

therefore not penetrate the coordination sphere as effectively. The delocalized nature of the acetate ion pair outer sphere may also account for the marked preference shown by the cation for acetate.

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## Mechanism and Steric Course of Octahedral Aquation. XII. The Kinetics and Steric Course of Aquation of Some Isomers of the Dichloro(1,4,8,11-tetraazaundecane)cobalt(III) Cation

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The kinetics and steric course of the aquations of the isomeric *trans*-(*RR,SS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup> and *trans*-(*RS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup> (2,3,2-tet = 1,4,8,11-tetraazaundecane; *R* and *S* refer to the chirality of the coordinated secondary nitrogens) in dilute acid are reported. The more labile (*RR,SS*) isomer ( $k_{25} = 2.9 \times 10^{-4} \text{ sec}^{-1}$ ,  $\Delta H^\ddagger = 25.9 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = 12 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ) initially forms a mixture of *trans*- and  $\beta$ -*cis*-(*RR,SS*)-Co(2,3,2-tet)H<sub>2</sub>OCl<sub>2</sub><sup>+</sup> containing  $50 \pm 20\%$  of the unstable *trans* isomer which then rapidly changes to the  $\beta$ -*cis* form. The *trans*-(*RS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup> cation ( $k_{25} = 1.5 \times 10^{-5} \text{ sec}^{-1}$ ,  $\Delta H^\ddagger = 24.3 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = 1 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ) aquates with complete retention of configuration. The mercuric ion catalyzed aquation of the *trans*-(*RR,SS*)-dichloro isomer yields initially  $30 \pm 5\%$  *trans*- and  $70 \pm 5\%$   $\beta$ -*cis*-chloroaquo complex, whereas the analogous reaction of the *trans*-(*RS*) isomer yields 100% *trans* product. A *cis*-dichloro isomer (presumed to be  $\beta$ -*cis*-(*RR,SS*)-dichloro) aquates with complete retention of configuration ( $k_{25} = 1.1 \times 10^{-3} \text{ sec}^{-1}$ ,  $\Delta H^\ddagger = 22.3 \text{ kcal mol}^{-1}$ ,  $\Delta S^\ddagger = 2 \text{ cal deg}^{-1} \text{ mol}^{-1}$ ). The  $\beta$ -*cis*-(*RR,SS*)-chloroaquo complex undergoes chloride anation in hydrochloric acid to give only the *trans*-(*RR,SS*)-dichloro complex, but in less acid solution it isomerizes at a rate inversely proportional to [H<sup>+</sup>], to the more stable *trans*-(*RS*) form. These reactions are discussed in connection with those of analogous complexes of the cyclic 1,4,8,11-tetraazacyclotetradecane (cyclam) and 1,4,7,10-tetraazadecane (trien). A dissociative mechanism is assigned in all cases and some conclusions are drawn concerning the nature of the five-coordinate intermediate.

### Introduction

In the last three parts of this series<sup>2-4</sup> the kinetics of the substitution and isomerization reactions of *trans*- and *cis*-Co(cyclam)Cl<sub>2</sub><sup>+</sup> have been reported. In spite of the many possibilities of isomerism arising from the various combinations of the secondary nitrogens, we were only able to isolate one *trans* form and one *cis* form. In an attempt to differentiate effects arising from the use of a macrocyclic ligand from those due to the presence of secondary nitrogen atoms, we have examined the behavior of complexes of an open-chain fragment of the macrocycle 2,3,2-tet. This ligand is closely related to triethylenetetramine whose complexes of the type Co(trien)Cl<sub>2</sub><sup>+</sup> and their aquoderivatives have been elegantly characterized and studied by Sargeson, *et al.* This work, therefore, serves as a link between the substitution reactions of the macrocyclic complex and those of the stereorestrictive trien ligands. Sargeson<sup>5</sup> has pointed out the need to take account of the configurations of the secondary nitrogens and has isolated and characterized certain of the isomers and reported the kinetics and steric courses of their spontaneous and induced aquation reactions.<sup>6</sup>

The somewhat more flexible ligand 2,3,2-tet should allow more of the possible isomers to be isolated, and, in the case of the *trans*-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup> complex, Hamilton and Alexander<sup>7</sup> were able to isolate and characterize both the (*RS*) (*meso*) and (*RR,SS*) (racemate) complexes. They showed that, on aquation, the *trans*-(*RS*) complex gave only *trans*-chloroaquo product, whereas the *trans*-(*RR,SS*) isomer gave the  $\beta$ -*cis*-chloroaquo species. They were also able to separate the *trans*-(*RS*)-chloroaquo complex, produced by the mercury(II)-catalyzed aquation of the dichloro complex, into two isomeric forms, thereby demonstrating the (*RS*) configuration. The (*RS*) form of the analogous trien complex is unknown. It is thus possible to examine the effect that the configuration of the secondary nitrogen exerts upon the kinetics and steric course of aquation of the dichloro complexes.

### Experimental Section

*trans*-Dichloro-(*RS*)-(1,4,8,11-tetraazaundecane)cobalt(III) chloride-2.5-water was prepared by the method of Bosnich, *et al.*<sup>8</sup> *Anal.* Calcd for C<sub>14</sub>H<sub>30</sub>Cl<sub>2</sub>Co<sub>2</sub>N<sub>8</sub>O<sub>5</sub>: C, 22.7; H, 6.8; Cl, 28.7; N, 15.1. Found: C, 23.0; H, 6.7; Cl, 28.9; N, 15.6.

