Ring Size Effects among Metal Complexes with Macrocyclic Ligands. The Kinetics of Aquation of Dichlorotetraamine Complexes of Cobalt(III) Involving Macrocyclic Ligands

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Abstract: Ring size is the structural parameter most distinctly characteristic of macrocyclic ligands and the present work reports on the kinetics of aquation and isomerization in acidic media of the cobalt(III) complexes with a series of unsubstituted, saturated tetraaza macrocyclic ligands of varying ring sizes. Significantly, the rates of the first aquation step vary from 2.6 to 1.1×10^{-6} s^{-1} and ln k_1 correlates well with the strain energy for planar chelation. The ligands range from 12 to 16 members and are abbreviated by $[X]$aneN_4, where X is a number corresponding to ring size. The complexes studied are *cis*-Co([12-13]aneN_4)Cl_2^+ and *trans*-Co([13-16]aneN_4)Cl_2^+ (except [14]aneN_4 which was studied by others). Two configurational isomers of Co([15-16]aneN_4)Cl_2^+ were studied. In all cases, the first sequential reaction involves replacement of a chloride by water with total retention of configuration. In the second step, the [13]aneN_4 complex suffers replacement of the second chloride, after which the diaquo complex rapidly isomerizes to the cis complex (which partially anates). This reaction requires inversion of a coordinated chiral nitrogen. The most stable isomer (I) of *trans*-Co([15]aneN_4)Cl_2^+ and the complex with [16]aneN_4 simply undergo successive aquation reactions. The less stable isomer of *trans*-Co([15]aneN_4)Cl_2^+ first aquates, followed by isomerization of the chloroaquo complex to the trans isomer having the most stable macrocycle configuration. The likelihood that the required nitrogen inversion does occur in this case is demonstrated by deuterium exchange studies. The rates of the first aquation step for the trans isomers vary in the sequence [16]aneN_4 > [15]aneN_4 (isomer II) > [15]aneN_4 (isomer I) > [13]aneN_4 > [14]aneN_4. The range over which the rates vary is considered to be remarkable for species having the same leaving group, the same central atom, the same donor atoms, and the same charge type. Further, the sequence of rates disagrees with the possibility that an electronic cis effect might be predominant, but correlates well with the strain energies calculated for the macrocycles in the starting complexes. The strain energy is presumed to be largely relieved in the transition state. The corresponding cis isomers show a very modest range of rates and a clear isokinetic effect. The latter is attributed to solvational differences.

Ring size is the single structural parameter that is uniquely characteristic of all macrocyclic ligands.[1] Consequently, the exploration of the relationships between ring size and the physical and chemical properties of metal complexes with macrocyclic ligands should eventually provide a number of partial answers to the general question "What is special about macrocyclic ligands?" The synthesis[2-4] of the saturated unsubstituted tetraaza macrocycles shown in Figure 1 has provided an ideal set of ligands for such studies.[5] These ligands are uncomplicated amines that form classical coordination compounds with many metal ions.

Earlier studies[1-4] have shown that the ligand field strengths of the secondary amine donor atoms are greatly affected by ring size in a way that depends on the relative fit of a particular metal ion into the intra-ring tetradentate chelation site. Rings that fit a given metal ion well produce normal ligand field strengths. Those that are smaller than the ideal size may still encompass the metal ion, but exhibit abnormally large ligand field strengths. Still smaller rings fail to encompass the metal ion and must fold in order to chelate in a tetradentate manner or, alternatively, the metal ion may be extruded above the intra-ring site.[6] Macrocyclic ligands that are larger than the best-fit size form complexes in which they exert abnormally weak ligand fields.[1-4] These stereostrictive and stereodilative effects have been observed for the ions of Ni^{2+}, Fe^{2+}, and Co^{3+}. A strain energy model has been developed[6,7] for the complexes of the ligands shown in Figure 1. The strain energies of the macrocycles that are chelated to a metal ion may be expected to affect the chemical and physical properties of the complexes. The strain energy calculations have been used to predict an ideal M-N distance for a given macrocyclic ligand[1,2] and the spectrochemical properties described above correlate well with the variation between the normal M-N distance for a given metal ion (from x-ray crystallography) and the ideal M-N distance for each macrocycle. It has also been found that the half-wave potential for the Co^{3+}/Co^{2+} couple for the complexes *trans*-Co([13-16]aneN_4)Cl_2^+ correlates well with the strain energy calculated for the cobalt(III) complex.[1] This is rationalized by assuming that the strain energy is essentially relieved when the metal ion is reduced to the divalent state, a possibility supported by the common occurrence of reduced coordination numbers and labile, distorted structures among such cobalt(II) complexes. Similar relationships between ring size and redox properties have been reported for nickel complexes.[8]

Rorabacher and associates[9] have studied the rates at which a related series of ligands are dissociated from their Cu^{2+} complexes. They used the complexes of a broad series of ligands very similar to those in Figure 1 but having only thioether donors in place of the secondary amines. They found that the rates of dissociation tend to be remarkably slow and that there is a very strong dependence of the rate on the ring size of the macrocyclic ligand.

Earlier studies[1,10] with [13]aneN_4, [15]aneN_4, and [16]aneN_4 have led to the isolation and characterization of two configurational isomers of the *trans*-Co(L)Cl_2^+ complexes with the latter two ligands and to the detailed assignment of structures to all of the complexes. Structural intricacies derive from the chiralities of the coordinated secondary amine donors and the possible chelate ring conformations. The structural assignments are shown in Figure 2.[1] The + and − signs indicate the orientations, with respect to the plane of the nitrogen donors, of the hydrogen atoms that are attached to nitrogen. The numbers indicate the chelate ring sizes along the respective edges of the coordination plane. The remaining symbols indicate the chelate ring conformations: δ, delta chirality (implies twist six-membered ring or gauche five-membered ring); λ, lambda chirality (same constraints as δ); γ, chair-form six-

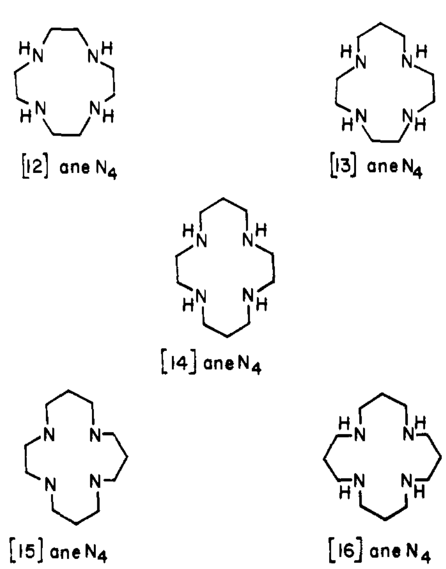

Figure 1. The saturated, unsubstituted tetraaza macrocyles used in this study.

