1. All oxidative dehydrogenation reactions are base-catalyzed.
2. The imine group formed is conjugated with an aromatic ring (no dehydrogenation with aliphatic polyamines).
3. Conformation of polyamine ligands in a dioxygen complex must be compatible with the formation of a trigonal R—C=N—R′ group (R = aromatic).
4. When isomers are possible, only the configuration with the α-CH adjacent to coordinated dioxygen undergoes dehydrogenation.
5. There is a large deuterium isotope effect.

A tentative reaction mechanism for the oxidative degradation of coordinated AMP in the dioxygen complex at high pH is illustrated by Scheme II. It is seen that subsequent to the deprotonation reaction, reflecting base catalysis, homolytic O–O bond scission is suggested as occurring with concerted proton transfer to coordinated oxygen and with simultaneous electron transfer through the metal ion from the organic center undergoing dehydrogenation to the coordinated oxygen. All of these changes are expressed in transition state **9**.

It is obvious that this mechanism predicts the existence of a large kinetic deuterium isotope effect corresponding to the rate-determining transfer of a proton from the α-carbon of AMP to coordinated dioxygen. The reaction kinetics for the mixed-ligand dioxygen complex **3**, containing completely α-deuterated AMP, was carried out at three pH values in the high-pH range. The ratios $k_2^f(H)/k_2^f(D) = 16$ and $k_2^s(H)/k_2^s(D) = 13$ are considerably higher than expected. Also, the value of $k_1^f(H)/k_1^f(D) = 9$ is also compatible with the suggested proton-transfer mechanism. The much lower magnitude of $k_1^s(H)/k_1^s(D)$ is indicative of a different reaction mechanism for the slow step and is compatible with the suggested rate-limiting conversion of inactive coordination isomers to the active forms, **6** and **6A**, for this phase of the reactions. The large values of the measured isotope effects are not unreasonable in view of recent results in the field.[20-26] The large values of the observed isotope effects also open up the possibility that quantum-mechanical tunneling makes a contribution to proton transfer, thus further supporting the proposed mechanism.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

Registry No. AMP, 3731-51-9; $C_5H_4NCD_2NH_2 \cdot 2HCl$, 100366-77-6; 2-cyanopyridine, 100-70-9.

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Oxidation of Cobalt(II) Pentaamine Complexes through the Formation of Dioxygen Complex Intermediates

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The oxidation of cobaltous complexes containing tetraethylenepentamine (TETREN), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (IMDIEN), 2,6-bis(3,6-diazahex-2-yl)pyridine (EPYDEN), 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN), or 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT) with molecular oxygen takes place through the formation of μ-peroxo-bridged cobalt(III) dioxygen complexes and ultimately results in either oxidative dehydrogenation of the coordinated ligand or simple "metal-centered" oxidation to form cobalt(III) complexes of the unchanged ligand and hydrogen peroxide. These reactions are shown to be first order with respect to the concentration of both the μ-peroxo-bridged cobalt(III) dioxygen complex and the hydroxide ion concentration. The cobalt(II) complexes of TETREN, IMDIEN, and EPYDEN undergo metal-centered oxidation, while the cobalt(II) complexes of PYDIEN and PYDPT undergo oxidative dehydrogenation of the coordinated amines to imines conjugated to the pyridine ring and coordinated to cobalt(II). The cobalt(II) complexes that have undergone oxidative dehydrogenation react with dioxygen to form new dioxygen complexes that undergo further oxidative dehydrogenation. It is proposed that the differences in reaction pathways and mechanisms of the oxidation reactions are dependent on the conformations of the aromatic and aliphatic amino groups in the coordination spheres of the μ-peroxo cobalt(III) dioxygen complexes having pyridyl-containing pentadentate polyamines as ligands.

Introduction

Recently attention has been focused on the mechanism of degradation reactions of μ-peroxo-bridged complexes of cobalt since the rates of such reactions are the limiting factors in catalytic oxidation and oxygenation studies involving cobalt dioxygen complexes as intermediates and determine the number of reversible oxygenations possible in the use of dioxygen complexes for oxygen separation processes. It has been proposed[2] that the degradation reaction involves remittal of oxygen as the result of the disproportionation of hydrogen peroxide[3] released from the oxygen complex and that the slow uptake of oxygen observed after initial rapid formation of the dioxygen complex is indicative of oxidation of the ligand. With the ligands 1,9-bis(2-pyridyl)-2,5,8-triazanonane (PYDIEN, **1**) or 1,11-bis(2-pyridyl)-2,6,10-triazaundecane (PYDPT, **2**) in the coordination sphere of the corresponding cobalt(II) dioxygen complexes, oxidative dehydrogenation of the coordinated ligand has been found to occur during the degradation

