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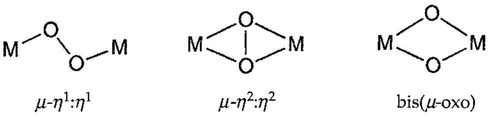
[20] The values for the helical twisting power (HTP) of the newly synthesized compounds are as follows: **33**: −8.3 μm^{-1}; **34**: +35.0 μm^{-1} (determined from a 1% w/w solution in the Merck mixture MLC-6260 at 20°C).

[21] The application-oriented evaluation of liquid crystals for use in LCDs is centered around "virtual" clearing temperatures, electrooptic parameters, and viscosities. These data are obtained by extrapolation from a standardized nematic host mixture: $T_{\mathrm{NI,extr}}$, $\Delta\varepsilon$, Δn, and γ_1 were determined by linear extrapolation from a 10% w/w solution in the commercially available Merck mixture ZLI-4792 ($T_{\mathrm{NI}} = 92.8$°C, $\Delta\varepsilon = 5.27$, $\Delta n = 0.0964$). The values thus obtained are empirically corrected for changes in the order parameter. For the pure substances the mesophases were identified by optical microscopy, and the phase transition temperatures by differential scanning calorimetry (DSC).

A Short Copper–Copper Distance in a (μ-1,2-Peroxo)dicopper(II) Complex Having a 1,8-Naphthyridine Unit as an Additional Bridge**

Chuan He, Jennifer L. DuBois, Britt Hedman,*
Keith O. Hodgson,* and Stephen J. Lippard*

Proteins that utilize transition metal ions to activate molecular oxygen perform a variety of functions.[1–4] Peroxo-bridged dimetallic species are important intermediates in these processes. The geometry of a bound peroxide group may play an important role in determining its reactivity and thus the function of the protein. Comparison of synthetic dinuclear peroxo complexes with the protein cores has helped elucidate the structures and properties of many such biological species. The μ-η^2:η^2 side-on geometry is presently known only in dicopper-containing proteins,[2] whereas the μ-η^1:η^1 (μ-1,2-peroxo)-bridged structure occurs in diiron-containing proteins (Scheme 1).[3]



Scheme 1. Selected geometric units formed upon the reaction of dioxygen with dimetallic transition metal centers.

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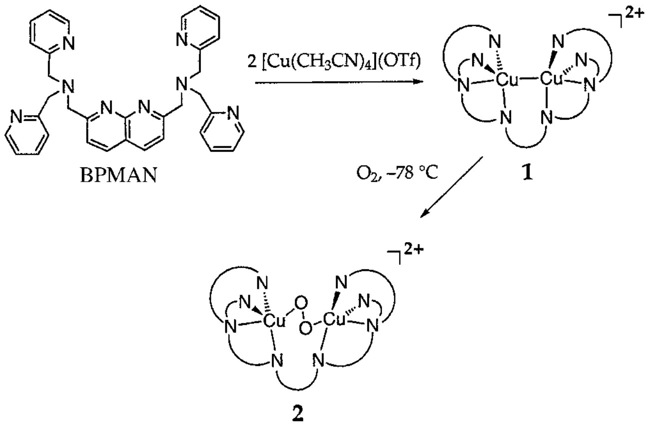
0044-8249/01/11308-1532 $ 17.50+.50/0

Dicopper(II) model complexes with μ-η^2:η^2 side-on-bound peroxide groups have metal–metal separations of about 3.5 Å,[5,6] whereas a *trans*-(μ-1,2-peroxo)dicopper(II) model complex exhibits a substantially longer copper–copper separation (4.36 Å).[7] The structures of three (μ-1,2-peroxo)diiron(III) complexes were determined several years ago, and the metal–metal distances ranged from 3.327 to 4.000 Å.[8–10] A recent extended X-ray absorption fine structure (EXAFS) study of a (μ-1,2-peroxo)diiron(III) intermediate in ferritin oxidation revealed a unique, μ-1,2-type peroxide bridge with a very short iron–iron separation of about 2.53 Å, a value thus far unprecedented for such species.[11] The unusual geometry was suggested to favor release of H_2O_2 from the (peroxo)diiron(III) intermediate, and the presence of two additional single-atom bridges was postulated to account for the short metal–metal distance.