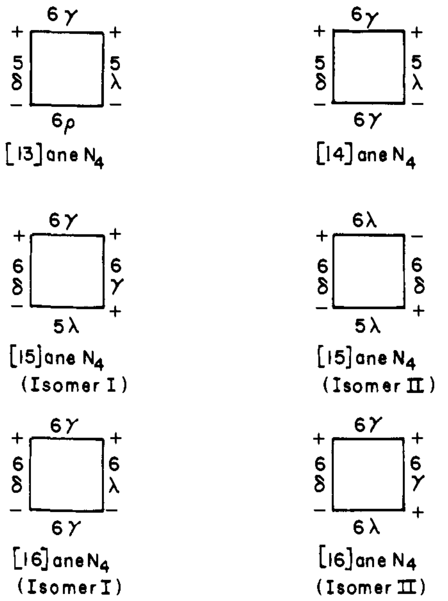

Figure 2. Configurations of the macrocyclic ligands in the complexes *trans*-Co([13-16]aneN_4)Cl_2^+.

membered ring; ρ, eclipsed five-membered ring.

The complexes *trans*-Co([13–16]aneN_4)Cl_2^+ (except the [14]aneN_4 derivative) and the related *cis*-Co([12–13]aneN_4)Cl_2^+ have served as the materials that were studied during the course of the work reported here. These families of compounds have been applied to the study of the effect of ring size on the rates of substitution at a metal ion center. The ring-size effects previously reported have been large, but the effects studied have generally involved the macrocycle directly (i.e., its rate of dissociation or its ligand field strength). The present studies reveal that ring size effects can also be very large in processes where the role of the macrocycle is less obvious. The present case involves the rates of aquation of the dichlorotetraamine complexes. Because they have been so heavily studied and are so well understood, the aquation reactions of the haloamines of cobalt(III) are quite appropriate for studies directed toward the understanding of new structural effects. The kinetics of aquation of the cobalt(III) complexes of a number of 14-membered macrocyclic ligands, including [14]aneN_4, have been reported.[11-14] The results of these earlier studies will be incorporated in the discussions that follow.

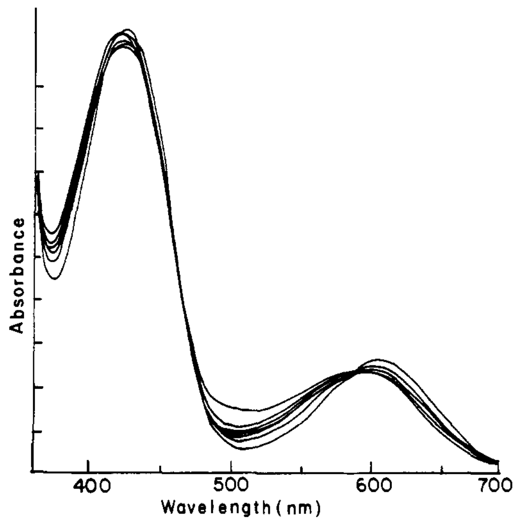

Figure 3. Changes in absorption spectra that accompany the first aquation reaction for *trans*-Co([13]aneN_4)Cl_2^+.

Results

The kinetics of the aquation reactions of the complexes *cis*-Co([12–13]aneN_4)Cl_2^+ and *trans*-Co([13–16]aneN_4)Cl_2^+ (except [14]aneN_4) have been studied. The complexes of [14]aneN_4 have been subjected to similar investigations by others and their data is used in discussions that follow. As has been reported elsewhere,[1,10] only the 12-, 13-, and 14-membered macrocycles form *cis*-dichloro complexes with cobalt(III). All of these ligands except [12]aneN_4 form *trans*-dichloro complexes. Two configurational isomers of *trans*-Co([15]aneN_4)Cl_2^+ are included in the present report. Their structures have also been discussed earlier.

In all cases, the first sequential reaction of these cobalt(III) complexes in acidic aqueous solutions is replacement of one chloride by water and retention of geometric configuration (cis or trans) is characteristic of these first aquation steps. Subsequent reaction processes vary both in the extent to which they proceed and in the importance of isomerization processes. These subsequent reactions were investigated in a number of cases, in part, to add certainty to the assignment of rates to the first aquation steps.

Aquation of *trans*-[Co([13]aneN_4)Cl_2]$^+$. The aquation of *trans*-[Co([13]aneN_4)Cl_2]$^+$ in 0.1 N nitric acid proceeds in two stages as indicated by two spectrophotometrically distinctive changes. The first stage is the solvolytic displacement of one coordinated chloride, as verified by the titration of liberated chloride. The second reaction stage is the solvolytic displacement of the second coordinated chloride by water and the concomitant isomerization and further reaction of the product, *trans*-Co([13]aneN_4)$(H_2O)_2^{3+}$, to a mixture of the *cis*-diaquo and *cis*-chloroaquo complexes. Titration of the free chloride in the reaction mixture at the end of the reaction (several days) gives 2.6 mol of free chloride.

The electronic spectra taken at different times during the first aquation reaction are characterized by a well-defined isosbestic point at 588 nm (Figure 3). At the end of the first reaction, the visible spectrum shows band maxima at 415 and 580 nm and is identical with that of the *trans*-Co([13]aneN_4)Cl$(H_2O)^{2+}$ complex synthesized by direct means. There was no evidence to indicate the formation of the *cis*-chloroaquo complex. Thus, the first aquation proceeds without steric change. Titration of the free chloride after 10 half-lives indicates that aquation was 75% complete for the chloride salt and 91% for the nitrate salt, from which $K_{eq} \approx 1.4 \times 10^{-2}$ M. Since in the acidic medium, the second reaction is very slow, there is no interference from the second reaction stage. The first

Table I. Rate Constants for the First Aquation Step for *cis*- and *trans*-Co([12-16]aneN$_4$)Cl$_2^+$ in 0.1 N HNO$_3$[a]

