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Electron Transfer. 117. Copper Catalysis in Thiol Reduction of Bound Superoxide. A Second Mechanistic Variation[1]

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Reduction of the binuclear superoxo complex of cobalt(III) $[Co_2(O_2)(NH_3)_{10}]^{5+}$ by 2-aminoethanethiol is specifically catalyzed by dissolved Cu(II). Each superoxide cation oxidizes one RSH, yielding the disulfide R_2S_2 and the peroxo complex, $[Co_2(O_2)(NH_3)_{10}]^{4+}$. Although some kinetic profiles for this reaction, measured with the reductant ($RedH_2^+$) in excess, are nearly exponential, most exhibit a prominent nearly linear component during the initial stages of reaction. Curves for 17 runs, carried out at pH 2.9–4.3 with [thiol] = $(5–40) \times 10^{-4}$ M and $[Cu^{2+}] = (7–200) \times 10^{-7}$ M are consistent with a sequence (eqs 2–8 in text) featuring the generation of Cu(I) by internal electron transfer ($k = 12$ s^{-1}, 25 °C) within a Cu^{II}–thiyl precursor, followed by a rapid reduction of the superoxide ($k = 6 \times 10^4$ M^{-1} s^{-1}) by a Cu^{I}–thiyl complex. Detailed rate dependencies on [thiol] and pH indicate the precursor to be $Cu^{II}(Red^-)(RedH)$ and the reactive intermediate to be $Cu^{I}(Red^-)(RedH)$. The system is characterized by several very large association constants (10^{15}–10^{24}) for both oxidation states of copper with chelating thiyl ligands. Reductions of the superoxo complex by thiyl-ligated Cu^{I}, by Cr^{2+}, by Eu^{2+}, and by V^{2+} appear to be outer-sphere processes. Comparison of the rate constant for the Cu^{I}–superoxide reaction with the (very nearly equal) value for reduction by Eu^{2+}, in conjunction with the Marcus model for outer-sphere reactions, leads to an estimated self-exchange rate of 10^2–10^3 M^{-1} s^{-1} for Cu(I,II) in our system, a value slightly below that for S_4-ligated copper centers but over 10^{11} as great as that for aqua-substituted ions. The present system differs from copper-catalyzed reductions, using both ascorbate and organic thiols, of $[Co_2(O_2)(CN)_{10}]^{5-}$, for which past evidence supports inner-sphere attack by Cu(I). Unlike thiol reductions of the cyano-substituted oxidant, the present system exhibits no inhibition at high concentrations of the reductant.

The reactions of superoxides with thiols are of interest since the superoxide anion, O_2^-, has been implicated as a byproduct of the functioning of aerobic organisms[2] and thiol/disulfide couples are important in modulating the redox potential at biological sites.[3] Reductions of one of the more robust (μ-superoxo)metal complexes, the decacyanodicobaltate(III) anion I, by 2-aminoethanethiol (III) and L-cysteine (IV) are slow but are dramatically accelerated by Cu(II). This catalytic action has been found to lead to unusual kinetic situations, including a conversion which, under suitable conditions, is zero order in both redox partners.[4]

$$[(NC)_5Co{-}O_2{-}Co(CN)_5]^{5-}$$

I

$$[(H_3N)_5Co{-}O_2{-}Co(NH_3)_5]^{5+}$$

II

$$[H_3NCH_2CH_2SH]^+$$

III

$$HSCH_2CH(NH_3^+)COO^-$$

IV

The present contribution describes the reduction of the decaamminesuperoxo complex II, using 2-aminoethanethiol (III). This appears to be the first instance in which copper catalysis of bound superoxide has been observed in the absence of cyano ligands.

Experimental Section

Materials. Acetic acid and sodium acetate (Aldrich) were used as received. Sodium perchlorate solutions for kinetic experiments were prepared by treatment of $NaHCO_3$ with $HClO_4$. The (μ-superoxo)bis[pentaamminecobalt(III)] complex (II) was prepared as its perchlorate salt as described previously,[5] and solutions were stored in the dark in brown bottles. Since the kinetic behavior of the redox reaction of interest was found to be appreciably affected by dissolved chloride, 2-aminoethanethiol hydrochloride (Aldrich) was converted to its hydroperchlorate in solution by passage under N_2 through Dowex 1-X2 anion-exchange resin (200–400 mesh) in its perchlorate form. Thiol concentration in the resulting solution was estimated by titration with KI_3. Solutions for kinetic runs were made from Millipore water which was treated with zinc amalgam as described,[5b] filtered, and then sparged with N_2 for 2 h to remove dissolved O_2.

