(CHN), 80.3 (C), 95.7 (C), 127.5, 127.6, 128.3, 141.3, 172.2 (C=O), 173.2 (C=O); IR (film) ν 1731 cm^{-1}. Anal. Calcd for $C_{21}H_{31}NO_5$: C, 66.82; H, 8.28; N, 3.71. Found: C, 66.58; H, 8.06; N, 3.55.

Acknowledgment. Support for this research under Grant 2 RO1 GM26178-10 from the National Institutes of General Medical Sciences (Public Health Service) (chemistry in Scheme I and Table I) and Grant CHE 870152 from the National Science Foundation (chemistry in Scheme II) is gratefully acknowledged. Mass spectrometry determinations were performed by Midwest Center for Mass Spectrometry, a National Science Foundation Regional Instrumentation facility (Grant No. CHE-8620177). S. De Lombaert thanks NATO for financial support.

Registry No. 1a, 117041-11-9; **1b**, 117041-12-0; **1c**, 112044-04-9; **1d**, 124716-04-7; **1e**, 112068-80-1; **1f**, 124685-61-6; **1g**, 112044-05-0; **1h**, 124685-62-7; **1i**, 124685-63-8; **1j**, 124685-64-9; **1k**, 124685-65-0; **1l**, 124685-66-1; **1m**, 117041-17-5; **1n**, 117041-14-2; **1o**, 112044-01-6; **1p**, 124685-67-2; **1q**, 124815-34-5; **1r**, 117041-19-7; **1s**, 67012-34-4; **1t**, 32370-44-8; **2a**, 124619-63-2; **2b**, 124619-64-3; **2c**, 124619-65-4; **2d**, 124619-66-5; **2e**, 124619-67-6; **2f**, 18085-37-5; **2f′**, 124619-68-7; **2i**, 1690-74-0; **2j**, 124619-69-8; **2k**, 124619-70-1; **2l**, 124619-71-2; **2m**, 105394-78-3; **2n**, 124619-72-3; **2o**, 124619-73-4; **2t**, 124619-74-5; **3a**, 124685-68-3; **3b**, 124685-69-4; **3c**, 124685-70-7; **4a** (isomer 1), 124619-75-6; **4a** (isomer 2), 124619-76-7; **4b** (isomer 1), 124619-77-8; 4b (isomer 2), 124619-78-9; **4b′** (isomer 1), 124619-79-0; **4b′** (isomer 2), 124650-74-4; **4c**, 124619-80-3; **4c′**, 124619-81-4; **7**, 20540-69-6; **8**, 12289-28-0; **11a**, 124619-82-5; **11b**, 124619-83-6; **11c**, 124619-84-7; **11d**, 124619-85-8; **11e**, 124619-86-9; **12a**, 124619-87-0; **12b**, 124619-88-1; *syn*-**14**, 124619-89-2; *anti*-**14**, 124650-75-5; **15a**, 124619-90-5; **15b**, 124619-91-6; $Na_2Cr(CO)_5$, 51233-19-3; $(CO)_5Cr{=}C(CH_3)NHCPh_3$, 124685-71-8; $K_2Cr(CO)_5$, 107799-34-8; $(CO)_5Cr{=}C(CH_3)O^{-}NMe_4^{+}$, 15975-93-6; $(CO)_5Cr{=}C(OMe)C{\equiv}CPh$, 99824-96-1; $(CO)_5Cr{=}C(OMe)C_6H_4$-*p*-CF_3, 27637-27-0; $(CO)_5Cr{=}C(OMe)Ph$, 27436-93-7; Br_2NH, 103-49-1; *N*-isoindolineacetamide, 18913-38-7; *N,N*-dibenzylacetamide, 10479-30-8; *N*-acetylmorpholine, 1696-20-4; *N,N*-dimethylcyclopropanecarboxamide, 17696-23-0; *N,N*-dimethyl-α-(phenyloxy)acetamide, 10397-59-8; *N*-benzylazetidinone, 4458-64-4; *N*-methylpyrrolidin-2-one, 872-50-4; *N*-benzylpyrrolidin-2-one, 5291-77-0; *N*-methylpiperidin-2-one, 931-20-4; *N*-benzylpiperidin-2-one, 4783-65-7; *N*-benzyl-2-azacycloheptanone, 33241-96-2; *N*-benzyl-2-azacyclotridecanone, 41011-68-1; *N,N*-diethylbenzenecarboxamide, 1696-17-9; *N,N*-dimethyl-3-furancarboxamide, 14757-80-3; 2-chloro-*N,N*-dimethylbenzenecarboxamide, 6526-67-6; (*E*)-*N,N*-dimethyl-3-phenylpropenamide, 17431-39-9; 2(*S*)-*N*-acetyl-2-phenyl-1,3-oxazolidine, 124619-59-6; (*S*)-phenylglycinol, 20989-17-7; isobutyraldehyde, 78-84-2; 2(*R*)-4(*S*)-2-isopropyl-4-phenyl-1,3-oxazolidine, 124619-60-9; 2(*S*)-4-(*S*)-2-isopropyl-4-phenyl-1,3-oxazolidine, 124619-61-0; 2,2-dimethyl-4-phenyl-1,3-oxazolidine, 124619-62-1; tritylamine, 5824-40-8; 4-methoxybenzyl chloride, 824-94-2; bromoacetic acid ethyl ester, 105-36-2; isoindoline, 496-12-8; β-bromo-*N*-benzylpropionamide, 1665-47-0; bromoacetic acid *tert*-butyl ester, 5292-43-3.

