(4), $J = 33.30$ (10) cm^{-1}, and $j = 0.293$ (10) cm^{-1}, leading to triplet, quintet, and septet energies of 35.20 (10), 103.9 (3), and 202.4 (6) cm^{-1}, respectively. Application of model 3 significantly improves the fit, the value of var/f reducing to 1.16. The ratio of the fitting parameters (var/f) for models 2 and 3 (1.8/1.6) is 1.55, which is at the 99.95% fractile of the V^2 distribution; i.e., the improvement brought about by the inclusion of the additional variable is significant at the 99.95% confidence level. This model (model 3) gives $g = 1.981$ (4) and $E(1) = 34.64$ (6), $E(2) = 103.4$ (1), and $E(3) = 198.7$ (5) cm^{-1}.

The results obtained here for this trans erythro complex can be compared with those reported for other monol dimers of this general type. The singlet–triplet splitting in the presnt complex (approximately 35 cm^{-1}) is considerably larger than that of approximately 21 cm^{-1} reported[13] for two salts of the cis complex $[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$ and is also larger than the value of approximately 31 cm^{-1} reported[9,10] for the symmetric rhodo complex $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$. It is apparent that the difference between the magnetic properties of the present complex and those of the cis hydroxo complex may be explained in part by the increased value of the bridging Cr–O–Cr angle (Φ) from 142.8° in the cis hydroxo complex to 155.1° in the present complex. It is also noteworthy, however, that in the present case the bridging hydrogen atom is in the bridging plane, at least on a time average, while in the cis hydroxo complex it lies approximately 0.5 Å above the plane.[13] As will be demonstrated in a future publication from our laboratories and has been suggested in some earlier papers,[2,4,8,17] both of these parameters are of importance in determining the magnitude of the magnetic interaction.

Acknowledgment. We are very grateful to Mrs. Solveig Kallesøe, who collected the susceptibility data. S.J.C. gratefully acknowledges the receipt of a NATO postdoctoral fellowship. This research was also supported by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO), through Grant No. 1318 (to D.J.H., J.G., and E.P.), by the donors of the Petroleum Research Fund, administered by the American Chemical Society (to D.J.H.), and by the Danish National Science Research Council through Grant Nos. 511-742, 511-3993, and 511-10516 (to E.P.).

Registry No. *trans*-$[(NH_3)_4(H_2O)Cr(OH)Cr(NH_3)_5]Cl_5 \cdot 3H_2O$, 77550-02-8; *trans*-$[(H_2O(NH_3)_4Cr(OH)Cr(NH_3)_5](NO_3)_5$, 77550-03-9; *trans*-chloro erythro, 77550-04-0.

Supplementary Material Available: A list of observed and calculated structure amplitudes (electrons × 10) (10 pages). Ordering information is given on any current masthead page.

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Oxidation–Reduction Reactions of Complexes with Macrocyclic Ligands. Role of Intermediates in Reactions of μ-Peroxo-dicobalt Complexes[1]

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Received August 19, 1980

The $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ complex decomposes slowly in acidic aqueous solution. The solutions of this μ-peroxo complex have both oxidizing and reducing properties. The rates of oxidation *and* reduction reactions approach limiting first-order behavior for large concentrations of the counterreagent. The limiting first-order rate constants depend on the anionic composition of the medium but are otherwise independent of the counterreagent. This behavior is attributed to rate-limiting homolytic dissociation of the μ-peroxo complex, with the reactive intermediate species being $Co([14]aneN_4)(OH_2)_2^{2+}$ and $Co([14]aneN_4)(OH_2)O_2^{2+}$. It is further proposed that the same kind of intermediates mediate the decomposition of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$. More specifically, in acidic chloride solutions the decomposition products of the μ-peroxo complex were found to be $Co([14]aneN_4)Cl_2^+$ and $Co([14]aneN_4)Cl(O_2H)^+$ in about a 1:0.8 ratio. This suggests an inner-sphere (Cl^--bridged) attack of $Co([14]aneN_4)(OH_2)_2^{2+}$ on $[ClCo([14]aneN_4)]_2O_2^{2+}$. The relative inertness of the μ-peroxo moiety probably arises from a combination of thermodynamic and intrinsic barriers to electron transfer.

Introduction

Transition-metal complexes play crucial roles in mediating the utilization of molecular oxygen by many biological and synthetic systems.[2] Very often the initial uptake of dioxygen can be described by the two steps

$$ML^{n+} + O_2 \rightleftarrows O_2ML^{n+} \qquad k_1, k_{-1}, K_1 \qquad (1)$$

$$O_2ML^{n+} + ML^{n+} \rightleftarrows LMO_2ML^{2n+} \qquad k_2, k_{-2}, K_2 \qquad (2)$$

The second step is frequently described as "irreversible". Owing in part to the complications introduced by this second step, the role, if any, of the O_2ML^{n+} dioxygen adduct in metal-mediated oxidations and oxygenations has proved difficult to elucidate.

Cobalt(II) complexes are well-known for their reactivity toward dioxygen,[2] and cobalt-mediated oxidations (or oxygenations) are varied and generally complex. However, it is possible to minimize those complexities attributable to variations in the coordination sphere of the metal by use of macrocyclic ligand complexes. This approach is particularly advantageous for 14-membered macrocyclic N_4 ligands since the cobalt(II) complexes tend to be low spin and can persist for hours in acidic aqueous media. This contrasts markedly

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(1) Partial support of this research by the National Institutes of Health (Grant AM 14341) is gratefully acknowledged.

(2) For reviews see: (a) Taube, H. *J. Gen. Physiol.* **1965**, *49*, 29. (b) Wilkins, R. G. *Adv. Chem. Ser.* **1971**, *No. 100*, 111. (c) Schultz, J., Cameron, B. F., Eds. "The Molecular Basis for Electron Transport"; Academic Press: New York, 1972. (d) Bennett, L. E. *Prog. Inorg. Chem.* **1973**, *18*, 1. (e) Valentine, J. *Chem. Rev.* **1973**, *73*, 235. (f) Basolo, F.; Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1975**, *8*, 384. (g) Vaska, L. *Ibid.* **1976**, *9*, 175. (h) McLendon, G.; Martel, A. E. *Coord. Chem. Rev.* **1976**, *18*, 125. (i) Dunford, H. B.; Stillman, J. S. *Ibid.* **1976**. (j) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139. (k) Fee, J. A.; Valentine, J. S. In "Superoxide and Superoxide Dismutases"; Michelson, A. M., McCord, J. M., Fridovich, I., Eds.; Academic Press: New York, 1977; p 19. (l) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 235. (m) Lever, A. B. P.; Gray, H. B. *Ibid.* **1978**, *11*, 348. (n) Fidovich, I. *Science* **1978**, *201*, 875. (o) Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645.