Stoichiometry. The stoichiometry of the superoxide–thiol reaction with the reductant in excess was determined by adding a known excess of the thiol to the superoxo complex in the presence of 10^{-6} M Cu^{2+}, waiting until net reaction ceased (about 5 min), and then titrating the unreacted thiol with KI_3 solution. Results, summarized in Table I, point to the consumption of equimolar quantities of the reactants.

Kinetic Measurements. Rates were estimated from absorbance changes at 300 nm (resulting from the disappearance of the superoxide, $\epsilon_{max}^{295} = 2.2 \times 10^4$ M^{-1} cm^{-1}) using a Cary 14 or Beckman Model 5260 recording spectrophotometer. Ionic strength was controlled by addition of $NaClO_4$, and pH was established using $HOAc–OAc^-$ buffers. Virtually all runs were carried out with the thiol in at least a 10-fold excess. Reactions were markedly accelerated by added Cu^{2+}, but not by Fe^{2+}, Fe^{3+}, or VO^{2+}. Inhibition experiments with added EDTA could not be carried out since the superoxo complex is rapidly reduced by this reagent.

Results and Discussion

From the close approach to 1:1 stoichiometry (Table I), we may represent the primary redox reaction as (1).[6] Subsequent

$$2[Co_2(O_2)(NH_3)_{10}]^{5+} + 2RSH \rightarrow 2[Co_2(O_2)(NH_3)_{10}]^{4+} + R_2S_2 + 2H^+ \quad (1)$$

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[1] Sponsorship of this work by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] See, for example: (a) Fee, J. A.; Valentine, J. S. In *Superoxide and Superoxide Dismutase*; Michelson, A. M., McCord, J. M., Fridovich, I., Eds.; Academic Press: New York, 1979; p 19. (b) Fridovich, I. *Adv. Inorg. Biochem.* **1979,** *67,* 1. (c) Bannister, W. H.; Bannister, J. V. *Biological and Clinical Aspects of Superoxide and Superoxide Dismutase*; Elsevier: Amsterdam, 1980.

[3] See, for example: Ziegler, D. M. *Annu. Rev. Biochem.* **1985,** *54,* 305.

[4] Ghosh, S. K.; Saha, S. K.; Ghosh, M. C.; Bose, R. N.; Reed, J. W.; Gould, E. S. *Inorg. Chem.* **1992,** *31,* 3358.

[5] (a) Davies, R.; Mori, M.; Sykes, A. G.; Weil, J. A. *Inorg. Synth.* **1982,** *12,* 197. (b) Saha, S. K.; Ghosh, M. C.; Gould, E. S. *Inorg. Chem.* **1992,** *31,* 5439.

[6] When the superoxo complex was taken in excess, somewhat higher stoichiometries (Ox/Red = 1.2–1.4) were observed, doubtless reflecting partial further oxidation of the thiol under these conditions.

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Table I. Stoichiometry of the Reaction of $[Co_2(O_2)(NH_3)_{10}]^{5+}$ (Ox) with 2-Aminoethanethiol (Red)[a]

mol × 10^4		$10^4\Delta$[mol of Red][b]	Δ[mol of Ox]/ Δ[mol of Red]
Ox	Red		
0.34	1.00	0.322	1.06
0.123	0.30	0.125	0.98
0.123	0.40	0.125	0.98
0.123	0.60	0.130	0.95
0.246	0.60	0.230	1.07

[a] Reactions were carried out at 25 °C, pH = 4.45 (HOAc–OAc⁻), μ = 0.20 M ($NaClO_4$), and $[Cu^{2+}] = 10^{-6}$ M. [b] Obtained by titrating unreacted thiol with KI_3 (see Experimental Section).

