(13) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 4539 (1967); D. A. Buckingham, J. Dekkers, A. M. Sargeson, and M. Wein, *ibid.*, **94**, 4032 (1972).
(14) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **92**, 5701 (1970).
(15) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **91**, 4102 (1969).
(16) E. Baraniak, Ph.D. Thesis, The Australian National University, March 1973.
(17) D. A. Buckingham, D. M. Foster, and A. M. Sargeson, *J. Am. Chem. Soc.*, **92**, 6151 (1970).
(18) D. A. Buckingham, A. M. Sargeson, and A. Zanella, *J. Am. Chem. Soc.*, **94**, 8246 (1972).
(19) D. A. Buckingham, F. R. Keene, and A. M. Sargeson, *J. Am. Chem. Soc.*, **96**, 4981 (1974).
(20) J. Springborg and C. E. Schäffer, *Inorg. Synth.*, **14**, 63 (1973).
(21) J. Meisenheimer, *Justis Liebigs Ann. Chem.*, **438**, 217 (1924); D. A. Buckingham, C. E. Davis, and A. M. Sargeson, *J. Am. Chem. Soc.*, **92**, 6159 (1970), and references therein.
(22) See ref 17, and M. D. Alexander and D. A. Busch, *Inorg. Chem.*, **5**, 602 (1966).
(23) C. J. Boreham, D. A. Buckingham, and F. R. Keene, to be submitted for publication.
(24) M. Anbar and S. Guttman, *Int. J. Appl. Radiat. Isot.*, **5**, 223 (1959).
(25) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).
(26) I. K. Reid and A. M. Sargeson, unpublished results.
(27) C. J. Boreham, D. A. Buckingham, and D. J. Francis, unpublished results.
(28) D. A. Buckingham, I. I. Olsen, A. M. Sargeson, and H. Satrapa, *Inorg. Chem.*, **6**, 1027 (1967); D. A. Loeliger and H. Taube, *ibid.*, **5**, 1376 (1966).
(29) J. F. Remar, D. E. Pennington, and A. Haim, *Inorg. Chem.*, **4**, 1832 (1965).
(30) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6654 (1968).
(31) J. O. Edwards, F. Monacelli, and G. Ortaggi, *Inorg. Chim. Acta*, **11**, 47 (1974).
(32) S. C. Chan and F. K. Chan, *Aust. J. Chem.*, **23**, 1175 (1970).
(33) R. S. Nyholm and M. L. Tobe, *J. Chem. Soc.*, 1707 (1956).
(34) C. J. Boreham, Ph.D. Thesis, The Australian National University, 1978.
(35) D. F. Martin and M. L. Tobe, *J. Chem. Soc.*, 1388 (1962).
(36) A. Haim and H. Taube, *J. Am. Chem. Soc.*, **85**, 3108 (1963).
(37) D. A. Buckingham, L. G. Marzilli, and A. M. Sargeson, *J. Am. Chem. Soc.*, **89**, 2772 (1967).

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Kinetics and Mechanism of Oxidation of Cobalt(II) Macrocycles by Iodine, Bromine, and Hydrogen Peroxide[1]

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A series of cobalt(II) complexes of tetradentate, 14-membered macrocyclic ligands with nitrogen donor atoms is oxidized by bromine and iodine in acidic aqueous solution to the corresponding monohalocobalt(III) product. The rate law shows a first-order dependence on each reactant; rate constants and reduction potentials were determined for each substance. Only one of the cobalt(II) complexes, $Co^{II}([14]aneN_4)^{2+}$, reacts with hydrogen peroxide in the same manner, and in that reaction positive results were obtained in scavenging for a hydroxyl radical intermediate. The other peroxide reactions apparently do not produce HO·. The mechanisms of all of the reactions are considered and discussed.

Introduction

Complexes of cobalt(II) and macrocyclic ligands are known to act as mild reducing agents. A series consisting of 14-membered tetradentate macrocycles or pseudo-macrocycles having nitrogen donor atoms is shown in Figure 1. They constitute a series which makes possible systematic variations in ligand structure, steric effects, electrode potential, and ionic charge. Furthermore, they are stable in aqueous and semi-aqueous media. Despite these advantages, relatively little is known about the kinetics and mechanisms of their oxidation–reduction reactions.

The emphasis of the present work centers on their reactions with iodine, bromine, and hydrogen peroxide. All of the halogen reactions (but only one of the hydrogen peroxide reactions) conform to the stoichiometry of the net reaction shown in eq 1.

$$2(H_2O)_2(Co^{II}) + X_2 = 2X(Co^{III})H_2O + H_2O \qquad (1)$$

(For purposes of generalized notation, the macrocyclic ligand is symbolized by parentheses, and the ionic charge, which varies among the compounds, is omitted. The cobalt(II) reactant is written as a six-coordinate complex, a structure which is known from crystallographic determinations for some of the complexes but only surmised for others.)

Reactions such as this are termed noncomplementary, in that the oxidation state changes do not match. Many such reactions, not only for symmetrical reagents such as I_2, Br_2, and H_2O_2 but also for unsymmetric reagents such as HOBr, ROOH, $PhCH_2Br$, and ICN, are thought to proceed by a sequence of two steps in which a radical or atomic species occurs as an intermediate. (Evidence, however, is not always definitive.) For the symmetrical reagents, the first step of this mechanism, invariably the rate-limiting reaction, is

$$M^{II} + X_2 \rightarrow X\text{–}M^{III} + X\cdot \qquad k_2 \qquad (2)$$

This step is then followed by a much more rapid reaction, often presumed to be a further step of oxidation by X· (eq 3) but which could equally well be atom recombination (eq 4) or, for the halogen reagents in the presence of a trace of halide ion, disproportionation (eq 5).

$$M^{II} + X\cdot \rightarrow X\text{–}M^{III} \qquad (3)$$

$$2X\cdot \rightarrow X_2 \qquad (4)$$

$$2X_2^- \rightarrow X_2 + 2X^- \qquad (5)$$

Previous examples of M(II) complexes whose reactions with various reagents X–Y have been studied mechanistically include $Co(CN)_5^{3-}$,[2] Cr^{2+},[3] edta complexes of Mn(II), Fe(II), and Co(II),[4] V^{2+},[5] V^{3+},[5] U^{3+},[6] Fe_{aq}^{2+},[7] $Fe^{II}(CN)_5$ complexes,[8] and, to a much smaller extent, cobalt(II) complexes of tetradentate macrocyclic ligands with organic halides[9] and peroxides.[10]

The studies reported here consist of determinations of the stoichiometry, products, and kinetics of the reactions of the cobalt(II) complexes shown in Figure 1 with the symmetrical reagents I_2, Br_2, and H_2O_2. Our objective is an understanding of these observations in terms of reaction mechanisms and of the factors affecting the rates of the individual reactions.

