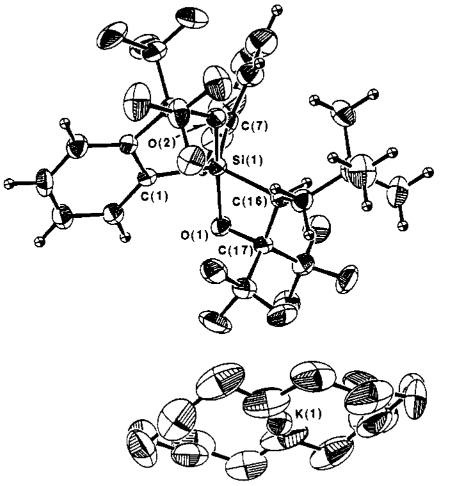
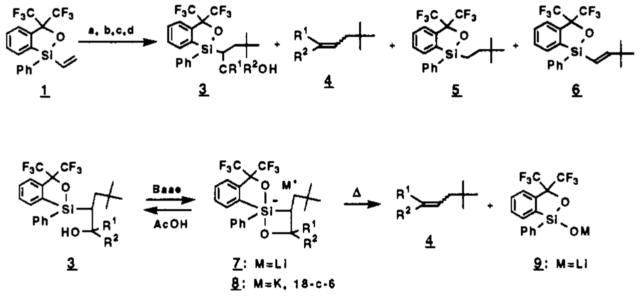


Figure 1. ORTEP drawing of **8a**. Selected bond lengths (Å) and bond angles (deg): Si(1)–O(1), 1.844 (4); Si(1)–O(2), 1.798 (4); Si(1)–C(16), 1.913 (5); O(1)–Si(1)–O(2), 166.3 (2); C(1)–Si(1)–C(7), 115.4 (2); C(1)–Si(1)–C(16), 132.7 (2); C(7)–P(1)–C(16), 111.1 (2); O(1)–Si-(1)–C(16), 73.9 (2); O(2)–Si(1)–C(1), 85.6 (2).

Scheme I

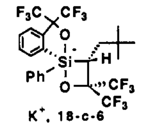


(a: $R^1=R^2=CF_3$; b: $R^1=H$, $R^2=Ph$)

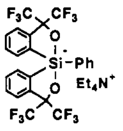
(a) 1.5 equiv *t*-BuLi, THF, -78 °C. (b) 5 equiv HMPA, -78 °C. (c) $R^1R^2C{=}O$ (2), -78 °C. (d) AcOH.

The use of KH instead of *n*-BuLi as base in the presence of 18-crown-6 in THF gave potassium 1,2-oxasiletanide **8a** in 91% yield as colorless needles after recrystallization from hexane–dichloromethane. Its ^{19}F and ^{29}Si NMR spectra are very similar to those of the lithium salt **7a**.

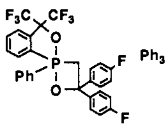
The X-ray crystallographic analysis of **8a** indicated that it has a distorted TBP (trigonal bipyramide) structure (Figure 1).[10,11] The phenyl group on silicon is trans to the neopentyl group, and as expected, two oxygen and three carbon atoms occupy apical and equatorial positions, respectively. The bond angle O(1)–Si(1)–O(2) between two apical bonds deviates by 13.7 (2)° from 180°. The bond length of Si–O(1) (1.844 (4) Å) is slightly longer than that of Si–O(2) (1.798 (4) Å), although both bonds are substantially longer than that of the Si–O bond (1.696 (6) Å) of a tetracoordinate 1,2-oxasiletane.[12] The structure of the Martin ligand moiety is very similar to that of pentacoordinate compounds such as **10**[8a] and **11**.[3] The strain of the four-membered ring seems to be reduced by elongating the apical Si–O(1) bond in contrast to a tetracoordinate oxasiletane with ususually long C–C and Si–C bonds.[12]



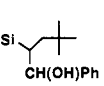
8a



10



11



12

Similarly, a single benzaldehyde adduct **3b** reacted with *n*-BuLi and KH to give **7b** (δ_{Si} −66.69) and **8b** (δ_{Si} −66.31), which decomposed slowly at room temperature and 50 °C, respectively, to give exclusively (*Z*)-**4b**.[13,14] Since the benzaldehyde adduct **12** prepared from triphenylvinylsilane instead of **1** gave no upfield signal characteristic of a pentacoordinate siletanide in ^{29}Si NMR under the same conditions, the Martin ligand is considered to play an important role in stabilizing a 1,2-oxasiletanide structure.

