Ligand-Templated Four-Metal Chains Dimerize into a Unique [Cu$^{II}_8$] Cluster**

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Within the context of what has been termed coordination supramolecular chemistry, remarkable progress has been made in the design and preparation of multidentate ligands capable of participating in complicated molecular structures upon complexation, in predetermined manners, with transition metals.[1] This approach is starting to take hold in the area of molecular magnetism. Thus, in recent years, a few important reports have appeared describing the formation of new magnetic transition metal clusters through the template action of specifically designed multinucleating ligands.[2] We have reported the synthesis of an O-pentadentate donor possessing a phenol and two β-diketone units (H$_3$L), which was conceived to direct the formation of chains
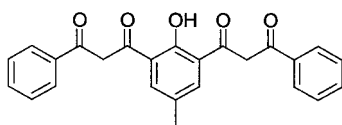
of closely spaced transition metals.[3] Initial efforts into the investigation of its coordination properties involved reactions with Mn^{II} ions, and led to the preparation of a trinuclear complex with formula [Mn$_3$(HL)$_3$] which displayed an asymmetric array of metals.[4] A significant step forward in the exploration of the templating capability of this new ligand is reported here with the fascinating methoxide-mediated aggregation of two ligand-templated [Cu$_4$] chains into an entirely new octanuclear Cu^{II} cluster held together by a fully deprotonated form of H$_3$L.

The title compound was prepared by treating a methanolic solution of Cu(NO$_3$)$_2\cdot$3H$_2$O with a solution containing 0.125 equivalents of H$_3$L and 1.8 equivalents of NtBu$_4$OH in MeOH. The green powder that precipitated was recrystallized from MeOH/Et$_2$O to yield green crystals of [{Cu$_4$(L)(OMe)$_4$-(NO$_3$)}$_2$] (1)[5] in an overall yield of 21%. The organic salt is introduced into the reaction mixture as the base necessary to deprotonate H$_3$L and also as the acceptor of the protons from

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methanol to give the MeO$^-$ ions that become incorporated into the complex. The fact that the complex binds methoxide instead of hydroxide ions despite the larger Brønsted basicity of the former can be explained by the stability of the final product combined with the large excess of methanol present in the system. The latter point is supported by the observation that, upon prolonged exposure to air, complex 1 changes color from green to brown, presumably following a process of complete hydrolysis of the methoxide ligands, as suggested by elemental analysis.[6]

The structure of 1[7] (Figure 1) shows a unique [Cu$^{II}_8$] cluster formed by the dimerization of two ligand-held four-metal-atom rows. Both metallic chains are bound to each other through eight methoxide ligands: six in a triply bridging
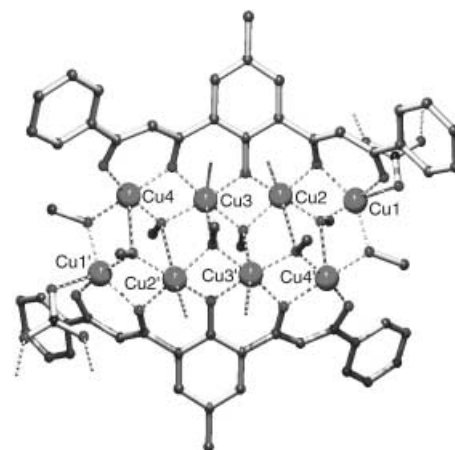

Figure 1. POV-Ray representation of [{Cu$_4$(L)(OMe)$_4$(NO$_3$)}$_2$] (1), where the axial bonds around the Cu^{II} ions are highlighted by striped lines.

manner[8] and two in a μ-OMe$^-$ fashion. The coordination around the Cu centers is completed by nitrate ions, which connect, in an extremely unusual $\eta^3:\mu_3$-NO$_3^-$ mode,[9] the [Cu$_8$] units into one-dimensional polymeric chains of clusters parallel to the a-axis (Figure 2). In fact, this compound represents a new and important addition to the small family of Cu-cluster polymers.[9–10] The octanuclear cluster possesses a crystallographic center of symmetry which relates one of the {Cu$_4$(L)(OMe)$_4$(NO$_3$)} units to the other. The core of complex
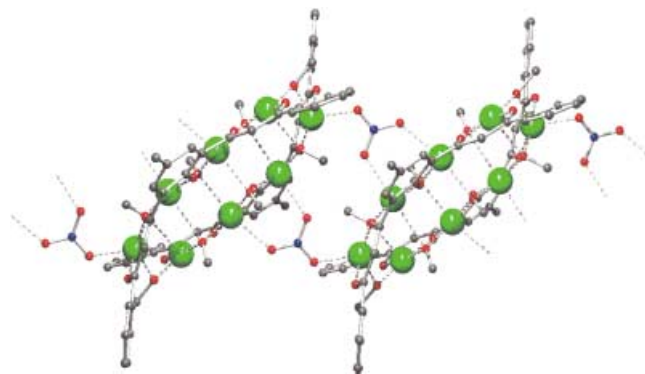

Figure 2. POV-Ray representation of 1 emphasizing the polymerization of [Cu$_8$] clusters in the solid state through $\eta^3:\mu_3$-NO$_3$ bridges. Green: Cu, red: O, blue: N, gray: C.

