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Oxo-Transfer Reaction from a Bis(μ-oxo)dicopper(III) Complex to Sulfides

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Abstract: Oxygenation of sulfides to the corresponding sulfoxides by a distinct bis(μ-oxo)dicopper(III) complex has been accomplished for the first time using 2-(2-pyridyl)ethylamine derivative L^{Py1Bz} (*N*-ethyl-*N*-[2-(2-pyridyl)ethyl]-α,α-dideuteriobenzylamine) as the supporting ligand. Detailed kinetic analysis has indicated that the reaction consists of two distinct steps, where the first quick process is association of the substrate to the bis(μ-oxo)dicopper(III) complex (k_1) and the second slow process is intramolecular oxygen atom transfer from the copper−oxo species to the substrate in the associated complex (k_2). The rate constant k_2 of the second process is rather insensitive to the oxidation potential of the substrates, suggesting that the oxo-transfer reaction proceeds via a mechanism involving direct oxygen atom transfer rather than a mechanism involving electron transfer.

Introduction

Oxygen atom transfer from metal−oxo species to organic or inorganic substances is ubiquitous not only in a wide variety of biological processes but also in numerous catalytic oxygenation reactions.[1] Much attention has so far been focused on the oxygen-transfer reactions catalyzed by iron porphyrin complexes as well as a series of model compounds of non-heme iron oxygenases.[1] Recently, a great deal of information on the structure and physicochemical properties of copper/dioxygen species has also appeared to provide valuable insight into dioxygen activation mechanism by copper monooxygenases.[2] Among a series of copper dioxygen complexes so far reported, (μ-η^2:η^2-peroxo)dicopper(II) and bis(μ-oxo)dicopper(III) complexes have recently attracted much attention, since they are considered as possible active oxygen intermediates of copper monooxygenases carrying a dinuclear metal active center.[2]

(μ-η^2:η^2-peroxo)Cu(II)$_2$ bis(μ-oxo)Cu(III)$_2$

With respect to the ability of oxygen atom transfer including hydroxylation reaction of these copper/dioxygen species, the (μ-η^2:η^2-peroxo)dicopper(II) complex has been demonstrated to hydroxylate aromatic ring of the supporting ligand[3] as well as phenolic compounds as external substrates.[4,5] Mechanistic studies have suggested that the aromatic hydroxylation by the (μ-η^2:η^2-peroxo)dicopper(II) complex proceeds via an electrophilic aromatic substitution reaction mechanism.[5,6] An oxo-transfer reaction mediated by a (μ-η^2:η^2-peroxo)dicopper(II) complex has also been reported recently, in which the amine moiety of the supporting ligand is converted into the corresponding *N*-oxide.[7]

The bis(μ-oxo)dicopper(III) complex, on the other hand, has been shown to undergo *intramolecular* aliphatic ligand hydroxylation via hydrogen atom abstraction and subsequent oxygen rebound mechanism or its concerted variant.[8,9] However,

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(1) (a) Valentine, J. S., Foote, C. S., Greenberg, A., Liebman, J. F., Eds. *Active Oxygen in Biochemistry*; Chapman & Hall: London, 1995. (b) Foote, C. S., Valentine, J. S., Greenberg, A., Liebman, J. F., Eds. *Active Oxygen in Chemistry*; Chapman and Hall: London, 1995. (c) Meunier, B., Ed. *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Imperial College Press: London, 2000. (d) Meunier, B., Ed. *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations*; Springer: Berlin, 2000. (e) Ortiz, de Montellano, P. R., Ed. *Cytochrome P-450. Structure, Mechanism, and Biochemistry*; Plenum Press: New York, 1986.

(2) (a) Karlin, K. D., Tyeklár, Z., Eds. *Bioinorganic Chemistry of Copper*; Chapman & Hall: New York, 1993. (b) Kitajima, N.; Moro-oka, Y. *Chem. Rev.* **1994**, *94*, 737−757. (c) Liang, H. C.; Dahan, M.; Karlin, K. D. *Curr. Opin. Chem. Biol.* **1999**, *3*, 168−175. (d) Tolman, W. B. *Acc. Chem. Res.* **1997**, *30*, 227−237. (e) Holland, P. L.; Tolman, W. B. *Coord. Chem. Rev.* **1999**, *190−192*, 855−869. (f) Blackman, A. G.; Tolman, W. B. In *Metal-Oxo and Metal-Peroxo Species in Catalytic Oxidations*; Meunier, B., Ed.; Springer: Berlin, 2000; pp 179−211. (g) Kopf, M.-A.; Karlin, K. D. In *Biomimetic Oxidations Catalyzed by Transition Metal Complexes*; Meunier, B., Ed.; Imperial College Press: London, 2000; pp 309−362. (h) Mahadevan, V.; Gebbink, R. K.; Stack, T. D. P. *Curr. Opin. Chem. Biol.* **2000**, *4*, 228−234. (i) Schindler, S. *Eur. J. Inorg. Chem.* **2000**, 2311−2326.

