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J. Am. Chem. Soc. **1997,** *119,* 8578−8579

Cu K-Edge XAS Study of the [Cu₂(μ-O)₂] Core: Direct Experimental Evidence for the Presence of Cu(III)

Jennifer L. DuBois,[†] Pulakesh Mukherjee,[†]
Andrea M. Collier,[§] James M. Mayer,[§]
Edward I. Solomon,*,[†] Britt Hedman,*,[‡]
T. D. P. Stack,*,[†] and Keith O. Hodgson*,[†,‡]

Department of Chemistry, Stanford University
Stanford, California 94305
Department of Chemistry, University of Washington
Seattle, Washington 98195
Stanford Synchrotron Radiation Laboratory
Stanford University, Stanford, California 94309

Received May 29, 1997

Copper in its infrequently observed Cu(III) oxidation state has gained attention recently, in particular as a proposed constituent of O_2-cleaving binuclear and trinuclear complexes.[1,2] A few discrete molecular species generally accepted as containing Cu(III) are known.[3] Assignment of the formal Cu(III) oxidation state in these compounds is based on a variety of spectroscopic, electrochemical, and structural evidence. In particular, their very short Cu−ligand bond distances relative to bond lengths in their Cu(II) counterparts suggest a higher oxidation state. However, a direct and unambiguous probe of the metal oxidation state is notably absent.[4] Metal K-edge X-ray absorption spectroscopy (XAS), because of its ability to probe directly the core-electronic environment of the absorbing metal, offers a means of explicitly examining the oxidation state of the copper. A specific probe of the *metal* oxidation state is particularly relevant, given the occurrence of ligand-centered oxidation in some Cu(II) systems.[5] More generally, defining differences between compounds with similar atomic compositions but differing electronic distributions, is potentially relevant to understanding variations in their reactivities. In particular, the $(\mu\text{-}\eta^2\text{:}\eta^2\text{-peroxo})$dicopper(II),[1b,6] bis-μ-oxyl dicopper(II), and bis-μ-oxo dicopper(III)[1] cores are all formally equivalent, though the latter two may be largely indistinguishable by most

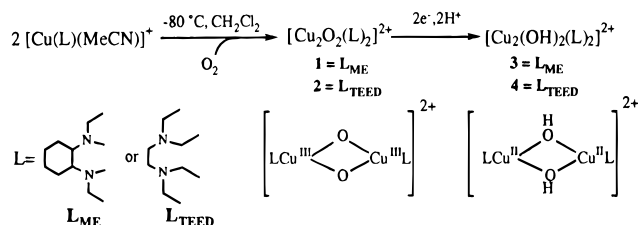**Figure 1.** Binuclear Cu(III) complexes **1** and **2**, and their $2e^-$/ $2H^+$ reduced, bis-μ-hydroxo bridged Cu(II) forms, **3** and **4**.

spectroscopic methods.[7] Here we report on a Cu K-edge XAS study of two binuclear copper complexes $[(L_{ME})_2Cu_2O_2]^{2+}$ (**1**) and $[(L_{TEED})_2Cu_2O_2]^{2+}$,[1,9] (**2**) (Figure 1) showing that these complexes are best formally described as $Cu(III)_2(\mu\text{-}O)_2$ and giving the first direct spectroscopic evidence of stabilized Cu(III) in a Cu_2O_2 rhomb.

The Cu(III) valence state for complex **1** may be proposed on the basis of its remarkably short, crystallographically determined metal−ligand bond lengths.[10] Cu K-edge EXAFS analysis[11] confirms these bond distances as well as the notably short Cu−Cu distance of 2.73 Å for **1**.[13,14] EXAFS analysis of **2** gives similar metrical details (Cu−O = 1.80 Å, Cu−N = 1.92 Å, Cu−Cu = 2.75 Å).[14] Verification of these structures by EXAFS provides an internal check against possible decomposition in these thermally sensitive molecules. Analogous Cu−ligand and Cu−Cu distances are 0.1−0.2 Å longer in the $2e^-$, $2H^+$ reduced bis-μ-hydroxo dicopper(II) forms of **1** and **2** (*i.e.*, **3** and **4**, respectively).[14,15] The Cu−Cu separation is ~0.05 Å longer in related, recently reported Cu_2O_2 complexes (*e.g.*, [(Bn₃-TACN)₂Cu₂O₂]²⁺).[1b,16] For comparison with **1**−**4**, two accepted Cu(III) species—the N₃O tripeptide chelate complex Cu(III)-(H₋₂Aib₃)[3a] and the solid state material KCuO₂[17] —have been