Formation and Homolysis of a Mononuclear Cobalt–Oxygen Adduct

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Abstract: The macrocyclic cobalt(II) complex $(H_2O)_nCo(C\text{-}meso\text{-}Me_6[14]aneN_4)^{2+}$ (L^2Co^{2+}) binds oxygen to yield $L^2CoO_2^{2+}$. The rate constants for the binding and release of O_2 in aqueous solutions at 25 °C have values 5.0×10^6 M^{-1} s^{-1} and 1.66×10^4 s^{-1}, respectively. There is no evidence for the formation of a binuclear μ-peroxo complex. The ESR parameters of the oxygen adduct in toluene at 120 K, $g_{\parallel} = 2.108$, $g_{\perp} = 1.96$, $A_{\parallel} = 3.81 \times 10^{-3}$ cm^{-1}, $A_{\perp} = 2.94 \times 10^{-3}$ cm^{-1}, are consistent with the formulation of the complex as a 1:1 adduct with the unpaired spin density residing on the oxygen. The laser flash photolysis of $L^2CoO_2^{2+}$ (λ_{irr} 490 nm) induces the cleavage of the cobalt–oxygen bond, $L^2CoO_2^{2+} \xrightarrow{h\nu} L^2Co^{2+} + O_2$.

A large number of cobalt–oxygen complexes are known both in solution and in the solid state.[1] The importance of these complexes lies in their being excellent models for metal–dioxygen binding, which should bring about a better understanding of the natural oxygen carriers, such as hemoglobin. Another important aspect of the cobalt–oxygen chemistry deals with the catalytic action of cobalt in the oxidation of a number of organic compounds.[2-4]

The affinity of oxygen for cobalt(II) varies greatly with the solvent and the ligands.[1] Both mononuclear and binuclear complexes are known. The former, usually referred to as superoxo complexes, are often only transients in the formation of the binuclear μ-peroxo complexes, eqs 1 and 2. The assignment of the

$$Co^{II} + O_2 \rightleftarrows Co^{III}O_2 \qquad k_1, k_{-1}, K_1 \tag{1}$$

$$Co^{III}O_2 + Co^{II} \rightleftarrows Co^{III}O_2Co^{III} \qquad k_2, k_{-2}, K_2 \tag{2}$$

3+ oxidation state to the cobalt and 1− or 2− to the oxygen is only a formalism of the ionic model, which can by no means account for all the spectral, structural, or chemical properties of these complexes. A better description of binding of O_2 to cobalt(II), at least for the low-spin, five-coordinate Co(II) complexes, is based on the molecular orbital scheme whereby an electron in the d_{z^2} orbital on the cobalt pairs up with an electron in the π^* orbital of O_2.[5]

There exists a wealth of thermodynamic information[1] on dioxygen binding to cobalt, but much less is known about the kinetics

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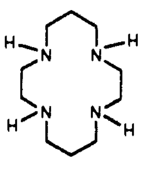
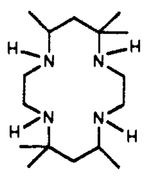
of these processes, especially in aqueous solution.[1a,6-8] The most detailed and extensive kinetic work has been reported by Endicott and co-workers on the reactions of several macrocyclic cobalt(II) complexes with oxygen.[9] The complex $[(H_2O)_2Co([14]aneN_4)^{2+}]$,[10] hereafter L^1Co^{2+}, reacts as in eqs 1 and 2.[9,11-13] The mononuclear superoxo complex, $L^1CoO_2^{2+}$, is a strong oxidant and it reacts with a number of inorganic reductants.[7,9] The high affinity of L^1Co^{2+} for oxygen,[6,7,9,11] coupled with the redox properties of $L^1CoO_2^{2+}$, is responsible for the catalytic role of L^1Co^{2+} in electroreduction of oxygen.[13] The direct kinetic studies of the reactions of $L^1CoO_2^{2+}$ with substrates of interest are, however, difficult to carry out owing to the complications imposed by the equilibrium of eq 2.

We have now studied the reaction of a closely related complex, $[(H_2O)_nCo(C\text{-}meso\text{-}Me_6[14]aneN_4)^{2+}]$, hereafter L^2Co^{2+}, with oxygen. We expected that the steric crowding, imposed by the six methyl groups at the periphery of the macrocycle, might reduce drastically the equilibrium constant K_2 for the formation of the binuclear peroxocobalt complex. Provided this alteration of the macrocycle does not cause too dramatic a decrease in oxygen affinity, i.e., if K_1 remains reasonably large, this cobalt(II) macrocycle should have some interesting oxygen-carrying properties. Moreover, the kinetic studies and mechanistic interpretations should be straightforward if reactions 2 and −2 are indeed negligible.



$[14]aneN_4 = L^1$



$Me_6[14]aneN_4 = L^2$

Experimental Section

Materials. The ligand C-*meso*-$Me_6[14]aneN_4$ (L^2) was prepared by a slight modification of a literature procedure.[14] After the reduction of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene dihydrobromide dihydrate (16 g) by $NaBH_4$ (3 g) was complete, 40 mL of 1.2 M KOH was added. The subsequent workup[14] yielded the compound with the correct melting point (146–148 °C). The ligand $[14]aneN_4$ (L^1) was obtained commercially (Strem). The complex $[L^2Co](CF_3SO_3)_2$ was prepared from the $CoCl_4^{2-}$ salt and $LiCF_3SO_3$ by a procedure analogous to that used in the preparation of the perchlorate salt.[15] The lack of structural information precludes a firm assignment of the coordination number (5 or 6) and stereochemistry around the nitrogens in L^2Co^{2+}. Our assumption that the complex contains two coordinated molecules of water and that the nitrogens have the 1*R*,4*R*,8*S*,11*S* configuration, does not affect the basic findings and conclusions in this work. The solutions of L^2Co^{2+} showed no signs of isomerization even after several days at room temperature. Kinetically and spectrally such aged solutions were identical with fresh ones, provided both had been handled anaerobically. The solutions of L^1Co^{2+} were prepared as described previously.[16] The organocobalt complexes L^1CoR^{2+} were prepared as the PF_6^- or ClO_4^- salts.[17] The complex $[L^2CoCH_3](CF_3SO_3)_2$ was prepared by the same method. The UV-visible spectrum of this complex [λ_{max} 500 nm (ϵ 72.4 M^{-1} cm^{-1}), λ_{max} 384 (ϵ 117)] matches that reported earlier [λ_{max} 498 (ϵ 74), λ_{max} 384 (ϵ 133)].[18]

Solutions of methyl viologen radical cation, MV^+, were prepared by the zinc amalgam reduction of MV^{2+} and standardized spectrophotometrically [λ_{max} 600 nm (ϵ 1.37×10^4 M^{-1} cm^{-1})].[19] These solutions were used to determine the concentrations of $CH_3^{\bullet}$ produced by the laser flash photolysis of $L^1CoCH_3^{2+}$.

