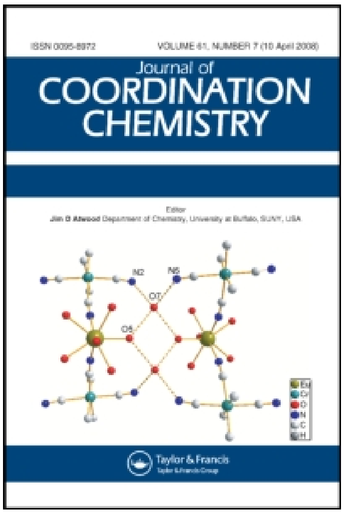


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

AXIAL LABILIZATION BY MACROCYCLIC LIGANDS. 5. AXIAL SUBSTITUTION IN Co(III) COMPLEXES OF A SERIES OF 14-MEMBERED TETRAAZA MACROCYCLIC LIGANDS

N. K. Kildahl[a]; G. Antonopoulos[a]
[a] Department of Chemistry, The Worcester Polytechnic Institute, Worcester, Massachusetts, USA

To cite this Article Kildahl, N. K. and Antonopoulos, G.(1986) 'AXIAL LABILIZATION BY MACROCYCLIC LIGANDS. 5. AXIAL SUBSTITUTION IN Co(III) COMPLEXES OF A SERIES OF 14-MEMBERED TETRAAZA MACROCYCLIC LIGANDS', Journal of Coordination Chemistry, 14: 4, 293 — 307

To link to this Article: DOI: 10.1080/00958978608075847

URL: http://dx.doi.org/10.1080/00958978608075847

J. Coord. Chem. 1986, Vol. 14, p.293-307
0095-8972/86/1404-0293 $18.50/0

AXIAL LABILIZATION BY MACROCYCLIC LIGANDS. 5. AXIAL SUBSTITUTION IN Co(III) COMPLEXES OF A SERIES OF 14-MEMBERED TETRAAZA MACROCYCLIC LIGANDS

N.K. KILDAHL[†] and G. ANTONOPOULOS
Department of Chemistry, The Worcester Polytechnic Institute, Worcester, Massachusetts 01609, USA.

The results of studies of the kinetics of (1) in acetonitrile solvent are presented.

$$\mathrm{CoL(An)_2}^{3+} + 2\mathrm{X}^- \longrightarrow \mathrm{CoLX_2}^+ + 2\mathrm{An} \qquad (1)$$

Here L= *any of three tetraaza-tetraimine macrocyclic ligands;* X^- = Br^- or Cl^-; and An = acetonitrile. Our results indicate that (1) occurs by a modified interchange mechanism involving formation of and interchange within both 1:1 and 2:1 ion pairs. The first-order rate constant for interchange within the 2:1 ion pairs, k_{i2}, increases from 0.873 for the least to 48.5 s^{-1} for the most electron-withdrawing macrocycle, L, at 30°. The activation parameters governing the temperature dependence of k_{i2} are $\Delta H^* = 45$ kJ/mole, $\Delta S^* = -98$ J/mol–K for $L=L^1$ (methyl substituents); $\Delta H^* = 33.6$ kJ/mole, $\Delta S^* = -111$ J/mole–K for $L=L^2$ (methyl and phenyl substituents); and $\Delta H^* = 46$ kJ/mole, $\Delta S^* = -64$ J/mole–K for $L=L^5$ (phenyl substituents) (*vide infra*). The data suggest that (1) occurs *via* associative interchange (I_a) rather than by the usual dissociative interchange (I_d) route.

Keywords: cobalt, macrocycles, kinetics, substitution, labilization

INTRODUCTION

The presence of a macrocyclic ligand in the first coordination sphere of a metal ion can lead to substantial labilization of the ligands in the remaining (so-called axial) coordination positions. This effect is thought to be an important aspect of the action of certain metal-porphyrin-containing enzymes and proteins whose substrates become bound at the active-site metal ion prior to being converted to products. To date, the effect has been studied for a variety of complexes, containing both porphyrin and synthetic macrocyclic ligands and a number of metal ions, by a variety of research groups.[1–28] In this paper, the focus will be on axial labilization in complexes of cobalt(III).[1–17]

The labilization of axial water in cobalt(III) porphyrin complexes has been well documented. Fleischer and co-workers first recognized it in 1968, when they reported that SCN^- substitutes for H_2O in diaquohematoporphyrincobalt(III) 10^6 times faster than in nitroaquobis(dimethylglyoximato)cobalt(III).[1] This was a particularly surprising result in view of the *trans*-labilizing ability of NO_2^-. Since then Pasternack and co-workers[2–5] and Ashley and co-workers[6–8] have examined axial labilization in a number of cobalt(III) porphyrin complexes, including tetracarboxyphenylporphinatocobaltate(III) ($CoTCPP^{3-}$), *tetrakis*(4-*N*-methylpyridyl)porphyrinatocobalt(III) $(CoTMpyP)^{5+}$, and tetra(*p*-sulfonatophenyl)porphyrinatocobaltate(III) ($CoTPPS^{3-}$). They have found that substitution of H_2O by SCN^- occurs 10^2–10^3 times faster in the anionic

---

[†] Author to whom correspondence should be addressed.

complexes than in the cationic complex, which they attribute to enhanced electron density on the cobalt(III) center in the anionic species. These results are consistent with dissociative activation.

Poon and co-workers have studied axial substitution rates in cobalt(III) complexes with synthetic macrocyclic ligands. In a series of reports,[9–15] they studied the hydrolysis of axial ligands in cobalt(III) complexes of the type *trans*-$[Co(N_4)X_2]^{n+}$, where (N_4) is a tetradentate tetraaza macrocyclic ligand and $X = Cl^-, Br^-, N_3^-, NH_3, H_2O, SCN^-$. They found that the rate of acid hydrolysis of analogous complexes increased with increasing extent of unsaturation in the macrocyclic ligand, N_4. For example, an increase of 10^4 in lability was observed for the dichloro complexes as (N_4) was changed from $[14]aneN_4$ to $[14]1,3\text{-diene}N_4$, to $[14]tetraeneN_4$.[29] They concluded that as the extent of unsaturation in the amine macrocycle increases, the softness of the central metal ion increases, probably due to increased delocalization of electrons from the macrocycle to the metal. Presumably this enhanced delocalization stabilizes the five-coordinate intermediates which occur along the dissociative reaction pathway.

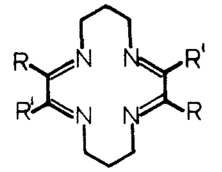
In contrast to the impressive number of reports dealing with axial labilization in cobalt(III) complexes in aqueous solution, no such studies in non-aqueous media have been reported. As part of our general programme of study of axial labilization by synthetic macrocyclic ligands,[30–33] we have examined the substitution of acetonitrile (An) by Br^- and Cl^- in a family of Co^{III} complexes containing related macrocycle ligands, in An solvent. The specific systems studied are detailed below.

$$CoL(An)_2{}^{3+} + 2X^- \xrightarrow{S} CoLX_2{}^+ + 2An \qquad (1)$$

$S = An$

$X^- = Cl^-, Br^-$

L =



$L = L^1$ when R, R' = CH_3

$L = L^2$ when R = ϕ, R' = CH_3

$L = L^5$ when R, R' = ϕ

Axial substitution according to (1) proceeds very rapidly by an interchange (I) mechanism, the interchange rate constant increasing in the order $L^1 < L^2 < L^5$ at 30°. This trend, and the temperature dependences of the rate constants, indicates that substitution occurs *via* associative activation. These systems thus differ substantially from most aqueous Co(III) systems, which substitute *via* dissociative activation.[1,2,4–8] As in our previous work with iron(II) complexes of the same macrocyclic ligands,[30,31,33] and consistent with the results of Pasternack and Ashley, the macrocyclic ligands exhibit a *cis*-labilizing effect upon the Co(III) ion. However, in our systems it is the relative withdrawing abilities of the macrocyclic ligands which should be emphasized.

