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Cluster Expansion

Cubane $\{Cu^{II}_4\}$ Cluster as a Precursor for the Preparation of a Mixed-Valent $\{Cu^{II}_{12}Cu^{I}_2\}$ Core**

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Current interests in the chemistry of high-nuclearity transition-metal complexes draw from their utility in the emerging science of nanomaterials,[1] as models for the multimetal active sites of metal-storage proteins,[2] and as single molecule magnets (SMMs).[3,4] In addition, such super-sized molecules often show a variety of supramolecular interactions.[5] The "self-assembly" process of generating a high-nuclearity cluster from a mono- or dimeric precursor generally involves low-dentate organic ligands.

Using a pentadentate Schiff base, *N,N'*-(2-hydroxypropane-1,3-diyl)bis(acetylacetoneimine) (H_3L), we have been successful in isolating a discrete tetranuclear copper(II) cubane cluster $[\{Cu^{II}(HL)\}_4]$ (**1**) which, unlike other clusters, has four pendant arms with eight donor sites (four imine nitrogen atoms and four hydroxy groups) available for binding to additional metal ions. Complex **1**, as a "molecular octopus", is a new precursor for high nuclearity copper clusters. This complex on reaction with copper(II) perchlorate in presence of KOH forms an octanuclear copper(II) species

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$[Cu_8L_4(OH)_3](ClO_4)$ that has already been prepared by us from a different reaction using a binuclear precursor.[6] The same metal-driven self-assembly process under different reaction conditions leads to the formation of a new discrete tetradecanuclear mixed-valent complex $[Cu^{II}_{12}Cu^{I}_2L_6(OH)_6](ClO_4)_2$ (**2**). Herein, we present the synthesis, crystal structures and magnetic properties of **1** and **2**. Complex **2** is a rare discrete molecular tetradecanuclear transition-metal complex with multidentate ligand system.[7] In addition two copper(I) atoms are encapsulated in a core containing twelve copper(II) atoms giving a prismatic propeller structure.

Complex $[\{Cu(HL)\}_4]$ (**1**), prepared from a reaction of $[Cu(H_2O)_6](ClO_4)_2$ with H_3L in presence of triethylamine in CH_2Cl_2/MeOH, crystallizes in the cubic space group $P\bar{4}3n$ with one copper center and one ligand along with one lattice water in the crystallographic asymmetric unit.[8] The structure consists of a tetranuclear core with the metal centers linked by μ_3 alkoxo oxygen atom, to form a cubic arrangement of the metal and the oxygen atoms (Figure 1). The copper centers are in an essentially square-pyramidal (4 + 1) geometry with one bridging Cu–O bond being the axial group (2.437(5) Å). The Cu···Cu distances are 3.438(1) and 3.124(1) Å. The potentially pentadentate ligand (H_3L) binds in a dianionic tridentate form through one imine nitrogen, one enolized oxygen as the terminal, and the anionic alkoxo-oxygen atom as the bridging site. This leaves the remaining hydroxy group and the imine nitrogen atom as pendant, noncoordinating sites suitable for cluster expansion through metal-driven self-assembly process (Figure 2). The nonbonded shortest Cu···O and Cu···N separations involving the pendant donor sites are 3.6 and 3.2 Å, respectively.

