On Cis and Trans Effects and the Mechanisms of Acid and Base Hydrolysis of Axial Ligands in Cobalt(III) Complexes Containing Macrocyclic (N_4) Ligands[1]

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Abstract: Rate constants and equilibrium constants have been determined in acidic solution for the replacement of an axial ligand by water in complexes of the type $Co^{III}(N_4)X_2$, where (N_4) is a nitrogen donor tetradentate macrocyclic ligand and X is variously Cl^-, Br^-, or NH_3. In complexes which do not contain methyl groups in the proximity of axial ligands X, there is a marked increase in axial ligand lability with increasing (N_4) unsaturation; a 10^4-fold increase seems characteristic of replacing a tetraamine by a sterically similar tetraimine. An increase in lability is also found in complexes in which methyl groups of the (N_4) ligand are constrained to be near the axial ligands X; two such axial methyls seem to result in about a hundredfold increase in lability compared with less strained systems. The apparent second-order rate constants for axial ligand hydrolysis are extremely large in basic solution in cases that some coordinated ligand, (N_4) or X, is an amine (or ammine) containing a labile proton. In the cases of $X = NH_3$ base hydrolysis rate constants are always relatively very large, even in the tetraimine complex where no labile protons are on nitrogen atoms cis to the leaving groups. Thus each of the isoelectronic ligands, CH_3^-, NH_2^-, and OH^-, can be considered to exert a trans-labilizing influence in six-coordinate complexes.

Hydrolytic reactions of the substitution inert complexes of cobalt(III) have been extensively investigated,[2] but there remain a number of important mechanistic problems. Very recently, Poon[3] has clearly summarized the problems and issues particularly pertinent to the hydrolysis of monodentate ligands in cobalt complexes containing macrocyclic (N_4) ligands. A problem of interest has been to assess the labilizing influence of progressive degrees of unsaturation in the macrocycle.[3,4] There are two important mechanistic aspects of this problem: (1) there have been frequent suggestions that unsaturated ligands may help stabilize five-coordinate cobalt(III) species, such as are expected to be intermediates in substitution reactions;[2g,3–5] and (2) there is some evidence that extensively unsaturated ligands result in an increase in the "soft"[5,6] character of the cobalt(III) center.[3] Examination of this type of mechanistic question is also relevant to a "model system" approach[7] to the chemical reactivity of vitamin B_{12} group of compounds.[8–10]

There have been several studies of axial ligand substitution in cyclic amine complexes[2–4] of cobalt(III) and a few similar studies of complexes containing diimine,[3,4] dimethylglyoximate,[2g,3] porphyrin,[3,11] and corrinoid[3,9,10] ligands. Comparisons of the results from studies of the latter classes of complexes with observations on the amine complexes have been greatly complicated by questions with regard to the steric promotion of labilization[3,4] and the variation of the overall charge type of the complex.[3]

Many complexes containing extensive unsaturation in their (N_4) ligands (*e.g.*, the *trans*-$Co^{III}(py)_4X_2$[12] and the *trans*-$Co^{III}(DH)_2X_2$[13–15] complexes) have proved to be relatively insensitive to base hydrolysis, presumably owing to a lack of ionizable amine protons and the consequent impossibility of forming a strongly labilizing coordinated amido group.[2,3,16] Dimethylglyoximate complexes of cobalt(III) which contain a coordinated ammine have been found to exhibit a base hydrolysis path,[17] but the mechanism in these cases is not clear[3] and no acid hydrolysis pathway was observed. Base hydrolyses in complexes of this type have some general mechanistic significance in view of Nordmeyer's[18] proposal that the hydroxide attack is stereospecific and cis to the leaving group.

Experimental Section

A. Preparation of Compounds. The Co^{III}([14]tetraene-

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(1) Partial support of this research by the Public Health Service (Grant AM 14341) is gratefully acknowledged.

(2) For useful reviews see (a) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed, Wiley, New York, N. Y., 1967; (b) R. D. Archer, *Coord. Chem. Rev.*, 4, 243 (1967); C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1966; (d) C. H. Langford and T. R. Stengle, *Annu. Rev. Phys. Chem.*, **19**, 193 (1968); (e) M. L. Tobe, *Accounts Chem. Res.*, 3, 377 (1970); (f) C. K. Poon, *Inorg. Chim. Acta Rev.*, 4, 123 (1970); (g) J. E. Byrd and W. K. Wilmarth, *ibid.*, 5, 7 (1971); (h) J. Burgess, "Inorganic Reaction Mechanisms," Specialist Periodical Report, The Chemical Society, Burlington House, London, 1970, Part II, Chapter 4; (i) C. H. Langford and M. Parris, "Comprehensive Chemical Kinetics," Vol. 7, C. H. Bamford and C. F. H. Tipper, Ed., Elsevier, New York, N. Y., 1972, p 1.

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(8) In the context of the present work, the reaction mode of interest is the appreciable lability of axial ligands[9,10] in the B_{12} series of compounds.

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(15) DH = dimethylglyoximate.

