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Oxidation–Reduction Reactions of Complexes with Macrocyclic Ligands. Oxygen Uptake Kinetics, Equilibria, and Intermediates in Aqueous Co^{II}(N$_4$) Systems[1]

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Abstract: The reactions of Co([14]aneN$_4$)(OH$_2$)$_2^{2+}$ and Co([15]aneN$_4$)(OH$_2$)$_2^{2+}$ with O$_2$ to form [H$_2$OCo([*n*]aneN$_4$)]$_2$O$_2^{4+}$ have been investigated in water at 25 °C. The reactions were found to occur in two stages. The initial stage involves the generation of a very reactive 1:1 adduct. At very low ionic strengths the initial step can be isolated from the second reaction stage and rate and equilibrium constants may be determined: $k_1 = (5.0 \pm 1.5) \times 10^5$ M^{-1} s^{-1} and $K_1 = (8 \pm 2) \times 10^3$ M^{-1} for the low-spin [14]aneN$_4$ complex; $k_1 = (3.8 \pm 1.1) \times 10^3$ M^{-1} s^{-1} and $K_1 \simeq 4 \times 10^3$ M^{-1} for the high-spin [15]aneN$_4$ complex. For the formation of the μ-peroxo product in the second reaction stage, the respective rate constants are $k_2 = (4.9 \pm 0.4)$ 10^5 and $(5 \pm 1) \times 10^4$ M^{-1} s^{-1} (μ = 0.4, 25 °C). More limited studies of several other reactions of macrocyclic cobalt(II) complexes with O$_2$ have demonstrated that the uptake steps are always rapid, but the extent of the overall equilibrium, Co^{II}(N$_4$)(OH$_2$)$_2$/O$_2$ with a μ-peroxo species, depends somewhat on the cobalt(III)–(II) reduction potential. Most of the variation appears to be due to the second reaction stage (K_2). The formation constant for Co(N$_4$)(OH$_2$)O$_2^{2+}$ (from Co(N$_4$)(OH$_2$)$_2^{3+}$ and O$_2^-$) is found to be surprisingly large, $K_f = 5 \times 10^{21}$ M^{-1}, suggestive of a significant covalent component to the Co–O$_2$ interaction. The intrinsic or reorganizational barrier to adduct formation is small and not very sensitive to variations in the nature of the cobalt complex. In particular, differences in the spin state of the cobalt complex probably affect the rate of substitution into the Co–OH$_2$ bond, but do not seem otherwise to influence the intrinsic reactivity of the complex.

Introduction

The reactions of dioxygen with transition-metal complexes have long been fascinating for chemists.[2] Among the problems of fundamental interest are the utilization of transition metals to relax the spin and symmetry constraints on the reactivity of molecular oxygen and the promotion of multiequivalent redox processes. Cobalt(II) complexes have a reputation for high reactivity toward dioxygen. Thus there are numerous studies of dioxygen–cobalt adduct formation at low temperatures and in nonaqueous media. Studies of the kinetic and equilibrium behavior of cobalt(II)–dioxygen systems in aqueous media at room temperature have for the most part been limited to the study of the rates of the initial uptake step, the magnitudes of the overall equilibrium quotient for oxygen uptake, and/or studies of the reactivity of μ-peroxo products.[2-10] In no previous study has it been possible to obtain kinetic and thermodynamic parameters for each individual step of the uptake process. As a consequence, the stability and reactivity of dioxygen–cobalt(II) adducts in reacting systems have remained obscure.

Fourteen-membered tetraaza macrocyclic ligands tend to remain equatorially coordinated to low-spin cobalt(II)[11] in acidic, aqueous solution, resulting in systems with four relatively well-defined coordination positions. The axial (low spin) Co(II)–ligand bond lengths tend to be much longer than the corresponding axial Co(III)–ligand bond lengths.[11,12] The reorganizational barrier resulting from this difference in bond lengths has been shown to be the major factor in determining the rate patterns for outer-sphere electron-transfer reactions of Co(N$_4$) complexes.[13,14] Reactions at the axial coordination site (e.g., inner-sphere electron-transfer reactions[14,15]) also exhibit reactivity patterns reflecting these structural parameters provided that there is appreciable transfer of charge (to or from the metal) across the reaction coordinate.[15] While somewhat controversial,[2f,k,16] careful thermochemical considerations have tended to support the view that charge transfer is relatively incomplete on formation of 1:1 adducts from cobalt(II) and dioxygen.[5,17] The macrocyclic cobalt complexes comprise a useful series of complexes for probing dioxygen–metal reactivity since intrinsic redox reactivities, as well as spin changes across the reaction coordinate,[18] can be altered systematically by structural changes in the equatorial ligand.[19]

In our studies of low-spin Co(N$_4$)(OH$_2$)$_2^{2+}$ complexes, we have observed that many of the systems (e.g., N$_4$ = Me$_4$[14]tetraeneN$_4$

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[18] For example, the Co^{II}([15]aneN$_4$) and Co^{II}([16]aneN$_4$) complexes appear to be high spin (Busch, D. H., private communication); see also the following text.

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or $Me_6[14]4,11\text{-diene}N_4$)[20,21] have persisted for hours in aerated aqueous solutions while others (e.g., N_4 = $[14]aneN_4$)[20-24] are very efficient oxygen scavengers. While some of these $Co^{II}(N_4)$ complexes seem to have little affinity for dioxygen in fluid solution at room temperature,[16] nearly all of them readily form dioxygen adducts in nonaqueous solvents at very low temperatures.[23-25] The differences in apparent reactivity of the $Co^{II}(N_4)$ complexes toward O_2 could arise from differences in driving force or in intrinsic reaction barriers. In this paper, we report our studies of the early steps in the reactions of several $Co^{II}(N_4)$ complexes with O_2. Succeeding papers will report on our studies of subsequent oxidation-reduction reactions of the $Co^{II}(N_4)/O_2$ mixtures.[26]

Experimental Section

A. Preparation of Complexes and Solutions. Literature procedures were employed for synthesis of most of the materials used in this study. The $[15]aneN_4$ ligand was obtained from Strem Chemical Co. Synthesis and characterization of the macrocyclic complexes have been described elsewhere;[26b,27-32] elemental analyses and infrared, visible, and ultraviolet spectra were in agreement with literature reports.

Preparation of $[Co(Me_2[14]4,11\text{-diene}N_4)(OH_2)_2](ClO_4)_3$. To a hot slurry of $[Co(Me_2[14]4,11\text{-diene}N_4)Cl_2]ClO_4$[31b] (5 g in 20 mL of 1 M $HClO_4$) a solution of $AgClO_4$ (4.6 g in 10 mL of water) was added slowly. The mixture was heated with stirring until all the AgCl precipitate had coagulated, then filtered. The filtrate was evaporated to about 10 mL, using a rotovap. Upon cooling, blue crystals formed. These were separated, washed with ethanol and diethyl ether, and dried under vacuum at 60 °C. Anal. Calcd for $CoC_{12}H_{28}O_{14}N_4Cl_3$: C, 22.66; H, 4.72; N, 8.81; Cl, 17.3. Found: C, 22.64; H, 4.81; N, 8.69; Cl, 17.82.

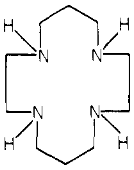
Preparation of $[Co(Me_2[14]4,11\text{-diene}N_4)(OH_2)_2](ClO_4)_2$. A solution of 1 g of $[Co(Me_2[14]4,11\text{-diene}N_4)(OH_2)_2](ClO_4)_3$ in 15 mL of 1 M $HClO_4$ was purged with Cr^{2+}-scrubbed N_2 for ~45 min. A slight excess of a 1 M Cr^{2+} solution was added by syringe. Brown, needle-shaped crystals formed and were separated and washed with a 1:5 ethanol-ether mixture. Anal. Calcd for $C_{12}H_{28}N_4O_{10}Cl_2$: C, 27.8; H, 5.41; N, 10.8; Cl, 13.71. Found: C, 29.6; H, 5.27; N, 10.65; Cl, 14.13.

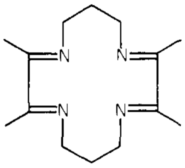
Solutions of Cr^{2+} were prepared by means of Zn(Hg) reduction of $Cr(ClO_4)_3 \cdot nH_2O$ in deaerated $HClO_4$ solutions.

Solutions of $Co([14 \text{ or } 15]aneN_4)(OH_2)_2^{2+}$ were prepared by (1) mixing deaerated aqueous solutions of $Co(ClO_4)_2 \cdot 6H_2O$ and free ligand (~10% stoichiometric excess); (2) Cr^{2+} reduction of $Co^{III}([14]aneN_4)X_2$ ($X = Cl^-$ or H_2O) in deaerated acidic solution.

