chelation. Reactions of ethylenediamine with metal ions in water generally have positive entropy changes because of the additional release of water that was initially hydrogen bonded to the ligand. Thus, our interpretation of these results indicates the importance of ligand solvation as well as metal ion solvation.

The effect of ligand solvation on metal ion complex stability constants should be very important in biological systems where donor groups are frequently forced to be close to one another or in some way are shielded from solvation. In this respect the terminology suggested by Busch[58] of *multiple juxtapositional fixedness* is an appropriate description. As with the macrocyclic effect the cause of enhanced metal binding is a combination of more favorable enthalpy terms from diminished solvation of donor groups and smaller loss of ligand configurational entropy. It is important to keep in mind that the magnitude of metal binding constants to larger molecules could be increased by many orders of magnitude due to these factors as well as the possibility that steric hindrance might have just the opposite effect.

The hydrophobic effect[59] is another aspect of ligand solvation which could be important in determining the stability constants of complexes. However, this effect should not increase the stability of a macrocyclic ligand over an open-chain ligand. In the case of the polyamines, differences in the extent of hydrogen bonding of water to the nitrogen atoms appear to be the dominant ligand-solvation effect.

Finally, if ligand solvation is important in the thermodynamics of metal complexation, then it should also be important in the kinetics of metal complexation, but once again very little attention has been directed to this effect.

Acknowledgment. This work was supported by National Science Foundation Grant GP 14781X.

Registry No. [14]ane$N_4Ni^{II}(ClO_4)_2$, 38643-78-6; C(5,12)-*ms*-Me_2[14]ane$N_4Ni^{II}(ClO_4)_2$, 52610-58-9; C(5,12)-*rac*-Me_6[14]aneN_4-$Ni^{II}(ClO_4)_2$, 52553-45-4; C(5,12)-*ms*-Me_6[14]ane$N_4Ni^{II}(ClO_4)_2$, 25504-25-0; 2,3,2-tet$Ni^{II}(ClO_4)_2$, 27537-50-4.

(58) D. H. Busch, K. Farmery, V. Goedken, V. Katovic, A. C. Melnyk, C. R. Sperati, and N. Tokel, *Advan. Chem. Ser.*, No. **100**, 52 (1971).

(59) C. Tanford, "The Hydrophobic Effect: Formation of Micelles and Biological Membranes," Wiley-Interscience, New York, N. Y., 1973, p 21.

Contribution from the Department of Chemistry,
University of Canterbury, Christchurch, New Zealand

Kinetics and Steric Course of the Acid Hydrolysis of *trans*-(Ammine)(diethylenetriamine)(dichloro)cobalt(III) Cation

M. CLAIRE COULDWELL and D. A. HOUSE*

Received May 2, 1974 AIC40286V

Solutions of the title cation, when treated with excess OH^- and then acidified, form the *trans*-diaqua ion. This slowly ($t_{1/2}$ = *ca.* 30 min at 25.0°) isomerizes to an isomeric diaqua ion which we believe is the *a*-ammine-*bc*-diaqua-*dfe*-(diethylenetriamine)cobalt(III) cation, with the diethylenetriamine in the facial configuration (henceforth designated cis). The final products in the uncatalyzed acid hydrolysis of the *trans*-dichloro ion are an equilibrium *cis*-diaqua–*cis*-aquachloro mixture. The rate of acid hydrolysis of the *trans*-dichloro ion has been measured both spectrophotometrically and by chloride release. In 0.3 *F* HNO_3 at 25.0°, the first-order rate constants for the primary hydrolysis are 10^5k_{spectro} ($\sec^{-1}$) = 39.8 ± 0.3 and 10^5k_{Cl} ($\sec^{-1}$) = 52.1 ± 0.8. These data have been interpreted in terms of a mechanism whereby the *trans*-dichloro cation hydrolyzes in acid solution to produce three five-coordinate intermediates. Aquachloro products from two of these have been detected spectrophotometrically in solution (as an 80:20 isomeric mixture) and the slower reacting major component has the above cis configuration. The other aquachloro ion isomerizes rapidly ($t_{1/2}$ = *ca.* 9 min at 25.0°) to the *cis*-aquachloro form and is assigned a *trans*-aquachloro configuration with the secondary NH proton of the meridional diethylenetriamine ligand adjacent to the aqua ligand. It is estimated that 50 ± 10% of the *cis*-aquachloro is formed directly from the *trans*-dichloro complex. The rate of acid hydrolysis of the *cis*-aquachloro isomer has been measured by chloride release and in 1.0 *F* HNO_3 at 25.0°: 10^5k_{Cl} ($\sec^{-1}$) = 7.89 ± 0.28, E_a (kJ mol^{-1}) = 96.3 ± 2.1, $\Delta S°_{298}$ (J K^{-1} mol^{-1}) = −8.4 ± 4.2, log *PZ* ($\sec^{-1}$) = 12.75. The *cis*-aquachloro–*cis*-diaqua equilibrium lies substantially (90%) toward the diaqua product.

Introduction

Recent studies[1] of the rate and steric course of the acid hydrolysis of tetraaminedichlorocobalt(III) complexes have been concentrated on systems containing linear[2-5] or macrocyclic[6-8] polyamines. In particular, in the primary hydrolysis of *trans*-$CoCl_2(N_4)^+$ complexes,[9] with N_4 = trien = 2,2,2-tet,[3] 2,3,2-tet,[4] and 3,2,3-tet,[5] there is 0%, *ca.* 50% (meso isomer), and 100% retention of configuration, respectively. However, with N_4 = cyclam = 2,3,2,3-tet[6] and Me_6-2,3,2,3-tet,[7,8] the trans configuration is retained in the aquachloro product.

To provide further insight into these processes, we have investigated the rate of acid hydrolysis and the steric course in the aquation of *trans-af,b,cde*-$CoCl_2(NH_3)(dien)^+$.[10]

Experimental Section

Commercially available diethylenetriamine was used without

(1) C. K. Poon, *Inorg. Chim. Acta, Rev.*, 123 (1970).

(2) A. M. Sargeson and G. H. Searle, *Nature (London)*, 200, 356 (1963).

(3) A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 2172 (1967).

(4) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, 8, 1589 (1969).

(5) M. D. Alexander and H. G. Hamilton, *Inorg. Chem.*, 8, 2131 (1969).

(6) C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967).

(7) J. A. Kernohan and J. F. Endicott, *Inorg. Chem.*, 9, 1504 (1970).

(8) W. K. Chau and C. K. Poon, *J. Chem. Soc. A*, 3087 (1971).

(9) Abbreviations used: en = $NH_2(CH_2)_2NH_2$, tmd = $NH_2(CH_2)_3$-NH_2, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, trien = $NH_2(CH_2)_2NH(CH_2)_2$-$NH(CH_2)_2NH_2$, 2,3,2-tet = $NH_2(CH_2)_2NH(CH_2)_3NH(CH_2)_2NH_2$, 3,2,-3-tet = $NH_2(CH_2)_3NH(CH_2)_2NH(CH_2)_3NH_2$, cyclam = 1,4,8,11-tetraazacyclotetradecane = 2,3,2,3-tet, Me_6-2,3,2,3-tet = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, ox = $C_2O_4^{2-}$.

further purification. All other chemicals were reagent grade quality. The ion-exchange material used was Zeo-Karb 225, SRC-6 cation-exchange resin in the Na^+ form (52–100 mesh). The dichloro cation was isolated using a 6 × 1 cm column cooled by a jacket of circulating ice water, and all other cations were isolated using a 10 × 1 cm ice-jacketed column. The preparation and analyses of cationic complexes were repeated at least three times to check the reproducibility of the ion-exchange separations and the visible absorption spectral parameters.

