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Electron Transfer. 115. Reduction of Cobalt-Bound Superoxide with Ascorbate[1]

S. K. Saha, M. C. Ghosh, and E. S. Gould*

Department of Chemistry, Kent State University, Kent, Ohio 44242

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The binuclear superoxo complexes of cobalt(III), $[Co_2(O_2)(NH_3)_{10}]^{5+}$ and $[Co_2(O_2)(CN)_{10}]^{5-}$, are reduced by ascorbic acid at pH 3.5–5.2. Reaction of the decacyano complex, but not of the decaammine, is catalyzed markedly and specifically by dissolved copper. Each ascorbate reduces 2 equiv of superoxide, yielding the corresponding binuclear peroxo complex, which decomposes rapidly, either to Co(II), NH_3, and O_2 or to $Co(CN)_5(H_2O)^{2-} + H_2O_2$. The rate law for reduction of the decaammine oxidant points to formation of a 1:1 complex of the ascorbate anion, HA^-, with the oxidant ($Q_{Ox \cdot HA} = 1.1 \times 10^3\ M^{-1}$), within which $1e^-$ transfer takes place at a rate constant 59 s^{-1} (25 °C), yielding the radical $HA^{\bullet}$, which then reacts rapidly with a second unit of superoxide. Agreement between the observed rate and that calculated on the basis of the Marcus model points to an outer-sphere path for this reaction. Copper-catalyzed reductions of the decacyano complex proceed at rates independent of [oxidant], reflecting an initial rate-determining reduction of Cu^{II} to Cu^{I}, the latter of which has been shown independently to reduce the superoxo derivative at a rate constant $> 1.4 \times 10^4\ M^{-1}\ s^{-1}$. The Cu(II)–ascorbate reaction in this system is 10^3 as rapid as that in the absence of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$, an acceleration attributed to enhanced reactivity of a tightly bound ion pair, $Cu^{2+}Ox^{5-}$ ($Q > 10^7\ M^{-1}$). Changes in the electronic spectrum of the superoxo complex in the presence of Cu^{2+} confirm the formation of such an adduct. The reaction of Cu^{I} with the decacyano oxidant proceeds about 10^5 as rapidly as estimated for a straightforward outer-sphere transaction. Here an unusually facile inner-sphere path predominates. The specificity of copper catalysis to CN-substituted superoxo systems suggests a transition state featuring a cyano bridge for this fast step.

Interest in the reactions of superoxide and its derivatives continues to be keen, due principally to the participation of this anion in metabolic processes.[2] Superoxide has been shown to intervene in some autoxidations[3] and as a byproduct in the metabolism of aerobic organisms.[4] It survives only briefly in biosystems, undergoing rapid disproportionation into H_2O_2 and O_2, a conversion dramatically catalyzed by bimetalloproteins known as superoxide dismutases.[5] Such proteins are presumed to protect the organism from superoxide toxicity, but the precise nature of such toxic effects has not yet been established.[5,6]

Superoxide is a strong nucleophile which can form reasonably robust metal complexes in the absence of facile decomposition paths. In addition to an array of superoxo derivatives of substitution-inert centers,[7] several less persistent superoxo derivatives of d^0 ions have been described[8] and have been studied in solution. Problems in preparation and handling are generally minimal in work with binuclear (μ-coordinated) superoxo derivatives, for these may frequently be stored in the crystalline state.

Although the reductions of $(Co^{III})_2$-bound superoxide by metal ions at low pH have been examined in some detail,[9] much less attention has been devoted to reactions with nonmetallic reductants.[10] Reductions with organic thiols, of interest because of the role assumed by RSH/R_2S_2 couples in mediating redox potentials at biological sites,[11] are favored thermodynamically. They have been found to be slow but are strikingly catalyzed by traces of dissolved copper, even at the 10^{-7} M level.[12]

Reductions by ascorbic acid merit attention in view of the part played by this molecule as an antioxidant[13] and as a hydroxylase cofactor[14] in biosystems. We here describe its reactions with two dimeric superoxo complexes, the decacyano anion, I, and the decaammine analog, cation II. Both of these yield, as the primary reduction product, the related μ-peroxo complex, but the associated kinetic pictures are quite different.

$$\underset{\text{I}}{[(NC)_5Co\text{-}O_2\text{-}Co(CN)_5]^{5-}} \qquad \underset{\text{II}}{[(H_3N)_5Co\text{-}O_2\text{-}Co(NH_3)_5]^{5+}}$$

Experimental Section

Materials. Ascorbic acid (Aldrich Chemicals, 99+%), sodium acetate (Baker and Adamson), acetic acid (MCB), and hydrated copper sulfate (J. T. Baker) were used as received. Sodium perchlorate solution, used as a supporting electrolyte in kinetic experiments, was prepared by treatment of $NaHCO_3$ with $HClO_4$. Because the redox reactions of cobalt(III)-bound superoxides are sometimes strikingly catalyzed by dissolved copper,[12] all kinetic runs were carried out in solutions which were made from "Millipore" water and which were stirred in contact with

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[2] See, for example: (a) Fridovich, I. *Adv. Inorg. Biochem.* **1979**, *67*, 1. (b) Fee, J. A.; Valentine, J. S. *Superoxide and Superoxide Dismutase*; Michelson, A. M., McCord, J. M., Fridovich, I., Eds.; Academic Press: New York, 1979; p 19.

