4.8
C6	4609(10)	4502(7)	8370(8)	8.3
C7	3092(5)	4854(4)	5337(6)	3.4
C8	3145(7)	5921(5)	5218(7)	5.3
C9	448(5)	910(4)	961(5)	3.3
C10	−728(5)	1247(5)	1299(5)	3.4
C11	−1651(5)	1282(4)	3158(6)	3.2
C12	−1802(5)	1357(4)	4450(5)	2.9
C13	−2957(5)	1404(5)	4752(6)	3.5
C14	−3321(6)	1827(6)	6008(7)	4.9
C15	−915(5)	1325(4)	5268(5)	3.1
C16	−981(6)	1134(5)	6566(6)	4.3
C17	3695(5)	3010(4)	1709(6)	3.2
C18	4599(5)	2310(4)	2162(5)	3.1
C19	4945(5)	557(4)	1712(5)	2.8
C20	4710(5)	−442(4)	1447(5)	2.9
C21	5648(6)	−1191(4)	1370(5)	3.6
C22	6780(6)	−861(5)	1369(7)	4.7
C23	3638(5)	−721(4)	1265(5)	3.2
C24	3364(6)	−1745(5)	803(6)	4.4
C25	94(6)	4058(5)	3691(6)	3.9
C26	−787(5)	3993(5)	2723(6)	4.1
C27	−746(5)	3955(5)	547(6)	3.7
C28	−353(6)	3731(4)	−662(6)	3.8
C29	−1112(7)	3912(5)	−1662(7)	5.4
C30	−2188(8)	4480(7)	−1409(8)	6.8
C31	732(6)	3339(5)	−859(6)	3.8
C32	1200(7)	3148(6)	−2110(6)	5.5

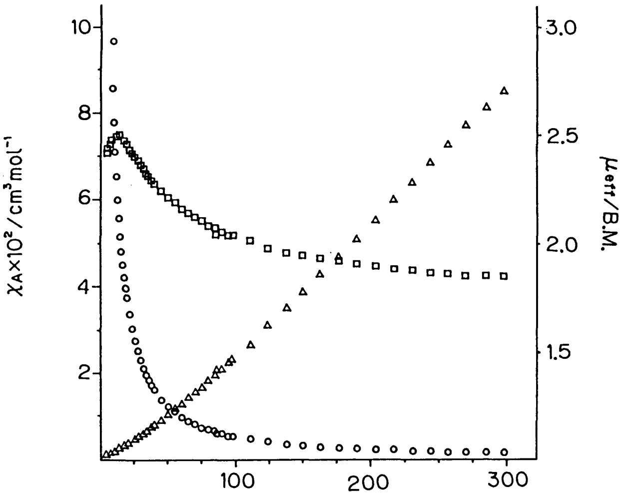

Fig. 1. The plots of χ_A vs. T (○), $1/\chi_A$ vs. T (△), and μ_{eff} vs. T (□) for $[\mathrm{CuL}]_4$.

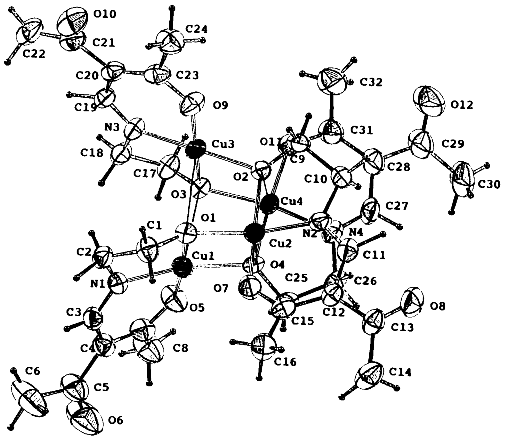

Fig. 2. Molecular Structure of Cubane-like Tetranuclear Copper(II) Complex $[\mathrm{CuL}]_4$ with the atom numbering scheme.

Table 2. Selected Bond Distances(Å) and Angles(deg)

(a) Bond distance/Å			
Cu1-Cu2	3.092(1)	Cu1-Cu3	3.337(1)
Cu1-Cu4	3.100(1)	Cu2-Cu3	3.126(1)
Cu2-Cu4	3.316(1)	Cu3-Cu4	3.094(1)
Cu1-O1	1.963(4)	Cu2-O1	1.929(4)
Cu2-O2	1.983(4)	Cu3-O2	1.930(4)
Cu3-O3	1.961(4)	Cu4-O3	1.952(4)
Cu4-O4	1.955(4)	Cu1-O4	1.945(4)
Cu1-O3	2.370(4)	Cu2-O4	2.414(4)
Cu3-O1	2.477(3)	Cu4-O2	2.382(4)
(b) Bond angle/deg			
Cu1-O1-Cu2	105.2(2)	Cu2-O2-Cu3	106.0(2)
Cu3-O3-Cu4	104.5(2)	Cu4-O4-Cu1	105.3(2)
Cu1-O1-C1	108.9(3)	Cu2-O1-C1	124.4(3)
Cu2-O2-C9	108.3(3)	Cu3-O2-C9	127.4(3)
Cu3-O3-C17	108.7(3)	Cu4-O3-C17	128.6(3)
Cu4-O4-C25	107.1(4)	Cu1-O4-C25	125.8(4)

ture. The coordination geometries of the four copper(II) ions are best described as a square pyramid. The apical positions of the square pyramids of Cu1, Cu2, Cu3, and Cu4 are occupied by O3, O4, O1, and O2, respectively, where the Cu-O(apical) bond distances fall in the range 2.370(4)—2.477(3) Å. The basal coordination sites of each copper(II) ion are occupied by the NO_2 donor set of the tridentate ligand L and an alkoxo-oxygen atom of the neighbouring ligand, where the bond distances are in the range 1.892(5)—1.983(4) Å. Adjacent copper(II) ions are bridged by two alkoxo-oxygen atoms inequivalently. For example, Cu1 and Cu2 atoms are doubly bridged by two alkoxo-oxygen atoms O1 and O4 with the bond distances of Cu1-O1 1.963(4) Å, Cu2-O1 1.929(4) Å, Cu1-O4 1.945(4) Å, and Cu2-O4 2.414(4) Å, indicating that one Cu-O bond among the four Cu-O bonds in Cu_2O_2 unit is elongated. The dihedral angle between the basal coordination planes of Cu1 and Cu2 is 78.7°, that of Cu2 and Cu3 94.9°, that of Cu3 and Cu4 92.6°, and that of Cu4 and Cu1 93.4°. Thus, the basal coordination planes are nearly perpendicular to each other.

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