ments for the nickel monoanions in crystalline samples.[6,9a] We are undertaking a complete structure determination of the cobalt complex to ascertain whether there is any pronounced dimerization present in the solid. However, even an arrangement similar to that in the copper case does not preclude the existence of dimeric dianions in solution. The apparent paradox of the different spin states of the cobalt species can now, at least qualitatively, be understood to be due to spin pairing in the dimer and is not simply due to a[18] smaller separation between the $\pi(yz)$ and $\pi(x^2 - y^2)$ orbitals in the toluene-3,4-dithiol complexes. The explanation of the diamagnetism of $[\{CoS_4C_4(CF_3)_4\}_2]$ and some of the related reactions associated with these dimeric units will clearly have to be postponed until the electronic structures of the dimeric units are understood.

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Substitution Reactions of Metallic Complexes of β,β′,β′′-Triaminotriethylamine. II. Kinetics of Aquation of *cis*-Dibromo(triaminotriethylamine)cobalt(III) Ion[1]

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The kinetics of the aquation of *cis*-$[Co(tren)Br_2]^+$ have been investigated in 0.1 *M* $HClO_4$ at 20.0, 25.0, 30.0, 35.0, and 40.0°. The pseudo-first-order rate constant for the release of one bromide ion at 25.0° was found to be 2.81×10^{-2} sec.$^{-1}$ The primary aquation rate constant, k_1, is independent of the initial concentration of the complex over the range 5.0–7.5 m*M*, of pH from 1.0 to 6.0, and of ionic strength from 0.0038 to 1.60. The Arrhenius activation energy is 15.1 kcal mole^{-1} and ΔS^* is -14.8 cal deg^{-1} mole^{-1}. Added sulfate ion accelerates the aquation. A value for the secondary aquation rate constant, $k_2 = 1.55 \times 10^{-6}$, for the loss of the second bromide ion has also been determined.

Introduction

An extensive amount of kinetic data has been reported for substitution reactions in octahedral complexes for the type $[MA_4XY]^{1+ \text{ or } 2+}$ where M has been Co(III), Cr(III), or Ir(III) and A represents a nonreplaceable ligand, which may be monodentate or polydentate, including N- and/or C-substituted polyamines. The ligands X and Y, with X representing the replaceable group, may be F, Cl, Br, OH, H_2O, or NH_3, although most commonly X has been Cl, Br, or F.[2]

A recent study of the aquation of the $[Co(tren)Cl_2]^+$ ion (tren = β,β′,β′′-triaminotriethylamine) showed its aquation rate to be greater than that of complex ions containing certain other organic amines.[1] It was assumed that the greater rate at which *cis*-$[Co(tren)Cl_2]^+$ aquated was attributable simply to steric strains produced by the peculiar geometry of the complex.[1] The purpose of the present investigation was to test this assumption by determining the rate constant and Arrhenius parameters for the first step of aquation of *cis*-$[Co(tren)Br_2]^+$ ion. In addition, we have also measured the second step of aquation for this cation.

The aquation reaction in 0.1 *M* acid solution takes place in two over-all steps

$$cis\text{-}[Co(tren)Br_2]^+ + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} cis\text{-}[Co(tren)BrH_2O]^{2+} + Br^- \quad (1)$$

$$cis\text{-}[Co(tren)BrH_2O]^{2+} + H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} cis\text{-}[Co(tren)(H_2O)_2]^{3+} + Br^- \quad (2)$$

Reaction 1 proceeds at a much greater rate than forward reaction 2, so that no serious interference is caused by forward reaction 2 in the study of reaction 1. Under the conditions of the experiments reported here, equilibrium was not observed either in reaction 1 or 2.

Experimental Section

Preparation of Compounds.—β,β′,β′′-Triaminotriethylamine trihydrochloride was synthesized according to a procedure outlined by Liu.[3]

***cis*-Carbonatotetraamminecobalt(II) Nitrate Hemihydrate.**—This compound was prepared by the method described by Schlessinger.[4]

***cis*-Dichloro(triaminotriethylamine)cobalt(III) Chloride.**—Described in a previous paper.[1]

***cis*-Dibromo(triaminotriethylamine)cobalt(III) Bromide.**—The new complex was prepared by adding a solution of 6.4 g of triaminotriethylamine trihydrochloride in 50 ml of water to 3.15 g

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(1) Part I: S. K. Madan, W. M. Reiff, and J. C. Bailar, Jr., *Inorg. Chem.*, **4**, 1366 (1965).