[3] (a) Bakac, A.; Espenson, J. H.; Creaser, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1983**, *105*, 7642. (b) Taube, H. *Prog. Inorg. Chem.* **1986**, *34*, 607.

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[5] See, for example: (a) Valentine, J. S.; de Frietas, D. M. *J. Chem. Educ.* **1985**, *62*, 990. (b) St. Clair, C. S.; Gray, H. B.; Valentine, J. S. *Inorg. Chem.* **1992**, *31*, 925.

[6] Fee, J. A. In *Oxygen and Oxy-Radicals in Chemistry and Biology*; Rodgers, M. A. J., Powers, E. L., Eds.; Academic Press: New York, 1981; pp 205–239.

[7] Review: Hill, H. A. O.; Tew, D. G. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon: Oxford, England, 1987; Vol. 2, Chapter 15.2.

[8] (a) Samuni, A.; Czaspski, G. *J. Phys. Chem.* **1970**, *74*, 4592. (b) Bourke, G. C. M.; Thompson, R. C. *Inorg. Chem.* **1987**, *26*, 903.

[9] (a) Davies, R.; Sykes, A. G. *J. Chem. Soc. A* **1968**, 2831. (b) Hoffman, A. B.; Taube, H. *Inorg. Chem.* **1968**, *7*, 1971. (c) Sasaki, Y. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1939.

[10] See, however: Edwards, J. D.; Yang, C.-H.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1974**, 1561.

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

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

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zinc amalgam for 7 days,[15] after which solutions were filtered and sparged with N_2 for 60 min.

μ-Superoxo complexes were prepared by the procedure of Davies and co-workers[16] with slight modifications. The μ-peroxo–bis(pentaammine) complex, $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{4+}$, was prepared from $Co(NO_3)_2 \cdot 6H_2O$ and was converted to the corresponding μ-superoxo derivative by oxidation with $(NH_4)_2S_2O_8$ as described.[16] The latter complex was isolated as its pentachloride salt and dissolved in 40% H_3PO_4. The resulting solution was filtered, and concentrated $HClO_4$ was added dropwise to the filtrate, precipitating the perchlorate salt, which was then recrystallized from 10% $HClO_4$. The green product was quickly dried and dissolved in 0.1 M $HClO_4$, and the solution was stored at 4 °C; λ_{max} values were at 670 (ϵ = 840 M^{-1} cm^{-1}; lit.[9b,17] ϵ = 838) and 295 nm ($\epsilon = 2.2 \times 10^4$ M^{-1} cm^{-1}).

The μ-superoxo–bis(pentacyano) complex, $K_5[(CN)_5Co(O_2)Co(CN)_5] \cdot H_2O$, was prepared from the μ-superoxo–bis(pentaammine) chloride by treatment with aqueous KCN,[16] a reaction which proceeded without formation of precipitate. After acidification with HNO_3 (hood!), the zinc salt was precipitated by addition of $ZnSO_4$, washed thoroughly with water, and then redissolved in a minimum volume of 10% aqueous KCN. The resulting solution was added, with stirring, to 10 times its volume of 1:1 C_2H_5OH/CH_3OH. The red microcrystalline precipitate so obtained was redissolved in a minimum volume of water, reprecipitated with EtOH/MeOH as above, washed with absolute EtOH, and air-dried. Further reprecipitations in the same manner led to partial decomposition, as did attempted chromatographic separation on Biogel P-2. The solid may be stored in the dark at −10 °C for 3 months without significant deterioration. Anal. Calcd for $K_5[(CN)_5Co(O_2)Co(CN)_5] \cdot H_2O$: K, 31.4; C, 19.3, N, 22.5; H, 0.32; Co, 18.8. Found: K, 32.4; C, 18.8, N, 22.8, H, 0.29, Co, 18.7.[18] ϵ_{max}^{311} was found to be 2.15×10^4 M^{-1} cm^{-1} (1.08×10^4 per Co), well above the reported values of 1.15×10^4 and 1.725×10^4.[19] Other maxima were at 202 ($\epsilon = 3.4 \times 10^4$) and 485 nm (930 M^{-1} cm^{-1}).

The analogous μ-peroxo complex, $K_6[(CN)_5Co(O_2)Co(CN)_5] \cdot H_2O$, as prepared by the method of Haim,[20] was contaminated with the μ-superoxo derivative, as shown by strong absorbance at 311 nm. The latter impurity was removed by treatment with dilute ascorbate at pH 11. As reported,[20] the light brown peroxo complex, when dissolved in water in the absence of CN^-, very rapidly decomposes to $[(CN)_5Co(H_2O)]^{2-}$ ($\epsilon_{max}^{375} = 2.7 \times 10^2$ M^{-1} cm^{-1}) and H_2O_2.

Stoichiometric Studies. The stoichiometries of the superoxo–ascorbate reactions were determined spectrophotometrically, either at 315 nm (for the decacyano complex) or 670 nm (for the decaammine derivative). Measured deficient quantities of ascorbic acid were added to a known excess of the superoxo complex; after net reaction ceased (about 2 min), decreases in absorbance were noted. These changes were then compared to those resulting from addition of an excess of the reductant. Reductions of the decacyano complex were carried out in the presence of 10^{-6} M Cu(II), for without this catalyst conversions were inconveniently slow. Results are summarized in Table I.

