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A Bis(μ-oxo)dicopper(III) Complex with Aromatic Nitrogen Donors: Structural Characterization and Reversible Conversion between Copper(I) and Bis(μ-oxo)dicopper(III) Species

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Transformation of (μ-η^2:η^2-peroxo)dicopper(II) complexes bearing sterically bulky tridentate *N,N′,N″*-trisubstituted tacn[2] to square pyramidal bis(μ-oxo)dicopper(III) complexes has been reported by Tolman et al.[3] In certain instances, they have observed a monooxygenase activity of the bis(μ-oxo)dicopper(III) complexes for the coordinated ligand as substrate. A different type of square planar bis(μ-oxo)dicopper(III) complexes having peralkylated-1,2-cyclohexanediamine ligands have been also prepared by Stack et al.[4] Very recently, partial formation of a bis(μ-oxo)dicopper(III) complex with a tridentate ligand containing two pyridyl sidearms[5] and a bis(μ-oxo)dicopper(III) complex with a bidentate ligand containing a pyridyl group have been reported.[6] However, there is no crystallographically characterized bis(μ-oxo)dicopper(III) complex having aromatic nitrogen donors. Thus, it is important to explore how the nature of the donor atoms and the stereochemistry of supporting ligands influence the formation, structure, and reactivity of bis(μ-oxo)dicopper(III) complexes.

Karlin et al. have demonstrated that a copper(I) complex having a tetradentate tripodal tpa ligand, $[Cu(tpa)(NCCH_3)]^+$, reacts with O_2 to form a *trans*-(μ-1,2-peroxo)dicopper(II) complex ($[Cu_2(O_2)(tpa)_2]^{2+}$) in a trigonal bipyramidal structure (λ_{max} (ϵ, M^{-1} cm^{-1}) = ~440 nm (4000), 525 nm (11500), and ~590 nm (7600)).[7] Previously we found that $[Cu(Me\text{-}tpa)]^+$ in acetone at −70 °C generates a *trans*-(μ-1,2-peroxo)dicopper(II) species, whereas the reaction of $[Cu(Me_2\text{-}tpa)]^+$ (**1a**) with O_2 ($Cu:O_2 = 2:1$) in acetone at −70 °C does not form a *trans*-(μ-1,2-peroxo)dicopper(II) species, but produces a brown species (**1b**, λ_{max} (ϵ, M^{-1} cm^{-1}) = 378 nm (~22 000, 0.1 mM), 494 nm (330, 10 mM)).[8] Thus, introduction of two 6-methylpyridyl groups into the tpa ligand prevents the formation of *trans*-(μ-1,2-peroxo)dicopper(II) species in a trigonal bipyramidal structure, probably due to a steric requirement of two 6-methylpyridyl groups. However, it is difficult to presume the structure of **1b** from its electronic spectrum, since the spectral feature of **1b** is somewhat different from those of (μ-η^2:η^2-peroxo)dicopper(II)[9] and bis(μ-oxo)dicopper(III) complexes.[3,4] Herein, we report a crystal structure of a brown bis(μ-oxo)dicopper(III) complex, $[Cu_2(O)_2(Me_2\text{-}tpa)_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**) and reversible conversion between **1a** and **1b**.

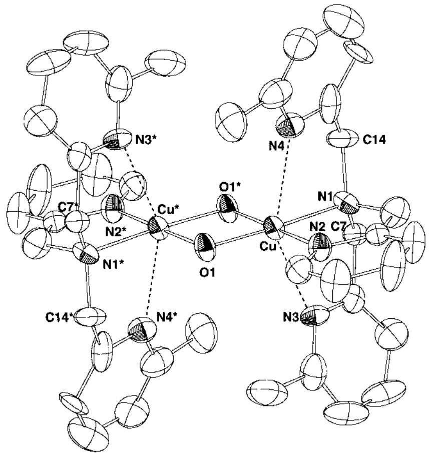

Figure 1. ORTEP view (50% probability) of the complex cation of $[Cu_2(\mu\text{-}O)_2(Me_2\text{-}tpa)_2](PF_6)_2 \cdot 2(CH_3)_2CO$ (**1b**). Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (deg): Cu−O1, 1.806(9); Cu−O1*, 1.799(8); Cu−N1, 1.97(1); Cu−N2, 1.91(1); Cu−N3, 2.48(1); Cu−N4, 2.55(1); O1···O1*, 2.32(1); Cu···Cu*, 2.758(4); Cu−O1−Cu*, 99.8(4); O1−Cu−O1*, 80.2(4).