(2) For review see D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 78.

(3) C. F. Liu, Doctorate Dissertation, University of Illinois, 1957.

(4) G. Schlessinger, *Inorg. Syn.*, **6**, 173 (1960).

of lithium hydroxide monohydrate. This solution was added to a solution of 6.45 g of $[Co(NH_3)_4CO_3]NO_3\cdot 0.5H_2O$ in 150 ml of water. With a small amount of charcoal as catalyst, the mixture was refluxed on a steam bath for 48 hr, after which no more ammonia gas could be detected. The mixture was filtered and the solution was evaporated to a small volume on the steam bath. During evaporation, 25 ml of concentrated hydrobromic acid was added in small portions. The resulting solution was evaporated to dryness and a green crystalline residue was extracted with 100 ml of absolute alcohol five or six times to remove lithium chloride. The product weighed 4.0 g, which corresponds to a 52% yield. The product was recrystallized either from dilute (1:1) hydrobromic acid or from a dilute hydrobromic acid–alcohol mixture. The "green color" in the dibromocobalt(III)–tren complex does not necessarily mean that the complex has the *trans* configuration. Linhard and Weigel[5] report *cis*-$[Co(en)_2Br_2]^+$ to be a dichroic, dark olive-green solid. Recently Buckingham[6] provided infrared evidence that the green *trans*-$[Co(trien)Br_2]Br$ isomer prepared by Selbin and Bailar[7] is mainly *cis*-α-contaminated by cis-β-$[Co(trien)Br_2]Br$. *Anal.* Calcd for *cis*-$[Co(tren)Br_2]Br$: C, 16.15; H, 4.05; N, 12.60. Found: C, 16.23; H, 3.94; N, 12.80.

Infrared Spectra.—Infrared spectra were obtained with a Perkin-Elmer Model 521 or 137 recording spectrophotometer. Spectra (4000–650 cm^{-1}) were obtained by using sodium chloride windows with Nujol mull smears.

Electronic Absorption Spectra.—The spectra in the visible region of various species were obtained with a Cary Model 14M recording spectrophotometer. Approximately millimolar solutions in an appropriate solvent were scanned in matched cells of 1-cm light path.

Kinetic Measurements. (a) Spectrophotometric Method.—The change in absorbance was followed with time, and the wavelength chosen for the study of this reaction was the one at which a substantial absorption difference occurs between the reactant and product. For instance, this difference between the dibromo complex and aquobromo complex occurs at 450 mμ, which was therefore the wavelength used to determine the rate of reaction 1. Reaction 1 was also followed at 600 and 650 mμ to confirm the assumption that no other unexpected side reactions were complicating the reaction. Measurements were made on a Cary Model 14M recording spectrophotometer using matched cells of 1-cm path length. The temperature was controlled to within ±0.05° by circulating thermostated water through the compartment surrounding the cells. The concentration of the complex in these runs was 3.6–13.0 m*M*. Experimental infinity absorptions were obtained after 7–8 half-lives.

Owing to the rapid rate of aquation of the dibromocobalt(III)–tren species ($t_{1/2}$ ~25 sec at 25°) and the relatively slow rate of dissolution of the complex, the concentration of each run could not be preset. A fixed weight of the complex could not be dissolved to give a solution of known molarity, since about 150 sec elapsed from time zero until all of the weighed sample dissolved.

To determine the concentration of dibromo species for each run, weighed samples of the solid complex were dissolved to give a definite volume of solution, and after 250 sec (the time when the first aquation step is virtually 100% complete) an A_∞ reading was taken for each sample at 450 mμ. The only complex present after 250 sec is the monoaquo species, since $k_1 \gg k_2$ and its concentration is the same as the concentration of the initial dibromo species would have been had dissolution been immediate. A plot of A_∞ at 450 mμ *vs.* concentration of complex yields a straight line.

In each kinetic run an estimated amount of complex was added to the thermostated solvent in a beaker and the contents were swirled vigorously for 5 sec. The undissolved complex was allowed to settle and the solution was decanted into the cell. The whole operation took about 20 sec from the time of addition of solid complex until the recording of the kinetic run began. The A_∞ of each run was then used with a Beer's law plot to determine concentrations.