	$k_1 \times 10^4$, s^{-1}, complex indicated by isomer and ligand				
T, °C	*trans*-[13]aneN$_4$	*trans*(I)-[15]aneN$_4$	*trans*(II)-[15]aneN$_4$	*cis*-[12]aneN$_4$	*cis*-[13]aneN$_4$
15			49 ± 5	17 ± 1	31 ± 1[d]
20			63 ± 3		56 ± 3[d]
25	6.8 ± 0.2[b]	11.6 ± 0.6	99 ± 3	42 ± 2	9.5 ± 2[d,e]
					10.2 ± 5
30	12.9 ± 0.5	20.3 ± 0.6	188 ± 6		149 ± 5
35	25.2 ± 0.6	31 ± 2	250 ± 20	89 ± 8	249 ± 9
40		49 ± 6		153 ± 2[c]	
45	57 ± 2.0	79 ± 8			

[a] At least three runs unless otherwise specified. ± standard deviation. [b] In 0.1 N CF$_3$SO$_3$H a single run gave $k_1 = 5.4 \times 10^{-4}$ s^{-1}. [c] Average of two runs. [d] In 0.1 N CF$_3$SO$_3$H. [e] The same value was obtained for two runs in 0.1 N HCl.

reaction was monitored at 560 and at 620 nm and the observed rates were the same for the two wavelengths. Rate constants are reported in Table I.

The second sequential reaction is characterized by isosbestic points at 577, 453, and 393 nm. However, toward the end of this reaction, the isosbestic points disappear. The spectrum at very long times corresponds mainly to that of the *cis*-diaquo complex (λ_{max} at 495 and 365 nm) which has been obtained independently by acidifying *cis*-[Co([13]aneN$_4$)CO$_3$]$^+$ in aqueous solution with perchloric acid. Chloride titration demonstrated that chloride is released during this second reaction stage. Further confirmation of the nature of the reaction is provided by the fact that it is accelerated by the presence of mercuric ion. k_{obsd} is 1.9×10^{-5} s^{-1} at 35.0 °C, and 3.2×10^{-5} s^{-1} at 40.0 °C for the second spontaneous aquation process. The examination of the steric course of the second aquation step is complicated because of the fast isomerization (see next section) of the *trans*-diaquo species. However, the aquation is considered to be stereoretentive in view of the rigid nature of the macrocyclic ligand and the results of studies with *trans*-Co([13]aneN$_4$)(H$_2$O)$_2^{3+}$.

Isomerization of *trans*-Co([13]aneN$_4$)(H$_2$O)$_2^{3+}$. Because the product of the second stage of aquation of *trans*-[Co([13]aneN$_4$)Cl$_2$]$^+$ is mainly a mixture of cis complexes, the rate of isomerization of the *trans*-diaquo complex to the cis compound was studied. *trans*-Co([13]aneN$_4$)(H$_2$O)$_2^{3+}$ was produced in solution by passing the *trans*-Co([13]aneN$_4$)Cl$_2^+$ complex through an anion exchange column (OH$^-$ form). The pH of the eluent was adjusted to about 1 with nitric acid. The isomerization of the pure diaquo complex was then followed by repeatedly scanning the spectrum between 650 and 330 nm. Two well-defined isosbestic points were observed at 385 and 448 nm (Figure 4). The rate constant for isomerization is estimated to be 5.4×10^{-4} s^{-1} at 25 °C and 3×10^{-3} s^{-1} at 45 °C. These values are about 60 times faster than the observed rate constants for the second stage of the aquation of the *trans*-dichloro complex. It is therefore to be expected that the *trans*-diaquo complex is not observed during the second stage of the aquation.

Aquation of *trans*(I)-Co([15]aneN$_4$)Cl$_2^+$. This tan complex aquates to the chloroaquo complex and spectral scans show isosbestic points at 630, 562, and 468 nm. The second aquation stage is characterized by isosbestic points at 400 and 460 nm. The first aquation reaction was followed at 400 nm where the second aquation process does not interfere. The rates of the first aquation step are reported in Table I. Chloride titration after 10 half-lives indicates that the aquation is complete (≥99%). The product, the *trans*-chloroaquo complex, exhibits band maxima at 625, 500, and 408 nm. k_1 for the first aquation is 1.16×10^{-3} s^{-1} at 25 °C, $\Delta H^{\ddagger} = 19.3$ kcal mol^{-1}, and $\Delta S^{\ddagger} = -7.4$ cal deg^{-1} mol^{-1} at 25 °C. There is no complication in the aquation reactions of this compound and the second sequential process was not studied.

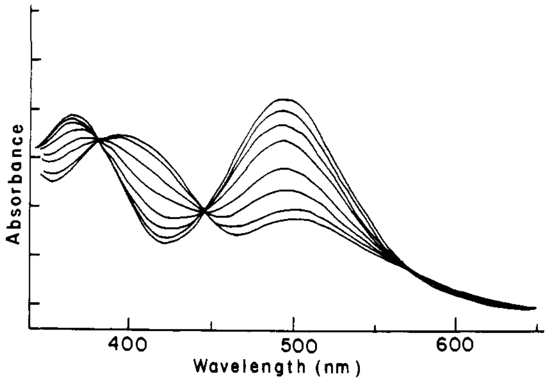

Figure 4. Changes in absorption spectra that accompany the isomerization of *trans*-Co([13]aneN$_4$)(H$_2$O)$_2^{3+}$ to *cis*-Co([13]aneN$_4$)(H$_2$O)$_2^{3+}$.

Aquation of *trans*(II)-Co([15]aneN$_4$)Cl$_2^+$. The spectral change accompanying the aquation of this green complex is characterized by the observation of isosbestic points at 425 and 621 nm for the first reaction stage. That one of the coordinated chloride ions is completely released is confirmed by chloride titration at the end of the reaction, at which time the spectrum shows bands at 615, 481, and 400 (sh) nm. As in the other cases, the presence of these three bands indicates that the product has the trans configuration. The rate constants are reported in Table I. The values were obtained by following the reaction at 569 and 670 nm.