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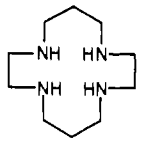
to the behavior of high-spin cobalt(II) complexes, even those containing macrocyclic ligands, which tend to equilibrate with the medium in a few seconds.[3,4] We have recently reported the nature of the oxygen uptake step for several macrocyclic N_4 cobalt(II) complexes.[4] For two of these complexes the magnitude of the overall equilibrium constant, K_1K_2, is sufficiently large *and* the rates of decomposition are sufficiently small that relatively stable μ-peroxo-dicobalt complexes can be isolated and characterized.[5-7] In contrast, the related μ-peroxo-dicobalt complex with N_4 = $Me_2[14]1,11$-dieneN_4[8] as the equatorial ligand has a comparable value of K_1K_2 but decomposes too rapidly to be isolated and characterized.[4,9] It has been stated that $[H_2OCo([14]aneN_4)]_2O_2{}^{4+}$ decomposes smoothly to $Co([14]aneN_4)Cl_2{}^+$ and H_2O_2,[5] presumably by means of simple heterolytic substitution. However, one must also consider redox decomposition pathways since the reduction potentials of the O_2/H_2O_2 (0.68 V),[10] $Co([14]aneN_4)Cl_2{}^{+,0}$ (~0.2 V),[9] and the $Co([14]aneN_4)(OH_2)_2{}^{3+,2+}$ (0.42 V)[4] couples are resaonably similar. In such an event, the μ-peroxo complexes in some systems might be able to function as reservoirs from which the relaitvely reactive O_2ML^{n+} superoxo complexes may be extracted.

Experimental Section

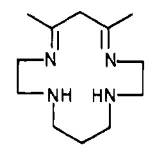
$[H_2OCo([14]aneN_4)]_2O_2{}^{4+}$[5] and $[H_2OCo(Me_2[14]4,11$-diene-$N_4)]_2O_2{}^{4+}$[6,7] were prepared according to procedures described in the literature cited. Elemental analyses were in good agreement with theoretical, and absorption spectra were in accord with the literature reports. Other macrocyclic complexes have been prepared as described previously.[12,13] Literature methods were also used to prepare $Fe(bpy)_3(ClO_4)_3$[14] and $[Ru(NH_3)_5py](ClO_4)_2$;[15] $Ru(NH_3)_6Cl_3$ was purchased from Matthey-Bishop Co. and recrystallized as the perchlorate salt. Chromous perchlorate solutions were prepared by Zn(Hg) reduction of acidic $Cr(ClO_4)_3{\cdot}nH_2O$ under a stream of nitrogen. Ferrous sulfate was recrystallized[16] and solutions were prepared and used immediately after purification of the salt. Ferric nitrate solutions were standardized by the thiocyanate method.[17]

Solutions for kinetic studies were prepared by dissolving a known amount of $\{[H_2OCo([14]aneN_4)]_2O_2\}(ClO_4)_4$ in a prethermostated aliquot of the reaction medium. Deaeration was accomplished by means of a Cr^{2+}-scrubbed nitrogen stream. Slower reactions were followed spectrophotometrically in serum-capped spectrophotometer cells. Rapid reactions were followed in an Aminco stopped-flow apparatus.

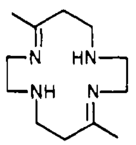
Concentrations of dissolved oxygen were determined from the literature values of oxygen in air or oxygen-saturated solutions[18] or by direct measurement using the Radiometer D616/E5046 P_{O_2} electrode and Orion Model 801A Research Digital Ionalyzer as described previously.[4]



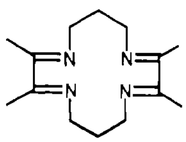
$[14]aneN_4$



$Me_2[14]1,11$-dieneN_4



$Me_2[14]4,11$-dieneN_4



$Me_4[14]$tetraeneN_4

In the kinetic studies of the reactions of $[XCo([14]aneN_4)]_2O_2{}^{n+}$ ($X = Cl^-$ or H_2O), the wavelengths monitored were 540 nm with $Co(Me_4[14]tetraeneN_4)Cl_2{}^+$ and $Co(Me_4[14]tetraeneN_4)(OH_2)_2{}^{2+}$, 500 nm with $Fe(bpy)_3{}^{3+}$, 430 nm with Fe^{3+}, 360 nm with $S_2O_8{}^{2-}$, 430 nm with Fe^{2+}, 400 nm with Cr^{2+}, and 370 nm with $Ru(NH_3)_5py^{2+}$.

Warning! The perchlorate salts used in this study are potentially explosive and should be handled with care.

Results

A. Thermal Decomposition of μ-Peroxo Complexes. All the $[XCo(N_4)]_2O_2{}^{4+}$ complexes generated were found to be metastable species in acidic aqueous solutions at room temperature. The decomposition reactions were always complex and were different in their principal features for each of the substrates studied.

1. $[H_2OCo([14]andN_4)]_2O_2{}^{4+}$ in Perchlorate Media. This complex has about a 1-h lifetime ($k = 3 \times 10^{-4}\ s^{-1}$) in 0.1 M $HClO_4$ at 25 °C. The absorbance of reactant solutions decreased at all visible wavelengths, and no isosbestic points were found. The final product spectra were different at 25 and 55 °C. At the higher temperatures (in an open beaker) the final product spectrum corresponded to that of the stoichiometric quantity of an authentic sample of $Co([14]aneN_4)(OH_2)_2{}^{3+}$, while at lower temperatures the "product" spectrum had relatively strong ultraviolet absorbancies. Pseudo-first-order plots of absorbance changes were reasonably linear over 2–3 half-lives at all temperatures ($E_a \simeq 77$ kJ mol^{-1}; Figure S-I[19]). The reaction rate was found to be acid independent (5×10^{-3} M $\leq [H^+] \leq 0.1$ M). Oxygen evolution in this system proceeded so slowly ($k < 10^{-4}\ s^{-1}$) at 25 °C that it could not be unequivocally distinguished from air leaks in our apparatus. We detected no H_2O_2 among the initial products of reaction at 25 °C.

2. $[H_2OCo([14]aneN_4)]_2O_2{}^{4+}$ in Chloride Media. This system was relatively more easily investigated and most of our studies of $[H_2OCo([14]aneN_4)]_2O_2{}^{4+}$ decompositions have been performed in chloride media. Two stages of reaction were identified: (a) the initial rapid stages identified as stepwise anation to form $[ClCo([14]aneN_4)]_2O_2{}^{2+}$ and discussed previously[4] and (b) decomposition of the μ-peroxo complex to form monomeric products. The final reaction stage (or stages) is described in this section.

In solutions with $[Cl^-] \geq 0.02$ M, the absorption spectra of the reaction products was very similar to the spectrum of $Co([14]aneN_4)Cl_4{}^+$; for smaller $[Cl^-]$, absorption spectra indicated more complex product mixtures. The product solutions did oxidize I^- in the presence of the molybdate catalyst, whereas $Co([14]aneN_4)Cl_2{}^+$ did not. When the product

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(8) Ligand abbreviations: $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; $Me_2[14]1,11$-dieneN_4 = 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,11-diene; $Me_2[14]4,11$-dieneN_4 = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; $Me_4[14]$tetraeneN_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; bpy = 2,2′-bipyridine.

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(19) Supplementary material. See paragraph at end of paper.