EXPERIMENTAL

Reagents.

Reagent grade acetonitrile (J.T. Baker, photrex grade) was refluxed over and distilled from P_2O_5 under nitrogen. Tetrabutylammonium bromide, Bu_4NBr, (Alfa Products) was recrystallized from ethanol by addition of ether and dried under vacuum. Tetraethylammonium chloride, Et_4NCl, (Aldrich) was purified by the following procedure. Tetraethylammonium chloride monohydrate (5g) was dissolved in 50 cm^3 of ethanol and 5 cm^3 of triethylorthoformate was added. The flask was stoppered and the solution was stirred overnight. The solution was then reduced in volume to about 10 cm^3, and 25 cm^3 of diethyl ether was added. This resulted in partial crystallization of the salt and the formation of two layers. About 3 cm^3 of acetone was added to cause mutual miscibility of the layers. This caused formation of solid Et_4NCl. The mixture was filtered in a N_2-filled glove bag and the solid was washed twice with ether and dried under vacuum. Anhydrous tetrabutylammonium perchlorate, Bu_4NClO_4, (G.F. Smith) was used as received. Analytical reagent grade *p*-toluenesulfonic acid hydrate, PTSA, (MCB) was purified by recrystallization from ethanol and dried under vacuum. All other chemicals were reagent grade and were used without further purification. All reagents used for kinetics studies were dried under vacuum at ambient temperatures in a vacuum oven for at least 48 hours prior to use.

Syntheses.

$[CoL^1Br_2]Br$,[34] $[CoL^2Br_2]Br$,[35] and $[CoL^5Br_2]Br$.[36]

These compounds were synthesized by the indicated literature procedures or modifications thereof. All three products were characterized by IR and electronic absorption spectroscopy.

$[CoL(An)_2](ClO_4)_3$.

(CAUTION. Perchlorate salts are potentially explosive). All three compounds, with L = L^1, L^2 and L^5, were synthesized according to the following procedure. $[CoLBr_2]Br$ (2.0g) was slurried in 60 cm^3 of acetonitrile for 10 min. A slight stoichiometric excess of solid $AgClO_4 \cdot H_2O$ (2.2g, 0.01 mol) was then added, causing the precipitation of AgBr and a change in solution color to orange-red. The solution was stirred overnight in a stoppered flask at room temperature to insure complete formation of AgBr, which was then removed by filtration, washed with 2 cm^3 of acetonitrile, and discarded. To the filtrate, 2 cm^3 of 70% $HClO_4$ was added and oxygen was bubbled through the solution until the volume was reduced by half. The orange-yellow product was collected by suction filtration, washed twice with small amounts of ethanol, then ether, and air dried. The product $[CoL(An)_2](ClO_4)_3$ was dissolved in hot acetonitrile, and the solution was filtered, cooled, and treated with 1.5 cm^3 of 70% $HClO_4$. Oxygen was bubbled through the solution for about 1.5 hours, resulting in the formation of a yellow-orange product. This was collected by filtration, washed with ether, and dried under vacuum in a drying oven at room temperature. (Treatment with $HClO_4$ and O_2 was deemed necessary to insure complete oxidation of $Co(II)L(An)_2^{2+}$ to $Co(III)L(An)_2^{3+}$. The former is formed spontaneously from the latter by reduction by small amounts of H_2O present in the solvents and in the atmosphere). The complexes $[CoL(An)_2](ClO_4)_3$, $L = L^1$, L^2 and L^5, were characterized by elemental analysis, IR, NMR, and electronic absorption spectroscopy. Analytical and electronic spectral data are presented in Table I. NMR spectra are consistent with data reported in the literature for Co(III) complexes containing the TIM ligand.[34–36]

Table I
Characterization of $CoL(An)_2(ClO_4)_3$.

Complex	*Found*			*Calc*			$\lambda_{max}(\varepsilon)$ *in An*
	%C	*%H*	*%N*	*%C*	*%H*	*%N*	
$CoL^1(An)_2(ClO_4)_3$	31.53	4.59	12.11	31.44	4.40	12.22	408(67) 260(sh) $228(3.64\times10^4)$ $211(3.25\times10^4)$
$CoL^3(An)_2(ClO_4)_3$	41.25	4.48	10.38	41.42	4.22	10.35	$302(1.01\times10^4)$ $227(3.65\times10^4)$ $208(4.21\times10^4)$
$CoL^5(An)_2(ClO_4)_3$							$342(1.78\times10^4)$ 230(sh)

Physical Methods.

Characterization.

Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. IR spectra were obtained in nujol mulls and/or KBr pellets using a Perkin-Elmer 683 grating IR spectrometer. For the *bis*-acetonitrile cobalt complexes, spectra were obtained as nujol mulls, because attempts to prepare Br pellets resulted in axial substitution by Br^-. NMR spectra were obtained in deuterated nitromethane by using a Hitachi Perkin-Elmer model R-24B 60 MHz NMR spectrometer. Electronic absorption spectra in acetonitrile were measured with a Perkin-Elmer model 553 UV-visible spectrophotometer. Electron paramagnetic resonance spectra were obtained using a Varian E-9 spectrometer operating at x-band frequencies. Ligand substitution kinetics were studied with a Nortech SF-3A Canterbury stopped-flow system interfaced with a Digital Equipment Corporation MINC-23 microcomputer. Temperature variation and thermostatting were achieved using a Neslab ULT-80 low temperature bath and circulator. Cyclic voltammetry was performed at a platinum button electrode on a PAR 373 potentiostat-galvanostat with a PAR 175 universal programmer and a Houston Instruments 2000 X-Y recorder. Voltages were measured against the aqueous saturated calomel electrode (SCE).

Spectrophotometric Titration.

In order to verify the stoichiometry of (1), aliquots of 0.012 M Bu_4NBr were added through a serum cap to a solution initially 5.4×10^{-5} M in $CoL(An)_2{}^{3+}$, and the electronic spectrum was scanned after each addition. Bromide concentrations ranging from 0 to 1.5×10^{-4} M were achieved. The results indicate replacement of An by Br^- in both axial sites (*vide infra*), as indicated in (1).

EPR Studies.

To eliminate the possibility that (1) involves a redox reaction between Co^{III} and halide, we scanned the epr spectrum of a frozen solution initially containing $CoL^1(An)_2{}^{3+}$ and Br^-, immediately following reaction. No spectrum was observed, eliminating the possibility of redox.

Kinetic Studies.

