the reduced chelate effect in pydpt is reflected in its lability toward ligand exchange as previously noted.

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Registry No. $[Co(tetren)Cl]^{2+}$, 33847-43-7; $[Co(epyden)Cl]ZnCl_4$, 71462-56-1; $[Co(pydien)Cl]^{2+}$, 71462-57-2; $[Co(pydpt)Cl]^{2+}$, 71462-58-3; $[Co(imdien)Cl]^{2+}$, 71462-59-4; $[Co(imdpt)Cl]^{2+}$, 71462-60-7; $[Co(tetren)O_2Co(tetren)](ClO_4)_4$, 36502-66-6; $[Co(epyden)O_2Co(epyden)](ClO_4)_4$, 71462-61-8; $[Co(pydien)O_2Co(pydien)](ClO_4)_4$, 71462-63-0; $[Co(pydpt)O_2Co(pydpt)](ClO_4)_4$, 71485-78-4; $[Co(imdien)O_2Co(imdien)](ClO_4)_4$, 71462-64-1; $[Co(imdpt)O_2Co(imdpt)](ClO_4)_4$, 71462-65-2; $[Co(epyden)O_2Co(epyden)]^{5+}$, 71582-21-3.

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Electrochemical Investigation of a Series of Peroxo-Bridged Binuclear Cobalt Complexes

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Peak potentials have been measured for the oxidation of a series of cobalt(II) complexes of the following polyamines or amino acids: tetraethylenepentamine, 1,9-bis(4-imidazolyl)-2,5,8-triazanonane, 2,6-bis[5-(1,4-diazahexyl)]pyridine, 1,9-bis(2-pyridyl)-2,5,8-triazanonane, 1,11-bis(2-pyridyl)-2,6,10-triazaundecane, 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane, 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane. The peak potentials of the cobalt(II) complexes show a linear correlation with the logarithms of the equilibrium constants for the formation of the corresponding dioxygen complexes. Peak potentials were also measured for the reduction of a series of cobalt(III) complexes in which the metal was coordinated to the ligands triethylenetetramine, ethylenediamine-*N*,*N*′-diacetic acid, *N*,*N*-bis(2-aminoethyl)glycine, diethylenetriamine, ethylenediamine, and glycylhistidine. The cobalt(II) complexes of all of these ligands form either μ-peroxo or μ-peroxo-μ-hydroxo binuclear dioxygen complexes. The cobalt(III) → cobalt(II) peak potentials show a linear correlation with the logarithms of the oxygenation constants. The peak potentials of the dioxygen complexes are very similar to those observed for the corresponding cobaltous complexes and also display a linear correlation with the logarithms of the oxygenation constants. Cyclic voltammetry was employed to determine peak potentials for the oxidation of the μ-peroxo complexes to the corresponding superoxides. The values of the redox potentials are interpreted in terms of the nature of the metal–dioxygen bonding in cobalt–dioxygen complexes and the concept of charge transfer from cobalt(II) to dioxygen on oxygenation.

Introduction

The prominent role of metalloproteins in the biological transport and utilization of molecular oxygen has created considerable interest in the fundamental properties of metal–dioxygen complexes. Although natural systems appear to employ copper and iron exclusively for these functions, a great deal of useful information has been obtained from the study of cobalt complexes as models for biological systems.[2,3] Although much progress has been made toward understanding the kinetics[4–7] and thermodynamics[8–13] of reversible oxygenation reactions of cobalt as well as the structural[14–18] and spectroscopic[19–23] properties of the dioxygen complexes, the redox properties of these complexes have received much less study. Some papers have dealt with the chemical reduction of both peroxo and superoxo complexes by various metal ions, e.g., Cr^{2+} and Fe^{2+},[24–28] but few electrochemical data are available on the reduction potentials of peroxo-bridged cobalt complexes.

Carter et al. have measured the cobalt(II) → cobalt(III) oxidation potentials of several Co(L)B complexes, where L is either a porphyrin or a tetradentate Schiff base and B is a suitable axial base.[29] Such complexes form mononuclear 1:1 dioxygen complexes in aprotic solvents, and there is a linear correlation between $E_{1/2}$ and the log of the oxygenation equilibrium constant. The present paper reports similar studies for a series of polyamino and polyaminopolycarboxylic acid

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complexes that react with dioxygen to form either μ-peroxo or μ-peroxo-μ-hydroxo binuclear dioxygen complexes.

In addition to the study of the unoxygenated cobalt(II) chelates, polarographic and cyclic voltammetry data are also reported on the dioxygen complexes themselves. Previously, the only detailed reports on the electrochemistry of dioxygen complexes were two papers by Vlcek,[30,31] one of which dealt with the pentacyano–cobalt(II) system at high pH, while the other reported polarographic data on several polyamine complexes containing up to three bridging groups. A small amount of polarographic data on some amino acid–cobalt–dioxygen complexes was also reported by Munakata.[32] However, the present paper contains by far the most extensive collection of redox potentials of cobalt–dioxygen complexes yet reported and includes data for a wide variety of nonbridging ligands.

