(DPM)($o$-$CH_2C_6H_4NMe_2$)$_2$, 65930-47-4; Cr(DPM)($o$-$CH_2C_6H_4NMe_2$)$_2$, 64061-49-0; V(DPM)($C_6H_4CH_2NMe_2$)$_2$, 61818-22-2; $TiMe_2$(DPM)($PMe_3$)$_2$, 65930-53-2; Cr(DBM)(Cp)Cl, 65930-52-1; Ti(DPM)($HBpz_3$)Cl, 65930-51-0; Ti(DPM)($PMe_3$)$_2Cl_2$, 65930-49-6; Cr(DPM)($PMe_3$)$_2Cl_2$, 65956-91-4; $TiCl_2$(DPM)(bpy), 65930-54-3; $Li^+[N(SiMe_3)_2]^-$, 4039-32-1; Ti(DPM)$[N(SiMe_3)_2]_2$, 61818-23-3; Ti(DBM)$[N(SiMe_3)_2]_2$, 61818-24-4; V(DPM)$[N(SiMe_3)_2]_2$, 61818-25-5; V(DBM)$[N(SiMe_3)_2]_2$, 61818-26-6; $TiCl_3(THF)_3$, 18039-90-2; $VCl_3(THF)_3$, 19559-06-9; $CrCl_3(THF)_3$, 10170-68-0.

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# Mechanism and Steric Course of Octahedral Aquation. 19.[1] Aquation of a Labile Trans Isomer of the Dichloro(1,4,8,11-tetraazacyclotetradecane)cobalt(III) Cation

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A new method for the synthesis of a labile form of *trans*-$[Co(cyclam)Cl_2]ClO_4$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) with the ligand in the *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) configuration is reported. The kinetics and steric course of aquation are reported. $k_{aq} = 1.75 \times 10^{-3}\ s^{-1}$ at 25.0 °C, $\Delta H^{\ddagger} = 24.2 \pm 0.5$ kcal $mol^{-1}$, and $\Delta S^{\ddagger} = +\ 9.9 \pm 1.6$ cal $K^{-1}\ mol^{-1}$ (0.0100 M $HNO_3$, $\mu = 1.00$ ($NaNO_3$)). The immediate reaction product, a mixture of 75% *trans*- and 25% *cis*-$[Co(cyclam)ClH_2O]^{2+}$ isomerizes to 100% *cis*-$[Co(cyclam)ClH_2O]^{2+}$ with $k_i = 1.3 \times 10^{-2}\ s^{-1}$ at 25.0 °C, $\Delta H^{\ddagger} = 25.8$ kcal $mol^{-1}$, and $\Delta S^{\ddagger} = +19.3$ cal $K^{-1}\ mol^{-1}$. The rate of aquation is independent of the acid concentration ($[H^+] \geq 0.01$ M) but is retarded by chloride. This is due to a reversible anation of the *trans*-$[Co(cyclam)ClH_2O]^{2+}$ species which competes with the isomerization and which does not affect the *cis*-$[Co(cyclam)ClH_2O]^{2+}$ species. The *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) configuration of the ligand is retained throughout. This is the first example of an aquation of a complex with a macrocyclic tetraamine ligand that proceeds with stereochemical change.

