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1,3-Bis(2,5,8,11-tetraazaundecyl)benzene (MXTRIEN): Synthesis, Binucleating Chelating Tendencies, and Formation and Thermal Degradation of Its Cobalt Dioxygen Complex

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Synthesis and potentiometric equilibrium studies of the stabilities of the complexes of 1,3-bis(2,5,8,11-tetraazaundecyl)benzene (MXTRIEN) with Cu(II), Co(II), Ni(II), and Zn(II) are reported. Equilibrium constants are determined for the formation of mononuclear and dinuclear chelates of these metal ions, as well as several protonated and hydroxo chelates. Dioxygen combines with the cobalt(II) complex to form a stable dibridged (μ-hydroxo, μ-peroxo) dinuclear cobalt dioxygen complex. The autoxidation of the cobaltous complex through the formation of the dioxygen complex results in a metal-centered oxidation to form the dicobalt(III) chelate and hydrogen peroxide. The first step of the autoxidation reaction is first-order with respect to the concentration of both the dioxygen complex and hydroxide ion.

Introduction

Synthetic dioxygen carriers have been studied for the past two decades for three main reasons, their relevance to naturally occurring dioxygen carriers,[1] their possible use in industrial processes for the separation of dioxygen from air,[2] and the activation of dioxygen in various types of redox reactions.[3] Although insights have been gained about the relationships between structure and properties of these complexes, much is still to be learned about the irreversible degradation of dioxygen complexes. Such information is necessary to design more robust and efficient oxygen carriers. Among the synthetic carriers, the cobalt(II) complexes have received[4] particular attention since they can be relatively easily synthesized with a large variety of ligands. However, it was not until very recently that detailed studies of the degradation of cobalt(II) dioxygen complexes were carried out.[5] Oxidative degradation of these complexes can be classified in two categories: metal-centered and ligand-centered oxidations.

In some cases degradation of dioxygen complexes occurs in high enough yield to allow isolation and/or characterization of the products. Martell[7] and co-workers[6-8] studied the degradation in aqueous solution of (μ-peroxo)dicobalt(III) complexes with dipeptides and polyamines as ligands. Displacement of the peroxo group and irreversible production of an inert Co(III) complex was reported for some of these ligands while the others were found to undergo oxidative dehydrogenation of the coordinated ligand, yielding a Co(II) complex that can again bind dioxygen.

The first part of this paper reports equilibrium studies for the coordination of the ligand 1,3-bis(2,5,8,11-tetraazaundecyl)benzene (MXTRIEN, **1**) with Cu(II), Ni(II), Co(II), and Zn(II). The second part describes formation of the dioxygen adduct of the Co(II) complex of MXTRIEN, as well as kinetic measurements and product identification of its degradation to an inert complex.

Experimental Section

Materials. Triethylenetetramine. Technical grade triethylenetetramine (TRIEN) was purchased from Aldrich Chemical Co. It has been reported[9] that it is a mixture of several polyamines, and further purification was necessary. About 500 g of the liquid amine was dissolved in 1 L of 95% ethanol and cooled to 10 °C in an ice bath. A 200-mL quantity of concentrated HCl was added dropwise so that the temperature of the solution did not exceed 20 °C. The solution was left at room temperature for 12 h until yellow crystals formed. After the crystals were filtered off, the same procedure was repeated until no further crystallization occurred. At this stage, the total amount of added HCl was about 600 mL. The addition of HCl was then continued until the total volume added reached 900 mL. The thick, creamy precipitate that formed was filtered off and recrystallized two times from a mixture of acidified water and ethanol. Colorless crystals were obtained. A weighed sample of each precipitate was titrated with standard sodium hydroxide. The yellow salt that precipitated first was found to require 3 equiv of KOH (2.97 equiv based on the molecular weight of 2,2′,2″-triaminotriethylamine, TREN) and was assumed to be TREN·3HCl. The colorless salt that precipitated last was found to require 4 equiv of KOH (3.98 based on the molecular weight of TRIEN) and was thus assumed to be TRIEN·4HCl. The yield was about 50 g for TREN·3HCl and 200 g for TRIEN·4HCl. A total of 126 g of the tetrachloride salt of TRIEN was neutralized with an excess of KOH. The liquid amine was extracted with $CHCl_3$. About 40 g of pure liquid TRIEN was obtained after evaporation of the chloroform solvent.

***N*-Acetyltriethylenetetramine.** A homogeneous solution of TRIEN (73 g, 0.50 mol) and ethyl acetate (126 g, 0.143 mol) was stored at room temperature without stirring for 2 weeks. Unreacted starting material was distilled off under vacuum at a temperature range of 84–90 °C. The residual light yellow oil was found to be at least 97% pure *N*-acetyltriethylenetetramine by NMR integration; yield 20.6 g, 0.11 mol (76%). A ^{1}H NMR spectrum (D_2O) gave δ 1.96 (singlet), 2.69 (quartet), and 3.34 (quintet) in the ratio of 3:8:4.

1,3-Bis(2,5,8,11-tetraazaundecyl)benzene (MXTRIEN). A mixture of *N*-acetyltriethylenetetramine (20.6 g, 0.11 mol) and 97% *m*-phthaldehyde (7.4 g, 0.055 mol) was dissolved in 50 mL of methanol and heated to 80 °C for about 30 min. After the methanol was evaporated, about 120 mL of benzene was added and the mixture distilled azeotropically until nearly all the water was removed. The product (Schiff base) was redissolved in 200 mL of methanol after having evaporated the benzene solvent. The solution was hydrogenated over 1 g of Pd on charcoal catalyst until the calculated amount of hydrogen was absorbed. The mixture was filtered, and the filtrate was concentrated by evaporation. The resulting oil was dissolved in 6 M HCl and the solution was refluxed for 48 h. The solid that formed on cooling was filtered off from the solution and washed with absolute ethanol. The octachloride salt was recrystallized twice from 80% methanol and dried under vacuum; yield 9.8 g (26%). The ^{1}H NMR spectrum gave δ 2.66 (multiplet), 3.65 (singlet), and 7.15 (singlet) in the ratio of 6:1:1. Anal. Calcd for $C_{20}H_{42}N_8\cdot 8HCl\cdot H_2O\cdot CH_3OH$: C, 34.25; H, 7.67; N, 15.21. Found: C, 33.95; H, 7.74; N, 15.14.