(3) (a) Karlin, K. D.; Dahlstrom, P. L.; Cozzette, S. N.; Scensny, P. M.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1981**, 881−882. (b) Karlin, K. D.; Hayes, J. C.; Gultneh, Y.; Cruse, R. W.; McKown, J. W.; Hutchinson, J. P.; Zubieta, J. *J. Am. Chem. Soc.* **1984**, *106*, 2121−2128.

(4) Santagostini, L.; Gullotti, M.; Monzani, E.; Casella, L.; Dillinger, R.; Tuczek, F. *Chem. Eur. J.* **2000**, *6*, 519−522.

(5) Itoh, S.; Kumei, H.; Taki, M.; Nagatomo, S.; Kitagawa, T. Fukuzumi, S. *J. Am. Chem. Soc.* **2001**, *123*, 6708−6709.

(6) (a) Nasir, M. S.; Cohen, B. I.; Karlin, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 2482−2494. (b) Karlin, K. D.; Nasir, M. S.; Cohen, B. I.; Cruse, R. W.; Kaderli, S.; Zuberbühler, A. D. *J. Am. Chem. Soc.* **1994**, *116*, 1324−1336. (c) Pidcock, E.; Obias, H. V.; Zhang, C. X.; Karlin, K. D.; Solomon, E. I. *J. Am. Chem. Soc.* **1998**, *120*, 7841−7847.

(7) Zhang, C. X.; Liang, H.-C.; Kim, E.; Gan, Q.-F.; Tyeklár, Z.; Lam, K.-C.; Rheingold, A. L.; Kaderli, S.; Zuberbühler, A. D.; Karlin, K. D. *Chem. Commun.* **2001**, 631−632.

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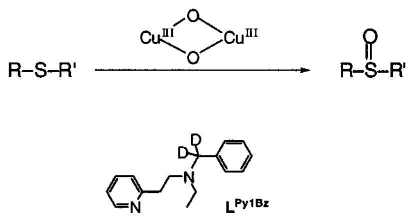
Scheme 1



little is known about the oxygen transfer reaction from the bis(μ-oxo)dicopper(III) complex to exogenous substrates.[10] Thus, it is highly desired to investigate the reactivity of bis(μ-oxo)dicopper(III) complex toward *intermolecular* oxygen atom transfer reaction not only to uncover the dioxygen activation mechanism by copper monooxygenases but also to develop an efficient catalyst for selective oxidation by dioxygen.

We report herein the first example of oxygenation of sulfides to the corresponding sulfoxides by a distinct bis(μ-oxo)dicopper(III) complex supported by bidentate ligand L^{Py1Bz} (*N*-ethyl-*N*-[2-(2-pyridyl)ethyl]-α,α-dideuteriobenzylamine) (Scheme 1).[11] Detailed kinetic analysis has indicated that the reaction proceeds via a direct oxygen atom transfer in a binary complex formed between the substrate and the metal−oxo species, providing further insight into the reactivity of non-heme dinuclear transition metal−oxo species. Reactivity of the (μ-η^2:η^2-peroxo)dicopper(II) and the bis(μ-oxo)dicopper(III) complexes in the oxo-transfer reaction has also been compared to provide valuable insight into the ongoing interest in the reactivity difference between the peroxo and the bis(μ-oxo) complexes.[10b]

Experimental Section

General. All chemicals used in this study except the ligand and the copper complex were commercial products of the highest available purity and were further purified by the standard methods before use.[12] Especially, the sulfide substrates were purified carefully to remove a trace amount of impurities. Synthesis and characterization of the bidentate ligand L^{Py1Bz} and the cuprous complex of L^{Py1Bz} have been reported elsewhere.[11] UV−vis spectra were measured using a Hewlett-Packard HP8453 diode array spectrophotometer with a Unisoku thermostated cell holder designed for low-temperature measurements. Mass spectra were recorded on a JEOL JMS-700T Tandem MS station. ^{1}H NMR spectra were recorded on a JEOL FT-NMR GX-300 spectrometer.