(b) Conductometric Method.—The reaction was also followed conductometrically. For these measurements, an RC-18 Industrial Instruments conductance bridge equipped with 1000- and 3000-c signals and a cathode-ray oscillograph as the null detector were used. The conductance cell was immersed in a thermostat which was kept at 25.00 ± 0.02°. The concentration of the complex was approximately 5.0–7.5 m*M*. Measurements were made at pH 5.0 and data corresponding to that obtained with the spectrophotometric method were obtained. The reason for lowering the concentration of perchloric acid in the conductometric procedure was to improve the sensitivity of the method (perchloric acid having a very high specific conductance in aqueous solution) and to allow comparison of the two methods.

Results

Infrared spectral data for *cis*-$[Co(tren)Cl_2]Cl$, *cis*-$[Co(tren)Br_2]Br$, and other related complexes are given in Table I. In Table II and Figures 1 and 2 visible spectral data are given and compared with those for the corresponding tetraammine,[8] bis(ethylenediamine), trien, and cyclen compounds.

Table I

CH₂ Rocking Frequencies (cm^{-1}) of the Cobalt–Chelate Rings in the Infrared Spectra of Some Complexes of Cobalt(III)

cis-$[Co(en)_2ClOH]Cl^a$	874		892
cis-$[Co(en)_2NH_3H_2O]Br^a$	881		892
cis-α-$[Co(trien)Cl_2]Cl^b$	871		905
cis-β-$[Co(trien)Br_2]Br^b$	879		903
cis-$[Co(tren)Cl_2]Cl^c$	870		900
cis-$[Co(tren)Br_2]Br^c$	860		897
trans-$[Co(en)_2ClOH]Cl^a$		893	
trans-$[Co(trien)Cl_2]Cl^b$		912	

[a] Values from ref 9. [b] Values from ref 6. [c] This work.

Spectrophotometric data were plotted as log $(A_\infty - A_t)$ *vs.* t where A_∞ was recorded at a time corresponding to 7 or 8 half-lives and A_t is absorbance at time t. The plots yield a straight line. The conductometric data were plotted as log $(G_\infty - G_t)$ *vs.* time t, where G_∞ and G_t are the conductances in mhos at infinity and time t, respectively. Data in that form gave a straight line. Results show a relative error of approximately 1.0% between the two methods; at pH 5.0 and 25° in $HClO_4$, by the conductometric method a rate constant of 3.01×10^{-2} sec^{-1} was obtained *vs.* a rate constant of 2.98×10^{-2}, 3.01×10^{-2}, and 2.97×10^{-2} sec^{-1} at 450, 600, and 650 mμ, respectively, by the spectrophotometric procedure.

The specific rate constants for reactions 1 and 2, k_1 and k_2, respectively (found by the spectrophotometric procedure), are given in Table III for the conditions specified. In all cases, quadruplicate runs gave straight-line plots whose k_1 and k_2 values agreed within 4%. The average values of k_1 and k_2 were found to be 2.81×10^{-2} and 1.55×10^{-6} sec^{-1}, respectively.

Discussion

In a previous study[1] we had assumed that dichloro(triaminotriethylamine)cobalt(III)chloride had a

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(5) M. Linhard and W. Weigel, *Z. Anorg. Allgem. Chem.*, **271**, 101 (1952).

(6) D. A. Buckingham and D. Jones, *Inorg. Chem.*, **4**, 1387 (1965).

(7) J. Selbin and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **82**, 1524 (1960).

(8) The following abbreviations are used in this article: cyclen for 1,4,7,10-tetraazacyclododecane, tetraammine for four ammonia molecules in complexes of cobalt(III), and tetramine for any four nitrogen atoms attached to cobalt(III).

TABLE II

COMPARISON OF THE ELECTRONIC SPECTRA OF A SERIES OF *cis*-TETRAMINE COMPLEXES

Complex	Solvent	λ, mμ	ε, M^{-1} cm^{-1}	λ, mμ	ε, M^{-1} cm^{-1}	Ref
cis-[Co(NH$_3$)$_4$Cl$_2$]$^+$	H_2O	540	45	. . .	. . .	*b, c*
cis-[Co(en)$_2$Cl$_2$]$^+$	H_2O	530	78	380	69	*c*
	H_2O	535	100	390	78	*b, d*
cis-α-[Co(trien)Cl$_2$]$^+$	50% $HClO_4$	549	130	381	135	*e*
cis-[Co(en)$_2$Br$_2$]$^+$	H_2O	560	110	. . .	. . .	*f*
cis-[Co(cyclen)Cl$_2$]$^+$	30% HCl	560	185	390	165	*g*
cis-[Co(cyclen)Br$_2$]$^+$	40% HBr	570	180	390	170	*g*
cis-[Co(tren)Cl$_2$]$^+$ [a]	50% HCl	565	125	390	120	
cis-[Co(tren)Br$_2$]$^+$ [a]	40% HBr	570	133	380 sh	640	
cis-[Co(tren)BrH$_2$O]$^{2+}$ [a]	0.1 *M* $HClO_4$	555	138	380 sh	143	
cis-[Co(tren)(H$_2$O)$_2$]$^{3+}$ [a]	0.1 *M* $HClO_4$	505	107	350	99	