Kinetic Procedures. All the kinetic determinations were carried out by use of the previously described[20] laser flash photolysis system and the LD 490 dye (Exciton). Typically some 20–100 μL of a 5–10 mM organocobalt(III) or diaquocobalt(II) stock solution were injected into 3–4 mL of an aqueous solution containing the desired concentration of oxygen and the electrolyte ($HClO_4$ and/or $LiClO_4$) in a 1-cm fluorescence cell. The concentration of O_2 was varied by combining aqueous solutions saturated with oxygen ($[O_2] = 1.26$ mM),[21] air ($[O_2] = 0.253$ mM),[21] and argon. In these experiments the cells were filled to capacity to avoid the reequilibration of the liquid and gaseous phases. The solutions were flashed and the absorbance monitored at 360 nm, a wavelength where the signal-to-noise ratio was the best. Owing to the reversibility of the reactions, the solutions could be flashed a number of times without a deterioration of the signal or a change in the rate constant.

The molar absorptivity of $L^1CoO_2^{2+}$ was determined at 360 nm, the wavelength where most of the kinetics were monitored. An argon-saturated solution of $L^1CoCH_3^{2+}$ (250 μM) and MV^+ (50 μM) was flashed by use of the laser ($\lambda_{excitation}$ 490 nm) to produce methyl radicals and L^1Co^{2+}. Under the experimental conditions most of the methyl radicals react with MV^+, ($k = 1.2 \times 10^9$ M^{-1} s^{-1}),[16] causing the absorbance at 600 nm to decrease. The concentration of $CH_3^{\bullet}$, calculated from this absorbance decrease, was corrected by an amount (<20%) that disappeared by dimerization,[22] $2k = 3 \times 10^9$ M^{-1} s^{-1}. The concentration of L^1Co^{2+} was taken to be equal to the concentration of the methyl radical. The experiment was then repeated under identical conditions, except that the solution was saturated with oxygen and the absorbance changes were monitored at 360 nm. All the methyl viologen is now present in the colorless MV^{2+} form. The methyl radicals and the cobalt(II) complex react with O_2 to yield $CH_3O_2^{\bullet}$ and $L^1CoO_2^{2+}$, respectively. Only the latter absorbs significantly at 360 nm. From the absorbance increase we obtain ϵ_{360} 2.6 (±0.2) × 10^3 M^{-1} cm^{-1}. Reference 9a reports a value of 2.2 (±0.1) × 10^3 M^{-1} cm^{-1}.

All the nonkinetic optical measurements were done by use of a Cary 219 spectrophotometer. All the experiments were performed at 25.0 ± 0.2 °C.

Results

All the preliminary experiments were carried out on the reaction of L^1Co^{2+} with O_2. The photochemical behavior of L^1CoR^{2+}, the precursor of L^1Co^{2+}, is well understood,[16,23] and a stopped-flow study of the reaction of this cobalt(II) complex with O_2 has already been reported.[9] This system thus seemed well suited to check out our kinetic procedure based on the photohomolysis of L^1CoR^{2+} in solutions containing O_2. The idealized reaction scheme is shown in eqs 3, 4, and 1-1. In order for the photochemical method to

$$L^1CoR^{2+} \xrightarrow{h\nu} L^1Co^{2+} + R^{\bullet} \tag{3}$$

$$R^{\bullet} + O_2 \rightarrow RO_2^{\bullet} \tag{4}$$

$$L^1Co^{2+} + O_2 \rightleftarrows L^1CoO_2^{2+} \tag{1-1}$$

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work well, the competing reaction of L^1Co^{2+} with $RO_2^{\bullet}$, eq 5, has

$$L^1Co^{2+} + RO_2^{\bullet} \rightarrow L^1CoO_2R^{2+} \qquad (5)$$

to be negligibly slow compared to reaction 1-1, so that all the L^1Co^{2+} reacts with O_2 and all the $RO_2^{\bullet}$ disappears in the self-reactions, eq 6.[24] This is a reasonable expectation, since the rate

$$2RO_2^{\bullet} \rightarrow \text{nonradical products} \qquad (6)$$

constants $k_{1\text{-}1}$, k_5, and k_6 probably all lie in the range 10^7–10^8 M^{-1} s^{-1},[16,24] but the concentration of O_2 is 20–100 times higher than that of either L^1Co^{2+} or $RO_2^{\bullet}$. This makes the *rate* of reaction 1-1 much larger than the rates of reactions 5 and 6. In that case the rate law of eq 7 should apply. In the presence of a large excess

$$\text{rate} = k_{1\text{-}1}[O_2][L^1Co^{2+}] - k_{-(1\text{-}1)}[L^1CoO_2^{2+}] \qquad (7)$$

of O_2 the rate constant k_{obs} is defined as in eq 8.

$$k_{obs} = k_{1\text{-}1}[O_2] + k_{-(1\text{-}1)} \qquad (8)$$

The laser flash photolysis of dilute, oxygen-free aqueous solutions of $L^1CoCH_3^{2+}$ (0.1–0.5 mM) causes no noticeable absorbance change at 360 nm. This is consistent with the low molar absorptivity of $L^1CoCH_3^{2+}$ (ϵ 91 M^{-1} cm^{-1}) and the formation of low concentrations (10–30 μM) of nearly nonabsorbing L^1Co^{2+} (ϵ 5 M^{-1} cm^{-1}) and $CH_3^{\bullet}$ in the flash.[16] If the same experiment is performed on an oxygen-saturated solution, the absorbance still does not change during the flash, but it increases after it in a first-order fashion, $k_{obs} = 1.48 \times 10^4$ s^{-1} at 25 °C. This rate constant is independent of the pH in the range 1–7 and the ionic strength (3×10^{-4}–0.1 M). The product has a molar absorptivity of 2.6×10^3 M^{-1} cm^{-1}; see Experimental Section. If other L^1CoR^{2+} complexes (R = C_2H_5, C_3H_7, CH_2Br, CH_2OCH_3) are substituted for the methyl derivative, the behavior of the system remains virtually the same, yielding an average rate constant of 1.46 (±0.07) × 10^4 s^{-1} for oxygen-saturated solutions. The absorbance changes are the same in air-saturated solutions, but the reaction is slower, $k_{obs} = 3.5 \times 10^3$ s^{-1}.