Product Analysis. Bis(μ-oxo)dicopper(III) complex, [Cu$^{III}_2$(L^{Py1Bz})$_2$(μ-O)$_2$](PF$_6$)$_2$ (**1**), was generated in situ by treating [Cu^I(L^{Py1Bz})(CH$_3$CN)]PF$_6$ (148 mg, 0.3 mmol) with O$_2$ gas at −80 °C in anhydrous acetone (200 mL) for 20 min.[11] Excess O$_2$ was then removed by bubbling Ar gas into the solution for 15 min. A cold solution (−80 °C) of thioanisole (124 mg, 1.0 mmol) in 3 mL of anhydrous acetone was added into the solution by cannulation, and the mixture was stirred for 3 h at this temperature. After evaporation of the solvent, 30 mL of ether was added to the remaining residue and the insoluble material was removed by filtration. The separated solid was further washed with additional ether (30 mL × 3), and the combined ether solution was concentrated to give an organic material, from which methyl phenyl sulfoxide was obtained in 83% yield by column chromatography (SiO$_2$, chloroform/ether).

Kinetics. Bis(μ-oxo)dicopper(III) complex, [Cu$^{III}_2$(L^{Py1Bz})$_2$(μ-O)$_2$](PF$_6$)$_2$ (**1**), was generated in situ by the reaction of [Cu^I(L^{Py1Bz})]PF$_6$ (1.0×10^{-4} M) and dry O$_2$ gas (introduced by gentle bubbling for a few minutes) in a UV−vis cell (1 cm path length) which was held in a Unisoku thermostated cell holder designed for low-temperature experiments (fixed within ±0.5 °C).[11] After generation of the bis(μ-oxo)dicopper(III) complex, excess O$_2$ was removed by bubbling Ar gas into the solution of the bis(μ-oxo)dicopper(III) complex for 10 min before addition of the substrate. During the bubbling of Ar gas, no spectral change of the bis(μ-oxo) complex was observed at this temperature. Then the reaction was initiated by adding an excess amount of the sulfide substrate into the solution, and the rate constants were determined by following the decrease in absorbance at 400 nm due to the bis(μ-oxo)dicopper(III) complex.

Electrochemical Measurements. Second harmonic ac voltammetry (SHACV) was employed to determine the one-electron-oxidation potentials (E^0_{ox}) of sulfides.[13] SHACV measurements were performed using a BAS 100B electrochemical analyzer in deaerated CH$_3$CN containing 0.10 M Bu$_4$N$^+$PF$_6^-$ as a supporting electrolyte at 298 K. The platinum working electrode was polished with alumina suspension and rinsed with acetone before use. The counter electrode was a platinum wire. The measured potentials were recorded with respect to an Ag/AgNO$_3$ (0.01 M) reference electrode. The E^0_{ox} values (vs Ag/AgNO$_3$) were converted to those vs SCE by addition of 0.29 V.

Theoretical Calculations. The heat of formation (ΔH_f) values of sulfides and the corresponding sulfoxides were calculated using the PM3 semiempirical molecular orbital method.[14] The calculations were performed using the MOL-MOLIS program, version 2.8, obtained by Daikin Industries, Ltd. Final geometries and energetics were obtained by optimizing the total molecular energy with respect to all structural variables.

Results and Discussion

Bis(μ-oxo)dicopper(III) complex **1** supported by the bidentate ligand (L^{Py1Bz}) was generated in situ by treating [Cu^I(L^{Py1Bz})(CH$_3$CN)]PF$_6$ with dry O$_2$ gas in acetone at a low temperature as reported previously.[11,15] Addition of thioanisole (1.0×10^{-3} M) to an acetone solution of **1** (5.0×10^{-5} M) at −80 °C under anaerobic conditions resulted in a spectral change shown in Figure 1. The characteristic absorption band at 400 nm (ϵ = 16 500 M^{-1} cm^{-1}) due to **1** (spectrum A) was rapidly converted to spectrum B (λ_{max} = 398 nm, ϵ = 8620 M^{-1} cm^{-1}), the intensity of which further decreased slowly as shown in the inset of Figure 1. Thus, the present reaction consists of two distinct steps. From the final reaction mixture, the oxygenation product, methyl phenyl sulfoxide, was isolated in 83% yield based on **1**.[16] An isotope-labeling experiment using ^{18}O$_2$ (95% pure) instead of ^{16}O$_2$ demonstrated that the oxygen atom source of

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(8) (a) Mahapatra, S.; Halfen, J. A.; Tolman, W. B. *J. Am. Chem. Soc*. **1996**, *118*, 11575−11586. (b) Itoh, S.; Taki, M.; Nakao, H.; Holland, P. L.; Tolman, W. B.; Que, L., Jr.; Fukuzumi, S. *Angew. Chem., Int. Ed*. **2000,** *39*, 398−400.