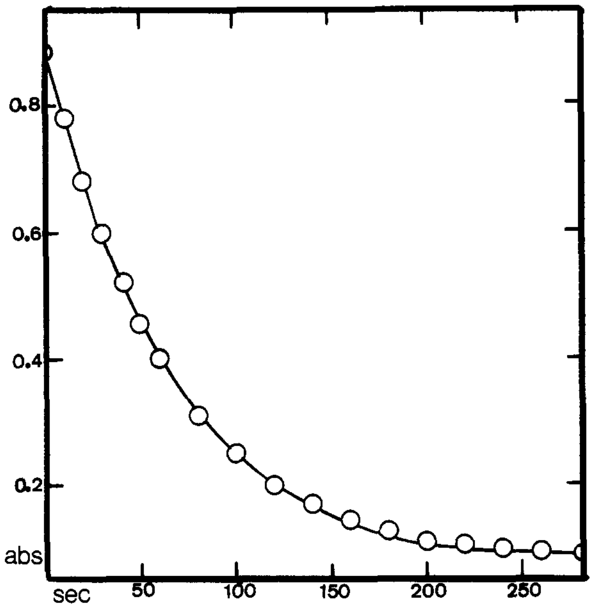

Figure 1. Kinetic profile at 300 nm for the reduction of $[Co_2(O_2)(NH_3)_{10}]^{5+}$ (3.8×10^{-5} M) with 2-aminoethanethiol (5.0×10^{-4} M) as catalyzed by Cu^{2+} (1.20×10^{-6} M) at 25 °C. $[H^+] = 3.2 \times 10^{-4}$ M; μ = 0.20 M ($NaClO_4$). The solid line is the experimental curve, whereas the circles are absorbances calculated from numerical integration of differential equations based on sequence (2)–(8) in the text, taking parameters listed in Table III. Extinction coefficients used (M^{-1} cm^{-1}): oxidant, 2.37×10^4; product, 2.27×10^3 per cobalt. Optical path length = 1.00 cm.

decomposition of the peroxo product to Co^{2+}, NH_4^+, and O_2[7] does not seriously affect the rate measurements of interest.

Kinetic patterns of this reaction are exponential at the more basic end (pH ≥3.7) of the acidity range examined. Exponential traces are also observed near pH 3.5 provided that [thiol]/[superoxide] > 40 and/or $[Cu^{II}]$/[superoxide] > 0.1. At higher acidities, and at lower concentrations of reductant and catalyst, decay profiles during the initial stages of reaction are much more nearly linear (Figure 1) than those characteristic of first-order curves.

Data obtained under exponential conditions are summarized in Table II. Although only a few runs are of this type, we see that the reaction is accelerated by increases in [thiol] and $[Cu^{II}]$ but that the kinetic dependencies are less steep than simple proportionalities. Conversion rates are also greater at higher pH's. Any suggested mechanistic picture must accommodate behavior observed both in this exponential region and in the "kinetically mixed" region, where nearly linear loss of the oxidant early in the reaction indicates that rates are determined mainly by a process not involving superoxide.

Our data point to a sequence in which the key intermediate, a Cu^I species, is generated by a Cu(II)–thiol reaction and then reduces Co^{III}-bound superoxide, regenerating Cu^{II}. At low concentrations of thiol and/or Cu^{II} and high [Ox], rates are set by the formation of Cu^I, but as the oxidant becomes depleted, the Cu^I–superoxide reaction becomes rate-determining.

Table II. Exponential Decay Curves Observed for the Reaction of $[Co_2(O_2)(NH_3)_{10}]^{5+}$ with 2-Aminoethanethiol[a]

10^4[thiol], M	$10^6[Cu^{2+}]$, M	$10^4[H^+]$	k, s^{-1}
15.0	1.20	3.2	0.030
25.0	1.20	3.2	0.039
40.0	1.20	3.2	0.048
5.0	4.2	3.2	0.054
5.0	10.2	3.2	0.110
5.0	20.2	3.2	0.173
5.0	1.20	0.59	0.053
5.0	1.20	1.29	0.040
5.0	1.20	2.04	0.026

[a] Reactions were run at 25.0 ± 0.2 °C and μ = 0.20 M ($NaClO_4$); solutions were buffered with HOAc–OAc⁻; λ = 300 nm. [Ox] = 3.8×10^{-5} M throughout. Solutions were Cl^--free.

Profiles obtained for each of the individual runs conform to this description. However, the entire series of 17 curves, for which $[Cu^{II}]$ is varied between 7×10^{-7} and 2×10^{-5} M, [thiol] between 0.00050 and 0.0040 M, and pH between 2.9 and 4.3, indicates that both components are [thiol]-dependent and that both exhibit kinetic saturation with respect to this reagent, telling us that copper–thiol complexes are involved, at both the Cu^{II} and the Cu^I stage. Moreover, both steps appear to be governed by prequilibria in which H^+ is released. Generation of Cu^I involves an $[H^+]^{-1}$ dependence, whereas the Cu^I–superoxide step entails an $[H^+]^{-2}$ dependence.