Experimental Section

Chemicals. The ligands $[14]aneN_4$, *ms*-$Me_6[14]aneN_4$, and $Me_6[14]$-4,11-dieneN_4[11] were purchased (Strem Chemical Co), and various cobalt complexes[12] were prepared by standard methods:

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Table I. Spectral Maxima[a] for Macrocyclic Cobalt Complexes λ_{max}/nm (ϵ/dm^3 mol^{-1} cm^{-1})

N_4 ligand	$(H_2O)_2(Co^{II})$	$(H_2O)_2(Co^{III})$	$Br(Co^{III})(H_2O)$	$I(Co^{III})(H_2O)$
[14]aneN$_4$	465 (22)	560 (28), 430 (46)[b]	610 (33)	650 (50), 433 (1.4 × 10^3)
ms-Me$_6$[14]aneN$_4$	483 (70), 330 sh[c]	565 (36), 449 sh, 257 (4 × 10^3)[c]	640 (14), 360 (670)	
Me$_6$[14]-4,11-dieneN$_4$	446 (130), 335 (2.5 × 10^3)[c]	582 (27), 431 sh[c]	625 (38), 363 (612)	
Me$_4$[14]teteneN$_4$	545 (4.0 × 10^3), 360 (1.0 × 10^3)[d]	575 sh, 505 (54), 425 sh[c]		
dpnH	505 (2.05 × 10^3)[d]			
(dmgH)$_2$[e]	460 (3.40 × 10^3)	340 (2.0 × 10^3), 240 (2.1 × 10^4)		
corrin	470 (1.09 × 10^4), 410 (6.46 × 10^3), 310 (2.41 × 10^4)	525 (9.9 × 10^3), 495 (9.9 × 10^3), 408 (3.2 × 10^3), 350 (2.6 × 10^4)	354 (2.04 × 10^4)[f]	373 (1.37 × 10^4), 363 (1.37 × 10^4)[g]

[a] This work, unless otherwise noted; values in acidic aqueous solution. [b] From aquation of $Cl_2(Co^{III})$. [c] Reference 14. [d] Reference 9. [e] In 0.1 M NaOAc. [f] Reference 27b. [g] J. M. Pratt and R. G. Thorp, *J. Chem. Soc. A*, 187 (1966).

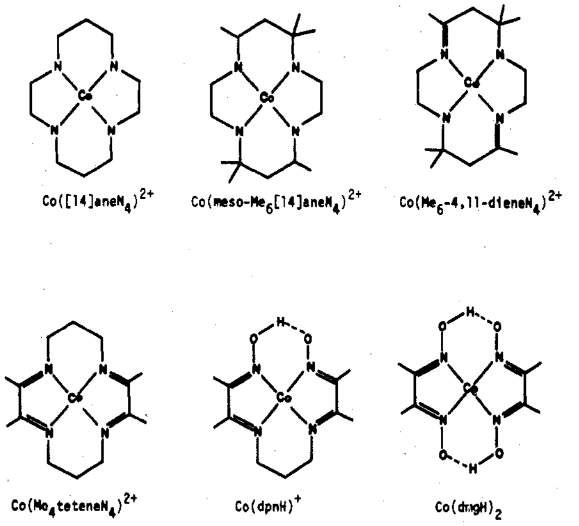


Figure 1. Molecular structures and abbreviated names for the cobalt macrocyclic complexes.

$[(H_2O)_2Co[14]aneN_4](ClO_4)_3$,[13] $[Co(ms\text{-}Me_6[14]aneN_4)](CoCl_4)$,[14] $[Co(ms\text{-}Me_6[14]aneN_4)](ClO_4)_2$,[14] $[Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)](ClO_4)_2$,[14] $[(H_2O)_2Co(Me_4[14]teteneN_4)](ClO_4)_2$,[6,15] $[I_2Co(dpnH)]$[16] and $[Cl_2Co(dmgH)(dmgH_2)]$.[17] The halide derivatives were converted to the known aquo compounds with silver perchlorate and crystallized as perchlorates: $[(H_2O)_2Co(dpnH)](ClO_4)_2$ and $[(H_2O)_2Co(dmgH)_2](ClO_4)$.

The cobalt(II) complexes, where not mentioned directly, were prepared as follows: $(H_2O)_2Co^{II}(dpnH)^+$ from the electrochemical reduction of the Co(III) complex in 0.1 M $LiClO_4$ at a mercury cathode; $(H_2O)_2Co^{II}(dmgH)_2$ by mixing equivalent quantities of dilute solutions of $Co(OAc)_2$ and $dmgH_2$ in 0.1 M NaOAc as well as by dissolution of solid $[(CH_3OH)_2Co(dmgH)_2]$;[17] $(H_2O)_2Co^{II}([14]aneN_4)^{2+}$ by mixing equal volumes of $Co(OAc)_2$ and 0.01 M ligand under prepurified nitrogen, followed (after the reaction appeared complete) by sufficient oxygen-free perchloric acid to provide 0.100 M H^+. Solutions of the cobalt(II) complex vitamin B_{12r} were prepared by reduction of aquocobalamin, B_{12a}, prepared by acidification of hydroxocobalamin (Sigma Chemical Corp.) with amalgamated zinc in 0.1 M perchloric acid.

The cobalt(II) complexes of $(dmgH)_2$ and $[14]aneN_4$ are especially oxygen sensitive, but the others are less so. Halide ions markedly accelerate the autoxidation of some cobalt(II) complexes in solution, especially that of $Me_6[14]aneN_4$.[18] In any event, all Co(II) solutions were carefully freed of oxygen by bubbling with Cr^{2+}-scrubbed nitrogen.

Two of the cobalt(II) complexes are unstable in acidic solution, forming Co_{aq}^{2+} and free ligand. Thus solutions of $Co^{II}(dmgH)_2$ were prepared and used in 0.1 M NaOAc, and solutions of $(H_2O)_2Co^{II}(dpnH)^+$ were prepared in 0.1 M $LiClO_4$. The former appears to decompose "instantly"[19] at pH <4 and the latter at a rate dependent upon $[H^+]$. (Decomposition of $Co^{II}(dpnH)^+$ to Co_{aq}^{2+} follows pseudo-first-order kinetics, with $k = 3.5 \times 10^{-3}$ and 6.2×10^{-3} s^{-1} at 0.033 and 0.050 F $HClO_4$, respectively, at ~22 °C and $\mu = 0.1$ M.)

Lithium perchlorate (used to adjust ionic strength) was prepared from the carbonate, and other materials were reagent grade chemicals.