Table I. Stoichiometry of the Reactions of $[Co_2(O_2)(CN)_{10}]^{5-}$ and $[Co_2(O_2)(NH_3)_{10}]^{5+}$ with Ascorbic Acid

superoxide (Ox)	pH	amt, 10^6 mol		Δ[mol of Ox] × 10^6	Δ[Ox]/Δ[Asc]
		Ox	Asc		
$(CN)_{10}$ (I)[a]	3.95	0.180	0.020	0.042	2.1
		0.140	0.020	0.040	2.0
		0.100	0.020	0.040	2.1
		0.060	0.020	0.039	1.95
		0.020	0.010	0.191	1.91
$(NH_3)_{10}$ (II)[b]	1.30[c]	2.28	0.20	0.44	2.2
		1.48	0.20	0.36	1.80
		0.72	0.20	0.38	1.90
	3.60[d]	2.28	0.20	0.40	2.0
		1.49	0.20	0.37	1.85
		0.70	0.20	0.35	1.75

[a] Reactions were carried out in $HOAc–OAc^-$ buffers; λ = 311 nm. $[Cu^{2+}] = 1.0 \times 10^{-6}$ M. [b] No Cu^{2+} added; λ = 670 nm. [c] Reactions in dilute $HClO_4$. [d] $HOAc–OAc^-$ buffers.

Kinetic Measurements. Rates were estimated from absorbance changes at or near λ_{max} for the superoxide complexes. Reductions of the decacyano oxidant (I) were monitored at 315 nm using a Beckman Model 5260 recording spectrophotometer, whereas the (more rapid) conversions of the decaammine complex (II) were followed at 305 nm using a Durrum-Gibson stop flow spectrophotometer interfaced with an OLIS computer system. Ionic strength was regulated by addition of $NaClO_4$, and pH was established by $HOAc–OAc^-$ buffers. Virtually all runs were carried out with ascorbic acid in at least a 10-fold excess. All reactions were carried out under N_2 since dissolved oxygen led to poorly reproducible results without, however, introducing any systematic trends.

Reductions of the decaammine superoxo complex yielded exponential decay curves and were not catalyzed significantly by Fe(II), V(IV), Fe(III), Cu(II), or Ni(II) (each at the 10^{-5} M level).[21,22]

In contrast, reductions of the decacyano derivative were accelerated dramatically by Cu^{2+} (but by no other metal ion centers examined). These reactions yielded linear kinetic profiles with very slight curvature only during the final 3–4% of reaction. No induction periods were evident. Reactions carried out in the absence of added Cu(II) proceeded about half as rapidly as those with 2.0×10^{-7} M Cu(II). Addition of 10^{-4} M EDTA at pH 4.0 lowered the rate by a further factor of 6.

Additional Observations. The spectrum of the product obtained from reduction of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ matched that of $[(CN)_5Co(H_2O)]^{2-}$ ($\epsilon_{max}^{375} = 2.7 \times 10^2$ M^{-1} cm^{-1}).[20] Reduction of $[(NH_3)_5(O_2)Co(NH_3)_5]^{5+}$ yielded Co(II) quantitatively.[9b,18]

Addition of dilute $CuSO_4$ to a solution of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ (5.0×10^{-5} M) in the absence of ascorbate resulted in a shift of the 311-nm peak to 302 nm and an attendant decrease in molar absorbance to 1.3×10^4 M^{-1} cm^{-1}. Maxima at 485 and 202 nm were not altered significantly. Plots of absorbance at 311 nm vs added $[Cu^{2+}]$ exhibited "break points" at Cu/Co ratios 0.97 ± 0.02.

The $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$–ascorbate reaction could be carried out in the absence of acetate using 0.015 M "MES" (*N*-morpholineethanesulfonic acid) in its protonated form. At pH 4.3, with [Red] = 5×10^{-5} M, [Ox] = 5×10^{-6} M, and $[Cu^{2+}] = 5 \times 10^{-7}$ M, $k_{obs} = 3.1 \times 10^{-7}$ M s^{-1}, a value comparable to 2.6×10^{-7} M s^{-1} obtained with an $HOAc/Ac^-$ buffer (0.020/0.015) under the same conditions.

Attempt was made to measure the rate of reduction of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ with Cu(I) by generating Cu^+ from treatment of Cu^{2+} with a deficiency of $Cr(ClO_4)_2$.[23] The reaction of this superoxide with excess (5×10^{-5} M) Cu^+ exhibited $t_{1/2} < 1$ s, corresponding to a bimolecular rate constant $> 1.4 \times 10^4$ M^{-1} s^{-1} (25 °C, μ = 0.20 M).

Results

Stoichiometric data for both superoxo complexes (Table I) indicate the consumption of very nearly 2 mol of superoxide/mol

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(15) This treatment was less cumbersome, and somewhat more effective, than passage through "Chelex" type cation-exchange resin. Runs carried out in the absence of added Cu(II) indicated that even after prolonged treatment with Zn–Hg, Cu^{2+} concentrations of $(2 \pm 1) \times 10^{-7}$ M remained in solution.

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(17) Linhard, M.; Weigel, M. *Z. Anorg. Allg. Chem.* **1961**, *308*, 254.