Experimental Section

Stock metal solutions were prepared from reagent grade cobaltous nitrate and standardized by titration with EDTA. Ethylenediamine (en), diethylenetriamine (dien), triethylenetetramine (trien), and glycyl-L-histidine (gly-his) as hydrochloride salts and ethylenediamine-*N*,*N*′-diacetic acid (EDDA) were obtained commercially, and their purities were confirmed by titration with standardized carbonate-free KOH. 1,10-Phenanthroline and 2,2′,2″-terpyridine were purchased and used as received.

The ligands *N*,*N*′-diglycylethylenediamine-*N*″,*N*‴-tetraacetic acid (DGENTA), *N*,*N*-bis(2-aminoethyl)glycine (DTMA), 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (4-IMDPT), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (4-IMDIEN), 1,11-bis(2-imidazolyl)-2,6,10-triazaundecane (2-IMDPT), 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN), 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT), and 2,6-bis[5-(1,4-diazahexyl)]pyridine (EPYDEN) were prepared in these laboratories according to published procedures.[33-36]

Tetraethylenepentamine (TEP) was purchased as the free base, distilled under vacuum, and isolated as the sulfate salt. The salt was then recrystallized from water by slow addition of methanol and tested for purity by titration with KOH.

Apparatus. Both sampled dc and differential pulse polarograms were recorded on a Princeton Applied Research Model 174 polarographic analyzer equipped with saturated calomel, platinum wire, and dropping mercury electrodes. The modulation amplitude and drop time were set at 50 mV and 1 s for all samples. The scan rates used were 2 and 5 mV/s. Measurements were made at room temperature with 0.10 M KNO_3 as supporting electrolyte, and solutions were kept under a blanket of flowing nitrogen during the measurements. The potentials were determined as the peak positions in the differential pulse polarograms and are reported vs. the saturated calomel electrode.

Cyclic voltammograms were recorded on an instrument constructed by R. Bess. Measurements were made on 5 mM samples in 0.10 M KNO_3 at room temperature with saturated calomel and platinum wire electrodes.

Analytical Potentiometry. $[(NH_3)_{10}Co_2\text{-}\mu\text{-}O_2](SO_4)_2$, $[(NH_3)_8Co_2\text{-}\mu\text{-}(O_2,NH_2)](NO_3)_4$, $[(CN)_{10}Co_2\text{-}\mu\text{-}O_2]K_6$, $[(NH_3)_{10}Co_2\text{-}\mu\text{-}O_2](NO_3)_5$, $[(NH_3)_8Co_2\text{-}\mu\text{-}(O_2,NH_2)](NO_3)_3$, and $[(CN)_{10}Co_2\text{-}\mu\text{-}O_2]K_5$ were prepared and purified by standard procedures. Potentiometric measurements were made on a Beckman Model 4500 pH meter fitted with platinum and calomel electrodes and standardized by using $Fe(CN)^{3-,4-}$ and $Co(phen)_3{}^{3+,2+}$ couples. Solid samples of the oxidized (superoxo) and reduced (peroxo) form of each complex were weighed out, dissolved in acid (superoxo) and base (peroxo), and mixed (to a final neutral pH) in a light-free thermostated cell. Potentials stabilized in 2–3 min, after which a very slow drift, due to decomposition of the superoxo species, became evident. Reported potentials are corrected for this drift. The $E°$ values were calculated from concentrations of [Ox] and [Red] by using E_m and the Nernst equation.

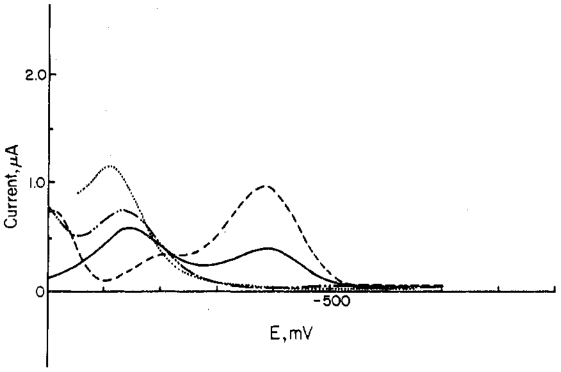

Figure 1. Differential pulse polarograms of cobaltous polyamine complexes in 0.10 M KNO_3 at 25 °C: (—) TEP, (···) 2-IMDPT, (-··-) PYDPT, (---) EPYDEN. $T_L = T_{Co} = 1.2 \times 10^{-3}$ M.

Sample Preparation. Solutions of cobaltous chelates were prepared in the polarographic cell by first dissolving ~0.04 mmol of the ligand and 5 mmol of KNO_3 in water, adding an amount of KOH equivalent to the sum of all dissociable ligand protons, and diluting to 50 mL. This solution was thoroughly degassed with nitrogen, followed by addition of sufficient 0.02 M cobaltous nitrate to obtain a 1:1 molar ratio of ligand to metal. Actual sample concentrations varied from 0.5 to 1.2 mM. The cobalt solution was separately deaerated prior to mixing, so that the sample solution was oxygen free, and was again deaerated at the potentiometric end point. Thus it contained no appreciable concentrations of either protonated or hydrolyzed chelates or free metal ion. Occasional contamination by oxygen was easily detected due to the immediate formation of the brown dioxygen complex.