Analyses. Hydrogen peroxide was determined volumetrically using acidified iodide and thiosulfate. Concentrations of bromine and iodine were determined spectrophotometrically: Br_2, λ 390 nm (ϵ 179 M^{-1} cm^{-1}); I_2, 460 (787).

Cobalt(II) concentrations were determined spectrophotometrically (see Table I), except for $(H_2O)_2Co^{II}([14]aneN_4)^{2+}$. In this case, formation of the complex is incomplete. Addition of perchloric acid converts any $Co(OH)_2$ to Co_{aq}^{2+} and protonates free ligand without decomposing the complex, which is the major species in solution. For purposes of analysis, portions of the solution were reacted with oxygen to form[20] $(Co[14]aneN_4)_2O_2^{4+}$, from which Co^{2+} was separated by ion exchange on Sephadex C-25 resin. The amount of Co^{2+} was determined spectrophotometrically using thiocyanate in 50% aqueous acetone (λ 623 nm, ϵ 1.84 × 10^3 M^{-1} cm^{-1}) and applied as a correction to the total cobalt taken.

Techniques. Products were often characterized spectrophotometrically by comparison with materials which are known or were independently synthesized; the spectra are summarized in Table I. In some cases products were separated using ion-exchange techniques.

Reaction stoichiometry was determined by spectrophotometric "titration", following an absorption band of a reactant or product as a function of reactant ratio and interpolating the absorbance to a "break point".

Reaction rates were determined spectrophotometrically using a Cary 14 instrument for slower reactions and a Durrum D110 stopped-flow instrument for faster ones. Most of the kinetic data were obtained under pseudo-first-order conditions, with one reactant present in substantial excess; these data were analyzed by standard methods. Two exceptions are to be noted: very fast reactions requiring a second-order kinetic analysis and certain reactions conforming to a pattern of consecutive pseudo-first-order processes were analyzed by standard methods.[21]

Half-wave potentials were determined for all of the complexes except B_{12} by cyclic voltammetry using a PAR Model 173 potentiostat/galvanostat and a Model 175 universal programmer. A platinum disk electrode was used for $(H_2O)_2Co(Me_4[14]teteneN_4)^{3+/2+}$ and a hanging mercury drop was used for the others; the reference was a saturated calomel electrode in all cases. The starting material was the available Co(II) or Co(III) complex, as appropriate for the given system, and the potentials were determined in 0.10 F $HClO_4$ except for the cobaloxime system, where 0.1 M $NaClO_4$ was used. The limited solubilities of the $Co(ms\text{-}Me_6[14]aneN_4)^{2+}$ and $Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+}$ complexes required 10^{-4} M concentrations, whereas other systems were studied at 10^{-3} M. A potentiometric method was also used for the $[14]aneN_4$ system, reducing the Co(III) complex with known quantities of Cr^{2+}; the system was calibrated with Fe^{3+}/Fe^{2+} as described by Liteplo and Endicott.[22]

Results

Reactions of Iodine—Stoichiometry and Products. Three of the more rapid iodine reactions were shown to occur with a 2:1 stoichiometry in accord with eq 1. These data are shown in Table II. Other workers[23] had previously shown this for the reaction of vitamin B_{12r} and iodine. Competition between the reaction with iodine and subsequent aquation of the $I(Co^{III})H_2O$ product prevented determinations in other cases, although we have no reason to suspect other than 2:1 stoi-

Table II. Stoichiometry of Oxidation of Co(II) Complexes[a]

reactants	range of init concn/M		Δ[Co]/Δ[I_2]
	$10^4[Co^{II}]_0$	$10^4[X_2]_0$	
I_2 + $(H_2O)_2Co^{II}$-([14]aneN_4)$^{2+}$	6.7–16.7	2.2–2.8	1.90 ± 0.08
I_2 + $(H_2O)_2Co^{II}$-(Me_4[14]tetaneN_4)$^{2+}$	3.08	0.51–1.19	1.76 ± 0.19
I_2 + B_{12r}	1.0	0.196–0.392	2.17 ± 0.09
H_2O_2 + $(H_2O)_2Co^{II}$-(Me_6[14]-4,11-dieneN_4)$^{2+}$	3.03	0.33–2.29	1.06 ± 0.06
H_2O_2 + $(H_2O)_2Co^{II}$-(Me_4[14]tetaneN_4)$^{2+}$	3.21	0.98–2.28	0.98 ± 0.03
H_2O_2 + $(H_2O)_2Co^{II}$-(Me_4[14]tetaneN_4)$^{2+}$ [b]	3.21	0.65–2.28	1.06 ± 0.05
H_2O_2 + $(H_2O)_2Co^{II}$-(Me_4[14]tetaneN_4)$^{2+}$ [c]	3.21	0.98–2.28	1.00 ± 0.08
H_2O_2 + $(H_2O_2)_2Co^{II}$-$(dmgH)_2$ [d]	1.33	0.33–0.98	0.99 ± 0.06
H_2O_2 + B_{12r}	0.67–1.00	0.33	1.20 ± 0.01
H_2O_2 + $(H_2O)_2Co^{II}$-(*ms*-Me_6[14]aneN_4)$^{2+}$	1.87	0.33–1.63	0.95 ± 0.34

[a] In aqueous perchloric acid, except as noted. [b] In 1 M *tert*-butyl alcohol. [c] In 50% aqueous *tert*-butyl alcohol. [d] In 0.1 M NaOAc.

chiometry for all iodine oxidations.

The product of the reaction of $(H_2O)_2Co^{II}([14]aneN_4)^{2+}$ and I_2 was readily separated from excess reactant and any Co_{aq}^{2+} present in the starting material (see Experimental Section) by ion-exchange chromatography on Sephadex C-25 resin, eluting with 0.3 F $HClO_4$. The product eluted as a single band identified as $ICo^{III}([14]aneN_4)H_2O^{2+}$ and confirmed by analysis for cobalt and iodine[24] (ratio I/Co = 1.02). The spectrum of the product (Table I) was then used to determine its yield in other runs (Table II).

Additional studies relating to $ICo^{III}([14]aneN_4)H_2O^{2+}$ were based on anation of the authentic diaquocobalt(III) complex with I^- and aquation of the iodo complex produced in the iodine reaction. Initial rate methods were used to estimate rate constants for both forward and reverse reactions, and absorption spectra, constant after ~60 h, were used to evaluate the equilibrium constant. These data are given in eq 6, but

$$(H_2O)_2Co^{III}([14]aneN_4)^{3+} + I^- \rightleftarrows ICo^{III}([14]aneN_4)H_2O^{2+} + H_2O \quad (6)$$

$$k_6 = 3 \times 10^{-3}\ M^{-1}\ s^{-1}, \quad k_{-6} = 9 \times 10^{-6}\ s^{-1}$$
$$(25\ °C,\ [H^+] = \mu = 0.5\ M)$$

$$K_6 = 5 \times 10^2\ M^{-1} \quad (\sim 23\ °C,\ [H^+] = \mu = 0.6\ M)$$

it must be noted that the kinetic data showed a strong inverse dependence upon $[H^+]$ and also gave indications of catalysis by $(H_2O)_2Co^{II}([14]aneN_4)^{2+}$, if present; thus the values are applicable only under the conditions stated.