Sample Preparation. The dicobaltic MXTRIEN complex was prepared by first oxidizing the hexaaquo cobaltous complex with hydrogen

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(9) Dixon, H. B. *Lancet* **1972**, *1*, 853.

peroxide in the presence of an excess of KOH. The resulting cobaltic black solid trihydroxide was separated and washed by repeated centrifugation and decantation. A 2-mmol portion of $Co(OH)_3$ was added to an 80%–20% ethanol–water mixture containing 1 mmol of MXTRIEN·8HCl. A 2-mmol amount of KOH was added to neutralize any excess of hydrogen ions released as a result of complexation. The solution was allowed to stand at 40 °C for 7 days. The complex was then isolated as a purple solid and purified by recrystallization from absolute ethanol. For polarographic analysis the purified complex was redissolved in dioxygen-free 0.100 M aqueous KCl.

Potentiometric Equilibrium Measurements. Potentiometric equilibrium measurements in the absence and in the presence of metal ions were carried out with a Corning Model 150 digital pH meter in a water-jacketed reaction vessel maintained at 25.0 ± 0.1 °C. The ionic strength of the medium was maintained at 0.100 M by the addition of KNO_3. The potentiometric cell was fitted with glass and calomel electrodes that were calibrated with standard aqueous HCl and KOH solutions to read $-\log [H^+]$ directly. In order to maintain the linearity of the EMF–hydrogen ion concentration calibration, the free H^+ and OH^- concentrations were limited to a small fraction of that of the supporting electrolyte by restricting the $-\log [H^+]$ measurements to the range 2–12. The titrant was delivered with a Metrohm piston buret. The potentiometric measurements were carried out under an atmosphere of nitrogen and dioxygen, respectively. Equilibrium measurements were made on solutions containing MXTRIEN free of metal and on solutions containing 1:1 and 2:1 molar ratios of metal ion to MXTRIEN. The amount of ligand in the 50-mL solutions was 0.00010 mol.

Computations. The equilibrium constants were determined by using the program BEST written in this laboratory.[10] No attempt was made to "invent" additional species for the purpose of obtaining a better fit of the experimental data. The species introduced were limited to those that could be justified on the basis of established principles of coordination chemistry in solution. Species distribution curves were generated with the aid of the program SPE written by R. J. Motekaitis, of this laboratory.

Kinetics. Reaction rates for the decomposition of the cobalt dioxygen complex were measured by following the decrease in absorbance of the strong ligand-to-metal charge-transfer band ($\pi^*_{O_2} \rightarrow d_{z^2}$) at ca. 366 nm. The UV-vis absorbance spectra were obtained with a Perkin-Elmer Model 553 fast-scan UV-vis spectrophotometer equipped with a thermostatically controlled cell unit and a remote-control time drive chart recorder. The solution samples were maintained at constant temperature and at constant p[H] during the measurements. The temperature was kept constant by the use of a water-jacketed reaction vessel and a thermostatically controlled quartz cell of 1.000 cm light path length connected together, the solution being circulated between the reaction vessel and the cell with the use of a Cole-Parmer Masterflex pump. The p[H] was maintained constant by continuous addition during running time of CO_2-free 0.100 M KOH. After preparation of the dioxygen complex and prior to the kinetic run, all excess dioxygen was removed with a flow of argon for a period of 30 min or more. A slower argon flow was allowed during running time to maintain anaerobic conditions. Anaerobic conditions were employed to simplify the kinetic data by avoiding continuous reoxygenation of the solution during experimental runs. The concentrations, p[H]'s, and temperatures of solutions for kinetic measurements ranged from 10^{-3} to 10^{-4} M, 9.00 to 11.00, and 50 to 70 °C, repspectively.

Product Identification. A solution of the dioxygen complex (0.100 mM) was digested at 50 °C and p[H] 11.00 for several half-lives in order to achieve complete decomposition under anaerobic conditions. The solution thus obtained was processed to isolate the ligand by precipitating the cobalt ion as CoS. The solution of the oxidation product was treated with amalgamated zinc under a constant N_2 atmosphere. After the mixture was stirred for 1 h, the amalgam was removed and H_2S was then bubbled through the solution. Addition of 1 M KOH to p[H] 11 precipitated the black cobalt sulfide, which was removed by filtration. The final solution was reduced in volume and the yellow oily liquid ligand was extracted with $CHCl_3$ and obtained in pure form by evaporation of the solvent.

Polarography. Redox potentials for the cobalt(II) and cobalt(III) complexes were obtained with a Princeton Applied Research electrochemical system. The instrument consists of a 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 0.100 M with KCl. Potential values were determined as the peak positions in the differential pulse polarograms and reported vs the Ag/AgCl electrode. The modulation amplitude and drop time were set at 50 mV and 1.0 s for all samples. The scan rates were 2 and 5 mV/s. Measurements were made at 25.0 ± 0.1 °C, and solutions were kept under a blanket of flowing nitrogen during the measurements. Sample concentrations were in the range of 10^{-3}–10^{-4} M.

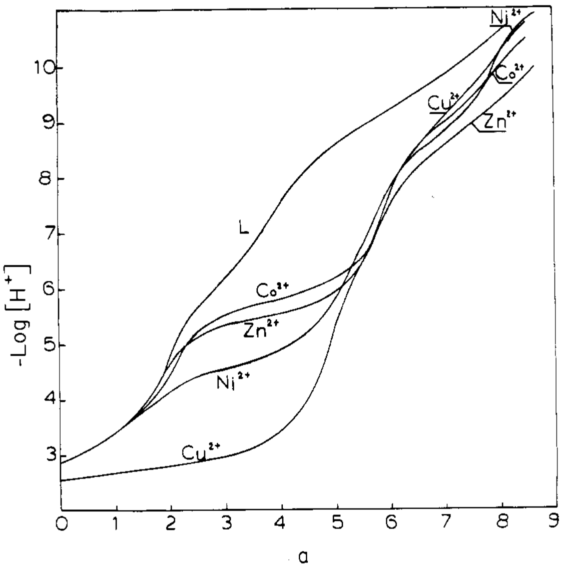

Figure 1. Potentiometric equilibrium data for MXTRIEN and for a 1:1 molar ratio mixture of metal to ligand. a = moles of KOH added per mole of MXTRIEN present. $T_L = 2.015 \times 10^{-3}$ M (L alone); $T_{Co} = 1.996 \times 10^{-3}$ M; $T_{Ni} = 1.976 \times 10^{-3}$ M; $T_{Cu} = 1.982 \times 10^{-3}$ M; $T_{Zn} = 2.002 \times 10^{-3}$ M; $T_L = 2.072 \times 10^{-3}$ M (L with metal). There are approximately 10 equilibrium points per a value.

