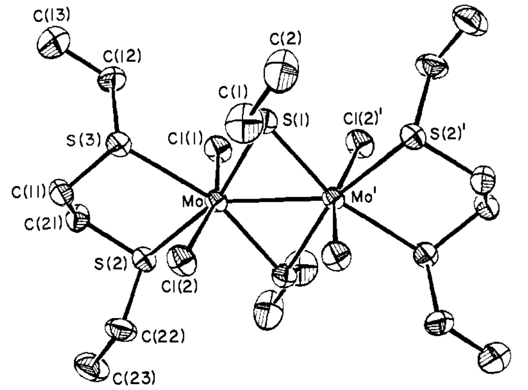

Figure 1. Molecular geometry and atom-labeling scheme for $Mo_2Cl_4(\mu\text{-}SEt)_2(dto)_2$ (**1**). The molecule resides on a center of inversion. Thermal ellipsoids represent 50% of the electron density. Selected bond distances and angles are Mo–Mo = 2.682 (1) Å, average $Mo\text{–}S_{bridging}$ = 2.402 [2] Å, average $Mo\text{–}S_{terminal}$ = 2.579 [1] Å, average Mo–Cl = 2.403 [1] Å, $Mo\text{–}S_b\text{–}Mo$ = 67.90 (3)°, average $Mo\text{–}Mo\text{–}S_t$ 138.8 [8]°, average Mo–Mo–Cl = 98.46 [4]°.

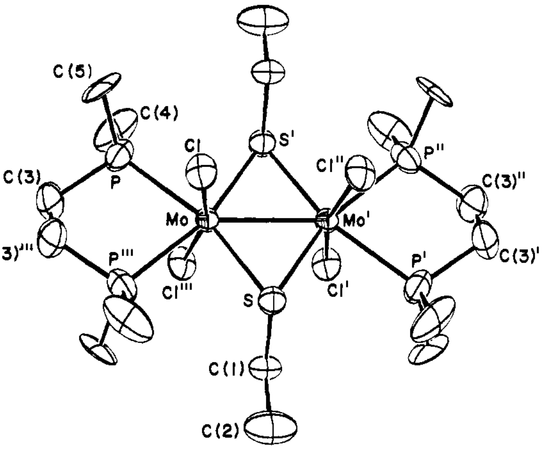

Figure 2. ORTEP view of $Mo_2Cl_4(\mu\text{-}SEt)_2(dmpe)_2$ (**3**) at the 50% probability level. The crystallographic symmetry of the molecule is $2/m$; singly primed, doubly primed, and triply primed atoms are related to unprimed atoms by an inversion center, a mirror plane, and a twofold axis, respectively. Selected bond distances and angles are Mo–Mo = 2.712 (3) Å, Mo–S = 2.411 (4) Å, Mo–P = 2.541 (3) Å, Mo–Cl = 2.417 (3)°, Mo–S–Mo = 68.5 (1)°, Mo–Mo–P = 140.25 (9)°, Mo–Mo–Cl = 98.55 (8)°.

dto.[8] Higher yields (40–45%) of **1** as a green-brown precipitate are obtained when a 1:2:1 ratio of $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$,[9] dto, and ethyl disulfide (EtSSEt) are refluxed together in methanol for 3–5 h; an IR spectrum[10a] is identical with that of the product from the first procedure. A similar reaction between $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$, dto, and phenyl disulfide (PhSSPh) yields a yellow-green solid which is probably $Mo_2Cl_4(\mu\text{-}SPh)_2(dto)_2$ (**2**) since its IR spectrum[10b] is similar to that of **1**.

Both **1** and **2** are most likely produced by initial formation of $Mo_2Cl_4(dto)_2$[11] followed by oxidative addition of RSSR. This pathway is supported by the fact that if $(NH_4)_5Mo_2Cl_9{\cdot}H_2O$ and EtSSEt are refluxed together for a few hours before adding dto, a compound with an IR spectrum quite different from that of **1** is formed. Moreover, the reaction of $\beta\text{-}Mo_2Cl_4(dmpe)_2$[12] with EtSSEt in refluxing toluene yields $Mo_2Cl_4(\mu\text{-}SEt)_2(dmpe)_2{\cdot}C_7H_8$ (**3**). Interestingly, $Mo_2Cl_4(PMe_2Ph)_4$[13] fails to react with EtSSEt in refluxing toluene, allowing for the recovery of starting material in ca. 95% yield.