(18) Gould, E. S.; Taube, H. *J. Am. Chem. Soc.* **1964**, *86*, 1318. Preliminary decomposition of this decacyano complex was carried out by heating with concentrated H_2SO_4 (rather than with 0.1 M NaOH). The resulting purple solution was then cooled and carefully diluted 10-fold with concentrated HCl, and Co(II) was estimated spectrophotometrically in the usual manner.

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(20) Haim, A.; Wilmarth, W. K. *J. Am. Chem. Soc.* **1961**, *83*, 509.

(21) The decomposition of solutions of the decaammine superoxo complex to $[Co(NH_3)_5(H_2O)]^{3+}$, Co^{2+}, and O_2,[22] which is negligibly slow below pH 5, but which competes with the reduction by ascorbate above pH 8, was examined briefly at pH 6.6–8.0 in solutions buffered by *N*,*N*-bis(2-hydroxyethyl)-2-aminoethanesulfonic acid ("BES") and its anion. The exponential profiles obtained were correlated by the rate law

$$-d[Ox]/dt = [Ox](k_0 + k_1[OH^-]) \qquad (1)$$

with $k_0 = (1.99 \pm 0.18) \times 10^{-3}$ s^{-1} and $k_1 = (2.33 \pm 0.10) \times 10^4$ M^{-1} s^{-1} (25 °C, μ = 0.20 M). The decomposition was found to depend also on the nature of the buffer used, being slower in *N*-morpholinepropanesulfonic acid ("MOPS") and still slower in *N*-(tris(hydroxymethyl)-methyl)-3-aminopropanesulfonic acid ("TAPS") buffers than in BES buffers with the same pH.

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(23) Parker, O. J.; Espenson, J. H. *J. Am. Chem. Soc.* **1969**, *91*, 1968. Since $CuClO_4$ solutions undergo rapid disproportionation to Cu^{2+} and metallic copper upon touching metal surfaces, this reaction could not be examined using our stop-flow equipment, in which reactant solutions come into brief contact with stainless steel valve parts.

Table II. Kinetic Data for Reduction of $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ with Ascorbic Acid (H_2A)[a]

$10^3[H_2A]$, M	$10^5[H^+]$, M	k,[b] s^{-1}	$10^3[H_2A]$, M	$10^5[H^+]$, M	k,[b] s^{-1}
0.050	9.3	2.7 (3.2)	60	28	116 (111)
0.070	9.3	4.2 (4.4)	0.20	32	6.0 (5.8)
0.10	9.5	5.7 (6.2)	0.20	25	7.3 (6.8)
0.20	9.5	11.3 (11.7)	0.20	20	9.1 (7.9)
0.30	9.5	15.6 (16.8)	0.20	8.3	12.5 (12.4)
0.50	9.3	25 (25)	0.20	7.6	12.9 (12.9)
1.00	9.3	46 (42)	0.20	5.6	13.0 (14.3)
2.0	9.3	63 (62)	0.20	4.9	15.8 (14.9)
5.0	9.5	87 (86)	0.20	4.6	16.4 (15.2)
7.0	9.5	89 (94)	0.20	2.2	18.8 (17.7)
10.0	9.3	97 (99)	0.20	1.14	21 (19)
20.0	11.4	105 (107)	0.20	0.67	24 (20)
40	24	107 (109)			

[a] Reactions at 25 °C in HOAc–OAc^- buffers; [HOAc] = 0.001–0.20 M; $\mu = 0.20$ M ($NaClO_4$); [oxidant] = 1.0×10^{-5} M throughout; $\lambda = 305$ nm. [b] Pseudo-first-order specific rates; parenthetical values were calculated by using eq 3 and parameters listed in the text.

Table III. Kinetic Data for Reduction of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ with Ascorbic Acid (H_2A) as Catalyzed by Copper[a]

10^7[Cu], M	$10^5[H_2A]$, M	[HOAc], M	10^8k,[b] M s^{-1}	10^7[Cu], M	$10^5[H_2A]$, M	[HOAc], M	10^8k,[b] M s^{-1}
0	5.0	0.050	2.7 (0)	5.0	5.0	0.100	4.3 (3.8)
0	5.0[c]	0.050	2.9 (0)	5.0	5.0	0.080	5.5 (5.0)
2.0	5.0	0.050	4.8 (3.4)	5.0	5.0	0.040	12.1 (11.9)
5.0	5.0	0.050	8.1 (8.6)	5.0	5.0	0.030	18.9 (17.4)
5.0	5.0[c]	0.050	9.6 (8.6)	5.0	5.0	0.025	29 (23)
10.0	5.0	0.050	15.3 (17.1)	5.0	5.0	0.020	35 (30)
15.0	5.0	0.050	22 (26)	5.0	5.0	0.0150	45 (40)
20.0	5.0	0.050	33 (34)	5.0	5.0	0.0125	59 (55)
5.0	10.0	0.050	16.0 (17.1)	5.0	5.0	0.0100	65 (65)
5.0	20.0	0.050	31 (34)	5.0	5.0	0[d]	31
5.0	30.0	0.050	48 (51)	0[e]	5.0	0.015	1.02
5.0	40.0	0.050	67 (69)	0[f]	5.0	0.015	0.15