After a reaction solution had already been exposed to one or two laser shots, the absorbance decreases somewhat during the next flash, indicating a photoactive species that absorbs at 360 nm had been formed. This happens only if the solution contains O_2. The subsequent absorbance increase takes place with a rate constant identical with that obtained from the first shot.

The most obvious species that might be responsible for the absorbance decrease in the flashes following the first one is $L^1CoO_2^{2+}$, formed in reaction 1-1. From the literature data on the reaction of L^1Co^{2+} with O_2,[9] and the rate constant $k_{1\text{-}1}$ obtained in this work (see later), we calculate that an oxygen-saturated solution that had originally contained 0.1 mM L^1Co^{2+} has 0.06 mM $L^1CoO_2^{2+}$ and 0.02 mM $(L^1Co)_2O_2^{4+}$. When such a solution is flashed the absorbance at 360 nm decreases, and then it increases to the precisely same value it had before the flash. The rate constant for the absorbance increase is 1.46×10^4 s^{-1}, identical with that obtained when L^1CoR^{2+} complexes were used as a source of L^1Co^{2+} in oxygen-saturated solutions. These oxygenated solutions of L^1Co^{2+} can be flashed dozens of times without any change in the rate constant, although aged solutions (>10 min) give smaller signals owing to the slow decay of $L^1CoO_2^{2+}$ and $(L^1Co)_2O_2^{4+}$. The rate constant for the reaction with O_2 is again dependent on $[O_2]$. Figure 1 shows a plot of k_{obs} against the concentration of O_2. All the points fell on the same line, irrespective of whether oxygenated solutions of L^1Co^{2+} or L^1CoR^{2+} were used as a photochemical precursor of L^1Co^{2+}. This finding also confirms that the alkylperoxy radicals, $RO_2^{\bullet}$, react negligibly slowly with L^1Co^{2+} under the experimental conditions, and that the slope of the line in Figure 1 represents the value of $k_{1\text{-}1}$, 1.18 (±0.03) × 10^7 M^{-1} s^{-1}. The intercept was fixed in this calculation at 100 s^{-1}, based on the reported estimates for the rate constant $k_{-(1\text{-}1)}$.[9] However, the intercept is so small relative to the slope, that changing the values of $k_{-(1\text{-}1)}$ in the range 0–1000 s^{-1} has only a negligible effect on the calculated value of $k_{1\text{-}1}$.

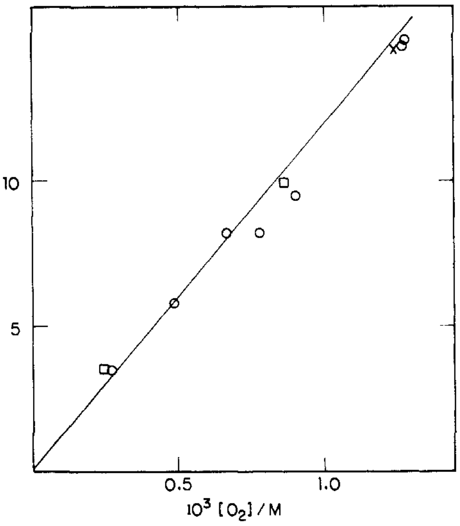

Figure 1. Plot of k_{obs} vs $[O_2]$ for the reaction of O_2 with L^1Co^{2+} generated by flash photolysis of $L^1CoO_2^{2+}$ (circles), $L^1CoCH_2CH_2CH_3^{2+}$ (squares), or $L^1CoCH_3^{2+}$ (crosses) at 25.0 °C, pH 1–7.

The kinetic behavior of oxygenated solutions of L^1Co^{2+} is that of an equilibrated system that upon the sudden disturbance (laser flash) returns to equilibrium according to the rate law of eq 8. Thus $L^1CoO_2^{2+}$ is apparently the only photoactive species in solution, eq 9. The other possible source of L^1Co^{2+} in the flash

$$L^1CoO_2^{2+} \xrightarrow{h\nu} L^1Co^{2+} + O_2 \qquad (9)$$

$$(L^1Co)_2O_2^{4+} \overset{h\nu}{\not\rightarrow} L^1Co^{2+} + L^1CoO_2^{2+} \qquad (10)$$

is the dicobalt species $(L^1Co)_2O_2^{4+}$, eq 10. This possibility can be clearly ruled out, since the combination of eqs 10 and 1-1 could not result in the same absorbance before the flash and after the reaction owing to the large difference in molar absorptivities at 360 nm of $L^1CoO_2^{2+}$ (ϵ 2600 M^{-1} cm^{-1}) and $(L^1Co)_2O_2^{4+}$ ($\epsilon \ll 1000$). Also, solutions of $(L^1Co)_2O_2^{4+}$, prepared by dissolving the solid perchlorate salt[11b] in 0.1 M $HClO_4$ under argon, show no absorbance change at 360 nm when exposed to a laser flash. When such solutions are saturated with air or oxygen the equilibrium amounts of $L^1CoO_2^{2+}$ form and the system becomes photoactive as expected.

When Fe^{2+} is added to solutions containing L^1CoR^{2+} and O_2 in 0.1 M $HClO_4$, the absorbance at 360 nm increases immediately after the flash, owing to the formation of $L^1CoO_2^{2+}$, and then decreases in a pseudo-first-order fashion. The plot of the pseudo-first-order rate constants for this absorbance decrease against $[Fe^{2+}]$ yields $k_{Fe} = 630$ M^{-1} s^{-1}. This value is in good agreement with that reported earlier (1.1×10^3 M^{-1} s^{-1})[9c] for the reaction of Fe^{2+} with $L^1CoO_2^{2+}$, once the difference in ionic strength in the two systems is taken into account. The agreement with the previous work is taken as evidence that the same isomer of the cobalt(II) complex is involved; see Discussion.

