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of the solution containing the complexes is usually interpreted in terms of a change of the electronic ground state of the complexes.

The electronic spectra were measured in the 300–1000-nm range for these complexes. A 550-nm band at 300 K is found to decrease steadily in intensity with decreasing temperature and is assigned to a high-spin state. Conversely a 700-nm band appears at low temperature (~230 K) and increases in intensity with decreasing temperature and is assigned to a low-spin state. These bands may be due to the metal–ligand charge transfer in origin because its absorption coefficients are about 10^4 l/(mol cm). The spin-state transition in solution is proceeded by the mechanism taking place in a molecule (intramolecular phenomenon). The existence of the bands due to the ^{2}T and ^{6}A states implies that the rate of the spin interconversion is slower than 10^{15} s^{-1} in solution. The rate of the spin interconversion in a solid state would be different from that in solution; however, these results would support the idea that the fast spin interconversion observed in the solid state proceeds fundamentally via an intramolecular mechanism (electronic factor) and also is influenced by the combined electron–phonon excitation.

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Oxidation–Reduction Reactions of Complexes with Macrocyclic Ligands. Electron-Transfer Reactivity of a 1:1 Cobalt(II)–Dioxygen Adduct[1]

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Received June 15, 1983

The 1-equiv oxidation–reduction reactions of the transient 1:1 $\mathrm{Co^{II}(N_4)–O_2}$ adduct, $\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+}}$ ($\mathrm{[14]aneN_4}$ = 1,4,8,11-tetraazacyclotetradecane), have been examined. The kinetic behavior with outer-sphere reduction agents, combined with the kinetics of oxidation of $\mathrm{Co([14]aneN_4)(OH_2)O_2H^{2+}}$ by $\mathrm{Ru(NH_3)_4phen^{3+}}$, implies that $E^f \simeq 0.3 \pm 0.1$ V and $k_{exch} \simeq 10^{3\pm1}$ $\mathrm{M^{-1}\ s^{-1}}$ for the $\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+,+}}$ couple. Reactions of the $\mathrm{Co^{II}(N_4)O_2}$ adduct with labile mildly reducing partners such as $\mathrm{Co^{II}(N_4)}$ or $\mathrm{Fe(OH_2)_6^{2+}}$ result in formation of μ-peroxo complexes. The rates of these "inner-sphere" reactions seem to be mostly a function of the equilibrium constant for adduct formation (k, $\mathrm{M^{-1}\ s^{-1}}$ (K, $\mathrm{M^{-1}}$)): 5×10^5 (8×10^5), 3.6×10^4 (10^4), 1.1×10^3 ($\leq 10^3$), respectively, for $\mathrm{Co([14]aneN_4)(OH_2)_2^{2+}}$, $\mathrm{Co([15]aneN_4)(OH_2)_2^{2+}}$, and $\mathrm{Fe(OH_2)_6^{2+}}$. The adduct did not exhibit significant radical character, nor was it significantly basic (pK_a < 0.1 for $\mathrm{Co([14]aneN_4)(OH_2)O_2H^{3+}}$).

Introduction

Reactions of dioxygen with organic and inorganic substrates are ubiquitous and of central importance in the chemistry of fuels, in aspects of synthesis, and in biological processes. Yet, molecular oxygen is notoriously sluggish in its reactions and often requires "activation", frequently by means of coordination in a transition-metal complex.[2] Neither the origins of the kinetic barriers to $\mathrm{O_2}$ reactions nor the means of their relaxation by coordination is well understood.

Simple, one-electron-transfer reactions of dioxygen moieties have recently received some attention.[2d,3-5] The advantage of study of such simple reactions is that one can make use of the highly sophisticated understanding of electron-transfer chemistry[6-11] to gain insight into the reactivity patterns of dioxygen species. Unfortunately, the initial studies of such reactions have reached somewhat contradictory conclusions, with the large intrinsic barrier to electron transfer in the $\mathrm{O_2–O_2^-}$ couple being attributed largely to solvent reorganization,[3] while that of the (μ-superoxo)–(μ-peroxo) couples has been attributed to the change in O–O bond length.[4]

The 1:1 dioxygen–transition metal adducts tend to exist only as reactive intermediates, or transient species in aqueous solutions at room temperature. As a consequence, there have been very few studies that directly investigate the chemical behavior of such adducts. Owing to a fortuitous combination of formation constants and absorptivities, we have been able to find conditions for which the transient dioxygen adduct of $\mathrm{Co([14]aneN_4)(OH_2)_2^{2+}}$[12] can be directly observed in reaction mixtures.[2d,13] Since the rate and equilibrium parameters in the $\mathrm{O_2–Co([14]aneN_4)(OH_2)_2^{2+}}$ system have been fully characterized,[13] it is possible to systematically investigate the

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[12] Abbreviations: $\mathrm{[14]aneN_4}$ = 1,4,8,11-tetraazacyclotetradecane; $\mathrm{[15]aneN_4}$ = 1,4,8,11-tetraazacyclopentadecane; $\mathrm{Me_4[14]tetraeneN_4}$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; $\mathrm{Me_6[14]4,11\text{-}dieneN_4}$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; sep = sepulchrate = (S)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; phen = 1,10-phenanthroline.

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electron-transfer chemistry of $Co([14]aneN_4)(OH_2)O_2^{2+}$. In the present study we report on the variations in reaction pathways of $Co([14]aneN_4)(OH_2)O_2^{2+}$ and our inferences about the intrinsic barrier to electron transfer in this species.

Experimental Section

Preparation of Complexes and Solutions. The ligand, $[14]aneN_4$, was prepared by using Barefield's procedure;[14] $[15]aneN_4$[12] was obtained from Strem Chemical Co. Solutions of the $Co^{II}(N_4)$ complexes were formed by mixing a 10% stoichiometric excess of the ligand with deaerated solutions of cobaltous perchlorate. We used a modification[15] of Sargeson's method[16] for the synthesis of $Co(sep)Cl_3$. Commercial (Matthey Bishop, Inc.) $Ru(NH_3)_6Cl_3$ was recrystallized before use.