[a] Reactions at 25 °C in HOAc–OAc^- buffers; $\mu = 0.50$ M ($NaClO_4$); [oxidant] = 5.0×10^{-6} M, [OAc^-] = 0.015 M unless otherwise indicated; $\lambda = 315$ nm. [b] Pseudo-zero-order rates; parenthetical values were calculated using (4) and parameters listed in the text. [c] [Ox] = 1.0×10^{-5} M. [d] Reaction in 0.015 M "MES"; pH = 4.3. [e] [EDTA] = 1.0×10^{-5} M. [f] [EDTA] = 1.0×10^{-4} M.

of reductant, H_2A. If, in keeping with other ascorbate oxidations,[24] the organic product is taken to be dehydroascorbic acid ("A"), we may represent both conversions schematically as (2).

$$2Co^{III}(O_2)^{-}Co^{III} + H_2A \rightarrow 2Co^{III}(O_2)^{2-}Co^{III} + A + 2H^+ \qquad (2)$$

The μ-peroxo product from reduction of the decaammine oxidant decomposes quickly, as reported,[9b] into Co^{2+} and O_2, whereas that from the cyano-substituted oxidant undergoes rapid aquation to $[(CN)_5Co(H_2O)]^{2-}$ and H_2O_2. The oxidation of ascorbate by H_2O_2 under our conditions is much slower than its oxidation by the superoxo complex, in accord with the close approach to 2:1 stoichiometry observed for the superoxo reaction and also with earlier reports.[25]

Kinetic data for the relatively rapid reductions of the ammine-substituted superoxide appear in Table II. Although rates rise with increases in pH and in [ascorbate], both dependencies are seen to be subject to kinetic saturation, leading to a limiting specific rate near 100 s^{-1}. The pH dependence doubtless reflects partition of the reductant, ascorbic acid ($pK_1 = 4.03$; $pK_2 = 11.3$),[26] into an active form (HA^-) and the unreactive protonated form (H_2A), whereas the [reductant] dependence points to a rate proportional to the concentration of a complex, Ox·HA^-, which reacts at the maximum rate constant, k_{lim}. Superposition of these two equilibria leads to the rate law (3), where $[asc]_T$ is the total

$$\text{rate} = \frac{k_{lim}[ox][asc]_T Q K_A}{[H^+] + K_A + Q K_A [asc]_T} \qquad (3)$$

concentration of added ascorbate, Q is the association quotient for the complex Ox·HA^-, K_A designates the first acidity constant for ascorbic acid (1.0×10^{-4}), and k_{lim} is the specific rate at high concentrations of HA^-. Refinement of data in terms of (3) yields $k_{lim} = 118 \pm 4$ s^{-1} and $Q = (1.08 \pm 0.05) \times 10^3$ M^{-1}. Table II also compares observed rates with those calculated by (3).

Reductions of the decacyano oxidant in carefully purified water are much slower than those of the decaammine analog and are further retarded by addition of EDTA. Like reductions by organic thiols,[12] however, catalysis by added copper is marked, with rates very nearly proportional to [Cu^{II}]. All decay curves observed in the presence of Cu are linear rather than exponential. Kinetic data for this system appear in Table III. Observed rates in the absence of added copper may be attributed to traces (ca. 2×10^{-7} M) of this metal center which persist despite our efforts at purification. As with the decaammine oxidant, rates increase with increasing pH, but in this case there is no tendency to level off at the highest basicities examined with this buffer system. Thus, a second deprotonation has come into play, yielding small quantities of a very reactive species.

Pseudo-zero-order rates for the decacyano complex are in accord with (4), where $[asc]_T$ is the total concentration of the

$$k_{obsd} = \frac{K_A(k_1[H^+] + k_2K_2)[Cu][asc]_T}{K_A[H^+] + [H^+]^2} \qquad (4)$$

reductant and k_1 and k_2 are specific rates pertaining to the two protonation levels. If K_A for ascorbic acid (K_1 at $\mu = 0.5$ M) is

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(24) See, for example: (a) Kustin, K.; Toppen, D. L. *Inorg. Chem.* **1973**, *12*, 1304. (b) Mushran, S. P.; Agrawal, M. C.; Mehrotra, R. M.; Sanehi, R. *J. Chem. Soc., Dalton Trans.* **1974**, 1460. (c) Pelizzeti, E.; Mentasti, E.; Pramauro, E. *Inorg. Chem.* **1976**, *15*, 2898. (d) Akhtar, M. J.; Haim, A. *Inorg. Chem.* **1988**, *27*, 1608. (e) Lannon, A. M.; Lappin, A. G.; Segal, M. G. *J. Chem. Soc., Dalton Trans.* **1986**, 619.

(25) See, for example: (a) Barteri, M.; Pispisa, B. *Biopolymers* **1982**, *21*, 1093. (b) Shurlatov, Y. *Int. J. Chem. Kinet.* **1980**, *12*, 347. (c) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 1538.

(26) (a) Martell, A. E.; Smith, R. M. *Critical Stability Constants*; Plenum: New York, 1979; Vol. 2, p 264. These values pertain to 25 °C and μ = 0.10 M. (b) See also: Ghosh, S. K.; Bose, R. N.; Gould, E. S. *Inorg. Chem.* **1987**, *26*, 2684.