Aqueous air-free solutions of L^2Co^{2+} have absorption maxima at 480 nm (ϵ 70 M^{-1} cm^{-1})[15] and 334 nm. The absorbance at the latter maximum, and at lower wavelengths, is quite sensitive to the presence of even minute amounts of O_2, such that reproducible values of ϵ_{334} (38 M^{-1} cm^{-1}) could be obtained only in the presence of small amounts of Cr^{2+} (1–5% of the amount of cobalt), or after a treatment of the cobalt solutions with Zn/Hg. Such behavior is indicative of the presence of the highly absorbing cobalt–oxygen species, similar to the case of $L^1CoO_2^{2+}$. Deliberate addition of O_2 to solutions of L^2Co^{2+} causes an immediate increase in absorbance throughout the range monitored (260–600 nm). The change in the spectrum is most dramatic at λ < 340 nm, Figure

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[24] (a) Adachi, H.; Basco, N.; James, D. G. L. *Int. J. Chem. Kinet.* **1979**, *11*, 1211. (b) Adachi, H.; Basco, N.; James, D. G. L. *Int. J. Chem. Kinet.* **1980**, *12*, 949. The idealized scheme requires that the alkoxy and hydroperoxy radicals, formed initially in the self-reactions of RO_2 radicals, also disappear in reactions not involving L^2Co^{2+}.

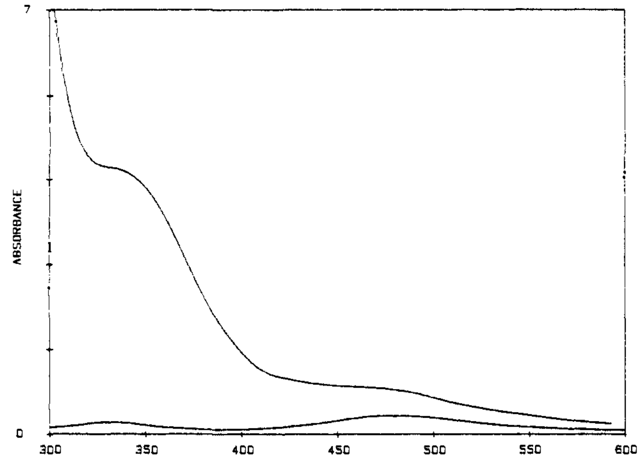

Figure 2. UV-visible spectrum (1-cm cell) of 4.0 × 10^{-4} M L^2Co^{2+} in a solution saturated with argon (lower) and oxygen (upper).

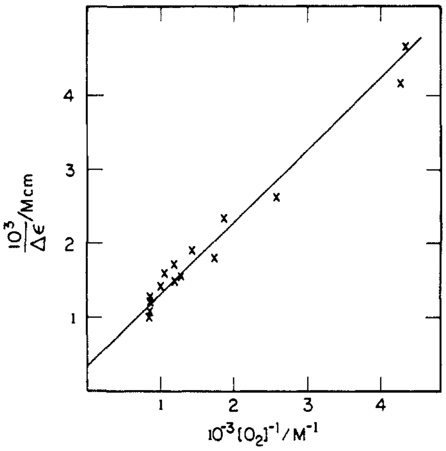

Figure 3. Plot according to eq 11 for the reaction of L^2Co^{2+} with O_2.

2. The reaction responsible for these observations, see later, is shown in eq 1-2. The equilibrium constant $K_{1\text{-}2}$ was determined

$$L^2Co^{2+} + O_2 \rightleftarrows L^2CoO_2^{2+} \qquad (1\text{-}2)$$

spectrophotometrically at 360 nm by recording the absorbance of solutions containing different initial concentrations of L^2Co^{2+} and O_2. The data were fitted to eq 11, where $\Delta\epsilon$ stands for the

$$\Delta\epsilon = \frac{K_{1\text{-}2}\Delta\epsilon_0[O_2]_{eq}}{1 + K_{1\text{-}2}[O_2]_{eq}} \qquad (11)$$

difference between the molar absorptivities of the equilibrated solutions and that of L^2Co^{2+}, $\Delta\epsilon_0$ is the difference between the molar absorptivities of $L^2CoO_2^{2+}$ and L^2Co^{2+}, and $[O_2]_{eq}$ is the equilibrium concentration of O_2. Figure 3 shows a plot according to the reciprocal of eq 11, which yields $K_{1\text{-}2}$ = 370 ± 120 M^{-1} and $\epsilon_{360}(L^2CoO_2^{2+})$ 2800 ± 700 M^{-1} cm^{-1}. The rather large errors reflect the fact that the equilibrium constant is small, such that under the experimental conditions ($[O_2]$ = 0 - 1.26 mM) only 0-28% of cobalt is present in the $L^2CoO_2^{2+}$ form.

The behavior of $L^2CoCH_3^{2+}$ (0.2 mM) in laser-flash photolysis experiments was qualitatively the same as that of $L^1CoCH_3^{2+}$, i.e., the absorbance did not change measurably at 360 nm during the flash, but it increased in a subsequent first-order reaction if oxygen was present. The absorbance changes were, however, smaller than in the L^1Co^{2+} reactions, mainly because only a fraction of L^2Co^{2+}, produced in the flash, reacted with oxygen, as determined by the low value of the equilibrium constant $K_{1\text{-}2}$. Consequently, the size and quality of the signals decreased significantly as the concentration of oxygen was lowered in the kinetic experiments. In oxygen-saturated solutions, where the signal was acceptably large, we obtain k_{obs} = 2.4 × 10^4 s^{-1} ($[L^2Co^{2+}]_0$ = 5 μM). A drastic increase in the initial concentration of $L^2CoCH_3^{2+}$, which would result in a corresponding increase in $[L^2Co^{2+}]$, and thus the kinetic signal, had to be avoided to prevent the equivalent of eq 5 from setting in.