(9) Tolman and co-workers reported an aromatic ligand hydroxylation with a distinct bis(μ-oxo)dicopper(III) complex: Holland, P. L.; Rodgers, K. R.; Tolman, W. B. *Angew. Chem., Int. Ed*. **1999**, *38*, 1139−1142. However, mechanistic details have yet to be clarified.

(10) For the reactivity studies of bis(μ-oxo)dicopper(III) complexes, see also: (a) Mahadevan, V.; DuBois, J. L.; Hedman, B.; Hodgson, K. O.; Stack, T. D. P. *J. Am. Chem. Soc.* **1999**, *121*, 5583−8854. (b) Mahadevan, V.; Henson, M. J.; Solomon, E. I.; Stack, T. D. P. *J. Am. Chem. Soc*. **2000**, *122*, 10249−10250.

(11) Taki, M.; Itoh, S.; Fukuzumi, S. *J. Am. Chem. Soc*. **2001**, *123*, 6203−6204.

(12) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 4th ed.; Pergamon Press: Elmsford, NY, 1996.

(13) The SHACV method provides a superior approach to directly evaluating the one-electron redox potentials in the presence of a follow-up chemical reaction, relative to the better-known dc and fundamental harmonic ac methods. See: (a) Bond, A. M.; Smith, D. E. *Anal. Chem.* **1974**, *46*, 1946−1951. (b) Arnett, E. M.; Amarnath, K.; Harvey, N. G.; Cheng, J.-P. *J. Am. Chem. Soc.* **1990**, *112*, 344−355. (c) Patz, M.; Mayr, H.; Maruta, J.; Fukuzumi, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1225−1227.

(14) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209, 221−264.

(15) In addition to the spectral data of **1** reported previously,[11] a *solution* resonance Raman spectrum of **1** in acetone was taken at −92 °C: ν(^{16}O-complex) = 609 cm^{-1}; ν(^{18}O-complex) = 578 cm^{-1} (S1).

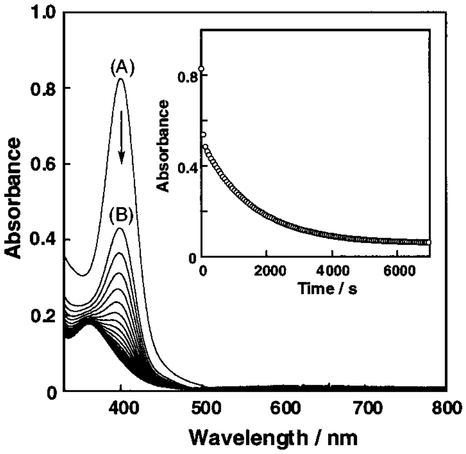

Figure 1. Spectral change (300 s interval) observed upon addition of thioanisole (1.0×10^{-3} M) into an acetone solution of **1** (5×10^{-5} M) at −80 °C. Inset: Time course of the absorbance change at 400 nm.

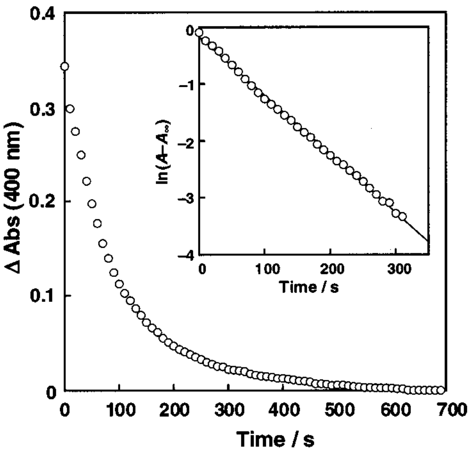

Figure 2. Time course of absorbance change in the first process of the reaction between $[Cu^{III}_2(L^{Py1Bz})_2(\mu\text{-}O)_2](PF_6)_2$ (5.0×10^{-5} M) and thioanisole (1.62×10^{-3} M) in acetone at −94 °C. Inset: First-order plot based on the absorption change at 400 nm.