We report here the discovery of a short (ca. 2.84 Å) copper–copper distance in a (μ-1,2-peroxo)dicopper(II) species having only 1,8-naphthyridine as an additional bridge. The rigid ligand scaffold used to assemble this unit seems well suited to afford short metal–metal distances in (μ-1,2-peroxo) dinuclear complexes. This finding is significant since it demonstrates that the presence of single-atom bridges may not be required to afford short metal–metal distances in (μ-1,2-peroxo)dimetallic centers. The short metal–metal separation observed here is very similar to those in bis(μ-oxo)dicopper(III) complexes (ca. 2.8 Å).[12–14] Thus the present complex may model key intermediates in the formation of μ-η^2:η^2 side-on peroxo structures in dicopper systems and in the conversion of (μ-1,2-peroxo) to bis(μ-oxo) species in dioxygen activation by diiron centers.

The 1,8-naphthyridine-based ligand 2,7-bis[bis(2-pyridylmethyl)aminomethyl]-1,8-naphthyridine (BPMAN) was employed as the dinucleating ligand.[15] The dicopper(I) compound $[Cu_2(bpman)](OTf)_2$ (**1**; OTf = $^-OSO_2CF_3$) was prepared by allowing one equivalent of BPMAN to react with two equivalents of $[Cu(CH_3CN)_4](OTf)$ in CH_2Cl_2 and was crystallized from CH_2Cl_2/Et_2O (Scheme 2). Each copper ion is coordinated to four nitrogen atoms from BPMAN and has distorted trigonal-bipyramidal geometry if a Cu–Cu interaction is included (Figure 1).[16] The copper–copper distance is short (2.5947(15) Å).



Scheme 2. Preparation of **1** and **2**; the OTf counterions for **1** and **2** are not shown.

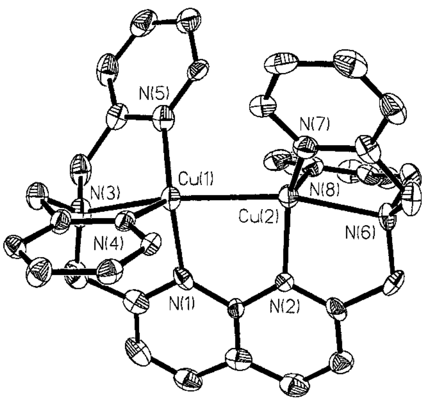


Figure 1. ORTEP diagram of $[Cu_2(bpman)](OTf)_2$ (**1**) showing 40% thermal ellipsoids and selected atom labels. Selected bond lengths [Å] and angles [°]: Cu(1)-N(1) 2.038(8), Cu(1)-N(3) 2.202(8), Cu(1)-N(4) 2.034(7), Cu(1)-N(5) 2.003(8), Cu(2)-N(2) 2.019(7), Cu(2)-N(6) 2.184(7), Cu(2)-N(7) 1.959(8), Cu(2)-N(8) 2.122 (8), Cu(1)···Cu(2) 2.5947(15); N(3)-Cu(1)-Cu(2) 162.5(2), N(1)-Cu(1)-N(3), 80.9(3), N(1)-Cu(1)-N(5) 126.5(3), N(1)-Cu(1)-N(4) 104.8(3), N(6)-Cu(2)-Cu(1) 167.6(2), N(2)-Cu(2)-N(6), 82.4(3), N(2)-Cu(2)-N(7) 140.5(3), N(2)-Cu(2)-N(8) 90.4(3).