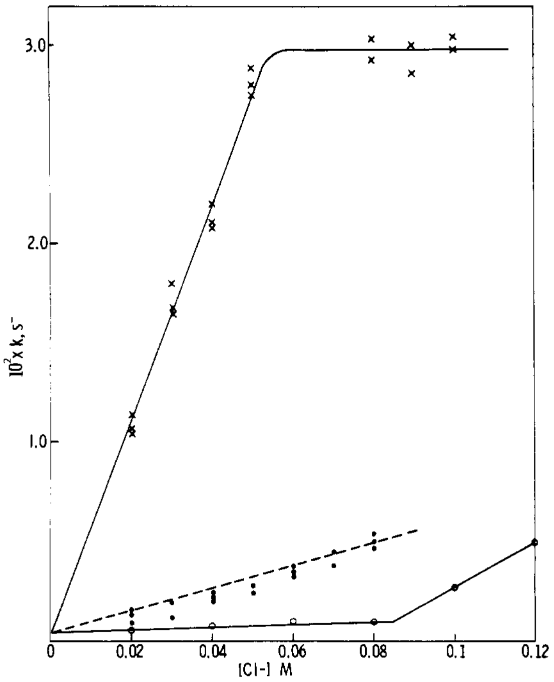

Figure 1. Variation with $[Cl^-]$ of the apparent first-order rate constant for decay of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ (25 °C; $\mu = 0.10$ M; $[H^+] = 0.01$ M): $[O_2]_i < 10^{-5}$ M, ×; $[O_2]_i = 1.3 \times 10^{-4}$ M, ●; $[O_2]_i = 2.6 \times 10^{-4}$ M, ○.

mixture (high $[Cl^-]$) was passed through a cation-exchange resin, the effluents obtained by washing the supernatant solution through the column with water exhibited no oxidizing activity; effluents from solutions of $Co([14]aneN_4)Cl_2^+$ and H_2O_2 treated in the same manner did exhibit the full oxidizing equivalents of the added peroxide. The green product isolated from a suspension of $\{[H_2OCo([14]aneN_4)]_2O_2\}(ClO_4)_4$ in 0.1 M HCl was analyzed to be approximately a 1:1 mixture of $[Co([14]aneN_4)Cl_2]ClO_4$ and $[Co([14]aneN_4)O_2HCl]ClO_4$. Anal. Calcd for $CoC_{10}H_{24}N_4Cl_3O_4$: C, 28.0; H, 5.63; N, 13.0; Cl, 24.8; O, 14.9. Calcd for $CoC_{10}H_{25}N_4Cl_2O_6$: C, 28.1; H, 5.9; N, 13.11; Cl, 16.6; O, 22.5. Found: C, 27.6; H, 5.42; N, 12.8; Cl, 22.2; O, 20.2. This solid did oxidize I^- in the presence of the molybdate catalyst and the oxidizing species could again be removed from solution by a cation-exchange resin; the amount of I_3^- formed was nearly twice that expected, but this could result from $Co^{II}([14]aneN_4)$-catalyzed oxidations of I^- in the aerated analytical solutions.

Oxygen was released, but much more slowly that the rate of decomposition of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ in chloride media. Thus a solution 2.3×10^{-4} M in the μ-peroxo complex and 0.25 M in HCl produced 10^{-4} M O_2 in slightly less than 2 h ($k \leq 6 \times 10^{-4}$ s^{-1}; see Table S-I[19]). Addition of oxidants to such solutions resulted in the rapid evolution of O_2 (see also below) even after the apparent decomposition of all the μ-peroxo complex; e.g., in the experiment noted above, addition of excess Ce^{IV} after 2 h resulted in the production of an additional 10^{-4} M O_2.

In a series of experiments in solutions 0.1 M in NaCl, 1.8×10^{-4} M $\leq [[H_2OCo([14]aneN_4)]_2O_2^{4+}] \leq 5.4 \times 10^{-4}$ M, we found the decomposition of the μ-peroxo complex to be accompanied by decreases in $[H^+]$, with the observed pH changes (pH changes in the ranges 3.0–3.8 and 3.4–4.0–6.0) depending on substrate concentration. These changes correspond to the consumption of 1.9 ± 0.1 mol of H^+/mol of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ decomposed (small corrections were made for sodium ion errors at the higher pHs). Almost all of this change in pH occurred in the first 10 min of reaction (see Figure S-II[19]).

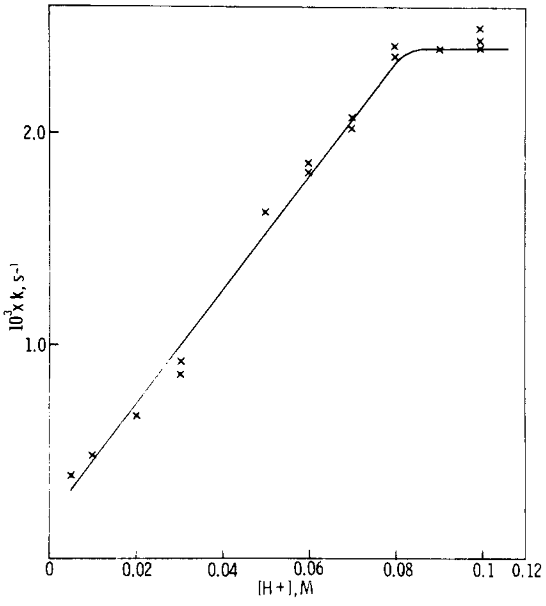

Figure 2. Variation with $[H^+]$ of the apparent first-order rate constant for decay of $[ClCo([14]aneN_4)]_2O_2^{2+}$ (25°; $\mu = 0.10$ M; $[Cl^-] = 0.10$ M).

The rate of decomposition of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ increased with $[Cl^-]$ (Figure 1) and $[H^+]$ (Figure 2) and increased when $[O_2]$ was reduced (Figures 1 and S-III[19]).

3. $[H_2OCo(Me_2[14]4,11\text{-}dieneN_4)]_2O_2^{4+}$. The acid decomposition of this complex was accompanied by absorbance decreases at all wavelengths. The product spectra exhibited a shoulder at about 450 nm ($\epsilon \simeq 25$ M^{-1} cm^{-1}) and strong ultraviolet absorptivity ($\lambda < 300$ nm). This differed from the case of the substrate ($\lambda_{max} = 325$ nm, $\epsilon = 6.8 \times 10^3$ M^{-1} cm^{-1}), $Co(Me_2[14]4,11\text{-}dieneN_4)(OH_2)_2^{3+}$ ($\lambda_{max} = 560$ nm, $\epsilon = 24$ M^{-1} cm^{-1}; shoulders at 415 nm and 360 nm with $\epsilon = 44$ and 73 M^{-1} cm^{-1}, respectively), or $Co(Me_2[14]4,11\text{-}dieneN_4)Cl_2^+$. The absorbance decay proceeded in two pseudo-first-order stages: $k_I = 0.115 \pm 0.003$ s^{-1} and $k_{II} = (7.3 \pm 1.6) \times 10^{-4}$ s^{-1}. Neither reaction stage was affected by variation of $[H^+]$ from 0.05 to 0.5 M or $[Cl^-]$ from 0 to 0.5 M. When the initial solution pH was ~2, the decomposition reaction consumed 6.9 ± 0.1 mol of H^+/mol of $[H_2OCo(Me_2[14]4,11\text{-}dieneN_4)]_2O_2^{4+}$ decomposed. Analyses by means of the NCS^- method indicated that the product solutions contained $Co(OH_2)_6^{2+}$, with the yield of $Co(OH_2)_6^{2+}$ equal to 2.0 ± 0.2 mol/mol of $[H_2OCo(Me_2[14]4,11\text{-}dieneN_4)]_2O_2^{4+}$ and independent of whether reactions were carried out in 0.1 M HCl or 0.1 M HF_3CSO_3. Finally the decomposition resulted in release of O_2 with $\Delta[O_2]$: $\Delta[[H_2OCo(Me_2[14]4,11\text{-}dieneN_4)]_2O_2^{4+}] = 0.51 \pm 0.01$ M.