the product was indeed dioxygen; the ^{18}O incorporation was 88%.[17]

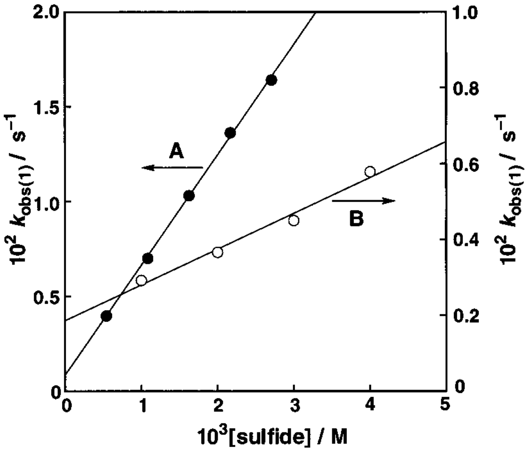

Figure 3. Plots of $k_{obs(1)}$ against substrate concentration for the first process of the reaction of $[Cu^{III}_2(L^{Py1Bz})_2(\mu\text{-}O)_2](PF_6)_2$ with (A) thioanisole and with (B) diethyl sulfide in acetone at −94 °C.

Scheme 2

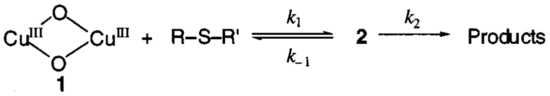

Table 1. Kinetic Parameters for the Reactions of **1** with Sulfides

sulfide	$E^0_{ox}{}^a$/V	$k_1{}^{b,d}$/M^{-1} s^{-1}	$k_{-1}{}^{b,e}$/s^{-1}	K^b/M^{-1}	$k_2{}^{c,d}$/s^{-1}
p-MeO−C_6H_4SMe	1.13	82.4	2.4×10^{-2}	3.4×10^3	1.6×10^{-3}
p-Me−C_6H_4SMe	1.24	34.4	1.2×10^{-2}	2.9×10^3	8.9×10^{-4}
C_6H_5SMe	1.34	5.7	9.6×10^{-4}	6.0×10^3	7.2×10^{-4}
p-Br−C_6H_4SMe	1.41	1.2	2.4×10^{-4}	5.2×10^3	6.5×10^{-4}
Ph_2S	1.43	0.03	6.1×10^{-5}	5.5×10^2	5.1×10^{-4}
Me_2S	1.37	13.1	3.5×10^{-4}	3.8×10^4	7.7×10^{-4}
Et_2S	1.57	0.94	1.8×10^{-3}	5.0×10^2	7.0×10^{-4}

[a] One-electron-oxidation potentials vs SCE determined by SHACV (see Experimental Section). [b] Determined at −94 °C. [c] Determined at −80 °C. [d] The experimental error is within ±5%. [e] The experimental error is within ±10%.

The time course of the initial rapid process [(A) to (B) in Figure 1] could be followed when the reaction was carried out at a lower temperature (−94 °C). Figure 2 shows the time course of the absorption change at 400 nm in the reaction with thioanisole at −94 °C, which obeys first-order kinetics as demonstrated in the inset of Figure 2. The initial rapid process in the reaction of **1** with other sulfides also followed first-order kinetics at −94 °C to give the pseudo-first-order rate constants $k_{obs(1)}$. Plot of the pseudo-first-order rate constant $k_{obs(1)}$ against the substrate concentration provided a linear line with an intercept as shown in Figure 3, where the plots for the reactions of thioanisole and diethyl sulfide are presented as typical examples. This indicates that the initial rapid decrease in absorbance at 400 nm is due to a process to reach an equilibrium between **1** and an intermediate complex **2** (see Scheme 2). The slope of the linear line corresponds to the rate constant for the forward reaction (k_1) and the intercept affords the rate constant of the backward reaction (k_{-1}). The rate constants for the reactions with other thioanisole derivatives (*p*-X−C_6H_4SMe, X = OMe, Me, Br) as well as those of diphenyl sulfide and dimethyl sulfide have also been determined similarly, and the values are listed in Table 1.