*cis*-Dichloro-(*RR,SS*)-(1,4,8,11-tetraazaundecane)cobalt(III)

- (1) On leave from the University of Ceylon, Peradeniya, Ceylon.
- (2) C. K. Poon and M. L. Tobe, *J. Chem. Soc., A*, 2069 (1967).
- (3) C. K. Poon and M. L. Tobe, *ibid.*, *A*, 1549 (1968).
- (4) C. K. Poon and M. L. Tobe, *Inorg. Chem.*, **7**, 2398 (1968).
- (5) A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 787 (1967).
- (6) A. M. Sargeson and G. H. Searle, *ibid.*, **6**, 2172 (1967).

(7) H. G. Hamilton, Jr., and M. D. Alexander, *J. Am. Chem. Soc.*, **89**, 5065 (1967).

(8) B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc., A*, 1331 (1966).

chloride was prepared by a modification of Bosnich's<sup>8</sup> method. A 5-g sample of the *trans*-(*RS*)-dichloro chloride was dissolved in water (50 ml) and the solution digested for 30 min with an excess of lithium carbonate on a steam bath. The undissolved lithium carbonate was filtered off, and the hot, red filtrate was treated with acetone (200 ml) and hydrochloric acid until a slight excess of acid was present. The mixture was digested for 1 hr on a steam bath and then set aside to cool. The violet crystals were filtered off, washed with acetone, and recrystallized rapidly by adding acetone to a fresh aqueous solution. *Anal.* Calcd for  $C_7H_{20}Cl_2CoN_4$ : C, 25.8; H, 6.1; Cl, 32.7; N, 17.2. Found: C, 26.1; H, 6.1; Cl, 32.9; N, 17.8.

*trans*-Dichloro-(*RR,SS*)-(1,4,8,11-tetraazaundecane)cobalt(III) perchlorate was prepared from the *cis*-dichloro complex by the method of Hamilton and Alexander.<sup>7</sup> *Anal.* Calcd for  $C_7H_{20}Cl_2O_4CoN_4$ : C, 21.6; H, 5.2; Cl, 27.3; N, 14.4. Found: C, 21.5; H, 5.2; Cl, 27.1; N, 14.2.

Other chemicals were reagent grade materials.

**Kinetics.**—Solutions, generally between  $2 \times 10^{-3}$  and  $4 \times 10^{-2}$  M in complex, were prepared by adding a known volume of the appropriate solvent mixture previously brought to the reaction temperature to a known weight of the required complex. The solutions were placed in a thermostated silica spectrophotometer cell and the reaction was followed, either by repeatedly scanning the visible and near-ultraviolet spectra or else, in the faster reactions, by fixing the spectrophotometer at the chosen wavelength and allowing the recorder bed to move at a known rate. The temperature of the reaction mixture was recorded during the reaction by a thermocouple actually placed in the cell, away from the light path. All measurements were made with a Unicam SP-800 spectrophotometer. Wherever possible, the reactions were carried out under pseudo-first-order conditions and the appropriate rate constants were determined from the change of optical density with time using standard graphical methods.

## Results

### (1) Aquation of *trans*-(*RS*)-[Co(2,3,2-tet)Cl<sub>2</sub>]Cl.—

A slightly acidified aqueous solution of this complex is remarkably similar in its behavior to that of the corresponding *trans*-(Co(cyclam)Cl<sub>2</sub>)Cl.<sup>2</sup> The aquation is slow and reversible at room temperature and reaches equilibrium before any of the second chloride is displaced. Titration of a solution that had been allowed to reach equilibrium at 65° showed that 98% of the first coordinated chloride was liberated, indicating that this dichloro complex is, thermodynamically, somewhat less stable with respect to aquation than the macrocyclic analog.<sup>2</sup> Addition of HCl to the equilibrium solution caused a slow anation back to the dichloro complex which could then be precipitated as its sparingly soluble perchlorate by adding perchloric acid. This salt is identical in every respect (uv, visible, and ir spectra, rate of aquation) with the perchlorate obtained directly from a freshly prepared solution of the *trans*-(*RS*)-dichloro complex and this, together with the characteristic "*trans* form" of the final spectrum (Figure 1), indicates that both aquation and anation take place with complete retention of configuration.

The aquation (and anation) is characterized by four isosbestic points at 592, 438, 408, and 355 m $\mu$ , and the change of optical density at 520 m $\mu$ , where *cis*-chloro-aquo species absorb much more strongly, shows no deviations consistent with their formation as labile intermediates. The optical density change follows a first-order rate law and the rate constants were determined from data taken at 530 m $\mu$ . The first-order rate

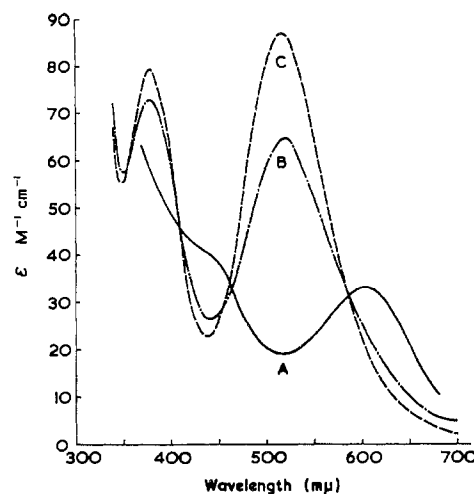


Figure 1.—Spectra of acid aqueous solutions of (A) *trans*-(*RS*)-Co(2,3,2-tet)H<sub>2</sub>OCl<sub>2</sub><sup>+</sup>, (B) the initial product of the Hg<sup>2+</sup>-catalyzed aquation of *trans*-(*RR,SS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup>; and (C)  $\beta$ -*cis*-(*RR,SS*)-Co(2,3,2-tet)ClH<sub>2</sub>O<sub>2</sub><sup>+</sup>.

constants, determined graphically in the usual way, are collected in Table I. Because of the general similarity of the spectra of the *trans*-dichloro and *trans*-chloro-aquo species, the fractional change of optical density is nowhere very large and the accuracy of the rate constants suffers accordingly.

