of the silane cation radical by both acetonitrile and methyl alcohol after diffusional separation from the geminate ion radical pair.[8] This conclusion is consistent with the lifetimes of **1b–d**•⁺ being considerably longer than those expected for the geminate pairs.[9]

The nucleophilic cleavage mechanism makes the additional prediction that the cleavage rates of the silane cation radicals should decrease as the steric demands of the nucleophile increase. This prediction is borne out by the steady decrease in the rate constants for the reaction of the silane radical cations with methyl alcohol (k_m), isopropyl alcohol (k_i), and *tert*-butyl alcohol (k_t) (Table I).

In summary, the cleavage of benzyltrialkylsilane cation radicals in acetonitrile is most consistent with a mechanism involving nucleophilic participation by the solvent. This mechanistic insight will undoubtedly be useful in more profitably utilizing silane cation radical cleavage reactions.

---

(8) Mariano and co-workers[5] found similar *product formation* quantum yields for a series of allyltrialkylsilane cation radicals with different substituents at silicon and concluded from this that, if a nucleophilic displacement mechanism was operating, it must be insensitive to the steric environment at silicon. Presumably their reactions, like ours, simply occur out of the geminate pair and thus the quantum yield for product fromation is an insensitive probe of cation radical reactivity.

(9) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

μ-η²:η²-Peroxo Binuclear Copper Complex, [Cu(HB(3,5-iPr₂pz)₃)]₂(O₂)

Nobumasa Kitajima,* Kiyoshi Fujisawa, and Yoshihiko Moro-oka*

Research Laboratory of Resources Utilization
Tokyo Institute of Technology
4259 Nagatsuta, Midori-ku, Yokohama 227, Japan

Koshiro Toriumi

Institute for Molecular Science
Okazaki National Research Institutes
Myodaiji, Okazaki 444, Japan

Received July 20, 1989

Considerable efforts have been made in the synthesis and structural characterization of μ-1,2-peroxo binuclear copper(II) complexes, since such a moiety is known to exist in oxygen binding states of hemocyanin (Hc) and tyrosinase (Tyr).[1] Very recently, Karlin et al. have reported the crystal structure of $[CuL]_2(O_2)^{2+}$ (L = tris[(2-pyridyl)methyl]amine), which definitely established the presence of trans μ-1,2 coordination of a peroxide ion.[2] However, the Cu···Cu distance (4.359 (1) Å) and the electronic spectrum of the complex are significantly different from those of oxy-Hc and oxy-Tyr. On the other hand, we[3] have reported the synthesis of a μ-peroxo binuclear complex, [Cu(HB(3,5-

(1) See the following reviews and papers and the references cited therein: (a) Solomon, E. I.; Penfield, K. W.; Wilcox, D. E. *Struct. Bonding (Berlin)* **1981**, *53*, 1. (b) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219. (c) Karlin, K. D.; Haka, M. S.; Cruse, R. W.; Meyer, G. J.; Farooq, A.; Gultneh, Y.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 1196. (d) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *Ibid.* **1987**, *109*, 2668. (e) Tyeklar, Z.; Karlin, K. D. *Acc. Chem. Res.* **1989**, *22*, 241.

(2) Jacobson, R. R.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690.

(3) Kitajima, N.; Koda, T.; Hashimoto, S.; Kitagawa, T.; Moro-oka, Y. *J. Chem. Soc., Chem. Commun.* **1988**, 151.
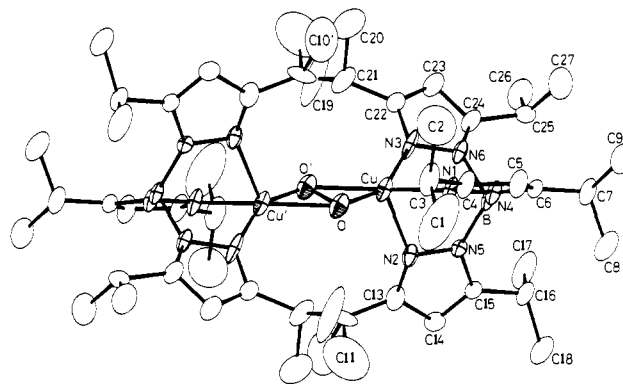

Figure 1. ORTEP view of **2** (30% probability). The molecule sits on the center of symmetry. CH₂Cl₂ molecules of crystallization were omitted. Selected bond distances (Å) and angles (deg) are as follows: Cu···Cu, 3.560 (3); Cu–O, 1.903 (11), Cu–O′, 1.927 (9); O–O′, 1.412 (12); Cu–N1 2.000 (8); Cu–N2, 2.258 (8); Cu–N3, 1.993 (14); O–Cu–O′, 43.3 (4); Cu–O–Cu′, 136.7 (5); Cu–O–O′, 69.3 (6); Cu′–O–O′, 67.4 (5); N1–Cu–O, 107.2 (4); N1–Cu–O′, 148.8 (4); N2–Cu–O, 114.2 (4); N2–Cu–O′, 111.5 (3); N3–Cu–O, 150.4 (4); N3–Cu–O′, 111.3 (4); N1–Cu–N2, 88.5 (3); N1–Cu–N3, 92.7 (4); N2–Cu–N3, 87.4 (4).