The k_1/k_{-1} ratio corresponds to the formation constant (K) of the intermediate **2**. The K value can also be obtained from the absorbance change ($\Delta A = A_0 - A$) in the first rapid process, which increases with increasing substrate concentration to reach a constant value as shown in Figure 4. Then the K values for C_6H_5SMe and Et_2S have been determined by fitting the data to eq 1 as $(6.2 \pm 0.7) \times 10^3$ M^{-1} and $(6.9 \pm 1.4) \times 10^2$ M^{-1}, respectively.[18]

$$\Delta A = \Delta A_\infty K[\text{sulfide}]/(1 + K[\text{sulfide}]) \qquad (1)$$

The K values thus determined from the absorbance change in Figure 4 agree within experimental errors with the values determined from the k_1/k_{-1} ratio, $(6.0 \pm 0.6) \times 10^3$ M^{-1} and $(5.0 \pm 0.5) \times 10^2$ M^{-1}, respectively. Such an agreement strongly supports the formation of an intermediate complex **2**.

In a series of thioanisoles, the k_1 value for the forward reaction increases with increasing electron donor ability of the para

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(16) Formation of the sulfoxide products from other sulfides has been confirmed by GC−MS, although limited quantity of the starting copper(I) complex supported by the deuterated ligand prevented us from performing the large-scale experiment for product isolation.

(17) A somewhat lower content of ^{18}O (88%) in the product could be attributed to a copper-mediated exchange of the oxygen atoms between the sulfoxide product and water molecule during the workup treatment. Oae, S.; Price, C. C. *Sulfur Bonding*; Ronald Press: New York, 1962.

(18) See Supporting Information (S2) for determination of the *K* values.

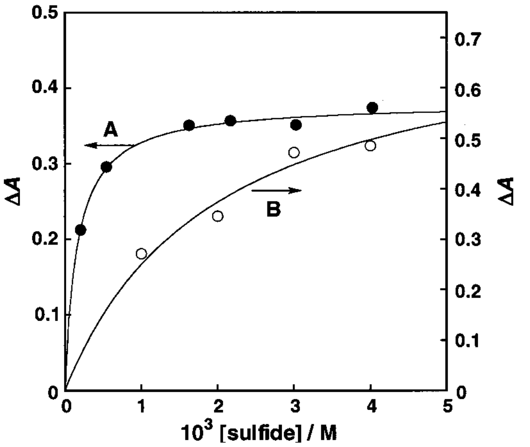

Figure 4. Plots of ΔA (= $A_0 - A$) against substrate concentration [(A) thioanisole, (B) diethyl sulfide] for the first process at −94 °C in acetone.

substituents (OMe > Me > H > Br), suggesting that the k_1 process involves coordination of the sulfur atom to the metal center. The order of k_1 values of MeSMe > PhSMe > EtSEt > PhSPh may reflect mainly the steric effects of the alkyl and/or aryl groups of the substrates in the coordination process of the sulfur to the copper. In contrast to the forward reaction, the k_{-1} value for the backward reaction decreases with decreasing donor ability of the para substituent of the thioanisole derivatives. Such an electronic effect of the para substituents on the backward reaction may implicate that there is a p_π–p_π or d–p_π type interaction to stabilize the intermediate **2** in which the aromatic ring of the substrate acts as an electron acceptor. The significantly smaller k_{-1} value of PhSPh (6.1×10^{-5} s^{-1}) as compared to that of PhSMe (7.0×10^{-4} s^{-1}) is consistent with such interpretation. The opposite substituent effects on the forward and backward reactions render the overall K values rather constant in the series of thioanisoles [$(2.9-6.0) \times 10^3$ M^{-1}, Table 1]. Overall, the least sterically hindered sulfide, i.e., dimethyl sulfide, exhibits the largest K value.

Stack and co-workers have suggested that coordination of exogenous substrates such as alcohols to the metal center of the bis(μ-oxo)dicopper(III) core is prerequisite for the *dehydrogenation* of the substrates.[10a] Such an interaction between the sulfide and the bis(μ-oxo)dicopper(III) core also plays an essential role in the *oxo-transfer reaction* (Scheme 1), although the structural details of the intermediate **2** have yet to be elucidated.[19]

The second slow process was then followed at the higher temperature (−80 °C), demonstrating that it was also a first-order reaction, but that the first-order rate constant ($k_{obs(2)}$) of this process is independent of the substrate concentration (Figure 5) (i.e., $k_{obs(2)} = k_2$ in Scheme 1). This clearly indicates that the second slow process is a *unimolecular* reaction of the intermediate **2** to the products. A plot of log k_2 vs the oxidation potentials of the substrates (E^0_{ox}) is shown in Figure 6, where the slope of the straight line is significantly small (−0.94).