Caution! Although we have experienced no difficulties with the perchlorate salt of the complex mentioned herein, this complex should be treated as potentially explosive and handled with care.

***trans*-(Ammine)dichloro(diethylenetriamine)cobalt(III) Perchlorate.**[11] Trinitro(diethylenetriamine)cobalt(III)[12] was converted to $CoCl(NO_2)_2$(dien) by the literature method,[12] and from this, *trans*(?)-[$Co(NO_2)_2(NH_3)$(dien)]Cl was prepared using a modification of the method of Crayton and Mattern.[12] A suspension of CoCl-$(NO_2)_2$(dien) (79 g) in water (400 ml) containing concentrated ammonia solution (100 ml, density 0.880 g cm^3) was evaporated to *ca.* 200 ml on a steam bath. The solution was allowed to cool overnight and the crystalline product was collected by filtration, washed with ethanol and ether, and air-dried. The mother liquors were evaporated to half-volume to obtain a second crop. The total yield was 33.7 g (41%). A suspension of *trans*(?)-[$Co(NO_2)_2(NH_3)$(dien)]-Cl (13.2 g) in HCl (200 ml, 12 *F*) was heated at boiling temperature for 15 min and then transferred to a steam bath. Perchloric acid (40 ml, 60%) was added and green crystals of the desired product were deposited. Steam bath heating was maintained for a further 15 min and the product (7.5 g, 60% yield) was collected by filtration from the ice-cooled solution. The material was recrystallized by dissolving in the minimum volume of 40° 0.1 *F* NaOH solution, filtering if necessary, and adding 3:1 12 *F* HCl–60% $HClO_4$ solution. The green product was collected from the ice-cooled solution, washed with 2-propanol and then ether, and air-dried. *Anal.* Calcd for [$CoCl_2$-(NH_3)(dien)]ClO_4: C, 13.74; H, 4.62; N, 16.03; Co, 16.86; ligand Cl, 20.28. Found: C, 14.17; H, 4.67; N, 16.09; Co, 16.55; ligand Cl, 19.70.

The *trans*-(Ammine)dichloro(diethylenetriamine)cobalt(III) Cation. The green *trans*-$CoCl_2(NH_3)(dien)^+$ cation was isolated by suspending *ca.* 100 mg of *trans*-[$CoCl_2(NH_3)$(dien)]ClO_4 in 0.025 *F* $HClO_4$ (30 ml). The unreacted solid was filtered from the solution which dripped directly onto the top of an ion-exchange column and was prewashed with 1.0 *F* and then 0.025 *F* HNO_3. The green band that formed at the top of the resin column was washed with 30 ml of 0.1 *F* HNO_3 and the green dichloro cation was then eluted with 50 ml of 0.3 *F* HNO_3 into an ice-cooled flask. The absorption spectrum was recorded immediately and analyses of solutions prepared in this manner (*ca.* 2 m*F* in complex) gave Co:NH_3:Cl ratios of 1:0.99 ± 0.04:2.07 ± 0.07 (10),[13] in acceptable agreement with the formula $CoCl_2(NH_3)(dien)^+$.

The *cis*- Plus *trans*-(Ammine)aqachloro(diethylenetriamine)cobalt(III) Cation Mixture. The pink *cis*- plus *trans*-$CoCl(NH_3)$(dien)-$(OH_2)^{2+}$ cation mixture was isolated by allowing *ca.* 120 mg of *trans*-[$CoCl_2(NH_3)$(dien)]ClO_4 to hydrolyze in 50 ml of 0.1 *F* HNO_3 for 6 hr at 13.5°. The solution was then adsorbed on an ion-exchange column which had been prewashed with 2 *F* and then 0.1 *F* HNO_3. The pink band was washed with 30 ml of 0.6 *F* and 20 ml of 0.8 *F* HNO_3, and the cation mixture was eluted with 50 ml of 1.0 *F* HNO_3. Absorption spectral parameters were measured immediately and analysis of the solutions (*ca.* 2 m*F* in complex) gave Co:NH_3:Cl ratios of 1:1.01 ± 0.03:1.03 ± 0.03 (8)[13] in agreement with the formula $CoCl(NH_3)(dien)(OH_2)^{2+}$. When this aquachloro mixture was left at room temperature until no further change in the absorption spectrum was observed (*ca.* 24 hr), an equilibrium *cis*-diaqua–*cis*-aquachloro mixture was obtained. Analysis of this equilibrium solution for total cobalt and free chloride ion showed that it contained about 90% diaqua ion.

The *trans*-(Ammine)(diaqua)(diethylenetriamine)cobalt(III) Cation. The yellow-orange *trans*-$Co(NH_3)(dien)(OH_2)_2{}^{3+}$ cation was generated by dissolving an accurately weighed amount of *trans*-[Co-$Cl_2(NH_3)$(dien)]ClO_4 in *ca.* 25 ml of 0.5 *F* NaOH solution and, after 3–4 min at room temperature, making up to 50 ml with 1 *F* HNO_3.

The same complex was formed by taking *ca.* 100 mg of *trans*-[$CoCl_2(NH_3)$(dien)]ClO_4 in 30 ml of 0.025 *F* HNO_3 and filtering the unreacted solid from the solution which dripped directly onto the top of an ion-exchange column (prewashed with 2 *F* and then 0.025 *F* HNO_3). The green band was washed with 30 ml of water and 30 ml of 0.1 *F* NaOH and then was eluted with 40 ml of 0.1 *F* NaOH into an ice-cooled 50-ml flask containing 10 ml of 1.0 *F* HNO_3. Both methods gave absorption spectra which were identical in the position of maxima and minima and molar absorbancy indices. Analyses of the effluent solutions (*ca.* 2 m*F* in complex) from the ion-exchange column, gave Co:NH_3 ratios of 1:1.00 ± 0.01 (6)[13] in agreement with the formula $Co(NH_3)(dien)(OH_2)_2{}^{3+}$.

The *cis*-(Ammine)diaqua(diethylenetriamine)cobalt(III) Cation. The orange-pink *cis*-$Co(NH_3)(dien)(OH_2)_2{}^{3+}$ cation was isolated in solution by dissolving *ca.* 150 mg of *trans*- [$CoCl_2(NH_3)$(dien)]ClO_4 in 50 ml of 0.3 *F* HNO_3 and leaving the solution at room temperature for 2 days. The solution was adsorbed on an ion-exchange column that had been prewashed with 2 *F* and then 0.3 *F* HNO_3. The resulting orange band was washed with 30 ml of 0.6 *F*, 50 ml of 0.8 *F*, and 30 ml of 1.0 *F* HNO_3 and then was eluted with 1.5 *F* HNO_3, the first 20 ml being discarded. The absorption spectrum was recorded immediately, and until no further change was observed (*ca.* 1 day). This latter spectrum could be interpreted in terms of a cis ⇌ trans equilibrium $Co(NH_3)(dien)(OH_2)_2{}^{3+}$ mixture containing 83 ± 4% *cis*-diaqua complex.