TABLE I  
FIRST-ORDER RATE CONSTANTS FOR THE  
AQUATION OF *trans*-(*RS*)-[Co(2,3,2-tet)Cl<sub>2</sub>]Cl IN  
DILUTE NITRIC ACID

Temp, °C	Ionic strength, M	pH	10 <sup>4</sup> k, sec <sup>-1</sup>
25.0	0.062	1.25	0.145
25.0	0.016	2.0	0.13
25.0	0.005	3.0	0.15
39.2	0.016	2.0	1.09
44.0	0.016	2.0	2.12
50.0	0.016	2.0	3.88
54.8	0.016	2.0	7.8
60.3	0.016	2.0	15.3
65.0	0.016	2.0	24.2

### (2) Aquation of *trans*-(*RR,SS*)-[Co(2,3,2-tet)Cl<sub>2</sub>]-ClO<sub>4</sub>.—

In acid aqueous solution (HClO<sub>4</sub>), the complex undergoes two major spectrophotometric changes. The first, corresponding to a green to purple transformation, is characterized by an isosbestic point at 588 m $\mu$  which remains throughout this stage and three others at 460, 415, and 359 m $\mu$  which disappear after about 1–2 half-lives. The second stage of the reaction corresponds to a purple to green change and takes place at a rate inversely proportional to the hydrogen ion concentration of the solution. At pH  $\leq 1$  the rates of the two stages are so different that it is possible to examine the spectrum at the end of the first stage before there is any marked interference from the second. This corresponds very closely to the spectrum at the end of the first stage of the aquation of the *cis*-dichloro complex and, from titration of the free chloride and comparison of the spectrum with those of analogous bis-ethylenediamine and triethylenetetramine complexes, allows one

to conclude that the product is one, or a mixture, of the *cis*-chloroaquo isomers. The kinetics and products of the second stage are independent of the way in which the *cis*-chloroaquo complex is generated, and, by isolating and characterizing crystalline materials, it is clear that the final product of the second stage is the equilibrium mixture of *trans*-(*RS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup> and *trans*-(*RS*)-Co(2,3,2-tet)ClH<sub>2</sub>O<sup>2+</sup>. This isomerization will be reported elsewhere. If concentrated HCl is added to the solution at the end of the aquation step (*i.e.*, to the *β*-*cis*-chloroaquo complex), the spectrum moves back toward that of the *trans*-(*RR,SS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup> complex and passes through the same isosbestic points. Addition of perchloric acid causes precipitation of the *trans*-(*RR,SS*)-dichloro perchlorate. This is true irrespective of whether the *cis*-chloroaquo complex is formed from the *cis*- or *trans*-(*RR,SS*)-dichloro substrate.

The first stage of the reaction, therefore, corresponds to the aquation of *trans*-(*RR,SS*)-Co(2,3,2-tet)-Cl<sub>2</sub><sup>+</sup>. The change in optical density at 520 mμ is large and, once a steady state is set up, follows a first-order rate law. The presteady-state behavior, which will be discussed below, makes it possible to say something of the steric course of this process. The spectrophotometric first-order rate constants are listed in Table II.

TABLE II  
FIRST-ORDER-RATE CONSTANTS FOR THE  
AQUATION OF *trans*-(*RR,SS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup>  
IN DILUTE PERCHLORIC ACID

Temp, °C	Ionic strength, <i>M</i>	pH	10 <sup>3</sup> <i>k</i> , sec <sup>-1</sup>
21.3	0.104	2.0	1.5
25.0	0.061	1.25	2.3
25.2	0.014	2.0	2.5
25.2	0.014	2.0	2.9
25.0	0.005	3.0	2.1
30.7	0.014	2.0	6.0
35.0	0.014	2.0	11.1
40.0	0.014	2.0	22.6
45.1	0.014	2.0	32.1

The value for *D*<sub>∞</sub> was determined at pH 1 (after 10 half-lives) and used as a calculated "infinity" at higher pH. The data at pH >3 become progressively less accurate because of increasing interference from the pH-dependent second stage.

(3) **Aquation of *cis*-[Co(2,3,2-tet)Cl<sub>2</sub>]Cl [Presumably *β*-(*RR,SS*)]**.—As with the *trans*-(*RR,SS*)-dichloro complex, two spectrophotometrically distinct changes can be observed. The first can be shown to correspond to the aquation of one of the chlorines. The second stage is the same as the *cis*-(*RR,SS*) → *trans*-(*RS*) isomerization that was mentioned above.

At pH ≤ 3, the first stage is characterized by isosbestic points at 516 and 444 mμ; at pH < 2 the second stage is too slow to interfere and the first-order rate constants were obtained from the very large change of optical density at 340 mμ. At pH ≥ 3, interference from the second stage is very marked and it was necessary to follow the aquation at 590 mμ which is an isos-

bestic point for the second step. With further increase in pH, the reaction takes on the properties of a single-stage reaction with isosbestic points at 474 and 431 mμ (since the second stage is very much faster than the first). The first-order rate constants for the aquation steps are collected in Table III.

TABLE III  
FIRST-ORDER RATE CONSTANTS FOR THE  
AQUATION OF *β*-*cis*-(*RR,SS*)-[Co(2,3,2-tet)Cl<sub>2</sub>]Cl  
IN DILUTE NITRIC ACID

Temp, °C	Ionic strength, <i>M</i>	pH	10 <sup>3</sup> <i>k</i> , sec <sup>-1</sup>
11.4	0.011	2.00	0.165
17.2	0.011	2.00	0.382
20.4	0.011	2.00	0.614
25.0	0.105	1.0	1.2
25.0	0.011	2.0	1.1
25.0	0.005	3.0	1.1
25.0	0.011	5.12 <sup>a</sup>	2.2
25.0	0.011	5.75 <sup>a</sup>	1.9
30.7	0.011	2.00	2.52
35.8	0.011	2.00	4.51

<sup>a</sup> In 2,6-lutidine-nitric acid buffer.