The structures of **1** and **3** have been determined by X-ray crystallography[14] and are illustrated in Figures 1 and 2, respectively. Both structures may be described as edge-sharing bioctahedrons, with metal-metal distances (ca. 2.7 Å) indicative of a Mo–Mo bond order of at least 1. Both **1** and **3** are diamagnetic.[15]

To our knowledge, these are the first examples of Mo(III) dimers doubly bridged by alkyl sulfide groups. Efforts are under way to obtain crystals of **2** and related species as we continue to investigate oxidative addition of various reagents to quadruply bonded bimetallic compounds.

Acknowledgment. We are grateful to the National Science Foundation for support.

Supplementary Material Available: Tables of crystallographic data and atomic positional parameters (3 pages). Ordering information is given on any current masthead page.

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[8] The fate of the C_2H_4 has not been established and it may not appear as such but rather in some other, as yet unidentified product. Since this procedure generates **1** slowly, it has the virtue of producing it in crystalline form whereas the reaction of $Mo_2Cl_8{}^{4-}$ with EtSSEt and dto does not.

[9] Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 346.

[10] Selected infrared absorption frequencies (cm^{-1}) for Nujol mulls. (a) $Mo_2Cl_4(\mu\text{-}SEt)_2(dto)_2$: 1400 s, 1247 m, 1170 w–m, 1145 w–m, 1059 m, 1048 sh, 1039 m, 1005 w, 962 m, 900 m–s, 840 m, 770 sh, 758 m. (b) $Mo_2Cl_4(\mu\text{-}SPh)_2(dto)_2$(?): 1400 s, 1258 m, 1241 m, 1150 sh, 1141 m, 1058 s, 1020 s, 970 m, 898 m, 836 w–m, 800 m, 757 sh, 751 s, 691 m–s.

[11] $Mo_2Cl_4(dto)_2$ was previously shown to form $Mo_2Cl_6(dto)_2$ spontaneously in CH_2Cl_2: Cotton, F. A.; Fanwick, P. E.; Fitch, J. W. III. *Inorg. Chem.* **1978**, *17*, 3254.

[12] Cotton, F. A.; Powell, G. L. *Inorg. Chem.* **1983**, *22*, 1507.

[13] San Filippo, J., Jr. *Inorg. Chem.* **1972**, *11*, 3140.

[14] Tables of crystallographic data and atomic positional parameters (3 pages) are available as supplementary material.

[15] Detailed magnetic measurements on **1** have shown that it has a partially populated triplet state.

Peroxide Coordination to a Dicopper(II) Center. Dioxygen Binding to a Structurally Characterized Phenoxide-Bridged Copper(I) Complex

Kenneth D. Karlin,* Richard W. Cruse, Yilma Gultneh,
Jon C. Hayes, and Jon Zubieta

Department of Chemistry
State University of New York at Albany
Albany, New York 12222

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There is considerable effort being undertaken to understand the binding, interaction, and subsequent reactivity of dioxygen at copper ion centers. This is in part due to the occurrence of copper-containing enzymes such as hemocyanin[1,2] that bind and transport O_2 and the monooxygenases tyrosinase[1,2b,3] and dopamine β-hydroxylase[3] that incorporate oxygen (from O_2) into organic substrates. Studies of biomimetic chemical models can be useful in elucidating structural and spectroscopic properties of the enzyme active sites as well as reactions occurring at these centers.[4] In addition, information gained in such model studies may apply to the development of useful synthetic systems for oxidation reactions.[5]

We have recently developed a model system which mimics the dioxygen reactivity found in the copper monooxygenases.[6,7] In

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[1] (a) Solomon, E. I. In "Metal Ions in Biology"; Spiro, T. G. Ed.; Wiley-Interscience: New York, 1981; Vol. 3, pp 41–108. (b) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding* (*Berlin*) **1983**, *53*, 1–57.

[2] (a) Lontie, R.; Witters, R. *Met. Ions Biol. Syst.* **1981**, *13*, 229–258. (b) Lerch, K. *Ibid.* **1981**, *13*, 143–186.