The *cis*-diaqua cation was also obtained by dissolving *ca.* 150 mg of *trans*-[$CoCl_2(NH_3)$(dien)]ClO_4 and 500 mg of mercuric acetate in 50 ml of 0.6 *F* HNO_3 and leaving the solution at room temperature in the dark for 1 day. The solution was then adsorbed on an ion-exchange column which had been prewashed with 2 *F* and then 0.6 *F* HNO_3. The orange band that formed was washed with 80 ml of 0.6 *F*, 100 ml of 0.8 *F*, and 50 ml of 1.0 *F* HNO_3, and the desired complex was eluted with 50 ml of 1.0 *F* HNO_3. Analyses of solutions prepared in the above manner (*ca.* 2 m*F* in complex) gave Co:NH_3 ratios of 1:1.02 ± 0.03 (12)[13] in acceptable agreement with the formula $Co(NH_3)(dien)(OH_2)_2{}^{3+}$.

Kinetic Measurements. For all hydrolysis studies, the cations were chromatographically isolated by elution from ion-exchange resins with HNO_3. These solutions were allowed to react at the appropriate temperature in glass-stoppered flasks which were wrapped in Al foil to exclude light. The titrimetric and spectrophotometric procedures followed were the same as those described previously.[14,15] To check the reliability of the chloride release data, the titrations were also carried out in a system where the free chloride ions were separated from the reaction mixture. Each 5-ml aliquot from a kinetic run at 13.6° was adsorbed on a 3 × 1 cm ice-cooled cation-exchange column which had been prewashed with 2 *F* and then 0.3 *F* HNO_3. The band was washed with distilled water to remove the free chloride ions and the combined effluent was titrated for halide ion in the normal manner.[14,15]

Chemical Analyses. Co and Cl were analyzed using the methods described previously.[15] NH_3 was determined using a micro Kjeldahl apparatus. The complex was decomposed with hot NaOH solution, and the liberated ammonia was steam distilled into 2% boric acid and titrated with standard HCl.[16] Diethylenetriamine was not distilled under the conditions used. Professor A. D. Campbell's laboratory at the University of Otago, Dunedin, New Zealand, performed the C, H, and N analyses of the solid complex. All spectrophotometric measurements were made with a Beckman DBG recording spectrophotometer.

---

(10) The nomenclature used is that recommended by the Commission on the Nomenclature of Inorganic Chemistry, *Pure Appl. Chem.*, 28, 1 (1971). The prefixed lower case letters refer to the position of the donor atoms in the octahedron (*a* and *f* in the axial positions) in the order which these are written in the cation name. The convention adopted here is that the polyamine ligands are coordinated stepwise from one end and in the order of the alphabetical letters. Unfortunately, this system gives rise to similar geometric isomers having different letter designations, due to changes in the alphabetical order of the ligands. Thus *a*-ammine-*bfc*-(diethylenetriamine)-*de*-(oxalato)cobalt(III), *a*-ammine-*b*-aqua-*c*-chloro-*dfe*-(diethylenetriamine)cobalt(III), and *a*-ammine-*bc*-diaqua-*dfe*-(diethylenetriamine)cobalt(III) all have the same geometry, *i.e.*, facial dien with the NH_3 trans to the secondary NH group. To avoid this confusion, the above configuration will be designated cis.

(11) During the course of this investigation, A. V. Ablov and E. V. Popa, *Russ. J. Inorg. Chem.*, 16, 1615 (1971); 17, 388 (1972), described the preparation of the chloride salt of this complex by essentially the same method.

(12) P. H. Crayton and J. A. Mattern, *J. Inorg. Nucl. Chem.*, 13, 248 (1960).

(13) The numbers quoted are the mean ± the standard deviation. The number in parentheses is the number of determinations.

(14) M. C. Couldwell and D. A. House, *Inorg. Chem.*, 11, 2024 (1972).

(15) M. C. Couldwell, D. A. House, and H. K. J. Powell, *Inorg. Chem.*, 12, 627 (1973).

(16) D. A. House, *Acta Chem. Scand.*, 26, 2847 (1972).

Table I. Visible Absorption Maxima and Minima (320–650 nm) of Some Diaqua-, Aquachloro-, and Dichloro(tetraamine)cobalt(III) Complexes in Aqueous Acidic Solution at 12–23°C

Cation	Acid (*F*)	Min[a]	Max[a]	Min[a]	Max[a]	Min[a]	Max[a]
trans-$CoCl_2(en)_2^{+\ b}$	MeOH–H_2O		385 (43.7)		450 (25.2)		625 (34.7)
trans-$CoCl_2(trien)^{+\ c}$	$HClO_4$ (0.01)			350 (65)	450 (135)	545 (20)	630 (52)
trans-$CoCl_2(NH_3)(dien)^{+\ d}$	HNO_3 (0.3 (10)[e])			376 (44.3 ± 0.7)	435 br[f] (77.5 ± 0.4)	545 (15.7 ± 0.9)	617 (40.5 ± 0.5)
cis-$CoCl(en)_2(OH_2)^{2+\ g}$	$HClO_4$ (0.012)		373 (67)	435 (15)	515 (84)		
Estimate of *cis*-$CoCl(NH_3)(dien)(OH_2)^{2+\ d}$		355 (63)	370 (67)	434 (32)	517 (80)		
Product mixture $CoCl(NH_3)(dien)(OH_2)^{2+\ d}$	HNO_3 (1.0 (7)[e])	354 (60.1 ± 0.9)	373 (65.9 ± 0.8)	433 (31.2 ± 1.0)	517 (70.0 ± 1.1)		
trans-$Co(en)_2(OH_2)_2^{3+\ h}$	HNO_3 (0.05) $NaNO_3$ (1)		~340 (~55)	410 (32.0)	444 (35.1)	492 (19.2)	520 (32.8)
trans-$Co(NH_3)(dien)(OH_2)_2^{3+\ d}$	HNO_3 (1.0 (6)[e])		380 (61.6 ± 1.5)	406 (58.7 ± 1.2)	453 (83.1 ± 1.2)		536 sh[i] (33.5 ± 1.2)
cis-$Co(en)_2(OH_2)_2^{3+\ h}$	HNO_3 (0.05) $NaNO_3$ (1)		355 (60)	410 (14.3)	492 (80.9)		
cis-$Co(NH_3)(dien)(OH_2)_2^{3+\ d}$	HNO_3 (1.0–1.5 (7)[e]		357 (79.2 ± 1.2)	418 (19.1 ± 0.5)	496 (101.7 ± 1.6)		
(*cis* ⇌ *trans*)-$Co(NH_3)(dien)(OH_2)_2^{3+\ d}$	HNO_3 (1.0 (4)[e])		357 (71.6 ± 1.6)	418 (25.1 ± 0.8)	496 (92.1 ± 0.8)		

[a] In nanometers (±2 nm for this work). Values in parentheses are the molar absorbancy indices, a_M, defined by $A = \log (I_0/I) = a_M cd$, in M^{-1} cm^{-1}. The data in this work are the mean ± the standard deviation (see footnote *e*). [b] H. Kawaguchi, N. Yano, and S. Kawaguchi, *Bull. Chem. Soc. Jap.*, **42**, 136 (1969). [c] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, **6**, 787 (1967), estimated from a plot of a_M *vs.* λ. [d] This work. [e] The number of individual determinations used to obtain the mean. [f] br = broad. [g] D. J. MacDonald and C. S. Garner, *J. Amer. Chem. Soc.*, **83**, 4152 (1961). [h] F. Woldbye, *Acta Chem. Scand.*, **12**, 1079 (1958). [i] sh = shoulder.