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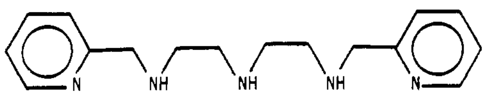
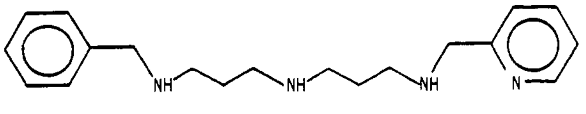
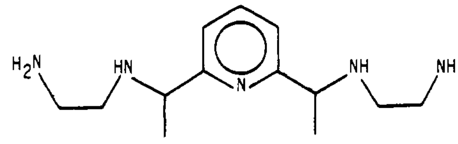


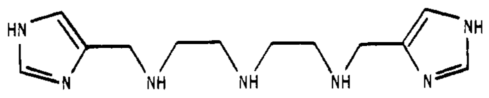
PYDIEN 1



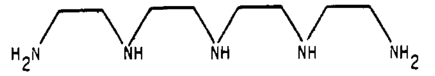
PYDPT 2



EPYDEN 3



4-IMDIEN 4



TETREN 5

process. A detailed study of this reaction for PYDIEN has been reported.[4]

With 2,6-bis(3,6-diazahex-2-yl)pyridine (EPYDEN, **3**), 1,9-bis(4-imidazolyl)-2,5,8-triazanonane (IMDIEN, **4**), or tetraethylenepentamine (TETREN, **5**) in the coordination sphere of Co(II), the degradation reaction is much different, in that these ligands are not oxidized by coordinated dioxygen. The oxidation pathway for these complexes involves release of peroxide and the formation of an inert cobalt(III) complex of the original ligand. This type of degradation is termed "metal-centered" oxidation. Some preliminary results on the degradation reaction involving the cobalt(II) EPYDEN complex have recently been described.[5,6] It is the purpose of this paper to report detailed studies of these reactions, to compare the results with the degradation reactions involving ligand dehydrogenation, and to suggest probable reaction mechanisms.

Experimental Section

Materials. Tetraethylenepentamine (TETREN) pentahydrochloride was prepared from redistilled tetraethylenepentamine (obtained from Pfaltz and Bauer Co.) by the addition of aqueous hydrogen chloride to a solution maintained below 20.0 °C. The crystalline hydrochloride obtained was filtered off, washed with absolute ethanol, and dried over potassium hydroxide pellets under vacuum. The pentahydrochloride was recrystallized three times from acidic aqueous solutions.

1,9-Bis(4-imidazolyl)-2,5,8-triazanonane (IMDIEN) pentahydrochloride was synthesized and characterized as described by Timmons et al.[7]

Table I. Pseudo-First-Order Rate Constants Calculated from the Disappearance of the LMCT Band of Cobalt(III) Dioxygen Complexes[a]

$-\log [H^+]$	$10^5 k_{obsd}$[b]	$-\log [H^+]$	$10^5 k_{obsd}$[b]
	TETREN		
11.00	12.5	10.50	3.5
10.75	7.6	10.02	2.2
	EPYDEN		
10.98	29	10.38	4.2
10.63	8.4	10.00	2.1
	IMDIEN		
11.01	42	10.21	6.7
10.68	20	10.03	4.4
10.50	13		
	PYDIEN[c]		
11.10	53	10.21	8.4
10.98	42	9.00	5.5
10.50	10.9	7.00	4.0
10.42	10.5	5.00	3.0
	PYDPT		
10.56	880	8.69	54
10.22	620	7.56	30
9.76	310	5.70	13
9.30	61		

[a] Reaction conditions: 35.0 °C, 0.10 M ionic strength. [b] Units of s^{-1}. [c] Previously reported in ref 4.

Table II. Second-Order Rate Constants Calculated from the Disappearance of the LMCT Band of Cobalt(III) Dioxygen Complexes at p[H] ≥ 10

ligand	$10^2 k$, $M^{-1} s^{-1}$	ligand	$10^2 k$, $M^{-1} s^{-1}$
TETREN	8.0	PYDIEN	27
EPYDEN	14	PYDPT	170
IMDIEN	26		

2,6-Bis(3,6-diazahex-2-yl)pyridine (EPYDEN) tetrahydrochloride monohydrate was synthesized and characterized as described by Harris et al.[8]

Iodo[2,6-bis(3(*S*),6-diazahex-2-yl)pyridine]cobalt(III) Iodide. EPYDEN·4HCl (1.2 mmol) and cobaltous iodide (2.3 mmol) were added to 5 mL of water. Sodium iodide (5 mmol) was added to the solution, and the p[H] was adjusted to 5.6 with 2 M KOH under a dioxygen atmosphere. Deep red, nearly black crystals formed from this solution at 15.0 °C after 2.5 days. The crystals were filtered off and washed with cool ethanol; yield 7%. Further crystallization resulted from the filtered solution by slow evaporation at ambient temperature. The crystals were filtered off and washed with ethanol; yield 52%. A crystal structure was obtained from the first crystallization product and is described elsewhere.[6]

