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A Novel μ_4-Oxo Bridged Copper Tetrahedron Derived by Self-Assembly: First Example of Double Helical Bis(Tridentate) Coordination of a Hexadentate Amine Phenol Ligand

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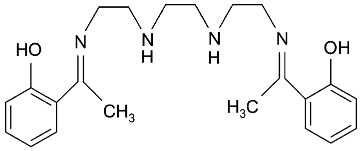
In methanol, the reaction of $Cu(ClO_4)_2 \cdot 6H_2O$ and the hexadentate amine phenol ligand (H_2bahped) in the presence of triethylamine affords a tetranuclear copper(II) complex having the formula $[Cu_4(\mu_4\text{-}O)(\text{bahped})_2](ClO_4)_2$. The X-ray structure of this complex shows a tetrahedral central $\{Cu^{II}{}_4(\mu_4\text{-}O)\}$unit coordinated to two hexadentate bridging (via the central ethylenediamine part) ligands. The compound is the first example of a μ_4-oxo tetranuclear copper(II) complex without any bridging ligand along the six tetrahedral edges. Variable-temperature magnetic data clearly show an $S_t = 0$ spin ground state for antiferromagnetic interactions between four $^2B_2$ copper(II) ions in a dimer of dimers.

Tetranuclear $\{Cu_4(\mu_4\text{-}O)\}$ cores have been known for some time and studied extensively.[1] The tetrahedral tetracopper assembly with the central oxo center is further stabilized by other bridging halides and phenolates. All complexes containing such cores have the same structural framework, with four copper atoms at the corners of a tetrahedron around the central μ_4-bridging oxygen and two to six μ_2-bridging halide/phenoxide atoms over each edge of the tetrahedron. The central $\{Cu_4(\mu_4\text{-}O)\}$ core is tetrahedral and has D_{2d} symmetry. An example of a $\{Cu_4(\mu_4\text{-}O)\}$ unit in a tetranuclear complex using a simple chelating nonbridging hexadentate ligand without any secondary bridging phenolate or halide ion is not known. Mononuclear cationic complexes of similar hexadentate ligands have shown potential as inexpensive metalloantimalarial drugs.[2] Currently, efforts are being made to rationalize the involvement of a novel tetranuclear copper cluster in the catalytic cycle of nitrous oxide reduction to dinitrogen. Cu_Z, the putative catalytic site, is a novel tetranuclear copper center never before found in biological systems.[3] Herein, we report a bridging halide-/phenolate-free, tetrahedral symmetric $\{M_4(\mu_4\text{-}O)\}$ unit in a tetracopper(II) complex cation, $[Cu_4(\mu_4\text{-}O)(\text{bahped})_2]^{2+}$, having square planar metal centers with a hexadentate bridging ligand, bahped^{2-} (1,3-bis-[3′-aza-4′-(3-methyl-2′--hydroxyphenyl)-prop-4-en-1′-yl]-ethane-1,2-diamine, H_2bahped, **I**).



(**I**)

The complex was synthesized in ~85% yield from methanolic medium under aerobic conditions at room temperature by stirring a reaction mixture consisting of $Cu(ClO_4)_2 \cdot 6H_2O$, H_2bahped (prepared by the condensation of 2 mol of 2-hydroxy acetophenone and 1 mol of triethylenetetramine), and $N(C_2H_5)_3$ in a 2:1:2 molar ratio for 1 h. The complex precipitates directly from the reaction mixture as a dark green solid. The elemental analysis data are consistent with the formula $[Cu_4(\mu_4\text{-}O)(\text{bahped})_2](ClO_4)_2$. For the complex, a sharp band of medium intensity at 566 cm^{-1} is characteristic of the T_2 vibrational mode of the $\{Cu_4O\}$ core.[4] This band is missing in the spectrum of the free ligand.