Cobaltic complexes were prepared by first oxidizing the hexaaquocobaltous complex with sodium peroxide. The resulting cobaltic hydroxide was separated and washed by repeated centrifugation and decantation and was then added to a solution of the hydrochloride salt of the appropriate ligand. Acid or base was added as needed either to protonate any remaining coordinated hydroxide groups or to neutralize any excess protons released into solution as a result of complexation. The complex was then isolated and purified by recrystallization. For polarographic analysis the purified complexes were redissolved in oxygen-free 0.10 M KNO_3.

Solutions of the dioxygen complexes were prepared by methods similar to the two described above. In one case, ligand, cobalt(II), and KOH were added in the appropriate stoichiometric ratios to a 0.10 M KNO_3 solution in the sample cell and oxygen was passed through the solution to completely form the dioxygen complex. This solution was then degassed with nitrogen and the polarogram was recorded immediately. Because of the fairly high pH (5–9), the oxygenation reaction was sufficiently irreversible to the removal of free oxygen that no appreciable dissociation of the complex occurred during the course of the measurement, as evidenced by the lack of a reduction peak around −0.1 V corresponding to the reaction $O_2 + 2H^+ \rightarrow H_2O_2$.

The superoxo complexes and some of the peroxo complexes were prepared and isolated as the perchlorate salts in accordance with published procedures.[37,38] About 10–20 mg of these salts was then dissolved in oxygen-free 0.10 M KNO_3 for immediate electrochemical analyses ([CoL] ≃ 3 mM). The superoxide solutions were adjusted to pH 1–2 to prolong the lifetime of these species in solution.

Results

The differential pulse polarograms of the cobaltous chelates all contain peaks in the −100 to −500 mV region and in the −1300 to −1500 mV region. Sample dc polarograms indicate that these peaks correspond to oxidation at the higher potential and reduction at the lower potential, and thus they are assigned

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Table I. Peak Potentials for the Oxidation of Cobaltous Chelates and Their Oxygenation Constants

ligand	formula	E_p, mV	log $K_{O_2}{}^a$	ref
TEP	CoL^{2+}	−400	15.83	35
4-IMDIEN	CoL^{2+}	−420	12.57	36
EPYDEN	CoL^{2+}	−410	14.66	35
PYDIEN	CoL^{2+}	−310	11.36	35
PYDPT	CoL^{2+}	−130	7.7	35
4-IMDPT	CoL^{2+}	−240	9.44	36
2-IMDPT	CoL^{2+}	−150	8.28	36
(histidine)$_2$	CoL_2	−30^b	6.5	42
(DAP)$_2$	CoL_2	−150^b	8.9	41

^{a} $K_{O_2} = [Co_2L_2O_2]/[CoL]^2[O_2]$. ^{b} Potentials from ref 32.

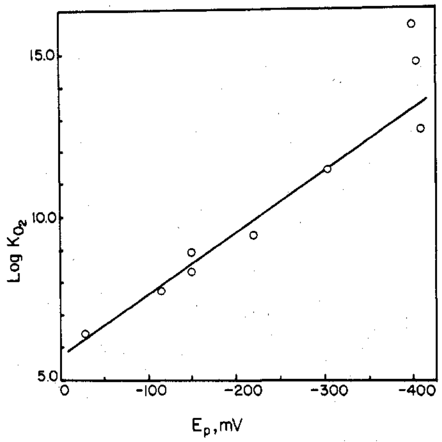

Figure 2. Co(II) → Co(III) peak potentials vs. the logarithms of the oxygenation constants for cobaltous chelates that form μ-peroxo-dioxygen complexes.

to $Co^{2+} \rightarrow Co^{3+}$ and $Co^{2+} \rightarrow Co^0$. Typical differential pulse polarograms in the 0 to −700 mV range are shown in Figure 1. In some systems there is a second oxidation wave around −150 mV, and in the 4-IMDIEN and 4-IMDPT systems this higher potential peak is by far the largest peak in the polarogram. Since the pH has been adjusted so as to eliminate any protonated or hydrolyzed chelates, it is not clear what reaction is responsible for this peak. It is possible that there is some direct interaction with the Hg electrode, since the potential of this peak does not appear to shift appreciably from system to system and since, in some cases, the intensity of the signal is unreasonably high to be assigned to a simple oxidation of a cobalt species in solution.

The observed cobalt(II) → cobalt(III) peak potentials are listed in Table I, along with the corresponding log K_{O_2} values from the literature. Plots of E_{dme} vs. log $[i/(i_d - i)]$ for these waves (where i is the current at the potential E_{dme} and i_d is the diffusion current) are linear with slopes of about 90 mV, indicating a quasi-reversible one-electron oxidation.[39] The relationship between peak potential and log K_{O_2} is shown in Figure 2. The Pearson correlation coefficient for these data is 0.944.[40]

Polarograms have also been recorded for a series of cobalt(III) complexes of ter- and tetradentate ligands. As expected, the only qualitative difference between these results and the polarograms of the cobaltous complexes is a shift from negative to positive current for the peak in the −300-mV region, corresponding to the reduction $Co^{3+} \rightarrow Co^{2+}$.