[a] Electronic spectra were measured at 25°; sh, shoulder. [b] J. P. Mathieu, *Bull. Soc. Chim. France*, **3**, 463 (1936). [c] R. C. Brasted and C. Hirayama, *J. Phys. Chem.*, **63**, 780 (1959). [d] F. Basolo, *J. Am. Chem. Soc.*, **72**, 4393 (1950). [e] G. H. Searle, Ph.D. Thesis, Australian National University, Canberra, A.C.T., Australia, 1963. [f] See ref 5. [g] See ref 10.

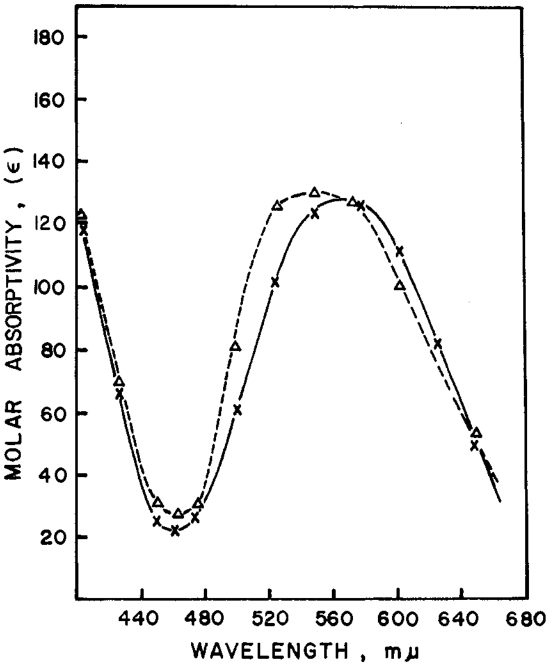

Figure 1.—Visible spectra of *cis*-[Co(tren)Cl$_2$]$^+$ (×) in 50% HCl and *cis*-[Co(trien)Cl$_2$]$^+$ (Δ) in 50% $HClO_4$.

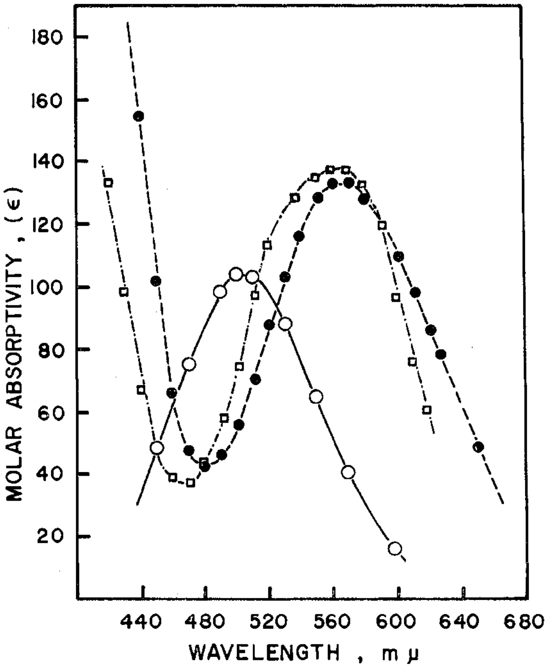

Figure 2.—Visible spectra of *cis*-[Co(tren)Br$_2$]$^+$ (●) in 40% HBr, *cis*-[Co(tren)BrH$_2$O]$^{2+}$ in 0.1 *M* $HClO_4$ (□), *cis*-[Co(tren)(H$_2$O)$_2$]$^{3+}$ in 0.1 *M* $HClO_4$ (○).