Acknowledgment. This work was partially supported by a Grant-in-Aid for Scientific Research on Priority Area of Organic Unusual Valency No. 02247205 (T.K.) from the Ministry of Education, Science, and Culture, Japan. We are grateful to Dr. N. Tokitoh of the University of Tokyo for the determination of the X-ray structure of **8a**. We also thank Central Glass and Tosoh Akzo Co. Ltd. for gifts of hexafluorocumyl alcohol and alkyllithiums, respectively.

Supplementary Material Available: Listing of physical and spectral data of **1**, **3a**, **4a**, **5**, **6**, **8a**, and **8b** and tables of X-ray crystallographic data including thermal and positional parameters, bond lengths, and bond angles for **8a** (14 pages). Ordering information is given on any current masthead page.

---

(9) The signals due to **7a** were also observed in the reaction mixture of the preparation of **3a**.

(10) $C_{36}H_{45}F_{12}KO_8Si$, FW = 900.91, crystal dimensions (mm) 0.560 × 0.650 × 0.440, triclinic, space group *P*1, $a = 14.063$ (2) Å, $b = 14.919$ (2) Å, $c = 11.451$ (2) Å, $\alpha = 97.78$ (1)°, $\beta = 114.27$ (1)°, $\gamma = 74.45$ (1)°, $V = 2104.8$ (6) Å^3, $Z = 2$, $D_{calcd} = 1.421$ g/cm^3, $R = 0.057$ ($R_w = 0.069$). Full details of the crystallographic structure analysis are described in the supplementary material.

(11) The percentage (TBP → SP) was calculated to be 37.4% by a reported method: Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318.

(12) Brook, A. G.; Chatterton, W. J.; Sawyer, J. F.; Hughes, D. W.; Vorspohl, K. *Organometallics* **1987**, *6*, 1246.

(13) Unexpectedly, the ^{19}F NMR spectra of **7b** and **8b** showed two sets of double quartets (2:1), indicating the presence of two diastereomers. For the ^1H and ^{19}F NMR spectra of **8b**, see the supplementary material.

(14) A single diastereomer **3b** was treated with a few drops of concentrated H_2SO_4 in THF at room temperature to give mainly (*E*)-**4b** (*E*:*Z*, 75:25), indicating that anti-elimination probably occurs under acidic conditions as with the usual Peterson reaction.

A Dinuclear Mixed-Valence Cu(I)/Cu(II) Complex and Its Reversible Reaction with Dioxygen: Generation of a Superoxodicopper(II) Species

Mohammad Mahroof-Tahir and Kenneth D. Karlin*

Department of Chemistry
The Johns Hopkins University
Baltimore, Maryland 21218

Received May 21, 1992

In this report, we describe a dinuclear mixed-valence Cu(I)/Cu(II) complex, which *reversibly* reacts with dioxygen (O_2) to form a Cu_2O_2 adduct, formally a superoxodicopper(II) complex.

The reaction of O_2 with copper(I) ion is of fundamental importance in a variety of chemical and biological processes.[1-4] The latter include O_2 transport by hemocyanin (Hc),[5,6] substrate

---

* Author to whom correspondence should be addressed.

(1) (a) Karlin, K. D.; Gultneh, Y. *Prog. Inorg. Chem.* **1987**, *35*, 219–327. (b) Tyeklár, Z.; Karlin, K. D. *Acc. Chem. Res.* **1989**, *22*, 241–248. (c) Karlin, K. D.; Tyeklár, Z.; Zuberbühler, A. D. In *Bioinorganic Catalysis*; Reedijk, J., Ed.; Marcel Dekker: New York, in press. (d) Karlin, K. D.; Tyeklár, Z. *Adv. Inorg. Biochem.*, in press.