Complex **1a** has a trigonal pyramidal structure with three pyridyl groups in the trigonal plane and tertiary amine in the apex.[10] Reaction of **1a** with O_2 in acetone/MeOH (10:1) at −78 °C gave a brown solution, from which brown crystals suitable for X-ray crystallography were obtained.[11] Figure 1 shows a crystal structure of the complex cation of **1b** which consists of a centrosymmetric $Cu_2(\mu\text{-}O)_2$ core with the Me_2-tpa nitrogens. Each copper ion has a square planar structure composed of a N_2O_2 donor set with two 6-methyl-2-pyridylmethyl sidearms which interact weakly with each copper ion in the axial positions (2.48(1) and 2.55(1) Å). The average Cu−O (1.803 Å) and Cu···Cu* (2.758(4) Å) distances are substantially shorter than those of bis(μ-hydroxo)dicopper(II) complex, $[Cu_2(OH)_2(Me_2\text{-}tpa)_2](ClO_4)_2$ (**1c**)[10] (1.942 Å and 2.9368(9) Å, respectively), and are comparable to those of bis(μ-oxo)dicopper(III) complexes, $[Cu_2(O)_2(Bn_3\text{-}tacn)_2]^{2+}$ (**3**; 1.806 and 2.794 Å)[3a,c] and $[Cu_2(O)_2(L_{ME})_2]^{2+}$ (**4**; 1.806 and 2.743 Å).[4] The resonance Raman spectrum of **1b** measured in acetone (~10 mM) at −80 °C with 488.0 nm laser excitation showed an isotope-sensitive band at 590 cm^{-1} with $^{16}O_2$ (564 cm^{-1} with $^{18}O_2$) shown in Figure 2 (inset), characteristic of those observed for the bis(μ-oxo)dicopper(III) complexes.[3c,4]

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(2) Abbreviations of ligands used: tpa = tris(2-pyridylmethyl)amine; Me-tpa = bis(2-pyridylmethyl)(6-methyl-2-pyridylmethyl)amine; Me_2-tpa = bis-(6-methyl-2-pyridylmethyl)(2-pyridylmethyl)amine; tacn = 1,4,7-triazacyclononane; Bn_3-tacn = 1,4,7-tribenzyl-1,4,7-triazacyclononane; L_{ME} = *N,N′*-dimethyl-*N,N′*-diethyl-*trans*-(1*R*,2*R*)-cyclohexanediamine; $HB(3,5\text{-}R_2pz)_3$ = hydrotris(3,5-dialkyl-1-pyrazolyl)borate.

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(10) Synthetic procedures, analytical data, and details for X-ray crystallography for **1a-BPh₄**, **1b**, and **1c** are available as Supporting Information.

(11) Crystal data for **1b**, $[Cu_2(O)_2(Me_2\text{-}tpa)_2](PF_6)_2 \cdot 2(CH_3)_2CO$, at −120 °C; monoclinic, $P2_1/c$ (No. 14), a = 11.426(5) Å, b = 15.616(8) Å, c = 15.768(4) Å, β = 107.05(2)°, V = 2689(1) Å^3, Z = 2, $R(R_w)$ = 0.078 (0.107) based on 1780 reflections ($I > 3.00\sigma(I)$) and 335 variable parameters.

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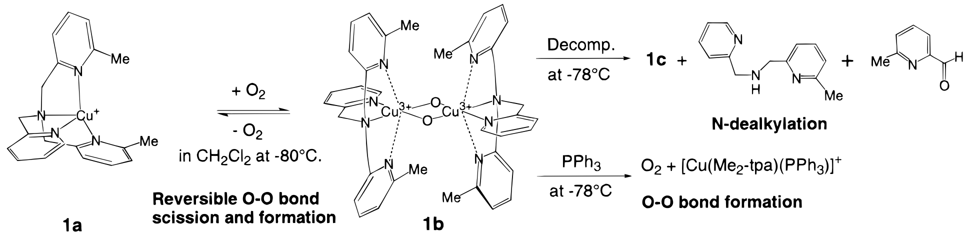
Scheme 1. Reaction Pathways of **1a** and **1b**



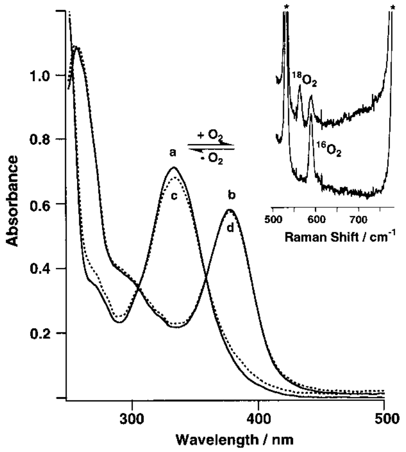


Figure 2. Electronic spectra of **1a** (**a** and **c**) and **1b** (**b** and **d**) in CH_2Cl_2 at -80 °C measured by an optical fiber apparatus with the corrected light path length of 0.315 cm (0.11 mM/Cu_2). The spectra, **a**, **b**, **c**, and **d** show the repetition of the reversible conversion cycle. See text for details (Supporting Information). Inset: Resonance Raman spectra of **1b** in acetone at -80 °C (~10 mM) with 488.0 nm laser excitation. The asterisk bands are solvent bands.

There is no evidence for the presence of a (μ-η^2:η^2-peroxo)dicopper(II) species which is expected to exhibit the O−O stretching vibration at 720−765 cm^{-1} and with an $^{18}O_2$ shift of 40−50 cm^{-1}.[9,12,13] These data indicate that **1b** is assigned as a bis(μ-oxo)dicopper(III) complex, $[Cu_2(O)_2(Me_2\text{-tpa})_2]^{2+}$. Thus, introduction of two 6-methyl group(s) into tpa has significant influence on the reactivity patterns.