Production of the monoiodo complex of B_{12} was demonstrated spectrophotomerically, as its subsequent aquation is known to occur too rapidly to permit isolation.[25] Thus in a stopped-flow determination at 535 nm (an isosbestic point for aquocobalamin, B_{12a}, and iodocobalamin) a single reaction is seen, whereas at 555 nm (a maximum for IB_{12}) the absorbance–time trace shows a distinct maximum. The second stage of reaction has a pseudo-first-order rate constant of 37 s^{-1}, agreeing with the directly determined value for aquation of IB_{12}, 35 s^{-1}.[25] These results are depicted in Figure 2.

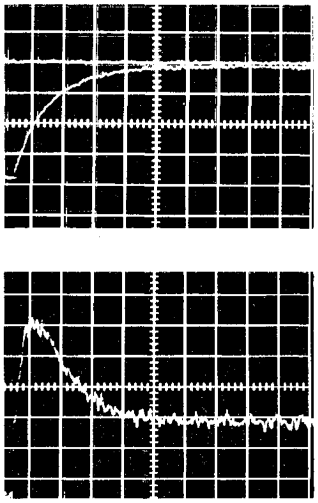


Figure 2. Stopped-flow traces for the reaction of vitamin B_{12r} and iodine: (a) at 535 nm, an isosbestic wavelength for aquocobalamin and iodocobalamin, (b) at 555 nm, an absorption maximum of iodocobalamin. The time scale is 20 ms/div.

Reactions between iodine and the cobalt(II) complexes of *ms*-$Me_6[14]aneN_4$ and Me_6[14]-4,11-dieneN_4 occurred quite slowly in two stages which we attribute to the oxidation–reduction process followed by aquation of the iodocobalt(III) complex. In view of this it was not possible to isolate the products, and the initial production of the iodo complexes was inferred from this biphasic reaction pattern and by analogy to the other reactions.

Reactions with Iodine—Kinetics. The kinetic data for each reaction were obtained under pseudo-first-order conditions, with the limiting reagent, wavelength, $[H^+]$, ionic strength, and concentration range chosen by circumstances specific to each. All kinetic data for the oxidation reactions are in accord with the rate law given in eq 7. The value of k was computed

$$-d[Co^{II}]/2dt = -d[I_2]/dt = k[(H_2O)_2(Co^{II})][I_2] \quad (7)$$

from the pseudo-first-order rate constant, k_{obsd}, as $k_{obsd}/2[I_2]_{av}$ or $k_{obsd}/[(Co^{II})]_{av}$ as appropriate in the given instance. The conditions for the various kinetic determinations and the results obtained are summarized in Table III; some typical kinetic data are shown in Figure 3. The variations shown in $[H^+]$ and in ionic strength have little if any effect, and comparisons of reactivity can be made between these systems. The reactions of $Co^{II}(dmgH)_2$ with I_2 and with Br_2 could not be studied owing to the rapid hydrolysis of the cobalt(II) complex at high $[H^+]$ and of the halogens at low $[H^+]$.

Since aquation of the product complexes $ICo(Me_6[14]aneN_4)H_2O^+$ and $ICo(Me_6[14]\text{-}4,11\text{-}dieneN_4)H_2O^{2+}$ occurred concurrently with their formation, the rates of the two stages over the narrow range of permissible concentrations were close enough to reduce the accuracy. The second-stage rates in both

Table III. Kinetic Data at 25.0 °C for Reactions between Cobalt(II) Complexes and Iodine

ligand	conditions	range of init concn/M		av k_2/$dm^3\ mol^{-1}\ s^{-1}$
	[H^+]/M; μ/M; λ/nm	$10^4[Co^{II}]_0$	$10^4[I_2]_0$	
dpnH	0.050; 0.10; 505	0.04–0.25	0.37–3.92	(9.2 ± 2.2) × 10^4
corrin	0.10; 0.10; 310, 535, 555	0.10–0.20	0.73–5.08	(6.1 ± 1.0) × 10^4
Me_4[14]teteneN_4	0.10; 0.10; 545	0.18	0.85–3.67	(6.9 ± 1.6) × 10^3
[14]aneN_4	0.13; 1.0; 430	2.6–18.4	0.28–0.46	(2.87 ± 0.25) × 10^3
ms-Me_6[14]aneN_4	0.01; 0.01; 460	3.8–10.5	0.27–1.02	5.0 ± 1.0
Me_6[14]-4,11-dieneN_4	0.01; 0.01; 460	3.8–7.6	0.51–1.0	4.0 ± 0.2

Table IV. Kinetic Data at 25.0 °C for Reactions between Cobalt(II) Complexes and Bromine

	conditions	range of init concn/M		
ligand	$[H^+]$/M; μ/M; λ/nm	$10^4[Co^{II}]_0$	$10^4[Br_2]_0$	av k_2/dm^3 mol^{-1} s^{-1}
dpnH	0.05; 0.10; 505	0.10	0.076	$(3.3 \pm 0.5) \times 10^7$
[14]aneN_4	0.10; 0.10; 300	1.0	0.65	$>1 \times 10^7$
corrin	0.10; 0.10; 350	0.14–0.28	0.038–0.076	$(6 \pm 1) \times 10^6$
Me_4[14]tetaneN_4	0.10; 0.10; 545	0.05–0.55	0.22–3.44	$(1.13 \pm 0.31) \times 10^5$
ms-Me_6[14]aneN_4	0.10; 1.0; 300	0.7–1.2	1.9–14.8	$(5.03 \pm 0.38) \times 10^4$
ms-Me_6[14]-4,11-dieneN_4	0.10; 1.0; 350	0.7	3.1–31.5	$(1.81 \pm 0.32) \times 10^4$
ms-Me_6[14]-4,11-dieneN_4	0.050; 0.050; 360	1.7	6.8–13.6	$(1.82 \pm 0.24) \times 10^4$

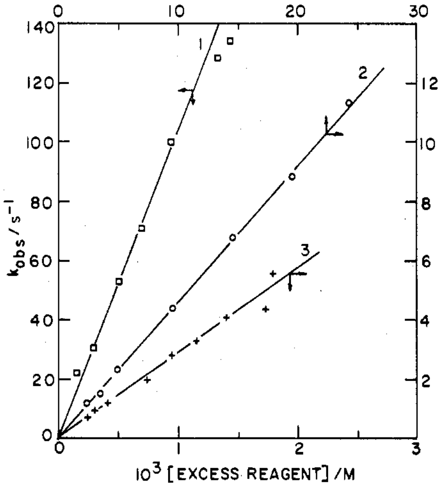


Figure 3. Plots of the pseudo-first-order rate constant vs. [excess reagent] for the reactions (1) Co^{II}(*ms*-Me_6[14]aneN_4) vs. $10^3[Br_2]$, (2) $Co^{II}(dpnH)^+$ vs. $10^2[H_2O_2]$, (3) I_2 vs. $10^3[Co^{II}[14]aneN_4{}^{2+}]$.

cases show a dependence on the concentration of the cobalt(II) excess reagent, as they were earlier shown to do in the [14]aneN_4 reactions, and thus rates of the uncatalyzed aquation step were not evaluated.