(2) Sorrell, T. N. *Tetrahedron* **1989**, *45*, 3–68.

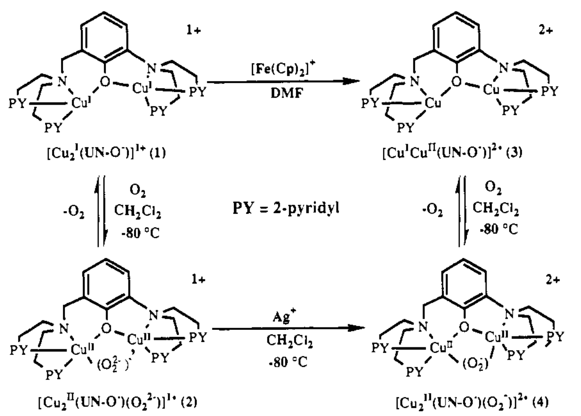
(3) Kitajima, N. *Adv. Inorg. Chem.*, in press.

(4) (a) Zuberbühler, A. D. In *Copper Coordination Chemistry: Biochemical and Inorganic Perspectives*; Karlin, K. D., Zubieta, J., Eds.; Adenine: Guilderland, NY, 1983; pp 237–258. (b) Gampp, H.; Zuberbühler, A. D. *Metal Ions Biol. Syst.* **1981**, *12*, 133–189.

(5) Volbeda, A.; Hol, W. G. J. *J. Mol. Biol.* **1989**, *209*, 249–279.

(6) (a) Solomon, E. I.; Baldwin, M. J.; Lowery, M. *Chem. Rev.* **1992**, *92*, 521–542. (b) Ross, P. K.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 3246–3259. (c) Solomon, E. I. In *Metal Clusters in Proteins*; Que, L., Jr., Ed.; ACS Symposium Series 372; American Chemical Society: Washington, DC, 1988; pp 116–150.

Scheme I



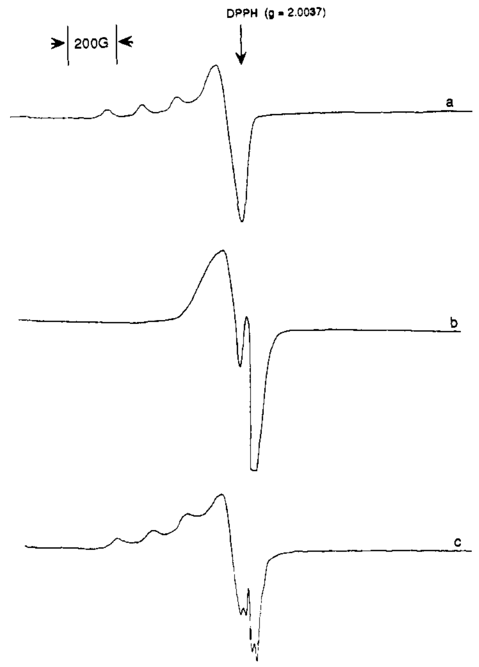


Figure 1. EPR spectra of (a) $[Cu^ICu^{II}(UN\text{-}O^-)]^{2+}$ (**3**), (b) $[Cu_2(UN\text{-}O^-)(O_2^-)]^{2+}$ (**4**), and (c) reaction of **4** plus 3 equiv of M_4PO. See text for further explanation.

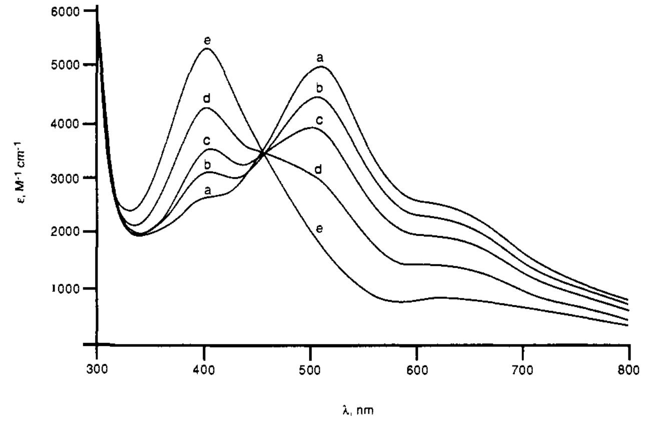


Figure 2.