cis configuration because the tertiary nitrogen atom must be *trans* to a chloro group. The same assumption is also applicable to the dibromocobalt(III) complex. However, the dibromo complex was olive-green instead of violet, a color which is usually associated with a *cis* configuration, and this prompted us to examine the assignment of configuration of these complexes more thoroughly. We have therefore attempted to assign a *cis* configuration to these complexes on the basis of spectroscopic evidence. Recently Baldwin has carried out an extensive spectral examination of *cis*- and *trans*-[Co(en)$_2$Cl$_2$]X (X = Cl, Br, I, SCN, ClO_4, 0.5S_2O_4) compounds and has concluded that the most consistent variation between the infrared absorption spectra of *cis* and *trans* isomers of bis(ethylenediamine)-cobalt(III) complexes is in the 850–900-cm^{-1} region. This region is assigned to the CH_2 rocking frequency of the cobalt–ethylenediamine chelate ring.[9] Here, for complexes with simple and small anions, such as chloride or bromide, *cis* isomers show two bands and *trans* isomers one.[9] More recently Buckingham[6] has shown that infrared spectroscopy can be used to differentiate between *cis*-α, *cis*-β, and *trans* isomers of several cobalt(III) complexes of triethylenetetramine (trien), which is an isomer of tren. Infrared absorption measurements on [Co(tren)Cl$_2$]Cl and [Co(tren)Br$_2$]Br show that the band in the region of 850–900 cm^{-1} is split. The splitting of the band in this region arises either from the lower symmetry of the *cis* isomer or from the reduction of symmetry caused by the interactions between the amine protons and the anions in the crystal lattice.[9] The CH_2 rocking frequencies of the chelate rings in our complexes are shown in Table I; those for the *cis*- and *trans*-haloamine complexes are included for comparison. We conclude that our assignment of a *cis* configuration to the halotren complexes on the basis of infrared evidence, although not unambiguous, is reasonable.

The visible spectra show small shifts in the absorp-

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(9) M. E. Baldwin, *J. Chem. Soc.*, 4369 (1960).

tion maxima to longer or shorter wavelengths in the cobalt(III)–tren complexes; there is a close similarity in character and shape of the spectra of cobalt(III)–tren complexes to those of the *cis* isomers of other tetramine compounds. Based on this evidence, the monodentate ligands (chloride, bromide, or aquo) in these tren complexes can be assigned a *cis* configuration (Table II, Figures 1 and 2). Comparison of the visible spectra of a series of tetramine complexes reveals a remarkable change in the molar absorptivity (ϵ). Comparing the ligands in the order of four ammonias, two en, trien, tren, and cyclen, the ϵ values increase by a factor of about 4 in the *cis*-dichlorocobalt(II) complexes.[10] The theory has been proposed that the intensities of d–d transition are enhanced by increasing the asymmetry of the ligand field.[11] There is experimental support for this postulation.[12] It seems reasonable that the rise in values accompanying the more rigid tetramine ligands is caused by increasing distortion of the octahedral field. Each additional ethylene bridge would be expected to result in further steric constraint.[10]

Table III exhibits the rate of aquation as determined spectrophotometrically in perchloric acid under various conditions of pH, complex concentration, temperature, and added electrolyte. It is obvious from Table III that the rate is independent of the initial concentration, pH, and ionic strength over the range at which these variables were studied. The fact that rate is independent of ionic strength was not unexpected (*e.g.*, NaCl) since this behavior is typical for the reaction between a univalent cation and a neutral molecule in dilute solutions. It is certainly evident that sulfate ion in concentrations 5 times the initial complex concentration, or greater, tends to increase the aquation reaction. This observation can be rationalized by assuming that the *cis*-dibromo(triaminotriethylamine)cobalt(III) cation forms ion pairs with the sulfate anion, $[Co(tren)Br_2]^+SO_4^{2-}$, which induces the removal of the coordinated bromide ion by an SN1 dissociation type of mechanism.

The activation parameters for reaction 1 were calculated from a linear Arrhenius plot of log k_1 *vs.* $1/T$ over the range 20.0–40.0°. The rate constants determined over this range are shown in Table III. The activation parameters calculated from these data are: $\Delta H^* = 15.1$ kcal, $\Delta F^* = 19.5$ kcal, and $\Delta S^* = -14.8$ cal deg^{-1} mole^{-1}. Corresponding values for the acid hydrolysis of the dichloro complex $[Co(tren)Cl_2]^+$ are:[1] $\Delta H^* = 17.8$ kcal, $\Delta F^* = 20.9$ kcal, and $\Delta S^* = -10.4$ cal deg^{-1} mole^{-1}.