## Introduction

Some years ago we examined the kinetics of aquation of a pair of cis and trans isomers of $[Co(cyclam)Cl_2]Cl$ (cyclam = 1,4,8,11-tetraazacyclotetradecane).[2,3] The cis species was some $10^4$ times more labile than the trans isomer and it was remarked at the time that this was a most unusual observation for the noncatalyzed aquation reactions of cobalt(III) acido–amine complexes. However, it was pointed out that the ligand configuration (arising from the various possible combinations of the chiralities of the four secondary nitrogen atoms) was different in the two isomers and it was shown that the isomerization of the cis species to the more stable trans isomer required proton exchange and the inversion of configuration of two of the nitrogens.[4] Although there has been no direct structural determination there is good reason to believe that the stable trans isomer has the same meso configuration $\underline{R\text{-}3\text{-}S\text{-}2\text{-}S\text{-}3\text{-}R\text{-}2}$[5] as in the Ni(II) complex, $[Ni(cyclam)Cl_2]$,[7] while the cis isomer is the racemic *R*,*R*,*R*,*R*,(*S*,*S*,*S*,*S*) form. This ligand configuration was found recently in the $[Co(cyclam)en]^{3+}$ cation[8] (en = 1,2-diaminoethane) and, although the structure has never been formally published, it is reported in a footnote to another paper[9] that the *cis*-dichloro complex does indeed have the predicted structure. Although it is unlikely that the above *RSSR* form of the ligand can be folded without excessive strain to form the cis complex, the *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) form of the ligand, despite remarks we have made to the contrary,[10] can be unfolded to give a somewhat strained trans complex which can retain the gauche conformations of the five-membered rings but which requires the six-membered rings to be skew (Figure 1). Some 4 years ago, Cragel and Douglas[11] prepared an optically active isomer of *trans*-$[Co(cyclam)Cl_2]^+$ by the action of methanolic hydrogen chloride on [Co(*R*,*R*,*R*,*R*-cyclam)($C_2O_4$)]$^+$ and they thought that the ligand might retain the *R*,*R*,*R*,*R* configuration throughout the reaction. The species was reported to be very labile, and our attempts to make it from racemic [Co(*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*)-cyclam)($C_2O_4$)]Cl were unsuccessful, yielding only the *cis*-dichloro species. Recently we found that the new isomer could be otained as a by-product in the preparation of *cis*-$[Co(cyclam)Cl_2]Cl$ from $[Co(cyclam)(CO_3)]Cl$, but only in small yield and always in the presence of small quantities of the *trans*-[Co(*R*,*S*,*S*,*R*-cyclam)$Cl_2$]$^+$ species. We now report a method in which the labile *trans*-dichloro complex is prepared directly from *cis*-[Co(*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*)-cyclam)$Cl_2$]Cl under conditions that retain the configurations of the nitrogens and we also report the kinetics and steric course of the aquation. Busch et al. have recently described a series of dichloro complexes of cobalt(III) with macrocyclic tetraamines of various ring sizes[12] and in one case they report two configurational trans isomers. The aquation kinetics of these species have also been reported.[13]

## Experimental Section

**Preparation.** ***trans*-Dichloro[(*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*))-1,4,8,11-tetraazaclotetradecane]cobalt(III) Perchlorate.** *cis*-$[Co(cyclam)Cl_2]Cl$ (1.9 g), prepared by the method of Poon and Tobe,[3] was added in small portions to 500 $cm^3$ of boiling absolute ethanolic hydrochloric acid (1 M) over a period of 1.5 h. After adding each portion it was advisable to wait until the color of the solution had changed from violet

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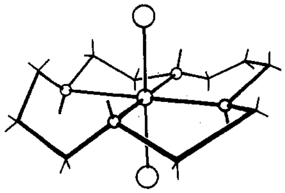

**Figure 1.** The *trans*-[Co(*R*,*R*,*R*,*R*-cyclam)$Cl_2$]$^+$ cation. Predicted structure showing the sequence of skew six-membered rings and gauche five-membered rings.

to blue-green before the next portion was added. The solution was left to reflux for 1 h more and then left to cool overnight. The unreacted violet *cis*-dichloro complex (1.2 g) was filtered off and the green filtrate was evaporated to 70 $cm^3$ in a rotary evaporator at reduced pressure, filtered, cooled, and treated with perchloric acid (4 $cm^3$, 60%). Although we have done this reaction many times and have no problems, the introduction of concentrated perchloric acid into organic solvents is a potentially hazardous process and should be treated with respect. Likewise, the perchlorate salts of these amine complexes should be handled with care. The solution was set aside in the refrigerator for 3 h and the green crystalline solid was filtered off. It was extracted from the filter with three portions (50 $cm^3$) of 0.2 M hydrochloric acid at room temperature, the solution being collected and cooled to 0 °C as soon as possible. (The insoluble *cis*-[Co(cyclam)$Cl_2$]$ClO_4$ remains on the filter.) Perchloric acid (2 M, 20 $cm^3$) and 10% sodium perchlorate solution (20 $cm^3$) were added, and the solution was kept at −5 °C for 15 min. The green crystals that formed were filtered off from a colorless mother liquor and washed with dry ethanol and diethyl ether and dried in a desiccator. Yield 0.39 g. Anal. Calcd for $C_{10}H_{24}N_4Cl_3O_4Co$: C, 27.96; H, 5.63; N, 13.04; Cl, 24.76. Found: C, 28.75, H, 5.63; N, 13.01; Cl, 24.91.

**Kinetics.** The appropriate solvent mixture (dilute $HNO_3$ + $NaNO_3$, $HNO_3$ + NaCl + $NaNO_3$, or dilute HCl) was brought to the reaction temperature in a silica cell in the SP 874 constant-temperature housing of a Pye-Unicam SP 1750 spectrophotometer and the reaction was started by adding a weighed amount of complex and stirring the solution with a thin glass rod until all had dissolved. The slower reactions were followed by scanning the spectrum over the range 350–700 nm at intervals or by following the change in absorbance with time at a single wavelength (535 nm). The faster reactions were followed by the second method only. The reaction temperature was monitored by a platinum resistance thermometer placed in an adjacent cell in the same housing, the system having previously been calibrated. The $Hg^{2+}$-catalyzed reactions and the subsequent isomerizations were studied in a similar fashion.

