Calculating from data for $\mu = 0.05$–2.5 gives values of $k_0 = 1.0 \times 10^{-3}$ M^{-1} s^{-1} for $[Co(NH_3)(\mu\text{-}O_2)]$ and $k_0 = 3.2 \times 10^{-3}$ M^{-1} s^{-1} for $[Co_2(NH_3)_8(\mu\text{-}O_2,NH_2)]$. Within the accuracy of this model, then, most of the large self-exchange difference between the monobridged and dibridged species can be explained by the charge differences of these complexes.

Finally, it is interesting to compare the values for the self-exchange rates derived here with those for free superoxide. Literature data are available for the reaction of O_2^- with several substrates.[23] From these data, a self-exchange rate for O_2^- of $\sim 10^{-3}$ M^{-1} s^{-1} can be derived.[22]

This rate is quite similar to that of metal-bound "superoxide" reported here. Thus, the reactivity of bound O_2 reinforces the structural evidence for a superoxide description. The common reactivity of free O_2^- and metal-bound O_2 might also suggest that a self-exchange rate of $\sim 10^{-3}$ M^{-1} s^{-1} may serve as a good approximation for many metal–O_2 systems (e.g., oxidases, superoxide dismutase). Studies to test this proposition are in progress.

Acknowledgment. We gratefully acknowledge support of this work by the Petroleum Research Fund, administered by the American Chemical Society, the Research Corp., who provided funds for the purchase of the stopped flow, and the National Institutes of Health. We wish to thank Barbara Fischer for her assistance with the CV measurements. G.M. is a Henry and Camille Dreyfus Teacher-Scholar.

Registry No. $[Co_2(NH_3)_{10}(\mu\text{-}O_2)]^{5+}$, 12259-09-5; $[Co_2(NH_3)_8(\mu\text{-}O_2,\mu\text{-}NH_2)]^{4+}$, 12381-36-1; $[Co_2(CN)_{10}(\mu\text{-}O_2)]^{5-}$, 12374-80-0; $[Co(trpy)_2]^{2+}$, 18308-16-2; $[Co(bpy)_3]^{2+}$, 15878-95-2; $[Co(phen)_3]^{2+}$, 16788-34-4.

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[22] For the cross reaction of O_2^- with cyt *c* $k_{12} = 5 \times 10^5$ M^{-1} s^{-1}. Taking $k_{22} = 5 \times 10^3$ M^{-1} s^{-1} and $K_{12} = 10^{13.5}$ gives $k_{11} = 10^{-3}$ M^{-1} s^{-1}.

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Electronic Structures of μ-Peroxo-bis[(pentadentate polyamine)cobalt(III)] Complexes

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Electronic spectral studies of $[CoLO_2CoL]^{4+}$ and $[CoLCl]^{2+}$, where L is 1,4,7,10,13-pentaazatridecane (tetren), 2,6-bis(5-(1,4-diazahexyl))pyridine (epyden), 1,9-bis(2-pyridyl)-2,5,8-triazanonane (pydien), 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (pydpt), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (imdien), and 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (imdpt) are reported. Chelate ring size has a noticeable influence on the ligand field strength, *Dq* ranging from 2630 to 2410 cm^{-1} in the series pydien > imdien > epyden $\gtrsim$ tetren $\sim$ imdpt > pydpt. A propensity for splitting of the $^1T_{1g}$ band in solutions containing high concentrations of weak field ligands seems to imply that the position transaxial to the peroxide moiety is rather labile. This is observed particularly for the pydien and pydpt complexes. The frequencies of the oxygen to cobalt charge-transfer bands are linearly related to the redox potentials of the complexes and to log K_{O_2}. While the base strength of the ligand is the major factor influencing the magnitude of K_{O_2}, ligand field strength may introduce a sizable perturbation.

Introduction

The past few decades have seen a growing interest in the study of cobalt–dioxygen complexes as models for biological oxygen carriers such as hemoglobin, hemerythrin, and hemocyanin.[2] Not only are the cobalt complexes more chemically tractable than the copper- and iron-containing systems they model but also they yield more easily interpreted electronic spectra. While considerable insight has been gained from the relatively few electronic spectral studies that have been conducted,[3-8] virtually no studies have been conducted on complexes that have been well characterized in terms of oxygen affinity, redox potentials, or the like. Thus any correlations between electronic structure and chemical behavior have, to date, been somewhat speculative.

Recently a series of pentadentate polyamine ligands consisting of 1,4,7,10,13-pentaazatridecane (tetren), 2,6-bis(5-(1,4-diazahexyl))pyridine (epyden), 1,9-bis(2-pyridyl)-2,5,8-triazanonane (pydien), 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (pydpt), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (imdien), and 1,11-bis(4-imidazolyl)-2,6,10-triazaundecane (imdpt) have been extensively characterized in these laboratories in terms of stability constants with various metals, oxygen affinities of the cobalt(II) complexes, redox potentials of the cobalt(II) and μ-peroxo-dicobalt(III) complexes,[9,10] and X-ray crystal structures of the μ-peroxo $(Co^{III}pydien)_2$ and $(Co^{III}pydpt)_2$ complexes.[11] The cobalt(II) complexes of these ligands cover a fairly wide range of oxygen affinity and yet are simple enough to allow spectral studies of the dioxygen complexes without extensive interference from intraligand or charge-transfer bands not involving the dioxygen.

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[1] Abstracted in part from a dissertation submitted by S. R. Pickens to the faculty of Texas A&M University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] See, for example, G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).

[3] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **5**, 1514 (1966).