Reductions of $Ru(NH_3)_6^{3+}$ and $Co(sep)^{3+}$ were carried out in neutral aqueous solutions, and V(IV) reductions were carried out in 0.1 M H^+, over zinc amalgam, and under a stream of Cr^{2+}-scrubbed N_2 or A (the latter for $Ru(NH_3)_6^{2+}$). Concentrations of reductants in stock solutions were determined spectrophotometrically from the reduction of $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$ or $Fe(phen)_3^{3+}$. Stock solutions of reductants were maintained over Zn-Hg for less than 1 h (less than 30 min for $Ru(NH_3)_6^{2+}$). Reducing titers were referenced to $\epsilon = 3.20 \times 10^3$ M^{-1} cm^{-1} at 540 nm for $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ and $\epsilon = 1.10 \times 10^4$ M^{-1} cm^{-1} at 510 nm for $Fe(phen)_3^{2+}$.

Ferrous perchlorate solutions were deaerated over Zn-Hg to remove any Fe(III). Solutions were standarized by conversion to $Fe(phen)_3^{2+}$.

The literature procedure[3,17] was used for synthesis of $Ru(NH_3)_4phen^{3+}$ from $Ru(NH_3)_6^{3+}$.

We found that acidic aqueous solutions of $Co([14]aneN_4)(OH_2)(O_2H)^{2+}$ were stable for periods in excess of 1 h. Solutions of this species were prepared as follows: (1) stoichiometric amounts of $Ru(NH_3)_6^{2+}$ and $Co([14]aneN_4)(OH_2)_2^{2+}$ were mixed in a nitrogen atmosphere; (2) O_2 was passed through the resulting solution for ~20 min. The reaction mixture was filtered, and the filtrate was characterized by its absorption spectrum.[18] In some studies characterizing the product of the $Co([14]aneN_4)(OH_2)O_2^{2+}$–$Ru(NH_3)_6^{2+}$ reaction, we separated components of the reaction mixture chromatographically. For these experiments, a column of Dowex 50W-X4, 100–200 mesh, in the H^+ form was pretreated with 3% H_2O_2 and then washed with 0.5 M $HClO_4$ and water. A green band was eluted with 6 M $HClO_4$, collected, and diluted to 25 mL. Product spectra compared well with those reported[18] for $Co([14]aneN_4)(OH_2)O_2H^{2+}$.

The following procedure was used to analyze products generated in $Co^{II}([14]aneN_4)$–O_2–Fe(II) mixtures. Oxygen was passed for about 15 min through an acidic aqueous solution ca. 0.5 mM in $Co^{II}([14]aneN_4)$ and ca. 20 mM in $Fe(OH_2)_6^{2+}$. The resulting mixture was Millipore filtered, and the absorption spectrum of the filtrate was recorded. The final product spectrum matched well with that reported for $Co([14]aneN_4)(OH_2)_2^{3+}$; on the basis of 100% conversion, we find the molar absorptivities (values from ref 18 in parentheses) ϵ(560 nm) = 28 (32) and ϵ(430 nm) = 40 (52). The reaction solutions had relatively intense UV absorptions, $\epsilon_{app}(240\ nm) = 2.48 \times 10^4$ (compared to 1.54×10^4 reported[18] for $Co([14]aneN_4)(OH_2)_2^{3+}$) owing to the presence of large amounts of iron(II) and iron(III) species.

Kinetic Methods. Rate measurements were performed with thermostated Aminco or Durrum stopped-flow instruments. Reaction conditions were adjusted so that the lifetimes for decay of $Co([14]aneN_4)(OH_2)O_2^{2+}$ into $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ [13] were in the range of 10–100 ms, depending on concentrations of O_2 and $Co([14]aneN_4)(OH_2)_2^{2+}$. Most of the reducing agents we employed (i.e., $Co(sep)^{2+}$, $Ru(NH_3)_6^{2+}$, V^{2+}, Fe^{2+}, etc.) have orders of magnitue smaller rate or/and equilibrium constants for reaction with O_2 than does $Co([14]aneN_4)(OH_2)_2^{2+}$. Consequently, the mixing of a solution containing $Co([14]aneN_4)(OH_2)_2^{2+}$ and another reducing species with solutions containing O_2 resulted in the very rapid formation of $Co([14]aneN_4)(OH_2)O_2^{2+}$ (usually at equilibrium in less than 10 ms). The reactions of other reductants, R, with the dioxygen adduct could then be inferred from their influence on the decay of the $Co([14]aneN_4)(OH_2)O_2^{2+}$ intermediate. These decays of intermediate absorbance were pseudo first order for more than 3 half-lives in each reaction studied: k_{obsd} $(s^{-1}) = a[R] + b$. In order to minimize $[Co([14]aneN_4)(OH_2)_2^{2+}]$, thus maximizing the lifetime of $Co([14]aneN_4)(OH_2)O_2^{2+}$, most of our studies have been carried out with the oxygenated solution saturated in O_2.

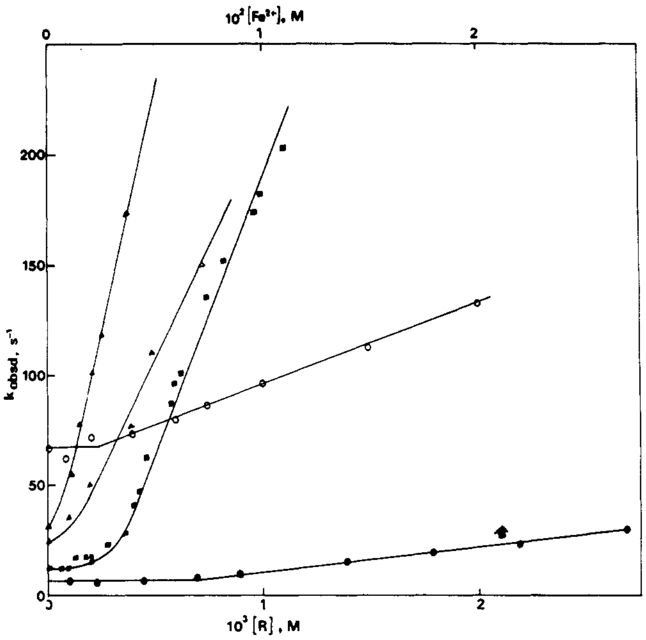

Figure 1. Variations in the $Co([14]aneN_4)(OH_2)O_2^{2+}$ decay rate in the presence of various reducing agents ($[Co([14]aneN_4)(OH_2)O_2^{2+}]$ in parentheses; from top to bottom): $Co(sep)^{2+}$ (6×10^{-4} M); $V(OH_2)_6^{2+}$ (5×10^{-4} M); $Ru(NH_3)_6^{2+}$ (5×10^{-4} M); $Co([15]aneN_4)(OH_2)_2^{2+}$ (8×10^{-4} M); $Fe(OH_2)_6^{2+}$ (5×10^{-4} M). All reactions are at 25 °C, $[O_2] = 6 \times 10^{-4}$ M, ionic strength 0.2 M ($NaClO_4 + HClO_4$).