Treatment of **1** with O_2 at $-78\,^\circ C$ in CH_2Cl_2 gave a deep violet species **2** after an induction period of several minutes. The low-temperature UV/Vis spectrum revealed the exact same features as those of a well-characterized *trans*-(μ-1,2-peroxo)dicopper(II) compound prepared in the presence of two tris[(2-pyridyl)methyl]amine (TPA) ligands (λ_{max} = 415 nm (sh), ε = 2333 $M^{-1}cm^{-1}$; λ_{max} = 505 nm, ε = 10500 $M^{-1}cm^{-1}$; λ_{max} = 620 nm, ε = 5400 $M^{-1}cm^{-1}$),[7] as depicted in Figure 2.

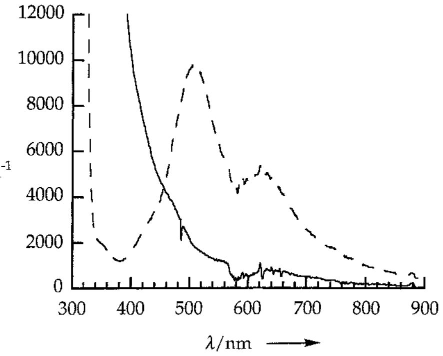


Figure 2. UV/Vis spectra for the reaction of **1** (0.06 mM) with O_2 in CH_2Cl_2. Solid line: **1** at $-78\,^\circ C$; dashed line: **2** generated from oxygenation of the solution of **1** at $-78\,^\circ C$.

A resonance Raman spectrum of **2** acquired in CH_2Cl_2 at $-78\,^\circ C$ with excitation at 514.5 nm displayed O_2-dependent bands at 831 cm^{-1} and 561 cm^{-1}, which disappeared when the solution was allowed to warm (Figure 3). The oxygenation experiment was repeated with an isotopically labeled 1:2:1 statistical mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$. The resulting purple solution exhibited three O_2-sensitive bands at 831 cm^{-1}, 813 cm^{-1} and 787 cm^{-1} having an intensity ratio of approximately 1:2:1, as shown in the inset of Figure 3. The values calculated based on a simple harmonic oscillator model for the $^{16}O^{18}O$ and $^{18}O_2$ derivatives are 808 cm^{-1} and 783 cm^{-1}, respectively. This result not only confirms the presence of a

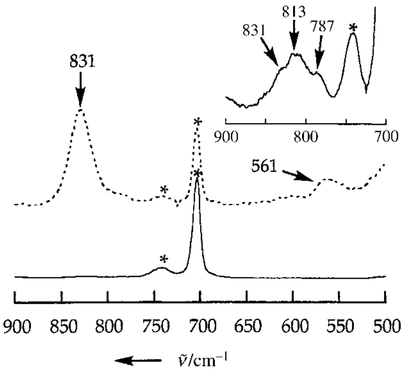


Figure 3. Resonance Raman spectra of **1** (lower curve) and **2** (upper curve) in CH_2Cl_2 at −78 °C. The inset shows the spectrum of the partially generated **2** from reaction of **1** with a 1:2:1 statistical mixture of $^{16}O_2$, $^{16}O^{18}O$, and $^{18}O_2$ (* solvent bands).

peroxide bridge, but also reveals it to bind in a symmetrical bridging fashion.

Different peroxide bridging modes between two copper(II) ions display very characteristic O–O stretching bands in Raman spectra. The O–O stretch band of **2** matches very well with that of a TPA-based *trans*-(μ-1,2-peroxo)dicopper(II) complex, which occurs at 832 cm^{-1} (788 cm^{-1} with $^{18}O_2$), and where there is also an O_2-sensitive band at 561 cm^{-1}.[17] These results strongly imply the existence of a symmetrical μ-1,2-peroxide bridge in **2**. Other bridging modes are inconsistent with the Raman results.