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[11] J. H. Timmons, R. H. Niswander, A. Clearfield, and A. E. Martell, *Inorg. Chem.*, **18**, 1042 (1979), for pydpt; for pydien the manuscript has been submitted for publication.

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Experimental Section

Preparation of Complexes. Ligands. Tetraethylenepentamine, "tetren", was commercially obtained (Aldrich) as the free amine. This was fractionally distilled under reduced pressure and precipitated from aqueous solution by addition of excess hydrochloric acid and the pentahydrochloride was recrystallized several times from dilute HCl. epyden·4HCl·H_2O, pydien·3HCl, pydpt·3HCl, imdien·5HCl, and imdpt·4HCl were supplied by Dr. Ichiro Murase of Kyushu University, Fukuoka, Japan. Their syntheses have been previously described.[9,10]

Chlorocobalt (III) Complexes. [Co(tetren)Cl]ZnCl$_4$ was prepared by hydrogen peroxide oxidation of the cobalt(II) complex as described by House and Garner.[12]

[Co(epyden)Cl]ZnCl$_4$. One gram (0.0025 mol) of epyden·4HCl·H_2O and 0.60 g of cobaltous chloride hexahydrate (0.0025 mol) were dissolved in 3 mL of water. Upon addition of 0.50 mL of 50% NaOH (0.060 mol) the solution changed from pink to dark reddish brown. The solution was heated on a steam bath for 15 min during which time the solution became red-violet. Upon addition of 0.75 g of $ZnCl_2$ (0.0055 mol) and 1.8 mL of 12 M HCl (0.022 mol) a rose colored precipitate formed. After an additional 45 min on the steam bath and cooling of the solution, 1.03 g (74% yield) of dull rose colored crystals were isolated, washed twice each with 75% ethanol and methanol, and air-dried. Recrystallization was accomplished by dissolving 0.50 g in 8 mL of 0.10 M HCl and adding 2 mL of 10% $ZnCl_2$ in 12 M HCl to precipitate 0.38 g of small shiny red platelets.

[Co(pydien)Cl]$^{2+}$, [Co(pydpt)Cl]$^{2+}$, [Co(imdien)Cl]$^{2+}$, and [Co(imdpt)Cl]$^{2+}$ proved to be more difficult to isolate as pure salts and air or peroxide oxidation proved to be unsatisfactory; thus these complexes were prepared from sodium cobaltic carbonate for use in situ. In a typical preparation 0.362 g (0.0010 mol) of freshly prepared (olive green) $Na_3Co(CO_3)_3·3H_2O$[13] was combined with 0.0010 mol of the ligand hydrochloride in 3 mL of 1 M HCl (for pydien and pydpt) or 0.3 mL of 1 M LiOH plus 1 mL of H_2O with 0.40 mL of 1 M HCl then added dropwise with stirring and heating (for imdien and imdpt). The solutions were volumetrically diluted to 100 mL with 0.30 M $HClO_4$ (for pydien or pydpt) or 0.1 M HCl (for imdien or imdpt since their perchlorates are insoluble). The resulting 0.010 M stock solutions were red, except for the $[Co(imdien)Cl]^{2+}$ solution which was golden orange.

μ-Peroxo-dicobalt(III) Complexes, [Co$_2$L$_2$O$_2$](ClO$_4$)$_4$, were prepared by neutralizing 1 mmol of the ligand hydrochloride with 10 M NaOH and adding this to a solution of 1 mmol of $Co(NO_3)_2·6H_2O$ in 4 mL of water. After the addition of about 1 g of $NaClO_4·H_2O$ and bubbling with oxygen in the solution on an ice bath was done, precipitates formed and were isolated. $[Co_2(epyden)_2O_2](ClO_4)_4$, $[Co_2(pydien)_2O_2](ClO_4)_4$, and $[Co_2(pydpt)_2O_2](ClO_4)_4$ were green solids. $[Co_2(tetren)_2O_2](ClO_4)_4$ was brown and $[Co_2(imdien)_2O_2](ClO_4)_4$ and $[Co_2(imdpt)_2O_2](ClO_4)_4$ were tan. The solids were washed with 2-propanol and ether and air-dried. Recrystallization resulted in little spectral change.

Spectral Measurements. Electronic spectra of freshly prepared solutions were measured on a Cary 14 UV-vis-near-IR spectrophotometer. Matched quartz (suprasil) cells were used for room-temperature spectra. Cells fabricated from square quartz tubing, with the light path spectrally calibrated, were immersed in a quartz Dewar containing liquid nitrogen for 80 K spectra. The level of the liquid nitrogen was brought to just below the light path. Solutions for low-temperature spectra were composed of equal parts of H_2O and saturated lithium chloride which on careful cooling forms a glass because of the disordering effects of the dissolved ions.[6] EPR spectra were obtained on a Varian E6S spectrometer using a flat quartz cell for room-temperature aqueous spectra and 3-mm i.d. quartz tubes for all other spectra.

