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Synthesis and Characterization of Spin-Delocalized Carboxylate-Bridged Cu(I)−Cu(II) Mixed-Valence Complexes Having Only Oxygen Donor Ligands

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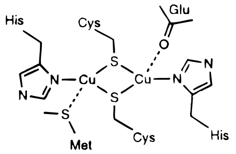
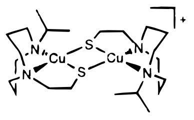
The discovery that the Cu_A centers in cytochrome *c* oxidase and nitrous oxide reductase contain bis(cysteinate)-bridged, fully spin-delocalized dicopper(1.5) units[1] has stimulated renewed interest in mixed-valence copper chemistry. Discrete dinuclear complexes of Cu(I)/Cu(II) have been known for many years,[2] including a handful of class II species,[3,4] but fully delocalized, class III mixed-valence moieties such as Cu_A are rare. The two types of class III complexes currently available either employ a tridentate N_2S ligand, $L^iPrdacoS$, which affords a thiolato-bridged dinuclear core,[5,6] or octaazacryptand macrobicyclic ligands, L^1−L^3 (Table 1).[7a−c] The electronic structures of the Cu_A center and these model complexes have recently been discussed.[8a−c] In the present communication we describe three new class III mixed-valence Cu(I)/Cu(II) complexes having exclusively oxygen-donor ligands, including two bridging carboxylate groups contributed by XDK and/or PXDK.[6,9−11] These complexes have been characterized fully by X-ray crystallographic, solid-state and solution EPR spectroscopic, cyclic voltammetric, electronic spectroscopic, reactivity, and extended Hückel molecular orbital studies. They significantly expand the family of delocalized Cu(I)/Cu(II) compounds and increase our insight into the factors governing the properties of such class III mixed-valent dicopper units.

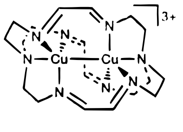
Table 1. Spectroscopic and Structural Data for Class III Mixed-Valence Copper Complexes



Cu_A **(a)**



$Cu(L^{iprdaco}S)_2(OTf)$ **(b)**



$(Cu_2L^2)^{3+}$ **(c)**

	vis/NIR (λ_{max}, nm (ϵ, M^{-1} cm^{-1}))	Cu−Cu dist (Å)	EPR[b] (g (A^{Cu}, G))	ref
a	363 (1200),[a] 480 (3000), 532 (3000), 808 (1600)	2.5−2.7	$g_{min} = 2.003$ (105),[c] $g_{mid} = 2.005$ (116), $g_{max} = 2.203$ (235)	1c−e
b	358 (2700), 602 (800), 786 (sh), 1466 (1200)	2.9306(9)	$g_1 = 2.010$, $g_2 = 2.046$ (36.3), $g_3 = 2.204$ (49.9)	5
c	600−650 (1500−3500),[d] 756 (5000)	2.448[e]	$g_{\parallel} = 2.004$ (11), $g_{\perp} = 2.148$ (111)	7a,b
6 or **7**[f]	536 (1600), 923 (1200)	2.4246(12)	$g_1 = 2.030$ (20.0), $g_2 = 2.158$ (55.0), $g_3 = 2.312$ (122.5)	this work

[a] From *Paracoccus denitrificans* C*c*O (see ref 1d). [b] All parameters were derived from simulated spectra. [c] ^{65}Cu- and [^{15}N]histidine-enriched N_2OR from *P. stutzeri*. [d] Only ranges were reported for the absorption maxima and molar absorptivities. [e] No esd reported. [f] UV−vis and EPR data are for **6**, and the X-ray data for **7**.

From the previously reported dinuclear precursors **1** and **2**,[9] complexes **3**−**7** were prepared by one-electron oxidation with the appropriate silver(I) salt in THF solution (Scheme 1).[12a] Structural studies revealed **3**, **5**, and **7** to have local C_{2v} symmetry with Cu−Cu distances ranging from 2.3988(8) Å in **5**, the shortest value yet reported for such a system, to 2.4246(12) Å in **7** (Table 1 and Figure 1).[12a,b] The X- and Q-band EPR spectra of powdered and frozen 2-Me-THF solution samples of **6** at 2, 9, and 77 K exhibited rhombic signals with readily discernible seven-line copper hyperfine lines. From the 77 K frozen solution spectrum (Figure 1), the parameters given in Table 1 were extracted by simulations.[13] These results and the similar appearance of the EPR spectra of **3** and **5** demonstrate that these $\{Cu_2(XDK)\}^+$ mixed-valence species are fully delocalized, providing the first example of a dicopper mixed-valence species *at 2 K.*