## Results

The infrared spectrum of the new green [Co(cyclam)$Cl_2$]$ClO_4$ has a single sharp peak at 3228 $cm^{-1}$, assigned to $\nu_{N-H}$ and three characteristic peaks in the region 900–800 $cm^{-1}$ at 891 (s), 865 (m), and 776 (m) $cm^{-1}$. The *trans*-[Co(*R*,*S*,*S*,*R*-cyclam)$Cl_2$]$ClO_4$ complex has two sharp peaks at 3228 and 3211 $cm^{-1}$ (the chloride has only a broadish single peak in this region[14]) and three equally sharp peaks at 905, 892, and 821 $cm^{-1}$, which are also observed in the chloride.[14] The absence of peaks at 3148 $cm^{-1}$ (characteristic of the *cis*-dichloro perchlorate) and 821 $cm^{-1}$ (characteristic of the trans *R*,*S*,*S*,*R* species) is an excellent criterion of purity. The $^1H$ NMR spectrum of a freshly prepared solution of the new complex in dimethyl sulfoxide has a single, typically broad, amine proton signal at $\tau$ 3.90 (cf. $\tau$ 3.68 for the *trans*-(*R*,*S*,*S*,*R*)-dichloro species). The spectrum of a freshly prepared solution of the labile green isomer in 0.10 M HCl has peaks at 634 (50) and 428 (56) (wavelength in nm; molar extinction coefficients in $cm^{-1}$ $M^{-1}$ in parentheses; cf. 633 (30) and 432 (42) for the trans *R*,*S*,*S*,*R* species[15]). Provided the solution is sufficiently acidic (>0.10 M $HNO_3$) and excess chloride is present (>0.10M), the spectrum changes, with excellent isosbestic points at 607 (39), 466 (29), 426 (55), and 364 (ca. 130) nm, to one with peaks at 537 (117) and 386 (130) nm, which closely resembles that of the initial product of the aquation of *cis*-[Co(*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*)-cyclam)$Cl_2$]$^+$ and which is typical of a *cis*-chloroaquotetraaminecobalt(III) complex. The subsequent changes are exactly the same as those previously reported for this species.[3] There is a slow reversible loss of the second chloride to give *cis*-[Co(cyclam)$(H_2O)_2$]$^{3+}$ and, at higher pH, the isomerization of *cis*-[Co(cyclam)$ClH_2O$]$^{2+}$ to a mixture of *trans*-[Co(cyclam)$Cl_2$]$^+$ and *trans*-[Co(cyclam)$ClH_2O$]$^{2+}$, with the ligand in the *R*,*S*,*S*,*R* configuration, dominates the reaction. This isomerization is retarded by chloride and has an inverse hydrogen ion concentration rate dependence[4] and seriously interferes with any attempt to follow the kinetics of the aquation at pH >3.

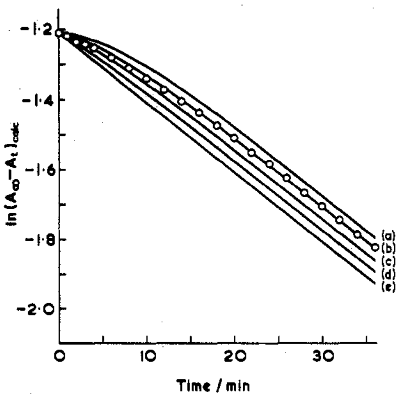

**Figure 2.** Plot of calculated values of ln ($A_\infty - A_t$) against time using $k_c + k_t = 3.32 \times 10^{-4}$ $s^{-1}$ and $k_i = 2.60 \times 10^{-3}$ $s^{-1}$ for the following values of $k_c(k_c + k_t)^{-1}$: (a) 0; (b) 0.25; (c) 0.50; (d) 0.75; (e) 1.00. The circles indicate experimental points for the reaction at 15.4 °C, $\mu$ = 0.10, [$H^+$] = 0.10 M ($HNO_3$).