Cobalt Dioxygen Complexes. Aqueous solutions of μ-peroxo cobalt(III) dioxygen complexes were prepared with equimolar amounts of cobaltous salts (nitrate or chloride) and the appropriate pentadentate ligand. The ionic strength of the solutions was adjusted with the appropriate potassium salt in a closed thermostated reaction cell. Carbon dioxide free oxygen was passed through the solution at 1 atm of pressure. The $-\log [H^+]$ (which is designated p[H]) was adjusted to the appropriate value by addition of carbon dioxide free potassium hydroxide. The nature and composition of the complexes formed, and the reaction conditions required for their formation, have been described previously.[7,8]

Measurements. Redox potentials for the cobalt(II) and cobalt(III) complexes and the ligands were obtained with a Princeton Applied Research electrochemical system. The instrumentation consists of the Model 303 static mercury-dropping electrode, a Model 305 stirrer, a Model 174A polarographic analyzer, and a Model RE 0074 Houston Instruments X-Y recorder. The supporting electrolyte was maintained at 0.10 M with KCl. Potential values were measured vs. the Ag/AgCl electrode with the aid of a polyethylene frit for highly alkaline conditions. The mercury drop times were set at 1-s time intervals, and sample concentrations were in the range 10^{-3}–10^{-4} M.

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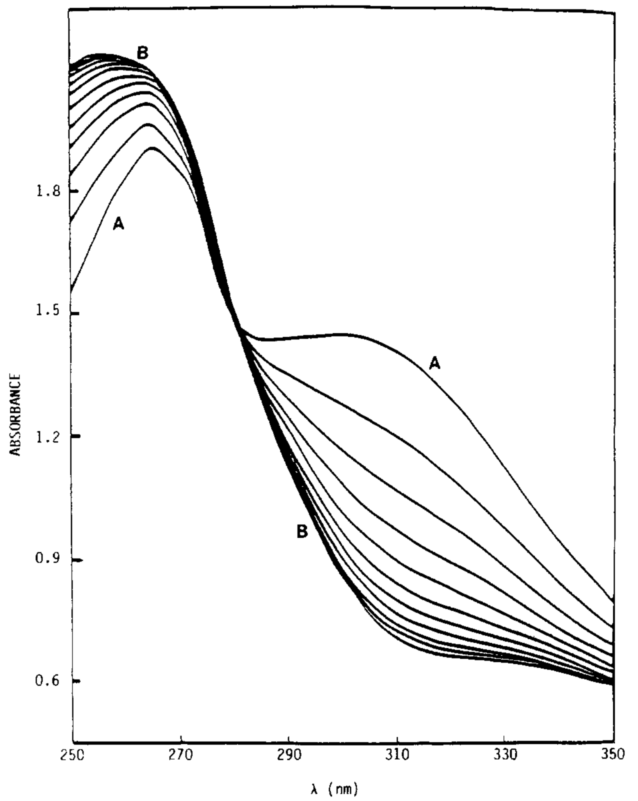

Figure 1. Absorbance of the EPYDEN cobalt dioxygen complex, illustrating conversion to the EPYDEN cobalt(III) complex (spectra taken at 20-min intervals; λ_{max} of dioxygen complex = 308 nm; λ_{max} of Co(III) complex = 266 nm; [Co] = [EPYDEN] = 1.63×10^{-3} M; [KCl] = 1.00 M; $-\log [H^+] = 11.00$; $T = 35.0$ °C); A, $t = 0$; B, $t = \infty$.

Table III. Observed Redox Potentials for Cobalt(II) Complexes and the Resulting Dissociative Oxidation Reaction Products[a]

	E_{obsd}[b,c]	
ligand	Co(II) complexes	oxidn products (Co(III) complexes)
TETREN	−0.425	−0.425
EPYDEN	−0.490	−0.490
IMDIEN	−0.610	−0.610

[a] $-\log [H^+]$ = ca. 11.00. [b] Units of volts. [c] Potentials were measured vs. the silver–silver chloride electrode (SSCE).

Table IV. Hydrolysis[a] Constants for Cobaltous and Cobaltic Chelates[b]

	p*K*	
ligand	Co(II)	Co(III)
EPYDEN	8.75[c]	4.93[c]
IMDIEN	8.7	5.5
PYDIEN	8.77[c]	5.6
PYDPT	9.2	5.6

[a] $LCo^{n+}(OH_2) \rightleftharpoons LCo^{n+}(OH^-) + H^+$ (n = 2, 3). [b] 0.10 M ionic strength; T = 35.0 °C. [c] μ = 0.05 M.

