Multinuclear Complexes

DOI: 10.1002/ange.201005232

Trinucleating Copper: Synthesis and Magnetostructural Characterization of Complexes Supported by a Hexapyridyl 1,3,5-Triarylbenzene Ligand**

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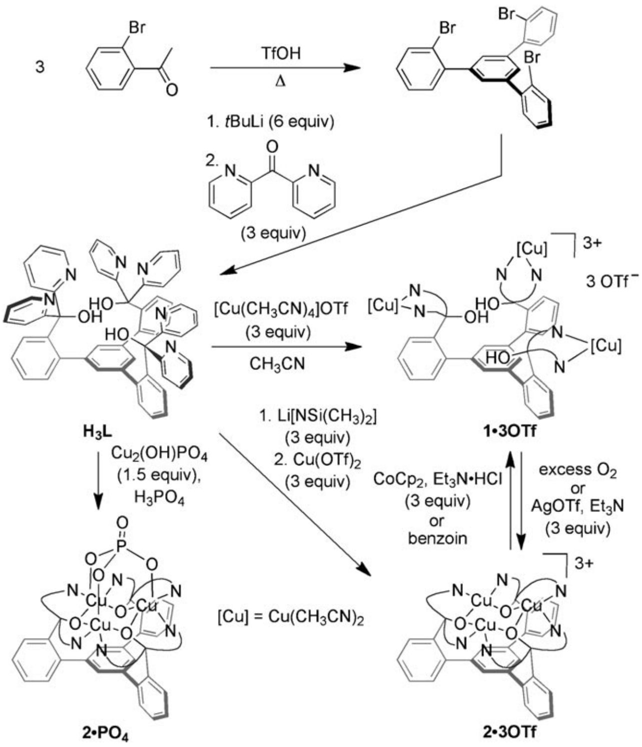
Multimetallic active sites are common in enzymes responsible for the catalysis of multielectron chemical reactions such as O_2 activation, H_2O oxidation, CO_2 reduction, and N_2 reduction.[1] In the context of reproducing the activity of such enzymes and understanding the electronic structure and reactivity of the active sites, the design of ligand architectures capable of nucleating several metal centers is of interest. The active sites of oxidases (laccase, ascorbate oxidase) and oxygenases (particulate methane monooxygenase), which are known or proposed to contain multicopper centers, have been appealing synthetic targets due to the potential applications in fuel cell technology, functionalization of organic substrates, and liquefaction of methane.[2] Treatment of mononuclear copper diamines with O_2 generates a self-assembled Cu_3O_2 moiety; reduction, however, causes the loss of the trinuclear core.[3] Multinucleating ligands represent an appealing alternate approach for accessing multinuclear copper complexes.[4] Of the variety of trinucleating ligands designed and investigated,[5] most are rather flexible and do not enforce cooperative trinuclear reactivity or a well-defined arrangement of the metal centers. Macrocyclic frameworks have shown promise for forming tricopper(II) complexes, but reactivity with O_2 has yet to be reported for most of these systems.[6]

We report here the design of a trinucleating ligand based upon a 1,3,5-triphenylbenzene core that can closely constrain three copper centers. In addition to three bidentate dipyridyl copper binding sites, the ligand variant discussed here (**H_3L**, Scheme 1) contains three hydroxy moieties that may serve as shuttles for the protons necessary for dioxygen reduction to water. The synthesis, oxygen reactivity, and spectroscopic characterization of trinuclear copper(I) and copper(II) complexes based upon this framework are reported.



Scheme 1. Synthesis and reactions of **1** and **2**.

The framework **H_3L** was prepared by lithium–halogen exchange of 1,3,5-tri(2′-bromophenyl)benzene[7] followed by addition of three equivalents of di(2-pyridyl)ketone. Variable-temperature ^{1}H NMR studies were conducted on a solution of **H_3L** in CD_2Cl_2 (see Supporting Information). At room temperature, the ^{1}H NMR spectroscopy signals are broad, indicating site exchange due to fluxional behavior. The spectrum at −50 °C has 24 signals corresponding to an isomer of **H_3L** with one dipyridyl moiety located on the opposite face of the central aryl ring from the other two. At lower temperatures other exchange processes are observed, possibly related to rotation about the aryl–alkyl bonds.