**Table I.** First-Order Rate Constants for the Spontaneous Aquation of *trans*-Dichloro[(*R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*))-1,4,8,11-tetraazacyclotetradecane]cobalt(III) Perchlorate[a,b]

| Temp/°C | [$Cl^-$]/M | $10^3k_{obsd}$/$s^{-1}$ |
|---|---|---|
| 15.4 | 0.00 | 0.332[c] |
| 19.7 | 0.00 | 0.746 |
| 20.5 | 1.006[d] | 0.265 |
| 25.5 | 0.00 | 1.96 |
| 29.8 | 1.000[d] | 1.23 |
| 29.9 | 0.00 | 3.35 |
| | 0.0200 | 3.18 |
| | 0.0333 | 3.07 |
| | 0.0500 | 2.97 |
| | 0.100 | 2.60 |
| | 0.300 | 2.17 |
| | 0.900 | 1.57 |
| 35.7 | 0.00 | 7.44 |
| 39.8 | 1.000[d] | 5.10 |
| 40.2 | 0.00 | 12.3 |
| 44.9 | 0.00 | 23.2 |
| 49.8 | 1.006[d] | 16.3 |

[a] In 0.100 M nitric acid, except where stated. [b] $\mu$ = 1.00 ($NaNO_3$). [c] $\mu$ = 0.100. [d] In 1 M hydrochloric acid.

The rate constants for aquation were determined from the change in absorbance at 535 nm where the absorbance change is maximum. The plot of ln ($A_\infty - A_t$) against time is linear for more than 3 half-lives if a sufficient excess of chloride is present but, in the absence of added chloride, there is a clearly defined induction period at the earliest stages of the reaction (Figure 2). The first-order rate constants (the negative slopes of the linear portion of the semilog plot) are sensitive to the concentration of chloride present and independent of the hydrogen ion concentration. These constants are collected in Table I. Parallel studies monitoring the release of chloride with a silver|silver chloride electrode and a mercurous sulfate reference electrode showed that the spectrophotometric change was due to the displacement of one of the coordinated chlorides from the complex.

**Table II.** First-Order Rate Constants for the Isomerization of *trans*-Chloroaquo[(*R,R,R,R*(*S,S,S,S*))-1,4,8,11-tetraazacyclotetradecane]cobalt(III) Cations[c]

| Temp/°C | $[Hg^{2+}]$/M | $10^3 k_i/s^{-1}$ |
|---|---|---|
| 11.0 | 0.0100 | 1.21 |
| | 0.0200 | 1.39 |
| 17.7 | 0.0100 | 3.66 |
| | 0.0200 | 4.35 |
| 23.5 | 0.0100 | 8.93 |
| | 0.0200 | 11.1 |
| 29.8 | 0.0100 | 19.6 |
| | 0.0200 | 24.8 |
| | 0.0300 | 24.7 |
| | 0.0400 | 26.7 |

[a] $[H^+] = 0.11$-$0.14$ M. [b] $\mu = 1.03$-$1.12$ ($NaNO_3$). [c] [Complex] = $1.2 \times 10^{-3}$ to $3.0 \times 10^{-3}$ M.

In the presence of $Hg(NO_3)_2$ a similar green to purple change is observed but there are significant differences. Spectrophotometric analysis indicates at least three subsequent processes. The first, which was too fast to follow by the techniques used, corresponds to a shift of the long-wavelength peak to shorter wavelengths (ca. 610 nm) without any significant increase in the absorbance. This change closely resembles that observed in the aquation of the *trans*-$[Co(R,S,S,R\text{-cyclam})Cl_2]^+$ cation, and the low absorbance at 535 nm ($\epsilon$ 6.0 $cm^{-1}$ $M^{-1}$) at a wavelength where the *cis*-chloroaquo species has a molar extinction coefficient of 117 $cm^{-1}$ $M^{-1}$ indicates that the first stage is the $Hg^{2+}$ ion catalyzed aquation of the *trans*-dichloro species to form only the *trans*-chloroaquo isomer. The second stage of the reaction is characterized by a large increase in the absorbance in the region 500–550 nm, with isosbestic points at 594, 452, and 414 nm, and corresponds to the isomerization of the *trans*-chloroaquo species to the cis form. The third stage of the reaction intervenes before the second stage is complete and corresponds to a shift in the peak to 508 nm. This stage is $[Hg^{2+}]$ dependent and is the catalyzed displacement of the chloride from *cis*-$[Co(cyclam)ClH_2O]^{2+}$ to give the *cis*-diaquo product. In none of these reactions is there any change in the configuration of the coordinated nitrogens.

The kinetics of the isomerization were studied at 535 nm where the third stage has an isosbestic point. The plots of ln $(A_\infty - A_t)$ vs. time are linear provided there is a sufficient excess of $[Hg^{2+}]$. Extrapolation to zero time gives $\epsilon_0$ 6.0 $cm^{-1}$ $M^{-1}$. The first-order rate constants are collected in Table II where it will be seen that for $[Hg^{2+}] \geq 0.02$ M ([complex] = $(1-2) \times 10^{-3}$ M) the rate constants are independent of mercuric ion concentration. It is not completely clear why the rate constant is not completely independent of $[Hg^{2+}]$ at the lower concentrations. Using the rate constants for $[Hg^{2+}] = 0.020$ M, $\mu = 1.04$, $[H^+] = 0.12$ M, $\Delta H^{\ddagger} = 25.8 \pm 0.9$ kcal $mol^{-1}$, and $\Delta S^{\ddagger} = 19.3 \pm 3.1$ cal $K^{-1}$ $mol^{-1}$.