[3] Freedman, T. B.; Loehr. *J. S.*; T. M. *J. Am. Chem. Soc.* **1976**, *98*, 2809.

[4] "Copper Coordination Chemistry: Biochemical and Inorganic Perspectives"; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1983.

[5] Sheldon, R. A.; Kochi, J. K. "Metal-Catalyzed Oxidations of Organic Compounds"; Academic Press: New York, 1981.

[6] (a) Karlin, K. D.; Dahlstrom, P. L.; Cozzette, S. N.; Scensny, P. M.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1981**, 881–883. (b) Karlin, K. D.; Gultneh, Y.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1982**, *104*, 5240–5242. (c) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *Ibid.* **1984**, *106*, 2121–2128.

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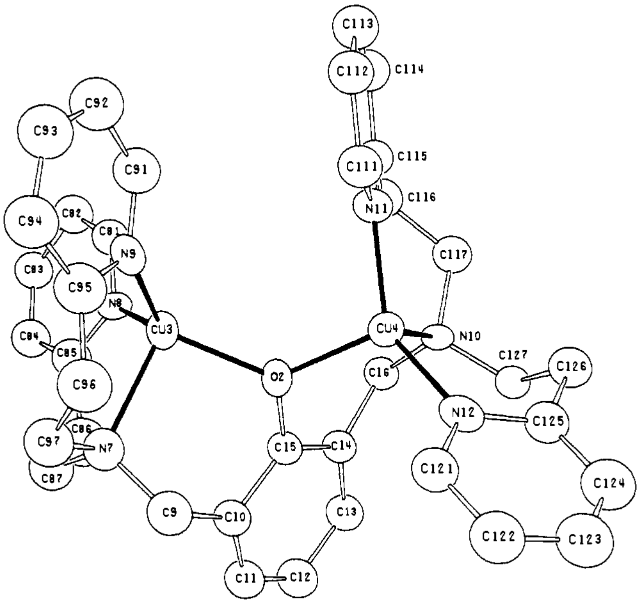
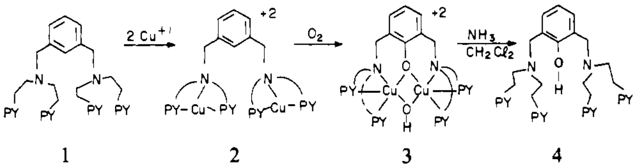


Figure 1. ORTEP diagram of one of the $[Cu_2(C_{36}H_{39}N_6O]$ monocations showing the atom labeling scheme. Labeling for the molecule containing Cu1 and Cu2 is analogous to that shown. Selected bond lengths (Å) and angles (deg): Cu1⋯Cu2, 3.715; Cu1–O1, 1.974 (9); Cu1–N1, 2.178 (10); Cu1–N2, 2.077 (11); Cu1–N3, 1.948 (10); Cu2–O1, 2.125 (9); Cu2–N4, 2.195 (11); Cu2–N5, 1.943 (10); Cu2–N6, 1.918 (10); Cu1–O1–Cu2, 130.0 (4); O1–Cu1–N1, 96.7 (4); O1–Cu1–N2, 105.8 (4); O1–Cu1–N3, 140.8 (4); N1–Cu1–N2, 95.7 (4); N1–Cu1–N3, 101.4 (4); N2–Cu1–N3, 106.7 (4); O1–Cu2–N4, 92.6 (4); O1–Cu2–N5, 108.0 (4); O1–Cu2–N6, 102.7 (4); N4–Cu2–N5, 99.7 (4); N4–Cu2–N6, 99.8 (4); N5–Cu2–N6, 142.5 (5). Cu3⋯Cu4, 3.619; Cu3–O2, 1.995 (9); Cu3–N7, 2.156 (12); Cu3–N8, 1.962 (11); Cu3–N9, 1.999 (11); Cu4–O2, 2.031 (9); Cu4–N10, 2.158 (10); Cu4–N11, 1.953 (11); Cu4–N12, 1.955 (12); Cu3–O2–Cu4, 128.0 (4); O2–Cu3–N7, 92.9 (4); O2–Cu3–N8, 119.8 (4); O2–Cu3–N9, 116.5 (4); N7–Cu3–N8, 101.2 (4); N7–Cu3–N9, 103.5 (4); N8–Cu3–N9, 116.2 (5); O2–Cu4–N10, 90.7 (4); O2–Cu4–N11, 109.5 (4); O2–Cu4–N12, 114.2 (4); N10–Cu4–N11, 103.0 (4); N10–Cu4–N12, 100.4 (4); N11–Cu4–N12, 129.7 (5).