Addition of three equivalents of a copper(I) salt such as $[Cu(CH_3CN)_4]OTf$ or $[Cu(CH_3CN)_4]BF_4$ to **H_3L** (Scheme 1) forms the yellow compounds $[Cu_3(H_3L)]\cdot3X$ (X = OTf, BF_4; **$1\cdot3X$**). The copper centers are each expected to bind two pyridyl nitrogens and solvent molecules or the counteranion.[8] Variable-temperature ^{1}H NMR spectra of **$1\cdot3BF_4$** indicate fluxional processes in solution similar to those of **H_3L**. The three copper centers are not constrained to remain

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[**] We thank Lawrence M. Henling for crystallographic assistance, David Vandervelde for help with NMR experiments, and Harry Gray, Jay Winkler and Liviu Mirica for stimulating discussions. We are grateful to Caltech and NSF GRFP (E.Y.T.) for funding. The Bruker KAPPA APEXII X-ray diffractometer was purchased through an NSF CRIF:MU award to Caltech, CHE-0639094. SQUID data were collected at the MMRC of the Beckman Institute of the California Institute of Technology.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201005232.

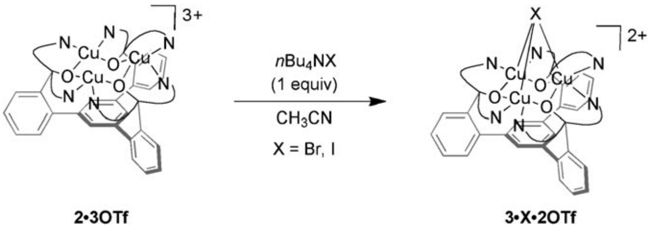
together and likely have rotational freedom about both aryl–aryl and aryl–alkyl bonds. At low temperatures, **1·3 OTf** likely adopts the same conformation as free **H_3L**, with one copper center located on the opposite face of the central aryl ring from the other two copper ions. Addition of excess dioxygen to a propionitrile solution of **1·3 OTf** at −78 °C does not result in a reaction within 24 h. However, the reaction of **1·3 OTf** with dioxygen in acetonitrile over 15 h at room temperature forms a green compound $[Cu_3L]\cdot 3OTf$ (**2·3 OTf**) quantitatively, as determined by ^1H NMR spectroscopy using an internal standard.

In the reaction with O_2, complex **1·3 OTf** formally acts as a source of both protons and electrons for the reduction of between 0.75 and 1 equivalent of O_2 (Toepler pump measurement). The product derived from O_2 in the oxidation of **1·3 OTf** has not been identified to date, but a peroxotitanyl test indicates that H_2O_2 is not present in solution when the conversion to **2·3 OTf** is complete.[9] In the absence of dioxygen, oxidation of **1·3 OTf** in acetonitrile with three equivalents of silver(I) triflate in the presence of triethylamine cleanly forms **2·3 OTf**. Addition of fewer equivalents of silver(I) does not form a mixed valence compound but rather a mixture of **1·3 OTf** and **2·3 OTf** in the expected ratio as judged by ^1H NMR spectroscopy. For the reverse reaction, **2·3 OTf** can be converted to **1·3 OTf** upon addition of three equivalents of cobaltocene in the presence of an acid such as triethylamine hydrochloride or upon treatment with benzoin.

Compound **2·3 OTf** was independently prepared by deprotonation of **H_3L** with three equivalents of base followed by addition of three equivalents of $Cu(OTf)_2$. The solid-state structures of **2·3 OTf** and of a phosphate analogue, **$2\cdot PO_4$**, show that the trinuclear complexes are pseudo-C_3 symmetric alkoxo-bridged trinuclear copper clusters capped by a triflate or phosphate anion (Figure 1).[10] The copper(II) centers and the alkoxo oxygens are linked in a chair-like $[Cu_3O_3]$ core and each copper(II) center is further coordinated by two pyridyl nitrogens from neighboring dipyridyl moieties. The Cu–O(alkoxide) and Cu–N distances are typical of other Cu^{II} compounds (1.91–2.01 Å), although the Cu–O(anion) distances are longer (2.4 and 2.2 Å, respectively), indicating weaker coordination of the triflate or phosphate.