Conversion of Isomer II to Isomer I in Aqueous Solution. After the completion of the displacement of one of the coordinated chloride ions from isomer II, the spectral bands shift to lower energies with isosbestic points at 559 and 602 nm. The final spectrum associated with this process corresponds to that of the product from the first aquation step of isomer I with λ_{max} at 408, 500, and 629 nm. Therefore, the reaction involves the isomerization of the chloroaquo complex of isomer II to that of isomer I. The rate constant for this isomerization is estimated to be 2.5×10^{-4} s^{-1} at 30.0 °C. No effort was made to determine the activation parameters. However, deuterium isotope exchange reactions were carried out in order to further demonstrate that this isomerization occurs with inversion of one or more secondary nitrogen atoms as required by the structural difference between the two configurational isomers. A small amount of sample was dissolved in 0.1 N HNO$_3$–D$_2$O solution at 30.0 °C to make a 0.002 M solution. This solution was thermostated at 30.0 °C for 45.8 min (approximately 1 half-life for the isomerization at this temperature) and then quenched in ice. The complex was isolated as the perchlorate salt, by adding lithium perchlorate to the solution, and freeze

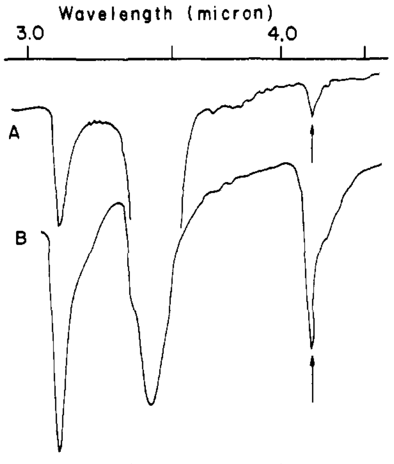

Figure 5. Infrared spectrum of the product of the isomerization reaction of *trans*(II)-Co([15]aneN_4)Cl$(H_2O)^{2+}$: A, after 45.8 min (~ 1 half-life) in 0.1 N HNO_3–D_2O; B, after 300 min in 0.1 N HNO_3–D_2O.

dried. The infrared spectrum exhibited a small N–D stretching peak at 2400 cm^{-1} (Figure 5), indicating that the breaking of nitrogen–hydrogen bonds had occurred to some extent in acidic media. Another portion of the sample was isolated after 300 min in the reaction bath. The infrared spectrum (Figure 5) shows that a greater extent of deuterium exchange has occurred, since the relative intensity of the infrared bands ν_{ND}/ν_{NH} has increased. It follows that nitrogen inversion is not prohibited at low pH, so that the isomerization can occur by the usual N–H exchange pathway.[15-17]

Aquation of *trans*-Co([16]aneN_4)Cl_2ClO_4 Complexes, Isomers I and II. Both of these isomers aquate so fast that it was not possible to follow their reactions by the method that was used for the investigation of the other compounds. Consequently, the reaction was studied in a different medium, a 1:1 mixture of water and acetonitrile, by the stopped-flow method. Due to solubility problems, the aquation of isomer II (the green complex) was not investigated thoroughly. From measurements at 670 nm at 25 °C, k_1 is estimated to be ~3 s^{-1}. The first aquation of isomer I (the brown complex) was followed at 680 nm where the absorption change is greatest. k_1 for the aquation of isomer I is 2.57 ± 0.09 s^{-1} at 25 °C. From rate measurements at a second temperature (19.8 °C where k_1 is 2.27 ± 0.07 s^{-1}) $\Delta H^{\ddagger}$ appears to be small.

Aquation of *cis*-Co([12]aneN_4)Cl_2^+. Spectral scans recorded during the first aquation reaction are characterized by one isosbestic point at 535 nm and those relating to the second stage by an isosbestic point at 427 nm. After 10 half-lives at 25 °C, the free chloride released in the first step was determined by potentiometric titration with silver nitrate. The chloride salt gives 1.85 M free chloride while the nitrate salt gives 0.93 M [Cl$^-$], from which K_{eq} = 0.12 M.

The aquation reaction was followed at 340 and 590 nm and both wavelengths gave the same rate constant, indicating that no other reaction occurs. The rate constants are reported in Table IV. The *cis*-chloroaquo complex absorbs at 530 and 370 nm.

Aquation of *cis*-[Co([13]aneN_4)Cl_2]Cl. Isosbestic points at 528 and 455 nm were observed in 0.1 N HNO_3 during the course of the first reaction. The first-order rate constant for the aquation in 0.1 N HCl is about the same value as that in 0.1 N HNO_3, indicating that the equilibrium for this reaction lies far to the right. In 0.1 N nitric acid, the second stage of reaction is characterized by three isosbestic points at 513, 436, and 378 nm. Chloride titration indicates that the second aquation is not complete; 2.61 mol of [Cl$^-$] was found in the solution at equilibrium. The *cis*-chloroaquo complex has peak maxima at 384 and 520 nm. The first reaction was followed at 340 and 490 nm. Rate constants appear in Table IV. The second aquation step has $k_{obsd} \simeq 2.4 \times 10^{-5}$ s^{-1} at 30.0 °C in 0.1 N CF_3SO_3H and 1.7×10^{-4} s^{-1} at 40.0 °C in 0.1 N HNO_3. The second reaction is about 1000 times slower than the first aquation process ($k_1 = 1.5 \times 10^{-2}$ s^{-1} at 30.0 °C) at this acid strength.

Discussion

The Kinetic Behavior of *trans*-Co([13–16]aneN_4)Cl_2^+. The aquation of complexes of the formula *trans*-Co([13–16]aneN_4)Cl_2^+ has been studied in 0.1 N HNO_3 as described in earlier sections. The first stage of the aquation of all the trans compounds is the release of one of the coordinated chloride ions with retention of the trans geometry. The rate constants for this stage fall in the order [16]aneN_4 > [15]aneN_4 > [13]aneN_4. The second stage of the reaction varies from system to system. The complex of [13]aneN_4 aquates stepwise to the *trans*-diaquo species, which isomerizes to the *cis*-diaquo complex and anates to the *cis*-chloroaquo complex (eq 1–4).

$$trans\text{-Co(L)Cl}_2^+ + H_2O \rightleftarrows trans\text{-Co(L)Cl(H}_2O)^{2+} + Cl^- \quad (1)$$

$$trans\text{-Co(L)Cl(H}_2O)^{2+} + H_2O \rightleftarrows trans\text{-Co(L)(H}_2O)_2^{3+} + Cl^- \quad (2)$$

$$trans\text{-Co(L)(H}_2O)_2^{3+} \rightleftarrows cis\text{-Co(L)(H}_2O)_2^{3+} \quad (3)$$

$$cis\text{-Co(L)(H}_2O)_2^{3+} + Cl^- \rightleftarrows cis\text{-Co(L)Cl(H}_2O)^{2+} + H_2O \quad (4)$$

The first aquation product of isomer I of *trans*-Co([15]aneN_4)Cl_2^+ aquates further to the diaquo complex with no complicating reactions (eq 1 and 2). Following the first aquation step, isomer II of the 15-membered ring system isomerizes to the first aquation product of isomer I (eq 1 and 5). Further reaction then simply follows eq 2.

$$trans\text{(II)-Co([15]aneN}_4\text{)Cl(H}_2O)^{2+} \rightleftarrows trans\text{(I)-Co([15]aneN}_4\text{)Cl(H}_2O)^{2+} \quad (5)$$

Within the limits of available data, the complex of [16]aneN_4 appears to undergo a simple two-step aquation sequence.