this system, a three-coordinate dimeric Cu(I) complex, **2**, of the binucleating ligand *m*-XYLpy2 (**1**) reacts with dioxygen, resulting in the oxygenation of the ligand and concomitant formation of the phenoxo- and hydroxo-bridged binuclear Cu(II) complex **3**.[6] The free phenol, **4**, can be isolated from compound **3**.[6c]



1 2 3 4

In hemocyanin and tyrosinase, binding of dioxygen is known to occur via intramolecular electron transfer to form a μ-1,2-peroxo-bridged Cu(II) species (Cu(II)⋯Cu(II) = 3.6 Å).[1-3] Our own experiments involving the reactions of Cu(II) complexes of **1** with hydrogen peroxide have shown that hydroxylation of **1** also occurs, suggesting that peroxo–Cu(II) intermediates are involved in the conversion of **2** to **3**.[7] Thus, because of the interest in stabilizing and characterizing peroxo–Cu(II) compounds formed by the reaction of O_2 with Cu(I),[8,9] we are investigating the intermediate products of the reaction of dioxygen with Cu(I) complexes of binucleating ligands such as **2** and **4**. Here, we report the synthesis and structural characterization of a novel phenoxo-bridged binuclear Cu(I) complex, **5**, which contains **4**.[10]

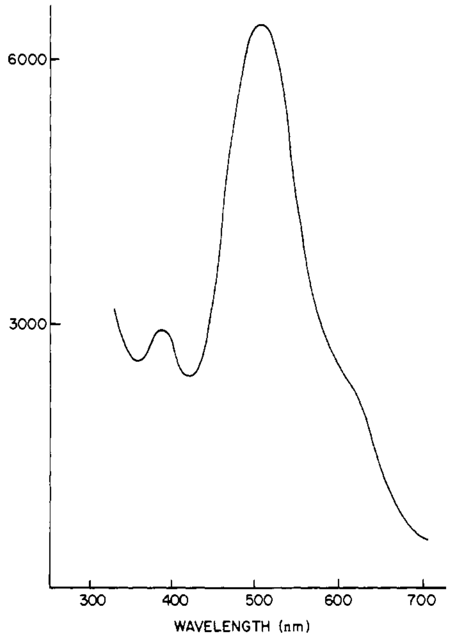


Figure 2. Visible absorption spectrum of the dioxygen–copper complex **6**. The spectrum was taken in dichloromethane at −80 °C. Band maxima λ (ε, M^{-1} cm^{-1}) are 385 (3000), 505 (6300), and 610 nm (2400).

Compound **5** reacts with O_2 resulting in the formation of a binuclear Cu(II)-peroxide complex, **6**, that is stable at low temperature.

Complex **5** was synthesized by the addition of a solution of **4** (3.94 g, 6.88 mmol) also containing 1.10 g of NaOH (27.7 mmol) in 100 mL of methanol (MeOH) to a warm (50 °C) solution of 5.13 g of $[Cu(CH_3CN)_4]PF_6$[11] (13.8 mmol) in deoxygenated MeOH (160 mL), giving an orange solution. After filtration, the solution was slowly evaporated under vacuum at 0 °C until about 50 mL remained. The crystals deposited were washed (under Ar) with cold MeOH, giving 4.2 g (72%) of **5** suitable for X-ray diffraction.[12]

The structure of the $[Cu_2(XYL\text{-}O\text{-})]$ cation is shown in Figure 1.[13,14] There are two crystallographically independent molecules in each asymmetric unit; each molecule consists of two four-coordinate Cu(I) ions ligated to the amino nitrogen and two pyridine donors of the py2 tridentate group. The fourth donor is the bridging phenoxo oxygen. The geometry about each Cu(I) ion is best described as pyramidal, similar to that found in Cu(I) complexes containing "tripod" tetradentate ligands.[15] Each Cu atom lies slightly above the basal plane formed by the two pyridine donors and the oxygen atom. The longer axial position is occupied by the tertiary amino nitrogen. The Cu⋯Cu distances in the two molecules are 3.619 and 3.715 Å with corresponding Cu–O–Cu angles of 128.0 (4)° and 130.0 (4)°. As can be seen in Figure 1, there is an empty "pocket" found in the area where a second

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[7] Blackburn, N. J.; Karlin, K. D.; Concannon, M.; Hayes, J. C.; Gultneh, Y.; Zubieta, J. *J. Chem. Soc., Chem. Commun.*, in press.