Data for all runs are consistent with the sequence represented schematically as (2)–(8), in which $RedH_2$, RedH, and Red

$$Cu^{2+} + RedH_2 \overset{K_2}{\rightleftharpoons} Cu^{II}(Red) + 2H^+ \tag{2}$$

$$2Cu^{II}(Red) \overset{K_3}{\rightleftharpoons} (Cu^{II}Red)_2 \quad \text{(inactive)} \tag{3}$$

$$Cu^{II}(Red) + RedH_2 \overset{K_4}{\rightleftharpoons} Cu^{II}(Red)(RedH) + H^+ \tag{4}$$

$$Cu^{II}(Red)(RedH) \xrightarrow{k_5} Cu^{I}(RedH) + Red^{\bullet} \tag{5}$$

$$Cu^{I}(RedH) + RedH_2 \overset{K_6}{\rightleftharpoons} Cu^{I}(Red)(RedH) + 2H^+ \tag{6}$$

$$Cu^{I}(Red)(RedH) + Ox \xrightarrow{k_7} Cu^{II}(Red)(RedH) + prod \tag{7}$$

$$2Red^{\bullet} \xrightarrow{k_8} (Red)_2 \tag{8}$$

designate the three protonation levels of the thiol reductant, and $Red^{\bullet}$ is the thiyl radical, $H_2NCH_2CH_2S^{\bullet}$.

In this sequence, step 2 is "kinetically silent", being included to attain the correct overall proton balance. The value of K_2 chosen is great enough to ensure virtually complete conversion to Cu^{II}(Red) in all runs. The dimerization of Cu^{II}(Red), reaction 3, reflects the substantial negative departure from first-order dependence on [catalyst] observed at high concentrations of the latter (Table II).[8,9] Association of Cu^{II}(Red) with $RedH_2$

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(7) See, for example: Hoffman, A. B.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1971.

(8) Alternatively, we can accommodate this deviation by assuming a dimerization equilibrium involving the Cu(I) intermediate, Cu^I(RedH) formed in step 5. Dimerization at the dipositive stage is considered more likely in view of the extensive monomer–dimer chemistry known to be associated with Cu(II) complexes.[9]

(9) See, for example: (a) Crawford, W. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107. (b) Kahn, O. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 834.

Table III. Rate Constants and Equilibrium Quotients Contributing to the Reaction of $[Co_2(O_2)(NH_3)_{10}]^{5+}$ with 2-Aminoethanethiol As Catalyzed by Cu(II)[a]

K_2	0.020	K_6	8.3×10^{-5} M^{-1} [d]
K_3	1.0×10^{5} M^{-1} [b]	k_7	5.5×10^{4} M^{-1} s^{-1} [d]
K_4	0.18[c]	k_8	10^{8} M^{-1} s^{-1}
k_5	12 s^{-1} [c]		

[a] Parameters pertain to sequence (2)–(8) in text. Reactions were run at 25 °C, $\mu = 0.20$ M ($NaClO_4$), pH = 2.9–4.3, $\lambda = 300$ nm, [Ox] = 3.8×10^{-5} M, [Red] = $(5\text{–}40) \times 10^{-4}$ M, and $[Cu^{2+}] = (7\text{–}200) \times 10^{-7}$ M. [b] The value for the dimerization constant K_3 was obtained from dependence of rate on $[Cu^{II}]$ at higher values of the latter. [c] Preliminary estimates of the association quotient K_4 and the rate constant k_5 were based upon the dependence of initial rates on [thiol] and $[H^+]$ for curves in the "kinetically mixed" region. [d] Estimates of the association quotient K_6 and the rate constant k_7 are based upon rate dependencies on [Red] and $[H^+]$ in the nearly exponential sections near the end of each of 17 profiles.

(reaction 4) prior to internal electron transfer generating Cu^I (reaction 5) is in accord with several reports[10] which demonstrate that the reduction of Cu^{II} to Cu^I with thiols proceeds through Cu^{II}–thiol complexes.

