is reasonable to assign this air-stable Tc–MDP complex as containing Tc(IV) centers. Further studies are now under way to verify this hypothesized structure and to probe the fundamental chemistry of this Tc–MDP complex.

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Supplementary Material Available: Figures A and B, including plots of the raw X-ray fluorescence data and the extracted EXAFS times $\mathbf{k}^3$, and Table A, listing the parameter values found in fitting the filtered EXAFS (3 pages). Ordering information is given on any current masthead page.

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(32) To whom correspondence should be addressed at the Department of Chemistry.

Biomedical Chemistry Research Center
Departments of Chemistry and Radiology
University of Cincinnati
Cincinnati, Ohio 45221-0172

John L. Martin, Jr.
J. Yuan
Craig E. Lunte
R. C. Elder*,[32]
William R. Heineman*,[32]
Edward Deutsch*,[32]

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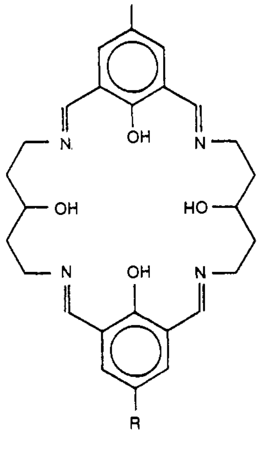
An Octacopper(II) Complex with μ_5-Oxo and Tripodlike Perchlorate Ligands: Formation and X-ray Structure of the $[Cu_4(L)O(ClO_4)]_2(ClO_4)_2 \cdot 2H_2O$ Dimer

Polynuclear complexes are of interest because of their bonding and magnetic interactions and also because of their potential value in catalysis. Recently[1] we reported the preparation of a planar tetracopper(II) complex, $[Cu_4(L')(OH)](NO_3)_3 \cdot 3H_2O$ (**1**), derived from the macrocyclic ligand H_4L'. We now record the dimerization of a copper complex of the related ligand H_4L, resulting in the formation of an octacopper(II) complex (**2**). The halves of the dimer are linked via a μ_5-oxo ligand in the center of each macrocyclic unit. Perchlorate anions are coordinated, in a new tripod bonding mode, to both open faces of the complex.



H_4L $R = CH_3$
H_4L' $R = C(CH_3)_3$

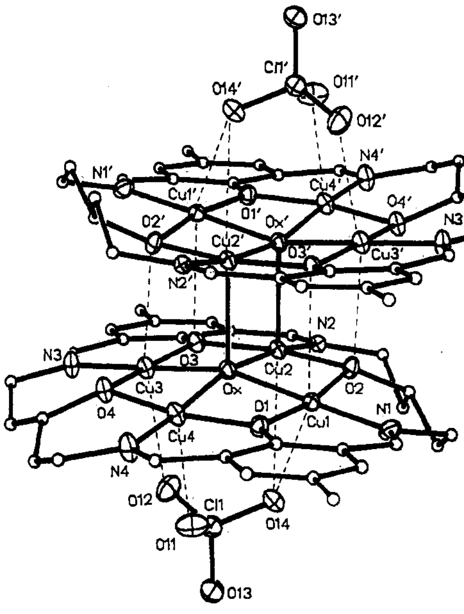


Figure 1. Perspective view of the $[Cu_4(L)O(ClO_4)]_2^{2+}$ dimer showing 30% probability thermal ellipsoids and atom labels for manganese, oxygen, and nitrogen atoms. Carbon atoms are shown as small spheres for clarity. Selected interatomic distances (Å): Cu(1)–Cu(2) = 2.852 (2), Cu(1)–Cu(4) = 2.876 (1), Cu(2)–Cu(3) = 2.918 (1), Cu(3)–Cu(4) = 2.844 (2), Cu(1)–Ox = 2.032 (6), Cu(2)–Ox = 2.066 (5), Cu(3)–Ox = 2.053 (6), Cu(4)–Ox = 2.054 (6), Cu(2)–Ox′ = 2.372 (7), Cu(1)–O(3′) = 2.84 (1), Cu(3)–O(2′) = 2.72 (1), Cu(1)–O(14) = 2.87 (1), Cu(2)–O(14) = 3.22 (1), Cu(3)–O(12) = 2.624 (8), Cu(4)–O(11) = 2.519 (8).