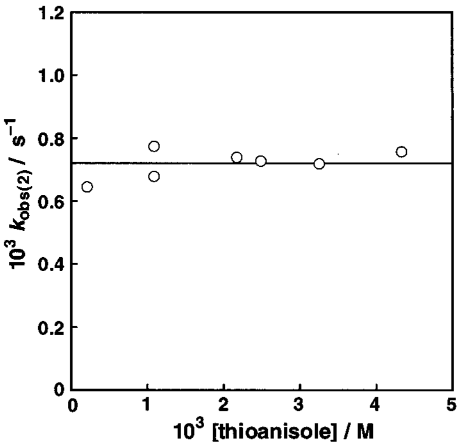

Figure 5. Plot of $k_{obs(2)}$ against substrate concentration for the second process of the reaction between [Cu$^{III}_2$(L^{Py1Bz})$_2$(μ-O)$_2$](PF$_6$)$_2$ and thioanisole in acetone at −80 °C.

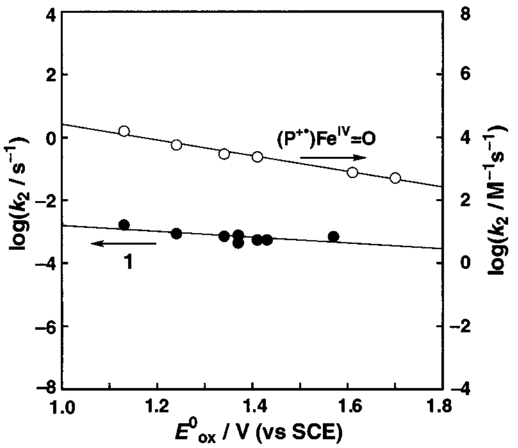

Figure 6. Plots of log k_2 against oxidation potential (E^0_{ox}) of sulfides for the oxo-transfer reaction by **1** in acetone at −80 °C (●) and by (TMP$^{+\bullet}$)Fe^{IV}=0 in CH$_2$Cl$_2$ at −50 °C (○) (Data are taken from ref 20).

Recently, Watanabe and co-workers have demonstrated that oxygenation of sulfides by compound I of horseradish peroxidase involves the electron-transfer process as the key step, in which the slope of the same type of plot is largely negative (−10.5).[20] If the variation of free energy change of electron transfer is directly reflected in the transition state of electron transfer, the slope will be equal to $-F(2.3RT)^{-1}$ (F is the Fraday constant), which is −16.9 at 298 K. The slope of −10.5 thereby indicates that 63% of the variation of free energy change of electron transfer is reflected in the transition state of electron transfer, which is commonly observed for electron-transfer reactions.[21] In contrast to this, the oxygenation of the same series of sulfides by an iron(IV)–oxo porphyrin π-cation radical in the model system proceeds via direct oxygen atom transfer, in which the slope becomes much smaller (−2.3).[20] This indicates that the rate of direct oxygen atom transfer is rather insensitive to the E^0_{ox} value, showing a sharp contrast with the oxygenation via electron transfer. Thus, the even smaller slope (−0.94) observed in Figure 6 indicates that the oxygenation of thioanisole by the bis(μ-oxo)dicopper(III) complex proceeds via a direct oxygen atom transfer mechanism rather than a mechanism involving an electron-transfer process. The similar reactivity of sulfides despite the large difference in the E^0_{ox} values may be ascribed to the small enthalpy change of the oxygen-transfer

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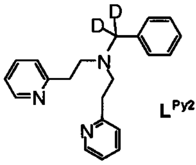
(19) The absorption maximum of **2** (λ_{max} = 398 nm) is only slightly red-shifted from **1** (λ_{max} = 400 nm), but the extinction coefficient (ϵ = 8620 M^{-1} cm^{-1}) becomes much smaller as compared to **1** (ϵ = 16 500 M^{-1} cm^{-1}). Resonance Raman band of **2** (ν(^{16}O-complex) = 609 cm^{-1}) is also slightly shifted to 598 cm^{-1} upon addition of the substrate at −92 °C in acetone.

(20) Goto, Y.; Matsui, T.; Ozaki, S.; Watanabe, Y.; Fukuzumi, S. *J. Am. Chem. Soc.* **1999**, *121*, 9497–9502.