hydroxylation by copper monooxygenases,[7-10] and oxidases where O_2 is reduced to H_2O_2 or water.[11-13] The primary interaction of O_2 with Cu(I) can lead to a 1:1 Cu/O_2 adduct, which may be thought of as a Cu(II)-coordinated superoxide, $[O_2^-]$. Such species are important in the Cu/Zn superoxide dismutase (SOD) reaction cycle,[14] and they may be present in dopamine-β-hydroxylase,[8] phenylalanine hydroxylase,[10] and cytochrome *c* oxidase.[15] Chemical studies involving the $Cu^{II}O_2^-$ species are of considerable interest;[16-24] we recently reported the first kinetic parameters for formation of a primary 1:1 Cu/O_2 adduct in a synthetic model system.[25]

One of several classes of copper dioxygen complexes we have previously studied[1] involves phenoxo-bridged dicopper species.[26-28] This includes the unsymmetrical dicopper(I) species $[Cu_2(UN\text{-}O^-)]^+$ (**1**), which reacts reversibly with O_2 at -80 °C to give peroxodicopper(II) complex $[Cu_2(UN\text{-}O^-)(O_2^{2-})]^+$ (**2**) (Scheme I).[28,29] Recently, we studied the redox behavior of **1** and observed

---

[7] (a) Wilcox, D. E.; Porras, A. G.; Hwang, Y. T.; Lerch, K.; Winkler, M. E.; Solomon, E. I. *J. Am. Chem. Soc.* **1985**, *107*, 4015–4027. (b) Robb, D. A. In *Copper Proteins and Copper Enzymes*; Lontie, R., Ed.; CRC: Boca Raton, FL, 1984; Vol. 2, pp 207–241. (c) Lerch, K. *Metal Ions Biol. Syst.* **1981**, *13*, 143–186.

[8] (a) Brenner, M. C.; Klinman, J. P. *Biochemistry* **1989**, *28*, 4664–4670. (b) Stewart, L. C.; Klinman, J. P. *Annu. Rev. Biochem.* **1988**, *57*, 551–592.

[9] (a) Zabriskie, T. M.; Cheng, H.; Vederas, J. C. *J. Chem. Soc., Chem. Commun.* **1991**, 571–572. (b) Reddy, K. V.; Jin, S.-J.; Arora, P. K.; Sfeir, D. S.; Feke Maloney, S. C.; Urbach, F. L.; Sayre, L. M. *J. Am. Chem. Soc.* **1990**, *112*, 2332–2340. (c) Merkler, D. J.; Kulathila, R.; Consalvo, A. P.; Young, S. D.; Ash, D. E. *Biochemistry* **1992**, *31*, 7282–7288.

[10] (a) Pember, S. O.; Villifranca, J. J.; Benkovic, S. J. *Biochemistry* **1986**, *25*, 6611–6619. (b) Pember, S. O.; Johnson, K. A.; Villafranca, J. J.; Benkovic, S. J. *Biochemistry* **1989**, *28*, 2124–2130.

[11] Messerschmidt, A.; Ladenstein, R.; Huber, R.; Bolognesi, M.; Avigliano, L.; Petruzzelli, R.; Rossi, A.; Finazzi-Agrò, A. *J. Mol. Biol.* **1992**, *224*, 179–205. (b) Messerschmidt, A.; Huber, R. *Eur. J. Biochem.* **1990**, *187*, 341–352.

[12] (a) Clark, P. A.; Solomon, E. I. *J. Am. Chem. Soc.* **1992**, *114*, 1108–1110. (b) Cole, J. L.; Ballou, D. P.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 8544–8546. (c) Cole, J. L.; Avigliano, L.; Morpurgo, L.; Solomon, E. I. *J. Am. Chem. Soc.* **1991**, *113*, 9080–9089. (d) Cole, J. L.; Clark, P. A.; Solomon, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 9534–9548. (e) Cole, J. L.; Tan, G. O.; Yang, E. K.; Hodgson, K. O.; Solomon, E. I. *J. Am. Chem. Soc.* **1990**, *112*, 2243–2249.