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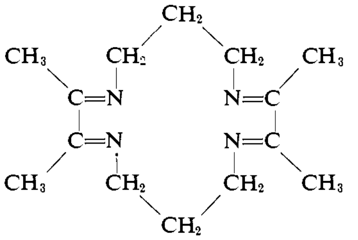
Table I. Microanalytical Data for [*trans*-$Co(N_4)X_2$]Y Complexes

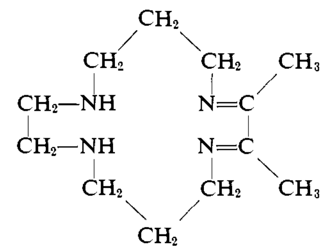
(N_4)	X	Y	Weight % calcd (% found) C	H	N	Cl	Br
[14]tetraeneN_4	Cl	ClO_4	35.2 (34.5)	5.0 (5.0)	11.7 (12.3)	22.3 (22.2)	
	Br	ClO_4	28.8 (31.0)	4.5 (4.4)	9.6 (9.5)	6.1 (6.0)	27.3 (27.2)
	Br	Br	30.7 (30.6)	4.4 (4.4)	10.2 (10.3)		43.9 (43.6)
[14]-1,3-dieneN_4	Cl	ClO_4[a]	30.7 (31.8)	5.2 (5.5)	11.9 (11.9)	22.6 (22.7)	
	Br	ClO_4	26.6 (26.5)	4.1 (4.3)	10.4 (10.3)	6.6 (6.6)	29.6 (29.8)
	H_2O	ClO_4[b]	22.7 (22.7)	4.8 (4.4)	8.8 (8.8)	16.7 (16.0)	

[a] Monohydrate. [b] [*trans*-$Co([14]\text{-}1,3\text{-diene}N_4)(OH_2)_2](ClO_4)_3 \cdot H_2O$.

$N_4)X_2$[19,20] and $Co^{III}([14]\text{-}1,3\text{-diene}N_4)X_2$ complexes were prepared according to the procedures provided to us by Farmery and Busch,[21] or in the case of the aquo complexes as we described previously.[22] Analytical information on the complexes prepared for this study is presented in Table I. Preparations of the remaining complexes used in this study have been described elsewhere.[23]



[14]tetraeneN_4



[14]-1,3-dieneN_4

B. General Techniques. Tap distilled water was redistilled over potassium permanganate, and all chemicals were reagent grade. Buffer solutions were made from organic ammines above pH 6 as described by Poon and Tobe[24] (pH in parentheses): (a) 2,6-lutidine + 0.1 *M* $HClO_4$ (5.6–7.2); (b) γ-collidine + 0.1 *M* $HClO_4$ (7.2–8.7); (c) 2,6-dimethylpiperidine (10.0–11.0). We used acetic acid–sodium acetate buffers in the range $4 < pH \leq 6.0$.

Solution spectra were obtained with a Cary 14 spectrophotometer. Solid-state spectra were determined with a Bausch and Lomb Spectronic-600 connected to an integrating-sphere reflectance attachment.[25] Absorption spectra of the complexes are summarized in Table II.

Kinetic determinations were made by observing changes of absorbance, using either a Cary 14 or an Aminco stopped flow apparatus. Solution temperatures were controlled with a Tamsen-T45 water bath.

C. Procedures for Equilibrium Studies. 1. Acid dissociation constants were determined at room temperature from the midpoints of the buffer regions determined in the titration of 0.05 *M* solutions of the $Co(N_4)(OH_2)_2^{3+}$ complex with standard NaOH. The pH values of the solutions were determined using an Instrumentation Laboratories Model 145 pH meter.

2. To determine the stability constants for the $Co(N_4)X_2^+$ complexes (eq 1), solutions containing 5×10^{-5} *M* $Co(N_4)X_2^+$ dissolved

$$Co(N_4)(OH_2)X + X^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Co(N_4)X_2^+ + H_2O \qquad (1)$$

in 0.1 *M* $HClO_4$ were allowed to equilibrate with known $[X^-]$. The absorbance of the halide to metal charge transfer band (see Table II) increased to a maximum at ~0.2 *M* and then remained constant with further added halide (*e.g.*, see Figure 1). The equilibrium constant was calculated from the initial rising portion of the curve, absorbance *vs.* $[X^-]$, assuming the only equilibrium species were $Co(N_4)(OH_2)X^{2+}$ and $Co(N_4)X_2^+$.

More generally one may assume an equilibrium such as (2) for

$$M^{m+} + nX^- \rightleftharpoons MX_n^{(m-n)+} \qquad (2)$$

which $K_f = [MX_n^{(m-n)+}]/[M^{m+}][X^-]^n$. Then $\log K_f + n \log [X^-] = \log \{[MX_n^{(m-n)+}]/[M^{m+}]\}$, and a plot of $\log \{[MX_n^{(m-n)+}]/[M^{m+}]\}$ *vs.* $\log [X^-]$ should be linear with slope, *n*, and intercept, $\log K_f$. Such plots were found to have slopes $= 1.0 \pm 0.1$ and intercepts not differing significantly from values of $\log K_f$ as determined by the graphical method. From the similarity of absorbance in $[X^-] > 0.2$ *M* and the reflectance spectra, we infer that eq 1 describes the equilibrium observed in each case.

We also attempted to determine the equilibrium constant for the second step. Spectral changes were observed in the visible region using a 0–0.2 absorbance slide wire and 5-cm cells. The $Co(N_4)X_2^+$ concentration was 2×10^{-4} *M*, $\mu = 1$ *M*, and pH <3. Absorbancies were recorded for solutions with different $[X^-]$. Two isosbestic points were found for solutions in which $[X^-] > 0.10$ *M* and only one for solutions with $[X^-] < 0.10$ *M*. This latter, long wavelength isosbestic point was observed at about the same wavelength (~570 nm) for both ranges of $[X^-]$. In addition we were unable to resolve a distinct visible absorption band for any species other than $Co(N_4)X_2^+$ (at very high $[X^-]$) or the mixture of species formed when $[Co(N_4)X_2]ClO_4$ was dissolved in perchlorate media.