1 (Figure 3) is the first of its kind amongst the family of alkoxide and hydroxide-bridged Cu clusters. The core has been identified, however, as a fragment of a 2D Cu/OH/OAc polymeric structure.[11] Other large transition metal aggregates, such as the tetraicosanuclear cluster $[Co_{24}(OH)_{18}$-$(OMe)_2Cl_6(mhp)_{22}]$ (Hhmp = 2-methyl-6-hydroxypyridine),
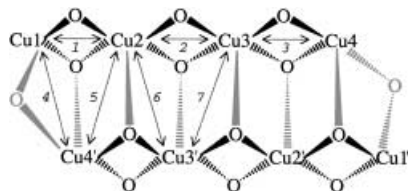

Figure 3. The $[Cu_8O_{14}]$ core of **1** showing in gray the Cu−O bonds linking both $[Cu_4O_6]$ structural units. The seven unique interactions between adjacent Cu ions necessary to describe the magnetic coupling in **1** are marked with arrows.

include this moiety as part of their structure.[12] The core of **1** contains two linear rows of four alkoxide-bridged Cu ions, each of which is described as a three-edge-sharing $\{Cu_2O_2\}$ unit. Both $[Cu_4]$ arrays are linked through six axially elongated bonds between the Cu ions and the μ_3-OMe⁻ groups, and two additional μ-OMe⁻ ligands. The Cu···Cu distances within the intrachain $\{Cu_2O_2\}$ units are 2.8999(8) (Cu1···Cu2), 2.8834(7) (Cu2···Cu3), and 2.9995(8) Å (Cu3···Cu4). The seven shortest interchain Cu···Cu vectors are described by four values by virtue of the symmetry of the cluster: 2.9610(9) (Cu1···Cu4′), 3.4677(8) (Cu2···Cu4′), 3.3225(8) (Cu2···Cu3′), and 3.2981(8) Å (Cu3···Cu3′). The presence of seven inequivalent, bridged Cu₂ pairs demonstrates the number of exchange parameters necessary for a rigorous description of the magnetic coupling within this cluster (see below). The templating action of the pentadentate ligand L³⁻ undoubtedly plays a crucial role in the formation of this unprecedented topology. The combination of unrestrained β-diketonate ligands and alkoxide groups has been reported to yield more-extended aggregates rather than linear arrangements.[13] The five strategically disposed oxygen donor atoms in L³⁻ direct the assembly of four Cu ions into metallic arrays, through the formation of four adjacent six-membered chelate rings. The structural constraints that derive from this assembly result in a marked bending of the ligand along its longest dimension as emphasized in Figure 2, which also translates into a curvature of the $[Cu_4]$ chain (the Cu1-Cu2-Cu3 and Cu2-Cu3-Cu4 angles are 159.78(2)° and 170.18(3)°, respectively). The four unique metal ions are accommodated within the structure of this cluster in three common geometric environments for Cu^{II} ions, namely, tetragonally elongated octahedral (Cu2 and Cu3), intermediate between square pyramidal and trigonal bipyramidal (Cu1, with $\tau = 0.50$),[14] and square pyramidal (Cu4, with $\tau = 0.01$). The axial positions of these ions correspond to the six long bonds connecting the $[Cu_4]$ chains through μ_3-OMe⁻ ligands, or are occupied by oxygen atoms from the nitrate groups (see Figure 1). The remaining Cu−O bonds lay in equatorial positions. All the bond lengths fall within the ranges usually observed for

the coordination of oxygen to Cu^{II} ions in such environments.[15]

Variable-temperature magnetic susceptibility measurements were performed over the 2–300 K range on a polycrystalline sample of **1** protected from air and under a constant magnetic field of 1 kG. A plot of the magnetic susceptibility (χ_m) per $[Cu_8]$ cluster, versus temperature T (Figure 4) shows a broad maximum at about 180 K. This
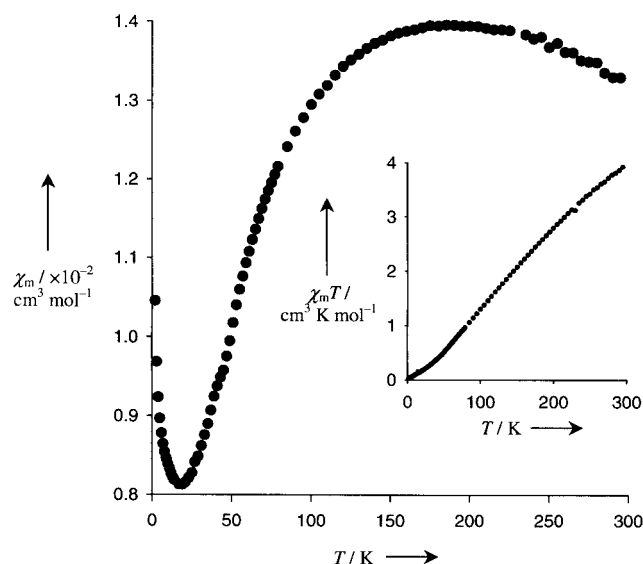