(21) Eberson, L. *Electron-Transfer Reactions in Organic Chemistry*; Springer-Verlag: Berlin, 1987.

reactions among sulfides employed in this study, since the calculated difference in heat of formation (ΔH_f) between sulfides and the corresponding sulfoxides (see Experimental Section) is rather constant (-27.3 kcal mol^{-1} for *p*-MeOC$_6$H$_4$SMe, which gives the largest k_2 value, and -27.0 kcal mol^{-1} for Ph$_2$S, which gives the smallest k_2 value; see Table 1).

Stack and co-workers have demonstrated that the reactivity of the (μ-η^2:η^2-peroxo)dicopper(II) supported by *N*,*N*′-dimethyl-*N*,*N*′-di-*tert*-butylethylenediamine in the oxygenation reaction of triphenylphosphine is much higher than that of the bis(μ-oxo)dicopper(III) with the same ligand in 2-methylhydrofuran.[10b] Although the mechanistic details about the oxo-transfer reaction have not been clarified yet, they suggested that the accessibility of the substrate (PPh$_3$) to the Cu$_2$/O$_2$ core is important for dictating such a difference in reactivity. Namely, the bis(μ-oxo)dicopper core is more condensed as compared to the (μ-η^2:η^2-peroxo)dicopper core, since the Cu−Cu distance in the former (∼2.8 Å) is significantly shorter than that in the latter system (3.5−3.6 Å).



L$^{\text{Py2Bz}}$

In our case (sulfoxidation reaction), however, the reactivity of the (μ-η^2:η^2-peroxo)dicopper(II) generated by using a tridentate ligand (L$^{\text{Py2Bz}}$: *N*,*N*-bis[2-(2-pyridyl)ethyl]-α,α-dideuteriobenzylamine)[22,23] is much lower than that of the bis(μ-oxo)dicopper(III) complex with the bidentate ligand (L$^{\text{Py1Bz}}$) (see Supporting Information, S3). In this case, the tridentate ligand may cover the Cu$_2$/O$_2$ core more efficiently than the bidentate ligand does, leading to the lower accessibility of the substrate to the (μ-η^2:η^2-peroxo)dicopper core as compared to that in the case of the bis(μ-oxo)dicopper core. The direct comparison of the intrinsic reactivity between the (μ-η^2:η^2-peroxo)dicopper(II) and the bis(μ-oxo)dicopper(III) is thereby difficult in the oxo-transfer reaction, which requires a precoordination of the substrate to the metal−oxo center. More systematic studies using outer sphere electron-transfer reactions will provide further insight into the intrinsic reactivity of the Cu$_2$/O$_2$ species.

In conclusion, the first detailed study on the oxo-transfer reaction by a distinct bis(μ-oxo)dicopper(III) complex has demonstrated that the sulfoxidation by the bis(μ-oxo)dicopper(III) complex proceeds via a direct oxygen atom transfer mechanism via formation of a binary complex between the substrate and the metal−oxo species. Although sulfoxidation reaction by the copper/dioxygen species has not been found in biological systems, the present results will shed light on the ongoing interest in the structure/reactivity relationships of the non-heme active oxygen complexes.

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Supporting Information Available: Resonance Raman spectra of the acetone solution of **1** (^{16}O and ^{18}O derivatives) measured at −92 °C (S1), double reciprocal plots (1/Δ*A* vs 1/[sulfide]) for determination of the *K* values (S2), and comparison of the reactivity between the bis(μ-oxo)dicopper(III) complex and the (μ-η^2:η^2-peroxo)dicopper(II) complex in the sulfoxidation reaction at −80 °C (S3). (PDF) This material is available free of charge via the Internet at http://pubs.acs.org.

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(22) Synthesis and characterization of ligand L$^{\text{Py2Bz}}$, [Cu$^{\text{I}}$(L$^{\text{Py2Bz}}$)]$^+$, and its (μ-η^2:η^2-peroxo)dicopper(II) complex have been reported by Karlin et al.: Sanyal, I.; Mahroof-Tahir, M.; Nasir, M. S.; Ghosh, P.; Cohen, B. I.; Gultneh, Y.; Cruse, R. W.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 4322−4332. More information is available in ref 5.

(23) Oxidative N-dealkylation of the ligand sidearm (self-decomposition) in the (μ-η^2:η^2-peroxo)dicopper(II) complex of L$^{\text{Py2Bz}}$, reported by Karlin et al.,[22] was much slower than the oxygenation reaction of thioanisole at −80 °C in acetone (S3).