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Synthesis and Properties of a Molecular Dumbbell with Bis-μ_4-oxo Copper(II/I) Hepta Metal Centers

Mi Young Han, Kil Sik Min, and Myunghyun Paik Suh*

Department of Chemistry Education and the Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Republic of Korea

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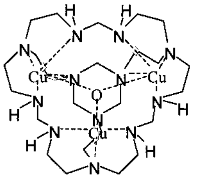
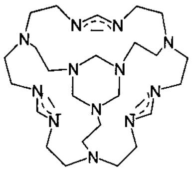
Large molecules with multi-paramagnetic metal centers have attracted considerable attention due to their interesting structures as well as potential applications as nanoscale molecular devices[1,2] and new inorganic magnetic materials that can be applied to memory devices.[3−5] Especially the polynuclear copper complexes are interesting not only because several oxidases contain multicopper active sites[6] but also because they may show magnetic interactions between the metal centers.[3−5,7] Previously, we have prepared molecular bowls with μ_3-oxo and μ_3-hydroxo tricopper(II) cores, $[(\mu_3\text{-O})\mathrm{Cu_3}(\mathbf{L})](\mathrm{ClO_4})_4\cdot2\mathrm{H_2O}$ (**1**) and $[(\mu_3\text{-OH})\mathrm{Cu_3}(\mathbf{L})]\mathrm{Cl_{0.5}}(\mathrm{ClO_4})_{4.5}\cdot1.5\mathrm{H_2O}$ (**2**), by the one-pot template reaction of tris(2-aminoethyl)amine and formaldehyde in the presence of $\mathrm{Cu^{II}}$ ion.[8] They exhibit unusually strong ferromagnetic interactions between the three $\mathrm{Cu^{II}}$ ions.[8] We have tried to interconnect molecular bowls to obtain bigger molecules with more paramagnetic metal centers, which might provide magnetic materials or insight into the magneto-structural relationship for the multicopper complexes.

Here, we report a dimerized molecular bowl containing seven metal centers, $\mathrm{Cu^I}[(\mu_4\text{-O})\mathrm{Cu^{II}}_3(\mathbf{L}^{3-})]_2(\mathrm{ClO_4})_3\cdot\mathrm{MeCOMe}$ (**3**). This is the first example of μ_4-oxo bridged species binding mixed valent $\mathrm{Cu^{II}}$ and $\mathrm{Cu^I}$ ions. The molecule has a dumbbell shaped structure of size 10.1 × 12.2 × 5.8 Å. Contrary to the molecular bowls, it shows antiferromagnetic interactions between the $\mathrm{Cu^{II}}$ metal centers.



$[(\mu_3\text{-O})\mathrm{Cu_3}(\mathbf{L})]^{4+}$, **1**



$\mathbf{L}^{3-}$

The compound was prepared under a nitrogen atmosphere as described in ref 9, and its crystal structure was determined.[10] Upon deprotonation of the secondary amine of **L** in **1**, the basicity of the μ_3-oxo ion becomes strong enough to bind an extra metal ion and thus a $\mathrm{Cu^{II}}_3{-}\mathrm{O}{-}\mathrm{Cu^I}{-}\mathrm{O}{-}\mathrm{Cu^{II}}_3$ linkage is formed, which gives rise to a dumbbell-shaped molecule. Although the synthesis has to be conducted under an inert atmosphere, the molecular dumbbell is insensitive to the air in the solid state and in solution. It is soluble in $\mathrm{Me_2SO}$, MeCN, MeOH, and $\mathrm{MeNO_2}$, but insoluble in water and acetone.[11] The molecular bowl **1** is green whereas the molecular dumbbell **3** is intense yellow. The properties and structural characteristics of **1**−**3** are compared in Table 1. The UV/vis spectrum of **3** shows a maximum absorption at 414 nm (ϵ = 5900 $\mathrm{M^{-1}\,cm^{-1}}$), which may be ascribed to the charge-transfer between $\mathrm{Cu^{II}}$ ion and negatively charged $\mathrm{N{=}C{-}N^-}$ linkages of the macrocycle $\mathbf{L}^{3-}$.