[8] Zuberbuhler, A. D. *Met. Ions Biol. Syst.* **1976**, *5*, 325–367.

[9] Our other recent studies in copper(I)–dioxygen reactivity include: (a) Karlin, K. D.; Shi, J.; Hayes, J. C.; McKown, J. W.; Huchinson, J. P.; Zubieta, J. *Inorg. Chim. Acta* **1984**, *91*, L3-L7. (b) Karlin, K. D.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *Inorg. Chem.* **1984**, *23*, 521–523. (d) Reference 6c.

[10] Few examples of structurally characterized phenoxo-bridged binuclear Cu(I) complexes are known. (a) Pasquali, M.; Fiaschi, P.; Floriani, C.; Gaetani-Manfredotti, A. *J. Chem. Soc., Chem. Commun.* **1983**, 197–199. (b) Gagne, R. R.; Kreh, R. P.; Dodge, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6917–6927.

[11] Kubas, G. J. *Inorg. Synth.* **1979**, *19*, 90–92.

[12] Anal. Calcd for $Cu_2(C_{36}H_{39}N_6O)(PF_6)$: C, 51.26; H, 4.66; N, 9.96. Found: C, 51.44; H, 4.66; N, 9.94.

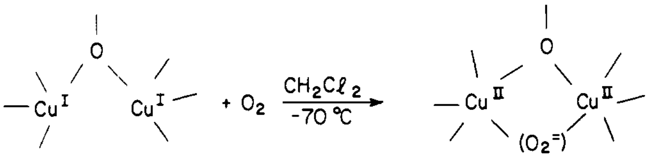
[13] The complex crystallizes in the monoclinic space group $P2_1/n$ with eight molecules per unit cell (2 per asymmetric unit): a = 13.861 (4) Å, b = 31.482 (8) Å, c = 16.956 (5) Å, β = 98.20 (2)°, ρ_{calcd} = 1.531 g/cm^3. The positional parameters of the copper atoms were obtained from solutions derived from SHELXL direct methods software. The remaining non-hydrogen atoms were located in subsequent difference Fourier syntheses. When 2927 unique observed reflections ($0° < 2\theta < 40°$, $F_o > 6\sigma(F_o)$) taken at 22 °C on a Nicolet R3m diffractometer using Mo Kα radiation are used, the structure was refined to a current value of 0.059 for the discrepancy index $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

[14] Supplementary material.

[15] (a) Karlin, K. D.; Hayes, J. C.; Hutchinson, J. P.; Hyde, J. R.; Zubieta, J. *Inorg. Chim. Acta* **1982**, *64*, L219–L220. (b) Zubieta, J.; Karlin, K. D.; Hayes, J. C. In ref 4, pp 97–108.

bridging ligand is observed for a number of doubly bridged Cu(II) binuclear compounds of this same ligand.[6a,c,16]

When an orange (λ_{max} = 380 nm) dichloromethane solution of **5** is exposed to O_2 below −70 °C, an intense violet color develops due to the formation of the peroxide–Cu(II) complex, **6**. Manometric measurements at −78 °C indicate that 1 mol of dioxygen is taken up per mol of **5** ($Cu:O_2$ = 2:1). The visible absorption spectrum (Figure 2) of the violet solution exhibits a new strong transition at 505 nm (ϵ = 6300 M^{-1} cm^{-1}) associated with the formation of **6**. In addition, a band at 385 nm is observed along with an absorption in the d–d region near 610 nm. Confirming evidence for the formulation of **6** as a copper(II)–peroxide complex comes from resonance Raman spectroscopy. Here, a peak at 803 cm^{-1} is assigned to the O–O stretching vibration of a coordinated peroxide group, based on (a) the $^{18}O_2$ isotopic perturbation observed[17a] and (b) a comparison to the O–O stretch values observed for oxyhemocyanins, oxytyrosinase, and ionic peroxides.[17]