[13] (a) Babcock, G. T.; Wikström, M. *Nature* **1992**, *356*, 301–309 and references cited therein. (b) Chan, S. I.; Li, P. M. *Biochemistry* **1990**, *29*, 1–12. (c) Malmström, B. G. *Chem. Rev.* **1990**, 1247–1260. (d) Capaldi, R. A. *Annu. Rev. Biochem.* **1990**, *59*, 569–596. (e) Scott, R. A. *Annu. Rev. Biophys. Biophys. Chem.* **1989**, *18*, 137–158.

[14] Bertini, I.; Banci, L.; Piccioli, M.; Luchinat, C. *Coord. Chem. Rev.* **1990**, *100*, 67–103.

[15] (a) Oliveberg, M.; Malmström, B. G. *Biochemistry* **1992**, *31*, 3560–3563. (b) Blackmore, R. S.; Greenwood, C.; Gibson, Q. H. *J. Biol. Chem.* **1991**, *266*, 19245–19249.

[16] Synthetic $Cu^{II}O_2^-$ complexes are included in the following: (a) Nappa, M.; Valentine, J. S.; Miksztal, A. R.; Schugar, H. G.; Isied, S. S. *J. Am. Chem. Soc.* **1979**, *101*, 7744–7746. (b) Thompson, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 4057–4059. (c) Thompson, J. S. In *Biological & Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, NY, 1986; Vol. 2, pp 1–10.

[17] There is some question or controversy concerning the formulation of the $LCu(O_2)$ 1:1 species described by Thompson.[16b,c] See ref 18.

[18] Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Toriumi, K.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277–1291.

[19] (a) Strothkamp, K. G.; Lippard, S. J. *Acc. Chem. Res.* **1982**, *15*, 318–326. (b) O'Young, C.-L.; Lippard, S. J. *J. Am. Chem. Soc.* **1980**, *102*, 4920–4924.

[20] Weinstein, J.; Bielski, B. H. J. *J. Am. Chem. Soc.* **1980**, *102*, 4916–4919.

[21] Roberts, J. L., Jr.; Sawyer, D. T. *Isr. J. Chem.* **1983**, *23*, 430–438.

[22] (a) Tait, A. M.; Hoffman, M. Z.; Hayon, E. *Inorg. Chem.* **1976**, *15*, 934. (b) Bailey, C. L.; Bereman, R. D.; Rillema, D. P. *Inorg. Chem.* **1986**, *25*, 3149–3153.

[23] Nishida, Y.; Unoura, K.; Watanabe, I.; Yokomizo, T.; Kato, Y. *Inorg. Chim. Acta* **1991**, *181*, 141–143.

[24] (a) Czapski, G.; Goldstein, S.; Meyerstein, D. *Free Radical Res. Commun.* **1988**, *4*, 231–236. (b) Goldstein, S.; Czapski, G. *Free Radical Res. Commun.* **1991**, *12–13*, 205–210 and references cited therein.

[25] Karlin, K. D.; Wei, N.; Jung, B.; Kaderli, S.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1991**, *113*, 5868–5870.

[26] (a) Karlin, K. D.; Cruse, R. W.; Gultneh, Y.; Farooq, A.; Hayes, J. C.; Zubieta, J. *J. Am. Chem. Soc.* **1987**, *109*, 2668–2679. (b) Pate, J. E.; Cruse, R. W.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1987**, *109*, 2668–2679. (c) Blackburn, N. J.; Strange, R. W.; Cruse, R. W.; Karlin, K. D. *J. Am. Chem. Soc.* **1987**, *109*, 1235–1237.

[27] Karlin, K. D.; Ghosh, P.; Cruse, R. W.; Farooq, A.; Gultneh, Y.; Jacobson, R. R.; Blackburn, N. J.; Strange, R. W.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 6769–6780.