Complex **2** was prepared in 55% yield by refluxing 2,6-diformyl-4-methylphenol, 1,5-diamino-3-hydroxypentane, and copper(II) perchlorate hexahydrate in ethanol for ca. 24 h. A green product, **3**, was filtered from the hot solution, and **2** was obtained by recrystallization from 1:1 dimethylformamide (dmf)–methanol by diffusion of diethyl ether.[2] Although we have experienced no difficulties with the perchlorate salts described here, *these should be regarded as potentially explosive and handled accordingly*; i.e., make only small quantities and handle behind an explosion shield.

Figure 1 shows the X-ray crystal structure[3,4] of $[Cu_4(L)O(ClO_4)]_2^{2+}$, the dimeric cation of **2**. Within each macrocycle the arrangement is similar to that reported for **1**; the four copper atoms are coplanar, and each is coordinated to an imine nitrogen atom, to bridging phenoxide and alkoxide donors, and to a central oxygen donor. In **1** the central species is a hydroxo group located in the plane of the four copper atoms. In the present complex the central

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(1) McKee, V.; Tandon, S. S. *J. Chem. Soc., Chem. Commun.* **1988**, 385.

(2) Copper(II) perchlorate hexahydrate (1.48 g, 4 mmol) and 2,6-diformyl-4-methylphenol (0.33 g, 2 mmol) were heated to reflux in dry ethanol (40 mL) on a steam bath. 1,5-Diamino-3-hydroxypentane dihydrochloride (0.38 g, 2 mmol), neutralized with KOH and dissolved in a 1:1 mixture of dry methanol and ethanol (20 mL), was added dropwise over 10 min. The resulting dark green solution was refluxed for 24 h, after which the dark green solid that separated was filtered from the hot solution, washed with dry ethanol (3 × 5 mL), and dried in vacuo at room temperature; yield of **3** 55%. Anal. Calcd for $C_{28}H_{33}Cl_3Cu_4N_4O_{17}$: C, 31.8; H, 3.1; N, 5.3; Cu, 24.0. Found: C, 31.8; H, 3.6; N, 5.1; Cu, 23.6. Recrystallization by slow diffusion of diethyl ether into a solution of this complex in 1:1 dimethylformamide–methanol gave crystals of the octanuclear complex **2**.

(3) Crystal Data: $C_{56}H_{62}Cl_4Cu_8O_{28}N_8$, green, dimensions 0.31 × 0.25 × 0.15 mm^3, triclinic, $a = 11.497$ (4) Å, $b = 12.714$ (3) Å, $c = 13.546$ (4) Å, $\alpha = 102.92$ (2)°, $\beta = 113.15$ (2)°, $\gamma = 100.36$ (3)°, $V = 1693$ (1) Å^3, space group $P\bar{1}$, $Z = 1$, $F(000) = 980$. Data were collected at 170 K on a Nicolet R3m four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71069$ Å). With use of 2° ω scans at 5.86° min^{-1}, 4049 unique reflections were collected in the range $4 < 2\theta < 45°$ and 2681 with $I > 3\sigma(I)$ were used in the structural analysis. The structure was solved by using Patterson methods, and refinement converged with $R = 0.0497$ and $R_w = 0.0642$. All programs used in the data reduction and structure solution are contained in the SHELXTL (Version 4.1) package. Full details will be published elsewhere.

(4) Sheldrick, G. M. *SHELXTL User Manual, Revision 4.1*; Nicolet XRD Corp.: Madison, WI, 1984.

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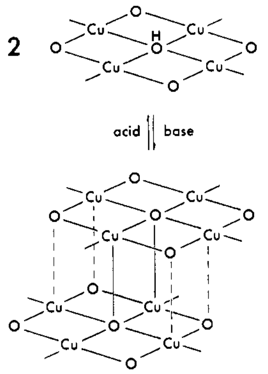
Scheme I



moiety is a five-coordinate oxo anion (Ox), which is displaced by 0.29 Å from the mean plane of the four copper ions. The coordination sphere of Ox is completed by Cu(2′), a copper atom from a second macrocyclic unit. This bond and the symmetry-related Cu(2)–Ox′ linkage hold the two macrocyclic units together in a centrosymmetric dimer. In addition, there are weaker interactions involving Cu(1) and Cu(3).