Expression of this sequence as a series of differential equations and numerical integration using an adaptation of the program KINSIM[11] yielded the concentrations of the participating species at 12.5-s intervals during the course of the reaction, and incorporation of the extinction coefficients of the superoxo reactant and its reduced peroxo product yielded calculated values for the absorbance of the reaction mixture at each point.

Values of rate constants and equilibrium quotients giving optimal agreement between calculated and observed absorbances for all curves are listed in Table III.[12] The rate constant assigned to the recombination of Red$^\bullet$ radicals (k_8) does not affect the quality of fit.[13] Absorbances calculated from these parameters are compared to a representative experimental curve in Figure 1.

Two aspects of the proposed sequence merit comment. The first is the remarkably strong affinity of the thiyl anion, $NH_2CH_2CH_2S^-$ (Red), for both states of copper. Although the successive acidity constants for $^+H_3NCH_2CH_2SH$ (pK_1 = 8.2; pK_2 = 10.7)[14a] must be reflected in very low concentrations (10^{-16}–10^{-14} M) of this anion in our media, kinetic saturation with respect to thiol is observed at both oxidation levels. Values of the equilibrium quotients K_2 and K_4 correspond to association constants of 2×10^{17} for Cu^{II}(Red) and 6×10^{24} for Cu^{II}(Red)(RedH), whereas K_6 leads to a similarly high constant for (11). The magnitudes of these K's, in conjunction with the

$$Cu^I(RedH) + Red \rightleftharpoons Cu^I(Red)(RedH) \qquad K = 9 \times 10^{14} \tag{11}$$

structure of the deprotonated thiol, strongly imply bidentate coordination in each case. Note that the calculated K for Cu^{II}(Red) exceeds the reported value for the analogous cadmium complex ($K_{Cd(Red)} = 10^{11.0}$),[14b] by over 10^6, the greater affinity for Cu^{II} shown by this S-donor being somewhat less one-sided than that shown by the more familiar nucleophile S^{2-}.[15–17]

The very rapid reaction of thiol-bound Cu^I with our superoxo complex ($k_7 = 6 \times 10^4$ M^{-1} s^{-1}) is comparably striking. Hoffman and Taube[7] have suggested that the reactions of this oxidant with Cr^{2+}, Eu^{2+}, and V^{2+} proceed through outer-sphere paths, and the relative rates reported by these authors, $k_{Cr}:k_{Eu}:k_V$ = 1:10:30, indeed correspond to those observed for the same dipositive centers with an array of oxidants having structures precluding bridging.[18] Extending this mechanistic assignment to (7), we note that our estimate of k_7 lies close to Hoffman's value for reduction by the much stronger reductant Eu^{2+} under comparable conditions ($k_{Eu} = 3 \times 10^4$ M^{-1} s^{-1} at 25 °C; $\mu = 1.0$ M).[7] The model of Marcus[19] then stipulates that the difference in potentials associated with the two reductants must be compensated by a much greater electron-self-exchange rate for the copper system.

The formal potential for Cu(I,II) in a N_2S_2 ligand environment may be taken as 0.0 V (vs NHE).[20] From the reported $E°$ for Eu(II,III) (–0.379 V),[21] we estimate that the self-exchange rate for Cu(I,II) should exceed that for the lanthanide center by 10^7. Chou and co-workers[22] have tabulated a range of rates for the latter, obtained from a variety of "cross-reactions" involving Eu^{2+}, but favor the figure 10^{-5}–10^{-4} M^{-1} s^{-1}. On this basis, we suggest a Cu(I,II) self-exchange rate of 10^2–10^3 M^{-1} s^{-1} in our system, a value slightly below $10^{3.8\pm0.2}$ listed by Meagher and co-workers[23] for S_4-ligated copper centers but 10^{11} times as great as the upper limit (10^{-9} M^{-1} s^{-1})[24] taken earlier to apply to aqua-substituted systems.

The striking catalytic effects exhibited by Cu(II) in our experiments may then be attributed jointly to (A) the ease with which it is reduced to the unipositive state by organic thiols and (B) the enhanced reactivity of Cu(I) when ligated by chelating thiol ligands, reflecting a pronounced drop in the Cu(I,II) self-exchange barrier.

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(10) See, for example: (a) Lappin, A. G.; McAuley, A. *J. Chem. Soc., Dalton Trans.* **1978**, 1606. (b) Davis, F. J.; Gilbert, B. C.; Norman, R. O. C.; Symons, M. C. R. *J. Chem. Soc., Perkin Trans. 2* **1983**, 1763.