The views of the cation of **3** are presented in Figure 1.[12,13] In the structure, two molecular bowls are connected by a $\mathrm{Cu^I}$ ion through their two oxo bridges, and the $\mathrm{Cu^I}$ ion locates at the inversion center. The average bond distance of $\mathrm{Cu^I{-}O}$ is 1.828(3) Å, and the bond angle of $\mathrm{O{-}Cu^I{-}O}$ is 180.0(3)°, which are comparable to those of the mineral cuprite consisting of linear $\mathrm{O{-}Cu^I{-}O}$ bonds.[14−17] The $\mathrm{Cu^I}$ ion is provided by the redox reaction between the macrocycle and the coordinated $\mathrm{Cu^{II}}$ ions. As all secondary amines of the $\mathrm{N{-}CH_2{-}N}$ linkages in the macrocycle are deprotonated and oxidized, the macrocycle $\mathbf{L}^{3-}$ of the molecular dumbbell contains three $\mathrm{N{=}CH{-}N^-}$ linkages.[18,19] Two N−C bond distances of the linkage are equivalent [av 1.304(2) Å] but shorter than the normal single bond distance (1.47 Å). The $\mathrm{N{-}CH{-}N^-}$ angle of the linkage is av 125.8(2)°, indicating sp^2 hybridization of the central carbon atom. Each deprotonated molecular bowl $\mathbf{L}^{3-}$ accommodates three $\mathrm{Cu^{II}}$ ions which are bonded to the μ_4-oxo ion.[20−22] The three $\mathrm{Cu^{II}}$ ions locate

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(1) Lindoy, L. F. *Nature* **1993**, *364*, 17−19.

(2) Ball, P. *Nature* **1993**, *362*, 123.

(3) *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; Kluwer Academic Publishers: Boston, 1996.

(4) Kahn, O.; Martinez, C. J. *Science* **1998**, *279*, 44−48.

(5) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993.

(6) *Encyclopedia of Inorganic Chemistry*; King, R. B., Ed.; John Wiley & Sons: New York, 1994; Vol. 2, pp 822−924.

(7) Journaux, Y.; Sletten, J.; Kahn, O. *Inorg. Chem.* **1986**, *25*, 439−447.

(8) (a) See Table 1. (b) Suh, M. P.; Han, M. Y.; Lee, J. H.; Min, K. S.; Hyeon, C. *J. Am. Chem. Soc.* **1998**, *120*, 3819−3820.

(9) $[\mathrm{Cu_3}(\mathbf{L})(\mu_3\text{-O})](\mathrm{ClO_4})_4\cdot2\mathrm{H_2O}$ (3.00 g, 2.61 mmol)[8] and finely pulverized KOH was placed in a flask. The experiment was performed in a drybox filled with dry nitrogen gas. Degassed $\mathrm{Me_2SO}$ (50 mL) was added to the mixture and the mixture was stirred vigorously for 30 min. The green solid went into a dark brown solution as the reaction proceeded. The solution was filtered to remove insoluble materials, and the solvent was evaporated under reduced pressure until the volume of the solution became 1/10 of the original volume. Acetone (10 mL) was then added to the solution to induce the precipitation of the product. The solution was allowed to stand at refrigerator until dark brown crystals formed, which were filtered off, washed with MeOH, and dried in vacuo. {Yield: 25%. Anal. Calcd for $\mathrm{Cu_7C_{51}H_{96}N_{24}Cl_3O_{15}}$: C, 33.35; H, 5.27; N, 18.30. Found: C, 33.08; H, 4.86; N, 17.95. IR (Nujol mull): $\nu_{\mathrm{N-C-N}}$, 1622 $\mathrm{cm^{-1}}$. UV/vis (in MeCN), $\lambda_{\max}$ (ϵ): 414 nm (5900 $\mathrm{M^{-1}\,cm^{-1}}$) and 771 nm (625 $\mathrm{M^{-1}\,cm^{-1}}$).

(10) Crystal data: $\mathrm{Cu_7C_{51}H_{96}N_{24}Cl_3O_{15}}$, fw = 1836.65, triclinic, space group $P\bar{1}$, a = 12.9778(2) Å, b = 13.1556(2) Å, c = 22.3756(2) Å; α = 75.259(1)°, β = 86.892(1)°, γ = 70.295(1)°; V = 3476.03(8) $\mathrm{Å^3}$; Z = 2, d_{calcd} = 1.755 g $\mathrm{cm^{-3}}$; λ(Mo Kα) = 0.710 73 Å; T = 295 K.; μ = 2.296 $\mathrm{mm^{-1}}$; Siemens SMART CCD diffractometer, Mo Kα (λ = 0.710 73 Å); corrections made for Lorentz polarization and absorption effects using SADABS program; anisotropic refinement for all nonhydrogen atoms, final cycle of full-matrix least-squares refinement on F^2 with 9949 independent reflections; R_{int} = 0.0446; 930 parameters; final R indices ($I > 2\sigma(I)$) R = 0.0554, R_w = 0.1265; R indices (all data) R = 0.0726, R_w = 0.1382, gof = 1.076.