Table I. Summary of Kinetic Data for Reductions of $Co([14]aneN_4)(OH_2)O_2^{2+}$ [a]

reductant	E^f, V (vs. NHE)	medium	k,[b] M^{-1} s^{-1}
$Ru(NH_3)_6^{2+}$	0.06[c]	0.1 M $HClO_4$	$(2.3 \pm 0.1) \times 10^5$
$Co(sep)^{2+}$	−0.30[d]	0.1 M $HClO_4$ and 0.2 M $NaClO_4$	$\sim 1 \times 10^6$
$V(OH_2)_6^{2+}$	−0.226[e]	0.1 M $HClO_4$	$(1.8 \pm 0.3) \times 10^5$
$Fe(OH_2)_6^{2+}$	0.74[f]	0.1 M $HClO_4$ and 0.2 M $NaClO_4$	$(1.1 \pm 0.1) \times 10^3$
$Co([15]aneN_4)(OH_2)_2^{2+}$	0.65[g]	0.1 M ($HClO_4$ + $NaClO_4$)	$(3.7 \pm 0.4) \times 10^5$
$Co([14]aneN_4)(OH_2)_2^{2+}$	0.421[h]	0.1 M $HClO_4$	$(4.9 \pm 0.4) \times 10^5$ [i]

[a] Reactions with initial concentrations $[Co([14]aneN_4)(OH_2)_2^{2+}] = (5–6) \times 10^{-4}$ M, $[O_2] = 6.3 \times 10^{-4}$ M; 25 °C; observed at 360 or 490 nm. Solutions of $Ru(NH_3)_6^{2+}$ and $Co(sep)^{2+}$ were at pH ~6 until mixing; V(II) and Fe(II) solutions were acidic. [b] Based on rates in the concentration limit where k_{obsd} is proportional to [reductant]. [c] Lim, H. S.; Barclay, D. J.; Anson, F. *Inorg. Chem.* 1972, *11*, 1460. [d] Reference 25b. [e] Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall, Englewood Cliffs, NJ, 1952. [f] Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* 1979, *101*, 1131. [g] Kumar, K.; Endicott, J. F., unpublished work. [h] Endicott, J. F.; Durham, B.; Glick, M. D.; Anderson, T. J.; Kuszaj, J. M.; Schmonsees, W. G.; Balakrishnan, K. P. *J. Am. Chem. Soc.* 1981, *103*, 1431. [i] Reference 13a.

Results

A. Outer-Sphere Electron-Transfer Reactions. The presence of strong, outer-sphere reducing agents (e.g., R = $Co(sep)^{2+}$, $Ru(NH_3)_6^{2+}$, V^{2+}, etc.) in the reaction medium greatly ac-

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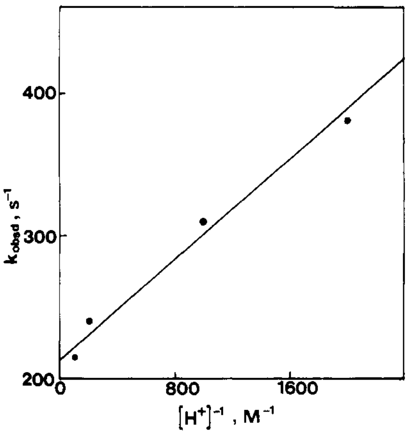

Figure 2. Acid dependence of the $Ru(NH_3)_4phen^{3+}$/Co([14]aneN$_4$)$(OH_2)O_2H^{2+}$ reaction at 25 °C, $\mu = 0.10$ M ($LiClO_4$ + $HClO_4$).

celerated the rate of Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ decay. For sufficiently large concentrations of the reductant, the apparent first-order rate constant for decay of the intermediate became proportional to [R] (Figure 1). The details of the kinetics experiments are summarized in Tables SI–SIII,[19] and second-order rate parameters for the limiting region, where $k_{obsd} = k[R]$, are summarized in Table I.

The reactions of $Co(sep)^{2+}$ and Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ were fast enough that we had to employ stoichiometrically small concentrations of $Co(sep)^{2+}$. When $[Co(sep)^{2+}]_0 \leq$ [Co([14]aneN$_4$)$(OH_2)_2^{2+}]_0$, there is a significant depletion in $Co(sep)^{2+}$ concentration as the reaction progresses, and the evaluation of rate constants becomes very complex. For these reactions we found a small dependence of the apparent second-order rate constant on the [Co([14]aneN$_4$)$(OH_2)_2^{2+}]_0$ (for $[O_2] \simeq 6 \times 10^{-4}$ M): for [Co([14]aneN$_4$)$(OH_2)_2^{2+}]_0 = 6 \times 10^{-4}$, 5×10^{-4}, 3×10^{-4}, and 1×10^{-4} M, respectively, $k = 3.5 \times 10^5$, 4.7×10^5, 6×10^5, and $\sim 1 \times 10^6$ M^{-1} s^{-1}. Unfortunately, the absorbance changes were very small at the lower limit of concentrations.

The second-order rate constants for R = $Ru(NH_3)_6^{2+}$ were independent of acidity in the range 1×10^{-4} M $\leq [H^+] \leq 0.1$ M (Table SII[19]). Potential radical scavengers (ascorbic acid, 2-propanol, allyl alcohol) did not affect the rates (R = $Co(sep)^{2+}$). While the transient decay in Co([14]aneN$_4$)$(OH_2)_2^{2+}/O_2$ solutions is not very sensitive to anionic composition of the electrolyte[13a] (Table SIII[19]), the transient decay is greatly enhanced in solutions containing $Co(sep)^{2+}$ and 10^{-3}–10^{-2} M NCS^- (Table SIII[19]). The dependence of the decay on [NCS^-] is of the form that suggests more than 10-fold greater reactivity of Co([14]aneN$_4$)$(NCS)O_2^+$ than Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ toward $Co(sep)^{2+}$.

Spectroscopic analysis of reaction products was consistent with the presence of various mixtures of Co([14]aneN$_4$)$(OH_2)O_2H^{2+}$, [Co([14]aneN$_4$)$OH_2]_2O_2^{4+}$, and Co([14]aneN$_4$)$(OH_2)_2^{3+}$. However the reactions of [Co([14]aneN$_4$)$OH_2]_2O_2^{4+}$ with most reducing agents[13b] precluded meaningful use of the product ratios.