Warning. The heavy metal perchlorate salts prepared in this study can be detonated and are potentially hazardous.

B. Techniques and Procedures. Most kinetic determinations were made by using standard spectrophotometric (Cary 14) or stopped-flow (Aminco-Bowman or Durrum) techniques with reactant solutions thermostated at 25 °C.[28,34]


$[14]aneN_4$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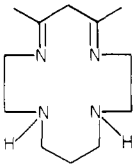
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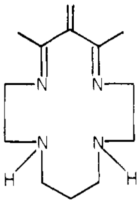
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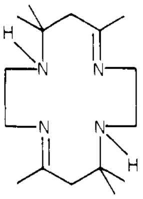
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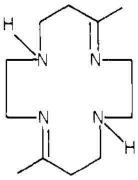
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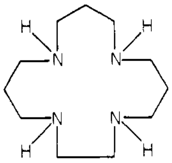
$[15]aneN_4$

Oxygen concentrations were determined by using a Radiometer D616/E5046 PO electrode and measuring circuit similar to that discussed by Hurst et al.[35,36] A constant polarizing voltage (~650 mV) was applied across the platinum cathode and Ag/AgCl anode of the cell. The current flow upon O_2 reduction ($O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$) was determined by following the iR drop across a precision resistor with a Model 801A Orion research digital ionalyzer. The electrode was calibrated by using solutions saturated with air, O_2, and Cr^{2+}-scrubbed N_2; literature values were used for the $[O_2]$ in these solutions.[37]

For the electrochemical determinations we modified the Chemtrix SSP-2[38] unit for use with a Houston Instruments Omnigraphic 2000XP recorder. The Pt working electrode was pretreated by soaking in hot, concentrated HNO_3 for 30 min. A positive potential was then applied to oxidize absorbed H_2. The counterelectrode was Pt and the reference was an aqueous calomel electrode made with saturated NaCl. Observed potentials were corrected[39] to NHE according to $E_{1/2}(\text{NHE}) = E_{1/2}(\text{SCE; NaCl}) + 0.236$.

The electrochemical cell was modified with a small side arm which allowed the attachment of a 50-mL buret for the amperometric titrations. The buret contained water that was continuously saturated with O_2. The residual current was determined from the cyclic voltammogram (0.1 V/s) of deaerated 1.0 M $LiClO_4$. An aliquot of $[Co(Me_2[14]1,11\text{-diene}N_4)(OH_2)_2](PF_6)_2$ in deaerated 1.0 M $LiClO_4$ was added under a stream of N_2, and the voltammogram was recorded. The N_2 pressure was increased so as to force the solution into contrast with the buret tip and an aliquot of O_2-saturated H_2O was added. The solution in the connecting tube was mixed several times with the bulk solution before the cyclic voltammogram was recorded. Three current measurements were averaged for each addition of O_2. A 10-min time interval was allowed between additions. The solution was stirred between additions, but stirring was stopped 20 s before a voltammogram was recorded. The current at the half-wave potentials (0.382 and 0.596 V vs. NHE, respectively, for $Co(Me_2[14]1,11\text{-diene-}N_4)$ and $Co(Me_2[14]1,11\text{-diene}N_4\text{-13-one})$) was determined by measuring the peak-to-peak distance in the voltammograms and subtracting the residual current. The current was corrected for dilution by using

$$\mu A = \left(\frac{V_{\text{init}} + V_{\text{titrant}}}{V_{\text{init}}}\right)(I_{\text{p,cathode}} + I_{\text{p,anode}} - I_{\text{residual}})$$

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[20] Ligand abbreviations are based on conventions described by Melson.[9] $Me_4[14]tetraeneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; $Me_6[14]4,11\text{-diene}N_4$ = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; $[14]aneN_4$ = 1,4,8,11-tetraazacyclotetradecane; $Me_2[14]4,11\text{-diene}N_4$ = 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; $Me_2[14]1,11\text{-diene}N_4$ = 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,11-diene; $Me_2[14]1,11\text{-diene}N_4\text{-13-one}$ = 12,14-dimethyl-1,4,8,11-tetraazacyclotetradeca-1,11-diene-13-one; sepulchrate = (*S*)-1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; $[15]aneN_4$ = 1,4,8,12-tetraazacyclopentadecane.

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Table I. Kinetic Data for the $Co([14]aneN_4)(OH_2)_2^{2+}/O_2$ Reaction (25 °C)

$10^4[Co^{II}(N_4)]$,[a] M	$10^4[O_2]$, M	$[H^+]$, M	$[Cl^-]$, M	μ[b]	wavelength monitored, nm	k_{obsd},[c] s^{-1}
3.1	1.3	0.010–0.10		0.10	430	27 ± 2 (4)
3.6	1.3	0.10		0.10	360–430	53 ± 2 (3)
4.8	1.3	0.10–0.005		0.10	360–430	113 ± 5 (11)
5.5	1.3	0.10–0.05		0.10	430	133 ± 2 (4)
6.4	1.3	0.10		0.10	360–430	190 ± 8 (5)
7.5	1.3	0.10–0.005		0.10	430	224 ± 3 (6)
7.5	1.3	0.10[d]		0.10[d]	430	406 ± 11 (3)
9.4	1.3	0.10		0.10	360	330 ± 3 (2)
0.73	1.3	0.10		1.0	360	50
1.5	1.3	0.10		1.0	360	81
0.37	6.3	0.10		1.0	360	8.8
0.73	6.3	0.10		1.0	360	16
2.9	6.3	0.10		1.0	360	37
5.8	6.3	0.10		1.0	360	65
0.73	1.3	6.2×10^{-3}		6.2×10^{-3}	360	9
0.73	1.3	0.10		0.55	360	37
0.73	1.3	0.10		2.50	360	108
1.9	1.3	0.10	0.10	0.10	430	12 ± 1 (2)
1.9	1.3	0.20	0.20	0.20	430	15
1.9	1.3	0.10[d]	0.02	0.12[e]	430	13 ± 1 (2)
5.8	1.3	0.10	0.02–0.08	0.10[e]	360	155 ± 2 (4)
5.8	1.3	0.01-0.005	0.10	0.10[f]	360	162 ± 2 (4)
6.4	1.3	0.10	0.10	0.10	360–430	152 ± 3 (3)
2.3	1.3	0.10	0.02–0.10	0.10[e]	360	27 ± 2 (5)
3.6	1.3	0.10	0.10	0.10	360–430	83 ± 4 (3)
4.8	1.3	0.10	0.02–0.05	0.10[e]	360	134 ± 2 (2)
4.8	1.3	0.10–0.008	0.10	0.10[f]	360	118 ± 5 (7)
9.4	1.3	0.10–0.01	0.02–0.10	0.10[e,f]	360	291 ± 3 (7)

[a] Generated from Co^{2+} + $[14]aneN_4$ complexation prior to mixing with O_2. [b] $HClO_4/LiClO_4$ except as indicated. [c] For multiple determinations, average and average deviation (number of determinations in parentheses). [d] HNO_3. [e] $LiClO_4/HCl$. [f] $HCl/NaCl$.

ESR spectra were obtained by using a Varian E-4 spectrometer. Solutions of $Co(N_4)^{2+}$ complexes were generated anaerobically by using solutions purged with Cr^{2+}-scrubbed N_2, and were transferred to degassed, serum-capped spectrometer cells by means of a syringe. While this procedure resulted in typical low-spin cobalt(II) spectra[11] for samples of $Co([14]aneN_4)(OH_2)_2^{2+}$, samples of $Co([15]aneN_4)(OH_2)_2^{2+}$ resulted only in broad, weak, and structureless signals very similar to those obtained for frozen solutions of cobaltous perchlorate. We were unable to detect significant ESR spectra in frozen solutions formed by mixing $Co([15]aneN_4)(OH_2)_2^{2+}$ with aerated H_2O, then freezing.

Solutions of $Co^{II}([15]aneN_4)$ were stable in neutral, aqueous media, but decomposed within minutes to Co^{2+} and free ligand upon acidification. This is strikingly in contrast to the behavior of solutions of $Co^{II}([14]aneN_4)$, which are stable at low pHs.

The absorption spectrum of $Co([15]aneN_4)(OH_2)_2^{2+}$ consisted of a complex cluster of partly resolved bands centered around 500 nm: 440 nm, sh (ϵ 8.4 M^{-1} cm^{-1}), 497, max (13.9), 535, sh ($\simeq$10). The low-spin cobalt(II) complexes with saturated ligands exhibit two to three well-resolved, nearly Gaussian absorption bands of moderate intensity (ϵ_{max} $\sim$20–10^2 M^{-1} cm^{-1}).[11,40]

Results

A. Reactions of Cobalt(II) Complexes with O_2. 1. $Co^{II}([14]aneN_4)$. Rapid ($\sim$4 ms) mixing of this complex with solutions containing O_2 resulted in the formation of a strongly absorbing intermediate species. This species then decayed to a "final" product whose absorption spectrum was indistinguishable from that of an authentic sample of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$. We found the largest absorbance changes to occur in the near ultraviolet.

