Structure and Magnetic Property of a Macrocyclic Tetranuclear Copper(II) Complex with Phenoxo- and Hydroxo-Bridges and Large and Small Cu–O–Cu Angles

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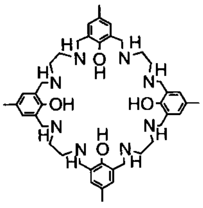
Reaction of a macrocyclic ligand of 36-membered octaaminotetraphenol with copper(II) triflate gave a tetranuclear complex with a large Cu–O(phenoxo)–Cu angle (130.8(1)°) and small Cu–O(phenoxo)–Cu (91.5(1)°) and Cu–O(hydroxo)–Cu angles (93.1(1)°). The magnetic behavior was interpreted based on the structural data.

The macrocyclic ligand of 36-membered octaaminotetraphenol H_4L (shown in Scheme 1) is very attractive in giving four metal ions arranged in a square with endogenous phenoxo-bridges and additional exogenous bridges. Nag et al. prepared its tetranuclear nickel(II) complexes $[Ni_4L(\mu_3\text{-}OH)(\mu\text{-}H_2O)_2(ClO_4)](ClO_4)_2{\cdot}2CH_3COCH_3{\cdot}H_2O$ (**1**) and $[Ni_4L(\mu\text{-}NCS)_2(\mu\text{-}H_2O)_2](ClO_4)_2{\cdot}2CH_3CN$ (**2**), of which structures were determined by X-ray crystal analyses.[1,2] Complex **2** has two bridging modes; one is for singly-bridged nickel ions with a phenoxo-bridge having a large Ni–O–Ni angle (131.6(3)°) and the other is for triply-bridged nickel ions with phenoxo oxygen, water oxygen, and thiocyanato nitrogen with Ni–O–Ni angles close to 90°. If the Cu–O(phenoxo)–Cu bond angles 130° and 90° are achieved for the copper(II) complex with L^{4-}, the angle values are located at the largest and the smallest ends reported for the phenoxo-bridged dinuclear copper(II) complexes.[3,4] The copper(II) complex having such large and small Cu–O–Cu angles within the same molecular core is unknown so far. Based on the experimentally established magneto–structural relationship between magnetic coupling constant *J* and Cu–O(phenoxo)–Cu angle,[5] the bond angles 130° and 90° give rise to fairly strong and small antiferromagnetic interactions. Although Nag et al. prepared $[Cu_4L(\mu\text{-}H_2O)_4](ClO_4)_4$ (**3**) and $[Cu_4L(\mu_3\text{-}OH)](ClO_4)_3{\cdot}MeOH$ (**4**),[6] no structural report has been presented. After our repeated efforts to obtain crystals suitable for the X-ray analysis, we have fortunately isolated single crystals when triflate ion was chosen as a counter ion in combination with a small amount of a base, triethylamine, on recrystallization in a methanolic solution. Here, we report the structure and magnetic property of a tetranuclear copper(II) complex of the ligand H_4L.



Scheme 1.

A solution of H_4L (0.192 g, 0.25 mmol) in methanol (10 mL) was added to a solution of NaOH (0.04 g, 1.0 mmol) in water (10 mL), to which a solution of $Cu(CF_3SO_3)_2$ (0.362 g, 1.0 mmol) in water (10 mL) was subsequently added. After the mixture was refluxed for 2 h, the solution was evaporated under reduced pressure and left at room temperature to give a green precipitate which was collected, washed with water, and dried over P_2O_5 in a vacuum desiccator. The green powder (0.2 g) was employed for recrystallization in a methanolic solution containing several drops of triethylamine. The green crystals (70 mg) were formed after a week. The elemental analysis was made for the sample after the magnetic measurement. Anal. Found: C, 39.76; H, 4.67; N, 7.96%. Calcd for $[Cu_4L(OH)_2](CF_3SO_3)_2{\cdot}H_2O$ ($\mathbf{5}{\cdot}H_2O$): C, 39.82; H, 4.79; N, 8.08%.

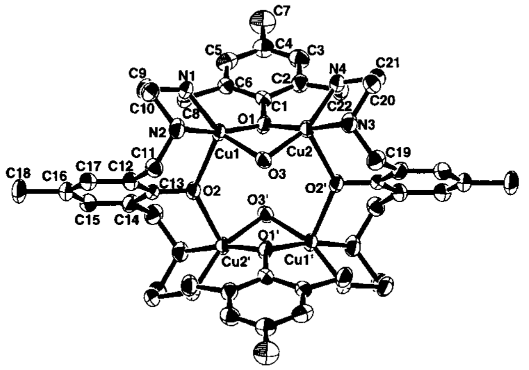


Figure 1. Perspective view of the teranuclear cation unit of $\mathbf{5}{\cdot}4MeOH{\cdot}2H_2O$. A crystallographic inversion center exists at the center of the cation.