The outer faces of the dimer are blocked by perchlorate ions, which are bound, in tripod fashion, to the Cu_4 array. Perchlorate oxygen atoms O(11) and O(12) are each coordinated to a single copper atom (O(11)–Cu(4) = 2.519 (8) Å, O(12)–Cu(3) = 2.624 (8) Å), and the interatomic distances, while rather long, are within the range observed for axial copper–oxygen bonds.[5] Atom O(14) has somewhat longer interactions with both Cu(1) and Cu(2). The inequivalence of these interactions is not surprising in view of the geometric mismatch between the square-planar Cu_4 array and the tetrahedral perchlorate anion. It is significant, however, that the shortest Cu–$OClO_3$ distance involves Cu(4), which has no significant axial interaction on the opposite side of the macrocycle, while the longest Cu–$OClO_3$ distance is that to Cu(2), which has a strong axial bond to Ox′. These observations support the suggestion that distinct bonding interactions are present, rather than more generalized electrostatic interactions or crystallographic packing effects. To our knowledge, this is the first structurally characterized example of perchlorate binding as a tripod ligand, although a number of bridging perchlorate ions involving one[6] or two[7] oxygen atoms have been reported. Neither the second perchlorate anion nor the solvate water molecule exhibits any significant intermolecular contacts.

The electronic reflectance spectrum of solid **2** (λ_{max} = 620 nm) corresponds closely to the solution spectrum (λ_{max} = 621 nm in dmf), suggesting that the octacopper structure is maintained in solution. The reflectance spectrum of the unrecrystallized material **3** (λ_{max} = 648 nm) is also similar to that of a fresh dmf solution (λ_{max} = 647 nm); however, the solution spectrum changes slowly with time and, after approximately 3 days, is identical with that of **2**. The same spectral change is accomplished within a few seconds in the presence of a noncoordinating base such as triethylamine. Addition of small amounts of acid will reverse the reaction, but excess acid leads to other, as yet unidentified, products. Very similar behavior is observed for the tetracopper complex **1** (λ_{max}(solid) = 670 nm, λ_{max}(in dmf) = 672 nm fresh, changing to 627 nm). Recrystallization of **1** from dmf yields an octacopper complex[8] with a structure very similar to that of **2**. These results will be discussed in detail in a subsequent paper.

The spectroscopic data imply that both **1** and **3** undergo slow dimerization in dmf to yield octacopper complexes and that the reaction is promoted by base and reversed by acid. This behavior can be ascribed to competition for the central atom (Ox) between protons and macrocycle-bound copper atoms (Scheme I). In protic solutions such as ethanol the tetracopper monomer with hydroxide at the center is favored. In less protic dmf solution the octacopper species is preferred but the rate of the interconversion is slow; addition of base increases the rate by promoting dissociation of the hydroxo proton. It might be expected that the dimerization would be reversed in protic solvents; however, due to the very low solubility of **2** in these solvents, we have been unable to test this hypothesis. The core of the octacopper complex (Scheme I) resembles a fragment of a metal oxide structure with Cu–Cu distances of approximately 2.9 Å; it might therefore be expected to show some adsorptive or catalytic properties. This suggests the interesting possibility of carrying out metal-promoted reactions on the open faces of the dimer. Investigations on the binding of substrates other than perchlorate are in progress. Interactions between the metal centers are also of interest; preliminary magnetic studies indicate strong antiferromagnetic coupling within the complex. The total magnetic moment for the system falls from 2.303 μ_B at 300 K to 0.149 μ_B at 6 K; the corresponding figures for the tetranuclear complex **1** are 2.512 and 0.737 μ_B. The slight increase in antiferromagnetic coupling in the octacopper complex may indicate some exchange between the two macrocycles, via the Cu(2)–Ox′ and Cu(2′)–Ox bridges. A detailed study and theoretical analysis of the magnetic results is under way.[9]

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Supplementary Material Available: Tables of atomic coordinates, bond lengths and angles, anisotropic thermal parameters, and H atom coordinates, a fully labeled diagram, and crystallographic details for **2** and electronic spectra (8 pages); a table of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(6) Taylor, I. F.; Amma, E. L. *J. Cryst. Mol. Struct.* **1975**, *5*, 129.

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Department of Chemistry
University of Canterbury
Christchurch, New Zealand

Vickie McKee*
Santokh S. Tandon

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Conductive Molecular Crystals from Three-Dimensional Building Blocks: Synthesis and Characterization of Tris(bis(ethylenedithio)tetrathiafulvalenium) Bis(tris(2-thioxo-1,3-dithiole-4,5-dithiolato)vanadate), $[ET]_3[V(dmit)_3]_2$, and the Corresponding Tetramethyltetraselenafulvalenium Salt

In recent years planar transition-metal bis(dithiolene) and bis(diselenolene) complexes have received attention as building blocks for the design of highly conducting molecular solids[1-5]

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