B. Oxidation–Reduction Properties of $[XCo(N_4)]_2O_2^{n+}$ Complexes. 1. Reactions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ with Oxidizing Agents. Solutions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ exhibit *both* oxidizing and reducing properties. In general oxidations by solutions of this complex proceed more slowly than do the reductions. For example we have found the relatively rapid reductions of Fe^{3+} or $Co(Me_4[14]tetraeneN_4)Cl_2^+$ to be followed by much slower oxidations of Fe^{2+} and $Co^{II}(Me_4[14]tetraeneN_4)$, respectively, when $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ was in excess or in aerated solutions. These reactions were kinetically complex with the observed rate constants (for oxidations or reductions) approaching a limiting first-order value for large concentrations of the counterreagent, [X], as indicated in Figures 3 and 4. The kinetic data are collected in Table S-II.[19]

Some oxygen was freed to solution when $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ reacted with various oxidants. For $Fe(bpy)_3^{3+}$,

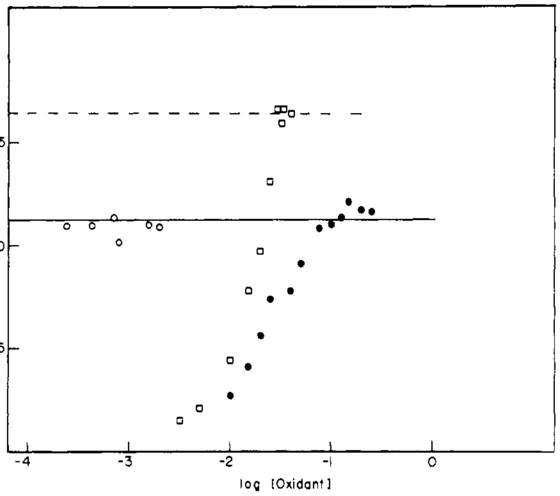

Figure 3. Variations with oxidant concentration in the pseudo-first-order rate constants for oxidations of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$. For oxidants: $Fe(bpy)_3^{3+}$, open circles, $\mu = 0.1$; Fe^{3+}, closed circles, $\mu = 2.0$; $S_2O_8^{2-}$, squares, $\mu = 1.0$; all in aerated perchlorate or trifluoromethylsulfonate media. $[H_2OCo([14]aneN_4)]_2O_2^{4+}] \approx 10^{-4}$ M. Limiting first-order rates are indicated by solid and dashed horizontal lines.

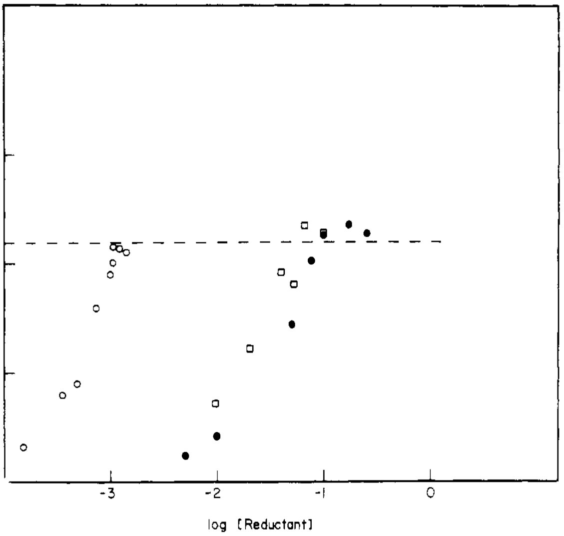

Figure 4. Variations with reductant concentrations in the pseudo-first-order rate constants for reductions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$. For reductants: Fe^{2+}, closed circles, $\mu = 2.0$, aerated; $Ru(NH_3)_5py^{2+}$, open circles, $\mu = 1.0$, deaerated; Cr^{2+}, squares, deaerated; all in ClO_4^- or $CF_3SO_3^-$ media. Limiting first-order rate is indicated by horizontal, dashed line.

Ce^{IV}, $Co(Me_4[14]tetraeneN_4)Cl_2^+$, and Fe^{3+}, O_2 was released within about 2 min after mixing reagents, and the stoichiometry of the oxygen generated was 1 mol of O_2/mol of the limiting reagent (Table S-III[19]). The cobalt product of oxidations with Fe^{3+} had an absorption spectrum corresponding to that of $Co([14]aneN_4)(OH_2)_2^{3+}$. In the oxidations with $Fe(bpy)_3^{3+}$, we found 2.1 ± 0.1 mol of $Fe(bpy)_3^{2+}$/mol of $[H_2OCo[14]aneN_4)]_2O_2^{4+}$ oxidized (Table S-IV[19]).

2. Reactions of $[H_2OCo([14]aneN_4)O_2]O_2^{4+}$ with Reducing Agents. These reactions were all slow (kinetic data summarized in Table S-V[19] and Figure 4) and stoichiometrically peculiar. For example, mixtures of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ and reducing agents resulted in net oxygen uptake in each case. In some cases this effect might be attributable to the reaction of the reducing agent with O_2, but in others the oxygen uptake was more rapid in the presence of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ than when only the reducing agent was present (e.g., as with $Co^{II}(Me_4[14]tetraeneN_4)$ or Fe^{2+}). Furthermore, the $[H_2OCo([14]aneN_4)]_2O_2^{4+}$-mediated oxygenation of $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ proceeded with no detectable net consumption of the μ-peroxo complex. Our studies have been more extensive with Fe^{2+} and $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ than with the other reducing agents.