The reactivity of solutions containing Co([14]aneN$_4$)$(OH_2)O_2H^{2+}$ toward $Ru(NH_3)_4phen^{3+}$ was investigated. These reactions were strongly pH dependent as shown in Figure 2. The reactions of $Ru(NH_3)_4phen^{3+}$ with [Co([14]aneN$_4$)$OH_2]_2O_2^{4+}$ were also investigated. These reactions were relatively slow and for our reaction conditions were less than 1% of the rates of the $Ru(NH_3)_4phen^{3+}$/Co([14]aneN$_4$)$(OH_2)O_2H^{2+}$ reactions (Tables SIV and SV[19]).

B. Reactions Resulting in μ-Peroxo Complex Formation. Several mild reducing agents with labile coordination positions were found to react rapidly with Co([14]aneN$_4$)$(OH_2)O_2^{2+}$. The prototypical reaction, with axially labile Co([14]aneN$_4$)$(OH_2)_2^{2+}$, has already been reported and discussed in some detail.[13a] We have made a few additional studies of this reaction, finding that the rate is nearly independent of pH in the range 0.2 M $\geq [H^+] \geq 5 \times 10^{-4}$ M. Since the inner-sphere pathway, which results in μ-peroxo complex formation, would require predissociation of a proton from coordinated O_2H, our observations indicate $pK_a < 0.1$ for Co([14]aneN$_4$)$(OH_2)O_2H^{3+}$. The previous study[13a] also indicated that reactions of coordinated O_2 in this system were insensitive to variations in pH.

We have also investigated the reactions of Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ with $Fe(OH_2)_6^{2+}$ and with Co([15]aneN$_4$)$(OH_2)_2^{2+}$. The kinetic parameters are summarized in Table I; details may be found in Tables SVI–SX.[19] The reaction of $Fe(OH_2)_6^{2+}$ with Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ proceeded in two stages. The first stage resulted in a new species with a unique absorption spectrum (λ_{max} = 415 and 490 nm; see Figure 2 of ref 2d). This species seems to be a mixed-metal μ-peroxo complex: [H_2O([14]aneN$_4$)Co–O_2–$Fe(OH_2)_5]^{4+}$. This initial product decomposes at a relatively slow ($t_{1/2} \sim$ 1 s) first-order rate (k_d). We have found k_d to be independent of [Fe(II)] (2.5×10^{-3}–5×10^{-2} M) and ascorbic acid, even though ascorbic acid apparently reacts with [H_2OCo([14]aneN$_4$)$]_2O_2^{4+}$. There is a slight increase in k_d when the reactant solutions contain $Fe(OH_2)_6^{3+}$ (Table SX;[19] k_d increases from 0.9 to 1.2 s^{-1} for 5×10^{-3} M $\leq$ [Fe(III)] ≤ 0.02 M). The initial reaction stage had a shorter lifetime in the presence of ascorbic acid.

The reactions of Co([15]aneN$_4$)$(OH_2)_2^{2+}$ with Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ were studied in solutions where initially [Co([14]aneN$_4$)$(OH_2)_2^{2+}$] > [O_2] in order to minimize complications originating from the Co([15]aneN$_4$)$(OH_2)_2^{2+}/O_2$ reaction.[13a]

No effect on the Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ decay rate was observed for [Co(Me_4[14]tetraeneN$_4$)$(OH_2)_2^{2+}$] or [Co(Me_6[14]4,11-dieneN$_4$)$(OH_2)_2^{2+}$ up to about 10^{-3} M (Tables SXII and SXIII[19]).

C. Other Reactions. Limited studies have been made of a few other reactions. Allyl alcohol (up to 0.02 M), ascorbic acid (up to 0.02 M), and 2-propanol (up to 0.5 M) have no effect on the rate of decay of Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ in acidic solution. Aqueous $Hg(ClO_4)_2$ (up to 0.02 M) also had no effect on the decay of the dioxygen transient.

Discussion

The coordinated superoxo ligand of Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ is a mild oxidizing center that seems to have only a modest intrinsic barrier to electron-transfer processes: very fast reactions are found with strongly reducing outer-sphere and mildly reducing inner-sphere electron-transfer reagents. On the other hand, the lifetime of the Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ reactant is so short and dependent on the conditions of formation(i.e., the lifetime is longer for excess O_2 than for excess Co([14]aneN$_4$)$(OH_2)_2^{2+}$ [13]) that only fast reactions can be investigated. Owing to reactant solubilities, reactant and product absorptivities, and the time resolution of our stopped-flow systems, the reductions of Co([14]aneN$_4$)$(OH_2)O_2^{2+}$ were generally run under conditions where the formation and decomposition kinetics contributed to the observed rate. The

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(19) See paragraph at end of paper regarding supplementary material.

(20) In aqueous solution, HN_3 and HO_2 have similar pK_a's (4.72[21] and 4.88,[22] respectively), and the pK_a of bound HN_3 has been estimated as −2.2 in $Rh(NH_3)_5N_3H^{3+}$.[23]

(21) Latimer, W. M. "Oxidation Potentials", 2nd ed.; Prentice-Hall: Englewood Cliffs, NJ, 1952; p 102.

(22) (a) Sawyer, D. T.; Gibian, M. J. *Tetrahedron* **1979**, *35*, 1471. (b) Sawyer, D. T.; Chiericato, J., Jr.; Angelis, C. T.; Nanni, E. J.; Tohru, T. *Anal. Chem.* **1982**, *54*, 1720.