D. Procedure for Kinetic Studies. 1. Acid Hydrolyses. Kinetic runs were carried out at 25°. For X = halide, a known amount of $[Co(N_4)X_2]ClO_4 \cdot xH_2O$ was dissolved in $1 < pH < 3$ perchloric acid or nitric acid solution and allowed to equilibrate with known concentrations of X^- (0.05 *M* $\leq [X^-] \leq 0.1$ *M*). Such solutions were diluted twofold with a $1 \leq pH \leq 2$ ($\mu = 0.1$

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(19) Abbreviations for macrocyclic ligands are based on suggestions by Busch and coworkers.[26] In this study we use [14]tetraeneN_4 = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene; [14]-1,3-dieneN_4 = 2,3-dimethyl-1,4,8,11-tetraazacyclotetradec-1,3-diene; [14]-4,11-dieneN_4 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene; Me_6[14]aneN_4 = *C-meso*-5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane; [14]aneN_4 = 1,4,8,11-tetraazacyclotetradecane.

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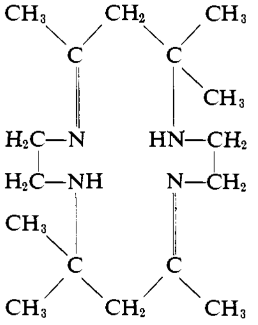
Table II. Absorption Spectra of Some *trans*-$Co^{III}(N_4)X_2$ Complexes

$(N_4)^a$	X	pH^a	Metal ion bands ν_{max}, kK(ϵ, M^{-1} cm^{-1}) IA	IB	II	Uv bands ν_{max}, kK(ϵ, M^{-1} cm^{-1})
[14]tetraeneN_4	OH_2	1.0	17.4 (sh)[b]	19.8 (54)	23.5 (sh)	26.7 (sh), 32.0 (sh), 44.7 (2.4×10^4)
	Cl^c		16.6 (sh)	17.4	23.2 (sh), 24.0	
	Cl^d	1.0	16.5 (sh)	17.8 (44)	Masked	26.7 (sh), 30.8 (1.6×10^3), 37.9 (1.6×10^4),[h] 40.7 (1.6×10^4)
	Cl^e	1.0		18.3 (39)	Masked	28.6 (sh), 40.8 (1.7×10^4), 49.3 (3.3×10^4)
	$Br^{c,f}$		15.1 (sh)	16.7	20.8, 22.2 (br)[b]	
	$Br^{d,f}$	3.0^g		16.9 (36)	Masked	27.2 (br, 2.2×10^3), 33.0 (2.0×10^4),[h] 38.8 (1.2×10^4)
	$Br^{e,f}$	3.0^g		18.2 (33)	Masked	27.8 (br, 1.1×10^3), 38.5 (9.6×10^3)
[14]-1,3-dieneN_4	OH_2	1.0		18.2 (35)	23.6 (sh)	28.2 (sh), 45.0 (2.1×10^4)
	Cl^c		15.2 (sh)	16.2	20.8 (sh), 23.5	
	Cl^d	1.0		16.3 (47)	Masked	32.2 (sh, 2.1×10^3), 38.9 (2.6×10^4)[h]
	Cl^e	1.0		17.6 (39)	Masked	38.5 (sh), 45.6 (2.3×10^4)
	Br^c		14.9 (sh)	16.4	21.3 (sh), 23.0	
	Br^d	3.0^g		15.8 (48)		27.1 (sh, 1.2×10^3), 33.6 (1.7×10^4), 38.3 (1.2×10^4)
	Br^e	3.0^g		18.0 (20)		

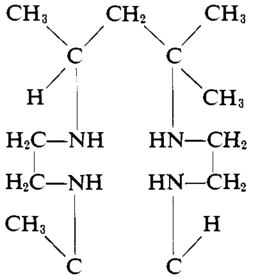
[a] Perchlorate salts in $HClO_4$ solution except as indicated. [b] Key: sh = shoulder, br = broad. [c] Solid-state spectrum. [d] $[X^-] = 0.5\ M$. [e] No added X^-. [f] Bromide salts. [g] HNO_3. [h] Halide to metal charge transfer.

M; $HClO_4$, $NaClO_4$) solution using stopped flow or syringe mixing techniques. The change in absorbance of the halide to metal charge transfer band was followed as the reactants reequilibrated.

For the diammine complexes absorbance changes were generally observed for 10^{-4} M $Co(N_4)(NH_3)_2^{3+}$ solutions at pH 0 and pH 1 in 1 M $NaClO_4$. These reactions were very slow even at 70°, and observations were generally made over a period of 3–5 days or about one reaction half-life. Measurements were recorded at λ 486 nm (ϵ 75 M^{-1} cm^{-1}) for $Co(Me_6[14]aneN_4)(NH_3)_2^{3+}$, at λ 338 nm ($\epsilon$ 80 M^{-1} cm^{-1}), for $Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}$, at λ 317 ($\epsilon$ 760 M^{-1} cm^{-1}) for $Co([14]\text{-}1,3\text{-}dieneN_4)(NH_3)_2^{3+}$, and at λ 326 nm ($\epsilon$ 1.9×10^3 M^{-1} cm^{-1}) for $Co([14]tetraeneN_4)(NH_3)_2^{3+}$.