Reactions of Bromine—Stoichiometry and Products. Several of the reactions were confirmed to occur in a stoichiometry corresponding to 2:1 $(H_2O)_2Co^{II}$:Br_2 by spectrophotometric titrations. B_{12r} constitutes a special case, discussed further below.

For complexes where oxidation by bromine occurs substantially more rapidly than subsequent aquation, we assumed that the product is the monobromocobalt(III) complex, and the spectral data in Table I are based upon this assignment. In support of this we note that the spectrum does not correspond to the diaquocobalt(III) complex; yet in all three cases in which this aspect was examined the immediate product underwent a subsequent reaction, producing ultimately materials whose spectra agreed with those of the authentic $(H_2O)_2(Co^{III})$ complexes. This subsequent reaction occurred with the maintenance of the isosbestic points and is most simply identified as aquation of the monobromocobalt(III) complex.

Oxidation of B_{12r} by bromine in only small (say, twofold) excess produced B_{12a}. We presume, by analogy to the other bromine reactions as well as the reaction of B_{12r} and iodine, that bromocobalamin was the primary product but is not detected owing to its aquation, which is known to be quite rapid (590 s^{-1}).[25]

A larger excess of bromine converted B_{12r} to a chromophore with a spectrum[26] that does not correspond to B_{12a}. Also, others have noted that reaction of B_{12a} and bromine yields an uncharacterized product in which the corrin ring or a side chain has been brominated. It should be noted that reaction between B_{12a} and bromine occurs slowly, whereas B_{12r} and bromine react very rapidly to produce a product other than B_{12a}.

Reactions of Bromine—Kinetics. Several of the cobalt(II) complexes reacted too rapidly to permit pseudo-first-order kinetics. Consequently these reactions were studied with comparable concentrations of reactants, and even then the reactions were so rapid as to reduce the accuracy of the kinetic data considerably. Other reactions occurred at easily measured rates, and in every case the kinetic data were consistent with a mixed-second-order rate law similar to that found for iodine (eq 7). The kinetic data are given in Table IV, and one set of experiments is shown in Figure 3.

The rates of aquation of the monobromo products of two reactions were determined. The complex BrCo(*ms*-Me_6[14]aneN_4)H_2O^{2+} aquates with $k_{obsd} = 1.4 \times 10^{-3}$ s^{-1} (25 °C, 0.007 M H^+, 1 run), and BrCo(Me_6[14]-4,11-dieneN_4) has $k_{obsd} = (6.5 \pm 0.3) \times 10^{-4}$ s^{-1} (25 °C, 0.10 M H^+, 2 runs, k independent of bromine concentration) and 1.1×10^{-3} s^{-1} (25 °C, 0.014 M H^+, 1 run).

Reactions of Hydrogen Peroxide—Stoichiometry and Products. Only the reaction of $(H_2O)_2Co^{II}([14]aneN_4)^{2+}$ occurred by the pattern seen for the halogen reactions. This reaction followed a clean 2:1 (Co^{II}):H_2O_2 stoichiometry and gave a product having a spectrum agreeing with that of $(H_2O)_2Co^{III}([14]aneN_4)^{3+}$. With added Br^- (0.01–0.08 M) the product was a mixture of this complex and the monobromo complex $BrCo^{III}([14]aneN_4)H_2O^{2+}$ (and possibly smaller amounts of $Br_2Co^{III}([14]aneN_4)^+$), consistent with scavenging of hydroxyl radical (reaction 8),[28,29] followed by eq 3 (X· = Br·).

$$Br^- + HO\cdot \rightarrow Br\cdot + OH^- \qquad (8)$$

$$k_8 = 3 \times 10^{10}\ \mathrm{dm^3\ mol^{-1}\ s^{-1}}$$

A similar experiment using 10^{-2} M I^- yielded, after ion-exchange separation, both the diaquo and the monoiodo complexes in respective yields of ca. 60 and 40%, again consistent with the stepwise reactions.

The remaining complexes react with a 1:1 stoichiometry; Table II shows data based on analysis, and other determinations were based upon spectrophotometric titrations. This is true not only for runs in aqueous *tert*-butyl alcohol, a scavenger for HO·, where a 1:1 stoichiometry is accounted for by the chemistry of the carbon-centered radicals, but also in strictly aqueous solution.[30]

The product spectra from these peroxide reactions do not correspond to the diaquocobalt(III) complexes. An ion-exchange separation of the products in the cobaloxime system gave two substances, one with a band at 230 nm, and the second, corresponding to $(H_2O)_2Co^{III}(dmgH)_2{}^+$ at 235 nm, in ca. 40% yield. The B_{12r} + H_2O_2 reaction has been reported[31] to yield products other than B_{12a}, with a spectrum resembling that of a "stable yellow corrinoid". Chromatography on Sephadex C-25 cation-exchange resin gave the yellow product along with B_{12a}. The 51% yield of B_{12a} was less at higher $[H_2O_2]$.