The rates of the first aquation step for the *trans*-dichloro complexes at 25 °C are collected in Table II along with the activation parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$. Data for the corresponding complex of [14]aneN_4[18] and those for related linear tetraamines,[19,20,21] bis(ethylenediamine),[22,23] and bis(trimethylenediamine)[24] complexes are also included for comparison. The rates of aquation of the unsubstituted, fully saturated macrocyclic ligand complexes *trans*-Co([13–16]aneN_4)Cl_2^+ fall in the order [14]aneN_4 < [13]aneN_4 < [15]aneN_4 (isomer I) < [15]aneN_4 (isomer II) < [16]aneN_4, while those of the linear tetraamine complexes follow the order:3,2,3-tet < 2,3,2-tet < 2,2,2,-tet. The range of rates (at 25 °C) for the macrocyclic ligand derivatives *trans*-Co([13–16]aneN_4)Cl_2^+ extends over six orders of magnitude from 2.6 s^{-1} for the [16]aneN_4 derivative to 1.1×10^{-6} s^{-1} for the [14]aneN_4 complex. This contrasts with the range of rates for linear tetradentate complexes, which covers less than a factor of 200 (Table II). Arbitrarily considering the ethylenediamine[22,23] complex *trans*-Co(en)$_2Cl_2^+$ to be the prototypic *trans*-dichlorotetraamine, the values for the series of macrocyclic ligand derivatives are seen to bracket the rate of aquation of this familiar reference compound ($k = 3.2 \times 10^{-5}$ s^{-1} at 25 °C, pH 1). The [14]aneN_4 derivative aquates more slowly, while the remaining complexes all react more rapidly;

Table II. Rate Constants and Activation Parameters for the Aquation of Selected Complexes of the Form *trans*-Co^{III}(L)Cl$_2$$^+$

L	k_1 (at 25 °C), s^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol	Steric change (% cis)
[13]aneN$_4$	6.76×10^{-4}	25.6	12.6	0
[14]aneN$_4$[a]	1.1×10^{-6}	24.6	−3	0
[15]aneN$_4$ (isomer I)	1.16×10^{-3}	19.6	−7.4	0
[15]aneN$_4$ (isomer II)	9.92×10^{-3}	15.8	−14.5	0
[16]aneN$_4$ (isomer I)	2.57			
Trien	3.5×10^{-3}	26.0	15.5	100
meso-2,3,2-Tet[b]	1.5×10^{-5}	24.6	1	0
d,l-2,3,2-Tet[b]	2.9×10^{-4}	24.7	9	50
3,2,3-Tet[c]	5.3×10^{-5}	24.5	4	0
(en)$_2$[d]	3.2×10^{-5}	26.2	14	35
(tn)$_2$[e]	5.33×10^{-2}			

[a] Reference 18. [b] Reference 20, 2,3,2-tet is 1,4,8,11-tetraazaundecane. [c] Reference 19, 3,2,3-tet is 1,5,8,12-tetraazadodecane. [d] Reference 23, en is ethylenediamine. [e] Reference 24, tn is 1,3-diaminopropane.

trans-Co([16]aneN$_4$)Cl$_2$$^+$, 10^5 more rapidly. Many other *trans*-dichlorotetraamines, including derivatives of lengthy series of substituted ethylenediamines[25] and the linear tetradentates of Table II, undergo aquation at rates within a factor of about 10^2 of that for *trans*-Co(en)$_2$Cl$_2$$^+$. It is therefore concluded that most of the macrocyclic ligands form complexes that have a tendency to aquate at accelerated rates. Only the [14]aneN$_4$ complex reacts at a rate that is slow compared to the reference compound. It is probably significant that electronic spectral studies on these same complexes have led to the conclusion that the [14]aneN$_4$ ligand is of the optimum size to encompass a cobalt(III) ion with minimum strain.[1,2] Accordingly, the other rings all provide nonideal cobalt(III) sites from the standpoint of size. Thus, the ring that fits cobalt(III) best produces a complex that aquates at a slightly retarded rate, while those rings that fit relatively poorly generate complexes that aquate at various accelerated rates. It is useful to explore this relationship between ring size and aquation rate further.

Correlation between the Rate for the First Aquation Step and Strain Energy. While one might look to electronic effects that have been described earlier for the parametric dependence of rate on macrocyclic ring size, the results presented here correlate with strain energies instead. It is useful, however, to examine the noncorrelation with electronic effects. Electronic spectral studies[1,3] show that there is a general interdependence between the ligand field strengths of such axial ligands as Cl$^-$ (as measured by the axial ligand field splitting parameter Dq^z) and those of the in-plane macrocyclic ligands (as measured by the corresponding Dq^{xy}) in complexes of the form *trans*-M([13–16]aneN$_4$)X$_2$$^{n+}$. As the in-plane ligand field strength Dq^{xy} increases, the interaction of the metal ion with the axial ligands is diminished (Dq^z decreases). These studies also show that Dq^{xy} generally increases and Dq^z decreases as the planar tetradentate tetraaza macrocycles become smaller in ring size. Since the mechanism of aquation of haloamines of cobalt(III) is essentially S$_N$1, one can predict the direction in which electronic effects would shift the rates of aquation as ring size changes. The rate should be greatest for the complexes having the smallest rings and least for the complexes with the largest rings; i.e., the electronic (cis) effect predicts that the rates of aquation would follow the sequence: [13]aneN$_4$ > [14]aneN$_4$ > [15]aneN$_4$ (isomer II) > [15]aneN$_4$ (isomer I) > [16]aneN$_4$. This most clearly is not the case (Table II). In fact, the experimental behavior shows more nearly the opposite behavior, since *trans*-Co([16]aneN$_4$)Cl$_2$$^+$ aquates, by far, at the most rapid rate. In fact, there is not even a monotonic relationship between the observed rates and the predictions based on an electronic cis effect. This does not deny the existence of the cis-effect phenomenon,[26,27] but rather requires that other effects dominate in this particular set of reactions. One might be tempted to seek a correlation with average ligand field strength. However, this is bound to fail, since Dq^{av} increases steadily as ring size decreases, while k_1 for aquation decreases from the 16-membered cases through the 14-membered ring derivative and then increases.