The redox properties of the mixed-valence solvento complex **6** and its dicopper(I) precursor[9] exhibit chemically reversible (i_{pa}/i_{pc} ∼ 1) and electrochemically quasi-reversible (average $E_{1/2} = -218$ mV vs Cp_2Fe^+/Cp_2Fe; $\Delta E_p = 118$ mV, scan rate = 50 mV/s) one-electron behavior as judged by cyclic voltammetry in THF solution. When the measured $E_{1/2}$ value was scaled with the aid of literature data for the SHE/SCE,[14] AgCl/Ag/SCE,[14] and SCE/Cp_2Fe^+/Cp_2Fe (in THF)[15] conversions, the resulting value

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(1) (a) Ferguson-Miller, S.; Babcock, G. T. *Chem. Rev.* **1996**, *96*, 2889−2907. (b) Beinhert, H. *Eur. J. Biochem.* **1997**, *245*, 521−532. (c) Neese, F.; Zumft, W. G.; Antholine, W. E.; Kroneck, P. M. H. *J. Am. Chem. Soc.* **1996**, *118*, 8692−8699. (d) Lappalainen, P.; Aasa, R.; Malmström, B. G.; Saraste, M. *J. Biol. Chem.* **1993**, *268*, 26416−26421. (e) Tsukihara, T.; Aoyama, H.; Yamashita, E.; Tomizaki, T.; Yamaguchi, H.; Shinzawa-Itoh, K.; Nakashima, R.; Yaono, R.; Yoshikawa, S. *Science* **1996**, *272*, 1136−1144. (f) Blackburn, N. J.; deVries, S.; Barr, M. E.; Houser, R. P.; Tolman, W. B.; Sanders, D.; Fee, J. A. *J. Am. Chem. Soc.* **1997**, *19*, 6135−6143.

(2) Dunaj-Jurco, M.; Ondrejovic, G.; Melnik, M. *Coord. Chem. Rev.* **1988**, *83*, 1−28.

(3) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247−422.

(4) (a) Hendrickson, D. N.; Long, R. C.; Hwang, Y. T.; Chang, H. In *Biological and Inorganic Copper Chemistry Volume I*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1985; pp 223−237. (b) Westmorland, T. D.; Wilcox, D. E.; Baldwin, M. J.; Mims, W. B.; Solomon, E. I. *J. Am. Chem. Soc.* **1989**, *111*, 6106−6123.

(5) Houser, R. P.; Young, V. G., Jr.; Tolman, W. B. *J. Am. Chem. Soc.* **1996**, *118*, 2101−2102.

(6) Abbreviations: $L^iPrdacoS$ = 1-isopropyl-5-(ethylthiolato)-1,5-diazocyclooctane; $L^1 = N(CH_2CH_2N{=}CH{-}CH{=}NCH_2CH_2)_3N$; $L^2 = N(CH_2CH_2{-}NH{-}CH_2{-}CH_2{-}NHCH_2CH_2)_3N$; $L^3 = N(CH_2CH_2CH_2N{=}CH{-}CH{=}NCH_2{-}CH_2CH_2)_3N$; H_2XDK = *m*-xylylenediamine bis(Kemp's triacid imide) and H_2PXDK is the propyl analogue; SOMO = singly occupied molecular orbital; SHOMO = second highest occupied molecular orbital.

(7) (a) Harding, C.; Nelson, J.; Symons, M. C. R.; Wyatt, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2499−2500. (b) Harding, C.; McKee, V.; Nelson, J. *J. Am. Chem. Soc.* **1991**, *113*, 9684−9685. (c) Barr, M. E.; Smith, P. H.; Antholine, W. E.; Spencer, B. *J. Chem. Soc., Chem. Commun.* **1993**, 1649−1652.

(8) (a) Williams, K. R.; Gamelin, D. R.; LaCroix, L. B.; Houser, R. P.; Tolman, W. B.; Mulder, T. C.; de Vries, S.; Hedman, B.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1997**, *119*, 613−614. (b) Farrar, J. A.; Grinter, R.; Neese, F.; Nelson, J.; Thomson, A. J. *J. Chem. Soc., Dalton Trans.* **1997**, 4083−4087. (c) Farrar, J. A.; McKee, V.; Al-Obaidi, A. H. R.; McGarvey, J. J.; Nelson, J.; Thomson, A. J. *Inorg. Chem.* **1995**, *34*, 1302−1303.

(9) LeCloux, D. D.; Lippard, S. J. *Inorg. Chem.* **1997**, *36*, 4035−4046.