TABLE III

RATES OF ACID HYDROLYSIS OF *cis*-$[Co(tren)Br_2]^+$ UNDER VARIOUS CONDITIONS IN $HClO_4$

Concn of complex, m*M*	Temp, °C	Added electrolyte	Ionic strength	pH	10^2k_1, sec^{-1}
8.8	20.0	None	0.109	1	2.32
5.5	25.0	None	0.105	1	2.82[a]
6.8	30.0	None	0.107	1	5.31
12.0	35.0	None	0.112	1	7.88
6.8	40.0	None	0.107	1	9.54
5.5	25.0	None	0.105	1	2.81
7.5	25.0	None	0.108	1	2.84
8.0	25.0	None	0.018	2	2.78
6.0	25.0	None	0.0070	3	2.84
13.0	25.0	None	0.013	4	3.01
6.8	25.0	None	0.0068	5	2.98
3.8	25.0	None	0.0038	6	2.98
6.2	25.0	0.025 *M* $Ca(ClO_4)_2$	0.181	1	2.99
9.2	25.0	0.025 *M* $Zn(ClO_4)_2$	0.184	1	2.85
6.3	25.0	0.05 *M* NaCl	0.157	1	2.88
10.5	25.0	0.05 *M* Na_2SO_4	0.210	1	3.11
6.0	25.0	0.10 *M* Na_2SO_4	0.406	1	3.24
3.6	25.0	0.50 *M* Na_2SO_4	1.600	1	3.64

[a] At 25°, $k_2 = 1.55 \times 10^{-6}$ sec^{-1}.

Tobe and co-workers[13,14] have investigated the steric course of a large number of octahedral aquation reactions of the type $[Co(en)_2AX]^{n+}$ where X represents a replaceable ligand and A is the orienting ligand. In every case the aquation of the *cis* complexes appears to be stereospecific and only the *cis* isomer of the product is formed. However, in the case of *trans* complexes, aquation occurs with a steric change if the orienting ligand can transfer electrons to the metal in the transition state. Since the latter conditions prevail in most reactions which have been investigated, steric change is usually noticed in aquation of *trans* complexes of cobalt(III). Quinn and Garner[15] have reported similar results for *cis* isomers of chromium(III) complexes, but the relatively small number of *trans* isomers which have been examined thus far were found to produce predominantly or wholly *trans* product. The aquation product in the present study must assume a *cis* configuration because the steric property of the molecule is fixed, since the tertiary nitrogen atom must be *trans* to a bromo or aquo group. This indeed is the case, as shown in Figure 2 by the electronic absorption spectra. Therefore, it is quite reasonable to say that the stereospecific rule for *cis* complexes in this case is also followed. Chan and Tobe[13] also observed a five- to sixfold increase in the aquation rate when X is changed from Cl to Br. This observation is consistent with the results obtained in the present study, though in this case the increase in aquation rate is greater than tenfold.

On comparison of the aquation rate of *cis*-$[Co(en)_2Br_2]^+$ at 25° (1.04×10^{-3} sec^{-1})[16] to *cis*-$[Co(tren)Br_2]^+$ at 25° (2.81×10^{-2} sec^{-1}) it is observed that the rate of the latter ion is 27 times faster than the rate of the former ion. Previous studies[1] have indicated that the greater rate of aquation of *cis*-$[Co(tren)Cl_2]^+$ as compared with the rates of certain other organic amines[1] is probably due simply to steric strain produced by the peculiar geometry of the complex. The same conclusion may be drawn in regard to the *cis*-$[Co(tren)Br_2]^+$ ion.

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(10) J. P. Collman and P. W. Schneider, *Inorg. Chem.*, **5**, 1380 (1966).

(11) See, *e.g.*, F. Basolo, C. J. Balihausen, and J. Bjerrium, *Acta Chem. Scand.*, **9**, 810 (1955), or F. A. Cotton, "Chemical Application of Group Theory," Interscience Publishers, Inc., New York, N. Y., 1963, p 231.

(12) R. L. Belford and W. A. Yeranos, *Mol. Phys.*, **6**, 121 (1963); P. W. Schneider and H. Brintzinger, *Helv. Chim. Acta*, **47**, 1717 (1964).

(13) S. C. Chan and M. L. Tobe, *J. Chem. Soc.*, 5700 (1963).

(14) C. Ingold, R. S. Nyholm, and M. L. Tobe, *Nature*, **187**, 477 (1960).

(15) L. P. Quinn and C. S. Garner, *Inorg. Chem.*, **3**, 1348 (1964).

(16) W. F. Cain and J. A. Mclean, Jr., *ibid.*, **4**, 1416 (1965).