Table III. Minimized Strain Energies of *trans*-Co([13–16]aneN$_4$)-Cl$_2$$^+$ [a]

	R	NB	θ	ϕ	*H*	Conformer[b]
[13]aneN$_4$	2.01	4.97	7.37	5.39	19.74	d r l g
[14]aneN$_4$	1.95	2.77	5.60	1.20	11.53	d g l g
[15]aneN$_4$(I)	4.26	5.32	8.02	3.73	21.33	g g d l
[15]aneN$_4$(II)	3.49	7.50	7.69	6.79	25.47	d l d l
[16]aneN$_4$(I)	7.81	10.18	10.98	6.60	35.56	d g l g

[a] All values in kcal/mol. *R* = energy associated with bond stretching; NB = energy associated with nonbonded interaction: θ = energy associated with bond angle deformation: ϕ = energy associated with bond torsions. [b] The symbols used to represent the chelate ring conformations are: d, the delta chirality; l, the lambda chirality; r, an eclipsed five-membered ring; g, a chair form six-membered ring.

We have found during the course of these studies that the rates of the first aquation reactions of the trans complexes correlate well with the strain energies of the chelated macrocycles in the starting complexes. The strain energies[1] for the theoretical gas phase ions *trans*-Co([13–16]aneN$_4$)Cl$_2$$^+$ are summarized in Table III. It is to be expected that when the five-membered rings are fused together in a macrocyclic ligand ([13]aneN$_4$), the resulting complex is strained because the complete ligand is too short for facile, planar tetradentate chelation to cobalt(III). The largest sources of strain arise from bond angle stretching and torsional deformation as indicated by the quantities θ and ϕ listed in Table III. In contrast, the fusion together of several six-membered chelate rings produces crowding in the structure. Huge nonbonding interactions and distortions of the bond angles result. Hence *trans*-Co([16]aneN$_4$)Cl$_2$$^+$ is the complex containing the most strained ligand and it is the substance which gives the most rapid rate of reaction, as reported above. The graph of ln k_1 vs. $H_{\text{strain energy}}$ is a fairly good straight line with a slope of 0.6 (Figure 6), indicating that the strain energy is a dominant factor determining the rates of aquation of these macrocyclic complexes.

The correlation of strain energy with ln k_1 for the first aquation step for *trans*-Co([13–16]aneN$_4$)Cl$_2$$^+$ represents a relationship between a theoretical property of the starting material and the free energy difference between the starting material and the transition state. In order for the correlation to be solely dependent on a property (strain energy) of the

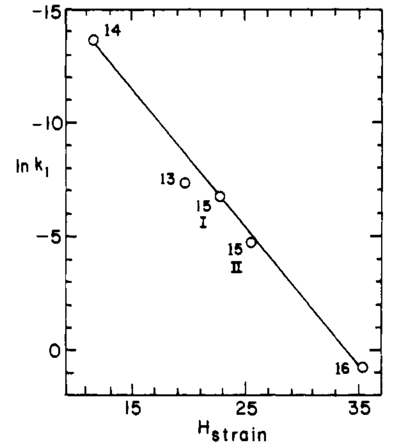

Figure 6. Correlation between the rates of aquation of the complexes *trans*-Co([13-16]aneN$_4$)Cl$_2^+$ and the strain energies for the chelated macrocycle in the starting complex.

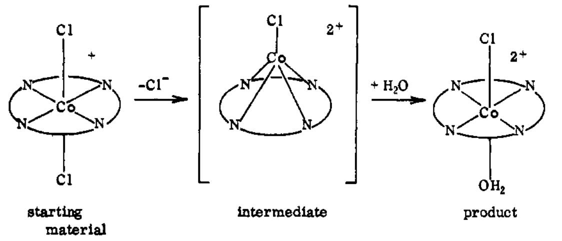

Figure 7. Model for the relief of strain energy during the aquation reaction.

starting material, it is apparent that the values for that property for the transition state are either relatively very small or do not change much from compound to compound. This leads to the logical suggestion that the strain energies of the several complexes are largely relieved in the transition state.

While it must be recognized that such a correlation could be fortuitous, it is not difficult to visualize a general model that would facilitate the understanding of the influence of strain energy on the rates of substitution reactions. Such a model, as outlined in Figure 7, provides the basis for further exploration for the effects of strain energies on the reactions of metal chelates. It must first be realized that the chloride ions of the complexes *trans*-Co([13-16]aneN$_4$)Cl$_2^+$ play a significant role in generating the values of the strain energies that have been calculated. This is apparent upon comparison of the various parameters derived from strain energy calculations for planar tetradentate macrocycles with[1] and without[2] the axial chlorides. The transition state usually presumed for substitution reactions at cobalt(III) is five-coordinate and for the present case involves the removal of a single chloride. Thus, the influence of one chloride on the exact conformation of the macrocycle is removed and the single remaining chloride exerts its force on one side of the planar macrocycle (Figure 7). This should remove the constraint for the metal ion to remain chelated in a site precisely within the N$_4$ plane of the macrocycle. The simplest change that could occur would involve displacement of the metal ion out of the N$_4$ plane toward the chloride ion, a distortion that is common in five-coordinate structures involving the porphyrin ring.[28] More complicated distortions resulting from the folding of the ring are also possible.

All of the macrocyclic complexes for which aquation studies have been reported,[11-14,18,29,30] whether the ligand is saturated, unsaturated, substituted, or not substituted, exhibit a characteristic property. This is the retention of configuration for the macrocyclic ligand in the product of aquation. This is consistent with the assumption that the intermediate in the aquation reaction of the macrocyclic complex has the tetragonal pyramidal geometry. For cases where the strain energy is modest, this is easily understood in view of the stereorestrictive nature of the ligand, a property which could oppose the trigonal bipyramidal structure for the five-coordinate intermediate state.[18] If the ring fits in a strain-free fashion, the enthalpy of the transformation from the octahedron to the trigonal bipyramid in the macrocyclic complex is considerably less favorable than that to the tetragonal pyramid because the ligand molecule is not required to change its conformation in the latter case.