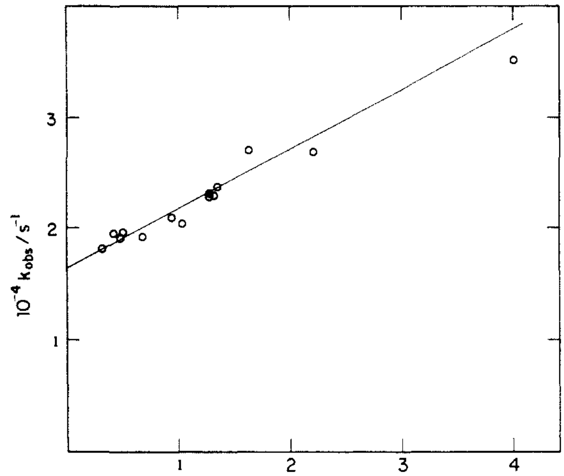

Figure 4. Plot of k_{obs} against the sum of the concentrations according to eq 12 for the reaction of L^2Co^{2+} with O_2.

Table I. Summary of Kinetic and Equilibrium Constants for the Oxygenation of Cobalt(II) Macrocycles[a]

reaction	k_f/M^{-1} s^{-1}	k_r/s^{-1}	K/M^{-1}
$L^1Co^{2+} + O_2 \rightleftarrows L^1CoO_2^{2+}$	1.18 (3) × 10^7	63 (6)[b,c]	2 × 10^5
$L^2Co^{2+} + O_2 \rightleftarrows L^2CoO_2^{2+}$	5.00 (47) × 10^6	1.66 (5) × 10^4	301 (40)
$L^1CoO_2^{2+} + L^1Co^{2+} \rightleftarrows (L^1Co)_2O_2^{4+}$	4.9 × 10^5[b,d]	0.6 (1)[b,c]	8 × 10^5[b]
$L^2CoO_2^{2+} + L^2Co^{2+} \rightleftarrows (L^2Co)_2O_2^{4+}$	e	e	<10^3

[a] Aqueous solution, 25 °C, pH 1-7, μ = 0.001-0.1 M ($HClO_4$ + $LiClO_4$). Values in parentheses represent 1 standard deviation of the last digit. [b] Reference 9. [c] μ = 1.0 M. [d] μ = 0.1 M; [e] No reaction observed.

The flash photolysis of $L^2CoO_2^{2+}$ turned out to be a superior method for the generation of L^2Co^{2+} for the kinetic determinations. Oxygen-containing solutions of L^2Co^{2+} are quite photosensitive, such that significant amounts of L^2Co^{2+} (5-25 μM) are formed in a flash under typical conditions ($[L^2Co^{2+}]_0$ = 0.1-0.3 mM, $[O_2]$ = 0.25-1.26 mM). The decrease in absorbance at 360 nm during the flash is followed by an absorbance increase to the exact preflash value. The kinetics of this reequilibration process, eq 1-2, were determined as a function of concentrations of O_2 and L^2Co^{2+}. In oxygen-saturated solutions the rate constant agrees well with that determined by use of $L^2CoCH_3^{2+}$ as a source of L^2Co^{2+}, k = 2.3 × 10^4 s^{-1} at $[L^2Co^{2+}]_{eq}$ = 0.1 mM. In many of the kinetic experiments the concentrations of O_2 and L^2Co^{2+} were comparable, such that eq 12 defines the rate constant for the approach to

$$k_{obs} = k_{1\text{-}2}([O_2]_{eq} + [L^2Co^{2+}]_{eq}) + k_{-(1\text{-}2)} \qquad (12)$$

equilibrium. A plot according to eq 12 is shown in Figure 4 and yields $k_{1\text{-}2}$ = 5.00 (±0.47) × 10^6 M^{-1} s^{-1} and $k_{-(1\text{-}2)}$ = 1.66 (±0.05) × 10^4 s^{-1}. The ratio of the two rate constants yields $K_{1\text{-}2}$ = 301 ± 40 M^{-1}. Within the error this value is the same as that determined from the equilibrium measurements, $K_{1\text{-}2}$ = 370 ± 120 M^{-1}. This finding strongly supports our contention that the same reaction, eq 1-2, is involved in the two types of experiments. The implication is that $L^2CoO_2^{2+}$, formed on a microsecond time scale, does not react with L^2Co^{2+} to form measurable amounts of $(L^2Co)_2O_2^{4+}$ in 5-30 s, the time frame of individual equilibrium measurements. This conclusion is also supported by the fact that the final absorbance readings in the kinetic experiments were constant in the presence of large amounts of unoxygenated L^2Co^{2+} for at least a second, the time limit imposed by our flash photolysis instrument. Apparently the equilibrium and/or rate constant for

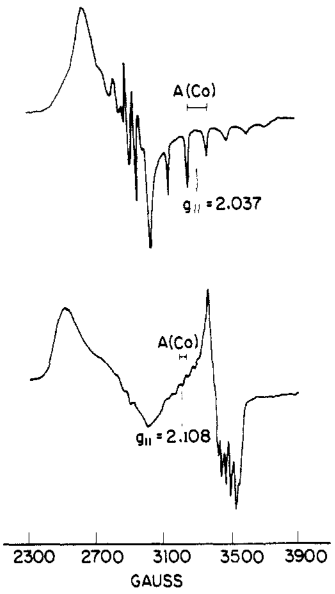

Figure 5. ESR spectra of L^2Co^{2+} (upper) and $L^2CoO_2^{2+}$ (lower) in 1:1:0.1 $C_6H_5CH_3/CH_2Cl_2/(CH_3)_2CO$ at 120 K.

reaction 2 are immeasurably small for L^2Co^{2+} under our experimental conditions. The summary of all the kinetic and equilibrium data is given in Table I.