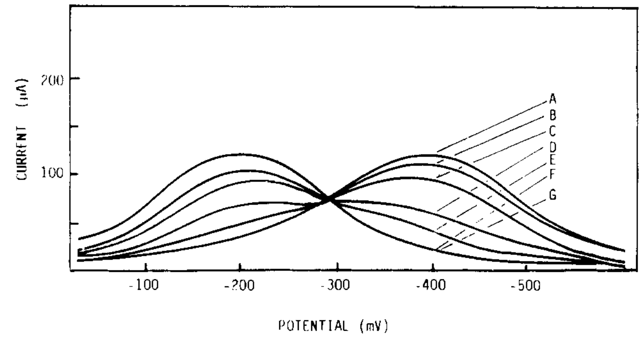

Figure 2. Differential pulse polarograms for solutions of cobalt(III) EPYDEN complexes (μ = 0.10 M (KCl)). p[H] values: A, 5.78; B, 5.57; C, 5.22; D, 4.73; E, 4.50; F, 4.14; G, 3.97. Potentials are obtained vs. the silver–silver chloride electrode.

Kinetic data were obtained from aqueous solutions in a jacketed reaction vessel thermostated at 35.0 °C. The concentrations of the dioxygen complexes in the solutions employed for rate measurements ranged from 10^{-3} to 10^{-4} M. The value of K_w employed for calculation of the second-order constants is 3.631×10^{-14}. The solutions were degassed prior to measurement to remove excess oxygen under conditions (sufficiently high p[H]) such that no appreciable dissociation of the dioxygen complex took place during the measurements.

Absorbance data on these solutions were taken with matched quartz cells having a path length of 1.000 ± 0.001 cm. The decrease in absorbance of the strong ligand-to-metal charge-transfer band ($O_2\ \pi^* \rightarrow d_{z^2}$) at ca. 350 nm was taken as a measure of the concentration of the dioxygen complexes formed initially. The ultraviolet and visible absorption spectra were obtained with a Perkin-Elmer Model 553 fast-scan UV/vis spectrophotometer equipped with a thermostated unit.

Results

The absorbances of the LMCT band of oxygenated 1:1 Co(II) complexes of TETREN, EPYDEN, or IMDIEN show a continuous decrease with time. The presence of an isosbestic point in the plot of absorbance vs. time for each pentadentate ligand is indicative of the fact that the observations involved the conversion of the μ-peroxo-bridged cobalt(III) complex to a single reaction product. An example of the spectra obtained is given for EPYDEN in Figure 1.

It was found that the change in absorbance of the ligand-to-metal charge-transfer band ($O_2\ \pi^* \rightarrow d_{z^2}$) may be described by a first-order rate expression for the initial step in the intramolecular redox process. Plots of $\ln (A_\infty - A_t)$ vs. time were linear for 2–3 half-lives, giving k_{obsd} values that fit expressions of the form $k_{obsd} = k_{OH}[OH^-]$ for L = TETREN, EPYDEN, and IMDIEN and of the form $k_{obsd} = k_{H_2O} + k_{OH}[OH^-]$ for L = PYDIEN and PYDPT. The values of k_{obsd} thus obtained are given in Table I.

The second-order rate constants for the cobalt(III) dioxygen complexes containing TETREN, IMDIEN, EPYDEN, PYDIEN, and PYDPT are given in Table II. The rate constants in Table I were obtained from three to five experimental runs for each pH value listed, with a reproducibility of about 5%. The significant numbers employed in reporting the constants in Tables I and II were selected on the basis of this degree of accuracy.

Hydrogen peroxide was detected chemically by iodide titration in the decomposition of the μ-peroxo-bridged cobalt(III) dioxygen complexes involving the ligands TETREN, EPYDEN, and IMDIEN with carbon tetrachloride. The efficiency of extraction of iodine from the aqueous phase depends on the concentration and the nature of the salts present and was therefore not quite quantitative (i.e., ca. 90–95%). The use of other quantitative methods for spectrophotometric determinations[9,10] of small amounts of hydrogen peroxide was prevented by the strong background absorbance of the cobalt complexes.

The peak reduction potentials taken from polarographic differential pulse polarograms measured at p[H] 11.00 are given in Table III for the cobaltous complexes of TETREN, EPYDEN, and IMDIEN and for the oxidation products obtained from the cobaltous complexes. There is no difference in the differential pulse polarograms; however, sampled dc measurements showed an anodic curve for the cobaltous differential pulse polarograms vs. a cathodic curve for the oxidation reaction products. It is noted that polarograms of Co(II) and Co(III) complexes of the corresponding monoimine are different from those of the completely saturated pentaamines. To accurately compare cobaltous vs. cobaltic waves for sampled dc polarograms, it was necessary to make measurements at p[H] values considerably higher than the p*K*'s of the cobalt(II) and cobalt(III) complexes (p[H] of about 11 was employed; Table IV). An example of the effect of p[H] on the polarographic waves of the Co(III) EPYDEN complex is