† Department of Chemistry, Stanford University.
§ Department of Chemistry, University of Washington.
‡ Stanford Synchrotron Radiation Laboratory, Stanford University.
(1) (a) Mahadevan, V.; Hou, Z.; Cole, A. P.; Root, D. E.; Solomon, E. I.; Stack, T. D. P. Manuscript in preparation. (b) Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Wang, X.; Young, V.; Cramer, C. J.; Que, L., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996,** *118,* 11555.
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(3) (a) Diaddario, L. L.; Robinson, W. R.; Margerum, D. W. *Inorg. Chem.* **1983,** *22,* 1021. (b) Ruiz, R.; Surville-Barland, A. A.; Anxolabehere-Mallart, E.; Journaux, Y.; Cano, J.; Munoz, M. C. *J. Chem. Soc., Dalton Trans.* **1997,** 745 (and refs. therein). (c) Hanss, J.; Kruger, H.-J. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 2827. (d) Will, S.; Lex, J.; Vogel, E.; Schmickler, H.; Gisselbrecht, J.-P.; Haubtmann, C.; Bernard, M.; Gross, M. *Angew. Chem., Int. Ed. Engl.* **1997,** *36,* 357.
(4) XAS has been performed on a few mixed Cu(II)/Cu(III) high T_c superconducting materials, with some very recent efforts at identifying solid-state Cu(III) XAS standards (*e.g.*, Stoll, S. L.; Bornick, R. M.; Stacey, A. M.; VerNooy, P. D. *Inorg. Chem.* **1997,** *36,* 1838.). At least one Cu K-edge for a discrete molecular Cu(III) complex has been published: Blumberg, W. E.; Peisach, J.; Kosman, D. J.; Mason, H. S. In *Oxidases and Related Redox Systems*; King, T. E., Mason, H. S., Morrison, M., Eds.; Proceedings of the Third International Symposium on Oxidases and Redox Systems; Pergamon Press: Oxford, 1982; pp 207−224.
(5) *E.g.*, Cu(II)−tyrosyl type of systems: (a) (galactose oxidase) Klinman, J. P. *Chem. Rev.* **1996,** *96,* 2541 (and references therein). (b) (glyoxal oxidase) Whittaker, M. M.; Kersten, P. J.; Nakamura, N.; Sanders-Loehr, J.; Schweizer, J. W.; Whittaker, J. W. *J. Biol. Chem.* **1996,** *271,* 681. (c) Wang, Y.; Stack, T. D. P. *J. Am. Chem. Soc.* **1996,** *118,* 13097. (d) Halfen, J. A.; Young, V. G., Jr.; Tolman, W. B. *Angew. Chem., Int. Ed. Engl.* **1996,** *35,* 1687.
(6) (a) Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994,** *94,* 737 (and references therein). (b) Magnus, K. A.; Ton-That, H.; Carpenter, J. E. *Chem. Rev.* **1994,** *94,* 727. (c) Sorrell, T. N.; Allen, W. E.; White, P. S. *Inorg. Chem.* **1995,** *34,* 952. (d) Lynch, W. E.; Kurtz, D. M.; Wang, S. K.; Scott, R. A. *J. Am. Chem. Soc.* **1994,** *116,* 11030.