(10) Herold, S. H.; Lippard, S. J. *J. Am. Chem. Soc.* **1997**, *119*, 145−156.

(11) Rebek, J., Jr.; Marshall, L.; Wolak, R.; Parris, K.; Killoran, M.; Askew, B.; Nemeth, D.; Islam, N. *J. Am. Chem. Soc.* **1985**, *107*, 7476−7481.

(12) (a) Experimental details are provided as Supporting Information, and a full account will be reported elsewhere. (b) X-ray data. **3**: space group $P2_1/n$, $a = 20.203(2)$ Å, $b = 12.0901(10)$ Å, $c = 22.130(2)$ Å, $\beta = 94.522(5)°$, $V = 5388.6(8)$ Å^3, $Z = 4$, $R = 0.0519$, w$R^2 = 0.1259$. **5**: $P2_12_12_1$, $a = 11.0246(1)$ Å, $b = 16.3138(1)$ Å, $c = 27.6753(1)$ Å, $V = 4977.49(6)$ Å^3, $Z = 4$, $R = 0.0471$, w$R^2 = 0.1245$. **7**: $P2_1/n$, $a = 17.4237(9)$ Å, $b = 21.5206(12)$ Å, $c = 18.857(1)$ Å, $\beta = 109.997(1)°$, $V = 6797.0(6)$ Å^3, $Z = 4$, $R = 0.085$, w$R^2 = 0.1814$.

(13) *WINEPR-SimFonia. 1.25*; Bruker Analytik GmbH: Karlsruhe, FRG, 1994−1996.

S0002-7863(98)00502-2 CCC: $15.00

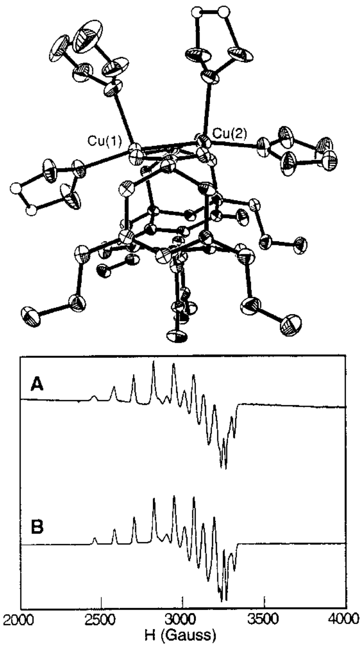
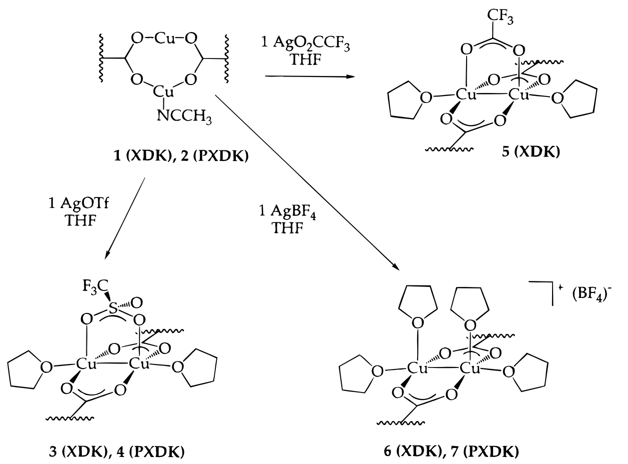


Figure 1. (top) ORTEP diagram of $[Cu_2(PXDK)(THF)_4](BF_4)$ (**7**) with 50% thermal ellipsoids. The PXDK-propyl groups proximal to the Cu centers have been removed for clarity, and the atoms designated as open circles were refined isotropically. (bottom) Experimental EPR spectrum of $[Cu_2(XDK)(THF)_4](BF_4)$ (**6**) acquired at 9.47 GHz in frozen 2-Me-THF solution at 77 K (A), along with a simulation (B), for which the parameters are listed in Table 1.

Scheme 1



of +583 mV vs NHE falls in the +200 to +800 mV range found for blue copper proteins[16] and near the value of +240 mV determined for the Cu_A domain of *Thermus thermophilus* cytochrome *ba*$_3$.[17] These proteins employ soft, nitrogen−sulfur donor sets and impose geometries on copper that are essentially unaltered between the 1+ and 2+ oxidation states.[18] The latter feature is generally assumed to be required to minimize the reorganization energy associated with electron transfer. Here we have achieved biologically relevant potentials and quasi-reversibility with simple carboxylate and oxygen donor ligands, albeit with significant structural reorganization.[9]