(4) **The Mercuric Ion Catalyzed Aquation of *trans*-(*RS*)-[Co(2,3,2-tet)Cl<sub>2</sub>]Cl**.—The addition of excess mercuric perchlorate to an acid aqueous solution of the *trans*-(*RS*)-dichloro complex causes precisely the same spectral changes as the spontaneous aquation, but at a much faster rate. However, the reaction does not stop when one chloride is displaced, and a slower subsequent reaction, with isosbestic points at 412 and 579 mμ, corresponding to the otherwise unobserved loss of the second chlorine to form *trans*-(*RS*)-Co(2,3,2-tet)-(H<sub>2</sub>O)<sub>2</sub><sup>3+</sup>, can be seen.

In the presence of excess Hg<sup>2+</sup> the spectrophotometric change follows a first-order rate law and the pseudo-first-order rate constants for the two steps, measured at 520 and 530 mμ, respectively, are collected in Table IV.

TABLE IV  
FIRST-ORDER RATE CONSTANTS FOR  
Hg<sup>2+</sup>-CATALYZED AQUATION OF *trans*-(*RS*)-  
[Co(2,3,2-tet)Cl<sub>2</sub>]Cl AT 25.0°

[Hg <sup>2+</sup> ], <i>M</i>	10 <sup>3</sup> <i>k</i> <sub>1</sub> <sup>a</sup> , sec <sup>-1</sup>	10 <sup>3</sup> <i>k</i> <sub>2</sub> <sup>b</sup> , sec <sup>-1</sup>	<i>k</i> <sub>1</sub> /[Hg], <i>M</i> <sup>-1</sup> sec <sup>-1</sup>	10 <sup>3</sup> <i>k</i> <sub>2</sub> /[Hg], <i>M</i> <sup>-1</sup> sec <sup>-1</sup>
0.015	3.7	...	0.25	...
0.020	4.7	...	0.24	...
0.025	6.0	...	0.24	...
0.050	12.0	0.25	0.24	5.0
0.10	...	0.48	...	4.8
0.25	...	1.64	...	6.5
0.40	...	2.15	...	5.4
0.75	...	5.2	...	6.9

<sup>a</sup> pH 1.0 and ionic strength 0.15. <sup>b</sup> pH 0.0 and ionic strength 4.0.

(5) **The Mercuric Ion Catalyzed Aquation of *trans*-(*RR,SS*)-[Co(2,3,2-tet)Cl<sub>2</sub>]ClO<sub>4</sub>**.—In the presence of excess Hg<sup>2+</sup> not only is the aquation of the coordinated chloride accelerated, but other features of the reaction, which were either obscured or prevented in the spontaneous reaction, become apparent. Four separate changes have been identified. The first, which

is rapid, is characterized by isosbestic points at 589, 461, 414, and 359  $m\mu$ . The change in optical density at 520  $m\mu$  is large enough to permit accurate determination of rate constants but is complicated by further changes at this wavelength corresponding to the second stage of the reaction. In the range of  $[Hg^{2+}]$  used, the process is first order in the complex and the first-order rate constants could be determined by Guggenheim's method under conditions where the second step did not interfere. The rate constant for the second step was determined in the usual way from absorbance data at 520  $m\mu$ . These constants are collected in Table V, where it will be seen that the first step is linearly proportional to  $[Hg^{2+}]$  whereas the second step is independent of  $[Hg^{2+}]$ .

TABLE V

PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE  $Hg^{2+}$ -INDUCED AQUATION OF *trans*-(*RR,SS*)- $Co(2,3,2-tet)Cl_2^+$  IN DILUTE PERCHLORIC ACID AT pH 0, IONIC STRENGTH ( $NaClO_4$ ) = 1.6, AND  $[COMPLEX] = 2 \times 10^{-3} M$

$[Hg^{2+}]$ , $M$	Temp, °C	$10^3k_1$ , sec $^{-1}$	$10^3k_2$ , sec $^{-1}$	$k_1/[Hg^{2+}]$ , $M^{-1} sec^{-1}$
0.005	11.5	5.0	...	1.00
0.010	11.5	9.3	...	0.93
0.015	11.5	15	...	1.00
0.020	11.5	21	...	1.05
0.025	11.5	24.5	...	0.98
0.050	11.5	51.4	...	1.03
0.100	11.5	96	...	0.96
0.005	25.0	15.8	3.6	3.2
0.0075	25.0	24	3.4	3.2
0.010	25.0	36	4.0	3.6
0.015	25.0	51	4.3	3.4
0.020	25.0	...	3.8	...

At 0.02  $M$  mercuric perchlorate, the first step is some 20 times faster than the second and it has been possible to measure the spectrum of the first reaction product. This is shown in Figure 1 together with the spectrum of the product at the end of the second stage of the reaction. This is identical with that observed when one chloride has been displaced from  $\beta$ -*cis*-(*RR,SS*)- and *trans*-(*RR,SS*)- $Co(2,3,2-tet)Cl_2^+$  under noncatalyzed conditions and is likely to be that of  $\beta$ -*cis*-(*RR,SS*)- $Co(2,3,2-tet)ClH_2O^{2+}$  (either or both stereoisomers). It has not been possible to determine the spectrum of *trans*-(*RR,SS*)- $Co(2,3,2-tet)ClH_2O^{2+}$  but that of the (*RS*) isomer is readily available and is also shown in Figure 1. From experience with the dichloro complexes, it is not likely that the two spectra will be greatly different.