We have been able to distinguish three stages of reaction: (1) an initial, very rapid ($\leq$30 ms in our experiments) primary reaction of $Co^{II}([14]aneN_4)$ with O_2 to form a very reactive intermediate; (2) a rapid (10–100 ms, depending on conditions) reaction of the initial intermediate with $Co^{II}([14]aneN_4)$ to form $[XCo([14]aneN_4)]_2O_2^{2+}$; (3) the much slower decomposition of this μ-peroxo "product". In this section we report our studies of the first two reaction stages.

Although the starting materials do not absorb appreciably at 360 nm and $[XCo[14]aneN_4)]_2O_2$ complexes do, we nearly always observed decays of the 360-nm absorbance in our stopped-flow experiments. Under our experimental conditions it was usually very difficult to isolate the initial step. However, the second step was much more dependent on ionic strength than the first (Table I, Figure SI[41]), and we were able to observe the increase of absorption of the intermediate species at very low ionic strengths. The absorbance of the intermediate increased in proportion to $[O_2]$ and $[Co([14]aneN_4)(OH_2)_2^{2+}]$ and is attributed to $Co([14]aneN_4)(OH_2)O_2^{2+}$. At very low ionic strengths, the intermediate absorbance was approximately constant for a short time (10–100 ms) and the absolute absorbance during this time period was used to determine the formation constant of the dioxygen adduct under ambient conditions. With the initial concentrations, $[Co([14]aneN_4)(OH_2)_2^{2+}]_i > [O_2]_i = 1.3 \times 10^{-4}$ M, a plot of $(\Delta Abs)^{-1}$ (ΔAbs = measured absorbance minus the measured absorbance of the starting materials corrected for dilution) vs. $[Co([14]aneN_4)(OH_2)_2^{2+}]_i^{-1}$ was linear: slope = $(4.6 \pm 1.0) \times 10^{-4}$ M cm, intercept = 3.6 ± 0.1 cm (least-squares fit, one standard deviation); Table SI.[41] For $K_1 = X/([A]_i - X)([O_2]_i - X) \simeq X/[A]_i([O_2]_i - X)$, $1/X \simeq 1/K_1[A]_i[O_2]_i + 1/[O_2]_i$ where $X = [Co([14]aneN_4)(OH_2)O_2^{2+}]$ and $A = Co([14]aneN_4)(OH_2)_2^{2+}$. Thus for the dioxygen adduct $\epsilon(360 \text{ nm}) = (\text{intercept}\cdot[O_2]_i)^{-1} = (2.2 \pm 0.1) \times 10^3$ M^{-1} cm^{-1} and $K_1 = (8 \pm 2) \times 10^3$ M_{-1}.

In several experiments the increased absorbance of the dioxygen adduct could be observed over a sufficient time period to estimate an apparent first-order time constant for the approach to equilibrium. As a check on our other determinations, we have treated the approach to equilibrium as a single-step relaxation process; $k_{app} \simeq k_1[Co([14]aneN_4)(OH_2)_2^{2+}]_e + k_{-1}$. A least-squares treatment of data from four experiments (see Table SI) gives $k_1 \simeq (4 \pm 1) \times 10^5$ M^{-1} s^{-1} and $k_1 \sim (1.4 \pm 0.8) \times 10^2$ s^{-1}.

The kinetics for absorbance decays at 360 nm were very well fitted to standard first-order plots. We found much poorer fits to second-order treatments of the absorbance data (linear to less than 2 half-lives). Nevertheless, the initial reaction rates were greater than first order in $[Co([14]aneN_4)(OH_2)_2^{2+}]_i$, Figure 1. This reaction was independent of H^+ in the range 0.05 M $\geq$ $[H^+]$ $\geq$ 0.0025 M (μ = 0.10, $LiClO_4$). When cobalt(II) was in excess,

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(40) Mok, C. Y.; Endicott, J. F. *J. Am. Chem. Soc.* **1978**, *100*, 123.

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

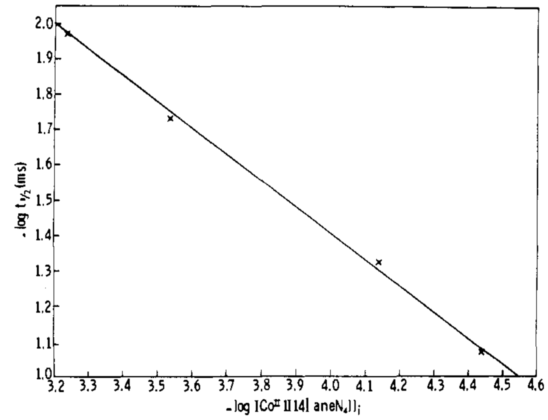

Figure 1. Determination of the order in $[\text{Co}^{\text{II}}(\text{N}_4)]_{\text{init}}$ of the intermediate absorbance decay (360 nm): 25 °C; $\mu = 1.0$ ($\text{LiClO}_4/\text{HClO}_4$); $[\text{H}^+] = 0.1$ M; $\text{Co([14]aneN}_4)(\text{OH}_2)_2^{2+}$ prepared by means of Cr^{2+} reduction of $\text{Co([14]aneN}_4)(\text{OH}_2)_2^{3+}$. Slope of correlation line is −0.74, implying that rate ∝ $[\text{Co}^{\text{II}}(\text{N}_4)]^{1.7}$.

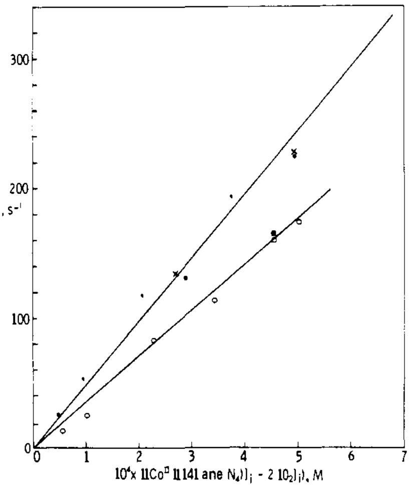

Figure 2. Dependence of the apparent first-order rate constant for intermediate absorbance decay on the initial reactant concentrations when $[\text{Co}^{\text{II}}(\text{N}_4)] > 2[\text{O}_2]$. Data from Table I. Upper line (●), perchlorate media (0.10 M, HClO_4); lower line (○), chloride media (0.10 M HCl). Crosses (X and □) for $[\text{H}^+] = 5 \times 10^{-3}$ M.

we found the apparent first-order rate constant (k_{obsd}) to be directly proportional to the difference between the initial $[\text{Co([14]aneN}_4)(\text{OH}_2)_2^{2+}]$ and twice the initial oxygen concentration (Figure 2).

In chloride solutions we found two steps for the absorbance decay. The first was a little slower in rate from the reactions observed in perchlorate media (see Figure 2). The second stage of decay observed in Cl^- media was dependent on $[\text{Cl}^-]$, with $k^{\text{II}}_{\text{app}} = (4.8 \pm 0.4\ \text{M}^{-1}\ \text{s}^{-1})[\text{Cl}^-]$ and $(0.07 \pm 0.02)\ \text{s}^{-1}$.

Similar final product species and final rate behavior were obtained when a perchloric acid solution of $[\text{H}_2\text{OCo([14]aneN}_4)]_2\text{O}_2^{4+}$ was mixed with HCl (see Tables SII and SIII[41]). Thus, the first-order plots for Cl^- anations of $[\text{H}_2\text{OCo([14]aneN}_4)]_2\text{O}_2^{4+}$ were curved. This curvature could very approximately be resolved into two components with the first corresponding to a rate of about twice the second: $k^{\text{I}}_{\text{Cl}^-} \sim (8 \pm 3)[\text{Cl}^-] + 0.18 \pm 0.1\ \text{s}^{-1}$ and $k^{\text{II}}_{\text{Cl}^-} = (4.5 \pm 0.5)[\text{Cl}^-] + 0.09 \pm 0.01\ \text{s}^{-1}$.

2. $\text{Co([15]aneN}_4)(\text{OH}_2)_2^{2+}$. For this complex also we observed the rapid decay of an intermediate absorbance in solutions of high ionic strength and it was possible to observe the buildup of absorbance of the intermediate species in solutions containing no added electrolyte. Over a period of about 1 h, the initial very rapid reactions were followed by a much slower reaction resulting in an absorbance increase.