Recently, in two independent studies,[8a,b] the electronic structures of Cu_A and its synthetic analogues were analyzed. Superexchange in these class III mixed-valence centers is facilitated by overlap between metal d or ligand p orbitals, or both, depending upon the energetic accessibility of a metal−metal vs a bridging exchange pathway. To investigate the electronic structures of **3**−**7**, we carried out extended Hückel molecular orbital calculations[19,20] on the model complexes $[Cu_2(\mu\text{-}O_2CCH_3)_2(OMe_2)_4]^+$ and $[Cu_2(OH)_2(OH_2)(OMe_2)_4]^+$, which were assigned core structures based on the crystallographic coordinates of **7**. The *z*-axis was taken along the apical copper−OMe_2 bond of one of the copper atoms, and the *x*- and *y*-axes along the copper−copper and copper−carboxylate (hydroxide/water) oxygen vectors, respectively. The SOMO has considerable Cu $d_{x^2-y^2}$/Cu $d_{x^2-y^2}$ σ-antibonding character (~60% for each copper atom), with a lobe from each metal pointed toward the other along the *x*-axis. The 4s (~11% for each copper) and d_{z^2} (~8% for each copper) orbitals also contribute significantly to the SOMO, with the same phases as the $d_{x^2-y^2}$ orbital on each metal. In addition, the p orbital contribution from each ligand is out-of-phase with respect to the adjacent copper orbital lobe. The SHOMO has more d_{z^2} (32%) and 4s (22%) character, with the ligand p orbitals again being out-of-phase with respect to the adjacent copper orbital lobe. In neither the SOMO nor the SHOMO do the carboxylate carbon atoms participate. The superexchange pathway for electron delocalization therefore appears to be accessible only through the Cu−Cu interaction. A reduced Mulliken overlap population analysis revealed a Cu−Cu overlap population of +0.1495 compared to the average overlap population of +0.5362 for CO single bonds in the same structure. Hence the short Cu−Cu distance in the mixed-valence complexes is indicative of a weak metal−metal bond.

The UV−vis spectra of **3**−**7** exhibit a relatively sharp and intense (ϵ = 1200−2000 M^{-1} cm^{-1}) feature which maximizes at ~545 nm (Table 1). In addition, the visible/near-infrared region contains broad absorptions between 700 and 2000 nm. Based on peak shapes, this latter feature appears to arise from a single transition for the BF_4^- complexes, but contains overlapping components in the OTf^- and $O_2CCF_3^-$ complexes. In all cases, these spectral features were unaltered when the complexes were allowed to stand in THF, benzene, or CH_2Cl_2 for several days under N_2. The conductivity of **3**−**7** in THF solutions similarly remained unchanged over the same time period; the OTf^- and $O_2CCF_3^-$ adducts are nonelectrolytes, whereas the BF_4^- salts are 1:1 electrolytes judging from the slopes of conductivity vs concentration plots. Taken together, these experiments demonstrate that the mixed-valence core is highly resistant to disproportionation, even in the absence of excess THF.

In conclusion, a series of dicopper mixed-valence complexes has been assembled with the XDK ligand system. Their fully delocalized class III behavior has been demonstrated experimentally through X-ray crystallographic studies and EPR experiments in the solid state and solution. These results contribute significantly to our understanding of the assembly, stability, and electronic structures of class III mixed-valence Cu−Cu systems such as Cu_A.

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Supporting Information Available: Experimental details on the preparation and characterization of **3**−**7**, including analytical and crystallographic data, ORTEP plots, bond distances and angles, and tables of positional and thermal parameters (45 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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(14) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods Fundamentals and Applications*; John Wiley & Sons: New York, 1980.

(15) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

(16) (a) Reinhammar, B. R. M. *Biochim. Biophys. Acta* **1972**, *275*, 245−259. (b) Tronson, D. A.; Ritchie, G. A. F.; Nicholas, D. J. D. *Biochim. Biophys. Acta* **1973**, *310*, 331−343.

(17) Immoos, C.; Hill, M. G.; Sanders, D.; Fee, J. A.; Slutter, C. E.; Richards, J. H.; Gray, H. B. *J. Biol. Inorg. Chem.* **1996**, *1*, 529−531.

(18) EXAFS studies have shown that the core structures of fully reduced and mixed-valent Cu_A are nearly identical, notwithstanding a slight lengthening of the Cu−Cu and Cu−S distances in the reduced form (ref 1f).

(19) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397−1412.

(20) Landrum, G. A. *YAeHMOP: Yet Another Extended Huckel Molecular Orbital Package. 2.0*; Cornell University: Ithaca, NY, 1995. YAeHMOP is freely available on the WWW.