To obtain further structural information about this species, X-ray absorption spectroscopy (XAS) was applied to examine frozen CH_2Cl_2 solutions of **1** and **2**. The Cu K-edge for **1** (Figure 4) features a weak 1s→4p transition at about 8982 eV, in accord with the value expected for a dicopper(I) complex. The K-edge for **2** has a weak 1s→3d transition at about 8979 eV, characteristic of Cu^{II}. The EXAFS data of **1** are well fit by a structural model that includes 2.5 nitrogen atoms at 2.02 Å and 1.5 nitrogen atoms at 2.17 Å. The Cu⋯Cu distance of 2.52 Å determined from fits to the EXAFS data for the frozen solution of **1** is slightly shorter than the distance of 2.59 Å found in the solid-state structure. The difference may reflect some degree of relative motion between the copper ions in solution. The Fourier transform (FT) of the EXAFS for **1** has two prominent features (Figure 5). The first peak is fit as scattering from coordinated ligands and the second peak is entirely compensated by scattering between the two copper ions. There are no additional prominent outer peaks due to longer distance Cu⋯C scattering.

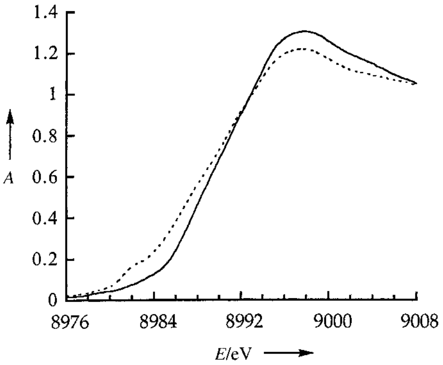


Figure 4. X-ray absorption Cu K-edges for **1** (dotted line), and **2** (solid line). A = normalized absorption.

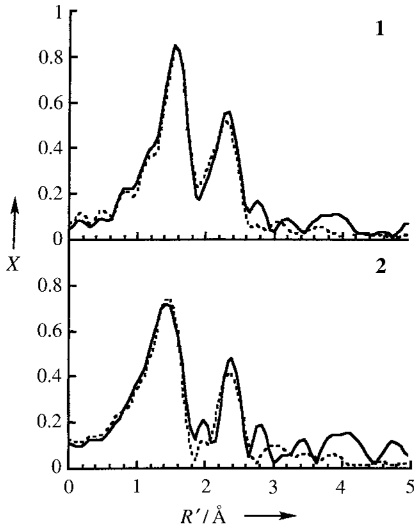


Figure 5. Fourier transforms of EXAFS data (solid lines) and representative fits to data (dotted lines) for **1** and **2**. X = Fourier transform magnitude.

The FT of the EXAFS data for **2** is similarly composed of two major peaks (Figure 5). The first peak is fit as scattering from three oxygen or nitrogen atoms at 1.95 Å plus an additional two at 2.08 Å. Contraction of the average Cu–ligand distance from about 2.07 Å in **1** to about 2.00 Å in **2** is consistent with copper oxidation. The second FT peak at R′ ~ 2.4 Å can be fit equivalently as scattering from 1 Cu or 4 C atoms (per Cu) at about 2.8–2.9 Å. Cu⋯C scattering did not contribute significantly to the fit for **1**, the Cu⋯Cu vector being well separated from the Cu⋯C contribution. Since complex **2** directly derives from **1**, the Cu⋯C contribution would be small owing to internal canceling, as in **1**. A fit including a Cu⋯Cu vector of about 2.84 Å is therefore the most reasonable interpretation.

Alternative peroxide structures, as well as tetranuclear species, are highly unlikely based on Raman and UV/Vis results. A tetranuclear species would also most likely be highly charged and insoluble in CH_2Cl_2. A tetranuclear species with a charge of +2 and having a related naphthyridine-based ligand does not dissolve in CH_2Cl_2.[18]

At −78 °C, compound **2** decays to another species **3** with a half-life of about 2.5 h. An isosbestic point was observed at 382 nm during the decay. The product **3** has absorption peaks at 345 nm ($\varepsilon = 4750\,M^{-1}cm^{-1}$) and 670 nm ($\varepsilon \sim 100\,M^{-1}cm^{-1}$), very similar to those in a putative (μ-oxo)dicopper(II) compound reported recently.[19] Compound **3** is unstable at higher temperatures and was not isolated.