Scheme I

3   2   4
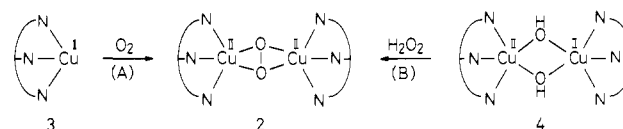
Me₂pz)₃)]₂(O₂) **(1)**, which shows remarkable physicochemical similarities to oxy-Hc and oxy-Tyr. In this communication, we report the crystal structure of the analogous complex [Cu(HB-(3,5-iPr₂pz)₃)]₂(O₂) **(2)**, which contains the novel coordination mode of the peroxide ion, μ-η²:η².

2 is prepared either by direct O₂ addition to copper(I) complex Cu(HB(3,5-iPr₂pz)₃) **(3)**[4] (method A) or by H₂O₂ treatment of [Cu(HB(3,5-iPr₂pz)₃)]₂(OH)₂ **(4)**[5] (method B) (Scheme I). The reaction of **3** with O₂ in acetone at −78 °C for 2 h gave the intensely purple colored solution of **2**. The manometric measurement of the consumed amount of O₂ conforms to the formation of **2**. The reduction of the solvent under vacuum at −20 °C followed by cooling at −78 °C afforded **2** as deep purple solids in an essentially quantitative yield. In a manner analogous to that for the preparation of **1**,[3] **4** was reacted with an excess amount (ca. 3 equiv) of H₂O₂ (30% aqueous solution) at −20 °C in CH₂Cl₂. The solution immediately turned deep purple. **2** was also isolable from the solution. The spectroscopic characterization of **2** established that the properties of **2** are closely similar to those of **1** and also oxy-Hc (-Tyr).[6]

Slow recrystallization from the CH₂Cl₂ solution at −30 °C, which was prepared by method B, gave single crystals of **2**·6CH₂Cl₂. As shown in Figure 1, two Cu(HB(3,5-iPr₂pz)₃)⁺ units bridged by a peroxide ion form a binuclear complex, which sits on a center of symmetry.[7] The O–O distance (1.412 (12) Å)

(4) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y. *Chem. Lett.* **1989**, 421.

(5) Kitajima, N.; Fujisawa, K.; Moro-oka, Y. *Inorg. Chem.* In press.

(6) A satisfactory elemental analysis was obtained for **2** dried under vacuum at −20 °C. Anal. Calcd for C₅₄H₉₂N₁₂O₂B₂Cu₂: C, 59.50; H, 8.51; N, 15.42. Found: C, 58.94; H, 8.54; N, 15.27. UV–vis (CH₂Cl₂, −12 °C): 349 (ε, 21 000), 551 nm (800). Raman (Me₂CO, −40 °C) (¹⁶O–¹⁶O): 741 cm⁻¹. The Raman study with the mixed-isotope dioxygen established the symmetric coordination of the peroxide ion as in oxy-Hc[1]: (¹⁶O–¹⁸O) 719, (¹⁸O–¹⁸O) 698 cm⁻¹. ¹H NMR (toluene-d₈, −10 °C, δ, ppm): 1.27 (d, 36 H, *Me*₂CH), 1.48 (d, 36 H, *Me*₂CH), 3.68 (m, 6 H, Me₂C*H*), 3.95 (m, 6 H, Me₂C*H*), 6.09 (s, 6 H, pz). (The chemical shifts of the pyrazole ring proton for the copper(I) complexes are 5.7–6.1 ppm.[4]) EPR: silent in CH₂Cl₂ at −196 °C; 0 μ_B by Evans method at −10 °C. These properties of **2** (as well as **1**[3]) closely mimic the characteristics of oxy-Hc[1] (mollusks): diamagnetic; UV–vis 345 (ε, ~20 000), 570 nm (~1000); Raman (¹⁶O–¹⁶O) 749, (¹⁶O–¹⁸O) 728, (¹⁸O–¹⁸O) 708 cm⁻¹. Further details of the preparation and properties of **2** will be reported elsewhere.