Results and Discussion

The complex *trans*-[$CoCl_2(NH_3)(dien)$]ClO_4 has been prepared as a green crystalline solid by the reaction sequence

$$trans\text{-}Co(NO_2)_3(dien)^{17} \xrightarrow{HCl} trans\text{-}CoCl(NO_2)_2(dien)^{18} \xrightarrow{NH_3}$$

$$trans\text{-}Co(NO_2)_2(NH_3)(dien)^{+\ 19} \xrightarrow{HCl} trans\text{-}CoCl_2(NH_3)(dien)^+$$

A *trans*-dichloro configuration is assigned[11] on the basis of the similarity of the visible absorption spectra with other *trans*-$CoCl_2(N_4)^+$ species (Table I), and is supported by the observed spectral changes and kinetics results. With the *trans*-dichloro configuration, the diethylenetriamine ligand must adopt the meridional arrangement and only one isomeric form is possible.

Acid (HNO_3) solutions of *trans*-$CoCl_2(NH_3)(dien)^+$ undergo two major spectrophotometric changes corresponding to the loss of one (Figure 1) and then both chloro ligands. The final spectrum corresponds to an equilibrium *cis*-diaqua-*cis*-aquachloro mixture with about 90% diaqua. Two sets of isosbestic points are observed in this forward reaction at 588 (30.0), 487 (60.9), 399 (53.0), 356 nm (59.2 M^{-1} cm^{-1}) and 526 (78.0), 445 (33.8), 375 nm (68.8 M^{-1} cm^{-1}), respectively. Addition of chloride ions (3 *F* Cl^- as LiCl) causes a reverse reaction, but only one set of isosbestic points is observed and these do not correspond to those in the forward reaction. The final spectrum after the addition of LiCl can be accounted for in terms of a *cis*-aquachloro-*trans*-dichloro mixture.

The Diaqua Ions. Base hydrolysis of *trans*-$CoCl_2(NH_3)(dien)^+$ using the ion-exchange technique outlined in the Experimental Section followed by acidification produces a $Co(NH_3)(dien)(OH_2)_2^{3+}$ ion with an absorption spectrum characteristic of a *trans*-diaqua species (Figure 2, Table I). A second diaqua ion is formed from the *trans*-dichloro after 3 days at room temperature in the presence of excess Hg^{2+}. The absorption spectrum indicates that the H_2O groups are now in the cis configuration (Figure 2, Table I). The *trans*-diaqua ion isomerizes ($t_{1/2}$ = *ca.* 30 min at 25.0° with the rate depending on [H^+] and ionic strength[20]) to give an equilibrium mixture of the above *cis*-diaqua ion and the original *trans*-diaqua ion containing 83 ± 4% *cis*-diaqua.

As there are three possible $Co(NH_3)(dien)(OH_2)_2^{3+}$ isomers with the OH_2 cis to one another,[21] the key to the interpretation of the steric course of the acid hydrolysis reaction lies in establishing the configuration of this *cis*-diaqua ion. Unfortunately, we have not been able to do this entirely to our satisfaction, but all the evidence we have points to the *a*-ammine-*bc*-diaqua-*dfe*-(diethylenetriamine)cobalt(III) configuration (Figure 3).

Attempts to isolate this *cis*-diaqua (or its *cis*-aquachloro precursor) in a crystalline form have been unsuccessful. We have, however, been able to isolate a $Co(ox)(NH_3)(dien)^+$ isomer from the reaction between sodium oxalate and *trans*-$CoCl_2(NH_3)(dien)^+$ as the ClO_4^- or PF_6^- salt. The infrared spectrum of this suggests that the dien ligand is in the facial configuration,[22-24] and if it is assumed that the nitrogen atoms in the *cis*-diaqua ion do not rearrange on chelate formation with oxalate, then this dien configuration is the one adopted in the diaqua. Our attempts to determine the X-ray crystal structure of this oxalato isomer have been thwarted by the poor crystal quality of the isolated salts. We have, in addition, isolated a second $Co(ox)(NH_3)(dien)^+$ isomer by the reaction sequence

$$CoCl_3(dien) \xrightarrow{ox} CoCl(ox)(dien) \xrightarrow{NH_3,\ NO_3^-} Co(ox)(NH_3)(dien)^+$$

---

(17) Y. Kushi, K. Watanabe, and H. Kuroya, *Bull. Chem. Soc. Jap.*, **40**, 2985 (1967).

(18) A. V. Ablov and E. V. Popa, *Russ. J. Inorg. Chem.*, **8**, 161 (1963).

(19) A. V. Ablov and E. V. Popa, *Russ. J. Inorg. Chem.*, **16**, 1615 (1971).

(20) M. C. Couldwell and D. A. House, unpublished research.

(21) These are the *a,bc,dfe*-$Co(NH_3)(OH_2)_2$(*fac*-dien)$^{3+}$, *a,bc,def*-$Co(NH_3)(OH_2)_2$(*fac*-dien)$^{3+}$ and *a,bf,cde*-$Co(NH_3)(OH_2)_2$(*mer*-dien)$^{3+}$ cations.

(22) D. A. House, *Inorg. Nucl. Chem. Lett.*, **3**, 67 (1967).

(23) S. H. Caldwell and D. A. House, *J. Inorg. Nucl. Chem.*, **31**, 811 (1969).

(24) H. H. Schmidtke and D. Garthoff, *Inorg. Chim. Acta*, **2**, 357 (1968).