[28] Mahroof-Tahir, M.; Murthy, N. N.; Karlin, K. D.; Blackburn, N. J.; Shaikh, S. N.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 3001–3003.

[29] Nasir, M. S.; Karlin, K. D.; McGowty, D.; Zubieta, J. *J. Am. Chem. Soc.* **1991**, *113*, 698–700.

that it undergoes a facile quasi-reversible one-electron oxidation (cyclic voltammetry in DMF; $E_{1/2} = -587$ mV vs Ag/Ag^+; $n = 1$). Using ferricinium ion as oxidant, we were able to isolate a brownish-green mixed-valence compound $[Cu^ICu^{II}(UN\text{-}O^-)]^{2+}$ (**3**).[30] This $S = {}^1/_2$ species has a magnetic moment $\mu_{eff}/Cu_{RT} = 2.0 \pm 0.1\ \mu_B$, no low-energy intervalence charge-transfer band is observed,[31] and it exhibits a four-line EPR spectrum ($g_\parallel = 2.25$, $A_\parallel = 155 \times 10^{-4}$ cm^{-1}; 77 K, CH_2Cl_2/C_7H_8) (Figure 1a). This latter behavior suggests a localized valence-trapped Cu(I)/Cu(II) structure for **3**, similar to that seen for a number of other RO^- bridged mixed-valence dicopper complexes.[32]

As followed by UV-vis spectroscopy at −80 °C, bubbling $[Cu^ICu^{II}(UN\text{-}O^-)]^{2+}$ (**3**) with O_2 causes a change to bright green (spectrum e; $\lambda_{max} = 404$ nm, $\epsilon = 5400$ M^{-1} cm^{-1} (Figure 2); $O_2^- \rightarrow$ Cu(II) (LMCT?)). The product is formulated as a superoxodicopper(II) complex $[Cu_2(UN\text{-}O^-)(O_2^-)]^{2+}$ (**4**), consistent with manometric measurements indicating $\mathbf{3}/O_2 = 1.1 \pm 0.1$. The binding of O_2 to **3** is reversible; via the application of a vacuum (with brief warming), several oxygenation/deoxygneation cycles can be effected and followed spectrophotometrically. An EPR spectrum (77 K, CH_2Cl_2/C_7H_8) of $[Cu_2(UN\text{-}O^-)(O_2^-)]^{2+}$ (**4**) is shown in Figure 1b. The $g = 1.91\text{-}2.20$ absorptions occur over a broader range than those seen for free O_2^-,[33] superoxocobalt(III) and O_2^- bridged dicobalt(III) compounds,[34-36] or other MO_2^- species.[37] This may reflect delocalization and coupling to the two $I = {}^3/_2$ Cu(II) ions, but further EPR spectroscopic and electronic structural studies are required.[38] A further indication for the presence of the superoxo radical anion in $[Cu_2(UN\text{-}O^-)(O_2^-)]^{2+}$ (**4**) is that, when the complex is reacted with the spin-trapping agent M_4PO (M_4PO = 3,3,5,5-tetramethyl-1-pyrroline *N*-oxide),[39] a mixture[40] which includes a sharp triplet centered at $g = 2.006$ ($A_N = 20$ G) (Figure 1c, 77 K, CH_2Cl_2/C_7H_8) is generated, indicating the formation of a superoxo–M_4PO adduct which may or may not be coordinated to the coppers. Spin-trapping agents have been used similarly in detecting adducts with superoxocobalt[41] and -iron[42] complexes.

Further proof for the formulation and superoxo nature of $[Cu_2(UN\text{-}O^-)(O_2^-)]^{2+}$ (**4**) comes from its observed relationship to peroxo complex $[Cu_2(UN\text{-}O^-)(O_2^{2-})]^+$ (**2**). As is the case in the well-established $\{Co^{III}(O_2)Co^{III}\}^{4+,5+}$ compounds,[34] oxidation of the peroxo complex **2** directly produces **4**. A spectrophotometric titration where ${}^1/_4$ mol equiv of $Ag(CF_3SO_3)$ as oxidant is added successively (spectra b–e) shows that the 510-nm band associated with **2** (spectrum a) decreases with concomitant formation of the 404-nm absorption of **4**; $[Cu_2(UN\text{-}O^-)(O_2^-)]^{2+}$ (**4**) generated in this manner is spectroscopically identical to that obtained by addition of O_2 to $[Cu^ICu^{II}(UN\text{-}O^-)]^{2+}$ (**3**) (Figure 2).