Results

Chlorocobalt(III) Complexes. The spectra of the chlorocobalt(III) complexes of the ligands are shown in Figure 1. The bands at 20 × 10^3 cm^{-1} are the $^1A_{1g} \rightarrow {}^1T_{1g}$ ligand field bands for the respective complexes. Only in the tetren complex is the splitting of this band (due to the tetragonal reduction in symmetry) apparent. At 80 K the ^1E and $^1A_2$ components of this band show up at 18.8 × 10^3 and 21.3 × 10^3 cm^{-1}, respectively, in close agreement to the expectedly similar spectrum of the $[Co(NH_3)_5Cl]^{2+}$ complex.[14] The splitting of the $^1T_{1g}$ band is not so apparent for the other complexes from the equation.[15,16]

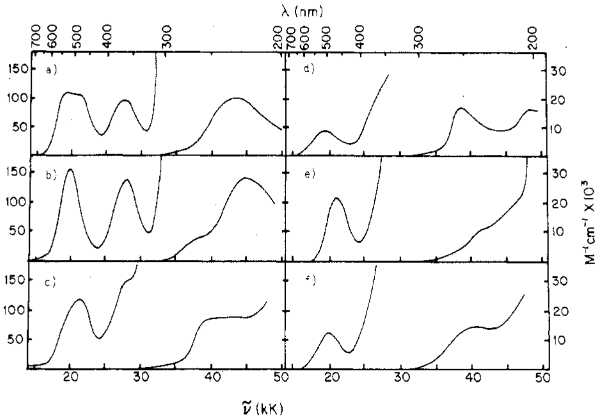

Figure 1. Electronic spectra of the chlorocobalt(III) complexes of (a) tetren, (b) epyden, (c) pydien, (d) pydpt, (e) imdien, and (f) imdpt in acidic solution (0.1 M HCl for a–d, 0.3 M $HClO_4$ for e and f; see Experimental Section). The extinction coefficients at the left apply to the low-energy portions (below 30 × 10^3 cm^{-1}) of the spectra while the extinction coefficients at the right apply to the high-energy portions. (10^3 cm^{-1} = 1 kK.)

Table I. Electronic Spectral Parameters for the Chloro(pentadentate polyamine)cobalt(III) Complexes[a]

ligand	d–d bands $^1A_{1g} \rightarrow {}^1T_{1g}$	 $^1A_{1g} \rightarrow {}^1T_{2g}$	intraligand and charge-transfer bands
tetren	18.0 (112), 20.6 (108)	27.3 (99)	43.8 (22 000)
epyden	19.7 (158)	27.8 (138)	37.5 (6800), ~45 (30 500), ~46 (28 800)
pydien	21.1 (119)	27.2 (148)	40.0 (17 200), 42.9 (17 700)
pydpt	19.2 (42)		38.6 (17 000), 48.7 (16 900)
imdien	20.9 (112)		41.2 (11 000)
imdpt	19.8 (76)		41.3 (12 700), 47.4 (15 100)

[a] Band positions are given in 1 cm^{-1} × 10^3, and the numbers in parentheses are extinction coefficients in M^{-1} cm^{-1}.

However the approximate ligand field strength of the polyamine ligand, Dq^{lig}, may be estimated

$$E(^1T_{1g}) = 10Dq - C \tag{1}$$

where

$$Dq = (5/6)Dq^{lig} + (1/6)Dq^{Cl^-} \tag{2}$$

Thus

$$E(^1T_{1g}) = (25/3)Dq^{lig} + (5/3)Dq^{Cl^-} - C \tag{3}$$

which, upon setting $Dq^{Cl^-} = 1.56$ and $C = 3.83$ based on values from similar complexes,[15,17] may be rearranged to yield

$$Dq^{lig} = (3/25)(\tilde{\nu}_{max}(^1T_{1g}) + 1.23) \tag{4}$$

where $\tilde{\nu}_{max}(^1T_{1g})$ is substituted for $E(^1T_{1g})$ to give Dq. Equation 4 and $\tilde{\nu}_{max}$ for the $^1T_{1g}$ bands in Figure 1 yield the approximate field strengths listed in Table I.

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(12) D. A. House and C. S. Garner, *Inorg. Chem.*, **5**, 2097 (1966).

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(16) These equations are somewhat crude in that they neglect the complicating effects of configuration interaction. However, for the present study this first-order approximation will be sufficient.

(17) The Racah parameter C is remarkably invariant for a wide range of cobalt(III) complexes. See ref 15.

Table II. Ligand Field Parameters for the Pentadentate Polyamine Ligands Used in this Study[a]

ligand	Dq^{lig}, cm^{-1} × 10^3	B,[b] cm^{-1} × 10^3
tetren	2.41	0.527
epyden	2.51	0.506
pydien	2.68	0.381
pydpt	2.45	*c*
imdien	2.66	*c*
imdpt	2.52	*c*

[a] Based on the chloro ligand cobalt(III) complex except where indicated. [b] For the overall complex. [c] Not calculable due to obscured $^1T_{2g}$ band.

The $^1A_{1g} \rightarrow {}^1T_{2g}$ bands appear at about 27.5 × 10^3 cm^{-1} (see Figure 1), although they are obscured in the spectra of the pydpt, imdien, and imdpt complexes. Since[15]

$$E(^1T_{2g}) = 10Dq + 16B - C \qquad (5)$$

the value of the Racah B parameter may be calculated in those cases where the $^1T_{2g}$ band is observed.

$$B = (1/16)[\nu_{\max}(^1T_{2g}) - \nu_{\max}(^1T_{1g})] \qquad (6)$$

These values of B, where obtainable, are also listed in Table II.

The more precise data which might have been available from sharper, low-temperature spectra were not in general available for these complexes, since, on exposure to the high chloride concentration of the LiCl solutions used for making low-temperature aqueous glasses, disubstitution tended to occur. This was especially true for the pydien and pydpt complexes, which on addition of LiCl, even in acid solution, changed from red to green in minutes (trans disubstitution) and more slowly to violet (trans to cis rearrangement).