Reactions of Fe^{2+} with $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ in aerated solutions resulted in formation of 4.0 ± 0.3 mol of Fe^{3+}/mol of μ-peroxo complex initially present in solution, $0.010\ M \le [Fe^{2+}] \le 0.20$ M and $0.82 \times 10^{-4}\ M \le [[H_2OCo([14]aneN_4)]_2O_2^{4+}] \le 9 \times 10^{-4}$ M (determination within a few minutes; Table S-VI[19]). There were systematic deviations from the average amount of Fe^{3+} produced, with $[Fe^{3+}]$ increasing when $[[H_2OCo([14]aneN_4)]_2O_2^{4+}]$ was decreased: the observed range was $2.13 \le [Fe^{3+}]/[[H_2OCo([14]aneN_4)]_2O_2^{4+}] \le 6.53$. Under similar conditions we also determined the amount of oxygen consumed in this process (Table S-VI). Evaluation of these measurements was somewhat complicated by the slow consumption of O_2 over a period of several hours in these relatively concentrated Fe^{2+} solutions. However, the observations cited refer to an initial, very rapid uptake of O_2 which was over in a few minutes, i.e., was of comparable lifetime to the Fe^{2+} reductions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$. The slower process was very likely due to an aerial oxidation of Fe^{2+} and may contribute to some of the scatter in estimated Fe^{3+} yields. We have extrapolated our measurements of O_2 consumption to the mixing time so that the numbers quoted (Table S-VII[19]) correspond to the initial, rapid uptake step. For this reaction, we find $\Delta[O_2]/[[H_2OCo([14]aneN_4)]_2O_2^{4+}] = 0.55 \pm 0.04$ with values ranging from 0.39 to 0.74.

Reactions of $Co^{II}(Me_4[14]tetraeneN_4)$ were performed in solutions sufficiently dilute that spectra of the $Co^{III}(Me_4[14]tetraeneN_4)$ species were obscured by other species in solution. Solutions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ were oxidizing toward $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ with the characteristic red color of the reducing agent ($\lambda_{max} = 542$ nm, $\epsilon = 3.4 \times 10^3\ cm^{-1}\ M^{-1}$) being bleached in about 0.5 h. After completion of this reaction in acidic, aerated solutions the $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ spectrum was nearly superimposable in the 600–350-nm region with the spectrum of a similarly aged solution not containing the reducing agent; i.e., there was little decomposition of the μ-peroxo complex. In these studies, we found that $[Co(Me_4[14]\text{-}tetraeneN_4)(OH_2)_2^{2+}]$ and $[O_2]$ decreased at the same rate. The reaction between $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ and H_2O_2 ($[HClO_4] = 0.1$ M; 25 °C) was found to have a second-order rate constant, $k = (2.0 \pm 0.5) \times 10^2\ M^{-1}\ s^{-1}$. ^1H NMR studies indicated that the ultimate cobalt(III) product of this reaction was $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+}$. The initial reaction product appeared yellow in these dilute solutions.

C. Related Electron-Transfer Reactions of $Co([14]aneN_4)(OH_2)_2^{2+}$. A few electron-transfer reactions of this complex were examined for purposes of comparison. The kinetic data are summarized in Table S-VIII.[19] In brief, we have the following for the oxidants given: $Co(Me_4[14]tetraeneN_4)Cl_2^+$, $k = (2.0 \pm 0.1) \times 10^4\ M^{-1}\ s^{-1}$ (0.4 M NaCl, 0.1 M HCl); $Fe(bpy)_3^{3+}$, $k = (1.6 \pm 0.2) \times 10^5\ M^{-1}\ s^{-1}$ (0.1 M $HClO_4$), $k = (0.98 \pm 0.04) \times 10^5\ M^{-1}\ s^{-1}$ (0.1 M HCl), $k = (0.95 \pm 0.05) \times 10^5\ M^{-1}\ s^{-1}$ (0.1 M HF_3CSO_3), ($k = (5.4 \pm 0.3) \times 10^4\ M^{-1}\ s^{-1}$ (0.1 M HCl, 0.1 M NaF_3CSO_3); $Fe(phen)_3^{3+}$, $k = (1.6 \pm 0.3) \times 10^5\ M^{-1}\ s^{-1}$ (0.1 M HCF_3SO_3, 0.1 M NaF_3CSO_3), $k = (1.1 \pm 0.1) \times 10^5\ M^{-1}\ s^{-1}$ (0.1 M HCl, 0.1 M NaF_3CSO_3).

Discussion

There are some complicating details of the reactions studied here. Many of these probably derive from the vagaries of radical reaction pathways. Despite the complications a number of important features of these systems stand out clearly.

All the oxidations *and* reductions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ approach limiting first-order behavior as the concentration of the counterreagent becomes sufficiently large (Figure 3 and 4). The limiting rates are the same regardless of the nature of the counterreagent: $k_{lim} = 0.6 \pm 0.1$ s^{-1}. The concentrations at which the limit is reached to depend upon the counterreagent. There is a limited medium dependence on the approach to the limiting rate and of the numerical value of the limiting rate. The numerical value of the limiting rate constant was somewhat larger in $S_2O_8^{2-}$ or Cl^- than in ClO_4^- media. This kinetic behavior clearly indicates that $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ is relatively unreactive and that its oxidation–reduction chemistry depends on its dissociation into more reactive intermediate species. We believe that the most plausible and the simplest process is the reverse of oxygen-uptake reactions of cobalt(II) complexes;[2,4] thus

$$[H_2OCo([14]aneN_4)]_2O_2^{4+} \rightleftharpoons Co([14]aneN_4)(OH_2)_2^{2+} + Co([14]aneN_4)(OH_2)O_2^{2+} \quad (2') \qquad k_{-2},\ k_2,\ K_2^{-1}$$

$$Co([14]aneN_4)(OH_2)O_2^{2+} \rightleftharpoons Co([14]aneN_4)(OH_2)_2^{2+} + O_2 \quad (1') \qquad k_{-1},\ k_1,\ K_1^{-1}$$

We have previously determined[4] $K_1 = (8 \pm 2) \times 10^3$ M^{-1} and $k_2 = (4.9 \pm 0.4) \times 10^5$ M^{-1} s^{-1} ($\mu = 0.1$; 25 °C). The present results imply for the limiting first-order dissociation rate of the μ-peroxo complex, $k_{-2} = 0.57 \pm 0.03$ s^{-1} ($0.10 \leq \mu \leq 2.0$; 25 °C; perchlorate media). Consequently $K_2 = (8.6 \pm 1.2) \times 10^5$ M^{-1} ($\mu = 0.1$; 25 °C; perchlorate media). In the sense that the μ-peroxo complex seems relatively unreactive but readily undergoes a redox dissociation (eq 2′), it can function as a reservoir of very reactive intermediate species, which are slowly leaked into solution.

Clearly the oxidations of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ fit this pattern of behavior. The reaction stoichiometries are consistent with 1:2 consumption of μ-peroxo complex and (one-electron) oxidants, forming $Co([14]aneN_4)(OH_2)_2^{3+}$ and O_2. Furthermore, $Co([14]aneN_4)(OH_2)_2^{2+}$ is a good reducing agent[20] and reacts very rapidly with most of the oxidants used. The order of decreasing oxidant concentrations required to reach the limiting first-order rate, and, thus, total scavenging of $Co([14]aneN_4)(OH_2)_2^{2+}$, are in the appropriate order for increasing reactivity of these oxidants toward $Co([14]aneN_4)(OH_2)_2^{2+}$: $Fe^{3+} < Co(Me_4[14]tetraeneN_4)Cl_2^+ < Fe(bpy)_3^{3+}$. The complicated kinetics observed for the approach to the limiting first-order condition in the Fe^{3+} oxidations reflect the orders of magnitude larger second-order rate constant for the reactions of $Co([14]aneN_4)(OH_2)_2^{2+}$ with $Co([14]aneN_4)(OH_2)O_2^{2+}$ than with Fe^{3+} [21] and the resulting kinetic competition for the cobalt(II) intermediate.