Attempts were made to scavenge any HO· produced in the reactions of $(H_2O)_2Co^{II}(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+}$ and $(H_2O)_2Co^{II}(dmgH)_2$ with hydrogen peroxide. Bromide ions and *tert*-butyl alcohol fail to alter the stoichiometry to 2:1 (and

Table V. Kinetic Data at 25.0 °C for Reactions between Cobalt(II) Complexes and Hydrogen Peroxide

	conditions	range of init concn/M		
ligand	$[H^+]$/M; μ/M; λ/nm	$10^4[Co^{II}]_0$	$10^4[H_2O_2]_0$	av k_2/dm^3 mol^{-1} s^{-1}
[14]aneN_4	0.10; 0.10; 300	2.5	9.8–94.5	$(3.97 \pm 0.80) \times 10^3$
$(dmgH)_2$	0.1; 0.10 (NaOAc); 460	0.60	4.9–49	$(1.92 \pm 0.20) \times 10^3$
dpnH	0.050; 0.10; 505	1.0	24–245	$(4.62 \pm 0.18) \times 10^2$
ms-Me_6[14]aneN_4	0.10; 0.10; 300	0.60	21–280	$(2.65 \pm 0.05) \times 10^2$
Me_4[14]tetaneN_4	0.10; 0.10; 545	0.58	3.7–187	$(1.42 \pm 0.10) \times 10^2$
corrin	0.10; 0.10; 468	0.50	49–980	$(1.32 \pm 0.08) \times 10^2$
Me_6[14]-4,11-dieneN_4	0.10; 0.10; 335	0.95	170–4760	$(7.7 \pm 0.7) \times 10^1$

fail to increase the reaction rate by a factor of 2), indicating HO· is not a reaction intermediate. Also, in the presence of 2 M CH_3OH the reaction fails to produce the transient of Co^{III}–CH_2OH as expected via reactions 9–11.

$$HO\cdot + CH_3OH \rightarrow H_2O + \cdot CH_2OH \quad (9)$$

$$k_9 = 7 \times 10^8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$Co^{II}(Me_6[14]\text{-}4,11\text{-diene}N_4)^{2+} + \cdot CH_2OH \rightarrow (Co^{III})\text{–}CH_2OH \quad (10)$$

$$k_{10} = 7 \times 10^7 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$(Co^{III})\text{–}CH_2OH \rightarrow (Co^I) + CH_2O \quad (11)$$

$$k_{11} = 0.10 \pm 0.02 \text{ s}^{-1}$$

Reactions of Hydrogen Peroxide—Kinetics. Kinetic data were obtained under pseudo-first-order conditions using excess peroxide and were in accord with the rate law in eq 12, where

$$\frac{-d[(Co^{II})]}{n\,dt} = \frac{-d[H_2O_2]}{dt} = k[(Co^{II})][H_2O_2] \quad (12)$$

n is the stoichiometry factor, 1 or 2, for the given reaction. The data are summarized in Table V, and one set of experiments is shown in Figure 3.

Some special effects were examined: addition of 10% *tert*-butyl alcohol gives the same rate constant for the cobaloxime (1.94×10^3 dm^3 mol^{-1} s^{-1}) as in its absence (($1.83 \pm 0.06) \times 10^3$ dm^3 mol^{-1} s^{-1}). Addition of Br^-, 0.2–0.5 M, causes a gradual increase in rate constant for the Me_4[14]teteneN_4 complex [$10^{-2}k_1$/dm^3 mol^{-1} s^{-1} ($[Br^-]$)]: 1.41 (0), 1.83 (0.2), 2.75 (0.3), 3.11 (0.4), 8145 (0.5). We attribute the increase to bromide catalysis, in which a bromocobalt(II) complex reacts more rapidly than the aquo complex.[29] In any event, the data do not follow the pattern for scavenging of HO·, which would be complete at 0.1 M Br^- and would have increased the rate by a factor of 2.0.

Electrode Potentials. The cyclic voltammogram for Co([14]aneN_4) was rather irreversible, although the value of $E_{1/2}$, 0.20 V vs. SCE or 0.44 V vs. NHE, agreed exactly with the accurate potentiometric value. The other complexes behaved rather reversibly and showed peak separations of 60–90 mV. Their values of $E_{1/2}$, which we take to approximate the standard reduction potentials, are (converted to the hydrogen scale) as follows: Co(*ms*-Me_6[14]aneN_4), 0.49 V (lit.[22] E^0 = 0.59 V); Co(Me_6[14]-4,11-dieneN_4), 0.51 V (lit.[22] 0.56 V; Co(Me_4[14]teteneN_4), 0.51 V; Co(dpnH), 0.41 V; Co$(dmgH)_2$, 0.36 V (0.1 M $HClO_4$, except Co$(dmgH)_2$, where 0.1 M $NaClO_4$ was used).

Discussion

The generally accepted mechanism for the reactions of halogens with many metal complexes consists of reaction 2 (rate-limiting) followed by (3) or (4) + (5). Our data on stoichiometry, products, and rate law for the bromine and iodine reactions appear to be in accord with either of these schemes. Indeed, the known[33] rapid reaction of Co(Me_6[14]-4,11-dieneN_4)$^{2+}$ with I_2^- would preclude any mechanism involving formation and disproportionation of the diiodide radical ion; thus eq 3 is favored over (4) + (5).

An analysis of the energetics of this mechanism in the cases for which complete data are at hand, or for which reliable estimates can be made, provides reason to propose a modified pathway in these instances.

The published one-electron reduction potential of iodine,[34] the potential for the Co([14]aneN_4)$^{3+/2+}$ couple, and the formation constant for the iodocobalt(III) complex permit calculation of the equilibrium constant for reaction 13, and

$$(H_2O)_2Co^{II}([14]aneN_4)^{2+} + I_2 \rightleftarrows ICo^{III}([14]aneN_4)H_2O^{2+} + I_{aq}\cdot \quad (13)$$

$$K_{13} = 1.1 \times 10^{-8}$$

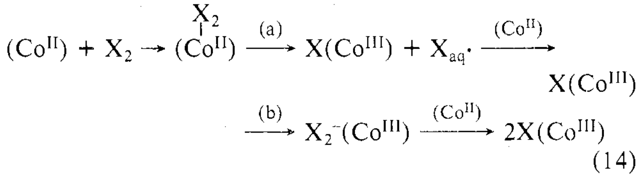
$$k_{-13} = k_{13}/K_{13} = 2.4 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

under the assumption that this is the rate-limiting step in the iodine oxidation, the reverse rate constant can be computed as shown.

The calculated value of k_{-13} exceeds the diffusion-controlled limit of ca. 10^{10} dm^3 mol^{-1} s^{-1} in water at 25 °C by a factor of ~24. Even after allowance is made for various sources of error in the experimental determinations or in the estimates[34] for $I_{aq}\cdot$ (the most severe of which appears to be that $\Delta H_{hyd}(I\cdot) = \Delta H_{hyd}(Xe\cdot)$), it is difficult to reconcile the difference. This is particularly so, since k_{-13} could hardly exceed 10^9 dm^3 mol^{-1} s^{-1} and still conform to the simple second-order kinetic pattern which requires that the second step be much faster than the reverse of the first ($R_3 >> R_{-13}$).

A similar estimate for the reaction of Co^{II}([14]aneN_4)$^{2+}$ and bromine gives, using an estimate of 10^3 M^{-1} for the formation constant of the bromocobalt(III) complex, $k_{12} > 3 \times 10^9$.