Table I. Protonation Constants of MXTRIEN, PXTRIEN, and TRIEN (I = 0.100 M (KNO_3); Temperature 25.0 °C)

	MXTRIEN[a]	PXTRIEN[b]		TRIEN[c]
$\log K_1^H$	9.96	9.98	$\log K_1^H$	9.68
$\log K_2^H$	9.46	9.47		
$\log K_3^H$	8.86	8.91	$\log K_2^H$	9.09
$\log K_4^H$	8.20	8.30		
$\log K_5^H$	6.53	6.54	$\log K_3^H$	6.58
$\log K_6^H$	5.73	5.79		
$\log K_7^H$	3.55	3.57	$\log K_4^H$	3.28
$\log K_8^H$	2.86	2.96		

[a] σ fit 0.004. [b] Reference 11. [c] Reference 12.

Results

Metal-Free MXTRIEN. In the absence of added complexing metal ions the potentiometric equilibrium curve of MXTRIEN·8HCl, illustrated in Figure 1, is seen to possess two smooth inflections at $a = 2$ and $a = 4$ (where a = moles of base added per mole of ligand) followed by an extensive buffer region from $a = 4$ to $a = 8$. The first inflection corresponds to completion of the neutralization of the two most acidic substituted ammonium ions. Between the first and the second inflection, two other substituted ammonium ions are neutralized. The buffer region occuring at high p[H] corresponds to the dissociation of the remaining four substituted ammonium groups of the ligand in sequential overlapping steps. All eight neutralization reactions were found to occur in a p[H] region suitable for the calculation of protonation constants from the potentiometric data. The log values of the protonation constants obtained at 25.0 °C and I = 0.100 M (KCl), as defined by eq 1 and 2, are 9.96, 9.46, 8.86,

$$H_{n-1}L^{(n-1)+} + H^+ \rightleftharpoons H_nL^{n+} \qquad (1)$$

$$K_n^H = [H_nL^{n+}]/[H_{n-1}L^{(n-1)+}][H^+] \qquad (2)$$

8.20, 6.53, 5.73, 3.55, and 2.86. These association constants are listed in Table I, with the corresponding values of 1,4-bis(2,5,8,11-tetraazaundecyl)benzene[11] (PXTRIEN, **2**) and tri-

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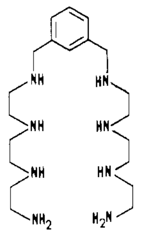
Table II. Logarithms of the Formation Constants of Cu(II), Ni(II), Co(II), and Zn(II) Complexes of MXTRIEN (I = 0.100 M (KNO_3); Temperature 25.0 °C; under Nitrogen)[a]

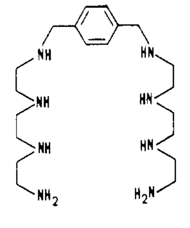
	Cu(II)		Ni(II)		Co(II)		Zn(II)	
quotient, Q	MXTRIEN	TRIEN	MXTRIEN	TRIEN	MXTRIEN	TRIEN	MXTRIEN	TRIEN
$[ML]/[M][L]$	20.15	20.10	14.13	13.80	10.53	10.95	12.20	12.03
$[M_2L]/[M][ML]$	18.40		11.37		8.82		8.84	
$[MHL]/[ML][H^+]$	9.38		8.73		9.26		8.93	
$[MH_2L]/[MHL][H^+]$	8.35		8.41		8.49		8.10	
$[MH_3L]/[MH_2L][H^+]$	5.99		6.33		6.20		6.04	
$[MH_4L]/[MH_3L][H^+]$	3.68		4.21		5.37		4.59	
$[M_2HL]/[M_2L][H^+]$	2.99		3.73		5.69		5.32	
$[MOHL][H^+]/[ML]$	*b*		*b*		−11.16		−9.53	
$[M_2OHL][H^+]/[M_2L]$	−10.95		−11.84		−9.76		−8.22	
$[M_2(OH)_2L][H^+]/[M_2OHL]$	*b*		*b*		−10.95		−8.79	

[a] Values for TRIEN are included for comparison from ref 12. [b] Species not found.

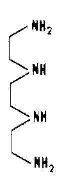
ethylenetetramine[12] (TRIEN, 3). The association constants of MXTRIEN and PXTRIEN were found to be very similar.