NMR spectroscopy data suggest that the $[Cu_3O_3N_6]$ geometry observed in the solid-state structures remains intact in solution allowing for three potentially accessible coordination sites on the same face of the tricopper unit. The ^1H NMR spectra of both **2·3 OTf** and **$2\cdot PO_4$** contain thirteen signals (see Supporting Information), indicating that the molecules are C_3-symmetric in solution; a higher-symmetry structure would give rise to nine peaks. The peaks are very well resolved, indicating the presence of low-lying excited states of the copper(II) complex that allow for fast electronic relaxation.[6b,11] The signals were assigned by comparing longitudinal relaxation times to distances in the X-ray diffraction structure, as well as using gCOSY experiments and NMR spectra of complexes with a deuterium-labeled ligand (Supporting Information).

To test the lability of the coordinated anions, a solution of **2·3 OTf** in CD_3CN was titrated with $n\mathrm{Bu}_4NX$ (X = Br, I) (Scheme 2). Addition of less than one equivalent of halide leads to gradual changes in the ^1H NMR spectra of the



Scheme 2. Synthesis of **3·X·2 OTf**.

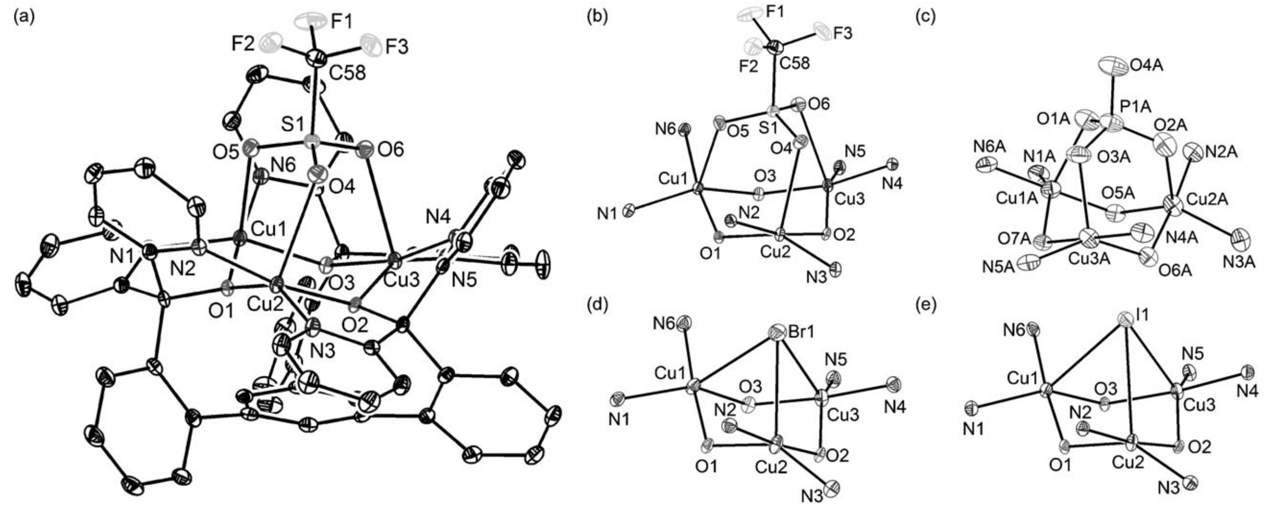


Figure 1. a) Solid-state structure of **2·3 OTf** as 50% thermal ellipsoids. Outer-sphere triflate anions and solvent molecules omitted for clarity. Truncated views of solid-state structures of b) **2·3 OTf**, c) **$2\cdot PO_4$**, d) **3·Br·2 OTf**, and e) **3·I·2 OTf**. Selected bond lengths [Å]: b) Cu–Cu 3.4426(3)–3.4624(3), Cu–O(alkoxide) 1.9087(9)–1.9544(10), Cu–N 1.9350(9)–1.9864(12), Cu–O(OTf) 2.4251(10)–2.5080(10). c) Cu–Cu 3.2948(5)–3.3309(5), Cu–O(alkoxide) 1.9307(15)–1.9944(16), Cu–N 1.972(2)–2.014(2), Cu–O(PO_4) 2.1945(17)–2.2147(16). d) Cu–Cu 3.2959(5)–3.3217(5), Cu–O-(alkoxide) 1.9072(18)–1.9752(19), Cu–N 1.965(2)–2.000(2), Cu–Br 2.8243(5)–2.8851(5). e) Cu–Cu 3.3192(5)–3.3612(5), Cu–O(alkoxide) 1.9086(19)–1.9688(19), Cu–N 1.959(2)–1.993(2), Cu–I 3.0442(5)–3.1308(4).