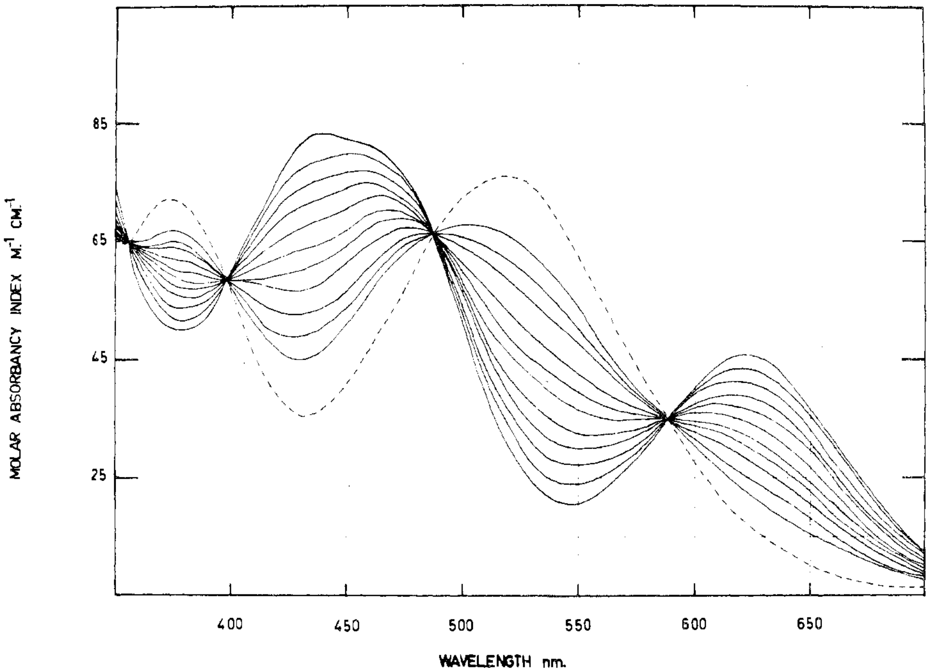

Figure 1. Spectral changes in the primary acid hydrolysis of *trans*-$CoCl_2(NH_3)(dien)^+$ (——) in 0.3 *F* HNO_3 at 15.2°. Reading downward at 450 nm (or upward at 525 nm), the reaction times are 0, 15, 30, 45, 60, 80, 100, 120, 150, 180, and 220 min. The final curve (- - - -) is that of the aquachloro product mixture.

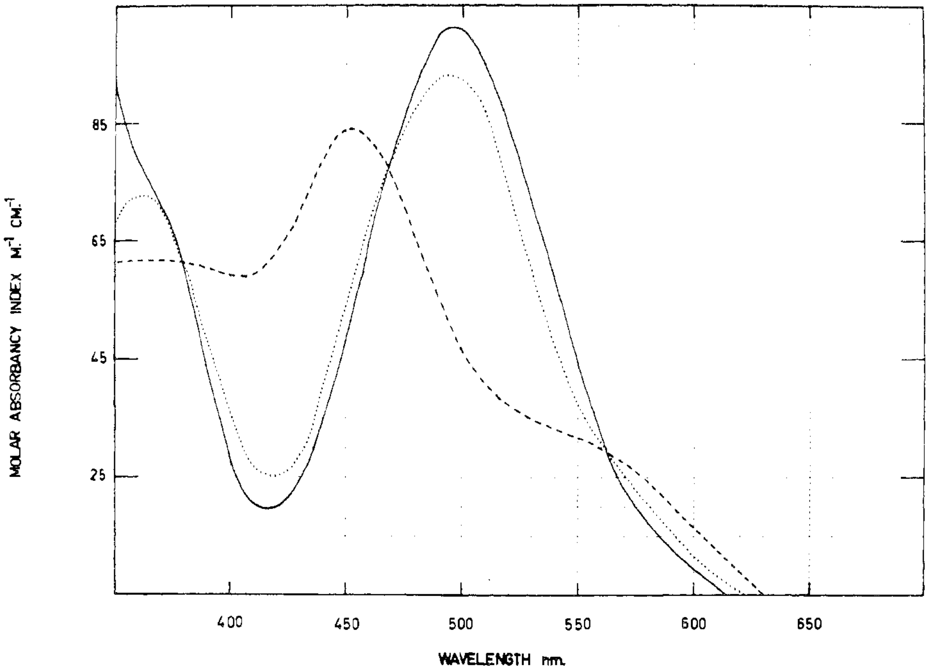

Figure 2. Visible absorption spectra of *trans*- (- - - -) and *cis*-$Co(NH_3)(dien)(OH_2)_2^{3+}$ (——) and the cis ⇌ trans equilibrium mixture (· · · ·) in 1.0–1.5 *F* HNO_3 at 20–23°.

as the NO_3^- or ClO_4^- salt. The X-ray structure of the nitrate[25] shows the dien ligand to have the meridional configuration and the salt is represented as *a*-ammine-*bcd*-(diethylenetriamine)-*ef*-(oxalato)cobalt(III) nitrate, with the NH proton on the secondary NH group of the meridional dien ligand adjacent to the NH_3 group (configuration *a,bf,cde* in Figure 3, with the two OH_2 groups replaced by ox). Thus we postulate dien movement rather than NH_3 in the isomerization of the *trans*-ammine(diaqua)(diethylenetriamine)-cobalt(III) ion.

Meridional to facial diethylenetriamine isomerism has been studied for the systems $Co(dien)(OH_2)_3^+$ [26] and *κ*-Co(en)-$(dien)(OH_2)^{3+}$.[27] Water-exchange mechanisms have been postulated[26,27] and the trigonal-bipyramidal transition state appears to be produced by movement of the NH_2 ends of the polyamine, rather than by movement of the secondary NH group into the trigonal plane.[27] End movement of the diethylenetriamine in the present system yields the *a*-ammine-

---

(25) M. C. Couldwell, D. A. House, and B. R. Penfold, unpublished reseach.

(26) P. Wilairat and C. S. Garner, *J. Inorg. Nucl. Chem.*, 33, 1833 (1971).

(27) K. T. Huan, J. N. Nulvihill, A. R. Gainsford, and D. A. House, *Inorg. Chem.*, 12, 1517 (1973).

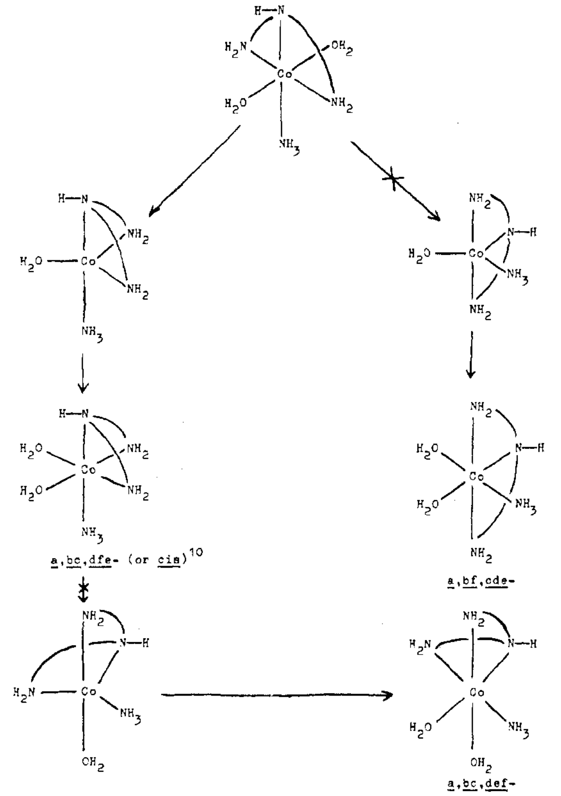

Figure 3. Mechanistic scheme for the production of ammine(diaqua)(diethylenetriamine)cobalt(III) isomers from the *trans*-diaqua. Routes involving movement of the secondary NH diethylenetriamine group to the trigonal plane of the five-coordinate transition states are marked $\nrightarrow$.

bc-diaqua-*dfe*-(*fac*-diethylenetriamine)cobalt(III) isomer while *secondary* NH-NH_3 movement yields the corresponding *a,bf,cde*-(*mer*-dien) isomer. Direct formation of the *a,bc, def*-(*fac*-dien) isomer from the *trans*-diaqua is apparently not possible using the above mechanistic schemes, and a second water exchange involving the unfavorable secondary NH(dien)-NH_3 movement into the trigonal plane is required to generate this isomer. These schemes are depicted in Figure 3. It should be noted that although the formation of the *a,bf,cde*-diaqua ion from the trans precursor is not favorable in terms of group movement, the reverse is not restricted in this manner. This is in accord with the observation that *both* of the oxalato isomers yield the *trans*-dichloro ion on treatment with concentrated hydrochloric acid.