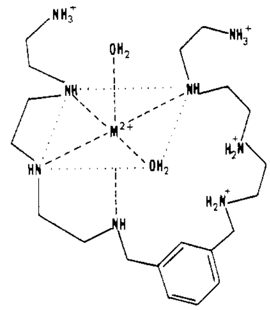
MXTRIEN 1



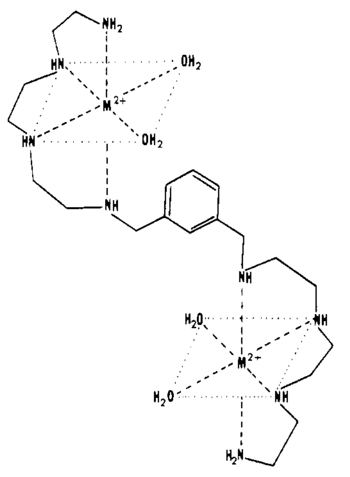
PXTRIEN 2



TRIEN 3



Proposed coordinate bonding of $M(H_4MXTRIEN)L^{6+}$, 4



Proposed coordinate bonding and conformation of $M_2(MXTRIEN)^{4+}$, 5

Metal Chelates of MXTRIEN. The potentiometric equilibrium curves of 1:1 and 2:1 ratios of metal ion to ligand (Figures 1 and 2) illustrate the type of behavior observed for Zn(II) ion and the transition-metal ions Co(II), Ni(II), and Cu(II). The curves for Ni(II), Zn(II), and Co(II) in Figure 1 indicate that these metal ions do not combine with the ligand until the first two protons of the ligand have almost been completely neutralized, whereas Cu(II) reacts more strongly at considerably lower p[H] and displaces protons from the octaprotonated form of the ligand. Above a = 8 the 1:1 equilibrium curves of these metals do not match the metal-free ligand curve, which indicates hydrolysis of the metal chelates at high p[H]. The equilibrium constants that were found necessary to account for the potentiometric equilibrium data of the type illustrated in Figures 1 and 2 are listed in Table II, together with the corresponding values of TRIEN (triethylenetetramine). It is seen that the computer analysis of the data reveals the existence of a considerably larger number of species than those that were obvious by visual inspection of the potentiometric equilibrium curves. The postulation of the presence of MH_nL species where n varies between 1 and 4 was required for a computer fit of the data. Only the monoprotonated form was necessary to be postulated for the dinuclear complexes, i.e. M_2HL. Both Cu(II) and Ni(II) were found to form the dinuclear monohydroxo complex $M_2(OH)L$; however, for Co(II) and Zn(II) three hydroxo forms were necessary to be able to fit the data: M(OH)L and $M_2(OH)_nL$ (n = 1, 2). This is in agreement with the difference between the potentiometric equilibrium curves of the ligand alone and those of the ligand–metal solutions for "a" values higher than 8.

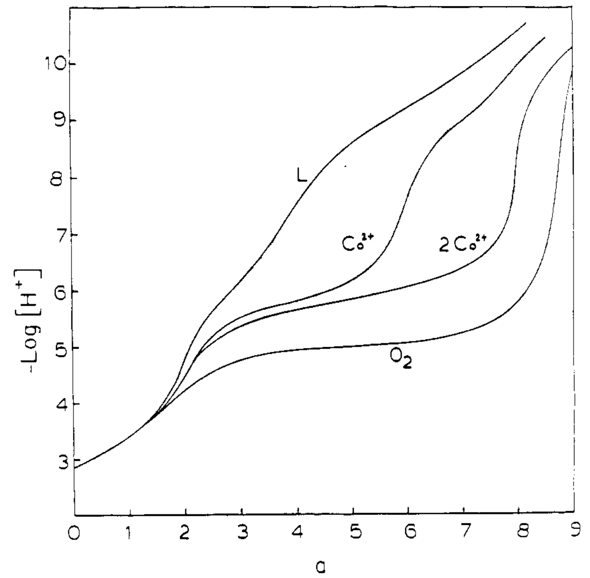


Figure 2. Potentiometric equilibrium data for the Co(II)–MXTRIEN system under anaerobic conditions and in the presence of dioxygen measured at 25.0 °C and I = 0.100 M (KNO_3). $T_L = 2.015 \times 10^{-3}$ M (ligand alone); $T_L = 2.072 \times 10^{-3}$ M (L with metal); $T_{Co} = 1.996 \times 10^{-3}$ M (1:1 Co–L, anaerobic); $T_{Co} = 3.992 \times 10^{-3}$ M (2:1 Co–L, anaerobic); $T_{Co} = 3.992 \times 10^{-3}$ M (2:1 Co–L, aerobic).

Cobalt Dioxygen Complex. Potentiometric equilibrium curves for MXTRIEN with Co(II) under dioxygen and under nitrogen are shown in Figure 2. The strong interactions of the Co(II) complexes with molecular oxygen are illustrated by the large difference in the equilibrium curves. The Co(II) solution of MXTRIEN exhibits under oxygen the dark brown color characteristic of cobaltous dioxygen complexes. The break at a = 9 in the curve under dioxygen indicates that an additional 1 equiv of base for every 2 mol of cobaltous ion was required to fully neutralize the hydrogen ions released in the oxygenation process. This observation is consistent with the formation of a dibridged μ-hydroxo μ-peroxo dinuclear cobalt(III) complex. The value of the formation constant for the dioxygen complex was obtained from the buffer region for the 2:1 system under 1 atm of dioxygen and is listed in Table III.

Species Distribution Curves. On the basis of the equilibrium data in Tables I and II the distributions of individual Co(II) complex species were calculated as a function of p[H] for 1:1 and

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(12) Smith, R. M.; Martell, A. E. *Critical Stability Constants*; Plenum Press: New York, 1975; Vol. 2.

Table III. Logarithms of the Oxygenation Constants and Dioxygen Affinities $P_{1/2}^{-1}$ of Co(II) Complexes of TRIEN, PXTRIEN, and MXTRIEN (I = 0.100 M (KNO_3); Temperature 25.0 °C; P_{O_2} = 1 atm)

L	quotient, Q	log Q	$P_{1/2}^{-1}$, atm^{-1} [d]	
			10^{-3} M[c]	1 M[c]
TRIEN	$[CoL(OH)(O_2)CoL][H^+]/[CoL]^2P_{O_2}$	3.22[a]	1.7×10^7	1.7×10^{10}
PXTRIEN	$[Co_2L(OH)(O_2)][H^+]/[Co_2L]P_{O_2}$	0.37[a]	2.3×10^7	2.3×10^7
MXTRIEN	$[Co_2L(OH)(O_2)][H^+]/[Co_2L]P_{O_2}$	0.60[b]	4.0×10^7	4.0×10^7

[a] Reference 11. [b] This work. [c] Initial concentration of ML or M_2L. [d] p[H] 7.00.