Table IV. Estimated Outer-Sphere Rates and Contributing Parameters for Reductions of $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$ (μ = 0.2 M) and $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$ (μ = 0.5 M)[a]

reductant	superoxide	$E°_{Ox}$, V	log k_{11}	log k_{22}	log K_{12}	log f_{12}[b]	log W_{12}[b]	(log $k_{12})_{calcd}$[c]
$HAsc^-$ ($E°$ = 0.70 V)	$(NH_3)_{10}$	0.95[d]	−6.2[d]	5.0[h]	4.26	0.0	3.73	5.2
		0.713[e]			0.22	−0.20		3.1
Cu^I ($E°$ = 0.15 V)	$(CN)_{10}$	0.09[d]	−6.2[f]	−5.0[i]	−1.02	0.0	3.98	−0.65
		0.27[g]			2.04	−0.10		−2.14

[a] Reactions at 25 °C. [b] Parameters log f_{12} and log W_{12} correspond to the second and third terms of (9) (see text and ref 28). [c] Calculated using (9). [d] Reference 29. [e] Reference 30. [f] Self-exchange rate assumed to be the same as that for the decaammine system. [g] Minimum value taken to be consistent with completion of reaction (see text). [h] Reference 31c. [i] Reference 28.

set at 4×10^{-4},[26a] refinement yields a value of $(5.9 \pm 1.4) \times 10^3$ M^{-1} s^{-1} for k_1 and 0.55 ± 0.10 s^{-1} for the product k_2K_2.[27] Since there is no approach to kinetic saturation, individual values of k_2 and K_2 cannot be determined.

Discussion

Reduction of $[(NH_3)_5Co(O_2)Co(NH_3)_5]^{5+}$. The 2:1 stoichiometry for reduction of the decaammine oxidant, II, in conjunction with the monophasic profiles obtained, tells us that we are dealing with a pair of 1e steps, the first of which is rate-determining. Rate law 3 further indicates that the mononegative reductant anion (HA^-), the reactive form of ascorbate in this reaction, is partially converted to the ion-pair, $Ox(HA^-)$. The suggested reaction sequence is thus represented as (5)–(8), where "P" is the

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_A = 1.0 \times 10^{-4} \tag{5}$$

$$HA^- + Ox \rightleftharpoons Ox(HA^-) \qquad Q = 1.1 \times 10^3 \tag{6}$$

$$Ox(HA^-) \rightarrow HA^\bullet + P \qquad k = 59\ s^{-1} \tag{7}$$

$$HA^\bullet + Ox \rightarrow A + P + H^+ \qquad \text{(rapid)} \tag{8}$$

μ-peroxo product. The rate constant listed for (7) is just half of k_{lim} appearing in (3), thus accommodating the net stoichiometry. The reaction is shown proceeding through the adduct $Ox(HA^-)$, although the rate law in itself does not require this.

The most notable facet of the decaammine reaction is the high redox reactivity of the anion HA^-, an aspect which is particularly striking in view of its weakly reducing $E°$ value. It is useful to consider this reaction in the framework of the Marcus model, but since the latter treats bimolecular redox reactions, it is desirable to select an effective second-order rate constant, 5×10^4 M^{-1} s^{-1}, applicable to low concentration of ascorbate where rates are very nearly proportional to $[HA^-]$. In view of the high charge on the reductant, we may use (9)[28] to estimate the rate of a purely outer-

$$\ln k_{12} = \frac{1}{2}\left[\ln (k_{11}k_{22}K_{12}) + \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln \frac{k_{11}k_{22}}{Z^2} + \frac{(w_{11} + w_{22})}{RT}\right]}\right] + \frac{w_{11} + w_{22} - w_{12} - w_{21}}{2RT} \tag{9}$$

sphere process involving the same redox partners. In (9), the rate constant, k_{12}, of an electron-transfer reaction is represented as the sum of three terms, where k_{11} and k_{22} are the self-exchange rates for the oxidant and reductant, K_{12} is the equilibrium constant for the redox reaction, Z is the collision frequency, 10^{11} M^{-1} s^{-1}, and the w's are electrostatic work contributions with the reactants, the products, and the two self-exchanging systems. Each w-term is, in turn, calculated by (10), where z's are the ionic charges on

$$w_{cd} = 4.23 z_c z_d / a_{cd}(1 + 0.33 a_{cd} \mu^{1/2}) \tag{10}$$

interacting species c and d, μ is the ionic strength of the medium, and a_{cd} is the distance of closest approach, as estimated from the presumed geometry of the encounter and reported atomic and ionic radii.

Calculated values for contributing terms are listed in Table IV. Consideration of this reaction is complicated by a substantial difference in formal potentials for the superoxide couple reported by McLendon (0.95 V)[29] and by Richens (0.713 V).[30,31] Nevertheless, the estimated rates pertaining to the "cross reaction" (log k_{12} = 5.2 or 3.1) lie near enough to the experimental value (log k = 4.7) so that we may reasonably assign an outer-sphere path to the decaammine reduction. As expected, much of the impetus for this reaction arises from the very favorable electrostatic attractive (log W_{12}) term.

Reduction of $[(CN)_5Co(O_2)Co(CN)_5]^{5-}$. Reduction of the decacyano oxidant, in the absence of added copper, is undetectably slow. Rates in the presence of copper are independent of [oxidant], telling us that the superoxide complex is reduced after the rate-determining step in the reaction sequence. Rates are then set by interaction of the reductant and catalyst to form Cu(I). The latter has been shown to be the reactive species in the analogous superoxo–RSH systems[12] and is found to react rapidly ($k > 10^4$ M^{-1} s^{-1}) with the decaammine oxidant in the present study.