(7) *E.g.*, complexes **1** and **2** (Figure 1) are EPR silent. Electronic descriptions consistent with this are two d⁸, low-spin Cu(III) centers with two oxide ligands or two Cu(II) antiferromagnetically coupled to two oxyl radical ligands.[8]
(8) Mahapatra, S.; Halfen, J. A.; Wilkinson, E. C.; Pan, G.; Cramer, C. J.; Que, L. Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1995,** *117,* 8865.
(9) L_{ME} = (1*R*,2*R*)-*trans*-N,N′-diethyl-N,N′-dimethylcyclohexanediamine; L_{TEED} = N,N,N′,N′-tetraethylethylenediamine: Thompson, J. S. *J. Am. Chem. Soc.* **1984,** *106,* 8303.
(10) Average Cu−O = 1.81 Å, Cu−N = 1.94 Å.[1a] The Cu−O distance is comparable to the 1.84 Å distance observed in the crystal structure for KCu(III)O₂.[17] Assignment of the +3 oxidation state also formally agrees with the 2:1 stoichiometry of the formation reaction and scission of the dioxygen bond; each copper center provides $2e^-$ to fully reduce the O_2 to two oxide ligands.
(11) Cu K-edge XAS spectra were obtained at Stanford Synchrotron Radiation Laboratory (SSRL): Si(220) double-crystal monochromator, detuned 50% at 9868 eV, transmission on solids in a matrix of BN, internal Cu foil calibration, first Cu foil edge inflection point assigned to 8980.3 eV. Theoretical EXAFS signals $\chi(k)$ calculated using *FEFF* (6.0)[12] and fit to the data using EXAFSPAK (G. N. George, SSRL).
(12) Mustre de Leon, J.; Rehr, J. J.; Zabinsky, S. I.; Albers, R. C. *Phys. Rev. B* **1991,** *44,* 4146.
(13) EXAFS data for **1** and **2** to $k = 15$ Å⁻¹ yield a first coordination shell easily resolvable into two average ligand distances and strong second shell scattering, indicative of (and fit as) a very short and somewhat rigid Cu−Cu unit. Excellent fit quality of the data indicates that the samples used were highly pure with minimal thermal decomposition. EXAFS has been reported for related compounds ([(Bn₃TACN)₂Cu₂O₂]²⁺, [(*i*Pr₃-TACN)₂Cu₂O₂]²⁺) in ref 1b where, possibly due to the limited data *k*-range (10.5 Å⁻¹), an average first coordination shell distance was obtained, and Cu−Cu distances deviated by ~0.07 Å from the crystallographic distances. Cu K-edges were not used to assign the oxidation state of the Cu in these molecules.
(14) EXAFS data and analysis to be published elsewhere.
(15) Crystallographically determined dimensions for the similar complex [(L_{TM})₂Cu(μ-OH)₂] (L_{TM} = (1*R*,2*R*)-*trans*-tetramethylcyclohexanediamine): Cu−Cu = 2.99 Å, average Cu−O = 1.92 Å, average Cu−N = 2.00 Å.
(16) The R₃-TACN ligand is three-coordinate rather than two-coordinate and has considerably greater steric bulk than the bidentate ligands of this study. The lesser steric bulk allows for closer Cu−Cu approach (~0.05 Å) and greater O−O separation (~0.05 Å) in the Cu₂O₂ core.
(17) Costa, G. A.; Kaiser, E. *Thermochim. Acta* **1995,** *269/270,* 591.
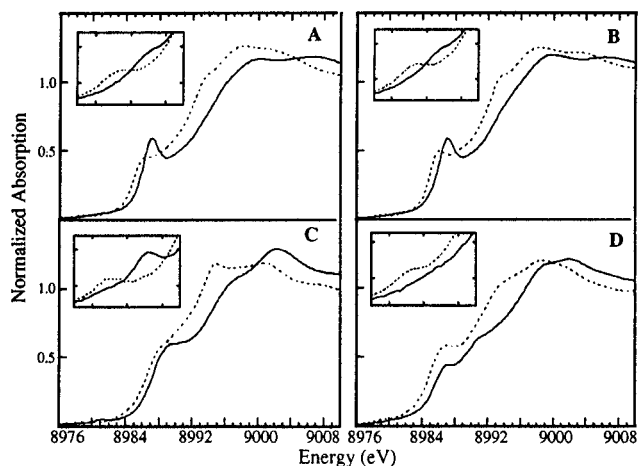
Figure 2. Cu K-edges for Cu(III) (—) and analogous Cu(II) species (- -): (a) complexes **1** and **3**; (b) complexes **2** and **4**; (c) tripeptide complexes Cu(III)(H$_{-2}$Aib$_3$) and Cu(II)(H$_{-2}$Aib$_3$); (d) solid state oxides KCu(III)O$_2$ and CuO. The insets amplify the pre-edges (1s → 3d transition). This is a weak, quadrupole-allowed transition which gains significant intensity via metal 4p$_z$ mixing into the 3d orbitals.[22] Complexes with rigorous centrosymmetry have no 4p$_z$ mixing. Hence the pre-edge for KCuO$_2$, with its rigorously square planar Cu centers, is of very low intensity. A feature at ∼8981 eV is, however, evident in the second derivative of the KCuO$_2$ edge (not shown).