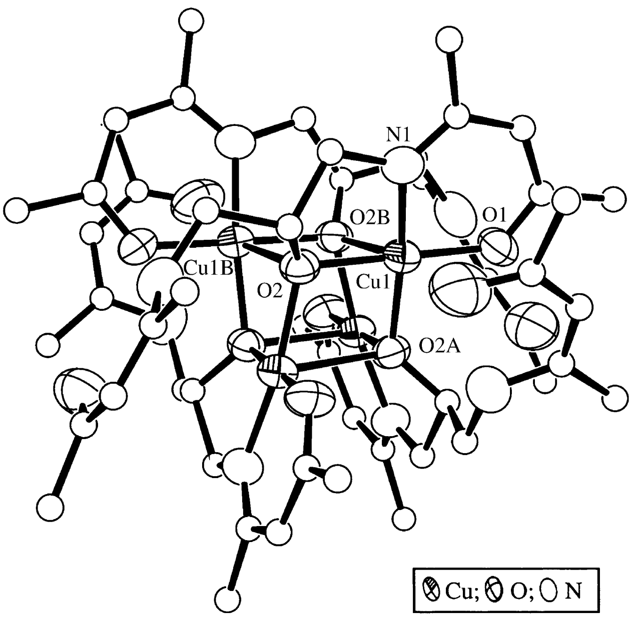

Figure 1. A perspective view of the complex in ($\mathbf{1}\cdot 4H_2O$) the thermal ellipsoids are set at 50% probability, the carbon atoms are shown as spheres with a reduced size for clarity. Selected interatomic distances [Å] and angles [°]: Cu1-O1 1.905(6), Cu1-O2 1.974(5), Cu1-O2A 1.971(5), Cu1-O2B 2.437(5), Cu1-N1 1.927(7); Cu1-O2-Cu1B 101.9(2), Cu1-O2-Cu1C 104.7(2), Cu1B-O2-Cu1C 89.61(19). Symmetry operations: A: $-x+3/2, z-1/2, -y+1/2$; B: $x, -y, -z+1$; C: $-x+3/2, -z+1/2, y+1/2$.

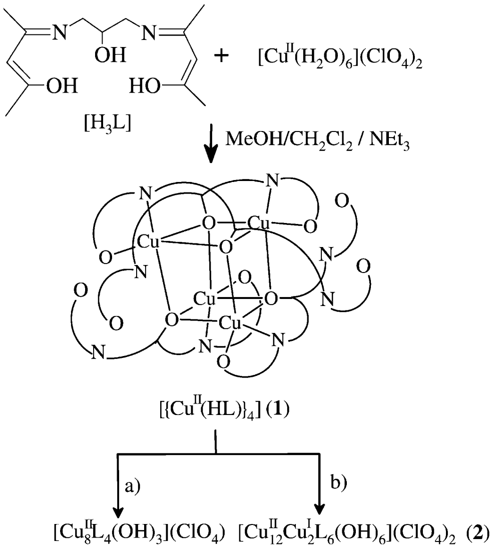

Figure 2. Reaction pathways in the self-assembly processes forming tetra-, octa-, and tetradecanuclear copper cores: a) $[Cu(H_2O)_6](ClO_4)_2$ and KOH in EtOH; b) $[Cu(H_2O)_6](ClO_4)_2$, H_3L, and piperidine in CH_2Cl_2/MeOH.

When **1** is treated with $[Cu(H_2O)_6](ClO_4)_2$ in a 1:4 molar ratio in presence of KOH in ethanol, the product is an octanuclear copper(II) complex $[Cu_8L_4(OH)_3](ClO_4)$, that has already been reported by us.[6] The reaction involves an addition of four copper(II) ions. Further addition of metal ions to **1** takes place on treatment of it with $[Cu(H_2O)_6](ClO_4)_2$ and H_3L in a 1:10:4 mole ratio in presence of piperidine in methanol and CH_2Cl_2 to form the tetradecanuclear mixed-valent complex $[Cu^{II}_{12}Cu^{I}_2L_6(OH)_6](ClO_4)_2$ (**2**). The cluster expansion process $\mathbf{1}\rightarrow\mathbf{2}$ involves the addition of ten copper atoms and two ligands to the cubane structure. Single crystals of $\mathbf{2}\cdot 3H_2O$, obtained by slow evaporation of the reaction mixture, belong to the trigonal space group $R\bar{3}c$ with six molecules in the unit cell.[8] The structure consists of six $\{Cu^{II}_2L\}^+$ units, each linked to two μ_3-OH groups attached to two copper(I) centers (Figure 3). The N_2O_3-donor Schiff base displays trianionic pentadentate mode of coordination. There are two central encapsulated copper(I) units that are presumably formed by the reduction of cupric ion owing to geometrical constraints within the core (see below). The Cu3 atom is bonded to three OH groups giving a threefold rotation axis with a propeller-shaped structure (see Supporting Information). In this essentially prismatic unit, the Cu3 atom has been assigned +1 oxidation state based on its trigonal-pyramidal structure in which the Cu3-O4 separation is 2.282(8) Å. The Cu3 atom is displaced 1.27(1) Å from the plane formed by three hydroxo oxygen atoms. The O-Cu3-O angle is 92.07(4)°. The deviation from the trigonal-planar structure could be due to the small size of the cavity accommodating the copper(I) atom. In addition, charge