(23) Davies, C. S.; Lalor, G. C. *J. Chem. Soc. A* **1970**, 446.

reactions that must be considered are (for a reducing agent R^{2+})

$$\mathrm{Co([14]aneN_4)(OH_2)_2^{2+} + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Co([14]aneN_4)(OH_2)O_2^{2+} + H_2O} \quad (1)$$

$$\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+} + Co([14]aneN_4)(OH_2)_2^{2+} \overset{k_2}{\rightleftarrows} [Co([14]aneN_4)OH_2]_2O_2^{4+}} \quad (2)$$

$$\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+} + R^{2+} \xrightarrow{k_3} Co([14]aneN_4)(OH_2)O_2^{+} + R^{3+}} \quad (3)$$

$$\mathrm{Co([14]aneN_4)(OH_2)O_2^{+} + H^+ \rightleftarrows Co([14]aneN_4)(OH_2)O_2H^{2+}} \quad (4)$$

In the absence of other reactants the nominal superoxo complex intermediate decays exponentially in time, with the transient decay adequately described as the relaxation of reactions 1 and 2 to equilibrium.[13] Pseudo-first-order decay kinetics are also observed in the presence of an additional reducing agent, eq 3. For present purposes, and to simplify the argument, we treat reactions 2 and 4 as irreversible (on the time scale of the observed relaxation process) and we assume that the ratio of adduct to reactants in eq 1 is approximately constant (but not necessarily at equilibrium); i.e.

$$\frac{[\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+}}]}{[\mathrm{Co([14]aneN_4)(OH_2)_2^{2+}}][\mathrm{O_2}]} \simeq C^{-1}$$

Then, for the observed, pseudo-first-order rate constant

$$k_{\mathrm{obsd}} \simeq -k_1C + k_{-1} + k_2[\mathrm{Co([14]aneN_4)(OH_2)_2^{2+}}] + k_3[\mathrm{R}] \quad (5)$$

For small $k_3[\mathrm{R}]$, k_{obsd}^{-1} is the relaxation time characteristic of the initial concentrations of O_2 and $\mathrm{Co^{II}(N_4)}$, while for sufficiently large [R], $k_{\mathrm{obsd}}/[\mathrm{R}] = k_3$. In the limit of very large values of k_3 and [R], reaction 1 becomes rate limiting and $k_{\mathrm{obsd}} \rightarrow k_1$; for our choice of reaction conditions this will occur for $k_{\mathrm{obsd}} \sim 3 \times 10^2\ \mathrm{s^{-1}}$ and may be approached by some of the fastest reactions. Overall, one expects an approximately sigmoidal dependence of k_{obsd} on [R]. Nearly all the systems investigated gave a good definition of the first two stages of this dependence, as illustrated by the examples of Figure 1. This has enabled us to make reasonable estimates of k_3 for a variety of systems. Specific systems are discussed below by reaction type.

A. Outer-Sphere Electron-Transfer Reactions. In order to evaluate the reactivity of coordinated dioxygen, it is necessary to estimate the potential for the couple

$$\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+} + e^- \rightleftarrows Co([14]aneN_4)(OH_2)O_2^{+}} \quad (6)$$

Owing to the short lifetime of the dioxygen adduct and the apparently large difference in acidity of O_2H and O_2H^- ligands, direct determination of this potential is very difficult. Thus, Geiger and Anson[18] have estimated the potential for irreversible couple

$$\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+} + H^+ + e^- \rightleftarrows Co([14]aneN_4)(OH_2)O_2^{2+}}$$

to be approximately 1 V (vs. NHE). It is possible to obtain an estimate of the potential for eq 1 from the kinetics of reductions of $\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+}}$ and oxidations of $\mathrm{Co([14]aneN_4)(OH_2)O_2^{+}}$ using the Marcus square root relation[6]

$$k_{\mathrm{ab}} = (k_{\mathrm{aa}}k_{\mathrm{bb}}K_{\mathrm{ab}}f_{\mathrm{ab}})^{1/2} \quad (7)$$

where k_{aa} and k_{bb} are outer-sphere self-exchange rate constants for the component couples, K_{ab} is the net equilibrium constant ($\log K_{\mathrm{ab}} = 16.9\Delta E°$ at 25 °C), and $\log f_{\mathrm{ab}} = (\log K_{\mathrm{ab}})^2/4 \log (k_{\mathrm{aa}}k_{\mathrm{bb}}/10^{22})$. If the subscripts refer to the oxidized and reduced species, respectively, then the rates of different reagents oxidizing or reducing a single couple may be compared (eq 8). If potentials and self-exchange parameters are known for the reference couples (here denoted "a" and "c"), then one can estimate the unknown potential.

$$k_{\mathrm{ab}}/k_{\mathrm{bc}} = (k_{\mathrm{aa}}K_{\mathrm{ab}}K_{\mathrm{cb}}f_{\mathrm{ab}}/k_{\mathrm{cc}}f_{\mathrm{bc}})^{1/2} \simeq (k_{\mathrm{aa}}K_{\mathrm{ab}}K_{\mathrm{cb}}/k_{\mathrm{cc}})^{1/2} \quad (8)$$

$$k_{\mathrm{ab}}/k_{\mathrm{bc}} = k_{\mathrm{bb}}(k_{\mathrm{aa}}k_{\mathrm{cc}}K_{\mathrm{ac}}f_{\mathrm{ab}}f_{\mathrm{bc}})^{1/2} \simeq k_{\mathrm{bb}}f_{\mathrm{ac}}(k_{\mathrm{aa}}k_{\mathrm{cc}}K_{\mathrm{ac}})^{1/2}$$

Table II. Comparison of Acidities of Coordinated Dioxygen Moietics

complex	pK_a	ref
$\mathrm{Co([14]aneN_4)(OH_2)O_2H^{2+}}$	8 ± 1	this work
$\mathrm{[(en)_2Co]_2(NH_2,O_2H)^{4+}}$	10.8	*a*
$\mathrm{[(CN)_5Co]_2O_2H^{5-}}$	12	*b*
$\mathrm{[(NH_3)_5Co]_2O_2H}$	~10	*c*

[a] Mori, M.; Weil, J. A. *Chem. Commun.* 1966, 534. [b] Haim, A.; Wilmarth, W. K. *J. Am. Chem. Soc.* 1961, *83*, 509. [c] Charles, R. G.; Barnart, S. *J. Inorg. Nucl. Chem.* 1961, *22*, 69.