is a typical value for the peroxide ion bound to a transition-metal ion.[8] All the Cu–O distances are equivalent within experimental error. Hence, the coordination mode of the peroxide ion can be described as μ-η^2:η^2. To our knowledge, this is the first example of a μ-η^2:η^2 peroxo binuclear complex of a d-block element,[9,10] although such coordination modes are known for the U and La complexes.[11,12] It is notable that the Cu$\cdots$Cu distance of 3.560 (3) Å is significantly shorter than that of the trans μ-1,2-peroxo binuclear Cu(II) complex (4.359 (1) Å)[2] and is consistent with the estimated values for oxy-Hc (3.58–3.66 Å)[13] and oxy-Tyr (3.63 Å)[14] by EXAFS analyses. Two of the Cu–N distances are normal, but the other Cu–N distance is considerably elongated. These indicate that the coordination geometry of the copper ion can be regarded as distorted square pyramidal with the N_3O_2 ligand donor set. The unusual coordination mode of the peroxide ion in **2** seems to reflect the strong preference of the copper(II) ion to penta-coordination (square pyramidal) rather than tetracoordination (tetrahedral) with the hindered tripod N_3 ligand such as in the present system.

A cis μ-1,2 coordination mode of the peroxide ion with an additional bridging ligand (such as OH⁻) has been proposed for oxy-Hc (or oxy-Tyr) on the basis of (1) the strong magnetic interaction (diamagnetism) between the two copper ions and (2) the extensive spectroscopic studies on met-Hc.[1] However, to date no direct evidence for the existence of such a bridging ligand has been provided. If there is no additional ligand in these proteins, one could also postulate the possibility of μ-η^2:η^2 coordination of the peroxide ion, since Hc contains three hystidyl nitrogens as ligands for each copper ion.[15] The close resemblance of the physicochemical properties between **2** and oxy-Hc (and oxy-Tyr), including the diamagnetism, may suggest the hypothesis, although more adequate investigations are required to lead to the conclusion.

Supplementary Material Available: An ORTEP drawing of the molecular structure with atomic numbering, a perspective view of the crystal structure, and tables of the summary of X-ray analysis, bond distances, bond angles, atomic coordinates, anisotropic thermal parameters, and hydrogen atom coordinates for **2**·6CH$_2$Cl$_2$ (12 pages); observed and calculated structure factors for **2**·6CH$_2$Cl$_2$ (7 pages). Ordering information is given on any current masthead page.

Unexpected Regioselectivity in the Reductive Cleavage of Epoxides: A Theoretical Rationalization

Andrea E. Dorigo,[†] K. N. Houk,*,[†] and Theodore Cohen*,[‡]

Department of Chemistry, University of Pittsburgh Pittsburgh, Pennsylvania 15260 Department of Chemistry and Biochemistry University of California Los Angeles, California 90024

The reductive cleavage of epoxides to alcohols is a reaction of general use in synthetic organic chemistry.[1] It has been observed recently that the reduction of epoxides of general formula **1** with lithium naphthalenide proceeds with regiochemistry that is intuitively unexpected,[2,3] but precedented by reductions of epoxides by means of metals dissolved in liquid ammonia or amines.[4] Unsymmetrical alkyl-substituted epoxides give mainly the more substituted carbinol, which requires cleavage of the C–O bond to the *less* substituted carbon atom (Table I, entries 1–6). Only a strongly radical stabilizing substituent causes ring opening to occur at the atom bearing that substituent (entries 7–10).[2,3]

Although the mechanism of the Birch reduction of epoxides[4] has been discussed in terms of a nucleophilic ring opening by a solvated electron,[4b] it is more likely that the mechanism is analogous to that of radical-anion reductions of organic halides,[5] aryl ethers,[1b] and phenyl thioethers.[1b,6] It thus involves electron transfer to the epoxide, followed by ring cleavage of the radical anion **2** to give a species containing an oxyanion and a radical. However, an apparent weakness of this mechanism is that, contrary to intuitive expectations, the less substituted radical must be formed in this step. One possible explanation, proposed by Bartmann,[3] is that the electron is localized in the antibonding

(7) **2**·6CH$_2$Cl$_2$ (C$_{60}$H$_{104}$N$_{12}$O$_2$B$_2$Cl$_{12}$Cu$_2$, MW 1599.71) crystallized in the monoclinic space group $C_{2/c}$ with $a = 22.36$ (2) Å, $b = 13.290$ (4) Å, $c = 29.29$ (2) Å, $\beta = 114.59$ (6)°, $V = 7915$ (9) Å^3, $Z = 4$. Intensity data were collected on a Rigaku AFC-5 diffractometer with graphite-monochromated Mo Kα radiation. The data collection was made at −75 ± 5 °C with a crystal sealed in a glass capillary, since the crystals were found to lose CH$_2$Cl$_2$ of crystallization very quickly at room temperature. The structure was solved by a heavy-atom method and refined by a block-diagonal least-squares technique with anisotropic thermal factors for non-hydrogen atoms. Hydrogen atoms on the boron, pyrazolyl rings, and tertiary positions of iPr groups were calculated and fixed in the refinement. The other hydrogen atoms were not included in the calculations. The weighting scheme is $w = [\sigma_c{}^2 + (0.05|F_o|)^2]^{-1}$. The current R and R_w values are 0.101 and 0.148 for 3003 reflections ($2\theta < 45°$, $F_o > 3\sigma(F_o)$). The slightly high residual values are probably due to the deterioration of the crystallinity during the mounting of the crystal, positional disorders of CH$_2$Cl$_2$ molecules and the isopropyl groups, and the fluctuation of the measurement temperature.