mixture. After the addition of one equivalent of $n\mathrm{Bu_4NX}$, the spectra of the mixture remain unchanged even upon adding three equivalents of halide. This behavior suggests that only one halide ion can bind to the $[\mathrm{Cu_3O_3}]$ cluster. X-ray diffraction studies of single crystals of **3·Br·2 OTf** and **3·I·2 OTf** confirm that a single halide atom bridges the three copper centers of each cluster, with the triflate anions remaining outer-sphere (Figure 1). Based on the ^{1}H NMR spectra, it is likely that these halide-capped structures are preserved in acetonitrile solution. Similar halide-bridged clusters have previously been observed in tricopper(II) complexes of other ligand systems.[12]

Alkoxo-bridged tricopper(II) clusters with similar $[\mathrm{Cu_3O_3}]$ motifs are known, but generally form by self-assembly of mononuclear copper(II) moieties.[12a,13] The magnetic behavior of these complexes has been studied because spin-frustrated triangular complexes may exhibit interesting ground states. It has been shown that varying the anion bridges of linear[14] and triangular[15] trinuclear copper(II) complexes changes the magnetic coupling, but no systematic study has been reported of these effects on μ-alkoxo-bridged trimers lacking a strongly μ_3-coordinated ligand.[12a,16] Since the synthesis of anion variants of the tricopper(II) complexes supported by the trinucleating ligand **L** described above is facile, a magnetostructural investigation of the effect of the capping anion the $[\mathrm{Cu_3O_3N_6}]$ core was performed.

The variable-temperature magnetic susceptibilities of compounds **2** and **3** were studied, and plots of $\chi_M T$ vs. T are shown in Figure 2. For **2·PO$_4$**, the $\chi_M T$ value at 300 K is close to $1.2\ \mathrm{cm^3\,mol^{-1}\,K}$ as expected for three nearly independent $S=1/2$ centers. The room temperature $\chi_M T$ values for the other complexes are below $1.2\ \mathrm{cm^3\,mol^{-1}\,K}$ due to antiferromagnetic exchange between the copper centers. The slope of these curves decreases at low temperatures, with most approaching a plateau around $\chi_M T = 0.4\ \mathrm{cm^3\,mol^{-1}\,K}$, which agrees with the spin-only value for an $S=1/2$ system. When cooled below 20 K, **2·3 OTf** and **2·3 BF$_4$** have $\chi_M T$ values below $0.4\ \mathrm{cm^3\,mol^{-1}\,K}$, indicating intermolecular antiferromagnetic interactions.[6d,12c,13b]

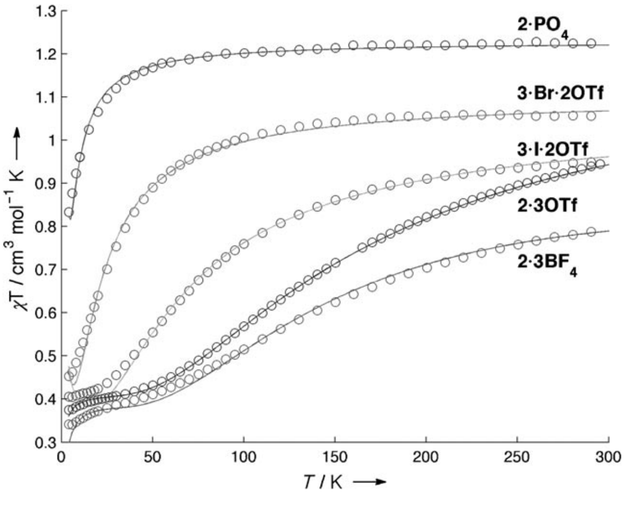


Figure 2. Plots of $\chi_M T$ vs. T for compounds **2** and **3** at an applied field of 0.5 T. Solid lines represent the best fits obtained.