Incoming ligand (X^-) solutions were prepared using Bu_4NBr as the source of Br^-, and Et_4NCl as the source of Cl^-. Reactions (1) were studied under conditions for pseudo-order kinetics in cobalt reactant. In all cases, appearance of product was monitored (λ = 305 nm for $CoL^1(An)_2{}^{3+}$; 300 nm for $CoL^2(An)_2{}^{3+}$ with $X^- = Br^-$; 265 nm for $CoL^2(An)_2{}^{3+}$ with $X^- = Cl^-$; and 440 nm for $CoL^5(An)_2{}^{3+}$) at temperatures giving convenient rates for the stopped-flow system. Reaction profiles were first-order over several half-lives. Pseudo-first-order rate constants were obtained from $\ln(A_\infty - A)$ *vs* time plots and standard least-squares-fitting programs. A_∞ values were measured directly from the stopped-flow traces. Addition of paratoluenesulfonic acid to prevent reduction of Co(III) to Co(II)[37,38] had no effect on measured rates. Consequently we omitted it in most studies.

Kinetic studies of (1) were performed with both constant and variable ionic strength (μ).[39] Constant ionic strength was maintained at 0.05 M for $CoL^1(An)_2{}^{3+}$, and 0.1 M for $CoL(An)_2{}^{3+}$, L = L^2 and L^5, using Bu_4NClO_4. Two approaches were tried to maintain constant ionic strength in the kinetic studies. In the first approach, electrolyte was added to both the metal complex and ligand solutions to give an ionic strength equal to 0.05 M or 0.1 M in each. The second approach was to initially place all the electrolyte in the Br^- ligand solution. In this case, the initial ionic strength of the ligand solutions was 0.1 or 0.2 M. Dilution by a factor of two in the stopped-flow cell gave a final ionic strength equal to 0.05 M for L = L^1, and 0.1 M for L = L^2 and L^5.

Kinetic studies of (1) using both of the above methods to maintain constant ionic strength resulted in faster rates of substitution of acetonitrile by bromide when the first aproach was used (*i.e.*, faster rates were observed when both solutions contained electrolyte). There are two possible explanations for the observed rate discrepancy, both requiring the presence of water, possibly introduced *via* the somewhat hygroscopic perchlorate salts. First, it is possible that water rapidly displaced acetonitrile in the axial sites to give the aquo complex, which then reacted with Br^- more rapidly than the An complex. Second, small amounts of water might have caused partial reduction of the Co(III) complexes to the corresponding Co(II) complexes, which are much more labile in the axial sites. This explanation is judged to be more likely based on experiments which indicate that both Co(III) and Co(II) complexes containing bis α-diimine macrocyclic ligands are readily reduced in acetonitrile.[45] In order to avoid this problem, the second approach for maintaining constant ionic strength was used.

RESULTS

Spectrophotometric Titrations.

To establish the stoichiometry of reaction between $CoL(An)_2{}^{3+}$ and X^-, and to determine the extent of reaction under the concentration conditions used in the kinetic studies, we performed spectrophotometric titrations of $CoL(An)_2{}^{3+}$ with X^-. In all cases, reaction of $CoL(An)_2{}^{3+}$ with X^- proceeds rapidly and completely to form $CoLX_2{}^+$, as indicated in (1). Spectrophotometric scans obtained during titration of $CoL^1(An)_2{}^{3+}$ with Br^- are shown in Figure 1a. The figure shows an isosbestic point at 264 nm, for $[Br^-]/[Co]$ ratios between 0 and 1, which shifts to 268 nm for $[Br^-]/[Co]$ ratios between 1 and 2. This is consistent with successive formation of the monobromo and dibromo complexes as the bromide concentration increases. Figure 1b shows that the absorbance at 305 nm increases linearly with $[Br^-]/[Co]$ until the ratio of $[Br^-]$ to [Co] equals 2, then levels off.

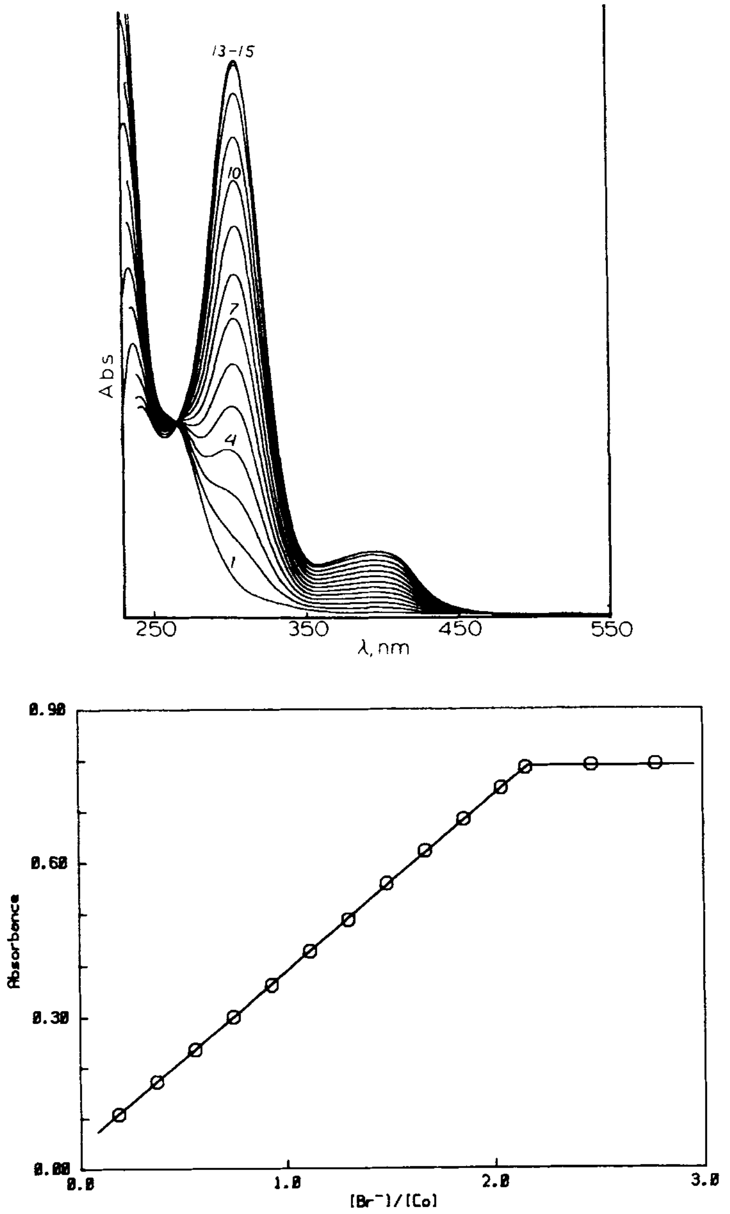


FIGURE 1 a: Titration of $CoL^1(An)_2^{3+}$ with Br^- in acetonitrile. [Co] = 5.4×10^{-5} M. Bromide concentrations ($\times 10^5$) are

1	OM	7	6.0
2	1.0	8	7.0
3	2.0	9	8.0
4	3.0	10	9.0
5	4.0	11	10.0
6	5.0	12	11.0
		13-15	12-15

b: Plot of absorbance at 305 nm *vs* $[Br^-]/[Co]$ for the $CoL^1(An)_2^{3+}$ system. [Co] = 5.4×10^{-5} M.