In the high-energy region the spectrum of $[Co(tetren)Cl]^{2+}$ is simplest, having a single band at 43.8 × 10^3 cm^{-1} (ϵ 22 000) which corresponds to a $Cl \rightarrow Co^{3+}$ charge-transfer transition, in close agreement with the $\sigma_{Cl^-} \rightarrow d_{z^2}(Co^{3+})$ transition of 43.9 × 10^3 cm^{-1} (ϵ 12 900) and $\pi_{Cl^-} \rightarrow d_{z^2}(Co^{3+})$ shoulder at 36.0 × 10^3 cm^{-1} (ϵ 400), assigned by Miskowski and Gray[18] for $[Co(NH_3)_5Cl]^{2+}$. The higher intensity and lower resolution in the spectrum of $[Co(tetren)Cl]^{2+}$ for which the $\pi_{Cl^-} \rightarrow d_{z^2}(Co^{3+})$ shoulder could not be discerned no doubt result from symmetry reduction and vibrionic effects of the chelate rings.

This portion of the spectrum is more complicated for the other complexes because of the possibility of ligand $\pi \rightarrow \pi^*$ and additional charge-transfer transitions. Pyridine itself, for example is known to have $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in this region and the free ligand, epyden, has peaks at 37.5 × 10^3 (ϵ 3100, shoulder), 38.4 × 10^3 (ϵ 3800), and 47.3 × 10^3 cm^{-1} (ϵ 6300). However, $[(Co(epyden)Cl]^{2+}$ has a band at about 45 × 10^3 cm^{-1} which is absent in the aquo complex, $[Co(epyden)H_2O]^{3+}$. Thus one might surmise that this corresponds to the $Cl^- \rightarrow Co^{3+}$ charge transfer. This band should be at somewhat lower energy than that in the tetren complex although the exact position of this band is difficult to ascertain because of the presence of bands involving the pyridyl group. The shift of the charge-transfer bands to lower energy on increasing the effective positive charge on the cobalt in the series $[Co(tetren)Cl]^{2+} < [Co(epyden)Cl]^{2+} < [Co(pydien)Cl]^{2+} < [Co(pydpt)Cl]^{2+}$ becomes more apparent with the pydien and pydpt complexes, the $^1T_{2g}$ band in fact being buried in the pydpt charge-transfer band.

The spectra of imdien and imdpt complexes are also plagued by tails of charge-transfer bands (the free ligands have no bands below 50 × 10^3 cm^{-1}) which bury the $^1T_{2g}$ bands. It is fortunate however that these tails do not obscure the intense $O_2^{2-} \rightarrow Co^{3+}$ charge-transfer bands in the peroxo complexes.

Peroxo Complexes. The spectra of the peroxo complexes at room temperature and at liquid-nitrogen temperature are presented in Figure 2. The log of the extinction coefficient is used as the ordinate to accentuate the weaker bands. A prominent feature in these spectra is a band in the vicinity of 31 × 10^3 cm^{-1} which was absent in the spectra of the chlorocobalt(III) complexes. This may confidently be assigned as a peroxide to cobalt charge-transfer band, its position and intensity agreeing well with expectations based on studies involving similar complexes.[6,7]

The bands at about 22–23 × 10^3 cm^{-1} might be expected to correspond to the $^1A_{1g} \rightarrow {}^1T_{1g}$ bands which were observed in the chlorocobalt(III) complexes. Similarly the shoulder at about 28 × 10^3 cm^{-1} might be either $^1A_{1g} \rightarrow {}^1T_{2g}$ bands or, more likely in view of their high intensities, additional $\pi^*_{O_2^{2-}} \rightarrow d_{z^2,Co}$ LMCT (ligand to metal charge transfer) bands. In view of the existence of two π^* orbitals on the peroxide there should be two $\pi^*_{O_2^{2-}} \rightarrow d_{z^2}$ LMCT bands, the more intense one being at higher energy.[19]

In addition, weak, low-energy bands occur at about 17 × 10^3 cm^{-1} in all of the spectra and are especially noticeable in the spectra of the pydien and pydpt complexes. A band in this region of the spectrum might conceivably arise from two sources: spontaneously formed superoxides,[4,19] which would have low-energy metal to ligand charge-transfer (MLCT) bands,[6,19] or a strong splitting of the $^1T_{1g}$ ligand field band which for a *trans*-chloro,peroxo complex would have the ^1E component at about 17 × 10^3 cm^{-1}.[3]

To test the former hypothesis, we took powder EPR spectra of the isolated perchlorate salts of the peroxo complexes. (The aqueous solutions gave no signal.) No signal was obtained for the tetren, pydien, or pydpt complexes but somewhat poorly defined signals were obtained for the epyden, imdien, and imdpt complexes, although in the imdpt case the signal was so weak as to be barely discernible. The EPR spectra for the epyden and imdien complexes are shown in Figure 3. Although the spectra are poorly resolved, it may be readily seen that they bear a strong resemblance to those of known mononuclear superoxides.[4,8,20] Moreover there is no similarity either to the spectra of the dinuclear superoxide (see Figure 4) or to the spectra of typical oxygen-free Co^{2+} complexes (e.g., see ref 4), and such complexes generally do not give sharp EPR signals at room temperature due to the rapid spin relaxation in the split $^4T_{1g}$ ground state.[21] Thus it is reasonably certain that the EPR spectra in Figure 3 result from mononuclear superoxides coprecipitated with the peroxides. Upon the dissolution of these perchlorates in water the EPR signal immediately disappears indicating total conversion to the dinuclear peroxide.

In view then of the probable absence of any superoxides in solution (or even in the solid state for the pydpt and pydien complexes which have the strongest 17 × 10^3 cm^{-1} bands) the 17 × 10^3 cm^{-1} band cannot be a $Co^{3+} \rightarrow O_2$ MLCT.