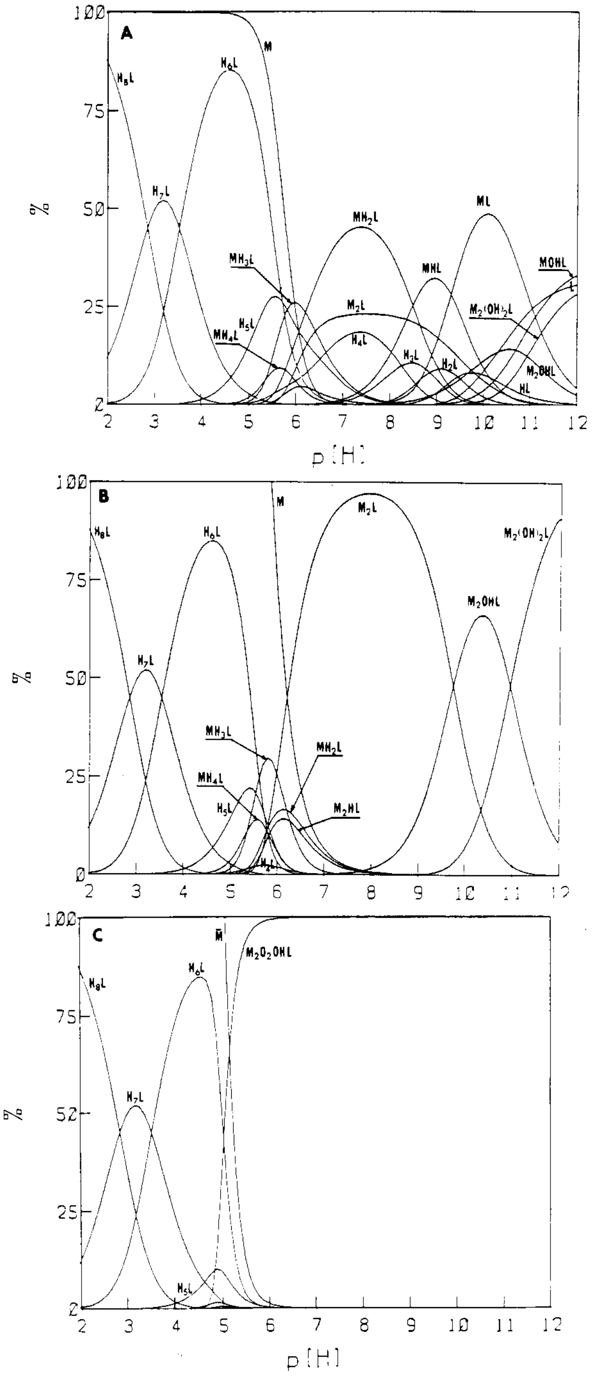

Figure 3. Species distribution diagrams for the cobalt(II)-MXTRIEN system as a function of $-\log [H^+]$ (M = Co^{2+}, L = MXTRIEN, H = H^+): (a) $T_L = T_M = 1.000 \times 10^{-3}$ M (anaerobic); (b) $T_M = 2T_L = 2.000 \times 10^{-3}$ M (anaerobic); (c) $T_M = 2T_L = 2.000 \times 10^{-3}$ M (aerobic).

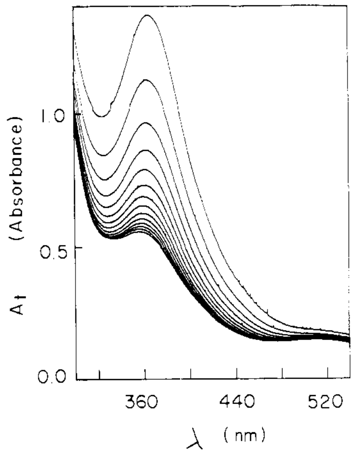

Figure 4. Absorbance of the MXTRIEN cobalt dioxygen complex as a function of time (λ = 366 nm, $T_{Co} = 2T_L = 4.14 \times 10^{-4}$ M, I = 0.100 M (KNO_3), $-\log [H^+]$ = 10.50, temperaure 70 °C, spectra taken at 10-nm intervals).

Table IV. Pseudo-First-Order Rate Constants Calculated from the Disappearance of the LMCT Band of the MXTRIEN Dioxygen Complex of Co(II) (Temperature 70 °C; I = 0.100 M (KCl))

p[H]	$10^3[OH^-]$,[a] M	10^4k_{obsd}, s^{-1}	$10^5k_{H_2O}$, s^{-1}	10^2k_{OH}, s^{-1} M^{-1}
9.00	0.20	1.70		
10.00	2.00	1.80	16.1	2.45
10.50	6.31	3.53		
10.80	12.6	4.63		
11.00	20.0	6.47		

[a] Calculation of $[OH^-]$ based on pK_w = 12.70 at t = 70 °C and at I = 0.100 M (KCl).

2:1 molar ratios of Co(II) to ligand in the presence of nitrogen and in the presence of dioxygen. The results are illustrated in Figure 3. The most striking feature of the 1:1 system (Figure 3a) is that the dinuclear complex Co_2L^{4+} is present at a nonnegligible concentration from p[H] 6 to 9. The 1:1 complex exists in several protonated forms from p[H] 5 to 10, but the deprotonated mononuclear complex becomes predominant only in the p[H] region from 9 to 11. According to the model, at higher p[H], the dinuclear monohydroxo and dihydroxo complexes also form. Thus, we have the situation such that all Co(II) is complexed while some of the ligand remains uncoordinated, because of its strong tendency to form dinuclear complexes in solution. For the 2:1 system the dinuclear chelate predominates above p[H] 7 (Figure 3b). The system containing a 2:1 molar ratio of Co(II) to MXTRIEN in the presence of dioxygen at 1 atm is much simpler (Figure 3c). In this case, it is seen that the μ-hydroxo μ-peroxo dinuclear cobalt(III) complex is the only species present above p[H] 7.

Oxidation Studies. The absorbance of the LMCT band ($\pi^*_{O_2} \rightarrow d_{z^2}$) of the μ-hydroxo μ-peroxo cobalt(III) complex at 70 °C shows a continuous decrease with time (Figure 4). It was found that the change in absorbance of the LMCT band of the dioxygen complex at constant p[H] may be described by a first-order rate expression for the initial step of the oxidation reaction. Both the linearity of these plots and the invariance of k_{obsd} with initial concentration of the cobalt dioxygen complex support the proposed order of the reaction. Plots of $-\ln (A_t - A_\infty)$ versus time were linear for 2–3 half-lives, giving k_{obsd} values that fit an expression of the form $k_{obsd} = k_{H_2O} + k_{OH}[OH^-]$. The values of k_{H_2O} and k_{OH} are listed in Table IV.