Margerum[4] has pointed out that halogen oxidations of Co^{II}(edta) and related complexes cannot be controlled either by ligand substitution rates at cobalt(II) (considering the magnitudes of the rates) or by halogen dissociation (considering the bond dissociation energies, $D(I_2) < D(Br_2)$, yet $k_{I_2} << k_{Br_2}$). He considers formation of a cobalt(II)–iodine adduct whose internal oxidation–reduction is rate limiting. Such an intermediate may be formed in the present situation as well, although whether its fate is transformation to a cobalt(III)–diiodide complex or to $I_{aq}\cdot$ cannot be resolved. Some of the alternatives are shown in eq 14; internal electron transfer (b) seems the most reasonable rate-limiting processes in the present reactions.



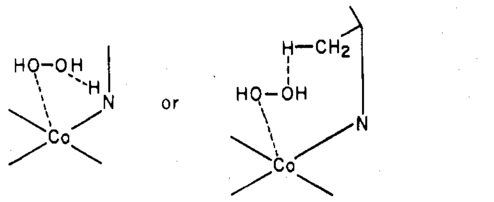
$$(Co^{II}) + X_2 \rightarrow \overset{X_2}{\overset{|}{(Co^{II})}} \xrightarrow{(a)} X(Co^{III}) + X_{aq}\cdot \xrightarrow{(Co^{II})} X(Co^{III})$$
$$\xrightarrow{(b)} X_2^-(Co^{III}) \xrightarrow{(Co^{II})} 2X(Co^{III}) \quad (14)$$

Production of ICo([14]aneN_4)$(H_2O)^{2+}$ in this reaction, given the known very slow anation of $(H_2O)_2$Co([14]aneN_4)$^{3+}$ by I^- (eq 6), definitely precludes an outer-sphere electron-transfer mechanism.

The oxidation of $Co^{II}([14]aneN_4)^{2+}$ by H_2O_2 may well proceed sequentially and involve the hydroxyl radical as an intermediate. Scavenging experiments using Br^- or I^- (via eq 8) were successful in yielding $XCo^{III}([14]aneN_4)H_2O^{2+}$, although for Br^- the results were complicated by anion catalysis of the first step.

The other peroxide reactions appear more complex, as shown most clearly by B_{12r}, where chelate modification occurs. Complications in the remaining peroxide reactions are also evident in their stoichiometry, and we note that the role of hydroxyl radical, generated by pulse radiolysis, toward $Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+}$ is not primarily metal oxidation but attack on the chelate structure, most probably at an imine nitrogen.[35] Walling[36] has reported that in the $Fe(edta)^-$-catalyzed decomposition of H_2O_2, HO· is scavenged by edta.

The failure to detect HO· except in the one case cited substantiates that this free radical is not an intermediate which then discriminates among various substrates in bimolecular processes, for, were this the case, scavengers such as Br^- and methanol would necessarily dominate over attack at a cobalt macrocycle position. Accordingly, it becomes necessary to postulate a modified mechanism, and we thus imagine that the attack occurs simultaneous with the initial step, or immediately following it, as shown pictorially for either of these hydrogen atom abstraction possibilities.



The kinetic effect of substitution of methyl groups at peripheral positions is quite marked. Of the two saturated systems $Co^{II}([14]aneN_4)$ reacts more rapidly than its hexamethyl analogue by substantial factors: 12 (H_2O_2), >200 (Br_2), and 570 (I_2). In part these differences arise from the 0.15-V difference in reduction potentials of this pair of Co(II) complexes. Likewise, self-exchange rates for the Co(II)–Co(III) couples are dependent upon such changes.[37] The added methyl groups block axial coordination quite markedly[18] and may be responsible for much of the rate retardations as well as the E^0 change in this case and possibly in the $Co(Me_6[14]\text{-}4,11\text{-}dieneN_4)$ complex as well.

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Registry No. $(H_2O)_2Co^{II}([14]aneN_4)^{2+}$, 65554-13-4; $(H_2O)_2Co^{II}$(*meso*-$Me_6[14]aneN_4)^{2+}$, 68170-27-4; $(H_2O)_2Co^{II}(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+}$, 38331-68-9; $(H_2O)_2Co^{II}(Me_4[14]teteneN_4)^{2+}$, 38337-82-5; $(H_2O)_2Co^{II}(dpnH)^+$, 47021-96-5; $(H_2O)_2Co^{II}(dmgH)_2$, 37115-10-9; $(H_2O)_2Co^{II}(corrin)^+$, 68108-77-0; $(H_2O)_2Co^{III}([14]aneN_4)^{3+}$, 46750-08-7; $(H_2O)_2Co^{III}$(*meso*-$Me_6[14]aneN_4)^{3+}$, 25259-86-3; $(H_2O)_2Co^{III}(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{3+}$, 17815-30-4; $(H_2O)_2Co^{III}(Me_4[14]teteneN_4)^{3+}$, 36452-48-9; $(H_2O)_2Co^{III}(dmgH)_2^+$, 28124-53-0; $(H_2O)_2Co^{III}(corrin)^{2+}$, 68108-78-1; $BrCo^{III}(H_2O)([14]aneN_4)^{2+}$, 68108-79-2; $BrCo^{III}(H_2O)$(*meso*-$Me_6[14]aneN_4)^{2+}$, 68108-80-5; $BrCo^{III}(H_2O)(Me_6[14]\text{-}4,11\text{-}dieneN_4)^{2+}$, 36530-66-2; $ICo^{III}(H_2O)([14]aneN_4]^{2+}$, 68108-81-6; Br_2, 7726-95-6; I_2, 7553-56-2; H_2O_2, 7722-84-1; Br_{12}, 14463-33-3.

References and Notes

(1) Based on the Ph.D. thesis of R.A.H., Iowa State University, Feb. 1978.

(2) (a) A. W. Adamson, *J. Am. Chem. Soc.*, **78**, 4260 (1956); (b) A. Haim, and W. K. Wilmarth, *ibid.*, **83**, 509 (1961); (c) P. B. Chock, R. B. K. Dewar, J. Halpern, and L.-Y. Wong, *ibid.*, **91**, 82 (1969); (d) P. B. Chock and J. Halpern, *ibid.*, **91**, 582 (1969).

(3) (a) H. Taube and H. Myers, *J. Am. Chem. Soc.*, **76**, 2103 (1954); (b) F. A. L. Anet and E. LeBlanc, *ibid.*, **79**, 2649 (1957); (c) G. Gordon and R. C. Thompson, *Inorg. Chem.*, **5**, 557,562 (1966); (d) J. K. Kochi and D. D. Davis, *J. Am. Chem. Soc.*, **86**, 5264 (1964); (e) G. Kramer, unpublished Ph.D. thesis, University of Sussex, 1974; (f) G. Davies, N. Sutin, and K. O. Watkins, *J. Am. Chem. Soc.*, **92**, 1892 (1970); (g) M. R. Hyde and J. H. Espenson, *ibid.*, **98**, 4463 (1976).