On the other hand, assignment of this band as the ^1E component of the $^1T_{1g}$ band for a trans chloro superoxo complex accords well with the following observations: (1) This band was most intense when the chloride concentration was high. (2) The band was especially intense for the pydien and pydpt complexes. The chlorocobalt(III) complexes of these ligands were previously noted to be substitution labile relative to the complexes of the other ligands. (3) The band appeared to shift ~1 × 10^3 cm^{-1} to higher energy when excess SCN^- (which

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(18) V. M. Miskowski and H. B. Gray, *Inorg. Chem.*, **14**, 401 (1975).

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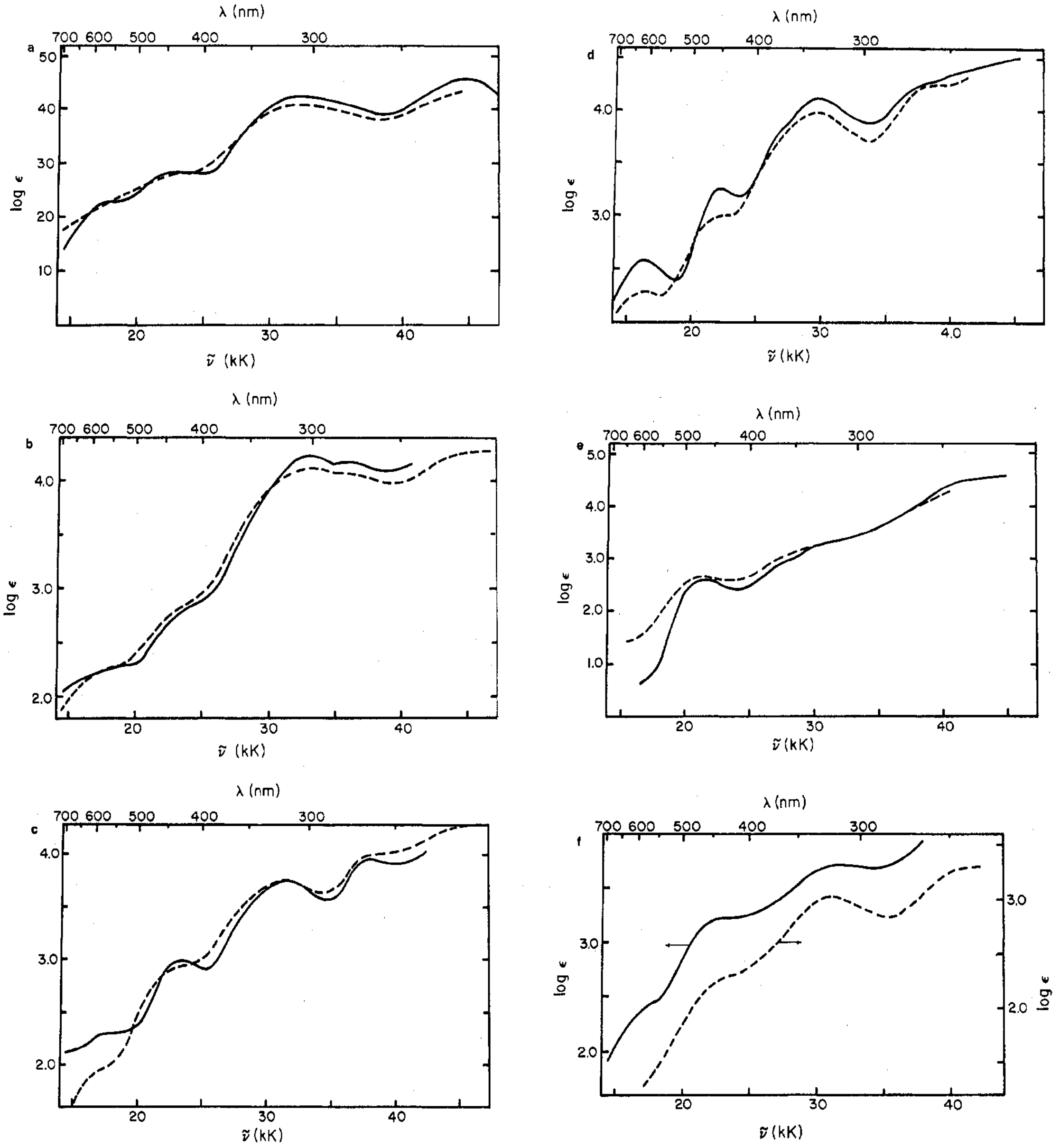

Figure 2. Electronic spectra of (a) $[Co(tetren)O_2Co(tetren)](ClO_4)_4$, (b) $[Co(epyden)O_2Co(epyden)](ClO_4)_4$, (c) $[Co(pydien)O_2Co(pydien](ClO_4)_4$, (d) $[Co(pydpt)O_2Co(pydpt)](ClO_4)_4$, (e) $[Co(imdien)O_2Co(imdien)](ClO_4)_4$, (f) $[Co(imdpt)O_2Co(imdpt)](ClO_4)_4$ in water at 300 K (dashed line) and in 50% saturated LiCl at 80 K (solid line).