The product of the decomposition of the dioxygen complex in aqueous solution at p[H] 11.00 and at 50.0 °C for several half-lives was investigated by polarographic techniques. In the differential

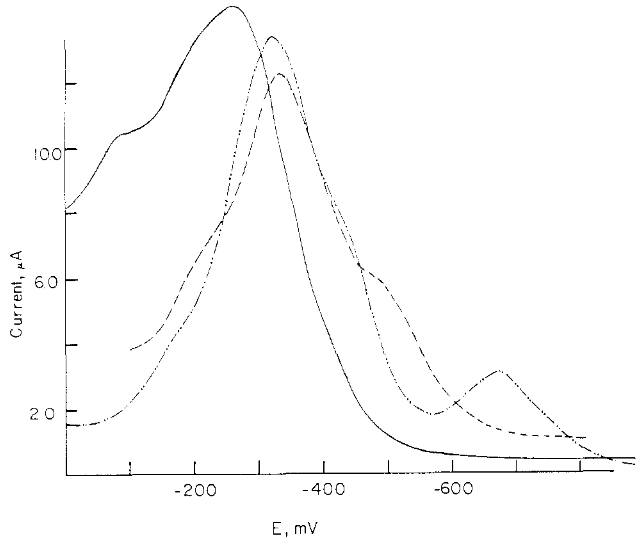

Figure 5. Differential pulse polarograms at I = 0.100 M (KCl) and 25 °C: (—) $Co^{II}_2MXTRIEN(OH)_n$; (-···-) degradation product; (-·-) synthetic $Co^{III}_2MXTRIEN(OH)_m$ ($1 \leq n, m \leq 4$).

pulse polarogram of the binuclear cobalt(II) complex formed at 25.0 °C in the absence of dioxygen, a peak potential at −270 mV vs Ag/AgCl was observed, corresponding to the oxidation of Co(II) to Co(III) as indicated by a negative current in the sampled dc polarogram.[13] A sampled dc polarogram of the oxidation product showed a positive current corresponding to the reduction of Co(III) to Co(II), indicating that Co(II) was oxidized to Co(III) during the degradation reaction. The peak potential corresponding to this reduction wave was found at −320 mV vs Ag/AgCl. In order to identify the nature of the cobaltic complex obtained by heating the dioxygen complex, the dicobaltic complex of MXTRIEN was prepared in a separate experiment from 2 equiv of Co(III) and 1 equiv of MXTRIEN. It was found that there was no difference in the position of the peak potentials in the differential pulse polarograms between the synthetic cobaltic complex and the oxidation product (Figure 5). It is suggested that the difference between the peak potential values of a solution at p[H] 11.0 and at 25.0 °C of the synthetic cobaltic complex (−320 mV vs Ag/AgCl) and the cobaltous complex (−270 mV vs Ag/AgCl) is probably due to a difference in the number of coordinated hydroxide ions or their nature (terminal versus bridging). Since the redox potential of the synthetic dicobaltic MXTRIEN complex and the one obtained from oxidation are the same at p[H] 11, it is apparent that the ligand has not changed and that metal-centered oxidative rearrangement is indicated.

The possibility that an alteration of the ligand during the oxidation reaction might have occurred was eliminated by comparing the ^1H NMR spectrum of the ligand isolated from the reaction mixture by precipitating cobalt as CoS with that of the starting ligand MXTRIEN. The two spectra were found to be identical. Attempts to isolate pure solid samples of the oxidized complex from the reaction mixture have not been successful.

Hydrogen Peroxide Formation. After 48 h, well beyond the time span of the oxidation reaction, the reaction mixture was analyzed for hydrogen peroxide by standard iodide titration but no H_2O_2 was detected. In quantitative titration of H_2O_2, excess iodide ions were added to the acidified solution, and the iodine formed was titrated with thiosulfate using starch as an indicator. The use of other quantitative methods such as spectrophotometric determination of a small amount of H_2O_2 was prevented by the strong background absorbance of the dicobalt dioxygen complex. When H_2O_2 was added initially to the reaction mixture before oxidation, no H_2O_2 was detected after completion of the oxidation. It is thus apparent that decomposition of H_2O_2 occurs under the conditions of the oxidation reaction. It was therefore decided to stop the reaction after periods of time corresponding to degradation of one-eighth and one-fourth of the initial dioxygen complex, in order to look for any amount of H_2O_2 that might have been formed and had not yet decomposed. The same experiment where 1 equiv of H_2O_2 was initially introduced was carried out, also. The results are summarized in Table V. The iodometric titration gave about the same percentage for the expected amount of H_2O_2 in both types of experiments, i.e. with and without initially added H_2O_2. Therefore, we have been able to titrate hydrogen peroxide in a semiquantitative way, using potassium iodide. Titration detected about 70% of the expected amount of H_2O_2 under the most favorable conditions, and the titer required decreased rapidly when the reaction was allowed to proceed substantially. The decomposition of H_2O_2 had previously been reported in other titrations of H_2O_2 in the presence of transition-metal complexes.[4,14] It is suggested that the main reason for the decomposition of hydrogen peroxide here is probably the catalase activity of one or more of the Co(II) complexes present.

Table V. Percentage of H_2O_2 Titrated after Decomposition of the Cobalt(II) Dioxygen Complex for a Period of Time t ($[Co_2MXTRIEN(O_2)(OH)^{3+}]_0 = 5 \times 10^{-4}$ M; p[H] 11.00; Temperature 60 °C; I = 0.100 M (KNO_3); $k_{obsd} = 15.0 \times 10^{-5}\ s^{-1}$ (Pseudo-First-Order Rate))

	reacn time t, min			
	0	15[c]	32[d]	t_∞ (48 h)
$Co_2MXTRIEN(O_2)(OH)^{3+}$	0[a]	65–70	55–60	0[b]
$Co_2MXTRIEN(O_2)(OH)^{3+} + H_2O_2$[e]	99	55–60	45–50	0[b]

[a] No H_2O_2 is expected, and none is found. [b] No H_2O_2 is found. [c] $t_{1/8} = k_{obsd}^{-1} \ln (8/7) = 15$ min. [d] $t_{1/4} = k_{obsd}^{-1} \ln (4/3) = 32$ min. [e] $[H_2O_2]_0 = 5 \times 10^{-4}$ M.

Discussion

The successive protonation constants (Table I) monotonically decrease, reflecting a general buildup of charge, whereby Coulombic repulsion lowers the basicity of the remaining donor groups. The stepwise addition of protons to MXTRIEN (**1**) can be seen as alternate protonation of two separate TRIEN (**3**) moieties. Therefore, the ligand MXTRIEN can be regarded as containing separated tetradentate moieties and its protonation constants can be described as a set of four pairs. The first protonation constant is higher than that of TRIEN. The increase in basicity can be explained in terms of a statistical effect, namely eight basic nitrogens being available for protonation in MXTRIEN as compared to four in the monomeric ligand TRIEN. It is interesting to note that all protonation constants of PXTRIEN[11] are higher than those of MXTRIEN. This effect is probably due mainly to the extent of charge separation between the two TRIEN moieties, which is larger in PXTRIEN (**2**).