In conclusion, by employing a 1,8-naphthyridine-based dinucleating ligand that can impose a rigid ligand scaffold, the peroxo-bridged dicopper(II) complex **2** was prepared by reacting the dicopper(I) precursor **1** with O_2 at low temperature. Spectroscopic properties and an isotope labeling experiment for **2** indicate that it contains a μ-η^1:η^1 peroxide. The EXAFS studies reveal a short Cu⋯Cu distance of about 2.84 Å, which supports a previous conclusion that (μ-1,2-

peroxo) dinuclear species can have quite short metal–metal distances.[11] This result suggests that a rigid ligand environment imposed at a protein active site could give rise to similar short metal–metal separations in (μ-1,2-peroxo) dinuclear species lacking single-atom bridges. The short metal-metal separation revealed in **2** is very close to those in bis(μ-oxo)dicopper(III) complexes (~2.8 Å)[12–14] and shorter than those in dicopper(II) species with μ-η^2:η^2 side-on peroxides (~3.5 Å).[5, 6] Such species could be present as intermediates in conversion of μ-1,2-peroxide to μ-η^2:η^2 side-on peroxides or bis(μ-oxo) species at biological and synthetic dinuclear centers.

Experimental Section

Preparation of compound **1**: A portion of BPMAN (50 mg, 0.090 mmol) in CH_2Cl_2 (0.5 mL) was added to $[Cu(CH_3CN)_4](OTf)$ (69 mg, 0.180 mmol) in CH_2Cl_2 (1 mL). The resulting brownish yellow solution was allowed to stir for 30 min. Vapor diffusion of Et_2O into this solution yielded yellow-brown plates suitable for X-ray crystallography (70 mg, 80 %). ^1H NMR (CD_2Cl_2, 300 MHz): $\delta = 4.485$ (s, 8 H), 4.684 (s, 4 H), 7.169 (t, $J = 6.5$ Hz, 4 H), 7.54–7.60 (m, 6 H), 7.820 (t, $J = 8$ Hz, 4 H), 8.366 (d, $J = 8$ Hz, 6 H); FT-IR (KBr): $\tilde{\nu} = 3066$ (m), 2938 (m), 2906 (m), 2855 (w), 1604 (s), 1506 (w), 1477 (w), 1440 (s), 1368 (w), 1277 (s), 1224 (m), 1155 (s), 1030 (s), 979 (w), 958 (m), 898 (w), 855 (w), 765 (s), 733 (w), 637 (s) cm^{-1}; elemental analysis calcd for $C_{37}H_{34}N_8O_6S_2F_6Cl_2Cu_2$ (**1**$\cdot CH_2Cl_2$): C 41.81, H 3.22, N 10.54; found: C 41.75, H 2.88, N 10.41.

XAS data collection: X-ray absorption spectra were measured on unfocused wiggler beamline 7-3 (sample **2**, 5 mM) and focused beamline 9-3 (sample **1**, 5 mM) at the Stanford Synchrotron Radiation Laboratory (SSRL), with the ring operating at 3 GeV and 50–100 mA. Samples were maintained at 10 K inside an Oxford Instruments CF1208 liquid He continuous flow cryostat. A Si(220) double-crystal monochromator was used, with harmonic rejection performed by detuning (beamline 7-3) or through a harmonic rejection mirror (beamline 9-3). Vertical 1-mm pre-monochromator slits were used to minimize beam divergence. Spectra were measured in fluorescence mode, using an ionization chamber Lytle detector for **1** with Ni filter and Soller slits and a 30-element Ge detector for **2**. Of the available 30 channels, 14 were operative. The spectrum of Cu foil was measured as an external calibrant before and after sets of four (beamline 7-3) or ten scans (beamline 9-3). External calibration was necessary as the sample matrix (CH_2Cl_2) was highly photoabsorbing such that minimal beam intensity was transmitted by the samples. The first inflection point of the Cu K-edge was set to 8980.3 eV. Multiple scans of the K-edge and EXAFS data were measured over the range 8668–9868 eV and averaged. Although EXAFS data were measured to $k = 15$ Å^{-1}, spectra were truncated at $k = 13$ Å^{-1} due to noise in the data at higher values of k.