(4) (a) W. H. Woodruff, D. C. Weatherburn, and D. W. Margerum, *Inorg. Chem.*, **10**, 2102 (1971); (b) W. H. Woodruff, B. A. Burke, and D. W. Margerum, *ibid.*, **13**, 2573 (1974); (c) W. H. Woodruff and D. W. Margerum, *ibid.*, **13**, 2578 (1974).

(5) (a) J. M. Malin and J. H. Swinehart, *Inorg. Chem.*, **8**, 1407 (1969); (b) R. D. Cornelius and G. Gordon, *Inorg. Chem.*, **15**, 997 (1976).

(6) A. Adegite, H. Egboh, J. F. Ojo, and R. Olieh, *J. Chem. Soc., Dalton Trans.*, 833 (1977).

(7) (a) P. R. Carter and N. Davidson, *J. Phys. Chem.*, **56**, 877 (1952); (b) W. G. Barb, J. H. Baxendale, P. George, and K. R. Hargrave, *Trans. Faraday Soc.*, **47**, 462 (1951); (c) C. Walling, *Acc. Chem. Res.*, **8**, 125 (1975), and references therein.

(8) (a) G. Davies and A. R. Garafolo, *Inorg. Chem.*, **15**, 1101 (1976); (b) M. L. Bowers, D. Kovacs, and R. E. Shepherd, *J. Am. Chem. Soc.*, **99**, 6555 (1977).

(9) (a) P. W. Schneider, P. F. Phelan, and J. Halpern, *J. Am. Chem. Soc.*, **91**, 77 (1969); (b) J. Halpern and P. F. Phelan, *ibid.*, **94**, 1881 (1972); (c) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *ibid.*, **93**, 1374 (1971); (d) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *ibid.*, **97**, 5752 (1970).

(10) J. H. Espenson and A. H. Martin, *J. Am. Chem. Soc.*, **99**, 5953 (1977).

(11) These ligands (see also Figure 1) have these systematic names, respectively: 1,4,8,11-tetraazacyclotetradecane, *meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetrazacyclotetradecane, 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene.

(12) Other ligands are as follows: $Me_4[14]teteneN_4$ = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,3,10-tetraene, $dpnH^-$ = monoanion of 3,3′-(trimethylenediimino)bis(butan-2-one oxime).

(13) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 1549 (1968).

(14) D. P. Rillema, J. F. Endicott, and E. Papaconstantinou, *Inorg. Chem.*, **10**, 1739 (1971).

(15) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972).

(16) G. Costa, G. Mestroni, and E. deSavorgnani, *Inorg. Chim. Acta*, **3**, 323 (1969).

(17) A. V. Ablov and N. M. Samus, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), **4**, 410 (1960); G. N. Schrauzer, *Inorg. Synth.*, **11**, 61 (1968).

(18) J. F. Endicott, J. Lilie, J. M. Kuszaj, B. S. Ramaswamy, W. G. Schmonsels, M. G. Simic, M. D. Glick, and D. P. Rillema, *J. Am. Chem. Soc.*, **99**, 429 (1977).

(19) A. Adin and J. H. Espenson, *Inorg. Chem.*, **11**, 686 (1972).

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

(21) (a) R. G. Wilkins, "The Study of Kinetics and Mechanism of Reactions of Transition Metal Complexes", Allyn and Bacon, Boston, Mass., 1974, pp 20–25; (b) J. H. Espenson and T.-H. Chao, *Inorg. Chem.*, **16**, 2553 (1977).

(22) M. P. Liteplo and J. F. Endicott, *Inorg. Chem.*, **10**, 1420 (1971).

(23) J. M. Brierly, J. L. Ellingboe, and H. Diehl, *Iowa State Coll. J. Sci.*, **27**, 425 (1953).

(24) Photodecomposition of the complex by a high-intensity mercury lamp converted it to Co_{aq}^{2+}, which was determined spectrophotometrically as $Co(NCS)_4^{2-}$. The I_2 produced was volatalized by a stream of nitrogen during the 90-min irradiation [R. G. Hughes, J. F. Endicott, M. Z. Hoffman, and D. A. House, *J. Chem. Educ.*, **46**, 440 (1969)]. Iodide was converted by reaction with excess iodate to iodine and determined spectrophotometrically.

(25) D. Thusius, *J. Am. Chem. Soc.*, **93**, 2629 (1971).

(26) The immediate product from B_{12r} (6.6×10^{-5} M) and Br_2 (5.7×10^{-4} M) has this spectrum: λ 530 nm (sh, ϵ 1080), 475 (2510), 450 (sh, 2030), 390 (sh, 2750), 390 (3700). Reaction of B_{12a} and Br_2 at the same concentrations requires ~2 h for completion, giving this spectrum: 550 (950), 470 (1470), 380 (sh, 2350), 350 (3260).

(27) (a) B. Ellis, V. Petrow, G. H. Beaven, and E. R. Holiday, *J. Pharm. Pharmacol.*, **6**, 60 (1953); (b) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}", Academic Press, New York, N.Y., 1972, pp 282–283.

(28) J. H. Baxendale and P. L. T. Bevan, *Trans Faraday Soc.*, **64**, 2389 (1968).

(29) The dibromo product might arise from the reaction of a bromocobalt(II) complex with atomic bromine. Halide accelerations of Co(II)–oxygen reactions have been noted.[18]

(30) The data in aqueous *t*-BuOH have been considered previously,[10] our earlier statement concerning a 2:1 stoichiometry in strictly aqueous solution is in error. (The ligand "$Me_4[14]teteneN_4$" of this paper is designated as "tim" in the earlier paper.)

(31) Reference 27b, p 288.

(32) H. Elroi and D. Meyerstein, *J. Am. Chem. Soc.*, **100**, 5540 (1978).

(33) S. D. Malone and J. F. Endicott, *J. Phys. Chem.*, **76**, 2223 (1972).

(34) W. H. Woodruff and D. W. Margerum, *Inorg. Chem.*, **12**, 962 (1973).

(35) A. M. Tait, M. Z. Hoffman, and E. Hayon, *Int. J. Radiat. Phys. Chem.*, **8**, 691 (1976).

(36) C. Walling, R. E. Partch, and T. Weil, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 140 (1975).

(37) D. P. Rillema, J. F. Endicott, and N. A. P. Kane-Maguire, *J. Chem. Soc., Chem. Commun.*, 495 (1972).