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Table V. R_f Values Obtained from Thin-Layer Chromatographic Separation of Standard Compounds and of Dehydrogenation Products

compd	R_f 80:20[a]	R_f 90:10[a]
products from the Co(III) dioxygen complex containing PYDPT after redox rearrangement	0.77	0.66
	0.67	0.46
	0.58	0.34
	0.40	0.14
	0.14	0.06
	0.03	0.01
PYDPT	0.13	0.06
2-pyridinecarboxaldehyde	0.73	0.68

[a] Ratio v/v of chloroform to isopropylamine.

illustrated in Figure 2. The results shown correspond to a pK of 4.93 ± 0.05 for reaction 1.

$$[\mathrm{Co(EPYDEN)OH_2}]^{3+} \rightleftharpoons [\mathrm{Co(EPYDEN)OH}]^{2+} + \mathrm{H}^+ \quad (1)$$

The use of the –log of the hydrogen ion concentration of 11.00 for these measurements sufficiently ensures the complete formation of cobaltous and cobaltic hydroxo complexes. Since the redox potentials of the Co(III)/Co(II) complexes involving TETREN, EPYDEN, or IMDIEN are not changed by the oxidation reactions at p[H] 11.00, it is apparent that the ligands have not changed and that metal-centered oxidative rearrangement is indicated. Thus, oxidative dehydrogenation of the coordinated ligands TETREN, EPYDEN, and IMDIEN does not occur through formation of the intermediate cobalt dioxygen complexes, in sharp contrast to the behavior of PYDIEN and PYDPT, discussed below.

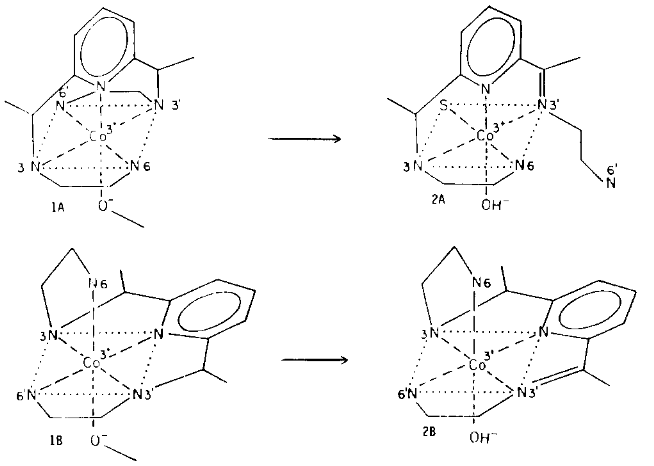
In the decomposition of the μ-peroxo cobalt(III) complex involving the ligand PYDPT, neither hydrogen peroxide nor dioxygen could be detected by polarographic methods or chemical methods (iodide titration). Under the reaction conditions employed about 1 × 10^{-3} M hydrogen peroxide was added to the solution and was found to be detected for at least 10 h. The absence of dioxygen was demonstrated by the use of a polarographic oxygen electrode. This indicates that hydrogen peroxide was not produced in the oxidation reaction and that therefore water is the probable reaction product. After 2–3 half-lives of the oxidation reaction a new ligand was identified by TLC analysis as the reaction product. The ligand formed was identified by removing the cobalt as CoS, extracting the reaction mixture with methylene chloride, and spotting the solution on a TLC plate. Separation of the products was accomplished by developing the TLC plate with a solution of chloroform and isopropylamine. The R_f values are listed in Table V for the separation of products extracted as well as the standard compounds 2-pyridinecarboxaldehyde and the starting ligand PYDPT. In separate experiments it was found that the quantity of 2-pyridinecarboxaldehyde (analyzed as the 2,4-dinitrophenylhydrazone) formed in the oxidative dehydrogenation reaction was equivalent to the amount of PYDIEN employed in dioxygen complex formation.

The pseudo-first-order rate constants for the oxidation reaction of Co(II) complexes of PYDIEN and PYDPT, measured by the disappearance of the LMCT (O_2 $\pi^* \rightarrow d_{z^2}$) for various p[H] values, are given in Table I. A marked increase in the rate constant can be observed above p[H] 10, with the reaction kinetics becoming first order in dioxygen complex and first order in hydroxide concentration.

Discussion

The redox rearrangement reactions of the cobalt dioxygen complexes containing EPYDEN, IMDIEN, and TETREN as ligands, which are classified above as metal-centered oxidations, are unlike the oxidation reactions of cobaltous complexes of PYDIEN and PYDPT, which are ligand-centered oxidative dehydrogenations. Despite the similarities in the donor groups of PYDIEN and EPYDEN, the ultimate oxidation products resulting from dioxygen complex formation are completely different.