## Discussion

The new, labile isomer of $[Co(cyclam)Cl_2]^+$ is clearly a trans species and its preparation from the *cis*-dichloro cation under strongly acidic conditions would indicate that the two species have the same ligand configuration; i.e., this is the racemic *trans*-$[Co(R,R,R,R(S,S,S,S)\text{-cyclam})Cl_2]^+$ isomer, as was suggested by Cragel and Douglas.[11] The aquation, under sufficiently acidic conditions to prevent nitrogen proton exchange and inversion of configuration yields the same chloroaquo species as the cis-$[Co(R,R,R,R(S,S,S,S)\text{-cyclam})Cl_2]^+$ cation. However, a careful spectrophotometric analysis of the absorbance changes at the earliest stages of the reaction (0.100 M $HNO_3$, no added chloride) at 15.4 °C shows that some *trans*-chloroaquo isomer is formed initially. In Figure 2 the experimental data, plotted as ln $(A_\infty - A_t)$ against time, are compared with similar plots calculated for 0, 25, 50, 75, and 100% initial *cis*-chloroaquo product ($k_{aquation} = 3.32 \times 10^{-4}$ $s^{-1}$; $k_{isom} = 2.60 \times 10^{-3}$ $s^{-1}$) using the equation in ref 16. It will be seen that the results indicate that some 25–30% *cis*-chloroaquo complex is formed initially while the rest is obtained from the isomerization of the *trans*-chloroaquo species. This aquation therefore resembles that of *trans*-$[Co(en)_2Cl_2]^+$,[17] *trans*-$[Co(R,R(S,S)\text{-2,3,2-tet})Cl_2]^+$ [16] (2,3,2-tet = 1,9-diamino-3,7-diazanonane) and *trans*-$[Co(S,S\text{-trien})Cl_2]$ [18] (trien = 1,8-diamino-3,6-diazaoctane) (Table III) where the aquation takes place with stereochemical change and has a reasonably large positive entropy of activation.[19] The *trans*-dichloro-(*R,S,S,R*)- and *trans*-dichloro-(*R,R,R,R*(*S,S,S,S*))-cyclamcobalt(III) complexes provide a second example of a pair of isomers, differing in the configurations of the secondary nitrogens, in which one reacts with complete retention of configuration and a low entropy of activation while the other reacts with steric change and a high entropy of activation.

The retardation of the aquation by chloride can be accounted for by the reversible anation of the *trans*-chloroaquo species in competition with its isomerization.

$$trans\text{-}[Co(cyclam)Cl_2]^+ \xrightarrow{k_c} cis\text{-}[Co(cyclam)ClH_2O]^{2+} + Cl^- \qquad (1)$$

$$trans\text{-}[Co(cyclam)Cl_2] \underset{k_{-t}}{\overset{k_t}{\rightleftharpoons}} trans\text{-}[Co(cyclam)ClH_2O]^{2+} + Cl^- \qquad (2)$$

$$trans\text{-}[Co(cyclam)ClH_2O]^{2+} \xrightarrow{k_i} cis\text{-}[Co(cyclam)ClH_2O]^{2+} \qquad (3)$$

**Table III.** First-Order Rate Constants, Steric Courses, and Activation Parameters for the Aquation of Some $[Co(L_4)Cl_2]^+$ Cations

| $L_4$[b] | Isomeric form | $10^4 k_{aq}/s^{-1}$ at 25 °C | $\Delta H^{\ddagger}$/kcal $mol^{-1}$ | $\Delta S^{\ddagger}$/cal $K^{-1}$ $mol^{-1}$ | % steric change | % steric change[c] | Ref |
|---|---|---|---|---|---|---|---|
| $(en)_2$ | Cis | 2.44 | 21.5 | −5 | 0 | 30 | 17, 20 |
| $(en)_2$ | Trans | 0.353 | 26.4 | +14 | 35 | 30 | 17, 20 |
| cyclam | Trans *R,S,S,R* | 0.011 | 24.6 | −3 | 0 | 0 | 2 |
| cyclam | Trans *R,R,R,R* | 17.5 | 24.2 | +10 | 25 | 0 | This work |
| cyclam | Cis *R,R,R,R* | 160 | 18.3 | −6 | 0 | 0 | 3 |
| 2,3,2-tet | Trans *R,R* | 2.9 | 25.9 | +12 | 50 ± 20 | 70 | 16 |
| 2,3,2-tet | Trans *R,S* | 0.15 | 24.3 | +1 | 0 | 0 | 16 |
| 2,3,2-tet | β-Cis *R,R* | 11 | 22.3 | +2 | 0 | 0 | 16 |
| 2,2,2-tet | Trans *S,S* | 35 | 25.5 | +16 | 100 | 0 | 18 |
| 2,2,2-tet | β-Cis *S,S* | 15 | 20.3 | −3 | 0 | 0 | 18 |
| $[13]aneN_4$ | Trans | 6.76 | 19.5 (25.6)[a] | −7 (+12.6) | 0 | | 13 |
| $[15]aneN_4$ | Trans I | 11.6 | 17.3 (19.6) | −14 (−7.4) | 0 | | 13 |
| $[15]aneN_4$ | Trans II | 99.2 | 14.7 (15.8) | −18 (−14.5) | 0 | | 13 |
| $[16]aneN_4$ | Trans I | 25 700 | | | 0 | | 13 |