[14]-4,11-dieneN_4



$Me_6[14]aneN_4$

2. **Base Hydrolyses.** The reactions of $Co(Me_6[14]aneN_4)(NH_3)_2^{3+}$ were observed at 300 nm, of $Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}$ at 290 nm, and the second step for $Co([14]\text{-}1,3\text{-}dieneN_4)(NH_3)_2^{3+}$ at 272 nm; all of these wavelengths correspond to shoulders on the charge transfer bands. The reactions of $Co([14]tetraeneN_4)(NH_3)_2^{3+}$ were observed at 326 nm, and the first step for hydrolysis of $Co([14]\text{-}1,3\text{-}dieneN_4)(NH_3)_2^{3+}$ was observed at 317 nm. For $Co([14]tetraeneN_4)X_2^+$ (X = Cl, Br) observations of the progress of hydrolysis were made at the charge transfer ($X^- \rightarrow Co(III)$) maxima. For the $Co([14]\text{-}1,3\text{-}dieneN_4)X_2^+$ (X = Cl, Br) complexes, we monitored changes of absorbance in the visible region of the spectrum (λ_{max} 609 and 635 nm, respectively) using the 0–0.2 absorbance slide wire.

Reactant solutions of $Co^{III}(N_4)X_2$ were made up to an ionic strength of 0.10 ($NaClO_4$, NaX) with 0.05 $M \leq [X^-] \leq 0.1$ M and pH 3 (for X = Cl, Br) or 0.10 M in $NaClO_4$ and pH 3 (for X = NH_3). The base hydrolyses of $Co(Me_6[14]aneN_4)(NH_3)_2^{3+}$, $Co([14]\text{-}4,11\text{-}dieneN_4)(NH_3)_2^{3+}$ (first step), $Co([14]\text{-}1,3\text{-}dieneN_4)Cl_2^+$, and $Co([14]\text{-}1,3\text{-}dieneN_4)Br_2^+$ had to be determined in buffered media.

E. Treatment of Kinetic Data. 1. For acid hydrolysis the rate of disappearance of $Co^{III}(N_4)X_2$ in (1) is given by

$$-\frac{d[Co^{III}(N_4)X_2]}{dt} = k_1[Co^{III}(N_4)X_2] - k_{-1}[Co^{III}(N_4)(OH_2)X][X^-] \quad (3)$$

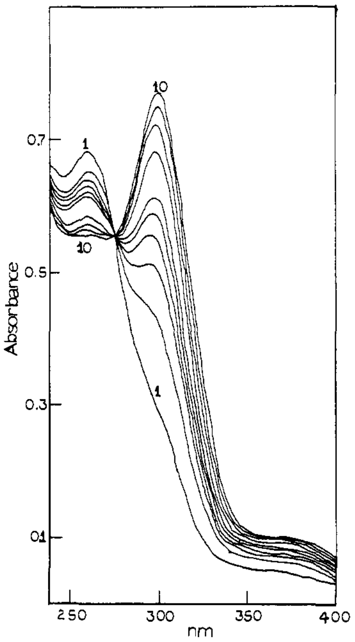


Figure 1. Titration of a pH 2 in HBr solution of $5 + 10^{-5}$ M $Co([14]\text{-}1,3\text{-}dieneN_4)(Br)(OH_2)^{2+}$ with $[Br^-]$. Concentrations (M) are respectively (1 → 10): 0.001, 0.03, 0.05, 0.07, 0.09, 0.11, 0.21, 0.31, 0.41, 0.51. The solution of $Co([14]1,3\text{-}dieneN_4)(Br)(OH_2)^{2+}$ was prepared from the $(Co([14]1,3\text{-}dieneN_4)Br_2)(ClO_4)$ salt. Isosbestic point is at 273 nm.

Since $[X^-]$ is constant, $k' = k_{-1}[X^-]$, and the above expression integrates to

$$\ln\left\{\frac{k_1[Co^{III}(N_4)X_2] - k'[Co^{III}(N_4)(OH_2)X]}{k_1[Co^{III}(N_4)X_2]_0 - k'[Co^{III}(N_4)(OH_2)X]_0}\right\} = -(k' + k_1)t \quad (4)$$

which can be written in terms of the equilibrium constant $K' = K_1/[X^-]$

$$\ln\left\{\frac{K'[Co^{III}(N_4)X_2] - [Co^{III}(N_4)(OH_2)X]}{K'[Co^{III}(N_4)X_2]_0 - [Co^{III}(N_4)(OH_2)X]_0}\right\} = k_1\left(1 + \frac{1}{K'}\right)t \quad (5)$$

Plots of the left-hand side of (5) *vs.* time were linear up to five half-lives. The forward rate constant, k_1, was calculated from the slope

Table III. Rate Constants for Acid and Base Hydrolyses of $Co^{III}(N_4)X_2$ Complexes[a]