This indicates that the final product is $CoL^1Br_2^+$. In agreement with this, the final spectrum matches very well the electronic absorption spectrum of an authentic sample of $CoL^1Br_2^+$.

The remaining systems, involving $CoL^2(An)_2^{3+}$ and $CoL^5(An)_2^{3+}$, behaved in similar fashion, each showing two sets of isosbestic points as the concentration of Br^- increased. The first set of isosbestic points, at low bromide concentrations, results from the simultaneous presence of $CoL(An)_2^{3+}$ and $CoL(An)(Br)^{2+}$ in solution. The second set of isosbestic points, which prevail at higher bromide concentrations, results from the presence of $CoL(An)Br^{2+}$ and $CoLBr_2^+$. Plots of absorbance versus $[Br^-]/[Co]$ for these systems are consistent with the stoichiometry indicated in (1).

Kinetic studies.

Reaction (1) ($L = L^1$, $X^- = Br^-$, Ionic Strength Variable).

Reactions of ~1.0 × 10^{-4} M An solutions of $CoL^1(An)_2^{3+}$ with An solutions of Br^- (0.001 M $\leq [Br^-] \leq$ 0.050 M) were monitored at 305 nm (λ_{max} for $CoL^1(Br)_2^+$) and 44.5° by stopped-flow spectrophotometry. Under these conditions, reaction is pseudo-first-order in cobalt reactant, as shown by linear plots of $\ln(A_\infty - A)$ *vs* t. Here A is the absorbance of the solution at time t, and A_∞ is the absorbance at infinite time, due entirely to $CoL^1(Br)_2^+$. The slopes of such plots yield pseudo-first-order rate constants, k_{obs}, which are plotted verus $[Br^-]$ in Figure 2a. The plot shows a decrease in the value of k_{obs} with increasing $[Br^-]$ until $[Br^-]$ reaches about 0.03 M, after which k_{obs} achieves a limiting value of 1.79 ± 0.03 s^{-1} (the mean value of k_{obs} for $[Br^-] \geq$ 0.03 M).

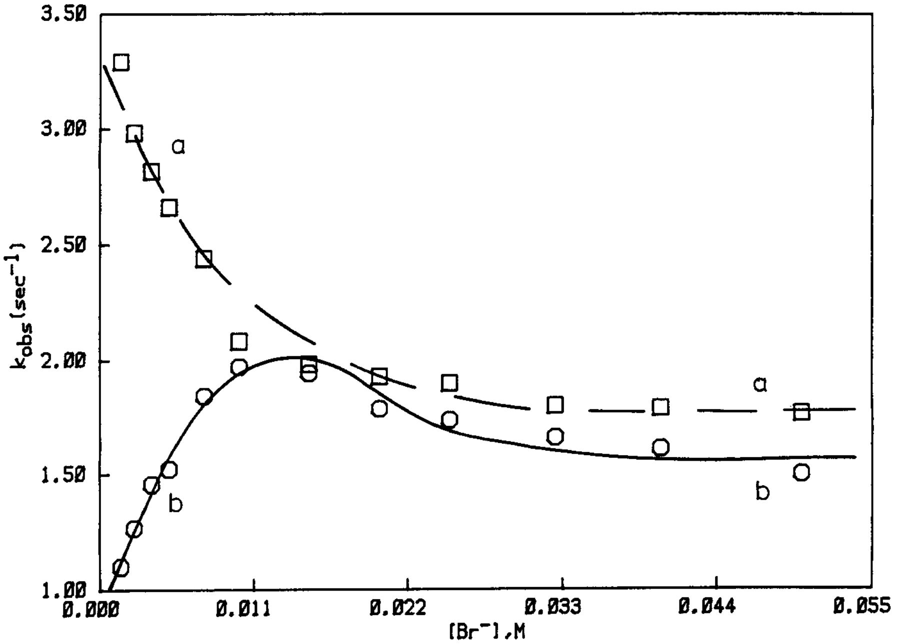


FIGURE 2 Dependence of k_{obs} on $[Br^-]$ for Reaction (1), L = L^1. Acetonitrile solvent, [Co] = 1.0 × 10^{-4} M, T = 44.5°. a: At a variable ionic strength (μ = $[Br^-]$); b: At a constant ionic strength (μ = 0.05 M).

TABLE II
k_{12} and activation parameters for $CoL(An)_2^{3+} + 2Br^- \longrightarrow CoLBr_2^+ + 2An$.

L	k_{12}, s^{-1}, *at 30°C*	ΔH* kJ/mol	ΔS* J/mol-K	$E_{1/2}(Co^{II}-Co^{III})$, V JS . SCE
L^1	0.873	45 ± 7	−98 ± 23	0.460
L^2	20.5	33.6 ± 2.2	−111 ± 8	0.549
L^5	48.5	46 ± 26	−64 ± 92	0.679

Reaction (1) ($L = L^1$, $X^- =$ Br$^-$, $\mu = 0.05$ M using Bu_4NClO_4).

Kinetic studies of the same system at an ionic strength of 0.05 M again yield first-order behavior with respect to cobalt complex. However, the dependence of k_{obs} on $[Br^-]$, shown in Figure 2b, is distinctly different under conditions of constant ionic strength. For $[Br^-] < 0.01$ M, k_{obs} increases linearly as $[Br^-]$ increases, reaching a maximum at about 0.012 M Br^-. At $[Br^-]$ in excess of 0.015 M, k_{obs} decreases in a manner similar to that observed when ionic strength was not maintained constant. For $[Br^-] > 0.03$ M, k_{obs} attains a limiting value of about 1.59 ± 0.08 s^{-1}.

The temperature dependence of k_{obs} between 25 and 60° at $[Br^-] = 0.04$ M and $\mu = 0.05$ M, conditions under which k_{obs} no longer depends markedly on $[Br^-]$, yields $\Delta H^* = 44.9 \pm 7.2$ kJ/mol and $\Delta S^* = -97.9 \pm 22.6$ J/mol-K. The rate and activation data are presented in Table II.

Reaction (1) ($L = L^2$, $X^- = Br^-$, Ionic Strength Variable).