Tobe proposed[31] that the structure of the intermediate formed during substitution reactions at Co(III) could be distinguished on the basis of the value of the entropy of activation. Positive values of $\Delta S^{\ddagger}$ were taken as evidence for a trigonal bipyramidal intermediate, while a negative entropy of activation was assumed to imply a tetragonal pyramidal intermediate. According to Tobe's concept, the aquation reaction of *trans*-Co([13]aneN$_4$)Cl$_2^+$, which has $\Delta S^{\ddagger} = 13$ cal deg^{-1} mol^{-1}, would be assigned a trigonal bipyramidal intermediate, whereas the reactions of the remaining macrocyclic ligand complexes would be assigned tetragonal pyramidal intermediates. In view of the rather regular charge of $\Delta S^{\ddagger}$ with ring size in this series of complexes it seems unlikely that Tobe's criterion applies.

The kinetic behavior reported by Rorabacher et al.,[9] for the rates of dissocation from Cu^{2+} of the closely related saturated, unsubstituted tetrathia macrocyclic ligands provides a supportive example. These rates of dissociation follow the same ring size order: [14]aneS$_4$< [13]aneS$_4$ < [15]aneS$_4$ < [16]aneS$_4$. This suggests that the two reactions, aquation of *trans*-Co^{III}(L)Cl$_2^+$ and dissociation of Cu^{II}(L)$^{2+}$, are influenced by a closely related set of strain energy considerations. Since a ring could not conceivably be removed from the metal ion without folding, this suggests that for the reactions studied here the more highly strained structures could involve some folding of the ring in the transition state.

Since the macrocyclic ligands discussed here can be considered to be derivatives of the linear tetraamines (for abbreviations see Table II), some similarities in the rates of aquation of the complexes of the two sets of ligands are to be expected. It is anticipated from the preceding discussion and other properties[1,2] of the complexes of the homologous cyclic ligands that strain energies will contribute to the differences in their behavior. This is also expected for the linear tetradentate derivatives. The trans complexes of 2,3,2-tet and 3,2,3-tet are relatively strain free,[7,32] while that of 1,4,7,10-tetrazadecane (abbreviated trien) is strained due to the small number of carbon atoms in its chelate rings, and it is this species (*trans*-Co(trien)Cl$_2^+$) which aquates most rapidly. Unfortunately, the complex *trans*-Co(3,3,3-tet)Cl$_2^+$ has not been successfully synthesized (3,3,3-tet is 1,5,9,13-tetraazatridecane). This complex would be expected to be strained and to react much faster than those of the strain-free complexes of 3,2,3-tet and 2,3,2-tet. It is also consistent with these considerations that k_1 for *trans*-Co(tn)$_2$Cl$_2^+$ is 1000 times[21] larger than that for *trans*-Co(en)$_2$Cl$_2^+$. With this in mind, it is interesting to note that k_1 for the 15-membered ring system is a 1000 times larger than that for the strain-free 14-membered ring system and 10^3 times smaller than that for the 16-membered ring system and that each pair of complexes compared differs by substitution of one six-membered chelate ring for a five-membered chelate ring.

Isomerization Reactions of the Trans Complexes. In contrast to the first aquation process for *trans*-Co([13]aneN$_4$)Cl$_2^+$, the loss of the second chloride is followed by rapid trans to cis isomerization of the product. Three experimental facts provide a ready rationalization for these relationships. In order for a cis isomer to be formed, the chiral nitrogen atoms must adopt relative configurations that permit folding of the macrocycle. As discussed elsewhere, the probable structure of the starting complex would not permit this.[1] Since the ligand does not have such an arrangement in the trans complex, inversion of at least one nitrogen must precede or accompany cis–trans isomerization. It has been well demonstrated that such inversions of nitrogen chiralities in coordinated macrocyclic ligands occur by ionization of the protons from the nitrogen atoms.[33,34] In turn, this leads to the conclusion that structural factors which increase the rates of exchange and/or the acidities of coordinated amines will facilitate nitrogen inversion. In the present case, ring folding, i.e., trans to cis isomerization, should be facilitated in this manner. It has long been known[35,36] that both the acidity and the rate of hydrogen exchange by coordinated amines increase as the charge on the complex ion becomes more positive. It follows that the tripositive ion *trans*-Co([13]aneN$_4$)(H$_2$O)$_2^{3+}$ should undergo more facile isomerization to the cis isomer than either of its precursors in the sequence of aquation reactions. It is apparent that proton exchange and trans–cis isomerization are slower than the alternate aquation reactions for *trans*-Co([13]aneN$_4$)Cl$_2^+$ and *trans*-Co([13]aneN$_4$)Cl(H$_2$O)$^{2+}$.

In the case of the less stable isomer of *trans*-Co([15]-aneN$_4$)Cl$_2^+$, a similar set of relationships has been observed. In this case, there is no tendency to form cis complexes, but the difference in strain energies provides a driving force for conversion of the trans(II) complex into the trans(I) complex. That isomerization occurs for the first aquation product *trans*(II)-Co([15]dieneN$_4$)Cl(H$_2$O)$^{2+}$ rather than for the starting material can again be explained in terms of the dependence of the reaction on the ionization of a proton from a chelated nitrogen atom. In this case we have demonstrated the occurrence of this necessary exchange reaction by deuteration studies (Results section).

The fact that rates of the first aquation reaction differ by almost an order of magnitude for the two configurational isomers of *trans*-Co([15]aneN$_4$)Cl$_2^+$ strongly emphasizes the role of strain energy in these reactions. The spontaneous conversion of isomer II to isomer I (for the chloroaquo species) accords with the results of strain energy calculations and other results in confirming the relative stabilities of the two isomers.[1] The fact that the least stable isomer reacts most rapidly requires that relief of strain energy in the transition state be a major factor, since electronic effects have been ruled out on other grounds (see above), while the associated solvational changes must be quite similar for the two isomers. The likelihood that solvation effects are of substantial significance in the rate variations discussed here is also discounted by the results of studies on the aquation of the cis isomers of some of these same substances.