The stability constants K_{ML} of 1:1 metal chelates of MXTRIEN are very close to the corresponding formation constants of TRIEN. This result reflects the fact that only four nitrogen donor groups (presumably from the same TRIEN group) are involved in 1:1 complex formation. It is interesting to note that although the values for K_{ML} for M = Cu(II), Co(II), and Zn(II) are slightly higher for MXTRIEN compared to those for TRIEN, the opposite is observed for Co(II). For all transition-metal ions studied and for Zn(II), MXTRIEN forms mono-, di-, tri- and tetraprotonated 1:1 metal chelates. The fourth chelate protonation constant of MXTRIEN complexes is higher than one would predict for the protonation constant of the fourth nitrogen of the uncoordinated side of MXTRIEN. This effect is the largest for Co(II). The same two observations about the unusual nature of the Co(II) complex have been made for PXTRIEN.[11] The suggestion proposed[11] to account for the second observation (unusually high $K^H_{MH_4L}$) involves a possible structure whereby on one side three nitrogens are coordinated to Co(II) in CoH_4L^{6+} (**4**) and the fourth

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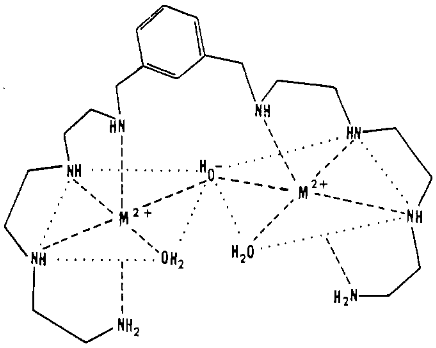
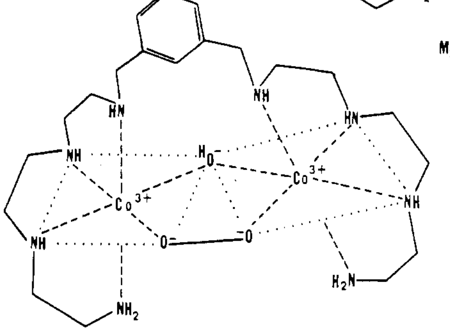
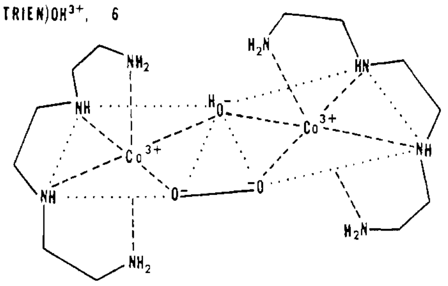
Chart I. Proposed Structures of **6–8**



$M_2(MXTRIEN)OH^{3+}$, 6

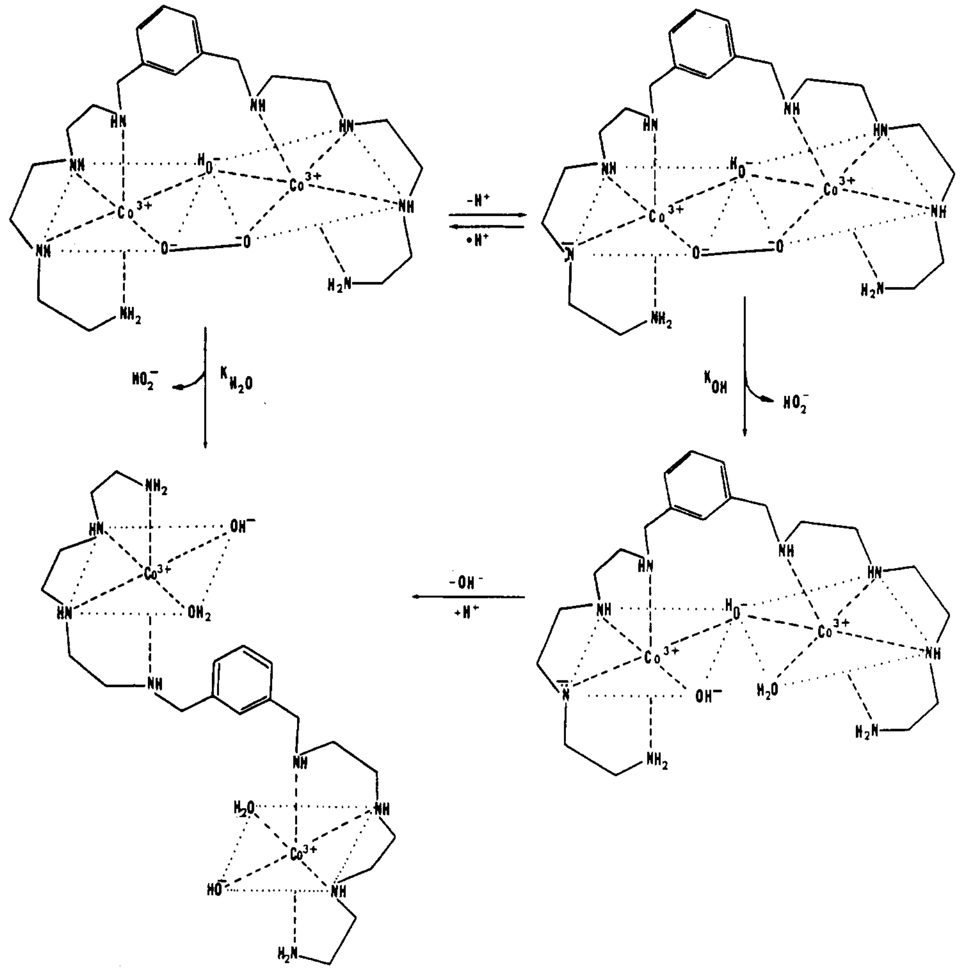


$Co_2MXTRIENO_2OH^{3+}$, 7



$Co_2(TRIEN)_2O_2OH^{3+}$, 8

Scheme I



is protonated while on the other side only three nitrogens are protonated and the fourth is perhaps coordinated to the metal ion. Another possible explanation is hydroxide ion binding between the metal ion coordinated to a tetraamine moiety and the tetraprotonated tetraamine group in MH_4L^{6+}, as was suggested for mononuclear protonated BISTREN complexes.[17] All the metal ions investigated form stable dinuclear complexes, M_2L^{4+} (**5**), which hydrolyze to give $M_2(OH)L^{3+}$ (**6**) (Chart I). However, the relatively high hydrolysis constants ($8 < pK < 11$) indicate that in this case one does not have a strongly bridged hydroxo ligand similar to those reported for Cu_2BISDIEN[16] and Cu_2BISTREN.[17] Therefore, all these hydroxo ligands are assumed to be monodentate or weakly bridging in these chelates.