In summary, we have described here still another type of dioxygen adduct of copper ion, a one-electron-reduced species formed at a dicopper center. Further elaboration of this type of chemistry is in progress. Fundamental structural and spectroscopic interest in such moieties is also relevant to O_2 reduction chemistry in proteins such as laccase and ascorbate oxidase, where binding of reduced O_2 intermediates occurs at a dicopper segment of a tricopper cluster.[6a,12a,b]

Acknowledgment. We thank the National Institutes of Health (GM 28962) for support of this research.

---

[30] (a) $[Cu^ICu^{II}(UN\text{-}O^-)](PF_6)_2\cdot{}^1/_4DMF$ (**3**): IR (Nujol) $\nu(PF_6) = 840$ cm^{-1}, ν(C═O; DMF) = 1645 cm^{-1}; UV–vis [CH_2Cl_2; λ_{max}, nm (ϵ, M^{-1} cm^{-1})] 348 (4000, sh), 680 (360). Anal. Calcd for $C_{35.75}H_{38.75}Cu_2F_{12}N_{6.25}O_{1.25}P_2$: C, 43.24; H, 3.90; N, 8.82. Found: C, 43.55; H, 3.97; N, 8.56.

[31] (a) The existence or intensity of intervalence charge-transfer bands (IT) can be quite variable.[32] For a recent example of a mixed-valence copper complex with an intense near-IR band, see: Harding, C.; McKee, V.; Nelson, J. *J. Am. Chem. Soc.* **1991**, *113*, 9684–9685.

[32] (a) Long, R. C.; Hendrickson, D. N. *J. Am. Chem. Soc.* **1983**, *105*, 1513–1521. (b) Hendrickson, D. N.; Long, R. C.; Hwang, Y. T.; Chang, H. R. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Adenine Press: Guilderland, New York, 1985. (c) Gagnê, R. R.; Koval, C. A.; Smith, T. J.; Comolino, M. C. *J. Am. Chem. Soc.* **1979**, *101*, 4571–4580. (d) Gagnê, R. R.; Henling, L. M.; Kistenmacher, T. J. *Inorg. Chem.* **1980**, *19*, 1226–1230. (e) Gagnê, R. R.; Koval, C. A.; Smith, T. J. *J. Am. Chem. Soc.* **1977**, *99*, 8367–8368.

[33] (a) Green, M. R.; Hill, H. A. O.; Turner, D. R. *FEBS Lett.* **1979**, *103*, 176–180. (b) Valentine, J. S. In *Oxygen: Biochemical and Clinical Aspects*; Caughey, W. S., Ed.; Academic Press: New York, 1979; pp 659–677.

[34] (a) Niederhoffer, E. C.; Timmons, J. H.; Martell, A. E. *Chem. Rev.* **1984**, 137–203. (b) Wilkens, R. G. In *Oxygen Complexes and Oxygen Activation by Transition Metals*; Martell, A. E., Sawyer, D. T., Eds.; Plenum: New York, 1988; pp 49–60. (c) Fallab, S.; Mitchell, P. R. *Adv. Inorg. Bioinorg. Mech.* **1984**, *3*, 311–377. (d) Jones, R. D.; Sommerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *2*, 139.

[35] Smith, T. D.; Ruzic, I. M.; Tirant, S.; Pilbrow, J. R. *J. Chem. Soc., Dalton Trans.* **1982**, 363–372.

[36] (a) Mori, M.; Weil, J. A.; Kinnaird, J. K. *J. Phys. Chem.* **1967**, *71*, 103–108. (b) Duffy, D. L.; House, D. A.; Weil, J. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2053–2058.