In summary, we believe that the simplest interpretation of the *trans*-diaqua to *cis*-diaqua isomerization is in terms of a meridional to facial diethylenetriamine configuration change with the *cis*-diaqua having the *a,bc,dfe*-(*fac*-dien) geometry. Consequently the aquachloro precursor of this diaqua species is expected to have a similar cis[10] configuration.

The Aquachloro Ions. Although *trans*-$CoCl_2(NH_3)(dien)^+$ has a plane of symmetry and is thus achiral, in any particular ion, the chloro ligands are nonequivalent, being adjacent to, and remote from, the secondary NH(dien) proton, respectively. Consequently, two nonequivalent (*mer*-dien)(H_2O)Cl ions (I and III in Figure 4) could be generated in the primary hydrolysis.[28] A similar situation occurs with *cis*-β-$CoCl_2(trien)^+$,[3] *trans*-*ms*-$CoCl_2(2,3,2\text{-tet})^+$,[4] and certain macrocyclic ligands.[8]

The excellent isosbestic points (Figure 1) that are maintained throughout (2 half-lives) the primary hydrolysis reaction and over a range of temperatures suggest that either one product is formed or a mixture of products is formed in a constant ratio. Ion-exchange chromatography failed to separate the aquachloro products, but subsequent spectrophotometric investigation (at 25.0°) of the effluent showed a rapid spectrophotometric change ($t_{1/2}$ = *ca.* 9 min) followed by a slower reaction. The rapid reaction was not reflected in chloride release studies and gives an estimate of k_e (Figure 4). These data suggest that two aquachloro species are produced in a constant ratio and the spectrophotometric changes are interpreted as a subsequent isomerization of one of these, followed by the expected aquachloro to diaqua hydrolysis to give an equilibrium mixture containing 90 ± 5% diaqua.

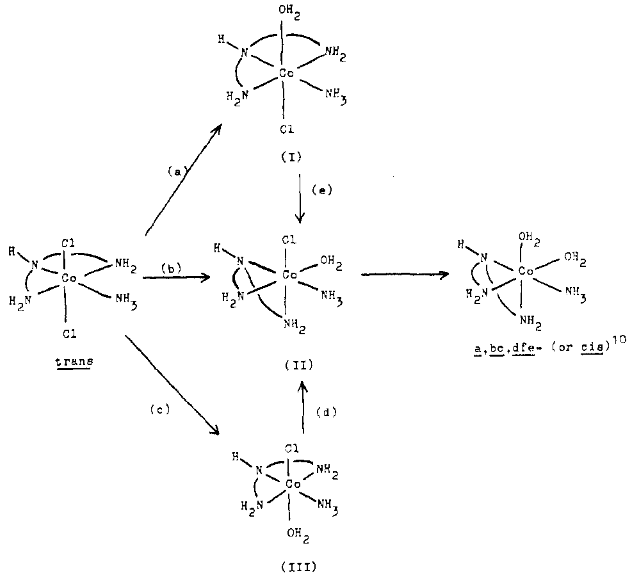

Figure 4. Reaction scheme for the acid hydrolysis of *trans*-$CoCl_2(NH_3)(dien)^+$.

Using the second set of isosbestic points in the hydrolysis of *trans*-$CoCl_2(NH_3)(dien)^+$, *i.e.*, those assumed to correspond to the aquachloro to diaqua hydrolysis, and the spectrum of the aquachloro products mixture, an estimate of the absorption spectral parameters of the major aquachloro product species was obtained (Table I). The estimated visible absorption spectrum of this aquachloro species suggests that the Cl and H_2O ligands are in a cis position, and as this is the precursor of the *cis*-diaqua[10] ion, it is assigned the *cis*-*a*-ammine-*b*-aqua-*c*-chloro-*dfe*-diethylenetriamine)cobalt(III) configuration.[10] Chloride release first-order rate constants for the loss of chloride for this complex are listed in Table III and were calculated on the basis of 90% reaction at "infinity." Kinetic parameters calculated from these data are E_a (kJ mol^{-1}) = 96.3 ± 2.1, log *PZ* (sec^{-1}) = 12.75 and ΔS°_{298} (J K^{-1} mol^{-1}) = −8.4 ± 4.2.

Primary Hydrolysis Kinetics Data. The characteristic isosbestic points and spectra changes for the first acid hydrolysis step in the forward reaction are shown in Figure 1. The final spectrum is that of the aquachloro product(s) isolated by ion-exchange chromatography from aged (3 spectrophotometric half-lives) solutions of the *trans*-dichloro ions. First-

---

[28] In fact, there are nine theoretical $CoCl(NH_3)(dien)(OH_2)^{2+}$ isomers possible, six of which are achiral. The potential isomers can be divided into two groups: (a) three containing the dien in the *edf* position (facial) and the NH_3, Cl, and H_2O in the *abc, bac,* and *cab* positions, respectively, which are potentially optically active; (b) three with the dien in the *cbe* position (meridional) and the NH_3, Cl, and H_2O in the *dfa, afd,* and *fda* positions. In class b, any particular isomer can exist in two potential configurations as the secondary NH(dien) proton can be adjacent to either of the two (different) ligands in the axial (*af*) positions.

Table II. First-Order Rate Constants for the Primary Hydrolysis of *trans*-$CoCl_2(NH_3)(dien)^+$ in 0.3 F HNO_3

Temp, °C	C_0,[a] mF	$10^5k_{spectro}$, sec^{-1} Obsd[b]	Calcd[d]	10^5k_{Cl}, sec^{-1} Obsd[b]	Calcd[c]	Method[d]
8.0	1.94-2.43			4.96 ± 0.06	4.93	H(3)
10.1	1.94-2.75	4.22 ± 0.05	4.23			SS(3)[e]
10.1	2.65	5.0 ± 0.3[f]				SS(1)[e]
13.6	2.39-2.58			10.9 ± 0.1	11.0	H(4)
13.6	2.21-2.23			10.9 ± 0.5[g]		H(2)
15.2	2.25-3.50	9.44 ± 0.11	9.36			SS(3)[e], CWS(1)[h]
17.0	3.68	12.3 ± 0.6	12.3			CWS(1)[h]
20.0	2.27-2.49			27.2 ± 0.2	26.8	H(3)
22.0	2.48-4.90	25.4 ± 0.6	25.8			CWS(4)[e]
25.0	2.72-3.22	40.6 ± 0.3	39.8			CWS(3)[e]
25.0	2.41-3.50			51.7 ± 0.8	52.1	H(5)
25.7	2.38-3.40	43.6 ± 3.5	44.0			CWS(4)[e]

[a] Initial complex ion concentration. [b] The numbers quoted are the mean ± the standard deviation. Where the number of determinations is ⩽2, an error of 5% is assumed. [c] Rate constants calculated using the E_a and log PZ values in eq 1 and 2. [d] Method used in monitoring the reaction: H = halide-release titration, SS = spectrophotometric scan, CWS = constant-wavelength scan. Numbers in parentheses are the number of individual determinations. [e] Data analyzed at 450 and 525 nm. [f] In 0.001 F HNO_3 ($\mu = 0.3$ ($NaNO_3$)). [g] Sample chromatographed prior to halide titration. [h] Data analyzed at 525 nm.