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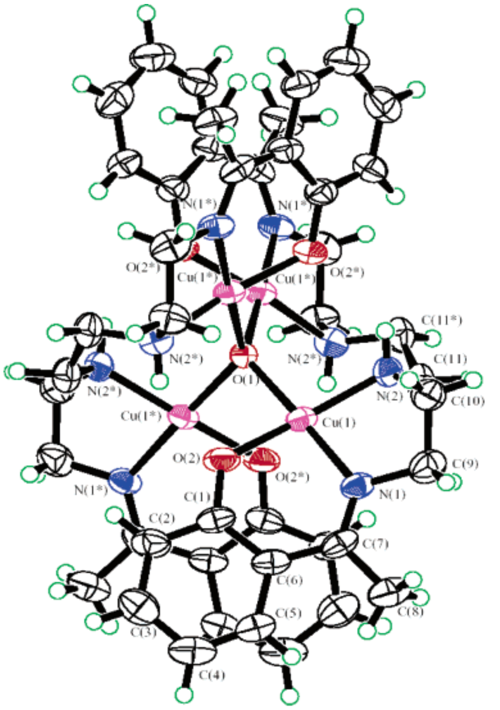

Figure 1. ORTEP plot of the cation $[Cu_4(\mu_4\text{-}O)(bahped)_2]^{2+}$ with atomic labeling and thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are shown as circles of arbitrary size. Selected bond lengths (Å) and angles (deg): Cu(1)−Cu(1), 2.797(3); Cu(1)−O(1), 1.935(1); Cu(1)−O(2), 1.936(8); Cu(1)−N(1), 1.956(9); Cu(1)−N(2), 2.026(9); O(1)−Cu(1)−O(2), 87.5(2); O(1)−Cu(1)−N(1), 178.1(3); O(1)−Cu(1)−N(2), 95.6(3); O(2)−Cu(1)−N(1), 90.9(4); O(2)−Cu(1)−N(2), 168.3(4); N(1)−Cu(1)−N(2), 86.2(4); Cu(1)−O(1)−Cu(1*), 92.58(7); Cu(1)−O(1)−Cu(1*), 130.59(7); Cu(1)−O(1)−Cu(1*), 107.72(7).

The strong unsplit band for $\nu(ClO_4^-)$ at around 1087 cm^{-1} suggests no coordination of perchlorate ions.[5]

One of the single crystals obtained by slow evaporation of an acetonitrile/dichloromethane (1:1) solution of the complex was used to determine the molecular structure by X-ray crystallography.[6] The complex cation is depicted in Figure 1. Each hexadentate N_4O_2 donor ligand binds two Cu centers on one side of the tetrahedron. The central ethylenediamine part of the ligands acts as a bridging unit for two copper centers within a seven-membered ring responsible for the ligand twisting. The μ_4-oxo atom satisfies the fourth coordination site of each of the four copper ions. The chelate bite angle for the terminal six-membered ring is 90.9(4)°, and that for the five-membered ring is 86.2(4)°. The C═N and C−O distances of the salicylaldimine fragments are consistent with the coordination of the deprotonated form of the salicylaldimine functionalities.[7]

The C−C distance at the bridgehead is 1.46(2) Å. The $Cu-N_{imine}$ [1.956(9) Å] and $Cu-N_{amine}$ [2.026(9) Å] distances are distinctly different. The longer $Cu-N_{amine}$ distances are mainly due to the different states of hybridization of the coordinating N_{amine} atoms in the molecule. The $Cu-N_{amine}$ distances are in the usual range for a bivalent metal ion and are not longer because of their participation in bridging. The Cu-to-central oxygen atom distances are comparable to those reported for other tetranuclear complexes having $\{Cu^{II}_4(\mu_4\text{-}O\}$ units.[1] The $Cu-O_{phenol}$ distance is slightly shorter than the $Cu-O_{oxo}$ distance.