Table II. Kinetic Parameters for the $\text{Co([15]aneN}_4)(\text{OH}_2)_2^{2+}/\text{O}_2$ Reaction

$\text{Co([15]aneN}_4)(\text{OH}_2)_2^{2+}$	O_2	k_{I}(obsd),[a] s^{-1}	k_{II}(obsd),[b] s^{-1}	k_{II}(calcd),[c] s^{-1}
0.8	6.3		12	12.6
1.1	6.3		20	16
2.2	6.3		34.5	30
3.0	6.3		35	41
0.8	1.3		3.2	5
2.2	1.3		8.6	10
3.0	1.3		11.5	12
12	1.3		66	56
21	1.3		112	105
27	1.3		161	131
35	1.3		182	171
4.0	6.3	301 ± 0.1		
6.5	6.3	4 ± 1		

[a] 25 °C, no added electrolyte; mean and average deviations of two determinations each. [b] 25 °C, 0.1 M NaClO_4. [c] For $[\text{O}_2] = 6.3 \times 10^{-4}$ M, $k(\text{calcd}) \sim 2[\text{Co}^{\text{II}}]_e [\text{O}_2]_e K_1 k_2 + k_{-2}$; otherwise, $k(\text{calcd}) = (a - d)/2 - \tfrac{1}{2}[(a + d)^2 + 4bc]^{1/2}$, where $a = k_1([\text{Co}^{\text{II}}]_e + [\text{O}_2]_e) + k_{-1}$; $b = [\text{O}_2]_e k_1 - k_{-1}$; $c = k_2[\text{Co}^{\text{II}}]_e$; $d = a + k_{-2}$; $k_1 = 4.2 \times 10^3\ \text{M}^{-1}\ \text{s}^{-1}$; $k_{-1} = 1\ \text{s}^{-1}$; $k_2 = 5 \times 10^4\ \text{M}^{-1}\ \text{s}^{-1}$; $k_{-2} = 2\ \text{s}^{-1}$.

We had some difficulties with this sytem which seem to be related to incomplete consumption of reactants when the initial oxygen uptake reactions reach equilibrium. We have been able to demonstrate the presence of cobalt(II) species by acidification of the $\text{Co([15]aneN}_4)(\text{OH}_2)_2^{2+}/\text{O}_2$ mixture at various time intervals after mixing the reactants. The resulting Co^{2+} was analyzed by the thiocyanate method.[42] In the presence of ~twofold stoichiometric excess of O_2 we did detect small amounts of Co^{2+} (2–8% of the total cobalt). The amount of Co^{2+} detected decreased with increases in the time interval between mixing and acidification. Extrapolation of $[\text{Co}^{2+}]$ to "zero" time, in this instance a time approximating completion of oxygen uptake steps, gave a value of $[\text{Co}^{2+}]_e$ from which a very crude estimate could be made of $K_1K_2 = [(\text{CoL})_2\text{O}_2^{4+}]_e/[\text{Co}^{\text{II}}\text{L}]_e^2[\text{O}_2]_e$. We obtained a value of "K_1K_2" $\sim 10^{9\pm0.5}\ \text{M}^{-2}$ in solutions containing no added electrolyte.

Extrapolation to "zero" time of the very slow absorbance changes also afforded a means of estimating the magnitude of K_1K_2 with an excess of $\text{Co([15]aneN}_4)(\text{OH}_2)_2^{2+}$, $[(\text{CoL})_2\text{O}_2^{4+}] \sim [\text{Co}^{\text{II}}\text{L}]_i^2[\text{O}_2]_i\, K_1K_2/(1 + K_1K_2[\text{Co}^{\text{II}}\text{L}]_i)$, and one may estimate ϵ and K_1K_2 for the μ-peroxo species from the variation of $(\text{abs})^{-1}$ vs. $[\text{Co}^{\text{II}}\text{L}]_i^{-1}$, where the absorbance has been extrapolated to the zero time of the slow step. By this means we found values of $K_1K_2 \sim 2 \times 10^7\ \text{M}^{-2}$ and $\epsilon \sim 500\ \text{M}^{-1}\ \text{cm}^{-1}$ (0.1 M NaClO_4, 25 °C, 400 nm). In solutions containing no added electrolyte, the apparent value of K_1K_2 was appreciably smaller, as expected, but ϵ was larger; we suspect that the long-term reactions in this system are in part hydrolytic, analogous to those which occur for complexes containing open-chain tetraamine ligands.[43-45]

The initial rapid, very small absorbance increase was only resolved in solutions relatively concentrated in O_2 and $\text{Co}^{\text{II}}([15]\text{aneN}_4)$. The observed relaxation times were reasonably first order, and when treated by the relaxation method described in the previous section the pseudo-first-order rate constants (Table II) gave $k_1 = (3.8 \pm 1.1) \times 10^3\ \text{M}^{-1}\ \text{s}^{-1}$.

The rapid absorbance decay, attributed to the reactions of $\text{Co([15]aneN}_4)(\text{OH}_2)\text{O}_2^{2+}$ with $\text{Co([15]aneN}_4)(\text{OH}_2)_2^{2+}$ to form the μ-peroxo complex, followed pseudo-first-order kinetics (Table II). For $[\text{O}_2]_i = 1.26 \times 10^{-4}$ M, the observed kinetic data fitted well to the expression

$$k(\text{obsd}) \simeq k_2[\text{Co}^{\text{II}}\text{L}]_e + k_{-2} + \frac{k_{-1}k_2[\text{Co}^{\text{II}}\text{L}]_e}{(k_1 + k_2)[\text{Co}^{\text{II}}\text{L}]_e + k_{-1} + k_{-2}}$$

obtained from the relaxation treatment of a system approaching

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(42) Kilson, R. E. *Anal. Chem.* **1959**, *22*, 664.
(43) (a) Fallab, S. *Chimia* **1967**, *21*, 538. (b) *Ibid.* **1969**, *23*, 177.
(44) Miller, F.; Wilkins, R. G. *J. Am. Chem. Soc.* **1970**, *92*, 2687.
(45) Nakon, R.; Martell, A. E. *J. Am. Chem. Soc.* **1972**, *94*, 3026.

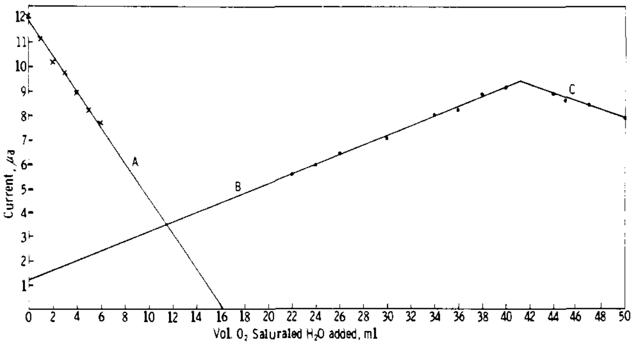

Figure 3. Amperometric titration of [Co(Me$_2$[14]1,11-dieneN$_4$)(OH$_2$)$_2$](PF$_6$)$_2$ with O$_2$. Initial mol of Co(Me$_2$([14]1,11-dieneN$_4$)(OH$_2$)$_2^{2+}$ = 4.45 × 10^{-5}; X, peak-to-peak current at potential ($E_{1/2}$ = +0.596 V vs. NHE) of Co(Me$_2$[14]1,11-dieneN$_4$-13-one)(OH$_2$)$_2^{2+}$. Slope of line A representing disappearance of the initial substrate is −0.729 ± 0.028 μA/mL; intercepts are 11.9 ± 0.1 μA and 16.3 ± 0.6 mL = 20.4 ± 0.7 μmol O$_2$.

equilibrium (see eq 4 in the Discussion section; the subscript "e" denotes an equilibrium concentration). For $[O_2]_i = 6.3 \times 10^{-4}$ M this approach did not work. We fitted these data assuming that the first equilibrium (K_1) was satisfied and that the relaxation time corresponded to the second equilibration (K_2), resulting in

$$k(\text{obsd}) = 2K_1k_2[\text{Co}^{\text{II}}\text{L}]_e[\text{O}_2]_e + k_{-2}$$

An iterative fit of the kinetic data to these two expressions was achieved by the parameters $k_1 = 4.2 \times 10^{-3}$ M^{-1} s^{-1}, $k_{-1} \simeq 1$ s^{-1}, $k_2 = 5 \times 10^4$ M^{-1} s^{-1}, and $k_{-2} = 2$ s^{-1} (see Table II). These parameters are in good agreement with the independent determinations of k_1 described above.