(11) The compound is soluble in the mixture of $\mathrm{Me_2SO}$ and $\mathrm{H_2O}$ but in which the complex is protonated at the macrocycle and turns into **2**, which can be identified by the UV/vis spectrum.

(12) There are two independent molecules in a unit cell, which are denoted as *a* and *b* in the atomic numbering scheme. In the figure, only the structure of *a* molecule is shown. In the text, bond distances and angles are averaged for both *a* and *b* molecules.

(13) Farrugia, L. J. *ORTEP-3 for Windows*, Version 1.02 Beta; University of Glasgow: Glasgow G12 8QQ, Scotland, UK, 1997.

(14) Drew, M. G. B.; Edwards, D. A.; Richards, R. *J. Chem. Soc., Dalton Trans.* **1977**, 299−303.

(15) Lopes, C.; Hakansson, M.; Jagner, S. *Inorg. Chem.* **1997**, *36*, 3232−3236.

(16) Lecloux, D. D.; Lippard, S. J. *Inorg. Chem.* **1997**, *36*, 4035−4036.

(17) Wells, A. F.*Structural Inorganic Chemistry*; Oxford: Clarendon, 1984; pp 127−129.

(18) Drew, M. G. B.; Wilkins, J. D. *J. Chem. Soc., Dalton Trans.* **1975**, 2611−2617.

(19) Abel, E. W.; Skittrall, S. J. *J. Organomet. Chem.* **1980**, *193*, 389−395.

10.1021/ic990555z CCC: $18.00

Table 1. Comparison of Structures and Properties of Molecular Bowls (**1** and **2**) and Dumbbell (**3**)

	IR^a, cm^{-1}		UV/vis^b	structural parameters			magnetism
compd	ν(NH)	ν(CN)	λ_{max}, nm (ϵ, M^{-1} cm^{-1})	Cu^{II}–O, Å	Cu^{II}–O–Cu^{II}, deg	Cu^{II}- - -Cu^{II}, Å	J (cm^{-1})
1	3230		623(792), 851(571)	1.876(2)	112.3(1)	3.115(1)	+109
2	3200, 3260		738(659), 660(sh)	1.959(2)	112.5(1)	3.258(1)	+37.8
3		1622	414(5900), 771(625)	1.956(2)	114.5(1)	3.290(1)	−125

[a] Nujol mull. [b] Measured in MeCN.

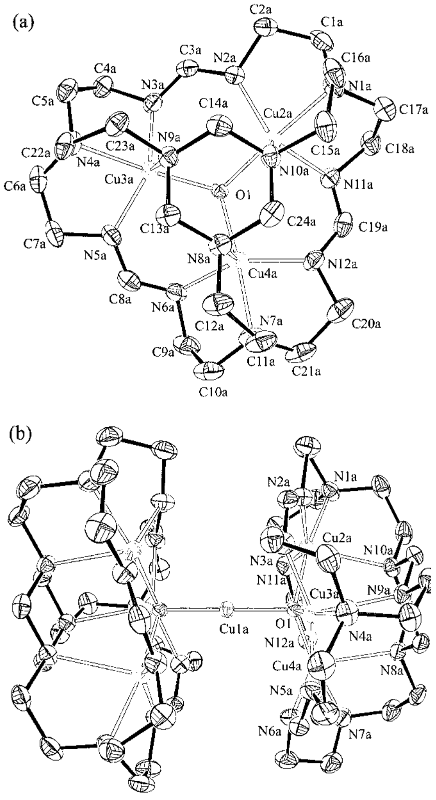

Figure 1. ORTEP drawings of top view (a) and side view (b) of the molecular dumbbell.[12,13] The atoms are represented by 30% probable thermal ellipsoid.

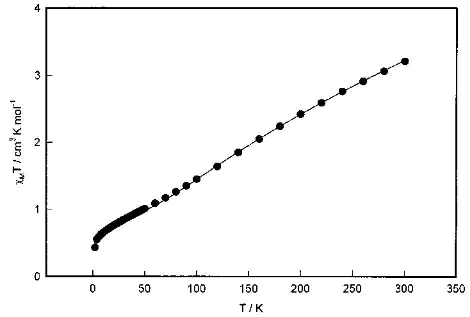

Figure 2. Plots of $\chi_M T$ vs T under 1.0 T. The solid line is the best fit curve to eq 2.[24]