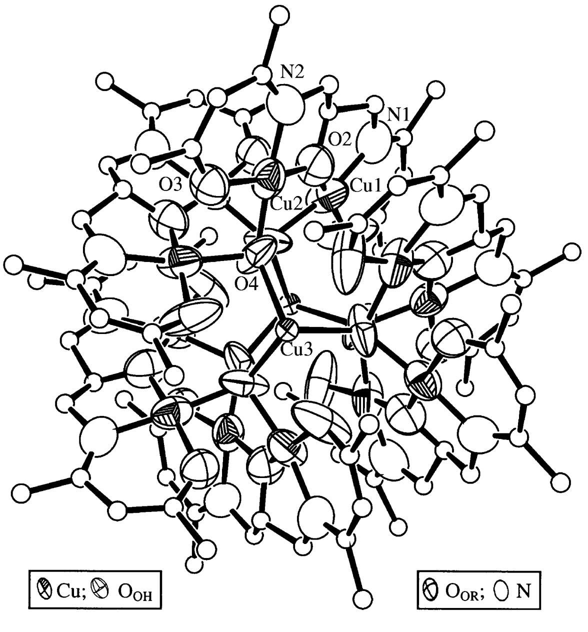

Figure 3. A perspective view of the complex in $\mathbf{2}\cdot 3\,H_2O$ with the thermal ellipsoids set at 50% probability the carbon atoms are shown as spheres with a reduced size for clarity. Selected bond lengths [Å] and angles [°]: Cu1-O1 1.899(11), Cu1-O2 1.941(11), Cu1-O4, 1.957(9), Cu2-O2 1.915(9), Cu2-O3 1.888(9), Cu2-O4 1.966(11), Cu1-N1 1.887(14), Cu2-N2 1.941(13), Cu3-O4 2.282(8); Cu1-O2-Cu2 136.5(6), Cu1C-O4-Cu2 101.8(4), Cu1C-O4-Cu3 100.4(4), Cu2-O4-Cu3 127.5(6). The prismatic structure involving the Cu^I centers can be seen. Symmetry operations: C:$-x+y+2/3$, $-z+1/6$, $-x+4/3$.

neutrality of this discrete molecular species requires two copper centers in +1 oxidation state. The Cu···Cu distance of 3.583(3) Å within the $\{Cu_2L\}^+$ units in **2** is similar to that observed in $[Cu_2L(O_2CMe)]$ (3.502(2) Å).[9] The dicopper(II) units in **2**, however, resemble the dialkoxo-bridged dicopper(II) complexes.[10]

The cluster expansion process is associated with a significant change in the magnetic properties as shown by preliminary magnetic data. The temperature dependence of the magnetic susceptibility of **1** and **2** is shown in Figure 4. The cubane cluster **1** has a μ_{eff} value of 1.76 μ_B and 2.31 μ_B per copper(II) center at 300 and 18 K, respectively (μ_{eff} per molecule: 3.51 μ_B, 300 K; 4.63 μ_B, 18 K). The observed increase in the $\chi_M T$ value on lowering the temperature suggests intracluster ferromagnetic interaction.[11] The contribution from the intercluster magnetic interaction should be negligible considering the large separation of the clusters from each other (intercluster Cu···Cu separation, ≈9.5 Å). The tetradecanuclear complex **2** shows, in contrast, strong antiferromagnetic (AF) behavior with singlet as a ground state. The magnetic moment values per copper(II) center are 1.12 and 0.17 μ_B at 300 and 18 K, respectively (μ_{eff} per molecule: 3.91 μ_B, 300 K; 0.62 μ_B, 18 K). Complex **2** has six $\{Cu_2L\}^+$ moieties with a Cu-O-Cu alkoxo bridge angle of 137°. Such an angle with a planar geometry of the alkoxo oxygen atom is likely to promote strong AF interactions within the dimeric unit.[10] The Cu1C-O4-Cu2 angle of 101.8(4)° with a pyramidal geometry of O4 atom (sum of angles 330°) is likely to promote weak AF interactions between two intracluster interdimer units.[12] Detailed magnetic studies are in progress.

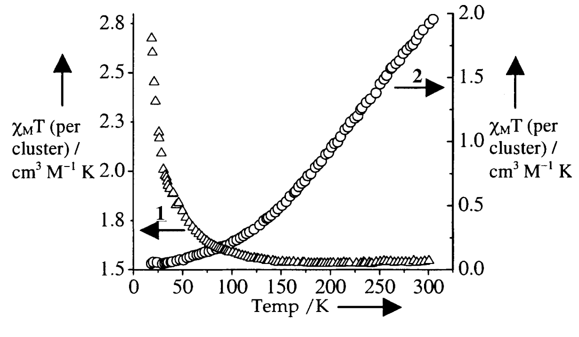

Figure 4. Plots of $\chi_M T$ (per molecule) versus T for complexes **1** (△) and **2** (○) in the temperature range 305–18 K.