Table II. Peak Potentials for the Reduction of Co(III) Chelates and the Oxygenation Constants of the Corresponding Co(II) Chelate

ligand	complex	E_p, mV	log $K_{O_2}{}^{a,b}$
trien, L	CoL^{3+}	−420	7.0
EDDA, H_2L	CoL^+	−200	−4.0
DTMA, HL	CoL^{2+}	−350	2.6
dien, L	CoL^{3+}	−310	1.1
en, L	$CoL_2{}^{3+}$	−470	10.8
gly-his, HL	$Co(H_{-1}L)^+$	−340	1.0^c

^{a} Values from ref 2a. ^{b} $K_{O_2}{}^{OH} = [Co_2L_2O_2(OH)][H^+]/[CoL]^2[O_2]$ or $[Co_2L_4O_2(OH)][H^+]/[CoL_2]^2[O_2]$. ^{c} $K_{O_2}{}^{OH} = [Co_2(H_{-1}L)_2O_2(OH)][H^+]/[CoH_{-1}L]^2[O_2]$.

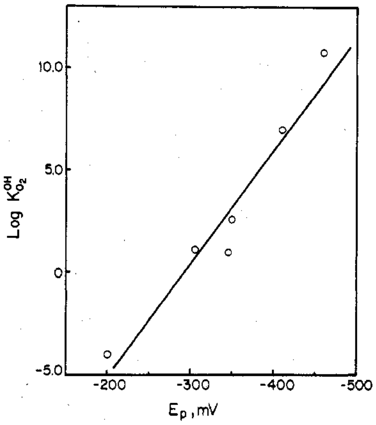

Figure 3. Co(III) → Co(II) peak potentials vs. log $K_{O_2}{}^{OH}$ for a series of cobaltous chelates that form μ-peroxo-μ-hydroxo–dioxygen complexes.

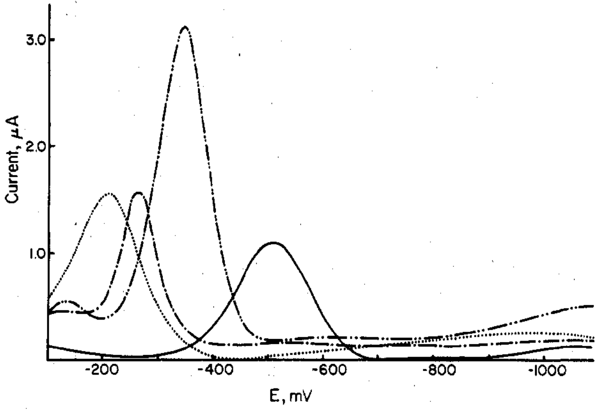

Figure 4. Differential pulse polarograms of a series of μ-peroxo-monobridged cobalt–dioxygen complexes in 0.10 M KNO_3 at 25 °C: (—) TEP, (···) 4-IMDPT, (-·-) PYDPT, $T_L = T_{Co}$ = 0.5 mM; (-··-) PYDIEN, $T_L = T_{Co}$ = 1.2 mM.

Because of the cis aquated coordination sites in the cobaltous complexes of these ligands, oxygenation of these species forms dibridged μ-peroxo-μ-hydroxo complexes. The equilibrium constant for this reaction is formulated as

$$2CoL + O_2 \xrightleftharpoons{K_{O_2}{}^{OH}} Co_2L_2(O_2)(OH) + H^+ \qquad (1)$$

$$K_{O_2}{}^{OH} = [Co_2L_2O_2(OH)][H^+]/[CoL]^2[O_2]$$

The observed values of the cobaltic → cobaltous peak potentials and the corresponding log $K_{O_2}{}^{OH}$ values from the literature are listed in Table II. The correlation between these parameters is shown in Figure 3, with a Pearson r for these data of 0.980.

Differential pulse polarograms of the cobalt–dioxygen complexes contain a set of three peaks in almost all cases.

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Table III. Peak Potentials for a Series of μ-Peroxo and μ-Peroxo-μ-hydroxo Complexes and the Shift in Potential from That of the Corresponding Unoxygenated Chelates

ligand	complex	E_p, mV	Δ, mV
	μ-Peroxo Complexes		
TEP, L	$Co_2L_2O_2^{4+}$	−490	−90
4-IMDIEN, L	$Co_2L_2O_2^{4+}$	−390	−10
EPYDEN, L	$Co_2L_2O_2^{4+}$	−410	0
PYDIEN, L	$Co_2L_2O_2^{4+}$	−340	−30
PYDPT, L	$Co_2L_2O_2^{4+}$	−240	−110
4-IMDPT, L	$Co_2L_2O_2^{4+}$	−210	+30
2-IMDPT, L	$Co_2L_2O_2^{4+}$	−180	−30
histidine, HL	$Co_2L_4O_2^{2+}$	−100[a]	
trpy, L, phen, L′	$Co_2L_2L'_2O_2^{4+}$	−190	
DGENTA, H_4L	$Co_2(H_{-2}L)_2O_2^{8-}$	−350	
$(NH_3)_5$, L	$Co_2L_2O_2^{4+}$	−280	
	μ-Peroxo-μ-hydroxo Complexes		
trien, L	$Co_2L_2(OH)O_2^{3+}$	−530	−110
DTMA, HL	$Co_2L_2(OH)O_2^{+}$	−370	−20
EDDA, H_2L	$Co_2L_2(OH)O_2^{-}$	−260	−60
dien, L	$Co_2L_2(OH)O_2^{3+}$	−430	−120
gly-his, HL	$Co_2(H_{-1}L)_2(OH)O_2^{-}$	−430	−90
	μ-Peroxo-μ-amido Complexes		
trien, L	$Co_2L_2(NH_2)O_2^{3+}$	−470	