[a] The values quoted are from a linear least-squares fit of the ln $(k/T)$ vs. $T^{-1}$ plots. The published values are in parentheses. [b] Key: en = 1,2-diaminoethane, cyclam = 1,4,8,11-tetraazacyclotetradecane, 2,3,2-tet = 1,9-diamino-3,7-diazanonane, 2,2,2-tet = 1,8-diamino-3,6-diazaoctane, $[13]aneN_4$ = 1,4,7,11-tetraazacyclotridecane, $[15]aneN_4$ = 1,4,8,12-tetraazacyclopentadecane, $[16]aneN_4$ = 1,5,9,13-tetraazacyclohexadecane. [c] Percent steric change for $Hg^{2+}$-catalyzed aquation.

Provided the concentration of the *trans*-chloroaquo complex remains small and obeys stationary-state conditions, the rate law takes the form

$$\ln (A_\infty - A_t) = -k_{\text{obsd}} t + c$$

and

$$k_{\text{obsd}} = \frac{k_t k_i}{k_{-t}[\text{Cl}^-] + k_i} + k_c$$

As $[\text{Cl}^-] \rightarrow 0$, $k_{\text{obsd}} \rightarrow k_t + k_c \equiv k_{\text{obsd}}(\text{lim})$. Therefore

$$k_{\text{obsd}}(\text{lim}) - k_{\text{obsd}} = k_t + k_c - \frac{k_t k_i}{k_{-t}[\text{Cl}^-] + k_i} - k_c = \frac{k_t k_{-t}[\text{Cl}^-]}{k_{-t}[\text{Cl}^-] + k_i}$$

and

$$(k_{\text{obsd}}(\text{lim}) - k_{\text{obsd}})^{-1} = k_t^{-1}(k_i/k_{-t})[\text{Cl}^-]^{-1} + k_t^{-1}$$

Therefore, a plot of $[k_{\text{obsd}}(\text{lim}) - k_{\text{obsd}}]^{-1}$ against $[\text{Cl}^-]^{-1}$ should be a straight line with slope $= k_t^{-1}(k_i/k_{-t})$ and intercept $k_t^{-1}$. This relationship is found to hold very well indeed and analysis of the data in Table I for the reactions at 29.9 °C gives a straight line of slope $(1.086 \pm 0.026) \times 10^2$ M s and intercept $= 399 \pm 66$ s. ($k_{\text{obsd}}(\text{lim}) = 3.35 \times 10^{-3}\ \text{s}^{-1}$.) It follows, therefore, that $k_t = 2.51 \times 10^{-3}\ \text{s}^{-1}$, $k_c = 0.84 \times 10^{-3}\ \text{s}^{-1}$, and $k_i/k_{-t} = 0.272$ M. The values of $k_c$ and $k_t$ tell us that *trans*-$[\text{Co}(R,R,R,R(S,S,S,S)\text{-cyclam})\text{Cl}_2]^+$ aquates to form 25% *cis*-chloroaquo product and 75% *trans*-chloroaquo product. This agrees well with the less precise value obtained from the spectrophotometric analysis in the absence of chloride. Independent studies of the product of the $[\text{Hg}^{2+}]$ catalyzed aquation give $k_i = 2.5 \times 10^{-2}\ \text{s}^{-1}$ at 29.9 °C, so that $k_{-t} = 9.2 \times 10^{-2}\ \text{M}^{-1}\ \text{s}^{-1}$. It is therefore possible to calculate the equilibrium constant for the stereoretentive solvolysis of the *trans*-dichloro complex, $K = k_t/k_{-t} = 2.7 \times 10^{-2}$ M. This equilibrium can be studied directly and without interference from subsequent change in the case of the *R,S,S,R* isomer and is found to be $7.8 \times 10^{-3}$ M at 60 °C.[2] The increased lability of the *R,R,R,R*(*S,S,S,S*) dichloro complex is not matched by its much smaller decrease in stability with respect to solvolysis. This explanation of the chloride retardation is also supported by the observation that the addition of a large excess of chloride to the immediate product of the reaction of the dichloro complex with mercuric nitrate slows down the rate of formation of the *cis*-chloroaquo species to the point where it approaches the rate of aquation of the *trans*-dichloro species. It has already been shown that the *cis*-chloroaquo species cannot anate back to the *cis*- or *trans*-dichloro species in the presence of high concentrations of chloride.[3] It is possible to obtain an identical rate law from a *D* mechanism in which the five-coordinate intermediate is trapped either by water to give aquochloro species or by chloride to give the starting material or else the much more labile *cis*-dichloro complex. While such a mechanism cannot be ruled out, we prefer the original mechanism which introduces no new mechanistic concepts and is fully consistent with the known behavior of these complexes.