(8) Gubelmann, M. H.; Williams, A. F. *Struct. Bonding (Berlin)* **1983**, *55*, 1.

(9) The possibility of μ-η^2:η^2 structure was suggested for several complexes: (a) Sakurai, F.; Suzuki, H.; Moro-oka, Y.; Ikawa, T. *J. Am. Chem. Soc.* **1980**, *102*, 1749. (b) Kim, K.; Collman, J. P.; Ibers, J. A. *Ibid.* **1988**, *110*, 4242. The novel coordination mode of bridged peroxide ion, μ_4-η^2:η^2, has been found recently in a tetranuclear iron complex. Micklitz, W.; Bott, S. G.; Bentsen, J. G.; Lippard, S. J. *J. Am. Chem. Soc.* **1989**, *111*, 372.

(10) Karlin et al. have proposed μ-η^2:η^2 coordination (nonplanar) as a possible structure for their peroxo binuclear copper complexes based on the EXAFS analyses. The complexes, as well as **1** and **2**, contain also N_3 ligands, and the copper ions are bridged solely by a peroxide ion. Blackburn, N. J.; Strange, R. W.; Farooq, A.; Haka, M. S.; Karlin, K. D. *J. Am. Chem. Soc.* **1988**, *110*, 4263.

(11) [(UO$_2$Cl$_3$)$_2$(O$_2$)]$^{4-}$: Haegele, R.; Boeyens, J. C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 648.

(12) [La(N(SiMe$_3$)$_2$)$_2$(PPh$_3$O)]$_2$(O$_2$): Bradley, D. C.; Ghota, J. S.; Hart, F. A.; Hursthouse, M. B.; Raithby, P. R. *Ibid.* **1977**, 1166.

(13) Woolery, G. L.; Powers, L.; Winkler, M.; Solomon, E. I.; Spiro, T. G. *J. Am. Chem. Soc.* **1984**, *106*, 86.

(14) Woolery, G. L.; Powers, L.; Winkler, M.; Solomon, E. I.; Lerch, K.; Spiro, T. G. *Biochem. Biophys. Acta* **1984**, *788*, 155.

(15) Gaykema, W. P. J.; Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1985**, *187*, 255.

[†] University of California.
[‡] University of Pittsburgh.

(1) (a) House, H. O. *Modern Synthetic Reactions*, 2nd ed.; Benjamin: Menlo Park, CA, 1972; p 103–105. (b) Maercker, A. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 972.

(2) Cohen, T.; Jeong, I.-H.; Mudryk, B.; Bhupathy, M.; Awad, M. M. A. *J. Org. Chem.* In press.

(3) Bartmann, E. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 653.

(4) (a) Birch, A. J. *J. Proc. Roy. Soc. N.S.W.* **1949**, *83*, 245. (b) Hallsworth, A. S.; Henbest, H. B. *J. Chem. Soc.* **1957**, 4604. (c) Hallsworth, A. S.; Henbest, H. B. *J. Chem. Soc.* **1960**, 3571. (d) Brown, H. C.; Ikegami, S.; Kawakami, J. H. *J. Org. Chem.* **1970**, *35*, 3243. (e) Kaiser, E. M.; Edmonds, C. G.; Grubb, S. D.; Smith, J. W.; Tramp, D. *J. Org. Chem.* **1971**, *36*, 330. (f) Benkeser, R. A.; Rappa, A.; Wolsieffer, L. A. *J. Org. Chem.* **1986**, *51*, 3391. See also ref 1a, p 227.

(5) Holy, N. L. *Chem. Rev.* **1974**, *74*, 243. Garst, J. F. *Acc. Chem. Res.* **1971**, *4*, 400. Garst, J. F. In *Free Radicals*; Kochi, J. F., Ed.; Wiley-Interscience: New York, 1973; pp 503–546. See also: Andrieux, C. P.; Gallardo, I.; Savéant, J. M.; Su, K. B. *J. Am. Chem. Soc.* **1986**, *108*, 638.

(6) Cohen, T.; Bupathy, M. *Acc. Chem. Res.* **1989**, *22*, 152 and citations therein.