We have chosen to investigate the oxidation of $\mathrm{Co([14]aneN_4)(OH_2)O_2H^{2+}}$ using an oxidant, $\mathrm{Ru(NH_3)_4phen^{3+}}$, which is about 0.5 V too mild to effect oxidation of the coordinated hydroperoxide according to the observations of Geiger and Anson.[18] As expected, these oxidations are complicated by the acid–base chemistry of the coordinated hydroperoxide. The observed behavior suggests the reactions in Scheme I. Since $K_a' \gg K_a$ so that the resulting difference

Scheme I

$$\mathrm{Co(N_4)(OH_2)O_2H^{2+} \overset{K_a}{\rightleftarrows} Co(N_4)(OH_2)O_2^{+} + H^+}$$

$$\mathrm{Co(N_4)(OH_2)O_2^{+} + Ru(NH_3)_4phen^{3+} \xrightarrow{k_4} Co(N_4)(OH_2)O_2^{2+} + Ru(NH_3)_4phen^{2+}} \quad (9)$$

$$\mathrm{Co(N_4)(OH_2)O_2H^{2+} + Ru(NH_3)_4phen^{3+} \xrightarrow{k_5} Co(N_4)(OH_2)O_2H^{3+} + Ru(NH_3)_4phen^{2+}} \quad (10)$$

$$\mathrm{Co(N_4)(OH_2)O_2H^{3+} \xrightarrow{K_a'} Co(N_4)(OH_2)O_2^{2+} + H^+}$$

in standard potentials of coordinated O_2^-–O_2^{2-} and O_2H–O_2H^- will result in $k_4 > k_5$ and since the protolytic equilibria are rapidly established, this scheme predicts that a plot of k_{obsd} vs. $1/[\mathrm{H^+}]$ has a slope of k_4K_a and an intercept of k_5 (Figure 2). We estimate $k_4K_a \simeq 0.09 \pm 0.01\ \mathrm{s^{-1}}$ and $k_5 \simeq 2 \times 10^2\ \mathrm{M^{-1}\ s^{-1}}$. If we assume similar self-exchange rates for the $\mathrm{Co(N_4)(OH_2)O_2H^{3+,2+}}$ and the $\mathrm{Co(N_4)(OH_2)O_2^{2+,+}}$ couples and since the potentials of these couples are related through K_a/K_a', eq 7 implies that $k_4/k_5 \simeq (K_a'/K_a)^{1/2}$ or $k_4K_a/k_5 \simeq (K_aK_a')^{1/2} \simeq 4 \times 10^{-4}$ M. For $K_a' \simeq 10^{1\pm1}$ M,[20-23] $K_a \sim 2 \times 10^{-8\pm1}$ M. This seems only slightly more acidic than some of the μ-peroxo complexes with more strongly reducing cobalt centers (Table II). We infer that $k_4 \sim 5 \times 10^{6\pm1}\ \mathrm{M^{-1}\ s^{-1}}$, and from eq 7 we infer that $k_{\mathrm{exch}} \sim 10^{3\pm2}\ \mathrm{M^{-1}\ s^{-1}}$ and $E^f \simeq 0.3 \pm 0.1$ V (vs. NHE) for the $\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+,+}}$ couple. The values of E^f and K_a inferred are reasonably consistent with an estimated potential of ~1 V for oxidation of $\mathrm{Co([14]aneN_4)(OH_2)O_2H^{2+}}$ found by Geiger and Anson.[18] In making these estimates we have used the rate and equilibrium constants for the $\mathrm{Ru(NH_3)_4phen^{3+}}$, $\mathrm{Ru(NH_3)_6^{2+}}$, and $\mathrm{V^{2+}}$ reactions with $\mathrm{Co([14]aneN_4)(OH_2)O_2^{2+}}$. Equation 8 implies a rate ratio of 0.5:1 for comparison of $\mathrm{V^{2+}}$ and $\mathrm{Ru(NH_3)_6^{2+}}$ outer-sphere reactions and 35:1 for comparisons of

Table III. Comparison of Electron-Transfer Rates for Reaction of Dioxygen Moieties

dioxygen substrate	counter reagent	k_{ab}, $M^{-1}\ s^{-1}$	$K_{ab}{}^{a}$	$k_{ab}/(K_{ab})^{1/2}$	prob pathway^{b}
O_2	$Ru(NH_3)_6{}^{2+}$	63 (1.0 M)^{c}	2.8×10^{-4}	3.6×10^{2}	OS
$Co([14]aneN_4)(OH_2)O_2{}^{2+}$	$Ru(NH_3)_6{}^{2+}$	2.4×10^{5} (0.1 M)^{d}	10^{4}	2.4×10^{3}	OS
$[(NH_3)_5Co]_2O_2{}^{5+}$	$Ru(NH_3)_6{}^{2+}$	3.7×10^{6} (0.1 M)^{e}	1.2×10^{11}	10.9	OS
$Co([14]aneN_4)(OH_2)O_2{}^{2+}$	V^{2+}	1.8×10^{5} (0.1 M)^{d}	8×10^{8}	6	OS
$[(NH_3)_5Co]_2O_2{}^{5+}$	V^{2+}	9.6×10^{4} (1.0 M)^{f}	8.3×10^{15}	1.1×10^{-3}	OS
O_2	$Co(sep)^{2+}$	45 (0.2 M)^{g}	3×10^{2}	2.4	OS
$Co([14]aneN_4)(OH_2)O_2{}^{2+}$	$Co(sep)^{2+}$	4.7×10^{5} (0.3 M)^{d}	1.4×10^{10}	4	OS
O_2	$Ru(NH_3)_4phen^{2+}$	7.7×10^{-3} (0.1 M)^{c}	6×10^{-12}	3×10^{3}	OS
$Co([14]aneN_4)(OH_2)O_2{}^{+}$	$Ru(NH_3)_4phen^{3+}$	$\sim 10^{7}$ (0.1 M)^{d}	4×10^{3}	$\sim 10^{5}$	OS
O_2	Fe^{2+}		9×10^{-16} (<10)		?
$Co([14]aneN_4)(OH_2)O_2{}^{+}$	Fe^{2+}	1.1×10^{3} (0.3 M)^{d}	4×10^{-8} ($\leqslant 10^{3}$)	$\geqslant 30^{j}$	IS
$[(NH_3)_5Co]_2O_2{}^{5+}$	Fe^{2+}	2.8×10^{-2} (2.0 M)^{h}	0.3	5.1×10^{-2}	?
O_2	$Co([14]aneN_4)(OH_2)_2{}^{2+}$	5.0×10^{5} (0.1 M)^{i}	2×10^{-10} (8×10^{3})	$6 \times 10^{3\,j}$	IS
$Co([14]aneN_4)(OH_2)O_2{}^{2+}$	$Co([14]aneN_4)(OH_2)_2{}^{2+}$	4.9×10^{5} (0.1 M)^{i}	1×10^{-2} (8×10^{5})	$5 \times 10^{2\,j}$	IS
O_2	$Co([15]aneN_4)(OH_2)_2{}^{2+}$	3.8×10^{3} (0.1 M)^{i}	3×10^{-14} ($\sim 4 \times 10^{4}$)	$\sim 2 \times 10^{j}$	IS
$Co([14]aneN_4)(OH_2)O_2{}^{2+}$	$Co([15]aneN_4)(OH_2)_2{}^{2+}$	3.7×10^{4} (0.1 M)^{d}	1×10^{-6} ($\sim 10^{4}$)	$\sim 4 \times 10^{2\,j}$	IS