The tetranuclear structure was confirmed by X-ray structure analysis.[7] Two water and four MeOH molecules are included as crystal solvents for a tetranuclear cation and two triflate ions. The cation unit of $\mathbf{5}{\cdot}4MeOH{\cdot}2H_2O$ is depicted in Figure 1. The coordination sites of copper(II) ion are occupied with two secondary amine nitrogens, two μ-phenoxo oxygens, and μ-hydroxo oxygen. The copper(II) ions are alternately singly- and doubly-bridged with phenoxo oxygen (O2, O2') and hydroxo and phenoxo oxygens (O1, O3, O1', O3'). As being expected from the crystal structure of **2**, large and small Cu–O(phenoxo)–Cu angles, ∠Cu1–O2–Cu2' = 130.8(1)° and ∠Cu1–O1–Cu2 = 91.5(1)° are achieved in the tetranuclear core. However, the phenoxo oxygen O2 (O2') is situated at an axial position of the square pyramidal configuration connecting copper(II) ions Cu1 and Cu2 (Cu1' and Cu2'). Basal angles close to 180° at each copper(II) ion, ∠O1–Cu1–N2 = 168.6(2), ∠O3–Cu1–N1 = 162.7(2), ∠O1–Cu2–N3 = 170.4(2), and ∠O3–Cu2–N4 = 161.8(1)°, indicate that the distortion from square pyramid to trigonal bipyramid is quite small because of weak axial interaction shown by relatively long axial contacts Cu1–O2 = 2.184(3) Å and Cu2–O2'= 2.165(3) Å. Hence, it is assumed that the phenoxo-bridges through O2 and O2' cannot propagate any important magnetic interaction.[8] The hydroxo-bridge is considered to be formed in the basic solution of methanol with triethylamine on recrystallization when taking into account that the recrystallization without triethylamine gave the water-bridged complex $[Cu_4L(\mu\text{-}H_2O)_2](CF_3SO_3)_4$ (**6**)[9] like the case of **3**. The bond angles through O1 and O3 between Cu1 and Cu2 (∠Cu1–O1–Cu2 = 91.5(1)° and ∠Cu1–O3–Cu2 = 93.1(1)°) are coincidentally close to 90°, which is magnetically interesting because, in the established magneto-structural relationship on the spin coupling through bridging oxygen for di-μ-hydroxo- and di-μ-phenoxodicopper(II) complexes between the Cu–O–Cu angle and coupling constant *J*, the angle 90° is in the range for antiferromagnetic (for phenoxo-bridge) and ferromagnetic (for hydroxo-bridge) interactions.[5,10]

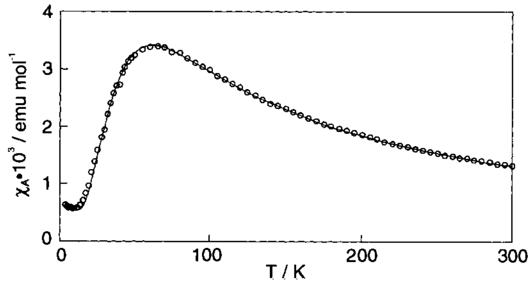
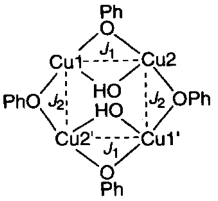


Figure 2. Temperature dependence of magnetic susceptibility per copper(II) ion of **5**·H_2O. The solid curve is drawn with J_1 = -35 cm^{-1}, J_2 = 0 cm^{-1}, J_3 = -3.5 cm^{-1}, g = 2.1, p = 0.017, and $N\alpha = 60 \times 10^{-6}$ emu mol^{-1} (see text).

The magnetic susceptibility measurement was performed in the temperature range 5–300 K (Figure 2). The magnetic moment per copper(II) ion at room temperature is 1.78 BM and decreases with lowering temperature, which is a typical behavior of antiferromagnetism. In the present case (Scheme 2), the spin Hamiltonian is described as

$$\mathcal{H} = -2J_1(S_1 \cdot S_2 + S_{1'} \cdot S_{2'}) - 2J_2(S_1 \cdot S_{2'} + S_2 \cdot S_{1'}).$$



Scheme 2.