(N_4)	X	k_1,[b] sec^{-1}	k_6,[c] $M^{-1}\ sec^{-1}$	k_7,[c] $M^{-1}\ sec^{-1}$
$Me_6[14]aneN_4$	NH_3	$(5 \pm 3) \times 10^{-6}$ [d] $(6 \pm 4) \times 10^{-6}$ [f]	$(3.2 \pm 0.5) \times 10^{6}$ [e]	Very slow
$[14]$-4,11-dieneN_4	NH_3	$(3.0 \pm 0.5) \times 10^{-6}$ [d] $(3 \pm 1) \times 10^{-6}$ [f] $(9 \pm 3) \times 10^{-7}$ [h]	$(3.2 \pm 0.3) \times 10^{6}$ [e]	0.34 ± 0.03 [g]
$[14]$-1,3-dieneN_4	NH_3	$\sim 9 \times 10^{-7}$ [d] 3×10^{-6} [f]	$(1.1 \pm 0.1) \times 10^{3}$ [g] $(4.3 \pm 0.3) \times 10^{3}$ [e]	0.84 ± 0.04 [g]
	Cl	$(2.3 \pm 0.1) \times 10^{-4}$	$(8 \pm 1) \times 10^{5}$ [i]	[j]
	Br	$(7.8 \pm 0.5) \times 10^{-2}$ [k]	$(1.1 \pm 0.5) \times 10^{6}$	[j]
$[14]tetraeneN_4$	NH_3	$(8 \pm 1) \times 10^{-7}$ [d] $(2.0 \pm 0.3) \times 10^{-6}$ [f] $(4 \pm 2) \times 10^{-7}$ [h]	36 ± 3 [g]	Fast
	Cl	$(2.1 \pm 0.3) \times 10^{-2}$	2.7 ± 0.3 [g,l]	[j]
	Br	0.12 ± 0.01 [m]	$(1.2 \pm 0.2) \times 10^{3}$ [g]	21 ± 5 [g]

[a] At 25° except as indicated. [b] At pH 2, $\mu = 0.075$, perchlorate media, except as indicated. [c] At $\mu = 0.10$, perchlorate media and buffered solutions, except as indicated. [d] Based on initial rate data, 68.5°, pH 0, $\mu = 1.0$ ($HClO_4$, $NaClO_4$). [e] At $\mu = 0.05$, perchlorate media. [f] Same as in footnote *d* but at pH 1. [g] In NaOH. [h] Same as in footnote *d* but at 59.6°. [i] At $\mu = 0.25$ (NaCl). [j] Not determined. [k] At pH 1.3, $\mu = 0.075$ (perchlorate medium). [l] At $\mu = 0.075$, perchlorate medium. [m] At pH 2, $\mu = 0.1$ ($NaClO_4$).

of the line, the independently determined values of K_1, and the concentration of halide (always present in great excess). The reverse rate constant, k_{-1} was determined from the equilibrium expression, $K_1 = k_1/k_{-1}$.

Hydrolysis rates of $Co(N_4)(NH_3)_2^{3+}$ were slow, so we used initial rates on pseudo-first-order plots ($\log (A_t - A_\infty)$ *vs.* t) to determine experimental estimates of the rate of aquation of the ammine ligands.

2. In the case of base hydrolysis, the second-order rate constants were determined from plots of k_{obsd} (pseudo-first order with $[OH^-]$ in excess or, in the case of buffered solutions, $[OH^-]$ constant) *vs.* $[OH^-]$.

Results

Rate constants for acid and base hydrolyses of the $Co(N_4)X_2^+$ complexes are summarized in Table III. In principle stepwise replacement of both ligands X is possible, and two hydrolysis rates might be observed. In practice both base hydrolysis steps, (6) and (7), were

$$Co^{III}(N_4)X_2 + OH^- \xrightarrow{k_6} Co^{III}(N_4)(OH)X + X \qquad (6)$$

$$Co^{III}(N_4)(OH)X + OH^- \xrightarrow{k_7} Co^{III}(N_4)(OH)_2 + X \qquad (7)$$

generally observed, whereas only one step was found for acid hydrolysis. In the cases of $Co(Me_6[14]aneN_4)(NH_3)_2^{3+}$ and $Co([14]tetraeneN_4)(NH_3)_2^{3+}$, we found only one base hydrolysis rate. In the former case this was associated with a small absorbance change similar to those observed for first step in base hydrolysis of the analogous $[14]dieneN_4$ complexes; on this basis we believe that k_7 is very small for $N_4 = Me_6[14]aneN_4$. In the case of $Co([14]tetraeneN_4)(NH_3)_2^{3+}$ the large absorbance changes observed can be accounted for by assuming that the single observed product was the dihydroxy complex and thus that $k_7 > k_6$ for this complex.

The case of $Co([14]tetraeneN_4)Br_2^+$ was complex. A two step base hydrolysis was observed but the first step was not directly proportional to $[OH^-]$; it rather had a base dependence suggestive of a preequilibrium step[2e,26] such as (8) so that the observed rate constant

$$Co(N_4)Br_2^+ + OH^- \overset{K_{IP}}{\rightleftharpoons} \{Co(N_4)Br_2^+, OH^-\} \qquad (8)$$

becomes a function of $[OH^-]$

$$k_{obsd} = \frac{K_{IP}k_9[OH^-]}{1 + K_{IP}[OH^-]}$$

At high $[OH^-]$ we find k_{obsd} becomes independent of $[OH^-]$ or $k_{obsd} \rightarrow k_9 \simeq 15\ sec^{-1}$. For low $[OH^-]$, $k'_{obsd} = K_{IP}k_0 \simeq 1.4 \times 10^3\ M^{-1}\ sec^{-1}$, so we infer that $K_{IP} \sim 93\ M^{-1}$. This inferred value of K_{IP} seems exceptionally large for an ion pair stability constant of ions of such low charge type[27] and the implicated reaction more likely involves hydrolysis of the tetraene ligand.[28]

$$\{Co(N_4)Br_2^+, OH^-\} \xrightarrow{k_9} Co(N_4)(OH)Br^+ + Br^- \qquad (9)$$

For $Co([14]tetraeneN_4)Cl_2^+$, we observed only one base hydrolysis reaction. We searched for a faster step using the stopped flow apparatus but could not find one. Since the half-life of the dissociative, acid hydrolysis path is 20 sec and the experimental half times for base hydrolyses were as short as 5 sec, we would have expected to see two rates if k_6 were strictly dissociative and k_{obsd} were associated with (7). However, since we observed the total absorbance change, we must conclude that k_{obsd} is associated with k_6 and that $k_7 \geq k_6$.