Scheme I. Possible Conformations of Dioxygen Complexes of CoEPYDEN (CoL^{2+}) and Requirements of Oxidative Dehydrogenation Reaction To Form $Co^{III}H_{-2}L$



First, the detection of hydrogen peroxide from solutions of the decomposed μ-peroxo cobalt(III) complex involving the ligand EPYDEN indicates that the μ-peroxo bridge dissociates from the dioxygen complex as hydrogen peroxide. This was not detected in the decomposition of the μ-peroxo cobalt(III) complexes involving PYDIEN or PYDPT as ligands.

Earlier work on Co(II)/Co(III) oxidation reduction potentials for complexes involving PYDIEN, PYDPT, EPYDEN, and IMDIEN showed that the potentials result from quasi-reversible one-electron oxidation or reduction.[11] In this research the cobalt(III) complexes obtained by degradation of the binuclear peroxo-bridged dioxygen complexes with EPYDEN, TETREN, and IMDIEN as ligands are compared with the cobalt(II) complexes from which the dioxygen complexes were formed. The polarographic waves observed were found to be reversible The pK_a's of hydrolysis for these cobaltous and cobaltic complexes and the measured potentials were found to be the same. Therefore, the equivalence of the potential of the cobalt(II) complex to the final product of the oxidation reaction indicates that there is no change in the coordinating ligand. Since the sampled dc polarograms indicate a change from negative to positive current, the only changes in the complexes involved are in the oxidation state of the metal ion.

The reaction pathway in the oxidation of $[\mathrm{Co(EPYDEN)OH}]^+$ is in sharp contrast to those of the analogous complexes of PYDIEN and PYDPT that undergo facile oxidative dehydrogenation. A probable rationale for this behavior may be seen in considering the possible conformations of the dioxygen complex intermediates in the oxidation process, conformations 1A and 1B in Scheme I. The aliphatic 3,3'-nitrogens would be expected to be approximately coplanar with the pyridine ring, with terminal nitrogens 6,6' either cis or trans to each other. The complex with conformation 1B has the lower energy dehydrogenation pathway through the formation of a conjugated imine, because it does not require that the coordinate bonds be broken upon oxidative dehydrogenation. Alternatively, imine formation from the complex with conformation 1A would result in the breaking of the terminal amine–cobalt(III) bond in the oxidative dehydrogenation process, because of the steric restraints of the trigonal imine nitrogen that would be formed, producing the complex illustrated by conformation 2A.

The crystal structure[6] of the iodide complex isolated from the decomposition reaction carried out on a solution of the μ-peroxo cobalt(III) complex involving EPYDEN indicates that the pyridyl group is trans to the oxygen and that no oxidation of the ligand occurs through the intermediate μ-peroxo cobalt(III) dioxygen complex. Thus, the lowest energy pathway for the oxidative decomposition of the dioxygen complex is simple dissociation of peroxide with the original ligand coordinated to cobalt(III) as indicated by 1A. In order that the crystal structure support this conclusion, it is essential that the iodide be formed with retention

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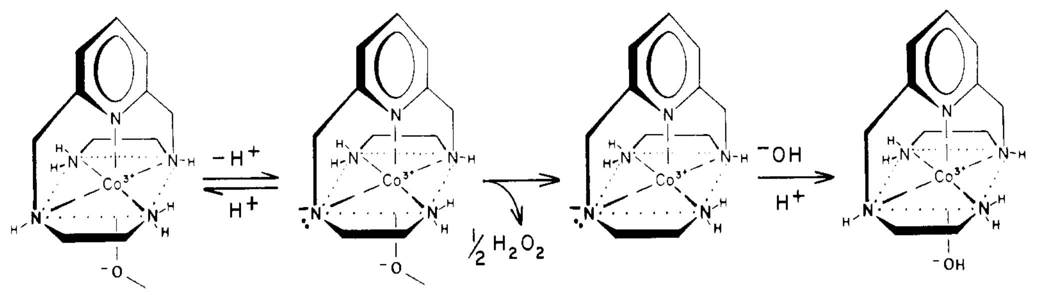
Scheme II



of the ligand configuration indicated by 1A.

For a dissociative process retention of configuration requires that the intermediate five-coordinate complex not form an intermediate with a trigonal-bipyramidal structure (C_{3v} or D_{3h}). For a purely dissociative process with retention of configuration, the five-coordinate intermediate must react with its immediate environment before trigonal complex formation or some amount of bond making associated with loss of the peroxo group can occur. An S_N1cB mechanism, generally accepted as the mechanism for base hydrolysis of various pentaamine complexes, is highly improbable in the oxidation of the cobaltous complex containing EPYDEN because a pyidyl group trans to a peroxo ligand cannot deprotonate to form the normally proposed conjugate-base intermediate. However, an interchange mechanism involving a conjugate base has been proposed for base hydrolysis of a cobalt(III) complex.[12,13]