The lability of the *trans*-dichloro *R,R,R,R*(*S,S,S,S*) isomer is some 1600 times greater than that of the *R,S,S,R* isomer at 25 °C but is still smaller than that of the *cis*-dichloro species with the same ligand configuration. The ratio $k_{\text{cis}}/k_{\text{trans}}$ is 9, and not greatly different from that found for the corresponding bis(ethylenediamine) isomers (6.9)[17] where conformational strain problems do not arise. Hung and Busch[13] have measured the rate constants for the aquation of a number of *trans*-dichlorotetraaminecobalt(III) complexes where "tetraamine" represents a macrocyclic quadridentate ligand like cyclam but with different ring sizes. In the case of 1,5,9,13-tetraazacyclopentadecane ([15]ane$N_4$), they have isolated two trans isomers which are identified as the

$$\begin{matrix} +3+ \\ 3\quad 3 \\ -2+ \end{matrix} \quad \text{and} \quad \begin{matrix} +3- \\ 3\quad 3 \\ -2+ \end{matrix}$$

forms (+ represents a hydrogen above the ligand plane and – one below it when the nitrogens are coordinated in a coplanar fashion). These differ in reactivity by a factor of less than 10. The latter, and more reactive, species is structurally similar to the labile trans *R,R,R,R*(*S,S,S,S*)-cyclam complex

$$\left(\begin{matrix} +2- \\ 3\quad 3 \\ -2+ \end{matrix}\right)$$

the less reactive *R,S,S,R*-cyclam complex can be represented as[21]

$$\begin{matrix} +2- \\ 3\quad 3 \\ +2- \end{matrix}$$

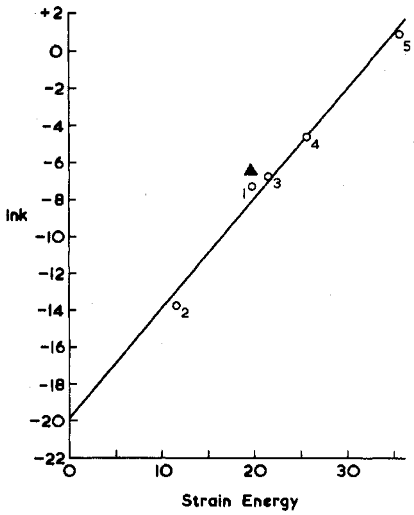

**Figure 3.** ln *k* for the aquation of *trans*-$[\text{Co}(\text{L}_4)\text{Cl}_2]^+$ plotted against the conformational strain energy in the macrocycle, $\text{L}_4$. Circles are data from ref 13 for varying $\text{L}_4$: 1, [13]ane$N_4$; 2, [14]ane$N_4$ (I) or *R,S,S,R*-cyclam; 3, [15]ane$N_4$ (I); 4, [15]ane$N_4$ (II); 5, [16]ane$N_4$ (I). ▲ indicates the value for *R,R,R,R*(*S,S,S,S*)-cyclam (or [14]ane$N_4$ (II)) using conformational strain energy from ref 12.