Table III. First-Order Chloride-Release Rate Constants for the Hydrolysis of *cis*-$CoCl(NH_3)(dien)(OH_2)^{2+}$ in 1.0 F HNO_3

Temp, °C	C_0,[a] mF	10^5k_{obsd},[b] sec^{-1}	10^5-k_{calcd},[c] sec^{-1}	Method[d]
25.0	1.31-2.55	7.89 ± 0.28	8.04	H(3)
30.0	2.07-2.23	15.9 ± 0.8	15.3	H(2)
35.0	1.86-2.59	27.7 ± 0.6	28.3	H(2)

[a] Footnote *a*, Table II. [b] Footnote *b*, Table II. [c] Rate constants were calculated using $E_a = 96.3$ kJ mol^{-1} and log $PZ = 12.75$ sec^{-1}. [d] Footnote *d*, Table II.

order rate constants calculated from these data were obtained in the 10.1-25.7° temperature range (0.3 F HNO_3) and are listed as $k_{spectro}$ in Table II.

Chloride release titration data in the 8.0-25.0° range (0.3 F HNO_3) also gave first-order rate constants and these are listed as k_{Cl} in Table II. In both cases, the first-order rate plots were linear for 0.75-2.0 half-lives. Change in the hydrogen ion concentration from 0.3 to 0.001 F ($\mu = 0.3$ ($NaNO_3$)) gave only a slight increase in $k_{spectro}$. Kinetic data obtained when titrations were carried out with the free chloride ions separated chromatographically from the reaction mixture gave rate constants which were no different from those obtained by the normal procedure. From the variation in k with temperature, the rate constants can be expressed[29] as

$$k_{spectro}\ (sec^{-1}) = PZ\ \exp(-105{,}500 \pm 1300/RT) \qquad \log PZ = 15.10 \qquad (1)$$

$$k_{Cl}\ (sec^{-1}) = PZ\ \exp(-96{,}700 \pm 1300/RT) \qquad \log PZ = 13.64 \qquad (2)$$

We interpret the non-equivalence of k_{Cl} and $k_{spectro}$ as due to a chloride-release path that is not detected spectrophotometrically. This suggests that one of the *trans*-aquachloro forms isomerizes to the *cis*-aquachloro almost as rapidly as it is produced. However, this rapidly isomerizing species must have a reasonable lifetime, otherwise k_{Cl} would equal $k_{spectro}$. On the other hand, its concentration must remain small so as to remain undetected spectrophotometrically. This is one of the few reported instances[30] where $k_{spectro}$ does not equal k_{Cl}, although quite often, in analogous systems, only one method has been used to monitor the extent of the reaction. In terms of Figure 4, isomer III can collapse directly to II *via* water exchange, whereas isomer I requires proton inversion prior to (or concurrently with) a water exchange isomerization. Thus k_d can be regarded as large compared with the other rate constants in the system, but its value cannot be obtained directly from the available data. It is noted, however, that k_e is about six times as fast as the most rapid chloride release path (k_b, Table IV) and k_d would have to be at least one order of magnitude greater, which gives $10^5k_d = 1300$ sec^{-1} at 25.0°, as a lower limit.

With this assumption, we regard k_{Cl} as the sum of the three possible chloride-release paths ($k_a + k_b + k_c$) and $k_{spectro}$ as equal to $k_a + k_b$. Thus k_c can be calculated directly as $k_{Cl} - k_{spectro}$ (Table IV) and can be expressed by the relationship[29]

$$k_c\ (sec^{-1}) = PZ\ \exp(-75{,}800 \pm 4200/RT) \qquad \log PZ = 9.35 \qquad (3)$$

The equation

$$a_M\ (\text{products}) = a_Mx(trans) + a_My(\text{I}) + a_Mz(\text{II})$$

represents the data in Figure 1 where, at time t, $a_M f(n)$ = molar absorbancy index (M^{-1} cm^{-1}) times the fraction of the species in parentheses (Figure 4), and $x + y + z = 1$.

Although a_M(I) and y are unknowns, analysis of the data at 0.5, 1.0, and 1.5 spectrophotometric half-lives with a_M(I) in the 10-40 M^{-1} cm^{-1} range at 520 nm gives a value of 20 ± 10% I in the aquachloro product mixture.[31]

The amount of *cis*-aquachloro directly formed can only be estimated if k_e (Figure 4) is known. Using the *ca.* 9 min half-life estimated for this reaction at 25.0°, and the fractions, F, of trans, I, and II at 1.0 half-life for the primary hydrolysis, k_a can be calculated from the expression

$$F(\text{I}) = k_a[F(\text{trans}) - \exp(-k_et)][k_e - (k_a + k_b)]^{-1} \qquad (4)$$

as $k_a + k_b$ is known. This calculation suggests that the *trans*-$CoCl_2(NH_3)(dien)^+ + H_2O$ = *cis*-$CoCl(NH_3)(dien)(OH_2)^{2+} + Cl^-$ reaction accounts for 50 ± 10% of the chloride release paths.

From k_a, the relative contribution of paths a, b, and c to the total primary chloride release can be estimated, and, assuming that these ratios are independent of temperature, the reverse calculations give the values of k_a, k_b, and k_c listed in

---

(29) Throughout this work $R = 8.314$ J K^{-1} mol^{-1}.

(30) C. S. Garner and D. J. MacDonald in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, pp 266-275.

(31) The I:II ratio is not particularly sensitive to the value of a_M(I) used. The fractions x, y, z of species trans, I, II (Figure 4) at 0.5, 1.0, and 1.5 half-lives are 0.75, 0.04, 0.21; 0.5, 0.08, 0.42; and 0.25, 0.12, 0.63, respectively, at 520 nm with a_M(I) = 10-40 M^{-1} cm^{-1}, giving an approximately constant I:II ratio of 5.25. At 520 nm, a_M(trans) = 24.3 and a_M(II) = 79.8 M^{-1} cm^{-1}, with a_M(products) = 36.0, 47.0, and 57.3 M^{-1} cm^{-1} at 0.5, 1.0, and 1.5 half-lives, respectively, at 15.0°.

Table IV. First-Order Rate Constants (sec^{-1}) Estimated for the Primary Hydrolysis of *trans*-$CoCl_2(NH_3)(dien)^+$ in 0.3 *F* HNO_3[a]

Temp, °C	10^5k_{Cl} ($=10^5(k_a + k_b + k_c)$)	$10^5k_{spectro}$ ($=10^5(k_a + k_b)$)	10^5k_c	10^5k_a	10^5k_b	10^5k_e
10.1	6.70	4.23	2.47	0.92	3.31	10
15.2	13.85	9.36	4.49	2.51	6.85	25
20.0	26.78	19.25	7.53	6.03	13.2	57
25.0	52.1	39.8	12.3	14.1	25.7	128

[a] Assuming 50 ± 10% of *cis*-$CoCl(NH_3)(dien)(OH_2)^{2+}$ as a directly formed product and 20 ± 20% *trans*-$CoCl(NH_3)(dien)(OH_2)^{2+}$ present in the aquachloro product mixture. Rate constants in the last three columns are probably accurate to ±20%.