Reactions of ~1.0 × 10^{-4}M solutions of $CoL^2(An)_2^{3+}$ in An with An solutions of

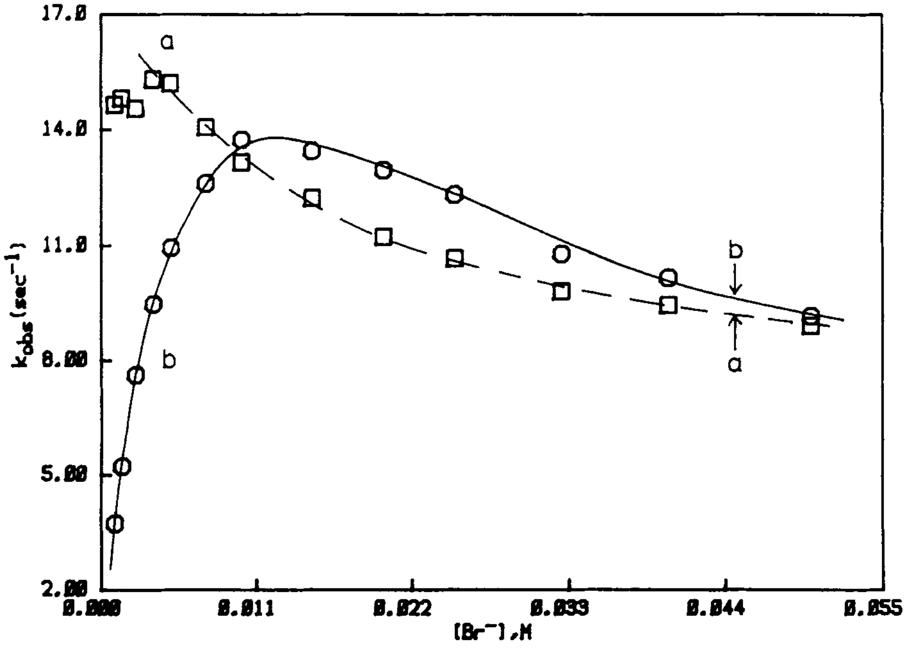


FIGURE 3 Dependence of k_{obs} on $[Br^-]$ for Reaction (1). $L = L^2$. Acetonitrile solvent, $[Co] = 1.0 \times 10^{-4}$ M, T = 15.6°. a: At a variable ionic strength ($\mu = [Br^-]$); b: At a constant ionic strength ($\mu = 0.1$ M).

Br^- (0.001 - 0.05 M) were monitored at 30 nm and 15.6°, again using stopped-flow methods. The reaction is first-order in $CoL^2(An)_2{}^{3+}$. A plot of k_{obs}, the pseudo-first-order rate constant, *versus* $[Br^-]$ is shown in Figure 3a. The profile is similar to that for the L^1 system under conditions of variable ionic strength, with k_{obs} decreasing with increasing $[Br^-]$ and gradually levelling off to 9.4 ± 0.5 s^{-1} at $[Br^-]$ = 0.04 - 0.05 M.

Reaction (1) ($L = L^2$, $X^- = Br^-$, $\mu = 0.10$ M).

Figure 3b shows the dependence of k_{obs} on $[Br^-]$ for the L^2 system at constant ionic strength (0.1 M). The profile, similar to that for the L^1 system at μ = 0.05 M, indicates that the reaction is first-order in Br^- at low $[Br^-]$, and inverse-first-order in Br^- at high $[Br^-]$ (*vide infra*). Values of k_{obs} approach a limiting value of 10.0 ± 0.8 s^{-1} at the highest bromide concentration used (0.05 M).

Studies of k_{obs} at $[Br^-]$ = 0.05 M, μ = 0.1 M, and temperatures in the range between −15 and 19° yield ΔH^* = 33.6 ± 2.2 kJ/mol and ΔS^* = −112 ± 8 J/mol-K. This information is summarized in Table II.

Reaction (1) ($L = L^2$, $X^- = Cl^-$, $\mu = 0.1$ M with Bu_4NClO_4).

This reaction was studied at λ = 265 nm under similar conditions of concentration and temperature as for the case $L = L^2$, $X^- = Br^-$. Chloride reactant solutions were prepared using Et_4NCl. Pseudo-first-order rate constants, k_{obs} are plotted as a function of $[Cl^-]$ in Figure 4. As for the case where the incoming ligand is Br^-, k_{obs} seems to approach a limiting value of about 10.5 ± 1.3 s^{-1} at $[Cl^-]$ = 0.05 M. The temperature dependence of k_{obs} was not studied.

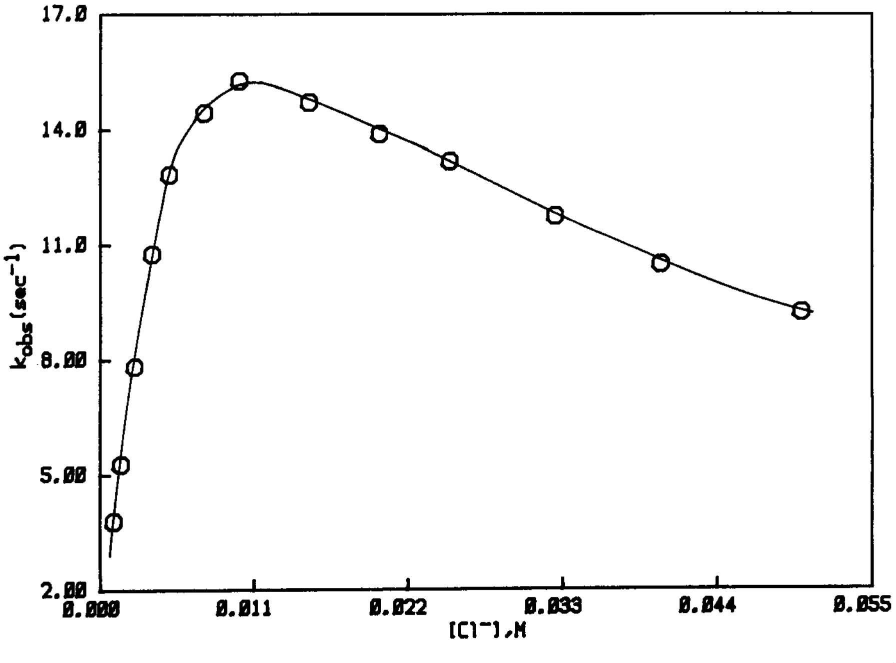


FIGURE 4 Dependence of k_{obs} on $[Cl^-]$ for Reaction (1), $L = L^2$ Acetonitrile solvent, [Co] = 1.0 × 10^{-4} M, T = 14.9°, μ = 0.1 M.

Reaction (1) ($L = L^5$, $X^- = Br^-$, $\mu = 0.1$ M).

Numerous studies of this system have resulted in disappointing reproducibiity. Although for studies using a single stock solution of $CoL^5(An)_2^{3+}$ and a series of solutions containing a range of bromide concentrations we obtain k_{obs} *vs* $[Br^-]$ profiles which are qualitatively similar to those for the systems described above, studies using a different cobalt stock solution yield quite different limiting values for k_{obs} at high $[Br^-]$. We attribute this to the facile reduction of $Co^{III}L^5(An)_2^{3+}$ to the corresponding Co(II) complex. The presence of a small amount of Co(II) in the solution gives rise to a marked increase in the apparent rate of substitution of the Co(III) species, presumably due to the sequence of reactions below.

$$Co^{II}L^5(An)_2{}^{2+} + 2Br^- \longrightarrow Co^{II}L^5Br_2 \qquad (2)$$

$$Co^{II}L^5Br_2 + Co^{III}L^5(An)_2{}^{3+} \longrightarrow Co^{III}L^5Br_2{}^+ + Co^{II}L^5(An)_2{}^{2+} \qquad (3)$$

Apparently small but variable quantities of water in the solvent give rise to variable quantities of Co(II) complex in the solutions, hence to irreproducible rate data for the axial substitution process. Kinetic experiments performed with solutions containing known concentrations of added Co(II) complex show a large increase in axial ligand substitution rate.