It is clear then that the spectrum of the first product is close to that of a mixture of  $\beta$ -*cis*- and *trans*- $Co(2,3,2-tet)ClH_2O^{2+}$  containing about 70% of the *cis* isomer and that the second, mercuric-independent, spectrophotometric change corresponds to the isomerization of the remaining *trans*-chloroaquo complex to the  $\beta$ -*cis* form.

At higher  $[Hg^{2+}]$  concentrations (0.1–1.0  $M$ ) two more spectrophotometric changes can be observed. The third stage is characterized by isosbestic points at 520, 436, 372, and 342  $m\mu$  and is conveniently followed at 560  $m\mu$ . The first-order rate constants are collected

in Table VI, where it can be seen that this step is first order in  $[Hg^{2+}]$ . The final stage is characterized by isosbestic points at 560, 445, 388, and 348  $m\mu$  and the first-order rate constants measured at 494  $m\mu$  are also collected in Table VI. This process is independent of  $[Hg^{2+}]$ .

TABLE VI

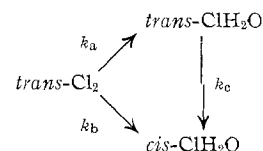
PSEUDO-FIRST-ORDER RATE CONSTANTS FOR THE THIRD AND FOURTH STAGES OF THE  $[Hg^{2+}]$ -INDUCED AQUATION OF *trans*-(*RR,SS*)- $Co(2,3,2-tet)Cl_2^+$  AT 25.0°, pH 0, AND  $\mu = 4.0$

$[Hg^{2+}]$ , $M$	$10^3k_3$ , sec $^{-1}$	$10^3k_4$ , sec $^{-1}$	$k_3/[Hg^{2+}]$ , $M^{-1} sec^{-1}$
0.10	0.50	5.1	0.050
0.25	1.05	5.1	0.042
0.40	2.0	...	0.050
0.50	2.5	5.1	0.050
0.75	3.8	5.5	0.051
1.00	5.2	5.3	0.052

These two processes, which probably comprise (1) the  $Hg^{2+}$ -catalyzed aquation of the  $\beta$ -*cis*- and *trans*-chloroaquo mixture and (2) the subsequent isomerization of the *trans*-(*RR,SS*)-diaquo to the  $\beta$ -*cis*-diaquo complex, will be considered in more detail elsewhere.

(6) **Steric Course of Aquation of *trans*-(*RR,SS*)- $Co(2,3,2-tet)Cl_2^+$ .**—In view of the fact that the rate constant for the isomerization of *trans*-(*RR,SS*)- $Co(2,3,2-tet)H_2OCl^+$  to the  $\beta$ -*cis* form is some 13 times faster than the rate of aquation of the *trans*-dichloro complex, there is little hope in obtaining accurate data for the steric course of aquation. Nevertheless, in the spectrophotometric studies of the aquation at 520  $m\mu$  it was clear that at the earliest stage of the reaction the optical density change was lagging behind a first-order behavior. Since, at this wavelength, the extinction coefficients of the *trans*-dichloro and *trans*-chloroaquo species are small (6.2 and 19  $M^{-1} cm^{-1}$ , respectively), compared to that of the *cis*-chloroaquo species (85  $M^{-1} cm^{-1}$ ), it seemed that this behavior might be due to the initial formation of some *trans*-(*RR,SS*)- $Co(2,3,2-tet)ClH_2O^{2+}$ . The extinction coefficient change at 25° for the first 25% of the aquation is shown in Figure 2.

The aquation and isomerization process was treated according to the sequence



Whence at time  $t$

$$\begin{aligned}
 [\textit{trans}\text{-}Cl_2]/A_0 &= F_1 = e^{-(k_a+k_b)t} \\
 [\textit{trans}\text{-}ClH_2O]/A_0 &= F_2 = \frac{k_a}{k_c - (k_a + k_b)} \left( e^{-(k_a+k_b)t} - e^{-k_c t} \right) \\
 [\textit{cis}\text{-}ClH_2O]/A_0 &= F_3 = 1 - \frac{k_c - k_b}{k_c - (k_a + k_b)} e^{-(k_a+k_b)t} + \\
 &\quad \frac{k_a}{k_c - (k_a + k_b)} e^{-k_c t}
 \end{aligned}$$

where  $A_0$  is the initial concentration of the complex. Experimental curves were determined for  $\epsilon$  as a function

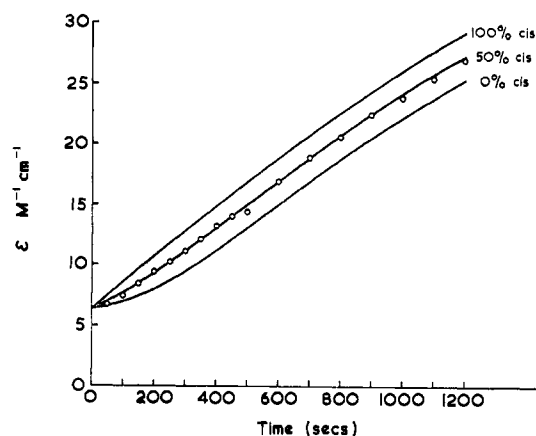


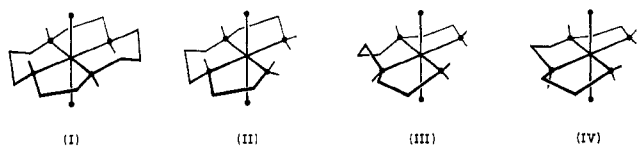
Figure 2.—Time dependence of the extinction coefficient at 520  $m\mu$  of a solution of *trans*-(*RR,SS*)-[Co(2,3,2-tet)Cl<sub>2</sub>]ClO<sub>4</sub> in 0.01 *M* HClO<sub>4</sub>, at 25.0° (O), together with curves calculated for 0, 50, and 100% initial formation of the *cis*-chloroaquo complex.