The $[H^+]$-dependence for reduction of the cyano-substituted oxidant (rate law 4) indicates that reaction is occurring at two acidity levels. In addition to that involving $HA^- + Cu^{2+}$ (specific rate k_1), a second act of deprotonation (K_2) has assumed importance, leading to an additional kinetic contribution, K_2k_2 (=0.55 s^{-1}). The latter cannot be attributed to the dinegative form of ascorbic acid, A^{2-}, for the very low acidity constant for HA^- (pK_2 = 11.3)[25] would imply a k_2 value exceeding 10^{11} M^{-1} s^{-1}, well above the diffusion-controlled limit for these species.[32] Neither can it reflect deprotonation of the oxidant, which, unlike its μ-peroxo analog,[20] exhibits no acid–base properties in the pH range 3–12. We suspect therefore that this term stems from deprotonation of a $Cu^{II}(HA^-)$ complex and that attachment of the metal center has increased the acidity quotient of HA^- by several powers of 10.

If the overall rate is determined by the generation of Cu(I), the value of k_1 (5.9×10^3 M^{-1} s^{-1}), obtained from refinement of

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(27) A small number of additional kinetic runs, in which both [HOAc] and $[OAc^-]$ were allowed to vary but their ratio (hence pH) was kept constant, indicated slight retardation at high values of [HOAc], consistent with formation of a weakly associated complex $H_2Asc{\cdot}HOAc$ ($Q = 9.9 \pm 2.1$ M^{-1}). This point was not pursued.

(28) Creutz, C.; Sutin, N. In *Inorganic Reactions and Methods*; Zuckerman, J. J., Ed.; VCH Publishers: Deerfield Beach, FL, 1986; Vol. 15, pp 13–51.

(29) McLendon, G.; Mooney, M. F. *Inorg. Chem.* **1980**, *19*, 12.

(30) Richens, D. T.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1982**, 1621. The superoxide–peroxide potential recorded by these authors lies very close to that reported for oxidation of HA^- to $HA^\bullet$ (0.70 V).[31] If correct, it would imply that the preponderance of the overall driving force for the superoxide–HA^- reaction arises from the second redox act (8) involving $HA^\bullet$, aided, perhaps, by the irreversible decomposition of the peroxide product to Co^{2+}, O_2, and NH_3.

(31) (a) Creutz, C. *Inorg. Chem.* **1981**, *20*, 4449. (b) Williams, N. H.; Yandell, J. K. *Aust. J. Chem.* **1982**, *35*, 1133. (c) Maccartney, D. H.; Sutin, N. *Inorg. Chim. Acta* **1983**, *74*, 221.

(32) See, for example: Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981; p 96.

rate law 4 and representing the specific rate of the Cu(II)–HA^- reaction, stands in marked contrast to the much lower rate, 5 M^{-1} s^{-1}, stemming from the work of Xu and Jordan.[33,34] These authors have pointed out that the acetato complex $Cu(OAc)^+$ (Q = 50 M^{-1})[26a] is much more rapidly reduced by ascorbate than is Cu^{2+}_{aq}. However, we are not seeing significant acetate catalysis in our system, for the reaction in acetate-free solutions is just as rapid as that in dilute acetate buffers, and high concentrations of acetate are seen to retard the overall reaction.[27]

At the same time, a substantial measure of ion-pairing involving Cu^{2+} and the –5-charged oxidant is anticipated, and the perceived shifts in the spectrum of the superoxide complex upon addition of Cu^{2+} are in accord with this expectation. Moreover, the sharp breakpoints in the spectrophotometric titration of the oxidant (5×10^{-5} M) indicate that, even at this level, this ion-pairing is very nearly complete. If the high catalytic effectiveness of Cu(II) in this redox system be attributed to its reactivity in the ion-pair form, the observed lack of kinetic dependence on [oxidant] requires that virtually all of the added Cu(II) in our kinetic runs is bound to the oxidant when the latter is at the 10^{-6} M level; i.e., that we are dealing with a formation quotient exceeding 10^7 M^{-1}.[35-37]

The proposed sequence for this copper-catalyzed reduction, which is in accord with rate law 4, is then (11)–(17). If, as suggested, both ascorbate and its derived radical forms ($HA^\bullet$ and $A^{\bullet-}$) reduce Cu^{II}, the rate constant assigned to (12) will be half of the empirical specific rate, k_1, in (4).[38,39]

Our experiments do not allow evaluation of k_{15}, the rate constant for the Cu(I)–superoxo reaction. This rate cannot lie much below 10^4 M^{-1} s^{-1} if the superoxo decay is to retain its observed zero-order character.