Lutidine buffered solutions were used in the studies of $Co([14]\text{-}1,3\text{-}dieneN_4)X_2^+$ (X = Cl, Br). In these cases the limiting value of k_{obsd} as $[OH^-] \rightarrow 0$ were much larger ($k_{obsd,\ lim}$ = 0.17 and 0.33 sec^{-1}, respectively) than the observed acid hydrolysis rates. The discrepancy is probably attributable to general base catalysis.[29]

Stability constants of the $Co(N_4)X_2^+$ complexes are summarized in Table IV.

Discussion

A. Axial Ligand Equilibria. The range of stability constants (or of acid dissociation constants) compared in Table IV is remarkably small for such a diverse collection of cyclic ligands. The stereochemistry of the geminal methyl groups of $Me_6[14]aneN_4$ and $[14]$-4,11-dieneN_4 complicates comparisons involving complexes with these ligands.[3,4,30] However, the tenfold decrease in stability of $Co(N_4)Cl_2^+$ complexes as (N_4) is changed from $[14]aneN_4$ to $[14]$-1,3-dieneN_4 to $[14]tetraeneN_4$ should be free of such steric complications and is systematic in progressive unsaturation of the

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[26] (a) S. C. Chan and F. Leh, *J. Chem. Soc. A*, 126 (1966); (b) S. C. Chan and O. W. Lau, *Aust. J. Chem.*, **22**, 1851 (1969).

[27] M. T. Beck, *Coord. Chem. Rev.*, **3**, 91 (1968).

[28] An irreversible decomposition occurs when the $Co^{III}([14]tetraeneN_4)X_2$ complexes stand in base for extended periods.

[29] C. K. Poon and M. L. Tobe, *Chem. Commun.*, 156 (1968).

[30] W. K. Chau and C. K. Poon, *J. Chem. Soc.*, 3087 (1971).

Table IV. Stability Constant for $Co(N_4)(OH_2)X^{2+} + X^- \overset{K}{\rightleftharpoons} Co(N)_4X_2^+ + H_2O$

	Stability constant, K, M^{-1} (or pK)[a]				
X	[14]aneN_4	Me_6[14]aneN_4	[14]-4,11-dieneN_4	[14]-1,3-dieneN_4	[14]tetraeneN_4
Cl	1.25×10^{2} [b]	34[c]	95 ± 5[d]	45 ± 3	15 ± 1
Br		37 ± 16[d]	43 ± 2[d]	13 ± 2	33 ± 5
OH(pK_1)	(2.9 ± 0.1)[e]	(2.7 ± 0.5)[d]	(4.02 ± 0.01)[d]	(3.0 ± 0.1)	(3.5 ± 0.1)
(pK_2)	(7.2 ± 0.1)[e]	(6.4 ± 0.05)[d]	(8.2 ± 0.1)[d]	(6.6 ± 0.1)	(6.5 ± 0.1)

[a] This work; pH 2, 25°, $\mu = 0.5\ M$; except as indicated. pK values are acid dissociation constants. [b] Reference 24, $T = 60°$. [c] Reference 30. [d] Reference 4. [e] References 24 and 30.

Table V. Comparison of Specific Rate Constants (k_1, sec^{1-}, at 25°) for Aquation of $Co(N_4)X_2^+$ Complexes

X	[14]aneN_4	Me_6[14]aneN_4	[14]-4,11-dieneN_4	[14]-1,3-dieneN_4[a]	[14]tetraeneN_4	$(DH)_2^{2-}$ [b]
Cl	1.1×10^{-6} [c]	$(9 \pm 1) \times 10^{-4}$ [e]	3.6×10^{-2} [f]	$(2.3 \pm 0.1) \times 10^{-4}$	$(2.1 \pm 0.3) \times 10^{-2}$	2.7×10^{-4}
Br	2.2×10^{-5} [d]	3.8×10^{-2} [f]	5.1×10^{-2} [f]	$(7.8 \pm 0.5) \times 10^{-2}$	0.12 ± 0.01	3.8×10^{-4}

[a] See Table III. [b] *trans*-Dimethylglyoximate complexes, ref 38 and 39. [c] References 24 and 31. [d] Reference 38. [e] Reference 30. [f] Reference 4.

ligand (N_4) so may reflect increasing "softness" of the cobalt(III) center (note that a similar order of stability of aquo hydroxy complexes is observed; Table IV and ref 31). Qualitative support for such a progressive increase in "soft" character of the metal with increase in ligand unsaturation is provided by our observation that the order of stabilities of dibromo and dichloro complexes, with respect to the corresponding aquo halo complexes, is reversed from the usual sequence for the ([14]tetraeneN_4)cobalt(III) complexes. It might also be noted that while Co([14]tetraene)I_2^+ can be prepared,[21] presumably owing to its exceptionally large stability constant,[32] the other cyclic (N_4) complexes of cobalt(III) enter into a redox equilibrium with iodide,[22,33-36] presumably a measure of the relative instability of these diodo complexes.