(11) Barshop, B. A.; Wrenn, R. F.; Frieden, C. *Anal. Biochem.* **1983**, *130*, 134. The original KINSIM program, for which we thank Dr. Carl Frieden, was developed for use on a VAX computer system. This was modified, using FORTRAN-77, to a "fixed-length" format and executed on an IBM 3081D system.

(12) Since the KINSIM procedure does not use equilibrium constants as such, these were expressed as ratios of rate constants for the forward and back reactions. Typically, for K_3 (=0.18) we included k_3 as 1.8×10^8 M^{-1} s^{-1} and k_{-3} as 1.0×10^9 M^{-1} s^{-1}.

(13) There is evidence that reactions 9 and 10 may compete with reaction 8 in the consumption of the intermediate radical, Red$^\bullet$ (see, for example:

$$Red^\bullet + Red \rightleftharpoons (Red)_2^{\bullet} \tag{9}$$

$$(Red)_2^{\bullet} + Ox \rightarrow (Red)_2 + \text{product} \tag{10}$$

Asmus, K.-D. *Methods Enzymol.* **1990**, *186*, 168). These occur after the rate-determining step(s), and alteration of the sequence (2)–(8) to include (9) and (10) should not affect the net kinetic profile. If the $(Red)_2^\bullet$ path is greatly favored over (8), the value of k_5 would be just half that listed in Table III.

(14) (a) Irving, R. J.; Nelander, L.; Wadso, I. *Acta Chem. Scand.* **1964**, *18*, 769. (b) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum: New York, 1975, 1976; Vol. 2, p 32; Vol. 4, p 76.

(15) A reviewer suggests an alternate treatment of individual runs in the "mixed kinetics region" which allows estimates of standard deviations of the proposed rate constants. Note, however, that values in Table III are those giving optimum agreement between calculated and observed absorbances of all 17 runs. Statistical analysis applying to the entire series appears to be a much more complex problem, for which we can devise no practicable approach.

(16) Reported[14b] K_{SP} values for CdS and CuS (25 °C, $\mu = 0$) are in the ratio 10^{10}.

(17) Although sequences involving the anionic form of the thiol, $H_2NCH_2CH_2S^-$, are thermodynamically equivalent to the indicated steps, e.g., (12)+(13) for (3), they are not kinetically admissible. The very

$$RedH_2 \overset{K_{11}}{\rightleftharpoons} Red + 2H^+ \tag{12}$$

$$Cu^{II} + Red \overset{K_{12}}{\rightleftharpoons} Cu^{II}(Red) \tag{13}$$

low value of K_{11} (10^{-19} M^2)[14b] ensures that [Red] in our media is so low that, even reacting at a diffusion-controlled rate, it cannot account for the necessary conversions within the time scale of our runs.

(18) See, for example: Fan, F.-R. F.; Gould, E. S. *Inorg. Chem.* **1974**, *13*, 2647.

(19) (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *24*, 970. (b) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(20) See, for example: Bernardo, M. M.; Heeg, M. J.; Schroeder, R. R.; Ochrymowycz; Rorabacher, D. B. *Inorg. Chem.* **1992**, *31*, 191.

(21) Biedermann, G.; Silber, H. R. *Acta Chem. Scand.* **1973**, *27*, 3761.

(22) Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1977**, *99*, 5615.

(23) Meagher, N. E.; Juntunen, K. L.; Salhi, C. A.; Ochrymowycz, L. A.; Rorabacher, D. B. *J. Am. Chem. Soc.* **1992**, *114*, 10411. This value applies to Cu(I,II) systems in which electron transfer is not delayed by conformational changes in the ligand system associated with the copper center.

(24) Pillai, G. C.; Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1988**, *27*, 1868.

Copper(I) has also been implicated in the Cu-catalyzed reductions, using both ascorbate and organic thiols, of the related decacyano-substituted superoxo complex I. However, it appears to assume a different role in these instances. Mechanistic examinations[4,5b] indicate that Cu(I) instead utilizes an inner-sphere path, probably with cyano bridging, in attacking this anionic oxidant. In line with this distinction, thiol reductions of I exhibit dramatic inhibiton by high concentrations of reductant, due presumably to competition between thiol and oxidant for sites at the Cu(I) center. Such inhibition plays no part in the present reaction.

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