To compare this lower limit to the rate, estimated on the basis of the Marcus model,[28] for an outer-sphere transformation, the self-exchange rate for the cyano complex (which apparently has not yet been recorded) may be reasonably taken to be very nearly the same as that of its decaammine analog.[29] Although the cyano-substituted superoxo species is a substantially weaker oxidant than the decaammine, the formal potential (0.09 V) for the cyano derivative recorded by McLendon[29] is not compatible with its quantitative reduction by Cu^+ ($E° = 0.15$)[28] observed in this study. We then feel justified in setting a minimum value of 0.27 V for the cyano potential (i.e., 120 mV greater than $E°_{Cu(I)}$).

$$H_2A \rightleftharpoons H^+ + HA^- \qquad K_A = 4 \times 10^{-4} \tag{5}$$

$$Cu^{2+} + Ox \rightleftharpoons Cu^{II}(Ox) \qquad K_{IP} > 10^7 \tag{11}$$

$$HA^- + Cu^{II}(Ox) \rightarrow HA^\bullet + Cu^I + Ox \qquad k = 3 \times 10^3\ M^{-1}\ s^{-1} \tag{12}$$

$$HA^- + Cu^{II}(Ox) \rightleftharpoons Cu^{II}(Ox)(A^{2-}) + H^+ \qquad K_2 \tag{13}$$

$$Cu^{II}(Ox)(A^{2-}) \rightarrow Cu^I + A^{\bullet-} + Ox \qquad k_2/2 \tag{14}$$

$$HA^\bullet + Cu^{II} \rightarrow Cu^I + A + H^+ \qquad \text{(rapid)} \tag{15}$$

$$A^{\bullet-} + Cu^{II} \rightarrow Cu^I + A \qquad \text{(rapid)} \tag{16}$$

$$Cu^I + Ox \rightarrow Cu^{II} + P \qquad \text{(rapid)} \tag{17}$$

Despite the very approximate nature of this analysis, the estimated outer-sphere rate (k_{12}, Table IV) is seen to fall 5–6 orders of magnitude below the lower limit based on our observations. The wide divergence in values leads us to infer that this transformation, unlike the superoxo–ascorbate reaction in the decaammine system, utilizes an inner-sphere path.

Although preassociation of Cu(I) with the decacyano oxidant is thus indicated, the site at which interaction occurs remains an open question. On one hand, myriad reports[34,40] have described copper catalysis of reductions of various O–O species which are devoid of cyano groups. If, however, we limit our attention to $(Co^{III})_2$-bound superoxo derivatives, marked catalysis by Cu has been confined thus far to cyano-substituted oxidants.[12] On balance, we favor, for the rapid electron-transfer step (17), a precursor complex in which Cu^I is attached to the softer cyano ligand.

In sum, the results of this study point to quite different routes taken by two superoxo complexes, which are closely related structurally, to attain substantial reduction rates. For the $(NH_3)_{10}$-substituted oxidant, close approach of the reactive centers of the two redox partners is taken to be favored by electrostatics and possible intermolecular hydrogen bonding. In the case of the $(CN)_{10}$-substituted derivative (which is by far the weaker oxidant)[30] effective copper catalysis appears to arise from activation of Cu^{2+} toward 1e reduction when incorporated with the superoxo complex in a tight ion pairs, in conjunction with the availability of an unusually facile inner-sphere path, involving cyano bridging, for reduction by Cu^I.

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(33) Xu, J.; Jordan, R. B. *Inorg. Chem.* **1990**, *29*, 2933. These workers present evidence that strongly implicates the $Cu^{II}(HA^-)$ ion pair as an intermediate in the redox process. The indicated value is obtained by multiplying the estimated rate of electron transfer within this ion pair (0.2 s^{-1}) by the reported formation quotient for this complex (2.6×10^2 M^{-1}).[34]

(34) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 1948.

(35) If, as suspected, virtually all Cu^{II} is present as a tightly bound ion pair, $[Cu^{II}Ox]^{3-}$, in these systems, diversion to the more loosely associated complex $Cu(OAc)^+$ (Q = 50)[26a] may be ignored.

(36) Among analogous, but less tightly bound, ion pairs involving highly charged anions are $La^{3+}Fe(CN)_6{}^{3-}$ ($Q = 10^{3.7}$)[37a] and $Fe^{3+}Mo(CN)_8{}^{4-}$ ($Q = 10^{4.1}$).[37b]

(37) (a) Stampfl, R.; Choppin, G. R. *J. Inorg. Nucl. Chem.* **1972**, *34*, 205. (b) Mentasti, E.; Secco, F.; Venturini, M. *Inorg. Chem.* **1982**, *21*, 2314.

(38) Since Fe^{III}, which is known to react with ascorbate to give the radical, $HA^\bullet$,[39] has been found not to catalyze the reduction of complex I, we conclude that direct reaction of $HA^\bullet$ with I does not contribute significantly to the overall reaction.

(39) See, for example: (a) Taqui Khan, M. M.; Martell, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 2286. (b) Ghosh, S. K.; Gould, E. S. *Inorg. Chem.* **1989**, *28*, 1538.

(40) See, for example: (a) Bhargava, A. P.; Swaroop, R.; Gupta, Y. K. *J. Chem. Soc. A* **1970**, 2183. (b) Kimura, M. *J. Phys. Chem.* **1973**, *77*, 1265. (c) Woods, R.; Kolthoff, I. M.; Meehan, E. J. *Inorg. Chem.* **1965**, *4*, 697. (d) Lyons, J. E.; Hsu, C.-Y. In *Biological and Inorganic Copper Chemistry*; Karlin, K. D., Zubieta, J., Eds.; Academic Press: New York, 1986; Vol. II, p 57. (e) Davies, M. B. *Polyhedron* **1992**, *11*, 285.