That the oxidations of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ proceed through dissociation to the cobalt(II) intermediate rather than direct oxidation to a μ-superoxo complex is not at all surprising in view of the large potentials and intrinsic ("reorganizational") barriers characteristic of μ-peroxo/μ-superoxo couples[22] and the relatively large value of k_{-2}.

The reductions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ are relatively slow, but, in common with the oxidation, the rates of reduction tend to approach a first-order limit. The numerical value of the limiting first-order rate constant is indistinguishable from that found for oxidations run in the same medium (0.55 ± 0.10 s^{-1} in 0.1 M perchlorate or $F_3CSO_3^-$ medium). The inescapable conclusion is that the various reducing agents scavenge a reactive oxidizing intermediate formed from the rate-limiting dissociation of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$. This very reactive oxidant must be $Co([14]aneN_4)(OH_2)O_2^{2+}$. The very small rate constants are an obvious consequence of the necessarily small stationary-state concentrations of $Co([14]aneN_4)(OH_2)O_2^{2+}$ ($k_{-2} = 4.9 \times 10^5$ M^{-1} s^{-1}, $k_{-1} = 63$ s^{-1}; $[Co([14]aneN_4)(OH_2)O_2^{2+}]_{ss} \approx k_{-2}[\mu\text{-peroxo}]/(k_2[Co^{II}] + k_{-1}) \approx 10^{-6}$ M) and the complex competition kinetics which must be involved in the decay of a very reactive intermediate species. Even the reductant concentrations required for rate saturation in Figure 4 are not simply interpretable. For example, the reaction products of Fe^{2+} reductions are Fe^{3+} and $Co([14]aneN_4)(OH_2)_2^{3+}$, while the products of the Cr^{2+} reductions are Cr(III) species and $Co([14]aneN_4)(OH_2)_2^{2+}$. Further, since Cr^{23} reacts more rapidly with the O_2 produced in eq 1 than does $Co([14]aneN_4)(OH_2)_2^{2+}$ (and much more rapidly with O_2 than does Fe^{2+}), rate saturation in the Cr^{2+} reactions cannot simply be attributed to the reaction of Cr^{2+} with $Co([14]aneN_4)(OH_2)O_2^{2+}$. The kinetic details of these reactions are being investigated by means of direct observations of the reactions of $Co([14]aneN_4)(OH_2)O_2^{2+}$.[23] For our present purposes it is sufficient that rate saturation is observed and that the limiting first-order rate is nearly independent of the nature of the counterreagent.

While the first step in reaction of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ with reducing agents is clearly identifiable, the mechanism of these reactions have not yet been established. The stoichiometric studies indicate that on the average for the Fe^{2+} reaction

$$4Fe^{2+} + [H_2OCo([14]aneN_4)]_2O_2^{4+} + {}^1/{}_2O_2 + 6H^+ \rightarrow 4Fe^{3+} + 2Co([14]aneN_4)(OH_2)_2^{3+} + H_2O$$

The small but systematic deviations from this stoichiometry are suggestive of some radical pathways; however, we do not yet know whether the principal reaction pathway does or does not involve any very reactive radical intermediates other than the monomeric superoxo complex. Perhaps the most striking feature of this reaction stoichiometry is the oxygen uptake, which is strongly supportive of the postulated, reactive $Co([14]aneN_4)(OH_2)O_2^{2+}$ intermediate. Obviously, direct reduction of the μ-peroxo linkage to two water molecules would require half the Fe^{2+} and involve no oxygen uptake.

That $Ru(NH_3)_5py^{2+}$ can be oxidized by the intermediate obtained from $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ suggests that the coordinated superoxo group is susceptible to outer-sphere reductions. Unfortunately, $Ru(NH_3)_5py^{2+}$ may be a powerful enough reductant to reduce the cobalt center[21,24] so the site of attack is ambiguous. It is important to observe that under our conditions, this complex does not reduce either the cobalt center or the μ-peroxo group of $[H_2OCo[14]aneN_4)]_2O_2^{4+}$.

In contrast to the ruthenium(II) complex, the Fe^{2+}, Cr^{2+}, and $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ complexes can in principle react with $Co([14]aneN_4)(OH_2)O_2^{2+}$ by means of

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(20) Yee, E. L.; Cave, R. J.; Guyer, K. L.; Tyma, P. D.; Weaver, M. J. *J. Am. Chem. Soc.* **1979**, *101*, 1131.

(21) We would estimate a rate constant of $\sim 10^2$ M^{-1} s^{-1} for this reaction on the basis of reorganizational parameters (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) and reactions of similar complexes (see ref 13).

(22) McLendon, G.; Mooney, W. F. *Inorg. Chem.* **1980**, *19*, 12.

(23) Endicott, J. F.; Kumar, K.; Balakrishnan, K. P.; Jeske, C.; Gilbert, T., work in progress. The stopped flow studies have shown that the $Ru(NH_3)_6^{2+}$ and Fe^{2+} reductions of $Co([14]aneN_4)(OH_2)O_2^+$ occur with rate constants $\sim 3 \times 10^5$ M^{-1} s^{-1} and $\sim 8 \times 10^2$ M^{-1} s^{-1}, respectively. The Fe^{2+} reaction appears to form a new intermediate as in eq 3–6. See also: Endicott, J. F.; Balakrishnan, K. P.; Wong, C. L. "Abstracts of Papers", 180th National Meeting of the American Chemical Society, Las Vegas, Nev., Aug 1980; American Chemical Society: Washington, D.C., 1980; INOR 319.

(24) For the $Ru(NH_3)_5py^{2+}/Co([14]aneN_4)(OH_2)_2^{3+}$ reaction $K = 110$ and we estimate (see references in footnote 21) $k \leq 35$ M^{-1} s^{-1}.