Due to the irreproducibility which we have experienced with this system we omit detailed kinetic data. Suffice it to say that temperature studies of k_{obs} under limiting rate concentration conditions between 0 and 25° yield activation parameters similar to those for the other systems, indicating that a similar mechanism is operative. Approximate values for ΔH^* and ΔS^* are included in Table II.

Cyclic voltammetry.

Cyclic voltammetric measurements were performed in acetonitrile solvent containing 0.1 M Bu_4NClO_4 for the series of complexes, $CoL(An)_2^{3+}$, L = L^1, L^2, L^5. Well-defined reversible redox cycles were observed for the Co(II)-Co(III) and Co(II)-Co(I) couples. The results of the electrochemical measurements are presented in Table II.

DISCUSSION

For all systems studied, (1) is first-order in cobalt complex, with the pseudo-first order rate constant, k_{obs}, exhibiting a complex dependence on the concentration of the incoming ligand, X^- ($X^- = Br^-$ or Cl^-). The dependence of the rate on the concentration of acetonitrile is indeterminable, since acetonitrile is the solvent. Before attempting to rationalize the observed rate behavior, it is necessary that we deal with a minor complication. Although we have written (1) as if it occurs in one step, it actually occurs as two successive axial substitution processes, given in (4) and (5). The question to be considered at this point is

$$CoL(An)_2{}^{3+} + X^- \longrightarrow CoL(An)(X)^{2+} + An \qquad (4)$$

$$CoL(An)(X)^{2+} + X^- \longrightarrow CoLX_2{}^+ + An \qquad (5)$$

which of the two reactions, (4) or (5), occurs slowly and thus determines the overall rate of (1). We cannot determine experimentally which reaction, (4) or (5), is slower, because both $CoL(An)(X)^{2+}$ and $CoLX_2^+$ absorb at the same wavelength in the electronic spectrum. Thus we cannot monitor reaction (1) at a wavelength characteristic of the mixed complex, CoL(An)(X), as we are able to do for similar Fe(II) systems.[30,31,33] Despite this, it is reasonable to assume that (4) occurs more rapidly than (5). The reason for this is that most ligand substitutions at Co(III) occur *via* an interchange mechanism, which involves prior formation of a reaction ion pair. As will be discussed, an interchange mechanism is operative in (1) as well. Since (4) involves ion pair interaction between a 3+ cation and a 1− anion, outersphere complex formation should be more favorable and the ion pair should be tighter than for (5), which involves a 2+, 1− interaction. We will therefore *assume* that (4) occurs much more rapidly than (5) and, further, that it proceeds virtually to completion. Our kinetic studies thus provide us with the rate of (5).

As indicated in the Introduction, many substitution reactions of 6-coordinte Co(III) complexes occur by the interchange (I) mechanism. In view of this, and keeping in mind the discussion above regarding the relative rates of (4) and (5), we at first thought that the simple I mechanism in equations (6) and (7) might apply to (1).

$$CoL(An)(X)^{2+} + X^- = CoL(An)(X)^{2+}...X^- \qquad K_o\text{, fast} \qquad (6)$$

$$CoL(An)(X)^{2+}...X^- \longrightarrow CoLX_2^+ + An \qquad k_i\text{, slow} \qquad (7)$$

The rate law demanded by this mechanism is given in (8), where $[Co]_T = [CoL(An)(X)^{2+}] + [CoL(An)(X)^{2+}...X^-]$.

$$\text{Rate} = \frac{k_iK_o[Co]_T[X^-]}{1 + K_o[X^-]} \qquad (8)$$

Our results are inconsistent with this mechanism. Although (8) can be used to rationalize the observed first-order dependence on cobalt, it does not adequately explain the complex dependence on incoming ligand concentration which we observe. To explain this dependence, we have found it necessary to invoke the formation of not only 1:1 ion pairs, but also of 2:1 ion pairs. This gives the revised mechanism in (9)–(12). The rate law

$$CoL(An)(X)^{2+} + X^- = CoL(An)(X)^{2+}...X^- \qquad K_{01}\text{, rapid} \qquad (9)$$

$$CoL(An)(X)^{2+}...X^- + X^- = CoL(An)(X)^{2+}...X_2^{2-} \qquad K_{02}\text{, rapid} \qquad (10)$$

$$CoL(An)(X)^{2+}...X^- \longrightarrow CoLX_2^+ + An \qquad k_{i1}\text{, slow} \qquad (11)$$

$$CoL(An)(X)^{2+}...X_2^{2-} \longrightarrow CoLX_2^+ + An + X^- \qquad k_{i2}\text{, slow} \qquad (12)$$

demanded by this mechanism is given in (13).

$$\text{Rate} = \frac{(k_{i1}K_{01}[X^-] + k_{i2}K_{01}K_{02}[X^-]^2)[Co]_T}{1 + K_{01}[X^-] + K_{01}K_{02}[X^-]^2} \qquad (13)$$

where

$$[Co]_T = [CoL(An)(X)^{2+}] + [CoL(An)(X)^{2+}...X^-] + [CoL(An)(X)^{2+}...X_2{}^{2-}] \qquad (14)$$

For all systems, that is, for $L = L^1$, L^2, and L^5, and $X^- = Br^-$, Cl^-, results are at least qualitatively consistent with this mechanism. Several points of correspondence between experiment and theory can be noted.

1) The observed first-order dependence on cobalt is rationalized by the mechanism.

2) The increase of k_{obs} with $[X^-]$ at low values of $[X^-]$ and constant ionic strength can be rationalized by assuming that at low $[X^-]$, the second term in the numerator and the second and third terms in the denominator of (13) are small enough to be ignored. The expression for k_{obs} then becomes

$$k_{obs} = k_{i1} K_{01} [X^-] \qquad (15)$$

Clearly, this predicts first-order behaviour in bromide.

3) The inverse dependence of k_{obs} on $[X^-]$ at higher X^- concentration can arise if certain terms in numerator and denominator of the k_{obs} expression become dominant as $[X^-]$ increases. Specifically, under conditions where the first term of the numerator and the last term of the denominator predominate, the expression for k_{obs} reduces to (16).

$$k_{obs} = \frac{k_{i1}}{K_{02} [X^-]} \qquad (16)$$

This would give a strict inverse dependence on the concentration of X^-. Realistically, there will probably be no concentration conditions under which the k_{obs} expression is this simple. Nonetheless, a decrease of k_{obs} with increasing $[X^-]$ is possible with a rate law of the form of (13), as computer simulations verify (*vide infra*).

4) The attainment of a limiting value for k_{obs} at high $[X^-]$ is consistent with the rate law in (13). At very high X^- concentration, the second term in the numerator and last term in the denominator are expected to predominate. The expression for k_{obs} becomes that in (17).

$$k_{obs} = \frac{k_{i2} K_{01} K_{02} [X^-]^2}{K_{01} K_{02} [X^-]^2} = k_{i2} \qquad (17)$$

Interpreted in terms of the mechanism in (9)-(12), the limiting value of k_{obs} obtained experimentally gives a direct measure of k_{i2}, the rate constant for interchange within the 2:1 ion pair.