XAS data reduction and analysis: For each spectrum, a smooth second-order polynomial was fit to the pre-edge region, then extrapolated across the entire energy range and subtracted from the data. A three-segment spline (polynomial curves of orders 2, 3, 3) was fit to and subtracted from the EXAFS region, and the data normalized at 9000 eV, using the SPLINE program (Ellis, SSRL). EXAFS data were k^3-weighted, where the photoelectron wave vector $k = [2m_e/(E - E_0)/(h/2\pi)^2]^{1/2}$, E = energy, E_0 = energy of the onset of the EXAFS, and m_e = the mass of an electron. Phase and amplitude functions ($\phi_{as}(k)$ and $A_s(k)$) calculated by feff 6.0[20] for each absorber–scatterer (a–s) pair were used in creating a simulated EXAFS spectrum, which was adjusted by a least-squares fitting process to match the data (using the EXAFSPAK programs).[21] Absorber–scatterer distances (R_{as}) and Debye–Waller factors (σ^2_{as}) were varied for each equivalent set of backscattering atoms. Coordination numbers (N_s) were generally kept constant, according to the known crystal structure for **1** and/or the hypothetical structural model being tested. Other parameters included in the fits were E_0 and S_0^2, where S_0^2 is the many-body amplitude reduction factor accounting for spectral dampening due to shake-up or shake-off processes. E_0 was allowed to vary within ranges defined by fits to similar, crystallographically characterized Cu complexes. S_0^2 was fixed at 0.9. Fits were constructed in a sequential process, where components to fits were included on the basis of visual improvement to the EXAFS fit and reduction in a goodness-of-fit parameter R, where $\mathrm{R} = R^2/[2\Delta k\Delta R'/\pi) -$ no. variables in fit], $R = [\Sigma k^6(\chi_{obs} - \chi_{calcd})^2/\mathrm{N}]^{1/2}$, N = the number of points in the EXAFS spectrum, Δk = the range over which the EXAFS was fit (3–13 Å^{-1}), and $\Delta R'$ = the range of the Fourier transform over which the fit was made ($\Delta R' = 0$–5 Å).

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[16] Crystal data for **1**: Yellow plates of dimensions 0.20 × 0.15 × 0.03 mm. Monoclinic, space group $P2_1/c$, $a = 22.6111(6)$, $b = 10.2211(3)$, $c = 16.8878(4)$ Å, $b = 98.2550(10)°$, $V = 3862.51(18)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.682$ mg m^{-3}. The data were collected at −85 °C on a Siemens SMART diffractometer equipped with a CCD detector ($2\theta_{max} = 45°$) using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$). A total of 15477 reflections were measured, of which 5040 were unique. The structure was solved by the direct methods program XS and refined by full matrix least-squares on F^2 and Fourier techniques using SHELXTL-PLUS. Absorption corrections were applied with the program SADABS. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned idealized positions and given a thermal parameter 1.2 times the thermal parameter of the carbon atom to which each was attached. Final residuals were $R = 0.0848$ and $wR^2 = 0.1947$ for 3350 observed reflections having $I > 2\sigma(I)$ and 477 variable parameters. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-149293. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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[21] This software was written by Dr. G. N. George, SSRL, and can be freely downloaded from the world wide web: http://www-ssrl.slac.stanford.edu/exafspak.html.