Table III. Band Positions and Intensities for the Peroxocobalt(III) Complexes with Some Pentadentate Polyamines[a]

ligand	temp, K	${}^1A_1 \to {}^1E$ (in trans Cl^- complex)	${}^1A_1 \to {}^1T_1$ (Cl^- free complex) or ${}^1A_1 \to {}^1A_2$ (trans Cl^- complex)	${}^1A_1 \to {}^1T_2$ or $\pi^*_{O_2,a} \to d_{z^2}$ (LMCT$_a$)	(LMCT$_b$) $\pi^*_{O_2,b} \to d_{z^2}$
tetren	80	17.5 (200)	22.6 (600)	27.6 (3000)	32.5 (16 000)
	300		22.3 (600)	28.6 (300)	32.4 (13 000)
epyen	80	~16.5 (160)	23.0 (500)	~29 (6000) sh	~32.4 (8020)
	300		~23 (800)		~32.0 (4033)
pydien	80	17.5 (200)	23.3 (1000)	~28 (2500) sh	31.5 (6000)
	300		23.5 (1000)		~31.3 (6000)
pydpt	80	16.4 (400)	22.3 (2000)	~26.5 (6000) sh	29.8 (13 000)
	300	16.5 (200)	22.0 (1000)	28.6 (6000) sh	29.9 (10 000)
imdien	80		21.5 (400)	~27.5 (800) sh	31.3 (2500)
	300		21.0 (500)		~31.3 (2500) sh
imdpt	80	17.0 (250)	23.2 (1000)		31.5 (5000)
	300		22.6 (500)		31.0 (2500)

[a] Band positions given in $cm^{-1} \times 10^3$, intensities given in parentheses in units of $M^{-1}\ cm^{-1}$.

has a greater ligand field strength than Cl^-) rather than Cl^- was present. (4) The spectrum of the tetren complex had an intense band at 45 × $10^3\ cm^{-1}$ which would not be expected in the simple peroxocobalt(III) complex. If, however, a

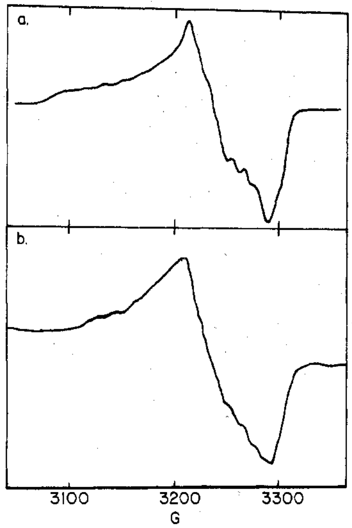

Figure 3. EPR powder spectra of paramagnetic impurities present in the rapidly precipitated (as perchlorates) cobalt–oxygen complexes of epyden at 80 K (a) and imdien at 300 K (b). The microwave frequency was 9.137 GHz in (a) and 9.145 GHz in (b).

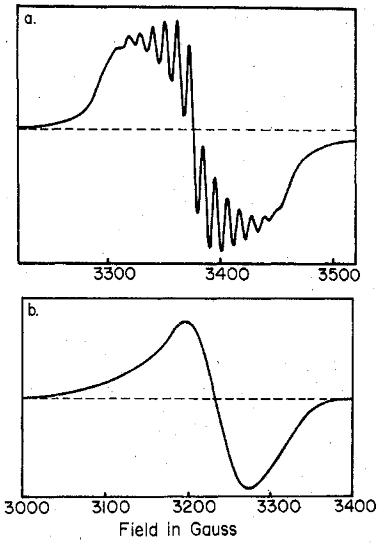

Figure 4. EPR spectra of $[Co(epyden)O_2Co(epyden)]^{5+}$ in water at room temperature (a) and 80 K (b). The microwave frequency was 9.551 GHz in (a) and 9.137 GHz in (b).

chloride is coordinated to the cobalt, a $Cl^- \rightarrow Co^{3+}$ CT band would be expected at about this frequency. The spectrum of $[Co(tetren)Cl]^{2+}$ had this band at 44×10^3 cm^{-1}. The 1×10^3 cm^{-1} shift to higher energy in the trans peroxo complex is reasonable in view of the high basicity of peroxide ($pK_{a,H_2O_2} = 12.13$, $pK_{a,NH_4^+} = 9.40$).

From the positions of the ^1E ($^1T_{1g}$) bands and the previously calculated values of Dq for the various ligands (see Table I) and the assumptions $C \simeq 3.83 \times 10^3$ cm^{-1} and $Dq^{Cl^-} \simeq 1.56 \times 10^3$ cm^{-1} as previously, one may calculate values for Dq for peroxide by using equations analogous to eq 1–3). So doing, one obtains an average value of $Dq^{O_2^{2-}} = 1.8 \times 10^3$ cm^{-1}. Thus the ligand field strength of peroxide appears to be slightly less than for water, in accord with expectation and in fair agreement with results obtainable on the basis of previous work.[3,6]

Discussion

Trans Substitution. The propensity for trans substitution in the peroxo cobalt(III) complexes implies that peroxide is a strong trans labilizing ligand, a "trans director". This is to be expected in view of the highly polarizable, dianionic, π-donating, and rather basic nature of O_2^{2-}. Crystal structures of both the pydien and the pydpt complexes show a longer than average Co–N bond length for the nitrogen trans to the peroxide (incidentally, in both cases this is one of the aliphatic nitrogens adjacent to a pyridine ring).[11]

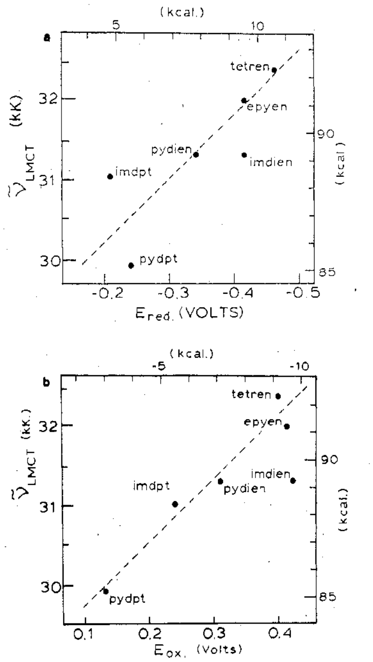

Figure 5. (a) $\tilde{\nu}_{max}$ for $LMCT_b$ vs. the reduction potential for the half-reaction $Co^{3+}LO_2^{2-}Co^{3+}L + e^- \rightarrow Co^{2+}LO_2^{2-}Co^{3+}L$. (b) $\tilde{\nu}_{max}$ of the $LMCT_b$ transition vs. the oxidation potential for $Co^{2+}L \rightarrow Co^{3+}L + e^-$.