B. Axial Ligand Aquation Kinetics. It is most instructive to compare first the sterically relatively unconstrained complexes. Thus the increase of about 10^4 in lability of chloro complexes as (N_4) is changed through the series [14]aneN_4, [14]-1,3-dieneN_4, and [14]tetraeneN_4 (Table V) must be an effect of the progressive unsaturation in the (N_4) ligands. This is consistent with the previous suggestions[3-5] that high degrees of unsaturation would tend to stabilize the five-coordinate dissociative intermediate.

The greater aquation rates of Co(Me_6[14]aneN_4)Cl_2^+ and Co([14]-4,11-dieneN_4)Cl_2^+ than the corresponding [14]aneN_4 and [14]-1,3-dieneN_4 complexes, respectively, can be attributed to stereochemical labilization by the geminal methyl groups present in the first pair of complexes.[2-4,30,37]

Very similar ranges of reactivity are observed for the bromo (Table V and ref 38) and chloro complexes, although there are some discrepancies of detail, especially in the relative reactivities of the complexes with hexamethylated ligands. It is clear that there is no general decrease in the ratio of k_{Br^-}/k_{Cl^-} with increasing unsaturation of the (N_4) ligand, such as Poon attributed[3] to a "delicate balance of "hard" and "soft" character" of the central metal. In fact this ratio is generally too small to provide useful mechanistic insight in these systems. The 10^4-fold increase in k_{X^-} as (N_4) is changed from [14]aneN_4 to [14]tetraeneN_4 is a striking manifestation of the effect of introducing extensive unsaturation into the "innocent" cyclic ligand.

It is also interesting to observe that the [14]tetraeneN_4 complexes are appreciably more labile than their dimethylglyoximate[39,40] analogs. This is so despite the formal structural similarity of the respective (N_4) ligands.

It seems evident that several factors (*e.g.*, (N_4) unsaturation, charge separation in the transition state, nonbonded repulsive interactions between coordinated ligands and (N_4)-ligand methyl groups, etc.) may contribute to the varying observed labilities. The balance of these contributions seems to vary with both the cationic residue and with the anionic leaving group. Although the acid hydrolysis rate constants approximately parallel the changes in stability of the complexes (Table IV), the hydrolysis rate constants are far more dependent on the nature of the cationic residue than are the stability constants. This suggests that variations in the labilities of the water molecules in $Co(N_4)(OH_2)X^{2+}$ complexes vary in approximately the same way as do the hydrolysis rates of $Co(N_4)X_2^+$ with changes in the equatorial (N_4) ligand; this inference may be quantified by examination of k_{-1} ($= k_1/K$) values.

C. Base Hydrolyses. With the exception of the Co([14]tetraeneN_4)X_2^+ (X = Cl, Br) complexes, the hydrolysis rates of all the $Co^{III}(N_4)X_2^+$ complexes are very greatly accelerated by base. In Table VI we have compared the ratios of base to acid hydrolysis rates, k_6/k_1, for several related *trans*-$Co^{III}(N_4)X_2$ complexes. The second-order rate constants for base hydrolysis of Co(Me_6[14]aneN_4)$(NH_3)_2^{3+}$ and Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$ (Table III) are even larger than the rate con-

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

(32) We have not included equilibrium and kinetic studies on Co([14]-tetraeneN_4)I_2^+ in this paper because we have been unable to obtain reproducible quantitative data for solutions of this complex. We suspect that some of the difficulties arise from extreme sensitivity of equilibration rates to redox catalysis. Further studies of this system are in progress.

(33) J. A. Kernohan, Ph.D. Dissertation, Boston University, 1969.

(34) Note that the $Co(N_4)(OH_2)_2^{3+,2+}$ and the I_2/I^- couples all occur at about 0.55 V.[35-36]

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

(36) W. M. Latimer, "Oxidation Potentials," Prentice-Hall, Englewood Cliffs, N. J., 1952.

(37) M. D. Alexander, *Inorg. Chem.*, **5**, 2084 (1966).

(38) W. K. Chau, unpublished results cited in ref 3.

(39) A. Y. Sychev and A. V. Ablov, *Russ. J. Inorg. Chem.*, **6**, 1163 (1961).

(40) Z. Finta, J. Zsako, and C. Varheli, *Z. Phys. Chem.*, **242**, 200 (1969).

Table VI. Reactivity Ratios (k_6/k_1, M) for Base and Acid Hydrolysis of *trans*-$Co^{III}(N_4)X_2$ Complexes[a,b]

	X =		
(N_4)	Cl^-	Br^-	NH_3
$(en)_2$	4.0×10^6 [c]	9.6×10^7 [c]	
$(14)aneN_4$	6.8×10^9 [d]		
Me_6-[14]aneN_4	6.3×10^8 [d]		5×10^{13}
[14]-4,11-dieneN_4	1.4×10^7 [e]		8×10^{13}
[14]-1,3-dieneN_4	4.0×10^9	1.6×10^7	10^{11}
[14]tetraeneN_4	90	1.4×10^4	3×10^9

[a] This study except as indicated. See Table III and references cited for values of k_6 and k_1. [b] Values of k_1 at 25° estimated assuming $E_a \simeq 20$ kcal. [c] Reference 40. [d] Data taken from ref 3. [e] Reference 4.