It has been shown that the electronic spectra of all of the bis(μ-oxo)dicopper(III) complexes exhibit two intense absorption bands at 390−448 nm and 296−324 nm.[3,4,6] The spectrum of **1b** in CH_2Cl_2 at -80 °C exhibits an intense absorption band at 378 nm ($\epsilon = \sim 19\,000\ M^{-1}\ cm^{-1}$, 0.11 mM/$Cu_2$) and a shoulder at ~490 nm, very similar to that in acetone, and shows an additional intense band at 258 nm ($\epsilon = \sim 36\,000\ M^{-1}\ cm^{-1}$) with a low-energy shoulder at ~300 nm ($\epsilon = \sim 12\,000\ M^{-1}\ cm^{-1}$) as shown in Figure 2. The band at 378 nm in **1b** is higher in energy than those of the corresponding bands of the other bis(μ-oxo)dicopper(III) complexes, indicating that the coordination environment can modulate the transition energy of this band in a wide range (378−448 nm).

It should be noted that a reversible conversion between **1a** and **1b** was observed in CH_2Cl_2 at -80 °C as exemplified in Figure 2; bubbling of N_2 gas into a brown solution of **1b** (spectrum **b**) for ~30 min regenerates **1a** (spectrum **c**) with some decomposition.[14] This cycle can be repeated several times. Thus, **1b** is the first example which exhibits the reversible conversion between copper(I) and bis(μ-oxo)dicopper(III) species depending on the dioxygen partial pressure, although a reversible conversion between copper(I) species and (μ-peroxo)dicopper(II) species,[7,15] and that between (μ-η^2:η^2-peroxo)dicopper(II) species and bis(μ-oxo)dicopper(III)[3a] by changing the solvent have been well demonstrated. A possible O−O bond formation pathway in **1b** may involve a preequilibrium between bis(μ-oxo)dicopper(III) and (μ-η^2:η^2-peroxo)dicopper(II) species, the latter of which appears to regenerate **1a** under N_2 atmosphere. Reaction of **1b** with PPh_3 in acetone at -78 °C under Ar atmosphere facilitated the O−O bond formation, and evolved O_2 in ~88% yield based on a dimer with production of $[Cu(Me_2\text{-tpa})(PPh_3)]^+$, and no measurable $O{=}PPh_3$ was detected, which were confirmed by GC and ^1H NMR measurements (Supporting Information). In the absence of PPh_3, about 20% of O_2 evolution was observed in the same conditions. There is a possibility that if (μ-η^2:η^2-peroxo)dicopper(II) species is present,[16] reaction with PPh_3 could release O_2 to give the corresponding copper(I) complex as observed for $[Cu_2(O_2)(HB(3,5\text{-}{}^iPr_2pz)_3)_2]$,[9a] although a ($\mu$-$\eta^2$:$\eta^2$-peroxo)dicopper(II) species, $[Cu_2(O_2)(N4)]^{2+}$, has been shown not to react with PPh_3 at low temperature.[17] Complex **1b** has a monooxygenase activity for the coordinated ligand as substrate (Supporting Information). Further study is in progress (Scheme 1).

In summary, the tetradentate Me_2-tpa ligand having aromatic nitrogen donors has been shown to produce the bis(μ-oxo)dicopper(III) species **1b**, that can be reversibly converted to the copper(I) species **1a** at -80 °C in CH_2Cl_2 by bubbling of N_2. Thus, reactivity patterns for copper−dioxygen chemistry significantly vary with ligand system. Me_2-tpa has a unique ability to stabilize both copper(I) and copper(III) oxidation states: it can take not only a square planar structure having weak ligation from the axial positions which can fit to the copper(III) oxidation state but also a trigonal pyramidal structure suitable for the copper(I) oxidation state.

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Supporting Information Available: Experimental details including Figures S1−S2, Tables S1−S12 listing crystallographic experimental details, final atomic coordinates, thermal parameters, and full bond distances and angles for **1a-BPh$_4$**, **1b**, and **1c**, and Figures S3−S5 displaying fully labeled ORTEP drawings for **1a-BPh$_4$**, **1b**, and **1c** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(13) We cannot eliminate a possibilty of the presence of (μ-η^2:η^2-peroxo)dicopper(II) species only from the resonance Raman spectrum, since the intensity of O−O stretching band is generally low.

(14) Previously, reversible conversion between **1a** and **1b** could not be found in acetone at -70 °C,[8] because of significant decomposition by bubbling N_2 gas. Reversibility in acetone is poor compared to that in CH_2Cl_2.

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(16) Similar dioxygen evolution was observed for the reaction of $[Cu_2(O_2)(tpa)_2]^{2+}$ with PPh_3,[7,17] although *trans*-(μ-1,2-peroxo) species may not be an active species for O_2 evolution in this system because its formation seems to be difficult due to steric requirement of Me_2-tpa mentioned above.

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