The intramolecular exchange coupling was modeled for a triangle of $S=1/2$ centers, and the energies of the spin states of the systems were calculated using the isotropic spin Hamiltonian [Eq. (1)]. The fits were not significantly improved by varying two coupling constants. As a result, it was assumed that $J=J_{13}$ in an approximately equilateral arrangement of the copper(II) centers. Application of the Van Vleck equation yields the magnetic susceptibility equation [Eq. (2)].[17]

$$H = -2J[(S_1 S_2) + (S_2 S_3)] - 2J_{13}(S_3 S_1) \tag{1}$$

$$\chi_M = \frac{Ng^2\beta^2}{4k(T-\theta)}\left[\frac{5+\exp(-3J/kT)}{1+\exp(-3J/kT)}\right] \tag{2}$$

The fitted magnetic susceptibility parameters for each complex are shown in Table 1. Except for **2·3 BF$_4$**,[18] the fits ($R \approx 10^{-4}$)[19] were obtained by varying only J, g, and the Curie–Weiss parameter θ.[20]

Table 1: Magnetic susceptibility and structural parameters.

Compound	Cu-O-Cu angle [°]	J [cm^{-1}]	g	θ [K]
2·PO$_4$	114.6–118.5	−2.7	2.09	1.7
2·3 OTf	125.9–126.5	−52.0	2.10	−0.6
2·3 BF$_4$	–	−52.2	2.10	−1.6
3·I·2 OTf	116.7–120.8	−22.0	1.95	1.0
3·Br·2 OTf	116.1–118.5	−7.3	1.98	0.8

The above data show that the antiferromagnetic exchange between spins varies considerably with the character of the coordinated anion. Triangular copper(II) complexes that couple through μ_3-hydroxy or μ_3-oxo groups display the strongest antiferromagnetic interactions in structures with large Cu-O-Cu angles, where the bridged clusters are more planar.[15a,b,16,21] Since compounds **2** and **3** contain more weakly coordinated capping anions, exchange between copper(II) centers is expected to occur primarily through the μ-alkoxo moieties. This is consistent with the fact that complexes **3·Br·2 OTf** and **3·I·2 OTf** display antiferromagnetic exchange and have longer Cu–halide bonds (by ca. 0.4 Å) compared to trinuclear copper complexes with μ_3-halide ligands in which ferromagnetic exchange is proposed to occur through the μ_3-halide.[15b] Furthermore, the complexes containing the least coordinating anions in the series, **2·3 OTf** and **2·3 BF$_4$**, show the largest exchange.

The facially coordinated capping ligand distorts the geometry of the $[\mathrm{Cu_3O_3}]$ core and changes the Cu-O-Cu angles (Table 1). As the capping ligand binds more strongly, the $[\mathrm{Cu_3O_3}]$ core distorts from a planar geometry by decreasing the Cu-O-Cu angles; this correlates with a weakening of antiferromagnetic exchange. This behavior is consistent with the solid- and solution-state EPR spectra of **2·PO$_4$** at temperatures below 20 K, which show the expected signal at $g \approx 2$ corresponding to the $S=1/2$ state as well as a broad lower field signal proposed to arise from a $S=3/2$ state (Supporting

Information).[22] The populations of the two states vary with temperature, indicating a spin equilibrium with the doublet being the ground state. Compound **2·3OTf**, with a more negative J and thus a larger doublet–quartet energy splitting, does not display an EPR signal arising from the $S = 3/2$ state at low temperatures.