3. **Co(Me$_2$[14]1,11-dieneN$_4$)(OH$_2$)$_2^{2+}$.** The amperometric titration of this complex with O$_2$ demonstrates that there is an initial oxygen uptake prior to formation of (Me$_2$[14]1,11-diene-N$_4$-13-one)-cobalt complexes (Figure 3, Table SIV[41]). Extrapolation of the initial line (A) in Figure 4 to zero current corresponds to an "end point" of 20.4 ± 0.7 μmol of O$_2$ (based on the solubility of O$_2$ in H$_2$O[37]). Thus, this initial stage of the oxygenation has stoichiometry of 2.19 ± 0.07 mol of Co(Me$_2$[14]-1,11-dieneN$_4$)(OH$_2$)$_2^{2+}$ consumed per mol of O$_2$ added.

We did not detect Co$^{\text{II}}$(Me$_2$[14]1,11-dieneN$_4$-13-one) until after the end point of the initial uptake (detection limit ~ 21μmol). The oxygenation of the ligand to form the final product species is a relatively slow and complex reaction which will be treated elsewhere.

In our detailed kinetic studies of this system we did not find any direct evidence for the buildup of appreciable amounts of the primary Co–O$_2$ adduct species. Rather, the disappearance of the cobalt(II) starting material was accompanied by formation of a relatively strongly absorbing metastable intermediate (believed to be the μ-peroxo complex). The absorbance increase followed simple pseudo-first-order kinetic behavior with

$$k = [(1.3 \pm 0.3) \times 10^5 \text{ M}^{-1} \text{ s}^{-1}] \times [\text{Co(Me}_2[14]1,11\text{-dieneN}_4)(\text{OH}_2)_2^{2+}]$$

(Figure 4, Table SV). This initial absorbance increase was followed by a much slower, kinetically complex absorbance decay (Table SVI).

4. **Co(Me$_2$[14]1,11-dieneN$_4$-13-one)(OH$_2$)$_2^{2+}$.** Although this complex had given us the impression of being relatively easy to handle in aerated solutions, we found a rapid initial uptake of O$_2$ ($t_{1/2}$ ~ 10–40 ms) in aqueous solutions of this complex. The extent of the initial, rapid reaction was found to be dependent on the concentration of the reagent in excess (Table SVII). The initial reaction kinetics are conveniently represented as

$$k^{\text{I}}_{\text{app}} = (3.6 \pm 0.4) \times 10^4 \times [\text{Co(Me}_2[14]1,11\text{-dieneN}_4\text{-13-one)(OH}_2)_2^{2+}]_i + (10 \pm 3) \text{ s}^{-1}$$

(25 °C, μ = 1.0 = [HClO$_4$]). The rate was not significantly changed in 0.5 M Cl$^-$ (μ = 1.0). As a consequence of the limited extent of uptake (relatively small value of K_1K_2), the rate of air oxidation of this complex appears to be slow: $t_{1/2}$ varied from 10 to 90 min depending on concentration conditions (Table SVIIB).

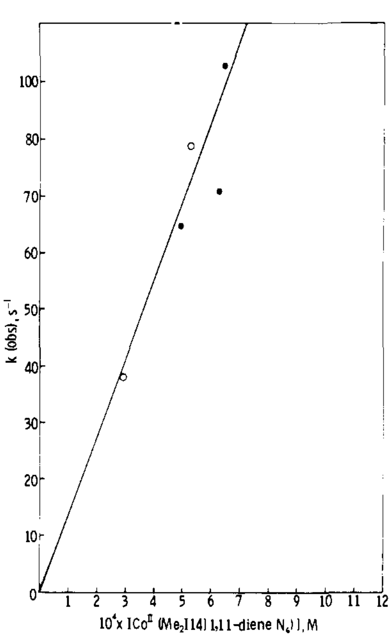

Figure 4. Cobalt(II) dependence of the apparent first-order rate of absorbance increase (μ-peroxo complex formation) for the Co(Me$_2$-[14]1,11-dieneN$_4$)(OH$_2$)$_2^{2+}$/O$_2$ system: 1.0 M HClO$_4$, ○; pH ~5.9, 1.0 M LiClO$_4$, ●. Least-squares fit gives slope = (1.3 ± 0.3) 10^5 M^{-1} s^{-1}.

5. **Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)$_2^{2+}$.** This complex is similar in its O$_2$ reactions to Co(Me$_2$[14]1,11-dienN$_4$-13-one)(OH$_2$)$_2^{2+}$. The initial absorbance changes and/or the equilibrium constants of the dioxygen adducts (K_1, K_2) are sufficiently small in this system that we have not been able to obtain definitive information about the initial reaction stages. Any initial O$_2$-uptake stages are followed by the very slow disappearance of the cobalt(II) substrate. The observed aerial oxidation was somewhat susceptible to catalytic effects and its rate increased with ionic strength. In 0.1 M LiClO$_4$/HClO$_4$ media at 25 °C we found the half-life for oxidation of Co(Me$_4$[14]tetraeneN$_4$)(OH$_2$)$_2^{2+}$ to be 2.6 × 10^4 s (Table SVIII).

6. **Co(Me$_2$14]4,11-dieneN$_4$)(OH$_2$)$_2^{2+}$.** While we have no quantitative kinetic data on the reactions of this complex with O$_2$, it seems qualitatively similar in behavior to Co([14]-aneN$_4$)(OH$_2$)$_2^{2+}$ and Co(Me$_2$[14]1,11-dieneN$_4$)(OH$_2$)$_2^{2+}$. The cobalt(II) complex appears to be an excellent oxygen scavenger. The apparently quantitative formation of the μ-peroxo complex was always complete in less than 1 min.

B. **Thermal Decompositions of μ-Peroxo Complexes.** All the μ-peroxo species we have observed have been thermally unstable. We have made an extensive study of the [H$_2$OCo([14]-aneN$_4$)]$_2$O$_2^{4+}$ system. This will be presented in detail elsewhere,[26a] with only a few pertinent observations being included in the supplementary material of this paper (Figures S2 and S3). In perchloric acid media this complex decomposed over a period of a few hours as manifested in decreases in the near-ultraviolet absorbance. This decomposition was greatly accelerated by Cl$^-$ and Br$^-$ and inhibited by NCS$^-$ or CN$^-$. The decomposition was accompanied by a somewhat slower release of oxygen. All these processes were kinetically very complex. Among our studies we have monitored the rate of evolution of O$_2$ when [H$_2$OCo([14]-aneN$_4$)]$_2$O$_2^{4+}$ was dissolved in a variety of media. In a study pertinent to the present report we found 1.1 × 10^{-4} M O$_2$ 2 h after mixing a solution initially anaerobic and 0.25 M in HCl and 2.3 × 10^{-4} M in [H$_2$OCo([14]aneN$_4$)]$_2$O$_2^{4+}$. Owing to difficulties of mixing, our initial determination of [O$_2$] = 0.55 × 10^{-4} M was made at 15 min; owing to the complex kinetic behavior we can only estimate a limit of the "initial" concentration of [O$_2$] ≤ 4 × 10^{-5} M 1 min after mixing. Assuming that this limit corresponds to equilibration of the μ-peroxo complex with O_2 and $Co^{II}([14]aneN_4)$, we find for a limit of the overall equilibrium constant $K_1K_2 \geq 7 \times 10^8\ M^{-2}$ ($\mu = 0.25$).

The metastable intermediate formed in oxygenations of $Co(Me_2[14]1,11\text{-diene}N_4)(OH_2)_2^{2+}$ had a lifetime of 1-5 s depending on medium conditions. In weakly acidic solutions the decomposition ultimately resulted in formation of $Co(Me_2[14]1,11\text{-diene}N_4\text{-}13\text{-one})(OH_2)_2^{2+}$ [12a,26b,33] in a reaction which is probably mediated by ligand to metal ($Co^{III} \leftarrow N_4^-$) electron transfer; the details of these following reactions will be discussed elsewhere. First-order plots of the absorbance decays were linear for 2-4 half-lives and were independent of the wavelength of observation in the range 390 nm $\leq \lambda \leq$ 570 nm. The apparent first-order rate constants were acid dependent in the low pH range: k_{app} = 0.99 ± 0.03 (12), 0.25 (1), and 0.15 ± 0.01 (4) for $[H^+] \sim 10^{-5}$ (no acid added), 0.50, and 1.0 M, respectively ($\mu = 1.0(LiClO_4)^{-1} \times (HClO_4)^{-1}$, number of determinations in parentheses; Table SVI[41]).