an "inner-sphere" pathway to form a mixed-metal μ-peroxo species as a further reaction intermediate. This is similar to the observed reaction pathway of the $Co([14]aneN_4)(OH_2)O_2^{2+}/Co([14]aneN_4)(OH_2)_2^{2+}$ reaction.[4] On the basis of the behavior of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$, it seems likely that such mixed-metal μ-peroxo complexes would undergo further oxidation–reduction reactions relatively slowly; this may be another reason for the small values of rate constants observed for many of the reductions. The existence of such a reaction pathway would greatly increase the number of possible reaction intermediates owing to the multiple decay modes possible for such species: e.g. for the Fe^{2+} reductions one would have to consider (3)–(6) among the possible

$$[H_2OCo([14]aneN_4)\text{–}O_2\text{–}Fe]^{4+} \xrightarrow{H^+} Co([14]aneN_4)(OH_2)_2^{3+} + FeO_2^{+} \quad (3)$$

$$[H_2OCo([14]aneN_4)\text{–}O_2\text{–}Fe]^{4+} \xrightarrow{H^+} Co([14]aneN_4)(OH_2)_2^{2+} + FeO_2^{2+} \quad (4)$$

$$[H_2OCo([14]aneN_4)\text{–}O_2\text{–}Fe]^{4+} \xrightarrow{H^+} Co([14]aneN_4)(OH_2)O_2H^{2+} + Fe^{3+} \quad (5)$$

$$[H_2OCo([14]aneN_4)\text{–}O_2\text{–}Fe]^{4+} \xrightarrow{H^+} Co([14]aneN_4)(OH_2)_2^{3+} + FeO_2H^{2+} \quad (6)$$

pathways not cleaving the O–O bond. Some of these pathways are clearly more likely than others; however, the systems are sufficiently complex that complete mechanistic elucidation must await studies which directly investigate the chemistry of the transient superoxo complexes.[23] It is interesting that the $[H_2OCo([14]aneN_4)]_2O_2^{4+}$-mediated oxygenation of $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ proceeds with little net consumption of the μ-peroxo substrate. This suggests that a pathway analogous to (4) followed by (1) is important for this cobalt substrate. The reactions of $Co^{II}(N_4)$ complexes with H_2O_2 are rapid,[25] and H_2O_2 or hydroperoxide complexes would not be expected to survive under these reaction conditions.

The $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ complex is only moderately stable in aqueous solution. The decomposition kinetics are very complex, but again some general features do stand out. The pseudo-first-order rate constant for decomposition of the μ-peroxo complex is always smaller than k_{-2}. Thus, the observed decompositions are likely to be mediated by $Co([14]aneN_4)(OH_2)_2^{2+}$ and/or $Co([14]aneN_4)(OH_2)O_2^{2+}$. In support of this view, we note that the stabilities of the μ-peroxo complexes are strongly affected by the anionic composition of the medium. Thus the decomposition of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ is more rapid in chloride than in perchlorate media and is effectively quenched in NCS^- or CN^- media. In chloride, the decomposition reaction is preceded by a rapid two-step reaction, which has been identified as the stepwise anation of the μ-peroxo complex.[4] We have also isolated the very stable $\{[SCNCo([14]aneN_4)]_2O_2\}(ClO_4)_4$ and $\{[NCCo([14]aneN_4)]_2O_2\}(ClO_4)_4$ complexes. Thus the rate of decomposition is most likely related to the nature of the axial ligand, and probably to variations in the Co(III)–Co(II) reduction potentials.[2,4] A correlation with redox potentials might be expected since it is thermodynamically easier to generate a cobalt(II) complex from a chloro than from an isothiocyanato or cyano complex.[26] In addition to the simple matter of redox thermodynamics, a mechanistic issue may also be involved. Thus the observation that the initial product mixture in chloride media contains $Co([14]aneN_4)(O_2H)Cl^+$ as well as $Co([14]aneN_4)Cl_2^+$ and the accelerated rate of decomposition in chloride media suggest that a major reaction pathway is (2′) and (1′) followed by the inner-sphere electron-transfer reactions (n = 1 or 0)

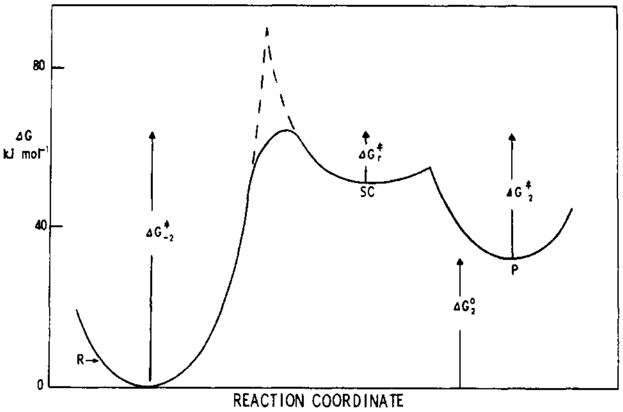
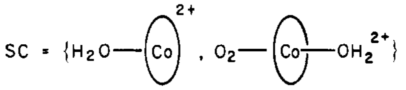


Figure 5. Schematic representation of the reaction coordinate for homolysis of the Co–μ-peroxo bond in $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ (=R), drawn to scale with free energy quantities measured as described in the text. The designation



$$SC = \{H_2O\text{—}\mathrm{Co}^{2+},\ O_2\text{—}\mathrm{Co}\text{—}OH_2^{2+}\}$$

is used to represent the immediate, solvent cage trapped homolysis products. The activation free energy for recombination of these immediate homolysis products is estimated to be $\Delta G_r^{\ddagger} \approx 8$ kJ mol^{-1}. The dissociation products, $Co([14]aneN_4)(OH_2)_2^{2+}$ and $Co([14]aneN_4)(OH_2)O_2^{2+}$, are designated by P.

$$Co([14]aneN_4)(OH_2)_{2-n}Cl_n^{(2-n)+} + [ClCo([14]aneN_4)]_2O_2^{2+} \xrightarrow{H^+} Co([14]aneN_4)(OH_2)_{1-n}Cl_{n+1}^{(2-n)+} + Co([14]aneN_4)(OH_2)_2^{2+} + ClCo([14]aneN_4)O_2H^{+}$$

and

$$Co([14]aneN_4)(OH_2)Cl^{+} + Co([14]aneN_4)(OH_2)Cl^{2+} \rightarrow Co([14]aneN_4)Cl_2 + Co([14]aneN_4)(OH_2)_2^{2+}$$

That most of the O_2 is released slowly compared to the disappearance of the μ-peroxo complex is attributed to the reactions forming and subsequently decomposing the hydroperoxo complex. Obviously there are many possible complications. Our observations point to a predominant reaction mode as described, but they do not preclude contributions from competing pathways.

This study has shown that the reactivity of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ depends on homolytic dissociation of the dimer into much more reactive monomer species. This reaction profile is schematically illustrated in Figure 5. It is instructive to consider the recombination process. So that the μ-peroxo complex can be formed, $Co([14]aneN_4)(OH_2)_2^{2+}$ and $Co([14]aneN_4)(OH_2)O_2^{2+}$ must be brought together and one water molecule must be displaced from the axially labile, low-spin cobalt(II) complex. This intermediate state of the reacting system may be regarded as a solvent cage trapped reactant pair (or as an "outer-sphere", ion-pair complex); we designate this species $\{H_2O\text{–}Co^{2+}, O_2\text{–}Co\text{–}OH_2^{2+}\}$. At ionic strengths of 0.1, we would estimate the free energy difference between the uncorrelated $Co([14]aneN_4)(OH_2)_2^{2+}$ and $Co([14]aneN_4)(OH_2)O_2^{2+}$ monomers and $\{H_2O\text{–}Co^{2+}, O_2\text{–}Co\text{–}OH_2^{2+}\}$ to be about 28 kJ mol^{-1}[27] (this assumes $k_w \approx 10^9$ s^{-1}

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(25) Heckman, R. A.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 38.