The Kinetic Behavior of *cis*-[Co(L)Cl$_2$]$^+$ Complexes. As is generally true of such isomers, the cis complexes studied here aquate with retention of the cis configuration. The aquation data for *cis*-[Co(L)Cl$_2$]$^+$ and several other related complexes are collected in Table IV. The rates of aquation of the cis-macrocyclic complexes do not differ as dramatically as do the rates for the trans complexes. The rate constants only differ by a factor of four as ring size changes from [14]aneN$_4$ to [12]aneN$_4$. The activation enthalpies of the cis complexes follow the order: [12]aneN$_4$ < [13]aneN$_4$ < [14]aneN$_4$; however, the order for the activation entropies follows the reverse trend. This results in a fairly constant activation free energy, hence only a small range for the rates. The *cis*-dichloro complexes of macrocyclic ligands display an isokinetic relationship. That is, the enthalpies and entropies of activation vary linearly (the slope is 366). The slope has units of absolute temperature and is equal to the isokinetic temperature (at that temperature the compounds would react at the same rate). This behavior suggests that the variation in a particular structural parameter gives rise to a single effect which dominates the variation in rate.[37] It has previously been suggested[31] that all cis complexes aquate via tetragonal pyramidal intermediate states. Since no steric change occurs during aquation, this structure is expected for the intermediate.

Table IV. Rate Constants for the Aquation of *cis*-Co^{III}(L)Cl$_2^+$

L	k_1, s^{-1} at 25 °C	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, cal/deg mol	$\Delta G^{\ddagger}$, kcal/mol
[12]aneN$_4$	4.2×10^{-3}	13.5	−24	20.8
[13]aneN$_4$	1.0×10^{-2}	15.2	−17	20.4
[14]aneN$_4$[a]	1.6×10^{-2}	18.3	−6	20.1
β-Trien[b]	1.5×10^{-3}	20.5	−3	21.9
β-2,3,2-Tet[c]	1.1×10^{-3}	22.3	2	21.7
(en)$_2$[d]	2.4×10^{-4}	21.5	−5	23.0

[a] From ref 14. [b] Reference 21. [c] Reference 20. [d] Reference 23.

The kinetic behavior reported here and the electronic spectral behavior described earlier[1] have demonstrated that the cis complexes are insensitive to the size of the macrocyclic ring. From this it may be concluded that when chelated in folded conformation, macrocycles do not exhibit the distinctive effects that derive from excessive strain energies. To reflect back on the behavior of the trans complexes of the composition [Co([13–16]aneN$_4$)Cl$_2$]$^+$, these conclusions support the view that the relief of strain energy may accompany the dissociation of a chloride ligand. Some folding of the macrocycle in the five-coordinate transition state may produce species in which the macrocyclic ligand can chelate while experiencing relatively little strain energy.

There remains to be considered the very tidy isokinetic behavior found in the rates of aquation of *cis*-[Co([12–14]-aneN$_4$)Cl$_2$]$^+$. Since the effect involves both strong enthalpy and entropy changes, the varying phenomenon most probably is *external* in character.[37] The entropy is expected to be relatively insensitive to such factors as stereorestrictivity, which vary *internally* with respect to the structure of the complex. It is therefore highly rational to suggest that the interaction generating the isokinetic behavior among *cis*-[Co(L)Cl$_2$]$^+$ complexes derives from solvent interactions. One might anticipate more extensive solvation in the polar transition state, in which case $\Delta S^{\ddagger}$ would become more negative as the hydrophobic structural component decreased in amount; i.e., $\Delta S^{\ddagger}$ should become more negative as ring size decreases. This is a rather compelling argument that the solvational effects of ring size are most simply and clearly seen in cis complexes. The relative importance of solvational effects and of those special strain energy effects that are aptly described by Rorabacher's term *stereorestrictivity*[38] continue to be matters of much interest as they relate to the reactions of complexes with macrocyclic ligands.[9,39,40]

Experimental Section

Materials. The preparation, properties, and characterization of the complexes used in this work are reported elsewhere except for *cis*-Co([12]aneN$_4$)Cl$_2^+$, which was synthesized by mixing the ligand with CoCl$_2$·6H$_2$O in methanol followed by acidification and air oxidation, instead of the literature method,[41] yield, 70%. Anal. Calcd for [Co(C$_8$H$_{20}$N$_4$)Cl$_2$]NO$_3$: C, 26.39; H, 5.54; N, 19.23. Found: C, 26.24; H, 5.21; N, 19.36.

Spectrophotometric Rate Studies. The Cary Model 14R spectrophotometer was used to follow the change in absorption during the aquation of *cis*- and *trans*-[Co(L)Cl$_2$]$^+$ complexes, except for the [16]aneN$_4$ derivatives. Cells with path lengths of 10 cm were used for the reactions of the trans complexes, while 5-cm cells were used for the aquation of the cis complexes. Each reaction was followed by setting the wavelength at an optimum value and the absorption at this wavelength was then recorded as a function of time by running the chart at a known speed. The optimum wavelength either corresponds to an isosbestic point of the second successive reaction, or to a wavelength where the change of absorption is the greatest. The solid sample of complex was weighed in the spectrophotometer cell. The 0.1 N acid solution (ionic strength, 0.1) was brought to reaction temperature and reaction was initiated by injection of the acid solution into the reaction cell. Temperature was controlled within ±0.1 °C by circulating water from a constant temperature bath through the compartment surrounding the cell. Kinetic runs were carried out at five different temperatures over a range of 20 °C. Graphs of ln $(A_\infty - A_t)$ vs. time were straight lines for at least 2 half-lives for all of the reactions investigated.

The aquation of *trans*-$[Co([16]aneN_4)Cl_2]ClO_4$ was followed by the stopped-flow method. A Durrum-Gibson Model 110 stopped-flow apparatus interfaced with a Nova mini-computer for data acquisition, storage, and evaluation was used. The instrument was fitted with Kel-F components and a 2-cm light path. Acetonitrile used in the stopped-flow measurements was dried over 4Å Linde molecular sieves and then distilled. Two solutions, one containing the complex dissolved in acetonitrile and the other containing 0.2 N HNO_3, were rapidly mixed in the mixing chamber of the instrument and the reaction was followed at 680 nm for isomer I of *trans*-$Co([16]aneN_4)Cl_2^+$ and 670 nm for isomer II of the same complex. Rate constants were calculated by a curve fitting method.

Titrimetric Studies of Chloride Release. Weighed samples were mixed with the acid solution which had previously been brought to the reaction temperature, and placed in a water bath at the reaction temperature. Samples were withdrawn at appropriate times and quenched with ice. Each sample was then passed through a cation exchange resin in the acidic form and eluted with ice-cold water. The eluent was titrated with $AgNO_3$ solution using a Corning Model 12 pH meter, a silver wire indicator electrode, and calomel reference electrode. Alternatively, the reaction mixture was titrated directly after quenching without passing through the cation exchange resin. The results were identical.

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