of time where  $\epsilon = (\text{optical density})/A_0l = \epsilon_1F_1 + \epsilon_2F_2 + \epsilon_3F_3$ ;  $\epsilon_1$ ,  $\epsilon_2$ , and  $\epsilon_3$  are the molar extinction coefficients of the three species *trans*-Cl<sub>2</sub>, *trans*-ClH<sub>2</sub>O, and *cis*-ClH<sub>2</sub>O at 520  $m\mu$ , and  $l$  is the length of the light path (4 cm). For the reaction at 25°  $k_a + k_b = 2.9 \times 10^{-4} \text{ sec}^{-1}$  and  $k_o = 3.8 \times 10^{-3} \text{ sec}^{-1}$ . The three curves shown in Figure 2 are for  $k_b = 0$  (i.e., 100% *trans*),  $k_b = k_a$  (i.e., 50% *trans*), and  $k_a = 0$  (i.e., 0% *trans*).

Within the limits of the experiment it would appear that, on aquation, *trans*-(*RR,SS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup> yields 50 ± 20% *cis*- (presumably  $\beta$ -*cis*-) chloroaquo product.

### Discussion

The main advantage of using 1,4,8,11-tetraazaundecane (2,3,2-tet) as the garland quadridentate is the existence of the two *trans*-dichloro isomers derived from the (*RS*) and (*RR,SS*) forms of the ligand. The (*RS*)-2,3,2-tet complex (II) is best looked upon as an open-



chain analog of the cyclic quadridentate (1,4,8,11-tetraazacyclotetradecane) complex (I)<sup>9,10</sup> whereas the (*RR,SS*) form (III) is clearly analogous to the only isolated *trans*-dichloro complex of triethylenetetramine (IV). Here the (*RR,SS*) racemate has been resolved and the (*SS*) form has been studied separately.

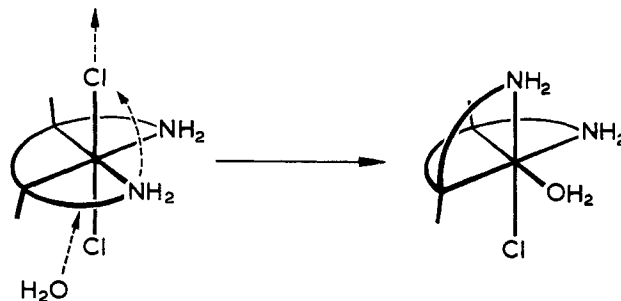
We find that the general kinetic and stereochemical features of the aquation reactions of these structurally related pairs reflect this similarity. Thus, the (cyclam)-Cl<sub>2</sub> and (*RS*)-(2,3,2-tet)Cl<sub>2</sub> complexes are relatively inert, have entropies of activation not far from zero (Table VII), and undergo aquation with complete retention of configuration, whereas the (*RR,SS*)-

(9) Although the structure of this *trans* isomer has not yet been reported there is evidence<sup>3,10a</sup> to suggest that the Co(III) complex has a structure similar to that of Ni(cyclam)Cl<sub>2</sub><sup>10b</sup> which is represented as I.

(10) (a) B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965); (b) B. Bosnich, R. Mason, P. J. Pauling, C. B. Robertson, and M. L. Tobe, *Chem. Commun.*, 97 (1965).

(2,3,2-tet)Cl<sub>2</sub> and (*RR,SS*)-(trien)Cl<sub>2</sub> complexes are considerably more labile, have much larger entropies of activation, and aquate with considerable stereochemical change.

The assignment of mechanism to these aquations deserves some consideration. Sargeson<sup>6</sup> has suggested that the stereospecific aquation of *trans*-(*SS*)-Co-(trien)Cl<sub>2</sub><sup>+</sup> is best explained in terms of a bimolecular attack by water, accompanied by an edge displacement of a terminal primary amine group



This is an attractive rationalization of the observation that each act of aquation leads to the  $\beta$ -*cis* isomer in which the water is *trans* to a secondary amine nitrogen but does not explain why this reaction does not occur with *trans*-Co(en)<sub>2</sub>Cl<sub>2</sub><sup>+</sup> or, as we now see, with the much more similar *trans*-(*RR,SS*)-Co(2,3,2-tet)Cl<sub>2</sub><sup>+</sup>. In both of these cases there is some *trans* product (Table VII); we cannot comment on the isomeric composition of the  $\beta$ -*cis*-chloroaquo complex in the latter case.

We wish to consider an alternative explanation which has the virtue of being generally applicable. It has been pointed out elsewhere<sup>11</sup> that, in the aquation of complexes of the type *trans*-MLACl<sup>n+</sup>, where L can be one quadridentate tetramine or two bidentate diamines, M either Co(III) or Rh(III), and A any of a number of monodentate ligands, those aquations accompanied by stereochemical change are invariably associated with a higher entropy of activation than those proceeding with retention of configuration. It was proposed that all of these reactions were essentially dissociative and that the lower entropy of activation and retention of configuration were associated with a square-pyramidal intermediate whereas the higher entropy of activation and stereochemical change arose from a trigonal-bipyramidal intermediate. The major objections to a trigonal-bipyramidal intermediate in the aquation of *trans*-(*SS*)-Co(trien)Cl<sub>2</sub><sup>+</sup> were (a) the stereospecific nature of the aquation and (b) the totally different steric courses of the spontaneous and mercury-induced aquation. Thus, even though the configurations of the secondary nitrogens do restrict the possible trigonal-bipyramidal forms, one might expect, at first sight, that in the form with the remaining chloride in the trigonal plane, Figure 3, there are three paths open for the entry of water: (1) that leading to the *trans*-chloroaquo product, (2) that leading to a  $\beta$ -*cis* product with the water *trans* to the secondary nitrogen, and (3) that leading to the  $\beta$ -*cis* product with water *trans* to the primary