(26) Rillema, D. P.; Endicott, J. F.; Papaconstatinou, E. *Inorg. Chem.* **1971**, *10*, 1739.

for the cobalt(II) complex[3] and ~8 kJ mol^{-1} in electrostatic work terms). Thus the observed $k_{-a} = 5 \times 10^5$ M^{-1} s^{-1} is somewhat smaller than the expected diffusional limit (~10^7 M^{-1} s^{-1}),[27c] and there appears to be a small ($\Delta G_r^* \approx 9$ kJ mol^{-1}) activation barrier to combination of the reactant pair in the solvent cage.[28]

In general, the activation free energy of a reaction depends on certain intrinsic components ΔG_i^*, modified by the driving force of the reaction, $\Delta G°$. A general functional dependence, $\Delta G^* = \alpha\Delta G° + \Delta G_i^*(M(\alpha))$, has been suggested for group-transfer reactions,[29,30] where α is the Brønsted coefficient and $M(\alpha)$ is some function of α. For small values of $\Delta G°$ this should reduce to $\Delta G^* \simeq {}^1/_2\Delta G° + \Delta G_i^*$. This approach has been useful in obtaining intrinsic parameters for inner-sphere electron-transfer reactions.[27] Application in the present system, to correct ΔG_r^* for the free energy change implies that $\Delta G_i^* \approx 25$ kJ mol^{-1}. A significant intrinsic barrier to adduct formation is very reasonable considering the magnitude of bond length changes which must occur at the Co^{II} [3] and O_2 centers.[4,21,22,31] It may be expected that future work will elucidate the nature of this barrier.

Registry No. $\{[H_2OCo([14]aneN_4)]_2O_2\}(ClO_4)_4$, 15661-33-3; $[H_2OCo(Me_2[14]4,11\text{-diene}N_4)]_2O_2^{4+}$, 58880-97-0; $[Co([14]aneN_4)Cl_2]ClO_4$, 15220-75-4; $[Co([14]aneN_4)O_2HCl]ClO_4$, 77495-52-4; $Fe(bpy)_3^{3+}$, 18661-69-3; Ce^{4+}, 16065-90-0; $Co(Me_4[14]tetraeneN_4)Cl_2^+$, 43225-24-7; Fe^{3+}, 20074-52-6; Fe^{2+}, 15438-31-0; $S_2O_8^{2-}$, 15092-81-6; $Ru(NH_3)_5py^{2+}$, 21360-09-8; Cr^{2+}, 22541-79-3; $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$, 38337-82-5; $Co([14]aneN_4)(H_2O)_2^{2+}$, 65554-13-4; $Fe(phen)_3^{3+}$, 13479-49-7; H_2O_2, 7722-84-1.

Supplementary Material Available: Figures of the temperature dependence of μ-peroxo decomposition in $HClO_4$, pH changes accompanying μ-peroxo decomposition in NaCl, and oxygen dependence of μ-peroxo decomposition and tables showing oxygen uptake or release during oxidations or reductions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ in aerated solutions, rate constants for oxidations of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$, oxygen released in reactions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ with oxidants in deaerated solutions, rate constants for reductions of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$, $[Fe^{3+}]$ produced in $Fe^{2+}/[H_2OCo([14]aneN_4)]_2O_2^{4+}$ reactions, oxygen uptake in $Fe^{2+}/[H_2OCo([14]aneN_4)]_2O_2^{4+}$ reactions, and rate constants for reactions of $Co^{II}([14]aneN_4)$ (23 pages). Ordering information is given on any current masthead page.

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[27] Similar considerations apply to any "inner-sphere" reaction. For example see: (a) Endicott, J. F.; Wong, C. L.; Ciskowski, J. C.; Balakrishnan, K. P. *J. Am. Chem. Soc.* **1980,** *102,* 2100. (b) Endicott, J. F.; Balakrishnan, K. P.; Wong, C. L. *Ibid.* **1980,** *102,* 5519. (c) Durham, B.; Endicott, J. F.; Wong, C. L.; Rillema, D. P. *Ibid.* **1979,** *101,*

[28] For comparison, combination of the adenosyl radical with a cob(II)-alamin fragment in a solvent cage has an apparent activation barrier of nearly 5 kcal mol^{-1}: Endicott, J. F.; Netzel, T. L. *J. Am. Chem. Soc.* **1979,** *101,* 4000.

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Transition-Metal Complexes of Pyrrole Pigments. 18. Redox Behaviors of Oxomolybdenum(V) Complexes Formed with Macrocyclic Tetrapyrroles

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Received July 7, 1980

The redox chemistry of (2,3,17,18-tetramethyl-7,8,12,13-tetraethylcorrolato)oxomolybdenum(V) [Mo(O)(MEC)] and (5,10,15,20-tetraphenylporphinato)oxomolybdenum(V) complexes [Mo(O)(TPP)(X), X = MeO, AcO, and Cl] was investigated in dichloromethane by means of cyclic voltammetry and controlled-potential electrolysis. One-electron oxidation and reduction of Mo(O)(MEC) at Mo^V were observed at +0.70 and −0.72 V vs. SCE, respectively. Such oxidation and reduction potentials for Mo(O)(TPP)(X) were very dependent on the nature of axial ligand X and consequently on the covalent character of the Mo^V–X bond: one-electron reduction becomes less facile as the covalent character increases and reaches the value of that in Mo(O)(MEC) for X = MeO. The TPP complexes were much more resistant to oxidation of Mo^V than the MEC complex. Two successive reductions of TPP were observed for Mo(O)(TPP)(X) at −1.1 and −1.5 V vs. SCE while no ligand reduction was detected for Mo(O)(MEC) in the cathodic region up to −2.0 V vs. SCE. On the basis of complete redox schemes for Mo(O)(MEC) and Mo(O)(TPP)(X), correlations between redox properties and ligand structures have been discussed. Coordination equilibria for reactions of Mo(O)(TPP)(MeO) with AcO$^-$, Cl$^-$, and ClO_4^- were investigated in dichloromethane, and the chloro complex was found to exist as a dimer while the others are monomers in solution.

Introduction

Several molybdenum(V) complexes of macrocyclic tetrapyrroles such as corrole and porphyrins have been prepared and characterized by various physical methods.[1-9] The molybdenum ion has been known to show strong affinity for oxygen in its higher oxidation states (+4 to +6), and pentavalent molybdenum complexes having an oxo group have been isolated as the most stable ones. Thus, porphyrin complexes involving tetra- and hexavalent molybdenum have been prepared from the pentavalent complexes by using appropriate oxidizing or reducing agents.[10-12] As a step toward preparation of one-dimensional electric conductors by stacking planar metal complexes with the formation of metal–metal bonds, molybdenum complexes of macrocyclic tetrapyrroles are plausible ones for this purpose since the metal ion has a strong tendency to form metal to metal bonds in its low oxidation states. The redox behaviors of molybdenum complexes need to be investigated in order to obtain chemical conditions

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