The higher affinity for dioxygen of the dibridged μ-peroxo μ-hydroxo dinuclear Co(III) MXTRIEN complex **7** (Chart I), compared to that of the corresponding PXTRIEN complex (Table III), is not of an electronic origin ($\sum pK_a$(MXTRIEN) = 55.15; $\sum pK_a$(PXTRIEN) = 55.52) and is probably due to the smaller amount of strain encountered by MXTRIEN when forming a double bridge between the two cobalt ions. Indeed, the atomic distance in MXTRIEN compared to that in PXTRIEN between the two first amine nitrogens substituted on both sides of the xylyl ring is shorter, bringing the two metal ions closer to each other.

It is interesting to compare also the dioxygen affinities of the binucleating ligands MXTRIEN and PXTRIEN with that of the mononucleating ligand TRIEN. The relevant equilibrium constants

$$K'_{O_2} = [ML(\mu\text{-}O_2)(\mu\text{-}OH)ML][H^+]/[ML]^2P_{O_2}\ (\text{atm}^{-1})$$

$$K''_{O_2} = [M_2L(\mu\text{-}O_2)(\mu\text{-}OH)][H^+]/[M_2L]P_{O_2}\ (\text{M atm}^{-1})$$

have different units and cannot be directly compared. However, it is possible to define $P_{1/2}$ as the pressure of oxygen at half-oxygenation for both types of ligands follows:

mononucleating ligand

$$[ML(\mu\text{-}O_2)(\mu\text{-}OH)ML] = \tfrac{1}{4}[ML]_0 \qquad [ML] = \tfrac{1}{2}[ML]_0$$

$$P_{1/2} = [H^+]/K'_{O_2}[ML]_0$$

binucleating ligand

$$[M_2L(\mu\text{-}O_2)(\mu\text{-}OH)] = \tfrac{1}{2}[M_2L]_0 \qquad [M_2L] = \tfrac{1}{2}[M_2L]_0$$

$$P_{1/2} = [H^+]/K''_{O_2}$$

Comparison of $P_{1/2}^{-1}$ for MXTRIEN and PXTRIEN with $P_{1/2}^{-1}$ for TRIEN at an initial complex concentration of 10^{-3} M and p[H] 7.00 shows that the binucleating ligands have higher affinity for dioxygen. Entropic factors for the formation of the binuclear dioxygen complex favor binucleating over mononucleating ligands. The sum of the ligand basicities of two TRIEN molecules (i.e. $\sum pK_a = 57.15$) is higher than the ligand basicities of MXTRIEN or PXTRIEN, and relative basicities would favor the TRIEN ligand with respect to dioxygen complex formation. It is also proposed that formation of the two μ-peroxo μ-hydroxo bridges is facilitated in the case of TRIEN because of the absence of steric effects caused by the xylyl bridge. At a high concentration of starting complex (1 M), where the entropic factor is much less pronounced, the $Co_2(TRIEN)_2(\mu\text{-}O_2)(\mu\text{-}OH)$ complex has a higher affinity for dioxygen (Table III).

Karlin et al.[18] reported that a dinucleating Cu(I) complex, upon addition of dioxygen, resulted in the hydroxylation of the arene ring of the ligand. The ligand MXTRIEN has some structural similarities with the binucleating ligand they employed, two terdentate polyamine units (bis[2-(2-pyridyl)ethyl]amine) connected to a *m*-xylyl group. Forty years ago, Basolo[19] noted that aeration of a mixture of TRIEN and an excess of $CoCl_2$ yielded a purple solid complex identified as $Co^{III}(TRIEN)Cl_3$. Given the previous reports on systems similar to Co_2MXTRIEN,[4-8,18,19] three types of degradation reactions through formation of a dioxygen complex are possible: oxidation of the metal to Co(III), oxidative dehydrogenation of the ligand with formation of an imine double bond, and hydroxylation of the arene. In the presence of dioxygen the dinuclear cobalt(II) chelate of MXTRIEN forms above p[H] 7 a μ-peroxo μ-hydroxo dinuclear cobalt(III) complex. This reaction is reversible at room temperature, and the dinuclear cobalt(II) complex can be recovered by lowering the p[H] and excluding dioxygen from the solution. However, if the temperature is raised, the dioxygen complex is converted irreversibly to the dinuclear cobalt(III) complex. Since the ^{1}H NMR spectrum of the ligand recovered after completion of the degradation is identical with that of the starting ligand, and since the current of the sampled dc polarogram corresponding to the Co(II)/Co(III) reduction potential of MXTRIEN is negative, it is concluded that metal-centered oxidative degradation of the dioxygen complex occurs. Semiquantitative titration of H_2O_2, as high as 0.7 mol of H_2O_2/mol of starting dioxygen complex, indicates strongly that the fate of the μ-peroxo bridge involves separation of hydrogen peroxide. However, H_2O_2 is not stable under the reaction conditions of the degradation reactions and decomposes totally, probably to give O_2 and H_2O.

A rate law of the form $k_{obsd} = k_{H_2O} + k_{OH}[OH^-]$ indicates that there are two parallel pathways for the metal-centered oxidative degradation reaction. The rate constant k_{H_2O} is associated with a spontaneous oxidation of the metal without the intervention of hydroxide ions. In a parallel pathway, deprotonation of an amine nitrogen, previously proposed by Martell et al.[5-8] for analogous systems, can account for the observed second-order rate constant k_{OH}. A plausible reaction mechanism, which is in conformity with all the reported findings in this paper, is proposed in Scheme I.

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