They have shown that there is a good linear correlation between ln *k* for aquation at 25 °C and *H*, the calculated minimized conformational strain energy. Using the value of *H* which they calculate for the *R,R,R,R*(*S,S,S,S*)-cyclam arrangement (19.51 kcal $\text{mol}^{-1}$) it appears that the labile cyclam complex lies off their line and is some 6 times more reactive than predicted (Figure 3). This is not surprising and it should be pointed out that conformational strain energies can only be related to reactivity if they are significantly relieved in the transition state and if there is a parallel relationship between the ring geometry and the configurational strain in the transition state. All of the complexes studied by Busch aquate with complete retention of configuration and with negative entropies of activation[22] and presumably with square-pyramidal intermediates; the transition states should therefore be geometrically similar. The *trans*-$[\text{Co}(R,R,R,R(S,S,S,S)\text{-cyclam})\text{Cl}_2]^+$ complex is unique in this series (and among most macrocyclic complexes) in aquating with stereochemical change, presumably through a trigonal-bipyramidal intermediate, and therefore it is unlikely that the conformational strain in this transition state is the same as that expected for the transition state leading to the square pyramid. The significant observation is not that the point for this complex lies off the ln $k$ vs. strain energy plot but that it lies so close to it. It would suggest that the overall energies of the two shapes of transition state (including their conformational strain energies) are fairly similar and that secondary considerations might tip the balance. Thus, although it is perfectly possible for the *cis*- and *trans*-dichloro complexes of the *R*,*R*,*R*,*R*(*S*,*S*,*S*,*S*) form of cyclam to form a common intermediate, this does not happen and the cis complex aquates with complete retention of configuration.[3] The $Hg^{2+}$ aquation of the trans species gives no *cis*-chloroaquo product and therefore cannot generate a common intermediate with the spontaneous aquation, where some 25% of the *cis*-chloroaquo is formed. This is very similar to the behavior of *trans*-$[Co(S,S\text{-trien})Cl_2]^+$ which aquates spontaneously to give stereospecifically one of the two possible *β*-*cis*-aquochloro products, whereas the $Hg^{2+}$-catalyzed aquation takes place with complete retention of configuration. There are cases where spontaneous aquation gives retention of configuration while the $Hg^{2+}$-catalyzed process gives steric change, e.g., D-*cis*-$[Co(en)_2Cl_2]^+$ [17,20] and innumerable examples where the catalyzed and spontaneous aquations have the same steric course, within experimental error.

Provided one uses the term "dissociative" to refer to the intimate mechanism[23] and to mean that there is no significant bonding between the incoming group and the reaction center in the transition state, the absence of a common intermediate cannot be used as evidence against a dissociative mechanism. It is vital to distinguish between the transition state, in which the leaving group is still loosely bound to the reaction center, and the intermediate, where it is not. If the intermediates do not differ greatly in energy, the leaving group may stabilize a transition state that leads to one of the less stable forms of the intermediate which may then be trapped before it has a chance to change to the most stable arrangement. The distinction between a D and an $I_d$ mechanism[23] can rest upon whether or not the intermediate can live long enough to equilibrate its own solvation environment and discriminate between individual nucleophiles[24] and an $I_d$ mechanism can account for different product ratios being obtained from a trigonal-bipyramidal intermediate. However, the time that is needed for an intramolecular twist to convert a square pyramid to a trigonal bipyramid is likely to be considerably longer than that needed for the equilibration of the solvation environment. In this way one can account for the observation that *cis*-$[Co(L_4)AX]^{n+}$ species can generate a square-pyramidal intermediate while the *trans*-$[Co(L_4)AX]^{n+}$ isomer gives a trigonal bipyramid without discarding a dissociative mechanism. Indeed one might also account for the cases where the $Hg^{2+}$-catalyzed aquation gives an intermediate of different geometry to that formed in the spontaneous aquation.

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**Registry No.** *trans*-$[Co(cyclam)Cl_2]ClO_4$, 15220-75-4; *cis*-$[Co(cyclam)Cl_2]Cl$, 20792-52-3.

## References and Notes

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(21) When one compares macrocycles containing different numbers of carbon atoms, this representation, first used in ref 10, provides a more readily recognizable method of labeling the complexes than the *R*,*S* nomenclature. For example, whereas

$$\begin{array}{ccc} + & 2 & - \\ 3 & & 3 \\ - & 2 & + \end{array}$$

is the $\underline{S\text{-}3\text{-}S\text{-}2\text{-}S\text{-}3\text{-}S\text{-}2}$ form,

$$\begin{array}{ccc} + & 3 & - \\ 3 & & 3 \\ - & 2 & + \end{array}$$

must be designated as the $\underline{S\text{-}3\text{-}R\text{-}3\text{-}R\text{-}3\text{-}S\text{-}2}$ form.

(22) It has been claimed[13] that the entropy of activation for the aquation of *trans*-$[Co([13]aneN_4)Cl_2]^+$ is +12 cal $K^{-1}$ $mol^{-1}$ in spite of the complete retention of configuration. Examination of the Eyring plot of the published data indicates that the best straight line with equal weighting to all points gives $\Delta S^{\ddagger} = -7$ cal $K^{-1}$ $mol^{-1}$. If the rate constant at 45 °C is ignored, $\Delta S^{\ddagger}$ becomes +6 cal $K^{-1}$ $mol^{-1}$. Clearly the data are insufficiently precise to be used in any argument concerning the relationship between the entropy of activation and the shape of the transition state.

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