The compound consists of four copper(II) ions bridged by a central μ_4-oxygen atom in a distorted tetrahedral environment. The Cu−O−Cu bond angles range between 92.58° and 130.39°. Each copper is, in turn, coordinated by the central oxygen atom, a phenoxy oxygen atom, and two amine nitrogen atoms from the hexadentate ligand, in a slightly distorted square-planar geometry with the copper about 0.064(4) Å from the basal ONNO(oxo) plane. The Cu···Cu distances range between 2.797 and 3.515 Å. This is comparable to the Cu···Cu distances in some of the μ_4-oxo tetracopper complexes that have been reported.[1,8,9] Interligand $\pi-\pi$ stacking [∼3.43(1) Å] between the terminal phenyl rings of the adjacent hexadentate ligands further stabilizes the copper tetrahedron. The double helical binding of the two hexadentate ligands actually hold the $\{Cu^{II}_4(\mu_4\text{-}O\}$ core as shown in Figure 2. Thus, the tetrahedral $\{Cu^{II}_4(\mu_4\text{-}O\}$ core stabilized by the double helical binding of the two hexadentate ligands having interligand $\pi-\pi$ stacking presents a new structural motif in the coordination chemistry.

Magnetic susceptibility data in the temperature range 2−300 K at a constant applied magnetic field of 0.8 T were collected for a polycrystalline sample of $[Cu_4(\mu_4\text{-}O)(bahped)_2](ClO_4)_2$ to identify the nature and magnitude of the exchange interaction propagated by the central μ_4-oxygen atom. A diamagnetic correction of 278.43×10^{-6} cgsu per complex,

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(6) X-ray analysis: The complex $[Cu_4(\mu_4\text{-}O)(bahped)_2](ClO_4)_2$ crystallizes in the orthorhombic system, space group *Ibam* (No. 72), with $a = 15.251(2)$ Å, $b = 15.389(2)$ Å, $c = 23.153(3)$ Å, $\beta = 90°$, $V = 5433(1)$ Å^3, $\rho_{calcd} = 1.503$ g/cm^3, and $Z = 4$. With the use of 16810 unique reflections $[I \geq 2\sigma(I)]$ collected at 298 K with Mo Kα radiation ($\lambda = 0.71073$ Å) to $\theta = 25°$ on a single-crystal X-ray diffractometer, the structure was solved on a PC 486 using the DIRDIF92-PATTY programme system (Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF Program System*; Technical Report of the Crystallography Laboratory; University of Nijmegen, Nijmegen, The Netherlands, 1992) and refined by full-matrix least-squares methods (Sheldrick, G. M. *SHELXS-97, Programme for the Refinement of Crystal Structures*; University of Göttingen, Göttingen, Germany, 1997. *TEXSAN, Crystal Structure Analysis Package*; Molecular Structure Corporation, The Woodlands, TX, 1992). The refinement converged to final R1 = 0.0965, wR2 = 0.1495 $[I > 2\sigma(I)]$, with GOF = 3.535 and the largest peak and hole differences as 3.76 and −1.10 e Å^{-3}, respectively.

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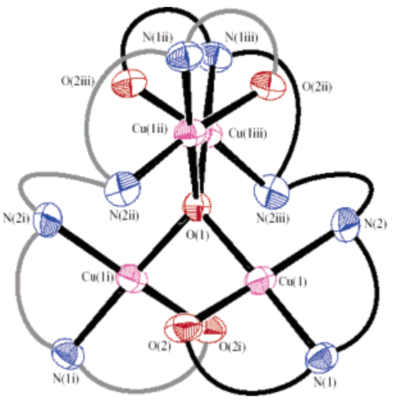


Figure 2. Atom connectivity in the core of $[Cu_4(\mu_4\text{-}O)(bahped)_2]^{2+}$. The μ_4-oxygen is in a distorted tetrahedral environment. [Symmetry code: (i) $-x$, y, $^1/_2 - z$; (ii) x, $1 - y$, $^1/_2 - z$; (iii) $-x$, $1 - y$, z.]