[a] Reference 32.

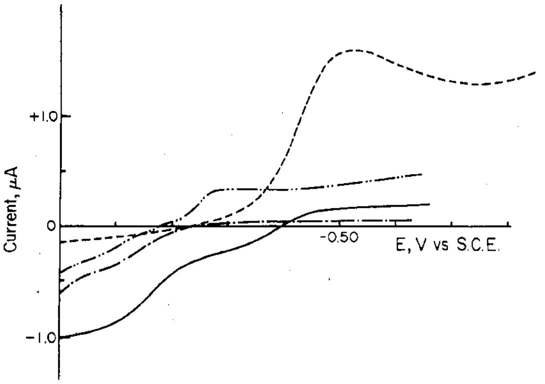

Figure 5. Sampled dc polarograms of solutions of cobaltous chelates of TEP and PYDPT prior and subsequent to the addition of oxygen to the solution: (—) TEP, (- - -) TEP + O_2, (–•–) PYDPT, (–••–) PYDPT + O_2.

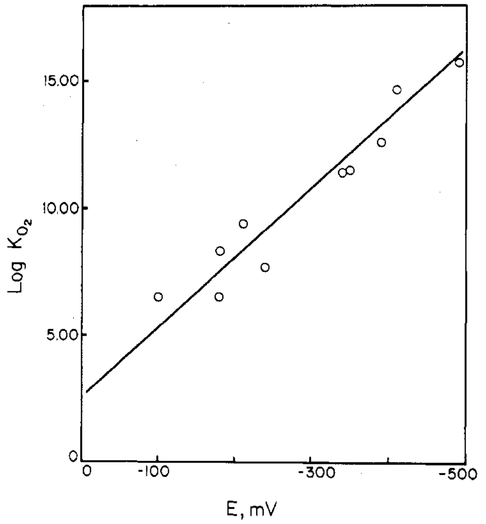

Figure 6. Plot of the cobalt(III) → cobalt(II) peak potentials vs. log K_{O_2} for a series of μ-peroxo-bridged cobalt–dioxygen complexes.

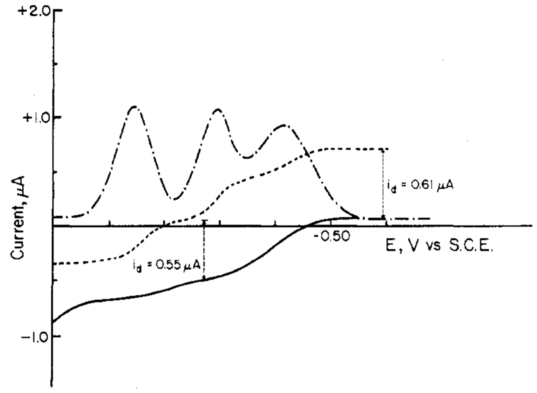

Figure 7. Sampled dc pulse polarogram of a solution of the cobaltous EPYDEN complex prior to the addition of molecular oxygen to the solution (–) and sampled dc (- - -) and differential (–•–) pulse polarograms subsequent to the addition of molecular oxygen to the solution. [Co(EPYDEN)] = 1.2×10^{-3} M.

There is a well-resolved reduction peak around −1400 mV which can be assigned to $Co^{2+} \rightarrow Co^0$. A second peak appears around −1000 mV which varies in height from system to system but which is always fairly small and poorly resolved. The potential and broad shape of this peak are both characteristic of $H_2O_2 \rightarrow H_2O$ reduction.

The third peak is in the −100 to −500 mV range, and typical differential pulse polarograms of this region are shown in Figure 4. Although this reduction peak is not electrochemically reversible, the potentials of these reduction peaks are very similar to the cobaltous → cobaltic oxidation potentials of the unoxygenated cobalt(II) complexes, as indicated by the small values of Δ in Table III, where $\Delta = E_p[Co_2L_2O_2] - E_p[CoL^{2+}]$. Although there is only a slight shift in the potential of this peak in going from the cobalt(II) to the dioxygen complex, there is a clear change from an oxidation in the cobalt(II) system to a reduction of the μ-peroxo complexes, as shown in Figure 5.

As expected, due to the small values of Δ, the peak potentials of the peroxo complexes also display a linear correlation with log K_{O_2}, as shown in Figure 6. The Pearson r for these data is 0.958.