characterized by Cu K-edge XAS, along with their analogous reduced [Cu(II)] compounds Cu(II)(H$_{-2}$Aib$_3$)[3a] and CuO.[18] EXAFS analysis agrees with crystal structures for Cu(III)-(H$_{-2}$Aib$_3$) and KCuO$_2$ and is consistent with a structure for Cu(II)(H$_{-2}$Aib$_3$) having two (axially) coordinated water molecules (at ∼2.30 Å) and bond lengths typical for Cu(II) bound to N and O.[14]

More directly relevant to the characterization of the oxidation state of the copper are the Cu K-edges for this series of compounds. The structures of metal K-edges have been shown to be sensitive to the oxidation state, coordination geometry, and ligand environment of the complexed metal ion.[19] The most unambiguous edge comparisons result from varying just one of these parameters. The 2e$^-$, 2H$^+$ reduced bis-μ-hydroxy dimers (**3** and **4**) are structurally and compositionally very similar to their oxidized counterparts (**1** and **2**). Edge comparisons for these pairs of complexes are almost ideally oxidation state dependent. For the other proposed Cu(III)/Cu(II) pairs, Cu(III)(H$_{-2}$Aib$_3$)/Cu(II)(H$_{-2}$Aib$_3$) and KCuO$_2$/CuO, the Cu(II) species have distant axially coordinated ligands at 2.30 and 2.78 Å, respectively.[14,18] The oxidized species are more rigorously square planar. Examination of the series of edges for these compounds (Figure 2) shows a dramatic general shift to higher energy in edges for both bis-μ-oxo copper complexes, Cu(III)(H$_{-2}$Aib$_3$), and KCuO$_2$, relative to the edges for their counterpart Cu(II) compounds.[20] Similar oxidation-state-dependent shifts in edge energy are also seen in other transition metal complexes.[19,21] These shifts result from the deeper binding energy of the 1s electron effected by the increased effective nuclear charge of the metal ion. Thus the shift in overall edge energy for Cu(III) *vs* a related Cu(II) complex is indicative of an increased copper oxidation state.

Analyses of oxidation-state-dependent changes in K-edge features in complexes of other transition metals have shown shifts in the energy of the pre-edge (*i.e.*, 1s → 3d transition).[21,22] The Cu(II) pre-edge energy is notably insensitive to changes in ligand environment, as demonstrated by a previous systematic study of 40 Cu(II) complexes with a diverse set of ligands.[19] Pre-edges for these complexes as well as for Cu(II) compounds included in this study appear at 8979 ±0.5 eV. Pre-edges for **1**, **2**, Cu(III)(H$_{-2}$Aib$_3$), and KCuO$_2$, however, are shifted by 1.8−2.0 eV to higher energies (inset Figure 2). This energy shift derives from a combination of the deeper binding of the 1s core donor orbital and the effect of the increased ligand field strength, which raises the energy of the Cu(III) 3d$_{x^2-y^2}$ acceptor orbitals. Given the parity of ligands for each Cu(II)/Cu(III) set of compounds and given that the magnitude of the shift is both large (*e.g.*, with respect to 0.5 eV) and similar for the four different Cu(III) species studied, the pre-edge shift appears to be a largely metal-determined phenomenon.[23] A pre-edge feature at 8981 ±0.5 eV thus itself appears diagnostic for the presence of Cu(III) in a molecular complex, *independent of comparisons* to the pre-edges/edges for otherwise identical, reduced compounds.