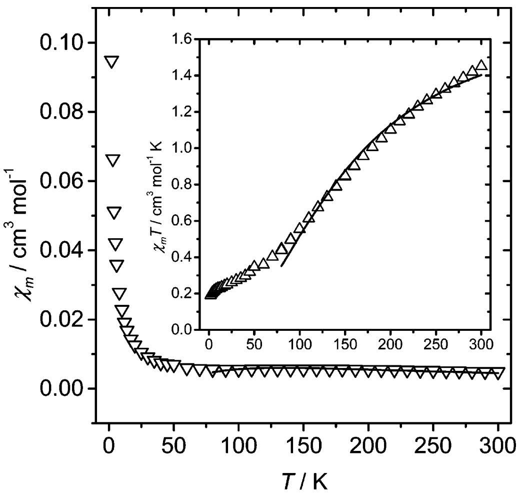
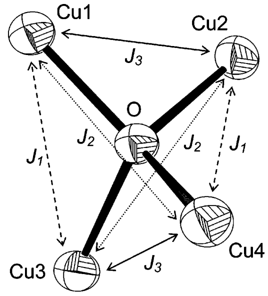


Figure 3. Plot of the thermal dependence of χ_m for complex $[Cu_4(\mu_4\text{-}O)(bahped)_2](ClO_4)_2$. Inset: plot of the thermal dependence of χ_mT for the complex $[Cu_4(\mu_4\text{-}O)(bahped)_2](ClO_4)_2$. The solid lines represent the best fit.

Chart 1



as calculated from Pascal's constants,[10] was applied to obtain the molar paramagnetic susceptibilities. The magnetic properties of the $[Cu_4(\mu_4\text{-}O)(bahped)_2](ClO_4)_2$ complex are represented in Figure 3 as χ_m and χ_mT (inset) versus T plots (χ_m is the molar paramagnetic susceptibility for four Cu^{II} ions). The antiferromagnetic nature of the coupling in the title complex can also be explained in terms of χ_mT (Figure 3, inset). At room temperature, χ_mT is 1.45 cm^3 mol^{-1} K, which is close to the value expected for four uncoupled copper(II) ions with $g = 2$ (1.5 cm^3 mol^{-1} K). As the temperature decreases, the value of χ_mT quickly decreases to 0.4 cm^3 mol^{-1} K at 75 K, followed by a less pronounced decline to reach 0.19 cm^3 mol^{-1} K at 2 K. The data clearly show that the spin ground state in this discrete system is $S_t = 0$.

Chart 1 shows the Cu_4O topology of the complex $[Cu_4(\mu_4\text{-}O](bahped)_2](ClO_4)_2$. The experimental magnetic data were analyzed as a first approximation with a three-J model. This model was adopted for fitting of the experimental χ_mT versus T data through an iterative numerical procedure that finds the best parameters to describe the system by diagonalizing the matrix for the corresponding spin Hamiltonian, using the irreducible tensor operator (ITO) formalism.[11] This procedure was performed by means of the program CLUMAG, which uses a Heisenberg spin Hamiltonian approximation. In this case, the magnetic energy operator takes the form

$$H = -2J_1(S_1S_2 + S_3S_4) - 2J_2(S_1S_3 + S_2S_4) - 2J_3(S_1S_4 + S_2S_3) \quad (1)$$

In eq 1, S_i is the spin operator of the ith Cu^{II} center, with an eigenvalue of $^1/_2$. The calculation provided the following results: $J_1 = J_2 = -60$ cm^{-1}, J_3 undetermined but positive (see below), $g = 2.22$, and $R = 1.2 \times 10^{-3}$ (R being the agreement factor defined as $\Sigma_i[(\chi_mT)_{obs} - (\chi_mT)_{calc}]^2/\Sigma_i[(\chi_mT)_{obs}]^2$ (Figure 3). Comparison of the above results with those obtained previously for similar systems is difficult because there seems to be no clear correlation between the J values and any particular structural parameter.[1,11−14] This is particularly true here, given that the complex $[Cu_4(\mu_4\text{-}O)(bahped)_2](ClO_4)_2$ is the first of this family not showing any additional bridge between Cu^{II} ions other than the $\mu_4\text{-}O^{2-}$ ion.

In conclusion, we have been able to isolate the $\{Cu_4(\mu_4\text{-}O)\}$ core in a bridging phenolate- and halide-free environment by using a nonbridging hexadentate Schiff base ligand. This complex might function as a chemical model for tetranuclear Cu_Z center of nitrous oxide reductase (N_2OR).

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Supporting Information Available: Experimental section describing the synthesis in detail, with characterization data, materials, and physical measurements; unit cell packing diagram (Figure S1); and X-ray crystallographic data (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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