Further support for the interchange mechanism in (9)-(12) comes from computer simulations using a rate law of the form of (13), reasonable values for the rate and equilibrium constants, and a range of values for $[X^-]$. A representative simulation is shown in Figure 5. As can be seen, this figure is similar in profile to Figures 2b and 3b, supporting our contention that 2:1 ion pairs play an important role in the pathway for (1).

We feel justified in invoking formation of 2:1 ion pairs on two grounds. First, from a theoretical viewpoint, the Fuoss equation[46] indicates that, in a solvent of low dielectric

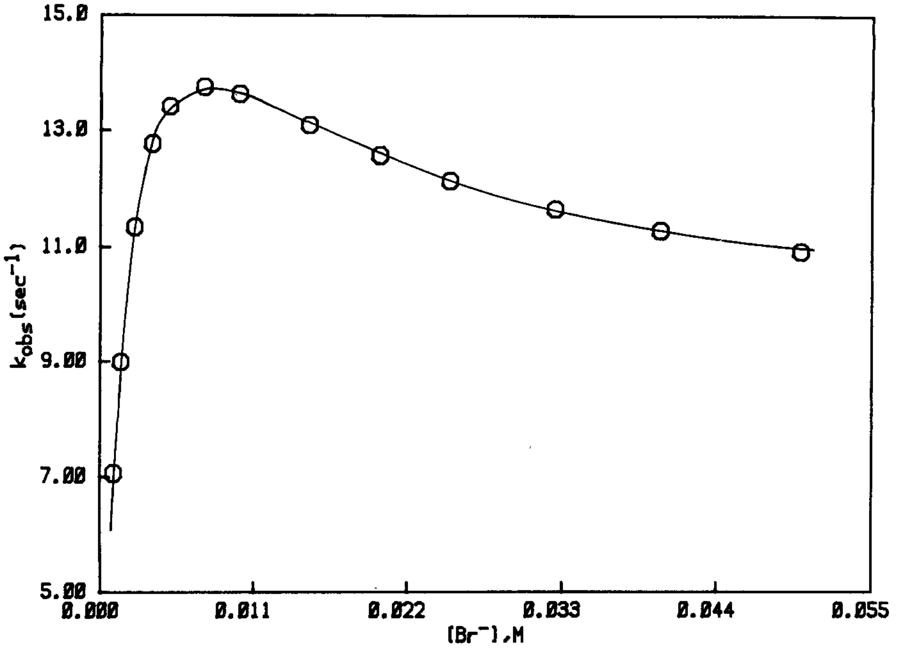


FIGURE 5 Computer simulation of the dependence of k_{obs} on [Br$^-$] for reaction (1), L = L^2. Fit to equation (13) with K_{01} = 500 M^{-1}, K_{02} = 100 M^{-1}, k_{i1} = *21* s^{-1}, k_{i2} = 9 s^{-1}.

constant (such as acetonitrile), the association constant for ion pair formation should be large. Further, the charges of the systems described here are fairly high, and in medium of low dielectric constant, one would expect 2:1 ion pairs to readily form. Second, our studies with variable ionic strength show that in the absence of a high concentration of ions, k_{obs} is large even at very low [Br$^-$] (see Figures 2a and 3a), that it decreases steadily as [Br$^-$] increases, and finally, that it becomes independent of [Br$^-$] at high [Br$^-$]. These results indicate that specific ion pair formation between CoL(An)(Br)$^{2+}$ and Br$^-$ takes place even at very low [Br$^-$]. At constant ionic strength, k_{obs} is small at low [Br$^-$], indicating that specific ion pair formation occurs less readily when perchlorate anions are present. At high [Br$^-$], the profiles of k_{obs} *vs* [Br$^-$] (one at constant and one with variable ionic strength) merge, indicating that, even in the presence of ClO_4^-, 2:1 ion pairs are present.

Based on the discussion above, we conclude that (1) occurs *via* the modified interchange mechanism in (9)-(12), involving formation of both 1:1 and 2:1 ion pairs. We further conclude that at high [X$^-$], k_{obs} gives a direct measure of k_{i2} (the rate constant for interchange within the 2:1 ion pair). Thus k_{i2} = 1.59 ± 0.08 s^{-1} at 40° when L = L^1; 10.0 ± 0.8 s^{-1} at 15.6° when L = L^2; and 35 ± 6 s^{-1} at 25° when L = L^5, under conditions of constant ionic strength.

Having established that (1) occurs *via* the interchange route, we are now in a position to discuss more intimate details of mechanism. Does ligand substitution at cobalt(III) occur by interchange which is primarily *dissociative* or *associative*? As discussed in the Introduction, there is substantial data in the literature supporting dissociative activation for substitution at Co(III) in aqueous solution. In most cases, substitution occurs *via* dissociative interchange (I_d).[6,37,38,47–49] In a few cases it occurs by the pure dissociative (D) route.[1-3,6] Our data are not consistent with a dissociative pathway. Instead we propose that (1) occurs *via* the associative interchange (I_a) mechanism.

Consider first the activation parameters, ΔH^* and ΔS^*, presented in Table 2. For all systems, ΔH^* is of relatively small magnitude, and ΔS^* is negative and of large magnitude. Small, positive values for ΔH^* usually arise when substantial bonding to the incoming ligand takes place in attaining the transition state. Thus bond formation compensates the partial rupture of the bond between metal and leaving ligand, giving rise to a small change in enthalpy. Similarly, large negative values for ΔS^* indicate an increase in order when the transition state is formed, as is expected for a process in which bond-making predominates.

Secondly, our data suggest a definite correlation between k_{i2} at 30° and the electron donor abilities of the macrocyclic ligands, L^1, L^2, and L^5. As we proceed along the series of macrocyclic ligands from L^1 to L^2 to L^5, there is a decrease in macrocyclic ligand donor ability resulting from systematic changes in the imine carbon substituents. This trend in donor abilities is seen quantitatively in the $E_{1/2}$ (Co(III-II)) values, presented in Table II. Table II also reveals that the values of k_{i2} at 30° follow a trend which parallels the trend in $E_{1/2}$ values. Specifically, k_{i2} increases as the electron donor ability of the macrocycle decreases. This trend in k_{i2} is not consistent with substitution via the I_d mechanism. The I_d mechanism, in which breaking of the bond to the leaving group is the important process preceding the transition state, demands the same trend of k_{i2} with macrocycle donor ability as was observed for the corresponding low-spin Fe(II) systems.[33] We observe just the opposite trend for substitution at Co(III). The substitution rate becomes faster as the donor ability of the macrocycle decreases, *i.e.*, as the metal center becomes more and more electron deficient. This is consistent with associative activation in these complexes.

Finally, we note that ligand substitution in the subject Co(III) complexes occurs much more rapidly than is typical for Co(III). The first-order rate constant for substitution of An by Br^- in the complex $CoL^1(An)_2^{3+}$ is about 1 sec^{-1} at 30°. This can be compared with a rate constant of 1.0×10^{-6} sec^{-1} for substitution of An by H_2O in $Co(NH_3)_5An^{3+}$ at 35°.[37] This remarkable difference presumably results from *cis*-labilization of the axial sites by the macrocyclic ligand, L^1. Substitutions in $CoL^2(An)_2^{3+}$ and $CoL^5(An)_2^{3+}$ are even more rapid indicating again a substantial labilization by the macrocyclic ligand.