stants previously[4] obtained for the corresponding dichloro complexes. These diammine complexes are about the most reactive cobalt(III) complexes known with regard to base hydrolysis rates. In contrast, the relatively small numerical value of k_6 found for Co([14]tetraeneN_4)$(NH_3)_2^{3+}$ makes this complex look relatively insensitive to base; however, this complex is in fact many orders of magnitude more reactive than $Co(NH_3)_6^{3+}$,[41] and the hydrolysis rate of this complex is extremely slow in acidic solution: $k_6/k_1 \simeq 3 \times 10^9$ M, a typically large value. The variations in the numerical values of k_6 for the different complexes may parallel differences in pK_a values of the various coordinated ammine and secondary amine ligands.[42]

The reaction of Co([14]tetraeneN_4)Br_2^+ in base is not simple and in fact may involve something more than dissociative replacement of coordinated Br^- by OH^-. In any case neither of the Co([14]tetraeneN_4)X_2^+ (X = Cl, Br) complexes exhibits anything approaching the sensitivity to base that is characteristic of complexes, including Co([14]tetraeneN_4)$(NH_3)_2^{3+}$, which contain amines (either primary or secondary) or ammonia coordinated to cobalt(III). It is therefore clear that labile N–H protons either cis or trans to the leaving group are sufficient to labilize a complex in basic solution. The contention[18,43] that the generation of an amido group cis to the leaving group is necessary to stabilize the kinetically significant intermediates (or transition states) is inconsistent with our results.

It does seem likely that the mechanism for labilization by amido groups cis to the leaving group does differ in its details from the mechanism of labilization by a trans amido group. Perhaps the 10^4-fold greater reactivity ratio (k_6/k_1) of Co([14]-4,11-dieneN_4)$(NH_3)_2^{3+}$ compared to Co([14]tetraeneN_4)$(NH_3)_2^{3+}$ reflects such differences in mechanism. On the other hand similar variations in the k_6/k_1 ratio are observed among complexes which can only generate an amido group cis to the leaving group, so that these differences in relative reactivities may not have profound mechanistic implications.

It is very interesting, and of mechanistic significance, that the isoelectronic ligands CH_3^-, NH_2^-, and OH^- all can exert a trans labilizing influence in six-coordinate complexes.[3] In fact the labilizing influence of CH_3^- appears to be so strong that five-coordinate alkyl complexes of cobalt(III) may be formed and isolated under relatively mild conditions.[7c,44–46] It appears that the ability of these ligands to labilize the trans position decreases in the order $CH_3^- > NH_2^- > OH^-$ and is more closely related to σ-donor ability (*i.e.*, the strength of the cobalt–ligand bond) of the labilizing ligand than to any variation in the tendencies of these ligands to stabilize dissociative transition states through π-donor interactions.

Finally we would like to point out that Gillard's suggestion,[47] that base hydrolyses of cobalt complexes operates by means of a redox mechanism, is incompatible with our observations.[48] We have previously demonstrated (1) that the reduction potentials of the $Co^{III}(N_4)X_2$–$Co^{II}(N_4)X_2$ couples depend more strongly on the axial ligands X than on the macrocyclic (N_4) ligands[22,23,35,49] and (2) that the rates of reduction of the $Co^{III}(N_4)X_2$ (X = Cl, Br)[22] complexes are always far faster than the rates of reduction of the $Co^{III}(N_4)(NH_3)_2$[22] complexes. Yet k_6 for Co([14]tetraeneN_4)$(NH_3)_2^{3+}$ is more than ten times larger than the value of k_6 found for Co([14]tetraeneN_4)Cl_2^+. Furthermore the equilibrium constant for (10) can be estimated from

$$Co(N_4)(NH_3)_2^{3+} + OH^- \underset{k_{-10}}{\overset{k_{10}}{\rightleftharpoons}} Co(N_4)(NH_3)_2^{2+} + OH\cdot \quad (10)$$

reduction potential data[23,36] to be $K_{10} \leq 5 \times 10^{-43}$ for each of the (N_4) ligands; thus our observations would require $k_{-10} > 10^{43}$ M^{-1} sec^{-1} if the Gillard mechanism were correct. This is clearly outrageous and the Gillard mechanism can be ruled out on both kinetic and energetic grounds.

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(41) A pseudo-first-order rate constant of 2.1×10^{-4} sec^{-1} has been reported for hydrolysis of $Co(NH_3)_6^{3+}$ in 1 M NaOH at 61.8°: J. H. Takemoto and M. M. Jones, *J. Inorg. Nucl. Chem.*, 32, 175 (1970).

(42) An equilibrium constant of 0.6 has been estimated for the reaction $Co(en)_3^{3+} + OH^- \rightleftharpoons Co(en)_2(en\text{-}H^+)^{2+} + H_2O$ by G. Navon, P. Panigel, and D. Meyerstein, *Inorg. Chim. Acta*, 6, 299 (1972).

(43) R. G. Pearson, R. E. Meeker, and F. Basolo, *J. Amer. Chem. Soc.*, 78, 709 (1956).

(44) J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}," Academic Press, New York, N. Y., 1971, pp 130–138.

(45) B. M. Higson and E. D. McKenzie, *J. Chem. Soc., Dalton Trans.*, 269 (1972).

(46) T. S. Roche and J. F. Endicott, *J. Amer. Chem. Soc.*, 94, 8622 (1972).

(47) R. D. Gillard, *J. Chem. Soc. A*, 917 (1967).

(48) As Tobe has observed (ref 2e, p 378) this mechanism has never had any evidence in its support. In fact consideration of the standard potentials of OH·/OH^- and cobalt(III)/cobalt(II) couples should have ruled this possibility out long ago. Unfortunately this has continued to be regarded as a feasible suggestion (*e.g.*, see ref 2h, pp 168, 255; ref 2i, p 17).

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