The formation of a trans disubstituted complex when the polyamine ligand is pentadentate strikes a contrast with a propensity for the formation of cis disubstituted complexes (frequently μ-hydroxo, μ-peroxo or μ-amido, μ-peroxo dibridged) when the amine ligands are mono-, di-, tri-, or tetradetnate.[2,8] This difference may be understood in terms of the routes by which the complexes are formed. In the case of the pentadentate polyamine ligands, oxygenation generally occurs with all five nitrogens coordinated to the cobalt. Once the oxygen is bound, the nitrogen most easily removed is the one trans to the peroxide moiety. In the case of polyamine ligands with fewer than five nitrogens capable of coordinating to the metal, oxygen uptake will preferentially occur on a site cis to the H_2O or Cl^- group where the lower basicity of the water of halide will least stabilize the orbital which loses an electron to the incoming oxygen.

Charge-Transfer Energy. The ligand to metal charge-transfer excitation is essentially an internal, Frank–Condon type redox process composed of the half-reactions:

$$O_2^{2-} \rightarrow O_2^- + e^- \quad E_{peroxo}$$

and

$$e^- + Co^{3+}L \rightarrow Co^{2+}L \quad E_{CoL}$$

Since E_{peroxo} is affected only secondarily by changes in the ligand, L, it will remain fairly constant throughout the series of ligands while E_{CoL} changes. Thus $\tilde{\nu}_{max}$ of the LMCT should be proportional to the reduction potential for $Co_2^{3+}L_2O_2^{2-}$ or minus the oxidation potential for $Co^{2+}L$. Figure 5 shows these relationships by using half-cell potentials previously measured by differential pulse polarography[22] and the $\tilde{\nu}_{max}$, LMCT values

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[22] W. R. Harris, Ph.D. Dissertation, Texas A&M University, College Station, Texas, Aug 1977.

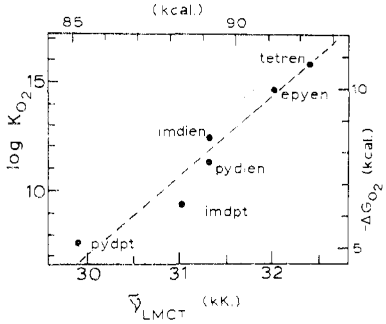

Figure 6. Log of the oxygenation constant (k_{O_2} = $[Co_2L_2O_2]/[CoL]^2[O_2]$) vs. the wavenumber of the $LMCT_b$ band.

from the room-temperature spectra which, though somewhat less resolved, have less of the trans chloro complex present to red shift the LMCT. While there is some scatter, which is due largely to experimental uncertainties in the positions of the broad charge-transfer bands, a fairly linear relationship is seen to exist. The energy scales, which are obtained from Planck's and Faraday's constants, point out the relationships between the Frank–Condon and the electrochemical redox processes. There is a difference of about 80 kcal/mol in the absolute energy required for the two processes. This is due to different competing half-reactions (e.g., $O_2^{2-} \rightarrow O_2^- + e^-$ as opposed to $Hg_2Cl_2 + 2K^+ + 2e^- \rightarrow 2Hg + 2KCl$) and changes in hydration and conformation which will minimize the energy required for the relatively slow electrochemical process but not the instantaneous Frank–Condon excitation. On the other hand, the relative change in energy resulting from changing the ligand, L, is roughly the same for both processes as indicated by the slope of ~1 kcal/kcal in Figure 5.

It has been observed that a linear relationship exists between the oxygen affinity of a cobalt(II) complex (log K_{O_2}) and the oxidation potential of the complex.[23,24] This relationship was seen to hold for the present series of pentadentate polyamine cobalt complexes.[22] Thus one would expect a linear relationship to exist between $\tilde{\nu}_{max}$ LMCT and log K_{O_2}. This relationship, which is depicted in Figure 6, may be readily understood if one considers the ligand to metal charge-transfer transition to be a reversal, though in Frank–Condon fashion, of the internal electron shift occurring upon oxygenation.

Structural and Electronic Factors Affecting Oxgenation. In the series of peroxocobalt(III) complexes, $[LCo\text{-}\mu\text{-}O_2\text{-}CoL]^{4+}$, changes in the ligand, L, should have a primary influence upon the electronic energy levels of the cobalt and only secondary effects transmitted through the metal to the peroxide. Given then the frequencies of the peroxide π^* to cobalt d_{z^2} charge-transfer bands in the spectra of Figure 2 and the assumption of a relatively invariant energy for the π^* orbitals of O_2^{2-}, one may estimate the relative changes in the energy of the d_{z^2} orbital resulting from changes in L. Then using the measured ligand field strengths of the pentadentate polyamine ligands in Table II and of peroxide, one may calculate the energies of the other d orbitals relative to the d_{z^2} orbital for each complex. The resulting comparative orbital diagram in Figure 7 serves to illustrate the electronic differences between the various complexes.