Just as in the cobalt(II) systems, some of the polarograms of the μ-peroxo complexes have an unexpected oxidation peak around −150 mV. Although it is possible to oxidize these complexes by one electron to the corresponding superoxo complex, in view of the cyclic voltammetry data discussed below, the potential of this peak appears to be too cathodic to be assigned to such a reaction. The peak may be due to some direct interaction of the complex with the mercury electrode.

In the EPYDEN system there is a second sharp reduction peak at −300 mV, just anodic of the expected peak at −400 mV. The sampled dc and differential pulse polarograms of this complex are shown in Figure 7, along with the polarogram of the cobalt(II) solution recorded just before the addition of oxygen. The sum of the heights of the two reduction waves (0.61 μA) is equal to the height of the Co(II) → Co(III) oxidation wave recorded for the oxygen-free solution (0.55 μA). Thus the two reductions represent a total of one electron per cobalt atom. Since the reduction waves are of roughly equal heights, the stoichiometry of each reaction is one electron per $Co_2O_2L_2$ unit. Thus the μ-peroxo complex of EPYDEN appears to undergo two sequential one-electron reductions.

In order to obtain potentials for the oxidation of the μ-peroxo complexes to the corresponding superoxides, we have recorded cyclic voltammograms for several systems, using a platinum wire electrode in place of the dropping mercury electrode. A single oxidation wave is observed in the voltage range 0 to +1500 mV. With the exception of the 4-IMDIEN complex, this wave is very weak, and in all cases the oxidation is irreversible. The peak potentials obtained for the peroxo → su-

Table IV. Peak Potentials for the Oxidation of a Series of μ-Peroxo Complexes

complex	E_p, mV
$Co_2(PYDPT)_2O_2^{4+}$	+860
$Co_2(EPYDEN)_2O_2^{4+}$	+500
$Co_2(4\text{-}IMDIEN)_2O_2^{4+}$	+1390
$Co_2(NH_3)_{10}O_2^{4+}$	+840,[b] +316[a]
$Co_2(NH_3)_8O_2(NH_2)^{3+}$	+570,[b] +466[a]
$Co_2(NH_3)_6O_2(NH_2)(OH)^{2+}$	+166[a]
$Co_2(bpy)_4O_2NH_2^{3+}$	+1000[c]
$Co_2(CN)_{10}O_2^{6-}$	+60[d]

[a] Reference 31. [b] Determined by analytical potentiometry. [c] S. R. Cooper, University of California, Berkeley, private communication (measured in acetonitrile). [d] Reference 30.

peroxo couple are listed in Table IV, along with the other values presently in the literature.

Discussion

It has been often noted that there is a qualitative relationship between the oxidation potential of a metal complex and its tendency to undergo a reversible oxygenation reaction. Metals such as Cu(II), Ni(II), or Zn(II), which have very low oxidation potentials, do not readily react with molecular oxygen. At the other extreme, metal complexes of Mn(II), Fe(II), or Cu(I) tend to be irreversibly oxidized by oxygen, although the oxidation may well proceed via a short-lived μ-peroxo-bridged intermediate. Thus the rather unique ability of cobalt(II) complexes to react reversibly with molecular oxygen at room temperature and in a variety of solvents may be due, in part at least, to intermediate values of the oxidation potentials of its complexes.

The possible relationship between the oxidation potential of a cobaltous complex and its oxygenation constant was initially put to a quantitative test by Carter et al.[29] as part of their study on mononuclear dioxygen complexes. They observed a rough linear correlation between $E_{1/2}$ and log K_{O_2}. The results presented above provide similar relationships for the binuclear dioxygen complexes, both for the μ-peroxo and for the dibridged μ-peroxo-μ-hydroxo species. These correlations are consistent with the formulation of these complexes as cobalt(III) centers bridged by a formally reduced peroxide group. Although it is probably an oversimplification to assign integral oxidation states to the cobalt and dioxygen moieties, the vast majority of the physical data reported to date indicates that the oxygenation reaction does involve the transfer of a considerable amount of electron density from the cobalt centers to the half-filled π^* orbitals of dioxygen. Thus the ΔG of oxygenation should be related to the ability of the cobalt(II) complex to donate electron density to the dioxygen, and the oxidation potential is directly proportional to this ability.

It should be noted that the observed correlations do not mean that the free energy change associated with the removal of electron density from the cobalt is the only factor in determining the absolute magnitude of log K_{O_2}. Other factors such as the reduction potential of molecular oxygen, substitution of coordinated water by "peroxide" or hydroxide groups, and electron delocalization over the four-atom Co–O$_2$–Co system undoubtedly make important contributions to the total ΔG of oxygenation. What the correlations do indicate is that these additional factors make essentially constant or relatively small contributions to most cobalt–dioxygen complexes and that the parameter which varies most from complex to complex is the oxidation potential of the reactant cobalt(II) chelate.