In conclusion, rapid ligand substitution according to (1) occurs *via* associative interchange (I_a) in acetonitrile solvent. To our knowledge, this is the first example of associative activation for cobalt(III). That it occurs with ionic reactants in acetonitrile solvent is not surprising, given the low dielectric constant (D = 36) of this solvent.

REFERENCES

1. E.B. Fleischer, S. Jacobs and L. Mestichelli, *J. Am. Chem. Soc.*, **90**, 2527 (1968).
2. R.F. Pasternack and M.A. Cobb, *J. Inorg. Nucl. Chem.*, **35**, 4327 (1973).
3. R.F. Pasternack and M.A. Cobb, *Biochem. Biophys. Res. Commun.*, **51**, 507 (1973).
4. R.F. Pasternack, M.A. Cobb and N. Sutin, *Inorg. Chem.*, **14**, 866 (1975).
5. R.F. Pasternack and G.R. Parr, *Inorg. Chem.*, **15**, 3087 (1976).
6. K.R. Ashley, M. Berggren and M. Cheng, *J. Am. Chem. Soc.*, **97**, 1422 (1975).
7. K.R. Ashley and A.Y. Shun, *Inorg. Chem.*, **15**, 1937 (1976).
8. K.R. Ashley, *J. Inorg. Nucl. Chem.*, **39**, 357 (1977).
9. C.K. Poon, *Coord. Chem. Rev.*, **10**, 1 (1973).
10. W.K. Lee and C.K. Poon, *JCS Dalton*, 2423 (1974).
11. C.K. Poon and C.L. Wong, *JCS Dalton*, 966 (1976).
12. C.K. Poon and C.L. Wong, *Inorg. Chem.*, **15**, 1573 (1976).
13. C.K. Poon and C.L. Wong, *JCS Dalton*, 523 (1977).
14. C.K. Poon and W.K. Wan and S.S.T. Liao, *JCS Dalton*, 1247 (1977).
15. C.K. Poon, C.L. Wong and P.W. Mak, *JCS Dalton*, 1931 (1977).

16. J.A. Kernohan and J.F. Endicott, *Inorg. Chem.*, **9**, 1504 (1970).
17. D.P. Rillema, J.F. Endicott and J.R. Barber, *J. Am. Chem. Soc.*, **95**, 6987 (1973).
18. J.G. Jones and M.V. Twigg, *JCS Dalton*, 1709 (1978).
19. I.W. Pang and D.V. Stynes, *Inorg. Chem.*, **16**, 2192 (1977).
20. C.E. Holloway, D.V. Stynes and C.P.J. Viuk, *JCS Dalton*, 124 (1979).
21. F. Pomposo and D.V. Stynes, *Inorg. Chem.*, **22**, 569 (1983).
22. J. Martinsen, M. Miller, D. Trojan and D.A. Sweigart, *Inorg. Chem.*, **19**, 2162 (1980).
23. R.F. Pasternack, B.S. Gilles and J.R. Stahlbush, *J. Am. Chem. Soc.*, **100**, 2613 (1978).
24. R.V. Snyder and G.N. LaMar, *J. Am. Chem. Soc.*, **98**, 4419 (1976).
25. K.R. Ashley, J.G. Leipoldt and V.K. Joshi, *Inorg. Chem.*, **19**, 1608 (1980).
26. K.R. Ashley, S.B. Shyu and J.G. Leipoldt, *Inorg. Chem.*, **19**, 1613 (1980).
27. M. Doeff and D.A. Sweigart, *Inorg. Chem.*, **20**, 1683 (1981).
28. A. Antipas, J.W. Buchler, M. Gouterman and P.D. Smith, *J. Am. Chem. Soc.*, **102**, 198 (1980).
29. Abbreviations for macrocyclic ligands are based on suggestions by Busch and co-workers. V.L. Goedkin, P.H. Merrell and D.H. Busch, *J. Am. Chem. Soc.*, **94**, 6987 (1972).
30. D.E. Hamilton, T.J. Lewis and N.K. Kildahl, *Inorg. Chem.*, **18**, 3364 (1979).
31. N.K. Kildahl, T.J. Lewis and G. Antonopoulos, *Inorg. Chem.*, **20**, 3952 (1981).
32. N.K. Kildahl, K.J. Balkus Jr. and M.J. Flynn, *Inorg. Chem.*, **22**, 589 (1983).
33. N.K. Kildahl, G. Antonopoulos, N.E. Fortier and W.D. Hobey, *Inorg. Chem.*, **24**, 429 (1985).
34. S.C. Jackels, K. Farmery, E.K. Barefield, N.J. Rose and D.H. Busch, *Inorg. Chem.*, **11**, 2893 (1972).
35. D.S. Eggleston and S.C. Jackels, *Inorg. Chem.*, **19**, 1593 (1980).
36. W.A. Welsh, G.J. Reynolds and P.M. Henry, *Inorg. Chem.*, **20**, 751 (1977).
37. M. Glavas, M. Seif El-Nasr and W.L. Reynolds, *Inorg. Chem.*, **20**, 751 (1981).
38. S.T.D. Lo, E.M. Oudeman, J.C. Hansen and T.W. Swaddle, *Can. J. Chem.*, **54**, 3685 (1976).
39. A referee has pointed out that unless the electrolyte, Bu_4NClO_4, is fully dissociated in An, use of the term ionic strength is inappropriate. Literature values of the ion pair association constant, K_A, for several electrolytes in An are given below

Electrolyte	K_A	Reference
Bu_4NBr	2	40
	10.6	41
Bu_4NI	3	40
	11.9	41
$Bu_4NB\phi_4$	<1	42
Et_4NClO_4	17.8	43

It is found generally that as ion size increases, the extent of association decreases.[42] This and the data above allow us to conclude that K_A for Bu_4NClO_4 is certainly less than 10 and probably near 1 M^{-1}. In support of this, Coetzee *et al.*, have reported that Bu_4NClO_4 is *not associated up to a concentration of 0.004 M.*[44] Assuming a value of 1 M^{-1} for K_A, we calculate that Bu_4NClO_4 should be 92% dissociated at 0.1 M. We will use the term ionic strength throughout this paper, while recognizing that some association occurs.

40. D.F. Evans, C. Zawoyski and R.L. Kay, *J. Phys. Chem.*, **69**, 3878 (1965).
41. A.C. Harkness and H.M. Daggett, *Can. J. Chem.*, **43**, 1215 (1965).
42. A.F.D. deNamor, L. Ghousseini and R.A. Schulz, *JCS Faraday*, **80**, 1323 (1984).
43. J.F. Coetzee and G.P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2534 (1965).
44. J.F. Coetzee and G.P. Cunningham, *J. Am. Chem. Soc.*, **87**, 2529 (1965).
45. N. Kildahl and P. Viriyanon, manuscript in preparation.
46. R.M. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).
47. C.H. Langford and H.B. Gray, "Ligand Substitution Processes", W.A. Benjamin, London, 1974.
48. T.W. Swaddle, *Coord. Chem. Rev.*, **14**, 217 (1974).
49. C.H. Langford, *Inorg. Chem.*, **18**, 3288 (1979).