5

6

The visible absorption spectrum of **6** is significantly different from that of oxyhemocyanin,[1] suggesting that the mode of coordination of the peroxo group must be different. The present study demonstrates that a binuclear Cu(I) center can react with dioxygen to give a stable peroxide-binding Cu(II) compound in a synthetic system. To our knowledge, this is the first example of O_2 binding to Cu(I) where a distinct and strong visible absorption band (505 nm) is observed and where the oxidation state of the coordinated dioxygen ligand (as O_2^{2-}) is confirmed by vibrational spectroscopy.[17,19] At this point, we cannot distinguish between μ-1,1-, μ-1,2-, or terminally bound peroxide.[1-3,21] The Cu(I)···Cu(I) separation of 3.6–3.7 Å observed in **5** compares with that found in oxyhemocyanin,[1,2] suggesting that a μ-1,2-peroxo complex is possible. On the other hand, we have already characterized several phenoxo and X doubly bridged (X = OH,[6b,c] OMe,[6a] Cl,[16] μ-1, 1-N_3[16]) Cu(II) complexes containing **4** where Cu(II)···Cu(II) is ca. 3.1 Å;[6,16,22] thus μ-1,1-O_2^{2-} bridging cannot be ruled out.[23] Further studies of the physical and chemical characteristics of **6** are in progress.

Acknowledgment. We thank the National Institutes of Health (K.D.K., GM28962; J.Z., GM27459) for support of this research. We are also very grateful to Professor E. I. Solomon, Jim Pate, and Rich Reem for helpful discussions and for obtaining the Resonance Raman data.

Supplementary Material Available: Listing of atomic coordinates and temperature factors, bond lengths, bond angles, and anisotropic temperature factors (15 pages). Ordering information is given on any current masthead page.

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(16) Karlin, K. D.; Hayes, J. C.; Hutchinson, J. P.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1983**, 376–378.

(17) (a) Pate, J.; Solomon, E. I.; Cruse, R. W.; Karlin, K. D., to be published. (b) The peroxide stretch in oxyhemocyanins occur between 744 and 752 cm^{-1}, while that for oxytyrosinase (*Neurospora crassa*) occurs at 755 cm^{-1}.[1,18] ν_{O-O} for ionic peroxides and superoxide (O_2^-) occurs at ca. 800 and 1100 cm^{-1}, respectively.

(18) Eickman, N. C.; Solomon, E. I.; Larrabee, J. A.; Spiro, T. G.; Lerch, K. *J. Am. Chem. Soc.* **1978**, *100*, 6529–6531 and references therein.

(19) a number of Cu(I) complexes bind dioxygen reversibly or quasireversibly with the stoichiometry $Cu:O_2$ = 2:1. No vibrational data that confirm the formation of bound peroxide to Cu(II) have been reported.[20]

(20) (a) Simmons, M. G.; Merrill, C. L.; Wilson, L. J.; Bottomley, L. A.; Kadish, K. M. *J. Chem. Soc., Dalton Trans.* **1980**, 1827–1837. (b) Bulkowski, J. E.; Burk, P. L.; Ludmann, M.-F.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1977**, 498–499. (c) Agnus, Y.; Louis, R.; Weiss, R. *J. Am. Chem. Soc.* **1979**, *101*, 3381–3384. (d) Nishida, Y.; Takahashi, K.; Kuramoto, H.; Kida, S. *Inorg. Chim. Acta* **1981**, *54*, L103–L104. (e) Bulkowski, J. E.; Summers, W. E., III In ref 4, pp 445–457.

(21) Although it would seem unlikely in the present system, terminal binding of peroxide to only one of the two copper ions cannot be ruled out. Recent data indicate that peroxide in the binuclear iron center in hemerythrin is only bound to one iron atom. Elam, W. T.; Stern, E. A.; McMallum, J. D.; Sanders-Loehr, J. *J. Am. Chem. Soc.* **1983**, *105*, 1919–1923 and references therein.

(22) Karlin, K. D.; Hayes, J. C.; Zubieta J. In ref 4, pp 457–472.