at the corners of a triangle of side av 3.290(1) Å. The μ_4-oxygen is on a C_3 axis of the whole molecule and it is 0.467(3) Å (av) above the plane made by three Cu^{II} ions. It displays sp^3 hybridization with Cu^{I}–O–Cu^{II} and Cu^{II}–O–Cu^{II} angle of av 103.8(1)° and av 114.5(1)°, respectively. Each Cu^{II} ion adapts a coordination geometry of distorted trigonal bipyramid (tbp). The apical sites are occupied by a μ_4-oxygen and a tertiary nitrogen donor belonging to the larger rim of the bowl. The average axial bond distances of Cu^{II}–O and Cu–N$_{ax}$ are 1.956(2) and 2.118(2) Å, respectively. This Cu^{II}–O bond distance is significantly longer than that [av 1.876(2) Å] of **1**. The trigonal plane is made by two short [av 1.976(1) Å] and one long [av 2.457(2) Å] Cu^{II}–N bonds involving the deprotonated secondary and the tertiary nitrogen donors, respectively. The average corresponding N–Cu^{II}–N bond angles are 104.5(1)° and 143.2(1)°, respectively. The Cu^{II} atom is displaced from the trigonal plane toward the apical μ_4-oxygen by av 0.310(1) Å.

Variable-temperature (2–300 K) magnetic susceptibility of **3** was measured, and the plot of $\chi_M T$ vs T is shown in Figure 2.[23] The value of $\chi_M T$ decreases with decreasing temperature, indicating an antiferromagnetic coupling between the Cu^{II} ions. The magnetic data are interpreted in terms of the spin Hamiltonian in zero field for a dimer of Cu$_3$ unit as described in eq 1,[24] where J and J' indicate the magnetic coupling constant between Cu^{II} ions in a Cu$_3$ unit and that between Cu^{II} ions belonging to the two different Cu$_3$ units, respectively. The χ_M of the molecule is expressed as eq 2.[24]

The best fit parameters for the magnetic susceptibility data to eq 2 are $g = 1.96$, $J = -125$ cm^{-1}, $J' = -2.22$ cm^{-1}, $tip = 0.00459$ cm^3 mol^{-1} with $R = 6.03 \times 10^{-4}$.[25] Although the molecular bowls **1** and **2** exhibited strong ferromagnetic interactions that are unusual for the tricopper complexes,[8] the present molecular dumbbell shows antiferromagnetic coupling. This different magnetic property may be attributed to the longer Cu^{II}–O bond distance [av 1.956(1) Å] and larger Cu^{II}–O–Cu^{II} bond angle [av 114.5(1)°] of the molecular dumbbell compared with those [av 1.876(2) Å and av 112.3(1)°, respectively] of molecular bowl **1**. It has been shown for the molecular bowls **1** and **2** that the intramolecular ferromagnetic coupling constant decreases as the Cu^{II}–O bond distance increases when their Cu^{II}–O–Cu^{II} angles are same.[8] The significant increase in the Cu^{II}–O bond distance as well as the enlarged Cu^{II}–O–Cu^{II} angle in **3** would result in completely different magnetic behavior as compared with the molecular bowls.

The present result suggests that structural changes occurring in the tricopper units of the system composed of two molecular bowls greatly alter the magnetic property. We are currently preparing supramolecules constructed by several molecular bowls and organic linkages to investigate further the magneto-structural relationship.

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Supporting Information Available: Equations describing magnetic susceptibility of **3**, Figure S1 showing packing diagram of **3**, and an X-ray crystallographic file, in CIF format, for the complex **3** are available free of charge via the Internet at http://pubs.acs.org.

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(20) Etheredge, K. M. S.; Hwu, S.-J. *Inorg. Chem.* **1996**, *35*, 5278–5282.

(21) Reim, J.; Griesar, K.; Hasse, W.; Krebs, B. *J. Chem. Soc., Dalton Trans.* **1995**, 2649–2656.

(22) Workie, B.; Dube, C. E.; Aksu, L.; Kounaves, S. P.; Robbat J, A.; Davies, G. *J. Chem. Soc., Dalton Trans.* **1997**, 1739–1745.

(23) The data were corrected for diamagnetic contribution. For **3**, the μ_{eff} values are 5.06 μ_B at 300 K and 1.85 μ_B at 2 K.

(24) See Supporting Information.

(25) If g value is fixed as 2.12, the best fit parameters become $J = -123$ cm^{-1}, $J' = -4.07$ cm^{-1}, and $tip = 0.00433$ cm^3 mol^{-1} with $R = 2.99 \times 10^{-3}$. In this case, the best fit curve shows slight deviations from the experimental data at the temperature range 2–50 K.