In conclusion, the ferromagnetic cubane cluster **1** with eight pendant binding sites presents a reactive precursor for the synthesis of high-nuclearity copper clusters by metal-driven self-assembly processes. Isolation of discrete molecular octanuclear copper(II) and tetradecanuclear mixed-valent copper complex with a propeller-shaped $\{Cu^{II}_{12}Cu^{I}_{2}\}$ core shows that the cubane complex can be used as a new precursor for the preparation of high-nuclearity clusters of nanometric size.

Experimental Section

1 was prepared from a reaction of $[Cu(H_2O)_6](ClO_4)_2$ (2.96 g, 8.0 mmol) with H_3L[9] (3.79 g, 14.9 mmol) in CH_2Cl_2/MeOH mixture (1:1 v/v, 40 mL) in presence of triethylamine (3.9 mL, 28.03 mmol) under reflux for 30 min. Dark blue crystalline product in ≈87% yield was obtained on slow evaporation of the solvent at 25 °C. Single crystals were obtained by slow diffusion of hexane to a CH_2Cl_2 solution of **1**. Complex **2** was prepared in ≈66% yield from a reaction of **1** (0.2 g, 0.16 mmol) in CH_2Cl_2 (10 mL) with $[Cu(H_2O)_6](ClO_4)_2$ (0.6 g, 1.6 mmol) in presence of H_3L (0.19 g, 0.64 mmol) and piperidine (0.15 mL, 1.5 mmol) in MeOH (10 mL). The octanuclear complex $[Cu_8L_4(OH)_3](ClO_4)$ was prepared from a reaction of **1** (0.21 g, 0.16 mmol) with $[Cu(H_2O)_6](ClO_4)_2$ (0.24 g, 0.64 mmol) and KOH (0.53 g, 0.94 mmol) in ethanol (15 mL) in 55% yield (0.14 g). The crystals of the octanuclear complex gave cell parameters similar to those reported earlier.[6] Elemental analysis (%) calcd for **1**: C 49.44, H 6.38, N 8.87; found C 49.21, H 6.54, N 9.02, (%) calcd for **2** C 34.72, H 4.48, N 6.23; found: C 34.88, H 4.68, N 6.33. UV/Vis in MeOH λ_{max},(ε, $M^{-1}\,cm^{-1}$)]: 233 (22500), 310 (43000), 630 nm (280) for **1** and 281 (60000), 315 (91000), 620 nm (1000) for **2**. $\chi_M T$ (per molecule) $cm^3\,M^{-1}\,K$: 2.675 at 18.54 K and 1.551 at 305.31 K for **1**; 0.048 at 18.41 K and 1.954 at 304.73 K for **2** (Supporting Information).

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[1] R. E. P. Winpenny, *Adv. Inorg. Chem.* **2001**, *52*, 1; V. G. Makhankova, O. Y. Vassilyeva, V. N. Kokozay, B. W. Skelton, J. Reedijk, G. A. Vanalbada, L. Sorace, D. Gatteschi, *New. J. Chem.* **2001**, *25*, 685.

[2] H. Oshio, N. Hoshino, T. Ito, M. Nakano, F. Renz, P. Gütlich, *Angew. Chem.* **2003**, *115*, 233; *Angew. Chem. Int. Ed.* **2003**, *42*,

223; A. Caneschi, A. Cornia, S. J. Lippard, *Angew. Chem.* **1995**, *107*, 511; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 467.

[3] D. Gatteschi, R. Sessoli, *Angew. Chem.* **2003**, *115*, 278; *Angew. Chem. Int. Ed.* **2003**, *42*, 268.

[4] W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, G. Christou, *Nature* **2002**, *416*, 408.

[5] J.-M. Lehn in *Supramolecular Chemistry - Concepts and Properties*, VCH, Weinheim, **1995**; R. W. Saalfrank, E. Uller, B. Demleitner, I. Bernt, *Struct. Bonding (Heidelberg)* **2000**, *96*, 149; F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759; M. Fujita, K. Umemoto, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509; G. J. E. Davidson, S. J. Loeb, *Angew. Chem.* **2003**, *115*, 78; *Angew. Chem. Int. Ed.* **2003**, *42*, 74; B. J. Holliday, C. A. Mirkin, *Angew. Chem.* **2001**, *113*, 2076; Angew . *Chem. Int. Ed.* **2001**, 40, 2022.