(23) μ-1,1-Peroxo bridging is known to occur in cobalt complexes. Durand, R. R., Jr.; Bencosme, C. S.; Collman, J. P.; Anson, F. C. *J. Am. Chem. Soc.* **1983**, *105*, 2710–2718 and references therein.

Oxidation of Alcohols to Aldehydes with Oxygen and Cupric Ion, Mediated by Nitrosonium Ion

M. F. Semmelhack,* Christopher R. Schmid,
David A. Cortês, and Chuen S. Chou

Department of Chemistry, Princeton University
Princeton, New Jersey 08544

Received February 15, 1984

Recent studies have demonstrated the ability of 2,2,6,6-tetramethylpiperidinyl-1-oxy (**1**, Tempo)[1] to mediate alcohol[2,3] and amine[4] oxidation by electrolysis, apparently via the nitrosonium ion **2**. Also under investigation are nonelectrochemical methods of nitroxyl-mediated oxidation. Here we report the room temperature oxidation of allylic and benzylic alcohols by *oxygen* using a catalyst mixture of cuprous chloride and nitroxyl **1**, as well as more general oxidations of primary alcohols, promoted by cupric chloride and mediated by the nitroxyl **1**.

A catalytic sequence for the oxidation by oxygen is proposed in eq 1-4, Scheme I. Cupric ion effects a one-electron oxidation of **1** to nitrosonium ion **2** (eq 1).[5,6] The alcohol is then oxidized by **2** (eq 2), generating the aldehyde and hydroxylamine **3**; rapid syn proportionation[3,4] of **3** with **2** regenerates **1** (eq 3). Finally, Cu(I) is regenerated by oxygen, in a process that consumes protons and gives Cu(II) and water (eq 4),[6] following a general method for recycling cupric ion.[7] The net reaction is alcohol oxidation by oxygen to afford aldehyde and water (eq 5). No net formation of acid is expected, and the usual requirement of added base in nitrosonium ion oxidations[3,4] might be avoided.

In the standard procedure, the alcohol (10 mmol), nitroxyl **1** or its 4-hydroxy analogue (1 mmol, 10 mol %),[8] and CuCl (1

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(1) This reagent has been studied extensively by Golubev, Rozantsev, and co-workers, including formation of nitrosonium **2** and its reaction with organic functional groups. For leading references, see: Golubev, V. A.; Rozantsev, E. G.; Neiman, M. G. *Izv. Acad. Nauk SSSR* **1978**, 1874–1881.

(2) A mixture of *m*-chloroperoxybenzoic acid and **1** has been used to oxidize alcohols to aldehydes: (a) Cella, J. A.; Kelley, J. A.; Kenehan, E. F. *J. Org. Chem.* **1975**, *40*, 1860–1862. (b) Ganem, B. *Ibid.* **1975**, *40*, 1998–1999.

(3) Semmelhack, M. F.; Chou, C. S.; Cortês, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 4492.

(4) Semmelhack, M. F.; Schmid, C. R. *J. Am. Chem. Soc.* **1983**, *105*, 6732.

(5) While a number of inorganic oxidants are known to convert **1** to **2**, this is the first report of Cu(II) providing this conversion. (a) With Sb(IV): Golubev, V. A.; Voronina, G. N. *Izv. Acad. Nauk SSSR* **1972**, 150. (b) With Sn(IV): Takaya, Y.; Matsubayashi, G.; Tanaka, T. *Inorg. Chem. Acta* **1972**, *6*, 339. (c) With Pd(II): Okunaka, M.; Matsubayashi, G.; Tanaka, T. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 907. (d) With Ti(IV) and Zr(IV): Golubev, V. A.; et al. *Bull. Acad. Sci.* **1977**, 1669.

(6) Electrochemical studies indicate that Cu(II) can indeed oxidize **1** to **2**. We find $E_{/2}$ = +0.7 V (vs. Ag/Ag(I)) for the reversible $CuCl/CuCl_2$ couple (cyclic voltammetry at Pt) in dry acetonitrile containing 0.5 M $LiClO_4$. Under the same conditions, the redox couple **1**/**2** shows $E_{1/2}$ = +0.33 V (vs. Ag/Ag(I)).

(7) For example, a similar cycle is observed in the well-studied Wacker process: Szoni, G. *Adv. Chem. Ser.* **1968**, *70*, 53.

0002-7863/84/1506-3374$01.50/0