Discussion

Our studies of the reactions of macrocyclic ligand complexes of Co(II) with O_2 are most conveniently discussed in terms of the traditional[2] reaction scheme

$$Co(N_4)(OH_2)_2^{2+} + O_2 \rightleftharpoons Co(N_4)(OH_2)O_2^{2+} + H_2O \qquad k_1, k_{-1}, K_1 \quad (1)$$

$$Co(N_4)(OH_2)_2^{2+} + Co(N_4)(OH_2)O_2^{2+} \rightleftharpoons [H_2OCo(N_4)]_2O_2^{4+} \qquad k_2, k_{-2}, K_2 \quad (2)$$

Our study of the Co^{II}([14 and 15]aneN_4)/O_2 systems is unique in that we have been able to obtain estimates of all the pertinent kinetic and thermodynamic parameters in fluid solution under ambient conditions. The information for the other macrocyclic ligand systems has been limited by problems of reactivity and absorptivity, similar to the limitations found for O_2 reactions with other kinds of complexes.

Kinetic treatments based on eq 1 and 2 result in coupled differential equations which are difficult to solve for the general case. In two of the cases studied here, the decay of an intermediate superoxo complex was observed and a stationary-state treatment would obviously be inappropriate. However, a great deal of insight into the kinetic details is afforded by consideration of small displacements of these coupled reactions from the equilibrium position. Thus, if we define displacement parameters α and β such that $[Co(N_4)(OH_2)O_2^{2+}] = ([Co(N_4)(OH_2)O_2^{2+}]_e - \alpha + \beta)$ and $[\{Co(N_4)OH_2\}_2O_2^{4+}] = ([\{Co(N_4)OH_2\}_2O_2^{4+}]_e - \beta)$, resulting first-order kinetic equations are (for α, β, and $[Co(N_4)(OH_2)O_2^{2+}]$ small)

$$d\alpha/dt = a\alpha + b\beta,\ d\beta/dt = (c\alpha - d\beta)$$

where $a = k_1[Co(N_4)(OH_2)_2^{2+}]_e + k_1[O_2]_e + k_{-1}$, $b = k_1[O_2]_e - k_{-1}$, $c = k_2[Co(N_4)(OH_2)_2^{2+}]_e$, and $d = k_2[Co(N_4)(OH_2)_2^{2+}]_e + k_{-2}$; the subscript "e" designates the ultimate equilibrium concentrations. One therefore expects two relaxation times[46-48] given by

$$\gamma_{I,II} = \{(a - d)/2 \pm \tfrac{1}{2}[(a + d)^2 + 4bc]^{1/2}\}^{-1} \qquad (3)$$

For the special case that $(a + b) > 4bc$, this results in

$$k_I \simeq a + bc/(a + d)$$

$$k_{II} \simeq d + bc/(a + d)$$

Clearly k_I corresponds to the buildup of the superoxo intermediate, while k_{II} corresponds to its decay. When the extent of the uptake reaction becomes very large (i.e., for K_1K_2 very large), the kinetic equations necessarily contain cross and other second-order terms which preclude a simple analytic solution.

A. The $Co^{II}([14]aneN_4)/O_2$ System. The very reactive intermediate observed in this system can be readily inferred to be $Co([14]aneN_4)(OH_2)O_2^{2+}$. Inspection of Table I shows the decay of this species to be inhibited by O_2. This and the rapid decay rates imply that K_1, k_{-1}, and k_2 are all reasonably large, so the small displacement treatment can only be useful over a limited range of conditions; e.g., for $[Co([14]aneN_4)(OH_2)_2^{2+}] \gg [O_2]$ eq 3 reduces to

$$k_{II} \sim k_2[Co^{II}L]_e + k_{-2} - \frac{k_2[Co^{II}L]_e(k_1[O_2]_e - k_{-1})}{(k_1 + k_2)[Co^{II}L]_e + k_{-1} + k_{-2}} \qquad (4)$$

Since K_1K_2 is large for this system,[49] the equilibrium concentration of $Co([14]aneN_4)(OH_2)_2^{2+}$ may be obtained from the stoichiometric conditions

$$[Co([14]aneN_4)(OH_2)_2]_i = [Co([14]aneN_4)(OH_2)_2^{2+}]_e + [Co([14]aneN_4)(OH_2)O_2^{2+}]_e + 2[\{Co([14]aneN_4)\}_2O_2^{4+}]_e$$

and

$$[O_2]_i = [O_2]_e + [Co([14]aneN_4)(OH_2)O_2^{2+}]_e + [\{Co([14]aneN_4)\}_2O_2^{4+}]_e$$

For $[O_2]_e$ and $[Co([14]aneN_4)(OH_2)O_2^{2+}]_e$ small these equations reduce to $[Co([14]aneN_4)(OH_2)_2^{2+}]_e \simeq [Co([14]aneN_4)(OH_2)_2^{2+}]_i - 2[O_2]_i$. Figure 2 then implies that the last two terms in eq 4 are small; thus, we find $k_2 = (4.9 \pm 0.4) \times 10^5\ M^{-1}\ s^{-1}$ (25 °C, $\mu = 0.1(HClO_4/LiClO_4)$; Figure 2). By means of chemical scavenging techniques, to be described elsewhere,[26a] we have shown that $k_{-2} = 0.6 \pm 0.1\ s^{-1}$ in perchlorate media (μ = 0.1, 25 °C); therefore, $K_2 = (8 \pm 2) \times 10^5\ M^{-1}$ (25 °C, μ = 0.1, perchlorate media).

When $2[O_2]_i > [Co([14]aneN_4)(OH_2)_2^{2+}]$, the small displacement approach to eq 1 and 2 is inappropriate, and we have found for the reciprocal of the apparent first-order rate constants

$$1/k_{app} \simeq a + b\frac{[O_2]_i}{[Co([14]aneN_4)(OH_2)_2^{2+}]_i}$$

where $a = (9.8 \pm 1.4) \times 10^{-3}$ s and $b = (6.1 \pm 0.2) \times 10^{-3}$ s. For a sufficient excess of O_2, and neglecting the product absorbance, these parameters may be interpreted in terms of a stationary state in $[Co^{II}]$ (25 °C, μ = 1.0):

$$a \simeq (k_2 - k_1)/k_2k_{-1},\ b \simeq k_1/k_2k_{-1};\ k_{-1} \simeq 63 \pm 6\ s^{-1},$$
$$k_1/k_2 \simeq 0.38 \pm 0.05\ M$$

From this value of k_{-1} and our determination that $K_1 = (8 \pm 2) \times 10^3\ M^{-1}$, we find $k_1 = k_{-1}K_1 = (5.0 \pm 1.5) \times 10^5\ M^{-1}\ s^{-1}$. This is in excellent agreement with the value of $k_1 = (4 \pm 1) \times 10^5\ M^{-1}\ s^{-1}$ found for the very rapid approach to equilibrium in the first step of the oxygen uptake reaction. The intercept in the relaxation treatment of the uptake kinetics is not well defined, but does agree in magnitude with the value of k_{-1} determined above.

B. The $Co^{II}([15]aneN_4)/O_2$ System. Analysis of the kinetic parameters for this system was more difficult owing to the relatively small magnitude of the equilibrium quotient, K_1K_2. Once again eq 4 provides the means of determining k_2, but for most conditions the equilibrium concentrations had to be determined by means of an iterative procedure. This procedure results in estimates of all four rate constants and is summarized in the Results section; the kinetic and equilibrium parameters are presented in Tables II and III. There is necessarily a great deal of uncertainty about the numerical values of the dissociation rate constants, k_{-1} and k_{-2}, estimated by this procedure. However,

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(49) McLendon and Mason[23] have estimated that $K_1K_2 \sim 10^8\ M^{-2}$ in a medium of lower ionic strength. These authors apparently waited several minutes for their system to "equilibrate". There is considerable irreversible decay of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ in a few minutes, and there is some oxygen release associated with this decay.[26a] A very recent claim that $K_1K_2 \sim 47\ M^{-2}$ (Kodama, M.; Kimura, E. *J. Chem. Soc.* **1980**, 327) is inconsistent with the observation of $[Co([14]aneN_4)OH_3]_2O_2^{4+}$ under the reported experimental conditions.