A linear dependence of the exchange interactions of dihydroxo-bridged copper(II) dimers with the Cu-O-Cu angles has been reported.[23] Similar trends extended to more complex systems have been complicated by the presence of multiple exchange pathways. Nevertheless, a non-linear trend has been reported for the Cu-(μ_3-X)-Cu angle for μ_3-bridged trimers.[15b,c] The present compounds allow for a systematic magnetostructural study. When the exchange parameters of compounds **2** and **3** are plotted against the average Cu-O-Cu angle in the respective structure, the data indeed follow an approximately linear trend (Figure 3). This dependence also holds when the available structural and magnetic data from other μ-alkoxo and μ-hydroxo copper(II) trimers of pseudo-C_3 symmetry are included.[6d,12a,13b,24] This behavior reflects the exchange through the μ_2-O donors rather than the weakly coordinated capping ligands. The exchange parameters for tricopper systems with μ_3-hydroxy or μ_3-oxo ligands do not lie along this trend. It is noteworthy that the linear trend holds despite significant variations in the nature of the non-bridging ligands (pyridines, alkyl amines, pyrrolides, and alkoxides). This magnetostructural behavior suggests that, as in hydroxo-bridged dimers, there is a Cu-O-Cu angle at which the copper centers switch from antiferromagnetic to ferromagnetic coupling. Such distorted structures may be difficult to access, however.

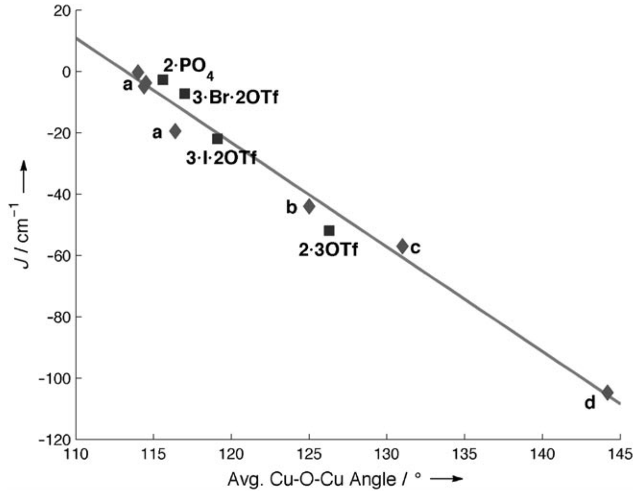


Figure 3. J vs. bridge angle (ϕ) for a series of alkoxo- or hydroxo-bridged copper(II) trimers. (■) This work. (◆) a) Ref. [12a]; b) Ref. [6d]; c) Ref. [13b]; d) Ref. [24]. Straight line was calculated from $J = -3.41\,\phi + 386$ cm^{-1}.

In summary, a trinucleating ligand containing six pyridine and three alcohol donors on a 1,3,5-triphenylbenzene platform has been used to assemble a tricopper(I) complex which, upon reaction with O_2, leads to alcohol deprotonation and oxidation of copper. The C_3-symmetric trinuclear core is robust by spectroscopy and chemical reactivity. Changing the capping anion facially coordinated to the tricopper(II) cluster alters the Cu-O-Cu angle to lead to changes of the antiferromagnetic exchange coupling between neighboring copper ions, providing a strategy for tuning the magnetism of the trinuclear core. The observed linear trend between the antiferromagnetic exchange coupling and the Cu-O-Cu angle holds for a variety of previously reported trinuclear species providing an extension to more complex systems of the classical dependence observed for dihydroxo-bridged copper(II) dimers. Complexes of the present ligand provide a versatile framework for mechanistic studies related to O_2 and other small-molecule reactivity at trinuclear centers and current studies are targeted toward further exploring Cu_3–O_2 chemistry as well as a variety of first-row transition metal trinuclear clusters.

Received: August 21, 2010
Revised: October 24, 2010

Keywords: copper complexes · dioxygen · magnetic properties · multinucleating ligands · trinuclear clusters

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[18] An improved fit for the magnetism susceptibility of compound **2·3BF**$_4$ was calculated by including a temperature-independent magnetism of -500×10^{-6} cm^{-1}. This discrepancy may be due to diamagnetic impurities such as an unknown number of solvent molecules or other salts.

[19] The data were fit by minimizing: $R = \sum|(\chi_{\mathrm{M}}T)_{\mathrm{obs}}-(\chi_{\mathrm{M}}T)_{\mathrm{calcd}}|^2/\sum(\chi_{\mathrm{M}}T)^2_{\mathrm{obs}}$.

[20] The parameter θ was included in the magnetic susceptibility equation to account for antiferromagnetic ($\theta<0$) or ferromagnetic ($\theta>0$) intermolecular interactions. See Ref. [15e], [23a] for examples.

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