The ESR spectra of L^2Co^{2+} and $L^2CoO_2^{2+}$ are shown in Figure 5. The parameters for the unoxygenated complex are quite similar to those for other low-spin cobalt(II) complexes,[25-31] $g_\parallel = 2.037$, $g_\perp = 2.33$, $A_\parallel = 11.0 \times 10^{-3}$ cm^{-1}, $A_\perp = 3.84 \times 10^{-3}$ cm^{-1}. Upon oxygenation of the complex the ESR spectrum changes drastically: $g_\parallel = 2.108$, $g_\perp = 1.96$, $A_\parallel = 3.81 \times 10^{-3}$ cm^{-1}, $A_\perp = 2.94 \times 10^{-3}$ cm^{-1}.[32] The parameters for the perpendicular region for both complexes are approximations owing to the incomplete spectral resolution. The ESR features of the oxygenated complex, $g_\parallel > g_\perp$, and the smaller $A_\parallel$ values relative to the unoxygenated complex, strongly suggest that the unpaired spin resides on the dioxygen and not on the cobalt.[5,26-33]

Discussion

The laser-flash photolysis of $LCoR^{2+}$ and $LCoO_2^{2+}$ yields the cobalt(II) complexes LCo^{2+} (L = L^1 and L^2), which react with O_2 to yield $LCoO_2^{2+}$. The photosensitivity of a number of alkylcobalt complexes, including those used in this work, has been well established.[16,23,34] On the other hand, the studies on the photochemical cleavage of mononuclear superoxocobalt(III) complexes are quite limited.[35,36] A number of observations confirm that eq 9 correctly describes the chemistry involved. The spectral changes during and after the flash are consistent with reaction 9 followed by reaction 1, as already mentioned under Results. For a given cobalt macrocycle the photolysis of the alkylcobalt and of oxygenated solutions of cobalt(II) yields the same species, as shown by its kinetic behavior in the reactions with oxygen and Fe^{2+}. The known photochemistry[16,23,34] of the alkylcobalt complexes requires that this species be the cobalt(II).

It is quite reasonable that the two superoxocobalt complexes should undergo photohomolysis. They absorb in the visible even more strongly than the corresponding (photoactive) alkylcobalt complexes, and the cobalt-oxygen bond in $LCoO_2^{2+}$ is much more labile than the cobalt-alkyl bond in $LCoR^{2+}$ complexes. This is demonstrated by the values of the equilibrium constants K_1 for the reversible binding of O_2 to L^1Co^{2+} and L^2Co^{2+}, $\sim 10^5$ and 301 M^{-1}, respectively, and the corresponding equilibrium constant for reaction 13, $K_{13} \gg 10^{12}$ M^{-1}. The latter was calculated from the

$$L^1Co^{2+} + CH_3^\bullet \rightleftarrows L^1CoCH_3^{2+} \qquad (13)$$

known rate constant for the capture of the radical ($k_{13} = 1.6 \times 10^7$ M^{-1} s^{-1}),[16] and by setting an upper limit of $\ll 8 \times 10^{-6}$ s^{-1} ($t_{1/2} \gg 1$ day) for the homolysis rate constant k_{-13}.

The kinetics of reaction 1-1 have been studied earlier by a stopped-flow technique under a limited set of conditions. The rate constant reported, 5.0×10^5 M^{-1} s^{-1}, is significantly smaller than the value determined in this work, 1.18×10^7 M^{-1} s^{-1}. The source of the discrepancy may lie in the fact that in the previous work[9] the data had to be collected under the conditions where all four reactions of eqs 1 and 2 contributed to the overall kinetics. Consequently, a complicated treatment of data was employed[9] to extract the values of the individual rate constants.

We discard the possibility that the species involved and/or the reactions studied were different in the two papers. The same isomer of the cobalt(II) complex should be involved, since we obtained identical results irrespective of which precursor of cobalt(II) we used, L^1CoR^{2+} or $L^1CoO_2^{2+}$. The former is known to have the macrocycle in the *R,R,S,S* configuration,[17,37] and the latter presumably does too, since it was produced immediately before the reaction from (*R,R,S,S*)-Co([14]aneN_4)$(H_2O)_2^{2+}$,[38] the same isomer that was used in the earlier stopped-flow work.

Reaction 1 is in many ways reminiscent of the reactions of cobalt(II) complexes with carbon-centered radicals, eq 14. Both

$$LCo^{II} + R^\bullet \rightleftarrows LCoR \qquad (14)$$

reactions 1 and 14 in the forward direction formally result in one-electron oxidation of the cobalt center, although in neither case is the transfer of the electron from the cobalt complete.[5,39]

The rate constant $k_{1\text{-}1}$, 1.18×10^7 M^{-1} s^{-1}, is almost identical with the values for the reactions of L^1Co^{2+} with the methyl (1.6×10^7 M^{-1} s^{-1}) and ethyl (1.1×10^7 M^{-1} s^{-1}) radicals.[16] The similarity of the three rate constants suggests that the substitution of coordinated water at the cobalt center takes place by dissociative activation, but the data are too limited to distinguish between a D and an I_D mechanism. Interestingly, Cr^{2+} also has comparable rate constants for the reaction with O_2 (1.6×10^8 M^{-1} s^{-1})[40] and with primary alkyl radicals, $k = (1-2) \times 10^8$ M^{-1} s^{-1}.[16] The radicals that are sterically more demanding have somewhat smaller rate constants.[41]

Steric effects of both the macrocycle and the alkyl group have a crucial influence on the magnitude of the equilibrium constant K_{14}.[42,43] Similarly, the methylation of the macrocycle L^1 causes

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(42) Bakac, A.; Espenson, J. H. *Inorg. Chem.* **1987**, *26*, 4305, and references therein. The importance of the steric effect of the alkyl groups has also been demonstrated in the study of the homolysis of a series of organochromium complexes.[43]

a ~300-fold decrease in the equilibrium constant for the binding of dioxygen. This is determined mainly by the ready homolysis of the oxygen adduct of the ligand-methylated complex, $L^2CoO_2^{2+}$ ($k_{-(1-2)} = 1.66 \times 10^4$ s^{-1}). Also, the rate constant for oxygen uptake by L^2Co^{2+}, $k_{1-2} = 5.0 \times 10^6$ M^{-1} s^{-1}, is smaller than the rate constants for the capture of akyl radicals by the same complex, $k = (3-5) \times 10^7$ M^{-1} s^{-1}.[16] The low affinity for oxygen thus seems to be reflected, although to a lesser extent, in the kinetics of the forward reaction as well.