^{a} Equilibrium constants for outer-sphere electron transfer (based on differences in potentials). Quantities in parentheses are measured or estimated equilibrium constants for adduct formation and have dimensions of M^{-1}. Potentials used are summarized in Table I for reductants. Other values used were −0.15 V for O_2-$O_2{}^{-}$ [2k] and 0.713 V for $[(NH_3)_5Co]_2O_2{}^{5+,4+}$.[32] ^{b} OS = outer-sphere; IS = inner-sphere (reaction forming μ-peroxo species). ^{c} Reference 3a. ^{d} This work. ^{e} Hand, T. D.; Hyde, M. R.; Sykes, A. G. *Inorg. Chem.* 1975, *14*, 1720. ^{f} Hoffman, A. B.; Taube, H. *Inorg. Chem.* 1968, 7, 1971. ^{g} Reference 25b–d. ^{h} Davies, R.; Sykes, A. G. *J. Chem. Soc. A* 1968, 283. ^{i} Reference 13a. ^{j} K_{ab} for adduct formation (i.e., quantity in parentheses) used in this calculation.

$Co(sep)^{2+}$ and $Ru(NH_3)_6{}^{2+}$ reactions; our observations are in reasonable accord with expectation for the $V^{2+}/Ru(NH_3)_6{}^{2+}$ comparison, but not for the $Co(sep)^{2+}/Ru(NH_3)_6{}^{2+}$ comparison. Crossreaction rates 1 order of magnitude or more smaller than expectation are quite common for reactions involving the $Co(sep)^{3+,2+}$ couple;[24] e.g., the reaction of O_2 with $Co(sep)^{2+}$ [25] is about $^{1}/_{60}$ of the rate expected based on eq 8 and the rate observed for the $O_2/Ru(NH_3)_6{}^{2+}$ reaction.[3a] This effect may originate from differences in the adiabaticity of the ruthenium and cobalt reactions.[24]

The self-exchange rate constant we have inferred for the $Co([14]aneN_4)(OH_2)O_2{}^{2+,+}$ couple, $10^{3\pm2}$ M^{-1} s^{-1}, does not differ significantly in magnitude from that inferred for the O_2–$O_2{}^{-}$ coupled (based on Ru(II) reactions),[3] although the intrinsic barrier to self-exchange may be slightly smaller for the coordinated than for the free dioxygen moieties if allowance is made for the differences in charge type.

The data now available, summarized in Table III, indicate that the greater outer-sphere electron-transfer reactivity of $Co([14]aneN_4)(OH_2)O_2{}^{2+}$ than O_2 toward a given substrate arises almost entirely from the difference in driving force (or equilibrium constant) for the reactions. *We find no dramatic,* purely *kinetic advantage* (as in reduced reorganizational barriers) *arising from the coordination of O_2 to this cobalt center.*

The nuclear reorganizational barriers to single electron transfer in O_2 moieties may be approximately evaluated. The change in O–O bond length should contribute ~12 kJ mol^{-1} to $\Delta G_{exch}{}^{*}$ for the O_2–$O_2{}^{-}$ couple,[26–29] and the solvent contribution would be ~43 kJ mol^{-1} for an effective mean size of 220 pm for O_2 and $O_2{}^{-}$. On the basis of Ru(II) reactions,[3] $\Delta G_{exch}{}^{*} \sim 46$ kJ mol^{-1}. Most of the barrier to exchange must originate from solvent reorganization, as noted by Stanbury et al.[3]; only ~25–30% of the observed barrier can be attributed to the change in O–O bond length.

For coordinated O_2 moieties, formally $O_2{}^{-,2-}$, the contribution of O–O bond length change to the nuclear reorganizational barrier should be comparable[30] to that estimated above for O_2–$O_2{}^{-}$. Since the change of electron density is localized on a ligand, not the metal center, estimation of the solvent contribution becomes very difficult.[31] However, a dramatic increase in solvent reorganizational energies can be ruled out. Similarities in self-exchange rates for O_2–$O_2{}^{-}$ and $Co([14]aneN_4)(OH_2)O_2{}^{2+,+}$ couples are quite plausible in view of the expected similarity in structural parameters. The somewhat smaller observed than calcuated activation barriers suggest that the simple classical model overestimates the magnitude of solvent reorganization for very small molecules such as O_2–$O_2{}^{-}$.

The huge barrier reported for electron transfer in (μ-superoxo)–(μ-peroxo) couples ($\Delta G_{exch}{}^{*} \sim 80$ kJ mol^{-1}) cannot be accounted for by O–O bond length changes or simple models of solvent reorganization. Some of the discrepancies may arise from errors in the values of potentials of the coordinated dioxygen moieties: the recently reported value of $E^{f} = 0.713$ V[32] (vs. NHE) for $[(NH_3)_5Co]_2O_2{}^{5+,4+}$ implies values of $\Delta G_{exch}{}^{*} \sim 70$ kJ mol^{-1} for this couple. Correction for charge type differences (i.e., work terms) would tend to further reduce the apparent discrepancy. Consequently, these reactions may not be as much out of line as was previously suspected.

Finally, we note that some or all of the reactions compared could be nonadiabatic (i.e., the classical transmission coefficient, κ, could be less than 1). Indeed the high-frequency vibrations of O–O moieties might be expected to result in

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(24) (a) Endicott, J. F.; Brubaker, G. R.; Ramasami, T.; Kumar, K.; Dwarakanath, K.; Cassel, J.; Johnson, D. *Inorg. Chem.* **1983**, *22*, 3754. (b) Endicott, J. F.; Ramasami, T.; Gaswick, D. C.; Tamilarasan, R.; Heeg, M. J.; Brubaker, G. R.; Pyke, S. C. *J. Am. Chem. Soc.* **1983**, *105*, 5301. (d) Endicott, J. F.; Ramasami, T. *Ibid.* **1982**, *104*, 5252.