[6] K. Geetha, M. Nethaji, A. R. Chakravarty, *Inorg. Chem.* **1997**, *36*, 6134.

[7] C. J. Milios, E. Kefalloniti, C. P. Raptopoulou, A. Terzis, R. Vincete, N. Lalioti, A. Escuer, S. P. Perlepes, *Chem. Commun.* **2003**, 819; G. Aromi, A. Bell, S. J. Teat, A. G. Whittaker, R. E. P. Winpenny, *Chem. Commun.* **2002**, 1896.

[8] Crystal data for $\mathbf{1}\cdot 4\,\mathrm{H_2O}$: $\mathrm{C_{52}H_{88}N_8O_{16}Cu_4}$, $M_r = 1335.46$, blue prisms ($0.265 \times 0.18 \times 0.145$ mm), cubic, $P\bar{4}3n$, $a = b = c = 22.421(4)$ Å, $V = 11\,272(3)$ Å^3, $Z = 6$, $\rho_{\mathrm{calcd}} = 1.180\ \mathrm{g\,cm^{-3}}$, $\mu = 1.174\ \mathrm{mm^{-1}}$, min/max trans. = 0.6341/0.8345, $2\theta_{\max} = 48°$, λ(Mo-Kα) = 0.71073 Å, $T = 293(2)$ K, 2961 unique reflections [R(int) = 0.1554], $R1 = 0.0693$, $wR2 = 0.1805$ [$I > 2\sigma(I)$], $R1 = 0.0953$, $wR2 = 0.1915$ (all data), GoF (F^2) = 1.077, $N_0/N_v = 2960/180$. Crystal data for $\mathbf{2}\cdot 3\,\mathrm{H_2O}$: $\mathrm{C_{78}H_{126}N_{12}O_{35}Cl_2Cu_{14}}$, $M_r = 2752.37$, green prisms ($0.325 \times 0.185 \times 0.09$ mm), trigonal, $R\bar{3}c$, $a = b = 16.318(2)$, $c = 70.22(2)$ Å, $V = 16\,193(6)$ Å^3, $Z = 6$, $\rho_{\mathrm{calcd}} = 1.693\ \mathrm{g\,cm^{-3}}$, $\mu = 2.824\ \mathrm{mm^{-1}}$, min/max trans. = 0.6133/0.8943, $2\theta_{\max} = 50°$, λ(Mo-Kα) = 0.71073 Å, $T = 293(2)$ K, 3077 unique reflections [R(int) = 0.0781], $R1 = 0.0879$, $wR2 = 0.2634$ [$I > 2\sigma(I)$], $R1 = 0.1228$, $wR2 = 0.2908$ (all data), GoF (F^2) = 1.048, $N_0/N_v = 3077/205$. X-ray diffraction data were measured in frames with increasing ω (width of 0.3 deg./frame) and with a scan speed at 6 s/frame for **1** and at 12 s/frame for **2** on a Bruker SMART APEX CCD diffractometer, equipped with a fine focus 1.75 kW sealed tube X-ray source. Empirical absorption corrections were carried out using MULTISCAN (for **1**) and SADABS (for **2**) program: R. Blessing, *Acta Crystallogr. Sect. A* **1995**, *51*, 33. The structures were solved by the heavy atom method and refined by full matrix least-squares using SHELX system of programs: G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, University of Göttingen, Göttingen (Germany), **1997**. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon atoms in the complex were generated and assigned isotropic thermal parameters, riding on their parent carbon atoms, and used for structure factor calculation only. CCDC 214522 and 214523 contain the supplementary crystallographic data for **1** and **2**, respectively. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk). ORTEP and packing diagrams in color for **1** and **2** are given as Supporting Information.

[9] Y. Nishida, S. Kida, *J. Chem. Soc. Dalton Trans.* **1986**, 2633.

[10] M. Handa, N. Koga, S. Kida, *Bull. Chem. Soc. Jpn.* **1988**, *61*, 6853.

[11] H. Oshio, Y. Saito, T. Ito, *Angew. Chem.* **1997**, *109*, 2789; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2673.

[12] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**.