The macrocycle-bound methyl groups exert both steric and electronic influence on the equilibrium constant K_{1-2}. There is little doubt that sterically the methyl groups will hinder the binding of oxygen. Since the reaction involves at least partial electron transfer to oxygen, the reduction potentials of the $Co^{III/II}$ couples, 0.42 V for $L^1Co^{3+/2+}$ [9] and 0.59 V for $L^2Co^{3+/2+}$,[44] work in the same direction. The potential of the ligand-methylated complex is higher than that of $L^1Co^{3+/2+}$, implying that the effect of methylation is again primarily a steric one and that LCo^{3+} is more destabilized relative to LCo^{2+} in the sterically more congested complex. The crystal structure data are not available to find out whether the congestion around the cobalt in L^2Co^{3+} is severe enough to cause an elongation of the axial $Co-OH_2$ bonds, in which case the axial bond-length changes would be expected to be smaller upon reduction of L^2Co^{3+} than L^1Co^{3+}.

The equilibrium constant K_2 has also decreased drastically from 8.6×10^5 M^{-1} ($L = L^1$) to $<10^3$ M^{-1} ($L = L^2$). The latter estimate is based on the assumption that the conversion of <10% of total $L^2CoO_2^{2+}$ (typically 50 μM) to $(L^2Co)_2O_2^{4+}$ would have caused an observable absorbance change at 360 nm in <1 s. The effect of ligand methylation on the value of K_2 is probably a cumulative one. Molecular models show that the approach of L^2Co^{2+} to the terminal oxygen of $L^2CoO_2^{2+}$ is made difficult by the macrocycle-bound methyl groups, at least for some orientations. In addition, the higher reduction potential of $L^2Co^{3+/2+}$ relative to $L^1Co^{3+/2+}$ will also result in a smaller value of K_2 for the formation of $(L^2Co)_2O_2^{4+}$.

The size of the effect of ligand methylation on the equilibrium constants becomes quite apparent if one compares the composition of oxygen-saturated 0.1 mM solutions of the two cobalt complexes. For $L = L^1$, 60% of the cobalt is present as $L^1CoO_2^{2+}$ and 40% as $(L^1Co)_2O_2^{4+}$; less than 0.5% contains no oxygen. For $L = L^2$, 28% is present as $L^2CoO_2^{2+}$, and 72% does not contain oxygen. The reaction of L^2Co^{2+} with O_2 is fully described by eq 1, and the binuclear peroxo complex is not formed to a measurable extent. This makes the L^2Co^{2+} a clean oxygen carrier on short time scales (minutes). At longer times both L^1Co^{2+} and L^2Co^{2+} are irreversibly oxidized by oxygen.

It has been noticed earlier[6,9] that reaction 15 has an unusually high equilibrium constant of 5×10^{13} M^{-1}. This value was

$$L^1Co^{3+} + O_2^- \rightleftarrows L^1CoO_2^{2+} \tag{15}$$

calculated from the equilibrium constant K_{1-1} and the reduction potentials for the couples O_2/O_2^- and $L^1Co^{3+/2+}$. Although our new value for k_{1-1} changes K_{1-1} to 2×10^5 M^{-1} and K_{15} to 1×10^{15} M^{-1}, this does not change the original argument, except perhaps to reinforce it. We note that a very similar situation occurs for L^2Co^{3+} as well. The equilibrium constant for the reaction $L^2Co^{3+} + O_2^- \rightleftarrows L^2CoO_2^{2+}$ has a value of 2×10^{15} M^{-1}, implying that this complex is also strongly stabilized by charge transfer.[6]

Acknowledgment. This work was supported by the U.S. Department of Energy, Chemical Sciences Division, under Contract W-7405-Eng-82. We are grateful to Dr. S. Lee for the synthesis of the macrocyclic ligand and to Dr. V. Rutar for his help with the ESR experiments.

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Synthesis of Porous Quantum-Size CdS Membranes: Photoluminescence Phase Shift and Demodulation Measurements

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Abstract: Optically transparent CdS membranes have been synthesized. Colloidal Q-CdS particles (particle diameter $d_p <$ 40 Å) carrying short phosphate chains and excess Cd^{2+} ions have been directly converted into a microporous membrane form. By controlling ionic strength and particle concentrations, one can link self-organized fusion-free aggregates and avoid formation of powder-like flocculation products. The resultant unsupported membranes exhibit different mechanical properties (e.g., rigidity, delayed elasticity, and solubility) in the presence of water depending upon the preparation method employed. The membrane form of CdS has distinctively different photophysical properties than the precursor colloidal form. Conversion of weakly red luminescent colloids (broad band at 700 nm) into membranes activated an intense room temperature band edge luminescence (BEL) (narrow bands between 450 and 500 nm) attributed to the recombination of excitons and/or shallowly trapped electron/hole pairs. A specific solvent effect has been observed indicating the major role of water and the related acid-base chemistry in producing radiationless recombination centers at the particle surface. In membrane/solvent experiments, water was found to be a very efficient quencher of the emission while alcohols and acetonitrile did not induce any changes in luminescence properties. A novel Multi-Harmonic Fourier Transform (MHFT) technique was used to determine the average lifetimes of the BEL decay process (≈10 ns in the colloidal form and ≈70 ns in the corresponding membrane form). Simultaneously detected (multiple-frequency domain) phase/modulation data have been used to describe the complex BEL decay, and a three-exponential law best fits the data.

Several recent reports have characterized the photocatalytic and optical properties of large surface area semiconductors.[1-6] One of the main findings is that in polymolecular dispersed metal chalcogenides and metal oxides these properties depend on particle size. Such materials are referred to as Q-materials (Q: showing quantum mechanical effect of exciton confinement).[7] A char-

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