Since there is a first-order increase with hydroxide ion concentration in the rate of the oxidation to inert cobalt(III) products for the cobaltous complex containing EPYDEN as well as for TETREN and IMDIEN, a conjugate-base mechanism is proposed. Thus the leaving group, peroxide, of a conjugated base dioxygen complex may leave the first coordination shell by an interchange reaction mechanism for retention of configuration. The rates for I_d reactions are not changed by nucleophiles competing with water; however, the intermediate may coordinate with any incoming ligand. The interchange mechanism, which is widely accepted for acid hydrolysis of cobalt(III) complexes, may also be applicable to the decomposition of peroxo-bridged cobalt(III) complexes. It is therefore proposed that the identification of the iodide trans to the pyridyl ring in the cobalt(III) complex containing EPYDEN indicates that it is a product of the dioxygen complex having configuration 1A in Scheme I. A five-coordinate intermediate state with an undistorted square-pyramidal geometry would also be expected to be favored over a trigonal bipyramid because of the relatively rigid structure formed by the pyridyl ring and the adjacent aliphatic nitrogen donor atoms.[14] Therefore, less energy is required in the formation of an intermediate with a square-pyramidal geometry than that required for the formation of a trigonal-bipyramidal arrangement of ligand donor atoms.

An important difference between the structure of the cobalt(III) dioxygen complex containing EPYDEN and other complexes for which the conjugate-base mechanism has been proposed (including IMDIEN and TETREN) is that in the latter a π-stabilizing orbital is not present trans to the leaving peroxo group. Second-order rate constants of these three complexes are very similar, and it is reasonable to expect that their activation energies are also comparable. Thus, similar mechanisms are expected for these three metal-centered oxidation reactions.

A plausible reaction mechanism, which is in conformity with the observed first-order increase in the rate of the reaction with the concentration of hydroxide ion, involves deprotonation of an amino nitrogen, as indicated in Scheme II. The increased negative charge in the coordination sphere would increase the donor character of the coordinated ligand and increase the peroxide character of the coordinated dioxygen, thus promoting the dissociation of the peroxide, stabilizing the cobalt(III) transition state, and leading to the formation of the final inert cobalt(III) complex.

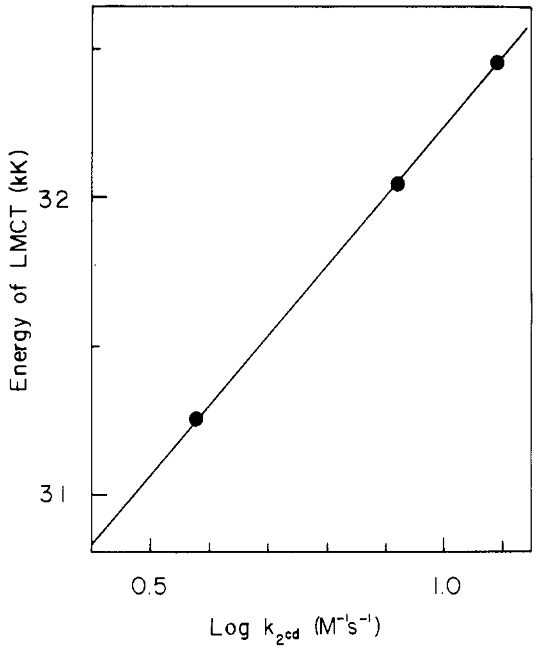


Figure 3. Plot of the energy of the LMCT band vs. the observed rate constants for the dissociation reactions of the cobalt(III) dioxygen complexes containing TETREN, IMDIEN, and EPYDEN (T = 35.0 °C; p[H] = 10.5; μ = 0.10 M).

If it is assumed that the frequency of the ligand-to-metal charge-transfer band of the oxygen π^* orbital to the metal d_{z^2} orbital is the reverse of the internal electron shift that occurs on dioxygen complex formation, then this energy may reflect a change in (Co–O–) bonding. Lever et al.[15] have pointed out a linear correlation between the energy of the oxygen-to-metal charge-transfer band and the charge properties of M(II) ions, concluding that there is a net increase in negative charge on the dioxygen as the electron affinity of the metal ion decreases. Thus for cobalt(II) complexes, a stronger electron-donating ligand should cause a decrease in the electron affinity of the cobalt(II), resulting in an increased negative charge on the dioxygen upon dioxygen adduct formation. The greater the negative charge on the dioxygen, the greater the cobalt(III) character of the metal ion and therefore, for the simple dissociative oxidation reaction, the energy of the oxygen-to-metal charge-transfer band, reflecting the σ-bond strength in the intermediate μ-peroxo cobalt(III) complexes, may be expected to correlate with the rate of peroxide dissociation. This relationship, shown in Figure 3, seems to hold for the complexes of EPYDEN, IMDIEN, and TETREN studied in this investigation.