From the small values of Δ shown in Table III, it is clear that the peak potentials of the dioxygen complexes are very close to those of the unoxygenated complexes. In addition, the sampled dc polarograms of the oxygen complexes have reduction waves with little if any anodic component. These results are consistent with a rather straightforward one-electron reduction of both metal centers to cobalt(II). The slightly negative values of Δ probably result primarily from the replacement of coordinated water by peroxide and hydroxide. Furthermore, the irreversibility and adsorption maxima associated with the reduction peaks of the dioxygen complexes introduce some uncertainty into the assignment of peak potentials, which adversely affects the precision of Δ.

The relative heights of the three reduction waves of the dioxygen complexes do not match the 1:1:2 ratio expected for reactions 2–4. Instead, the peroxide reduction wave is re-

$$2H^+ + Co_2L_2O_2^{4+} \xrightarrow{2e^-} 2CoL^{2+} + H_2O_2 \qquad (2)$$

$$2H^+ + H_2O_2 \xrightarrow{2e^-} 2H_2O \qquad (3)$$

$$2CoL^{2+} \xrightarrow{4e^-} Co^0 + 2L \qquad (4)$$

markedly reduced in height, with a related increase in the height of the cobalt(III) reduction wave. Very similar results were reported by Vlcek in his paper on polyammine–dioxygen complexes.[31] He proposed that the shift in peak height was due to rapid reoxidation of cobalt(II) by the hydrogen peroxide generated at the electrode. Similar results are observed in the polarograms of simple unoxygenated cobalt(III) salts in solutions containing hydrogen peroxide.[43]

The EPYDEN system is unique in that there appear to be two one-electron reductions at −300 and −400 mV. This raises the possibility that the Co–O$_2$–Co system may be reduced by one electron and remain intact. Sykes has detected an intermediate in the chromous reduction of $Co_2(en)_4(O_2)(NH_2)^{3+}$ which presumably contains an O_2H^- bridging group between cobalt and chromic ion, but this species has a half-life of only about 30 s.[44] The appearance of two separate EPYDEN reduction peaks implies a longer lived species under less favorable (more alkaline) conditions. An alternative explanation is that the initial reduction forms a cobalt(II) chelate and a stable mononuclear cobalt(III)–peroxo complex. Unfortunately, the data presented here are not sufficient to identify the product of the −300-mV reduction, and any discussion of these results must remain speculative pending further investigation.

The cyclic voltammograms of the peroxo complexes described above are of somewhat limited value due to the obvious irreversibility of the one-electron oxidation to the superoxo complexes. It has been observed during chemical syntheses of these superoxo species that they rapidly decompose in aqueous solution above pH 2. Since it is necessary to maintain the sample solutions above pH 4 to stabilize the initial peroxo complexes, the irreversibility of the cyclic voltammogram is probably due to the rapid acid-catalyzed decomposition of the superoxides. Vlcek was able to obtain reversible superoxo → peroxo reduction waves only for complexes containing two or three bridging groups, e.g., $Co_2(NH_3)_6(O_2)(NH_2)(OH)$.[31]

It should be noted that the results in Table IV for $Co_2(NH_3)_{10}O_2^{4+}$ and $Co_2(NH_3)_8O_2(NH_2)^{3+}$ differ appreciably from values reported by Vlcek. The values reported here were obtained by analytical potentiometry and are consistent with the reaction chemistry of the superoxo species (e.g., $Co_2(NH_3)_{10}O_2^{5+}$ will oxidize Fe^{2+} to Fe^{3+} ($E° = 0.7$ V)), whereas the Vlcek values are not. The different values reported by Vlcek may reflect the uncertainty in assigning potentials to an irreversible wave or may simply be a misassignment. In either case, there is little doubt that the present results are more nearly correct.

Unlike the cobaltic → cobaltous potentials, the peroxo → superoxo potentials do not correlate with log K_{O_2}. However,

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they may be sensitive to the relative π-bonding ability of the ligands, since the pyridyl- and imidazole-type ligands tend to form complexes which have higher peak potentials than the ammine complexes. Obviously additional data are needed to firmly establish such a trend.

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Registry No. $Co(TEP)^{2+}$, 64740-13-2; $Co(4\text{-}IMDIEN)^{2+}$, 71302-39-1; $Co(EPYDEN)^{2+}$, 64740-09-6; $Co(PYDIEN)^{2+}$, 64740-01-8; $Co(PYDPT)^{2+}$, 64740-05-2; $Co(4\text{-}IMDPT)^{2+}$, 71302-40-4; $Co(2\text{-}IMDPT)^{2+}$, 71302-41-5; $Co(trien)(OH_2)_2^{3+}$, 33865-40-6; $Co(EDDA)(OH_2)_2^{+}$, 55177-51-0; $Co(DTMA)(OH_2)_2^{2+}$, 71302-42-6; $Co(dien)(OH_2)_3^{3+}$, 25426-87-3; $Co(en)_2(OH_2)_2^{3+}$, 21247-59-6; $Co(gly\text{-}his)(OH_2)_2^{+}$, 71302-43-7; $Co_2(TEP)_2O_2^{4+}$, 71302-44-8; $Co_2(4\text{-}IMPIEN)_2O_2^{4+}$, 71302-45-9; $Co_2(EPYDEN)_2O_2^{4+}$, 71359-28-9; $Co_2(PYDIEN)_2O_2^{4+}$, 71328-32-0; $Co_2(PYDPT)_2O_2^{4+}$, 71328-33-1; $Co_2(4\text{-}IMDPT)_2O_2^{4+}$, 71302-46-0; $Co_2(2\text{-}IMDPT)_2O_2^{4+}$, 71302-47-1; $Co_2(trpy)_2(phen)_2O_2^{4+}$, 71302-48-2; $Co_2(DGENTA)_2O_2^{8-}$, 36002-59-2; $Co_2(NH_3)_{10}O_2^{4+}$, 16483-06-0; $Co_2(trien)_2(OH)O_2^{3+}$, 36431-46-6; $Co_2(DTMA)_2(OH)O_2^{+}$, 55701-24-1; $Co_2(EDDA)_2(OH)O_2^{-}$, 55177-53-2; $Co_2(dien)_2(OH)O_2(OH_2)_2^{3+}$, 36885-27-5; $Co_2(gly\text{-}his)_2(OH)O_2^{-}$, 71307-86-3; $Co_2(trien)_2(NH_2)O_2^{3+}$, 71302-49-3.