Figure 4. Plot of the magnetic susceptibility (χ_m) versus T for **1**. The inset shows a plot of $\chi_m T$ versus T of **1** over the same temperature range.

feature indicates that the magnetic exchange in this temperature interval is mainly influenced by antiferromagnetic interactions, and leads to a total spin ground state of $S_T = 0$. The small increase in the χ_m value below 19 K is typical for the presence of a small amount of paramagnetic impurity, which is very common in such systems.[16] A regime of uncoupled spins has not yet been reached at the highest measured temperature. This is clear from the plot of $\chi_m T$ versus T (Figure 4, inset), which does not show saturation at 300 K. The value of $\chi_m T$ at room temperature (4.09) is higher than that expected for eight uncoupled Cu^{II} ions with $g = 2$ (3.00).

A full investigation over a larger temperature range is under way to obtain a detailed description of the magnetic properties of **1**. An important point to elucidate is whether the high value of $\chi_m T$ at 300 K arises from the presence of strong ferromagnetic interactions in the cluster. The symmetry of this system shows that it is necessary to define seven independent coupling constants for the description of its magnetic exchange (Figure 3). This scheme does not allow for the application of the Kambe vector coupling method[17] to obtain the energy of its various spin states. Thus, a full-matrix diagonalization method will be necessary for a quantitative treatment. In addition, the possibility of nitrate-mediated intercluster interactions will need to be considered.

The potential of L³⁻ to assemble transition metals into unprecedented, magnetically coupled building blocks for the construction of new clusters has been demonstrated with complex **1**, and is currently being investigated with other

3d elements under a variety of conditions. The prospect of the preparation of mixed-metal moieties is also being explored.

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[5] Elemental analysis calcd for **1** · MeOH: C 41.50, H 3.66, N 1.64; found: C 41.11, H 3.30, N 1.75.

[6] Elemental analysis of **1** after hydrolysis calcd for [{Cu$_4$(L)(OH)$_4$-(NO$_3$)}$_2$] · 2.8 H$_2$O: C 36.09, H 3.22, N 1.68; found: C 35.82, H 2.87, N 1.69.

[7] Crystal data for **1**: C$_{29}$H$_{29}$Cu$_4$NO$_{12}$ · solvent (see below). Data were collected on a green block-shaped crystal ($0.2 \times 0.2 \times 0.3$ mm), triclinic, space group $P\bar{1}$ (no. 2) with $a = 10.5682(15)$, $b = 13.510(2)$, $c = 13.9695(14)$ Å, $\alpha = 100.964(9)$, $\beta = 98.654(10)$, $\gamma = 96.257(12)°$, $V = 1916.3(5)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.452$ g cm^{-3}, $\mu(Mo_{K\alpha}) = 2.24$ mm^{-1}. 30251 Reflections were measured, 6936 of which were independent ($R_{int} = 0.0600$, $R_\sigma = 0.0359$, no absorption correction applied) on a Nonius KappaCCD diffractometer with a rotating anode ($T = 150$ K, $1.6 < \theta < 25.25°$, Mo$_{K\alpha}$ radiation, $\lambda = 0.71073$ Å). The structure was solved by automated direct methods (SHELXS86), and refined on F^2 (SHELXS-97). The structure contains two sets of interconnecting channels that run in directions [100] and [101] that are filled with a mixture of disordered MeOH and Et$_2$O molecules. The electron density (240 e in 524 Å^3 for each unit cell) was taken into account in the refinement by PLATON/SQUEEZE. Where relevant, data cited above are given without disordered solvent contributions. One of the phenyl rings (C151–C156) is refined with a two-site disorder model. Hydrogen atoms were included on calculated positions riding on their carrier atoms. Refinement of 406 parameters converged at a final w$R2$ value of 0.1031, $R1 = 0.0403$ (for 6309 reflections with $I > 2\sigma(I)$) $S = 1.044$, $-0.86 < \Delta\rho < 2.09$ e Å^3. CCDC-171479 contains the supplementary crystallographic data for this paper. 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).

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[15] Axial Cu−O bond lengths: a) to μ_3-OMe: 2.743(3) (Cu2), 2.389(3) (Cu3), and 2.418(3) Å (Cu4) and b) to μ_3-NO$_3$: 2.226(3) (Cu1), 2.340(3) (Cu2), and 2.433(3) Å (Cu3). Equatorial Cu−O bond lengths: a) to μ-O(ligand): 1.906(3) – 1.994(3) Å, b) to μ-OMe: 1.958(3) (Cu1) and 1.921(3) (Cu4), and c) to μ_3-OMe: 1.935(2) – 1.954(3) Å.

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