The oxidation of the cobaltous complex containing PYDPT does not produce hydrogen peroxide, and the oxidation of this ligand must involve imine formation through dehydrogenation in a manner similar to that described for PYDIEN.[4] This type of oxidation is indicated by extensive uptake of dioxygen beyond the

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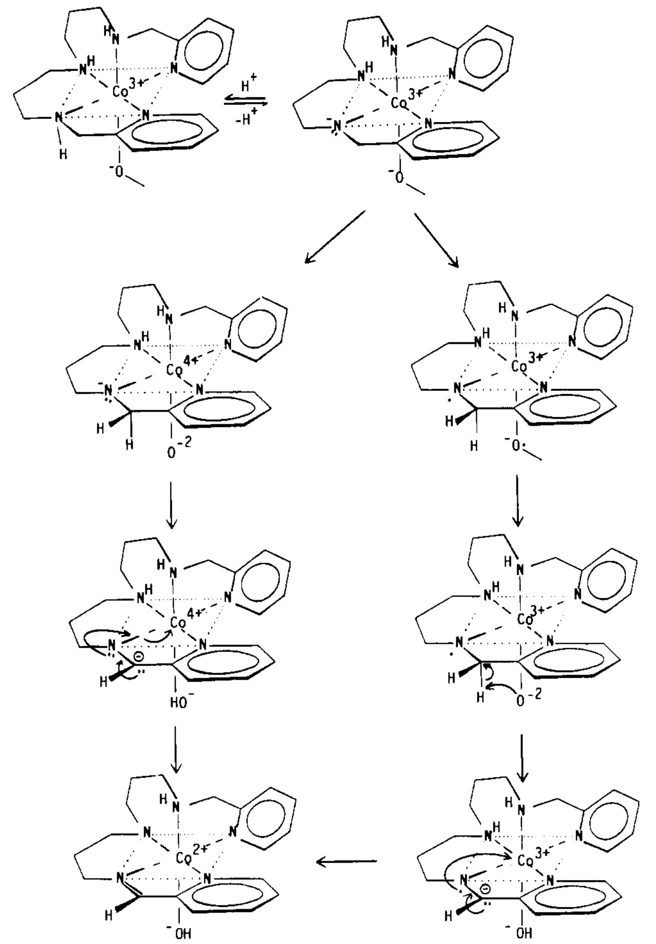
Scheme III



amount needed for initial dioxygen complex formation and by identification of 2-pyridinecarboxaldehyde as a reaction product (resulting from acid hydrolysis of the imine formed by ligand dehydrogenation after the removal of cobalt(II) from the reaction mixture).

The reaction mechanism suggested for oxidative dehydrogenation (Scheme III) takes into account the observed first-order increase in the rate of reaction with the concentration of hydroxide ion, as well as additional oxygen uptake required for ligand dehydrogenation. The rate-determining step suggested is the homolytic cleavage of the peroxo bridge, which is assisted by a one-electron transfer to the peroxo bridge. At p[H] values above the p*K* of the cobalt(III) complex, a hydroxo complex would be expected as the final product. The sequence of steps in the reaction mechanism shown beyond the rate-determining step involves some alternative choices, all of which would be promoted by the initial deprotonation of a coordinated aliphatic amino group. The oxo radical shown would be expected to be highly reactive and have a short lifetime. It would be stabilized by coordination to the Co(III) center and may be written in the form $Co^{IV}-O^{-II}$ (coordinated oxo). This structure would be further stabilized by the especially strong coordination of the metal ion by the deprotonated amino nitrogen.

Few cobalt(IV) complexes are known, and they are not well characterized;[16] therefore, it is highly probable that this transient oxidation state may be relieved by concerted donation of an electron pair to the metal from the coordinated nitrogen, imine double bond formation, and hydrogen ion dissociation from the α-carbon atom, illustrated in Scheme III. The proximity of the hydrogen atoms bound to the α-carbon, as seen by CPK precision molecular models, makes the whole process concerted, resulting in a single transition state in which all effects mentioned above are involved. It is seen that conjugation with the aromatic ring would also be a factor in the stabilization of the proposed transition state.

An alternative to the coordinated oxo radical shown in the reaction mechanism is to consider the possibility of a coordinated amido nitrogen radical, with an electron transferred to the oxygen to form the dinegative oxo group, which is subsequently protonated. The amido radical, which would be stabilized by Co(III), may then be converted through the appropriate transition-state complex to an imine nitrogen coordinated to cobalt(II), as indicated.

There is no clear distinction between two successive one-electron transfers and the hydrogen abstraction since both would involve formation of water, imine, hydrogen ion, and a cobalt(II) product. However, hydrogen ion abstraction may be less specific, whereas a ternary complex involving two subsequent one-electron transfers to the coordinated peroxo group may help avoid side reactions by shortening the lifetime of reactive intermediates. Further support for a ternary intermediate vs. a free-radical oxidation in the oxidative dehydrogenation reactions may be inferred from the generally seen conjugated-imine products. The buildup of the conjugated systems provides a low-energy pathway for an intramolecular oxidation, avoiding the less specific hydrogen atom abstraction pathway.

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