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

TABLE VII  
RATE CONSTANTS, ACTIVATION PARAMETERS, AND STERIC COURSES FOR THE AQUATION OF SOME DICHLORO  
QUADRIDENTATE TETRAMINE COMPLEXES OF COBALT(III)

Ligand	$k_{23}^0$ , sec <sup>-1</sup>	$\Delta H^\ddagger$ , kcal mol <sup>-1</sup>	$\Delta S^\ddagger$ , cal deg <sup>-1</sup> mol <sup>-1</sup>	% retention of configuration
<i>trans</i> Complexes				
( <i>RSSR</i> )-cyclam	$1.1 \times 10^{-6}$	24.6	-3	100 <sup>a</sup>
( <i>RS</i> )-2,3,2-tet	$1.5 \times 10^{-5}$	24.3	+1	100 <sup>b</sup>
( <i>RR,SS</i> )-2,3,2-tet	$2.9 \times 10^{-4}$	25.9	+12	$50 \pm 20$ <sup>b</sup>
( <i>SS</i> )-trien	$3.5 \times 10^{-3}$	25.5	+16	0 <sup>c</sup>
<i><math>\beta</math>-cis</i> Complexes				
( <i>RRRR,SSSS</i> )-cyclam	$1.6 \times 10^{-2}$	18.3	-6	100 <sup>d</sup>
( <i>RR,SS</i> )-2,3,2-tet	$1.1 \times 10^{-3}$	22.3	+2	100 <sup>b</sup>
( <i>SS</i> )-trien	$1.5 \times 10^{-3}$	20.3	-3	100 <sup>c</sup>

<sup>a</sup> Reference 2. <sup>b</sup> This work. <sup>c</sup> Reference 6. <sup>d</sup> Reference 3.

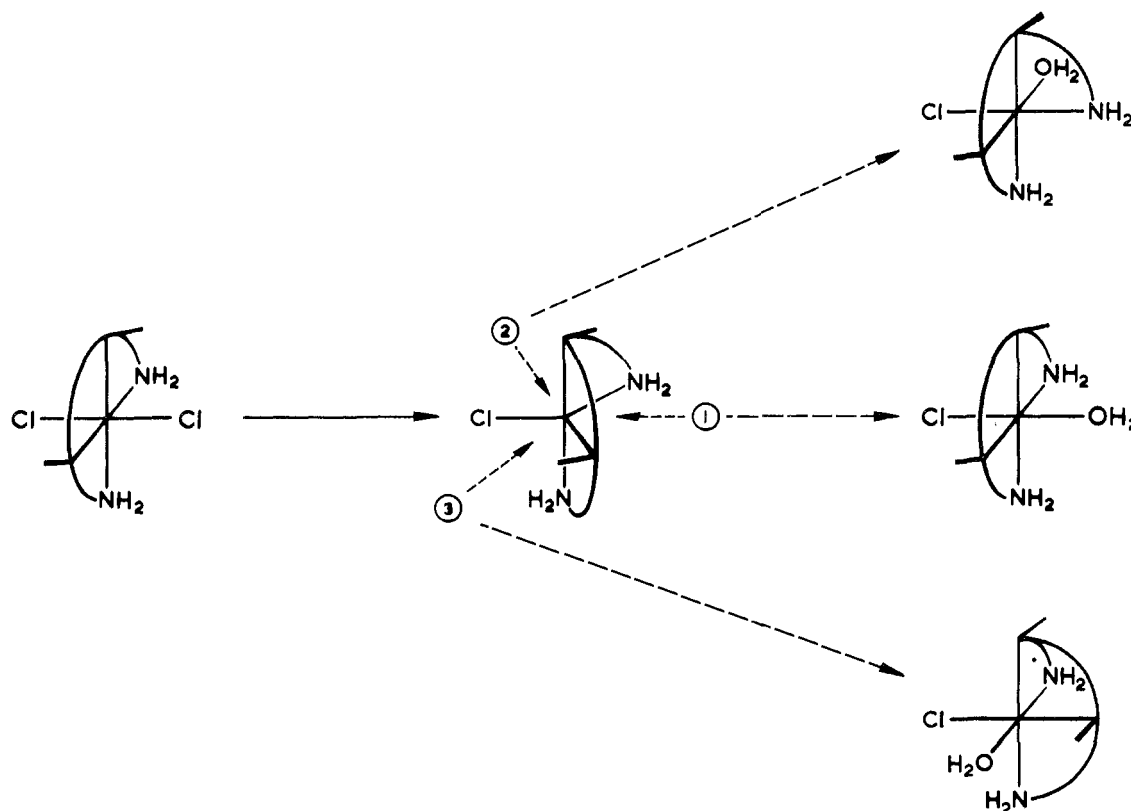


Figure 3.

nitrogen. However, examination of space-filling models shows that these paths are far from equivalent. Path 1 requires the incoming water to "push" against the strain that was released when the original chloride was expelled. Path 2 requires the incoming water to enter at the side that is rich with "hydrophilic" amine protons. Path 3, on the other hand, requires the water to enter at the side that is blocked by "hydrophobic"  $\text{CH}_2$  protons. It is not surprising, therefore, that path 2 predominates. The relative rates of aquation and isomerization would make it easy to detect significant amounts of *trans* isomer in the initial product but studies of the optical density changes at the early part of the reaction enable us to confirm Sargeson's statement<sup>6</sup> that no significant amount of *trans*-chloro-aquo complex is formed in the aquation.