Table IV. From these rate constants, the relative proportions of I:II:III produced directly from the *trans*-dichloro are estimated as 20 ± 10:50 ± 10:30 ± 10.

Although the rate data in Table IV give satisfactory Arrhenius plots, the activation parameters for the individual paths (apart from k_c, where $E_a = 75 \pm 4$ kJ mol^{-1}, log $PZ = 9.35$ sec^{-1}, and $\Delta S°_{298} = -74 \pm 8$ J K^{-1} mol^{-1}) are probably not of sufficient accuracy to justify any real theoretical significance. Nevertheless, it is interesting that for k_a, k_b, and k_e, the $\Delta S°_{298}$ values are all positive. Tobe[32] has argued that steric change is associated with a higher (and positive) $\Delta S°_{298}$ than is retention of configuration and these data, apart from that associated with k_a, support this hypothesis. Table V lists the kinetic parameters and steric course for the primary acid hydrolysis of some *trans*-$CoCl_2(N_4)^+$ systems. The apparently anomalous positive $\Delta S°_{298}$ values obtained for certain macrocyclic ligands showing no steric change has been discussed by Poon and Tobe.[33]

The mechanism of Niththyananthan and Tobe[34] for the hydrolysis of *trans-RR,SS*-$CoCl_2(N_4)^+$ [(N_4) = 2,3,2-tet, trien] is applicable to the present system, with modifications due to the formation of the *trans*-aquachloro (III) but only one *cis*-aquachloro (II) product. We would, however, prefer a five-coordinate transition state with the secondary NH proton position as in Figure 3, as the published[34,35] intermediate has one secondary NH proton in the sterically unsatisfactory position between the C-N-C angle of the polyamine. Such a position gives rise to a *cis*-β-$CoCl(N_4)(OH_2)^{2+}$ isomer with the opposite NH configuration to that found for *cis*-β-$CoCl(trien)(OH_2)^{2+}$ by X-ray methods.[36] However, the production of I (Figure 4) requires the formation of a square-pyramidal transition state, as postulated in the Hg^{2+}-catalyzed acid hydrolysis of *trans*-$CoCl_2(trien)^+$.[4] Thus the present system provides an example of an acid hydrolysis reaction where both square-pyramidal and trigonal-bipyramidal transition states contribute to the steric course, and as a consequence, both *cis*- and *trans*-aquachloro species are produced.

Table V. Kinetic Parameters and Steric Course for the Acid Hydrolysis of Some *trans*-Tetraaminedichlorocobalt(III) Complexes at 25°

trans-$CoCl_2N_4^+$	$[H^+]$, *F*	10^4k, sec^{-1}	E_a, kJ mol^{-1}	$\Delta S°_{298}$, J K^{-1} mol^{-1}	% steric change
$(NH_3)_4$[a,b]	0.1	18	98.8	+36.0	55 ± 10
$(en)(NH_3)_2$[a]	0.1	2.3			
$(en)_2$[c]	0.01	0.35	109.7	+58.6	35
(en)(tmd)[d]	0.3	3.96	101.3	+21.3	66 ± 5
$(tmd)_2$[e]		533	89.2	+28.9	
(NH_3)(dien)	0.3	5.21[f]	96.7	+7.9	50 ± 10
RR,SS-trien[g]	0.1	31.8	108.8	+64.9	100
RR,SS-2,3,2-tet[h]	0.01	2.5	108.4	+50.2	50 ± 20
RR,SS-2,3,2-tet[i]			105.1	+37.7	95
RR,SS-2,3,2-tet[j]			103.4	+37.7	100
RS-2,3,2-tet[h,j]	0.01	0.14	101.7	+4.2	0
RR,SS-3,2,3-tet[j]	0.01	0.54	102.6	+16.7	0
Cyclam[k]	0.01	0.011	103.0	−12.6	0
ms-Me_6-2,3,2,3-tet	0.01	9.3[l]	107.2	+54.4	0
rac-Me_6-2,3,2,3-tet	0.01	42[l]	118.5	+104.7	0

[a] R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, 59, 304 (1955). [b] R. G. Linck, *Inorg. Chem.*, 8, 1016 (1969). [c] S. C. Chan, *Aust. J. Chem.*, **20**, 595 (1967). [d] M. C. Couldwell, D. A. House, and H. K. J. Powell, *Inorg. Chem.*, 12, 627 (1973). [e] I. R. Jonasson, R. S. Murray, D. R. Stranks, and Y. K. Yandell, *Proc. Int. Conf. Coord. Chem.*, 12, 32 (1969). [f] The rate constant is that for chloride release and the activation parameters cited here are composite quantities. [g] A. M. Sargeson and G. H. Searle, *Inorg. Chem.*, 6, 2172 (1967). [h] R. Niththyananthan and M. L. Tobe, *ibid.*, 8, 1589 (1969). [i] M. L. Tobe, *ibid.*, 7, 1260 (1968). [j] M. D. Alexander and H. G. Hamilton, *ibid.*, 8, 2131 (1969). [k] C. K. Poon and M. L. Tobe, *J. Chem. Soc. A*, 2069 (1967). [l] W. K. Chau and C. K. Poon, *J. Chem. Soc. A*, 3087 (1971).

Acknowledgments. We acknowledge with thanks funds from the New Zealand Universities Grants Committee for the purchase of instruments used in this research. M. C. C. thanks British Petroleum (N. Z.) for the receipt of a scholarship and the University of Canterbury for Research Grant 73/2/5.

Registry No. *trans*-$[CoCl_2(NH_3)(dien)]ClO_4$, 52571-38-7; *trans*-$CoCl_2(NH_3)(dien)^+$, 49863-78-7; *cis*-$CoCl(NH_3)(dien)(OH_2)^{2+}$, 52571-41-2; *trans*-$Co(NH_3)(dien)(OH_2)_2{}^{3+}$, 52571-42-3; *cis*-$Co(NH_3)(dien)(OH_2)_2{}^{3+}$, 52612-69-8; *trans*-$[Co(NO_2)_2(NH_3)(dien)]Cl$, 35868-74-7.

---

(32) M. L. Tobe, *Inorg. Chem.*, 7, 1260 (1968).

(33) C. K. Poon and M. L. Tobe, *Coord. Chem. Rev.*, 1, 81 (1966).

(34) R. Niththyananthan and M. L. Tobe, *Inorg. Chem.*, **8**, 1589 (1969); see Figure 3.

(35) C. K. Poon, *Inorg. Chim. Acta, Rev.*, 123 (1970).

(36) D. A. Buckingham, P. A. Marzilli, I. E. Maxwell, A. M. Sargeson, M. Fehlmann and H. C. Freeman, *J. Chem. Soc., Chem. Comm.*, 488 (1968).