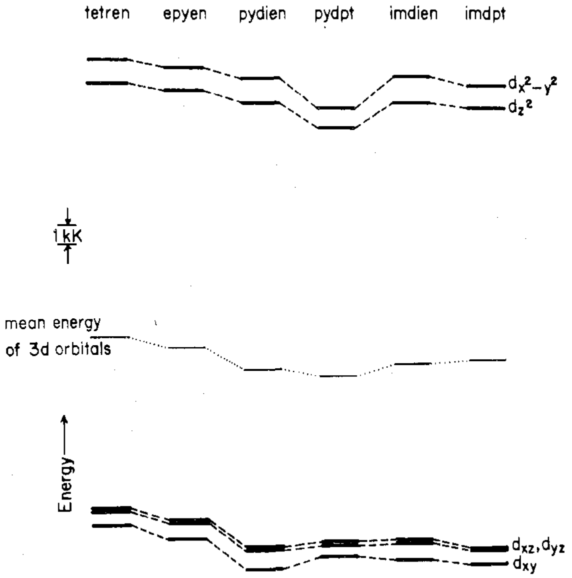

Figure 7. Relative energies of the d orbitals in $[CoL\text{-}\mu\text{-}O_2\text{-}CoL]^{4+}$, where L = tetren, epyden, pydien, pydpt, imdien, or imdpt, as indicated.

A rather linear correlation between ligand basicity (as expressed by the sum of the ligand p*K*'s) and oxygen affinity (as expressed by log K_{O_2}) has previously been noted for such complexes.[2,22] However, the oxygen affinities for the pyridyl-containing ligands were anomalously high, given the low basicities of these ligands. It may be seen from Figure 7 that this anomaly may be related to the high field strengths of the pyridyl-containing ligands. Thus, although the mean energy of the cobalt d orbitals drops considerably with decreasing ligand basicity in the series tetren > epyden > pydien as expected, the energy of the d_{z^2} orbital is much less perturbed due to the partially offsetting effect of increasing *Dq* in the series tetren < epyden < pydien. Oxygen affinity is most directly related to the energy of the d_{z^2} orbital since this is the orbital which loses an electron in the internal electron transfer accompanying oxygenation. The high field strength of the pyridine-containing ligands is most likely due to π acidity of the pyridine. Thus while pyridine behaves as a weak base toward protons, π donation from cobalt to the pyridine would electrically favor increased σ donation from pyridine to cobalt and vice versa in a symbiotic fashion. While net electronic donation to the cobalt is less with aromatic than with aliphatic amines, σ donation into the $d_{x^2-y^2}$ and/or d_{z^2} orbitals is nearly the same. Along these lines it may be pointed out that the Co–N distance is less for the pyridyl than for the aliphatic nitrogens in the pydien and pydpt complexes.[11]

Chelate ring size has a noticeable influence both upon ligand field strength and upon the net basicity of the ligand toward the metal. Thus pydpt, for which $\sum pK_a$ is actually greater than for pydien has a lower ligand field strength and yields a lower mean cobalt 3d orbital energy. This may be related to both static and dynamic effects. On the one hand, the steric disadvantages of six-membered chelate rings is reflected in longer average Co–N bonds in the pydpt complex than in the pydien complex (1.974 vs. 1.951 Å).[11] (In turn, on going from pydpt to pydien, the Co–O–O angle goes from 115 to 112.5°, the Co–O distance shrinks slightly from 1.89 to 1.876 Å and the O–O distance expands slightly from 1.456 to 1.489 Å[11] in line with a slight increase in peroxide character in the pydien complex relative to the pydpt complex.) In addition however,

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(23) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).

(24) Similarly a relationship exists between XPS binding energy and oxygen complex stability. See J. H. Burgess, J. G. Dillard, and L. T. Taylor, *J. Am. Chem. Soc.*, **97**, 6080 (1975).

(25) For these calculations, the energy of the peroxide π_h^* orbital is fixed at $E = 0$ for all complexes. Then $E(d_{z^2}) = E(LMCT, \pi^*_{O_2^{2-}} \rightarrow d_{z^2})$. The energies of the other d orbitals relative to the d_{z^2} orbital may then be derived via eq 4-33, 4-34, 5-14, and 5-15 in C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, 1962, pp 65, 101. While these equations rely on a knowledge of *Dq*, *Ds*, and *Dt*, *Dq* and *Dt* may be derived from Dq^{lig} (Table II) and $Dq^{O_2^{2-}}$ (1.8×10^3 cm^{-1} as indicated earlier) by using eq 4 in ref 15. Finally *Ds* is approximated on the basis that over a wide variety of complexes a clear splitting in the $^1T_{1g}$ band (which should be $(35/4)Dt$) is often observed whereas a splitting in the $^1T_{2g}$ band ($6Ds - (5/4)Dt$) is never observed (see ref 15). Thus we assume $Dt \neq 0$ in general whereas $6Ds - (5/4)Dt \simeq 0$. Thus $Ds \simeq (5/24)Dt$.

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$_2$Co(tetren)](ClO$_4$)$_4$, 36502-66-6; [Co(epyden)O$_2$Co(epyden)](ClO$_4$)$_4$, 71462-61-8; [Co(pydien)O$_2$Co(pydien)](ClO$_4$)$_4$, 71462-63-0; [Co(pydpt)O$_2$Co(pydpt)](ClO$_4$)$_4$, 71485-78-4; [Co(imdien)O$_2$Co(imdien)](ClO$_4$)$_4$, 71462-64-1; [Co(imdpt)O$_2$Co(imdpt)](ClO$_4$)$_4$, 71462-65-2; [Co(epyden)O$_2$Co(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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