Table III. Comparison of Thermodynamic and Kinetic Parameters for the Oxygen $Co^{II}(N_4)$ Reactions (1) and (2) in Water (25 °C, $\mu = 1.0$, Except as Indicated)

equatorial ligand, N_4	$k_1 \times 10^{-4}$, $M^{-1}\ s^{-1}$	k_{-1}, s^{-1}	$k_2 \times 10^{-4}$, $M^{-1}\ s^{-1}$	k_{-2}, s^{-1}	K_1, M^{-1}	K_2, M^{-1}	K_1K_2, M^{-2}	$k_{exch}^{1/2}$, $(M^{-1}\ s^{-1})^{1/2}$ [a]	$E^{(f)}$, V [b]
$[15]aneN_4$	0.38 ± 0.11	~1	(5 ± 1)[c]	~2	~4 × 10^4	~2 × 10^4	$10^{8\pm1}$		⩾0.6[d]
$Me_2[14]1,11$-diene-13-one	4 ± 1[e]	~10[e]	⩾10		~4 × 10^3 [e]		<10^7 [f]	0.066	0.600
$Me_6[14]4,11$-dieneN_4							(10^5)[g]	0.0067	0.564
$[14]aneN_4$	50 ± 15	63 ± 6	49 ± 4[h]	0.6 ± 0.1	(8 ± 2)10^3 [n]	(8 ± 3)10^5 [h]	(6 ± 3)10^9 [h]	0.028	0.421
$Me[14]1,11$-dieneN_4	13			>1[j]			>10^8 [k]		0.384[i]
$Me_2[14]4,11$-dieneN_4							>10^8 [l]		0.349
$(NH_3)_5$	1.5[m]			56[m]				0.021[n]	0.30[o]

[a] Self-exchange rate constants, k_{exch}, for $Co(N_4)(OH_2)_2^{3+,2+}$ electron exchange reactions from ref 13 except as indicated. [b] From ref 52 except as indicated. Formal potentials at 25 °C, $\mu = 0.1$ ($NaClO_4$) vs. NHE. [c] 0.1 M $NaClO_4$. [d] Based on the greater than 0.19 V difference of the half-wave potentials of $Co([14]aneN_4)Cl_2^+$ and $Co([15]aneN_4)Cl_2^+$ in acetonitrile solution: Hung, Y.; Martin, L. Y.; Tackels, S. S; Tait, A. M.; Busch, D. H. *J. Am. Chem. Soc.* 1977, *99*, 4029. [e] Assignment of the observed relaxation time is ambiguous. [f] Based on less than 10% consumption of $Co(Me_2[14]1,11\text{-dienN}_4\text{-13-one})(OH_2)_2^{2+}$ in the oxygen-uptake steps. [g] From ref 23. [h] $\mu = 0.1$; $HClO_4$. [i] This work. [j] Based on overall decomposition rate of μ-peroxo complex in neutral solution. Dissociation rate is probably not rate determining. [k] Based on detection limit of amperometric titration. [l] Estimate based on the apparently complete oxygenation of $Co^{II}(Me_2[14]4,11\text{-dieneN}_4)$ on mixing with O_2. [m] Reference 2b. [n] Based on the $Ru(NH_3)_6^{2+}/Co(NH_3)_5OH_2^{3+}$ reaction with corrections for $Ru(NH_3)_6^{3+,2+}$ self-exchange and driving force using $k_{12} = (k_{11}k_{22}K_{12})^{1/2}$. [o] Yalman, R. C. *Inorg. Chem.* 1962, *1*, 16.

the kinetic data cannot be fitted by parameters significantly different in magnitude from those cited.

C. Oxygen Uptake with the Remaining $Co^{II}(N_4)$ Systems. The detailed information about the remaining macrocyclic complexes is much more limited. The behavior of the $Co(Me_2[14]1,11\text{-dieneN}_4\text{-13-one})(OH_2)_2^{2+}/O_2$ system is again suggestive of a system approaching equilibrium with $k_{obsd} \simeq (4.0 \times 10^4)[Co^{II}L] + 10\ s^{-1}$. This relaxation process, corresponding to the observed consumption of Co(II), may alternatively be described by (1) eq 4 if $k_1 \geq 10^5\ M^{-1}\ s^{-1}$; or (2)

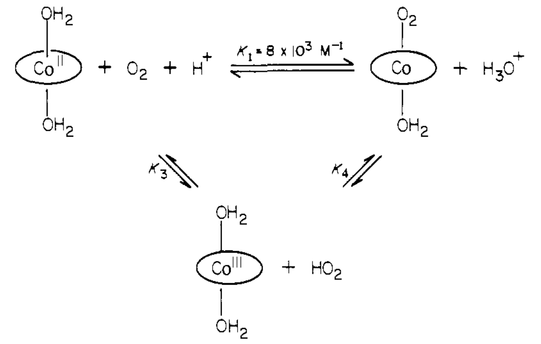
$$k_{obsd} \sim k_1[Co^{II}L]_e + k_{-1} + \frac{k_2[Co^{II}L]_e(k_1[O_2]_e - k_{-1})}{(k_1 + k_2)[Co^{II}L]_e + k_1[O_2]_e + k_{-1} + k_{-2}}$$

provided $k_2 \geq 10^5\ M^{-1}\ s^{-1}$. The experimental evidence itself is not adequate to distinguish these possibilities. We have tentatively assigned the observed relaxation process to τ_1 based on the greater similarity of the numerical value of the corresponding equilibrium quotient to K_1 than to K_2 found for other complexes.

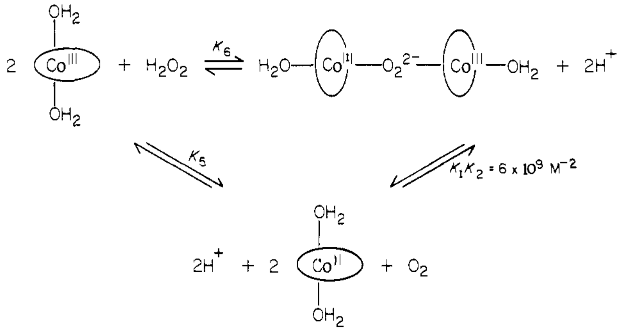
In contrast to the limited extents of reaction of O_2 with $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ and $Co(Me_2[14]1,11\text{-dieneN}_4\text{-13-one})(OH_2)_2^{2+}$, the oxygen-uptake reactions of $Co(Me_2[14]1,11\text{-dieneN}_4)(OH_2)_2^{2+}$ and $Co(Me_2[14]4,11\text{-dieneN}_4)(OH_2)_2^{2+}$ appear to go to completion rapidly. For the $Co(Me_2[14]1,11\text{-dieneN}_4)(OH_2)_2^{2+}/O_2$ system, we have observed only absorbance increases, presumably to form the μ-peroxo product, with no direct observations of the monomeric superoxo intermediate. This implies that $k_2 > k_1$ and that the uptake step (1) is rate limiting.

D. Comparisons and Conclusions. The kinetic and thermodynamic parameters for oxygen-uptake reactions in water are collected in Table III. While the uncertainties are large, there is a tendency for K_1K_2 to increase as the $Co^{III/II}$ couple becomes more reducing.[50-53] Our results for the $Co([14\text{ and }15]aneN_4)(OH_2)_2^{2+}/O_2$ systems suggest that most of this variation occurs in K_2. In contrast, the *rates* of oxygen uptake are rapid for all cobalt(II)–macrocycle complexes. However, the *extent* of the uptake reactions (e.g., as reflected in K_1K_2) becomes very small as the $Co^{II}(N_4)$ complex becomes a relatively poor reducing agent.

Scheme I



Scheme II



Most of our studies have centered on the $Co([14\text{ and }15]aneN_4)(OH_2)_2^{2+}/O_2$ systems, for which we have been able to isolate and characterize both steps (1) and (2). The large stability constant found for step (1), $K_1 \simeq 8 \times 10^3\ M^{-1}$, in water at 25 °C is very striking in view of the known oxidation-reduction thermodynamics of the $Co([14]aneN_4)(OH_2)_2^{3+,2+}$ and O_2/HO_2 couples ($E° = 0.42$ V, Table III; −0.05 V, ref 54–57); i.e., the

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(50) Unfortunately there is a dismaying range of emf values reported for some of these complexes. For example, the value of "$E°$" for the $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{3+,2+}$ couple has variously been reported as 0.54 (ref 28), 0.604 (ref 14), 0.51 (ref 51), and 0.564 V (ref 52; these authors reported half-wave potentials vs. SCE, with the correction (at $\mu = 0.1$, 25 °C) to NHE, including the junction potential, being estimated as 0.249 V. An even wider range of "$E°$" values has been reported for the $Co(Me_6[14]4,11\text{-dieneN}_4)(OH_2)_2^{3+,2+}$ couple (0.56,[53] 0.605,[14] 0.51,[51] 0.564,[52] and 0.33[23] V). To some degree the inconsistencies result from (1) variations in reference systems used (especially with regard to ionic strength); (2) differences in junction potentials, possibly complicated by such specific problems as precipitation of $KClO_4$ in glass frits, and differences in diffusion coefficients of Na^+ and ClO_4^-; (3) the very large variations of $E°$ with temperature for these cobalt(III)–(II) couples.[52] We have used the data of Weaver and co-workers[52] for most of the comparisons in this paper; these data are in reasonable agreement with much of the earlier literature and have been obtained with due consideration of the problems noted above. We are very grateful to Professor Weaver for making this information available to us prior to publication. The electrochemical measurements performed in the present study, using a thermostated cell, have been in excellent agreement with values from ref 52.