The presence of the extra carbon atom in the 2,3,2-tet

ligand reduces the steric restriction on the formation of the *trans*-chloro-aquo complex. However, the "hydrophilic" and "hydrophobic" sides remain and one would predict that the  *$\beta$ -cis* part of the product should consist entirely of the isomer with the water *trans* to the secondary nitrogen. Unfortunately, we have not been able to characterize this product in sufficient detail to examine this point.

The steric course of the mercuric ion induced aquation of the *trans*-(*RR,SS*)- $\text{Co}(2,3,2\text{-tet})\text{Cl}_2^+$  cation is essentially similar to that of the spontaneous aquation. The experimental errors do not allow us to say whether they are identical, as may be the case for the *trans*- $\text{Co}(\text{en})_2\text{Cl}_2^+$  system,<sup>12</sup> but identity would only be expected if the five-coordinate intermediate lived long enough to equilibrate its solvation environment and lose

(12) A. M. Sargeson, *Australian J. Chem.*, **17**, 385 (1964).

all memory of its origin. It has often been assumed that a fundamental criterion for the demonstration of a five-coordinate intermediate is that the steric course<sup>18</sup> and all other consequences of the subsequent reaction of the reactive intermediate (discrimination, competition, etc.) are independent of the nature of the leaving group, but, while this provides an operational definition of a dissociative mechanism that is readily open to experimental examination, it diverts attention from the mechanistically important part of the process, namely, the transition state for the slow step. A five-coordinate intermediate whose lifetime is so short that it combines with a component of the environment that it inherited from the parent substrate before this environment can fully reequilibrate is as much the product of a dissociative reaction as the longer lived species. In such a case

(13) D. A. Loeliger and H. Taube, *Inorg. Chem.*, **5**, 1376 (1966).

one would expect to find that the reactions of the intermediate were influenced by the nature of the leaving group.

The considerable difference between the steric courses of the spontaneous and mercuric ion induced reactions of the *trans*-(*SS*)-Co(trien)Cl<sub>2</sub><sup>+</sup> cation is extremely difficult to understand in the light of the normal behavior of the 2,3,2-tet analog. It is possible that the steric crowding and the subsequent loosening of the chloride by the attachment of Hg<sup>2+</sup> is sufficient to cause dissociation without conjugative assistance from the *trans* chloride so that the trigonal bipyramid need not be formed. The square pyramid as suggested by Sargeson<sup>12</sup> would lead to substitution with retention of configuration.

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## The Relationship between Base Hydrolysis and Racemization at the Asymmetric Nitrogen Center in Cobalt(III) Complexes of 4-(Aminoethyl)-1,4,7,10-tetraazadecane. $\pi$ Stabilization in the SN1CB Intermediate

BY D. A. BUCKINGHAM, P. A. MARZILLI, AND A. M. SARGESON

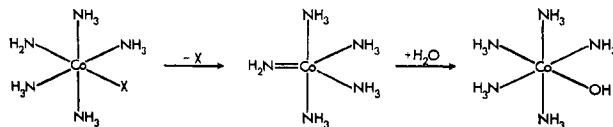
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The structures of *sym*-Co(trenen)Cl<sup>2+</sup>, *sym*-Co(trenen)N<sub>3</sub><sup>2+</sup>, and *sym*-Co(trenen)OH<sub>2</sub><sup>3+</sup> ions [trenen = 4-(aminoethyl)-1,4,7,10-tetraazadecane] are assigned along with the base hydrolysis and racemization rate constants of the optically active complexes. For the hydrolysis of the chloro complex some racemization occurs in the deprotonated reactant and in the hydroxo product. For the intervening steps, however, the reaction occurs with retention of configuration. This result eliminates for this complex the possibility of an sp<sup>2</sup> N center Co=N< *trans* to the leaving group. The general validity of  $\pi$  stabilization of the five-coordinate intermediate is discussed. The results also imply that inversion and conformational interchange are synchronous.

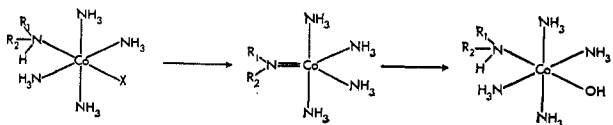
### Introduction

In the past few years the evidence in favor of the SN1CB mechanism for the base hydrolysis of substituted cobalt(III)-ammine type complexes has been substantial.<sup>1-3</sup> Competition and stereochemical studies have established some of the properties of the intermediates of reduced coordination number<sup>2,3</sup> but their stereochemistry is still obscure. In the original proposal for this mechanism Basolo and Pearson<sup>4</sup> accounted for the rapid rate of base hydrolysis (relative to aquation of ions of the same charge as the deprotonated reactant) by invoking the possibility of  $\pi$  bonding in the reaction intermediate: "This  $\pi$  bonding is of the type in which electrons move from ligand to metal" by overlap of a filled p orbital on the deprotonated N center with the vacant d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbital on cobalt. The movement aids

the loss of leaving group and stabilizes the five-coordinate intermediate



The proposal can be tested provided the center at which deprotonation occurs is optically active. The mode of stabilization of the intermediate requires the N center to adopt an sp<sup>2</sup> configuration with a plane of symmetry and the resulting hydroxo product must be racemic.



Recently three complexes have been prepared<sup>5</sup> which have the required asymmetry to test this proposal,

(5) P. A. Marzilli, to be submitted for publication.

(1) F. Basolo and R. G. Pearson "Mechanisms of Inorganic Reactions," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1967.

(2) M. Green and H. Taube, *Inorg. Chem.*, **2**, 948 (1963).

(3) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Am. Chem. Soc.*, **90**, 6654 (1968).

(4) R. G. Pearson and F. Basolo, *ibid.*, **78**, 4878 (1956).