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Preparation and Magnetic Characterization of the Linear-Chain Series $M^{II}L_2Cl_2$ with M = Mn^{2+}, Cu^{2+}, and Ni^{2+} and L = 4-Phenylpyridine

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Magnetic susceptibilities have been determined on powdered samples of the title compounds $M^{II}L_2Cl_2$. The data for the copper(II) compound may be fit by the Heisenberg linear-chain results of Bonner and Fisher with $\langle g \rangle = 2.06$ and $J/k = -12.2$ K. The data for the manganese(II) compound may be fit by the scaled form of the infinite-spin linear-chain results modified by a molecular field correction term with the parameters $g = 1.98$, $J/k = -0.39$ K, and zJ'/k (the molecular field term) = -0.133 K. Magnetic susceptibility data for the nickel(II) compound were field dependent with a maximum occurring at about 9 cm^{-1}. Magnetization data are consistent with a metamagnetic transition. At 50 kOe the material was not fully saturated ($\mu = 1.62\ \mu_B$). The magnetic data may be fit with the parameters $D/k = -52$ K, $J/k = 8.5$ K, and $g = 2.3$, where D is the zero-field splitting parameter of the ^3A state. Thus $Ni(4\text{-}Ph\text{-}Py)_2Cl_2$ exhibits ferromagnetic intrachain exchange, very large single-ion anisotropy, and antiferromagnetic interchain interactions which lead to metamagnetism.

Introduction

The magnetic and thermal properties of low-dimensional transition-metal ion complexes have been studied extensively over the last few years.[1] Theoretical studies of these interesting polymers have been primarily aimed toward providing an analysis of the properties of completely isolated one- or two-dimensional lattices. Even with this simplication, the problem is so intractable that only a few such models can be solved exactly, those being the one-dimensional Ising chain,[2] the 2-D Ising layer,[3] the 1-D *XY*,[4] and the 1-D Heisenberg model with infinite spin.[5] Several other models, especially those of isotropically interacting Heisenberg spins, are known to a high degree of accuracy through various degrees of approximation. Bonner and Fisher[6] have performed exact calculations on small systems of $S = {}^1/_2$ Heisenberg spins and have been able to extrapolate to the infinite 1-D limit. Also, Weng has utilized a similar procedure to calculate the properties of linear Heisenberg chains $S \geq 1$.[7] Furthermore, Wagner and Friedberg[8] have shown that the infinite-spin linear model of Fisher can be scaled to the "exact" results of the high-temperature series expansions[9] for the limiting case of large spins (i.e., $S = {}^5/_2$).

Unfortunately, from an experimental viewpoint, real magnetic systems rarely, if ever, obey the full spirit of the available theories for low-dimensional cooperative phenomena.[1] Generally one must also take into account additional interactions such as (a) *intrachain* exchange between next nearest neighbors, (b) *interchain* exchange, (c) anisotropy in the near-neighbor exchange,[10] (d) single-ion crystal field anisotropy (in magnetic ions with $S \geq 1$), and (e) antisymmetric exchange interactions between neighboring magnetic ions within a chain or between ions in different chains.[10] The above interactions are often strong enough to induce long-range three-dimensional (3-D) spin ordering at low temperatures.[1] Since the 3-D ordering process of an assembly of 1-D magnetic chains involves a "crossover" of either spin and/or lattice dimensionality, valuable information into the nature of cooperative phenomena can be gained by studying simple magnetic model systems.[1,11] Furthermore, it is of primary importance in such studies to eliminate or control as many of the complicating terms as possible.

A large number of transition-metal complexes of the general stoichiometry $M^{II}L_2X_2$ (where M = divalent first-row transition-metal ion, L = heterocyclic nitrogen-containing organic base, and X = Cl^- or Br^-) can be readily synthesized.[12] Crystallographic data have been obtained for several members of the above class of complexes including $Cu(py)_2X_2$ (X = Cl^-, Br^-),[13] $Mn(py)_2Cl_2$,[14] and $Mn(pz)_2Cl_2$[15] (pz = pyrazole). In all of the above structures, the metal ions are situated on

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