The theoretical equation was obtained using the van Vleck equation. The best fit[11,12] with J_1 = –35 cm^{-1}, $J_2 \approx 0$ cm^{-1} (or $J_1 \approx 0$ cm^{-1}, J_2 = –35 cm^{-1}), g = 2.1, p = 0.017, and $N\alpha = 60 \times 10^{-6}$ emu mol^{-1} (R = 0.016)[13] was obtained as the solid line in Figure 2.[14] It does not seem easy to predict which coupling constant value corresponds to the interaction through Cu1–(O1,O3)–Cu2 (J_1) or Cu1–O2–Cu2' (J_2) bridge. However, as mentioned in the structural description of **5**·4MeOH·2H_2O, the phenoxo-bridge through O2 is considered not to mediate any important magnetic interaction. Hence, the coupling constant J_2 can be assumed as ≈ 0 cm^{-1}. Consequently, J_1 is assumed as –35 cm^{-1}. According to the magneto-structural relationship for di-μ-phenoxo- and di-μ-hydroxo-bridged copper(II) complexes,[5,10] the bond angle ∠Cu–O–Cu = 90° is in the region for the antiferromagnetic interaction in the case of phenoxo-bridge and for ferromagnetic one in the case of hydroxo-bridge. These counter-complementary factors on the interaction could lead to the relatively weak interaction J_1 = –35 cm^{-1} through the μ-hydroxo-μ-phenoxo bridge.[8] A dinulear copper(II) complex having the angles ∠Cu–O(phenoxo)–Cu = 91.55° and ∠Cu–O(hydroxo)–Cu = 96.45° was reported to show a very weak interaction $J \approx 0$ cm^{-1}.[3] In this complex, the phenoxo oxygen adopts a distorted pyramidal geometry, the sum (ρ) of the bond angles around the phenoxo oxygens being 329.5 and 333.2°. The less pyramidal (more planar) geometry around the phenoxo oxygen (O1) in **5**·4MeOH·2H_2O (ρ = 345.2°) could make the interaction stronger (J_1 = –35 cm^{-1}) by enhancing the antiferromagnetic contribution through the phenoxo oxygen.[3,6]

The magnetic behavior of **6** was explained by a similar model as that in Scheme 2 with J_1 = –323 cm^{-1} (for phenoxo-water-bridge) and $J_2 \approx 0$ cm^{-1} (for single phenoxo-bridge)[15] on the condition that the tetranuclear core dimensions are basically maintained on protonation of the hydroxo-bridge to the water-bridge. In addtion to $J_2 \approx 0$ cm^{-1}, the estimated strong interaction J_1 = –323 cm^{-1} supports the above magnetic interpretation on **5**·H_2O because it is considered that the water-bridge cannot propagate any significant interaction; the strong antiferromagnetic interaction (J = –288 cm^{-1}) through the phenoxo-water-bridge was estimated for **3**.[2] In order to verify the interpretation, further study is now going on by changing the counter ion triflate or the subtituent methyl groups on phenyl rings of H_4L.

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7 Crystal Data for **5**·4MeOH·2H_2O: $Cu_4C_{50}H_{82}O_{18}N_8F_6S_2$ fw = 1515.53, triclinic, space group $P\bar{1}$, a = 12.4216(9), b = 12.5726(9), c = 11.7541(9) Å, α = 103.818(3), β = 104.251(4), γ = 100.190(3)°, V = 1672.6(2) Å^3, Z = 1, D_m = 1.58, D_c = 1.50 g cm^{-3}, μ(Mo Kα) = 14.03 cm^{-1}, crystal dimensions 0.5×0.5×0.1 mm, F(000) = 784, T = 298 K, R = 0.058, R_w = 0.068 for 5850 (I>3σ(I)) observed reflections from 7549 unique data. For the determination of structure, intensity data were collected on a Rigaku RAXIS-rapid imaging plate area detector with graphite monochromated Mo Kα radiation. The intensity data were corrected for Lorentz-polarization effects. The structure was solved by direct method and refined by the full-matrix least-squares method using teXsan program package.

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9 Elemental-analytical data of **6**. Found: C, 35.00; H, 3.73; N, 6.79%. Calcd for $[Cu_4L(H_2O)_2](CF_3SO_3)_4$ (**6**): C, 34.91; H, 3.91; N, 6.78%.

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11 The magnetic simulation was satisfactorily carried out by assuming the impurity to be a dimeric copper(II) species (D). The parameter p, which is fraction for the impurity, is defined as in the following equation: $\chi_A = \chi_A'(1 - p) + pD(g, J_3) + N\alpha$, where χ_A' is the theoretical susceptibility obtained from the spin Hamiltonian in the text and $D(g, J_3)$ is that for the Bleaney–Bowers equation (J_3 was estimated as –3.5 cm^{-1} with g = 2.1). Similar treatment can be seen for tetranuclear copper(II) complexes in ref 14, in which monomeric and dimeric impurities are taken into consideration.

12 Quality of the fitting is almost independent of J_1 (or J_2) as long as $|10J_1|$ (or $|10J_2|$) < 35 cm^{-1}(= $-J_2$ (or $-J_1$)).

13 $R = [\Sigma(\chi_{A\,obs} - \chi_{A\,calcd})^2/\Sigma\chi_{A\,obs}^2]^{1/2}$.

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15 The other magnetic parameters are g = 2.2, $N\alpha = 42 \times 10^{-6}$ emu mol^{-1} (R = 0.044).