(25) (a) Creaser, I. I.; Harrowfield, J. M.; Herit, A. J.; Sargeson, A. M.; Springborg, J.; Geue, R. J.; Snow, M. R. *J. Am. Chem. Soc.* **1977**, *99*, 3181. (b) Sargeson, A. M. *Chem. Br.* **1979**, *15*, 23. (c) Creaser, I. I.; Geue, R. J.; Harrowfield, J. M.; Herit, A. J.; Sargeson, A. M.; Snow, M. R.; Springborg, J. *J. Am. Chem. Soc.* **1982**, *104*, 6016.

(26) Owing to the large vibrational quanta in O_2 and $O_2{}^{-}$, nuclear tunneling makes a substantial contribution. We have estimated this quantity using the approach of Buhks et al.[10c] The parameters employed are $\nu(O_2) = 1556$ cm^{-1},[27] $\nu(O_2{}^{-}) = 1089$ cm^{-1},[28] $r(O_2) = 121$ pm,[29] and $r(O_2{}^{-}) = 134$ pm.[28] The classical[6] contribution to ΔG^{*} would be 19 kJ mol^{-1}.

(27) Barrow, G. M. "Introduction to Molecular Spectroscopy"; McGraw-Hill: New York, 1962; p 42.

(28) Celotta, R. J.; Bennett, R. A.; Hall, J. L.; Siegel, W. W.; Levine, J. *Phys. Rev. A.* **1972**, *6*, 631.

(29) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 3rd ed.; Interscience: New York, 1972.

(30) The differences in bond lengths are comparable. The smaller vibrational frequencies will tend to decrease the reorganizational contribution, but this will be partly compensated by a small contribution of nuclear tunneling.

(31) See: Cannon, R. D. "Electron Transfer Reactions"; Butterworths: Boston, MA, 1980; Chapter 6.

(32) Richens, D. T.; Sykes, A. G. *J. Chem. Soc., Dalton Trans.* **1982**, 1621.

(33) Kenne, J. P. *Radiat. Res.* **1964**, *22*, 14.

nonadiabatic effects based on Landau–Zener surface-crossing arguments, whether formulated in terms of the effect of very different slopes on the crossing probability of more explicitly by expressing κ as a function of the ratio of the frequencies of electronic to nuclear motion.[7,8] Unfortunately, the quality of data currently available for these systems does not permit evaluation of such factors.

B. Inner-Sphere Reactions. While very rapid reactions are frequently observed between $Co(N_4)(OH_2)O_2^{2+}$ and mild reducing agents (often reactions with very unfavorable equilibrium constants for outer-sphere electron transfer), these reactions invariably involve formation of metastable μ-peroxo complexes. Since peroxide is a very basic ligand[21] with a high affinity for metals (e.g., see ref 13), the free energy change associated with formation of the μ-peroxo adducts makes such a large contribution to the overall free energy change that adduct formation is the preferred reaction pathway (see Table III).

The contrasting reactivities of $Fe(OH_2)_6^{2+}$ and $Co^{II}(N_4)$ complexes toward dioxygen species are particularly interesting. It appears that the smaller reactivity of the aquoiron complex can be ascribed largely to a significantly smaller equilibrium constant. Thus, for

$$Fe(OH_2)_6^{2+} + O_2H \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Fe(OH_2)_5O_2H^{2+} + H_2O$$

$k_3 = 7.3 \times 10^5\ M^{-1}\ s^{-1}$,[33] $k_{-3} = 0.11\ s^{-1}$, and so $K_3 \sim 6 \times 10^6\ M^{-1}$. For the corresponding reaction of $Co([14]aneN_4)(OH_2)_2^{2+}$ with O_2H, k_3' would be about $10^7\ M^{-1}\ s^{-1}$ (based on the reaction with $Co([14]aneN_4)(OH_2)O_2^{2+}$ and allowing for the difference in charge types), while the hydroperoxo complex is sufficiently stable that we estimate $k_{-3}' < 10^{-3}\ s^{-1}$ or $K_3' > 10^{10}\ M^{-1}$. A similar pattern of stabilities would imply $K_4 \leq 10^3\ M^{-1}$ for

$$Co([14]aneN_4)(OH_2)O_2^{2+} + Fe(OH_2)_6^{2+} \overset{K_4}{\rightleftharpoons} H_2O([14]aneN_4)Co{-}O_2{-}Fe(OH_2)_5^{4+} + H_2O$$

We note that $H_2O([14]aneN_4)Co{-}O_2{-}Fe(OH_2)_5^{4+}$ can dissociate by means of either $Fe^{III}{-}O_2^{2-}$ or $Co^{III}{-}O_2^{2-}$ bond breaking. Since our experiments were performed in excess Fe(II), the H_2O_2 or hydroperoxo complexe products of dissociation would not be expected to survive long enough for analytical detection and the absorbance changes are small enough that stopped-flow detection of products was also difficult and ambiguous. Limited evidence for free-radical contributions to the decomposition (Table SX[19]) is consistent with Fe(II)/hydroperoxide reactions, which generate hdyroxyl radicals.[34] The different substitutional properties of Fe(III) and Co(III) argue strongly that the immediate product of dissociation must be $Co([14]aneN_4)(OH_2)O_2H^{2+}$.

Conclusions

In this study we have found a considerable enhancement of reaction rate, with electron-transfer substrates, for 1:1 $Co{-}O_2$ adducts compared to aqueous O_2. We have also found that this rate enhancement on coordination of O_2 arises predominantly from differences in equilibrium constants for the 1-equiv oxidation–reduction processes—whether outer sphere or inner sphere. The more favorable equilibrium constants for reaction of O_2 coordinated to Co(II) complexes can be associated with the relative stability and basicity of the peroxo reaction products. There seems to be little radical character and no special kinetic properties have been found for the 1:1 $Co(II){-}O_2$ adducts, more or less in keeping with the views recently expressed by Sawyer and Valentine.[35] That systems exist which possess unique kinetic features seems to be illustrated by some (μ-peroxo)–(μ-superoxo) couples. The dramatic variations in thermodynamic properties of these systems remain a bit perplexing.

Acknowledgment. Some of the preliminary experiments in this study were performed by Dr. K. P. Balakrishnan and by Clifford Jeske.

Supplementary Material Available: Tables SI–SXII of kinetic data (15 pages). Ordering information is given on any current masthead page.

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[34] Walling, C.; Goosen, A. *J. Am. Chem. Soc.* **1973**, *95*, 2987.

[35] Sawyer, D.; Valentine, J. *Acc. Chem. Res.* **1981**, *14*, 393.