[37] (a) Bear, J. L.; Yao, C.-L.; Capdevielle, F. J.; Kadish, K. M. *Inorg. Chem.* **1988**, *27*, 3782–3785. (b) Hasegawa, K.; Imamura, T.; Fujimoto, M. *Inorg. Chem.* **1986**, *25*, 2154–2160. (c) Raynor, J. B.; Gillard, R. D.; Pedrosa de Jesus, J. D. *J. Chem. Soc., Dalton Trans.* **1982**, 1165–1166. (d) Wayland, B. B.; Newman, A. R. *Inorg. Chem.* **1981**, *20*, 3093–3097.

[38] (a) Solomon and co-workers[6a,12d] have recently discussed electronic interactions occurring in a cluster with three $S = {}^1/_2$ spins (i.e., three Cu(II)), possibly analogous to that seen here, i.e., with two Cu(II) plus O_2^-. (b) As one possibility, Figure 1b may be the spectrum of a superoxide radical (sharp spike at $g \approx 2.0$) which is essentially uncoupled to the dicopper(II) center, i.e., with its broader signals plus a weak half-field line near $g = 4$. The latter weak $g \approx 4$ signal is indeed observed.

[39] Janzen, E. G.; Shetty, R. V.; Kunanec, S. M. *Can. J. Chem.* **1981**, *59*, 756–758.

[40] We speculate that the four-line signal observed in Figure 1c may be due to the presence of $[Cu^ICu^{II}(UN\text{-}O^-)]^{2+}$ (**3**), an M_4PO adduct with **3** ($g_\parallel = 2.26$, $A_\parallel = 162 \times 10^{-4}$ cm^{-1}, independently determined), or a dicopper(II) derivative if a superoxo–TEMPO adduct dissociates.

[41] Hamilton, D. E.; Drago, R. S.; Telser, J. *J. Am. Chem. Soc.* **1984**, *106*, 5353–5355.

[42] Herron, N.; Schammel, W. P.; Jackels, S. C.; Grzybowski, J. J.; Zimmer, L. L.; Busch, D. H. *Inorg. Chem.* **1983**, *22*, 1433–1440.

(*Z*)-3-Fluorophosphoenolpyruvate as a Pseudosubstrate of EPSP Synthase: Enzymatic Synthesis of a Stable Fluoro Analog of the Catalytic Intermediate

Mark C. Walker* and Claude R. Jones

New Products Division
The Agricultural Group
Monsanto Company
800 North Lindbergh Boulevard
St. Louis, Missouri 63167

Ronald L. Somerville

Department of Biochemistry
Purdue University
West Lafayette, Indiana 47907

James A. Sikorski

Monsanto Corporate Research
700 Chesterfield Parkway North
St. Louis, Missouri 63198

Received June 8, 1992

The critical plant enzyme EPSP synthase[1,2] (5-enolpyruvoylshikimate-3-phosphate synthase) catalyzes an unusual transfer of a carboxyvinyl moiety derived from phosphoenolpyruvate (PEP) to the 5-OH of shikimate 3-phosphate (S3P). The reaction proceeds through a single, kinetically competent tetrahedral intermediate[3] (I) which has been previously isolated.[4] While a variety of PEP analogs have been examined as alternate substrates

---

* Author to whom correspondence should be addressed.

[1] Sikorski, J. A.; Anderson, K. S.; Cleary, D. G.; Miller, M. J.; Pansegrau, P. D.; Ream, J. E.; Sammons, R. D.; Johnson, K. A. In *Chemical Aspects of Enzyme Biotechnology: Fundamentals*; Baldwin, T. O., Raushel, F. M., Scott, A. I., Eds.; Plenum Press: New York, 1991; pp 23–39.

[2] Anderson, K. S.; Johnson, K. A. *Chem. Rev.* **1990**, *90*, 1131–1149.

[3] Anderson, K. S.; Sikorski, J. A.; Johnson, K. A. *Biochemistry* **1988**, *27*, 7395–7406.

[4] Anderson, K. S.; Sikorski, J. A.; Benesi, A. J.; Johnson, K. A. *J. Am. Chem. Soc.* **1988**, *110*, 6577–6579.

0002-7863/92/1514-7601$03.00/0