Other features in the Cu K-edges, notably the intense peak at ∼8986−8988 eV customarily assigned as a 1s → 4p + LMCT shakedown transition,[19] likewise show shifts to higher energy for the oxidized species relative to their Cu(II) counterparts. The energy of this transition has been shown to be strongly influenced by ligand effects, shifting to lower energy in complexes with more covalent metal−ligand bonds.[22a] Therefore, its energy cannot be used as an indicator of oxidation state.[20] This transition appears at a low energy (8985.9 eV) and with marked intensity in the edges for **1** and **2** (Figure 2A), indicating that the Cu−oxide bond is very covalent. The appearance of this transition correlates with intense oxygen → Cu(III) LMCT bands observed for these complexes in the 400 nm region.[24] The final description of compounds **1** and **2** provided by Cu K-edge XAS is consistent with a di-Cu(III) bis-μ-oxo bridged core, with a highly covalent ground state molecular orbital. In the course of this work, structural features suggestive of Cu(III) have been verified by EXAFS and coupled to identifiable features in the Cu K-edge−*i.e.*, a shift in the edge energy and a pre-edge at 8981 ±0.5 eV. This work therefore provides a foundation for the systematic description of Cu(III) sites by XAS.

(18) Åsbrink, S.; Norrby, L.-J. *Acta Crystallogr.* **1970**, *B26*, 8.

(19) Kau, L. S.; Spira-Solomon, D. J.; Penner-Hahn, J. E.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 6433.

(20) The first inflection point of the rising edge is sometimes referred to as the *edge energy*. For Cu complexes, this region of the edge is complicated by a superimposed 1s → 4p + LMCT shakedown transition.[19] For a given Cu oxidation state, the transition, and consequently the first inflection point of the edge, appears at different energies depending on the ligand environment of the absorbing Cu (Figure 2). Therefore, the first inflection point energy is a poor indicator of Cu(II)/Cu(III) oxidation state. The Cu(III) edge shift is more evident at energies higher than the region where this transition occurs, *e.g.*, in the general region of the 1s → 4p main transition (∼8993 eV for Cu(II) complexes).[19]

(21) Examples of studies of oxidation-state dependent edge and/or pre-edge shifts in Cu, Fe, Mn, and V complexes include: (a) **19**. (b) Westre, T. E.; Kennepohl, P.; DeWitt, J. G.; Hedman, B.; Hodgson K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1997**, *119*, 6297. (c) Penner-Hahn, J. E.; Fronko, R. M.; Pecoraro, V. I.; Yocum, C. F.; Betts, S. D.; Bowlby, N. R. *J. Am. Chem. Soc.* **1990**, *112*, 2549. (d) Wong, J.; Lytle, F. W.; Messmer, R. P.; Maylotte, D. H. *Phys. Rev. B* **1984**, *30*, 5596.

(22) (a) Shadle, S. E.; Penner-Hahn, J. E.; Schugar, H. J.; Hedman, B.; Hodgson, K.O.; Solomon, E. I. *J. Am. Chem. Soc.* **1993**, *115*, 767. (b) Hahn, J. E.; Scott, R. A.; Hodgson, K. O.; Doniach, S.; Desjardins, S. E.; Solomon, E. I. *Chem. Phys. Lett.* **1982**, *88*, 595.

(23) At least two XAS studies on compounds with exceptionally short Cu(II)−O bonds exist. These show pre-edges in the expected Cu(II) energy range, indicating that the observed shift in pre-edge energy for the compounds in this paper is not merely an effect of short Cu−O bonds: (a) Sanyal, I.; Karlin, K. D.; Strange, R.W.; Blackburn, N. J. *J. Am. Chem. Soc.* **1993**, *115*, 11259. (b) Zhang, H. H.; Filipponi, A.; DiCicco, A.; Lee, S. C.; Scott, M. J.; Holm, R. H.; Hedman, B.; Hodgson, K. O. *Inorg. Chem.* **1996**, *35*, 4819 (Cu K-edges not published in paper).

(24) Optical data for **1**: ϵ_{406nm} = 28 000 M^{-1} cm^{-1}; **2**: ϵ_{400nm} = 24 000 M^{-1}cm^{-1} (CH$_2$Cl$_2$, −80 °C).