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Table IV. Intrinsic Reactivities of $Co^{II}(N_4)/O_2$ Couples

free-energy quantity, kcal mol^{-1}	N_4 = [14]-aneN_4	Me_2-[14]1,11-dieneN_4-13-one	[15]-aneN_4
$\Delta G_1^{\ddagger}$(obsd)[a]	8.7	10.2	11.6
ΔG_1° [b]	−5.4	−5.0	−5.0
$\Delta G_1^{\ddagger}$(intrinsic)[c]	11.4	12.7	14.1
$\Delta G_w^{\ddagger}$ [d]	~5	~5	~8
$\Delta G_1^{\ddagger} - \Delta G_w^{\ddagger}$	6	8	6
$^1/_2(\Delta G_{Co}^{\ddagger} + \Delta G_{O_2}^{\ddagger})$os[e]	15.0	14.6	

[a] Based on $k_{obsd} = K_0(kT/h)e^{-\Delta G^{\ddagger}/RT}$; $K_0 = 0.15\ M^{-1}$. [b] $\Delta G^{\circ} = RT \ln K_1$. [c] $\Delta G^{\ddagger}_{intrinsic} = \Delta G^{\ddagger}_{obsd} - 0.5\Delta G^{\circ}$. [d] Estimated activation free energy for $Co^{II}-OH_2$ bond breaking. Based on a water exchange rate of $\sim 10^9\ s^{-1}$ for low-spin complexes[11,15a] and $\sim 10^7\ s^{-1}$ for the high-spin $Co([15]aneN_4)(OH_2)_2^{2+}$. The latter is based on $Co(OH_2)_6^{2+}$ [63] and $Co(NH_3)_6^{2+}$.[64] [e] Based on self-exchange parameters for the cobalt complexes[13,14,19] and O_2/O_2^-.[65,68]

"outer-sphere" one-electron transfer oxidation of $Co([14]aneN_4)(OH_2)_2^{2+}$ by O_2 (Scheme I) is unfavorable by 0.47 V and $K_3 = 1.1 \times 10^{-8}\ M^{-1}$. This requires a formation constant (Scheme I) $K_4' \simeq 3.8 \times 10^{16}\ M^{-1}$ for the replacement of one water molecule in $Co([14]aneN_4)(OH_2)_2^{3+}$ by O_2^-. This may be compared to formation constants in the range of 10^7–$10^9\ M^{-1}$ for complexation of various iron(III) complexes by CN^-.[58] Since O_2^- does not appear to be a particularly strong base the extraordinarily large formation constant must be due to some factor unusual in the substitutional chemistry of trivalent complexes. Walker and co-workers[5] have drawn similar inferences based on other kinds of thermochemical information for cobalt–porphyrin/O_2 reactions.

Comparison of superoxide to peroxide coordination (Scheme II) in this system is very instructive. Using 0.68 V for the O_2/H_2O_2 couple,[59] we obtained $K_5 = 6 \times 10^8\ M^{-2}$ and $K_6 = 10$. To compare the mean stabilities per cobalt we may consider $K_4' = 3.8 \times 10^{16}\ M^{-1}$ and the ratio $[K_6(K_{a1}K_{a2})^{-1}]^{1/2}$ ($pK_{a1} = 11.6$, $pK_{a2} \sim 25$[59]) $\sim 6 \times 10^{18}\ M^{-1}$. Surprisingly, this comparison suggests similar Co–O binding energies in the superoxo and peroxo complexes. Since there is such a vast difference in the mean pK_as (4.88 [56,57] compared to ~ 18[59]), even in this comparison there is something very unusual about O_2^-.

The surprisingly large stability of the Co^{III}/O_2^- complex could be accounted for by appreciable $O_2^- \rightarrow Co^{III}$ charge transfer. This is in keeping with the adduct bonding models proposed by Drago[17] and by Goddard,[60] and with the small electron affinity of O_2 (~0.5 eV).[39] An alternative would be to postulate somewhat different bonding formulations for superoxo and peroxo complexes; e.g., an appreciable $Co \rightarrow O_2$ ($d\pi \rightarrow \pi^*$) bonding component in the superoxo complex could contribute to the differences in proton and complex stability constants.

Some detailed comparisons of reactivity are also possible. The rate constants of the dimerization step (2) for the $Co([14]aneN_4)(OH_2)_2^{2+}$ and $Co([15]aneN_4)(OH_2)_2^{2+}$ reactions with O_2 vary as the square root of the equilibrium constant: $k_2 \propto K_2^{1/2}$. This is as expected since the relationship $\Delta G^{\ddagger} = (a\Delta G^{\circ} + b\Delta G_i^{\ddagger})$ should be very general and $a \rightarrow 0.5$ for small values of ΔG°[61,62] ($\Delta G_i^{\ddagger}$ is the "intrinsic reactivity" associated with the reaction coordinate). Since this process involves substitution on cobalt(II), a component of $\Delta G_i^{\ddagger}$ must be $Co-OH_2$ bond breaking ($\Delta G_w^{\ddagger}$). We would expect the high-spin $Co([15]aneN_4)(OH_2)_2^{2+}$ complex to have a smaller tetragonal distortion than the low-spin $Co([14]aneN_4)(OH_2)_2^{2+}$ complex; i.e., all six cobalt–ligand bonds of the former are expected to be longer than in $Co([15]aneN_4)(OH_2)_2^{3+}$, while only the axial bonds of the low-spin cobalt complexes are lengthened.[13] Thus Co(II)–OH_2 bond breaking is expected to occur with a frequency $\sim 10^6$–$10^7\ s^{-1}$ for the [15]aneN_4 complex, similar to $Co(OH_2)_6^{2+}$ [63] or $Co(NH_3)_6^{2+}$,[64] and $\sim 10^9\ s^{-1}$ in the low-spin complexes.[11,15a] Since $\Delta G_i^{\ddagger} \sim 11.5$ kcal mol^{-1} for both complexes, the ~3 kcal mol^{-1} differences in $\Delta G_w^{\ddagger}$ are apparently compensated by differences in reorganizational paramters. Such a difference of a few kilocalories per mole is plausible since oxidation of Co(II) to Co(III) is likely to involve a bigger bond-length change on low-spin than on high-spin cobalt(II).

The oxygen uptake step, (1), can be analyzed in a similar manner, Table IV. For this step quantities ($\Delta G_i^{\ddagger} - \Delta G_w^{\ddagger}$) are the same for the [14]aneN_4 and [15]aneN_4 complexes. This suggests that the reorganizational parameters which determine the rates of outer-sphere electron-transfer reactions are not as important in determining the rates of adduct formation. In fact this ~6 kcal mol^{-1} barrier to adduct formation is much smaller than the intrinsic barrier $\lambda/4 \sim 15$ kcal mol^{-1} estimated for outer-sphere electron transfer between $Co([14]aneN_4)(OH_2)_2^{2+}$ and O_2.[65–68] Since transfer of charge to the small O_2 moiety must involve an appreciable change in solvation (e.g., contributing ~10 kcal mol^{-1} to the O_2/O_2^- self-exchange (Table SVIII); see also ref 65 and 68), the small observed barriers to adduct formation are suggestive of transfer of a relatively small fraction of charge.

One additional point of interest in the comparison of the $Co([14]aneN_4)(OH_2)_2^{2+}/O_2$ and $Co([15]aneN_4/(OH_2)_2^{2+}/O_2$ systems is that the change of spin multiplicity which occurs in the course of the latter reaction apparently affects the rate constant only through variations in the rates of Co–OH_2 bond breaking. There is no evidence whatsoever for any purely electronic spin constraint on the reactivity of these systems.

Supplementary Material Available: Figures of ionic strength dependence of absorbance decay rate constants for $Co([14]aneN_4)(OH_2)_2^{2+}/O_2$ reaction, decomposition rates of $[XCo^{III}([14]aneN_4)]_2O_2$ in chloride media (pH dependence), and decomposition rates of $[XCo^{III}([14]aneN_4)]_2O_2$ in chloride media (chloride dependence), and tables of anation rates of $[H_2OCo([14]aneN_4)]_2O_2^{2+}$, amperometric titration of $Co(Me_2[14]1,11\text{-}dieneN_4)(OH_2)_2^{2+}$, with O_2, kinetic parameters for the $Co(Me_2[14]1,11\text{-}dieneN_4)(OH_2)_2^{2+}/O_2$ system, reaction of $Co(Me_4[14]tetraeneN_4)(OH_2)_2^{2+}$ with O_2, and kinetic parameters for the $Co(Me_2[14]1,11\text{-}dieneN_4\text{-}13\text{-}one)(OH_2)_2^{2+}/O_2$ system (14 pages). Ordering information is given on any current masthead page.

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