Substitution Reactions of Metallic Complexes of β,β',β''-Triaminotriethylamine. VIII. Kinetics of Acid Hydrolysis Reaction of the Chlorobromo(β,β',β''-Triaminotriethylamine)Cobalt(III) Ion

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The stoichiometry and kinetics of the acid hydrolysis reaction of $Co(tren)ClBr^+$ (tren = β,β',β''-triaminotriethylamine) in 0.1 M $HClO_4$ have been investigated. In the acid hydrolysis process the data are consistent with two parallel reactions, probably due to the presence of two isomers in the reactant. One reaction is the release of Cl^- in the α-isomer, and the other is the release of Br^- in the β-isomer. The pseudo-first-order rate constants for these reactions in 0.1 M $HClO_4$ at 25.0°C were found to be $3.21 \times 10^{-3} sec^{-1}$ (k_α) and 3.38×10^{-2} (k_β), respectively. Both rate constants were independent of the acid concentration below pH value 6, and independent of ionic strength from 0.10 to 0.15. Added sulfate ion accelerates the reaction rate. The activation enthalpies and entropies were calculated: $\Delta H_\alpha^* = 18.3 \pm 08$ kcal mol^{-1}, $\Delta H_\beta^* = 16.0 \pm 0.2$ kcal mol^{-1}; and $\Delta S_\alpha^* = -13.5 \pm 2.7$ cal $mol^{-1} deg^{-1}$, $\Delta S_\beta^* = -9.0 \pm 0.7$ cal $mol^{-1} deg^{-1}$. The relative rate constants ($k_\beta/k_\alpha = 10$) provide further evidence of the effect of steric strain and crowding on the reactivities of dihalo cobalt(III) tren complexes.

Introduction

In this laboratory, we have studied the kinetics of reactions of octahedral β,β',β''-triaminotriethylamine cobalt(III) complexes, $Co(tren)X_2^+$ (X = F, Cl, Br,[2a,b,c] and tren = β,β',β''-triaminotriethylamine) and Co-$(tren)H_2OX^{2+}$ (X = Cl, Br).[2d,c]

The acid hydrolysis reactions of these tren-complexes were found to be faster than that of the reactions of other tetraamine cobalt(III) complexes presumably due to steric strains produced by the peculiar geometry of the tren-complexes. Furthermore, in the kinetic study of the acid hydrolysis reaction of the chloroaquo (triaminotriethylamine) cobalt(III) ion, two different reaction rates were observed, and the existence of two isomers of $Co(tren)H_2OCl^{2+}$, (i.e., α-isomer with the chloride *cis* to the tertiary ni-

trogen of the tren ligand, and β-isomer with the chloride *trans* to the tertiary nitrogen of the tren ligand) was suggested.[2d]

The present investigation had two goals. The first was to see whether the primary substitution reaction of $Co(tren)X_2^+$ complexes was influenced by changing the homodihalo complexes to a mixed halogen complex due to the unequal ligand field strengths of the chloride and bromide ligands. The second aim was to obtain further evidence of the existence of the two isomers in $Co(tren)H_2OCl^{2+}$ by synthesizing Co(tren)-$ClBr^+$ from $Co(tren)H_2OCl^{2+}$. With these purposes in mind, the kinetics of the acid hydrolysis reactions of $Co(tren)ClBr^+$ have been investigated under various conditions of temperature, ionic strength, and acid concentration, and the data are compared with those of related systems.

Experimental Section

Materials: Deionized water and reagent grade chemicals were used in all procedures.

Preparation of Compounds: (1) β,β',β''-*Triaminotriethylamide:* This compound was prepared by the method of Paoletti, Ciompolini, and Sacconi.[3]

(2) *Carbonato(triaminotriethylamine) cobalt(III) perchlorate monohydrate:* The method of H.A. Sheidegger[4] was used for the preparation of this complex.

(3) *Dichloro(triaminotriethylamine)cobalt(III) chloride:* The preparation of this complex was described in an earlier paper.[2d]

(4) *Dibromo(triaminotriethylamine)cobalt(III) bromide:* The preparation of this complex was also described in an earlier paper.[5]

(5) Chloroaquo(triaminotriethylamine) cobalt(III) sulfate: The preparation of the complex was previously reported.[2d]

(6) Chlorobromo(triaminotriethylamine) cobalt(III)

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(2) a. S.K. Madan, W.M. Reiff, and J.C. Bailar, Jr., *Inorg. Chem.,* **4**, 1366 (1965); b. S.K. Madan and J. Peone, Jr., *ibid.,* **6**, 464 (1967); c. K. Kuo and S.K. Madan, *ibid.,* **10**, 229 (1971); d. W.V. Miller and S.K. Madan, *ibid.,* **10**, 1250 (1971); e. W.V. Miller and S.K. Madan, *ibid.,* **9**, 2362 (1970).

(3) P. Paoletti, M. Ciampolini, and L. Saconi, *J. Chem. Soc.,* 3589 (1963).
(4) H.A. Scheidegger, *Doctoral thesis,* L.T.H., Zurich, 1966.
(5) K. Kuo and S.K. Madan, *Inorg. Chem.,* **8**, 1580 (1969).

bromide: Cholroaquo (triaminotriethylamine) cobalt(III) sulfate monohydrate (0.414 g) was dissolved in 10 ml of water, and a slight excess of barium bromide dihydrate (1.23 g) was added to the solution. The fine $BaSO_4$ precipitate was removed by centrifugation. Enough acetone was added to the clear solution to form the precipitate of chloroaquo(triaminotriethylamine) cobalt(III) bromide. After the solution was cooled in an ice bath, the pink solid was collected on a filter and heated in an oven at 100°C until the color change from pink to greenish-blue was complete. The resulting product was washed with methanol and dried in vacuo at room temperature. *Analytical* calculated for [Co(tren)ClBr]Br: C, 18.00; H, 4.50; N, 14.00. Found: C, 18.28; H, 4.66; and N, 14.20. Yield 80%.

Electronic absorption spectra: All visible spectra from 700.0 nm - 350.0 nm reported here were obtained with a Cary 14M recording spectrophotometer using matched cells with 1 cm path length.

Kinetic measurements: The acid hydrolysis reaction of $Co(tren)ClBr^+$ was carried out with a Cary Model 14M recording spectrophotometer using matched cells of 1 cm length. The temperature was controlled to within ±0.05°C by circulating thermostated water through the compartment surrounding the cells. The primary wavelength used for the study of this reaction was 529.4 nm, at which a substantial absorption difference occurs between the reactants and products. Expanded slidewire was used for the absorbance measurements. Because of the relatively slow rate of dissolution of the complex and the rapid rate of aquation of $Co(tren)ClBr^+$, the following procedure was used. In each kinetic run, a thermostated 0.10 M $HClO_4$ (5 ml) was added to the chlorobromo complex (~0.01-0.005 g) in a flask, which is also thermostated. The solution was swirled vigorously for several seconds, and the dissolved complex was removed by decanting the solution into a spectrophotometric cell through filter paper. The pseudo-first-order rate constants were obtained from the slopes of the plots of ln $(A_\infty-A_t)$ *vs* t where A_∞ is the final absorbance reading and A_t is the absorbance at time t. However, a curvature was noted during the initial part of the reaction. By extrapolating the linear portion of the plot to t = 0 and plotting the difference between a point on the curve at time t, *i.e.* $(A_\infty-A_t)_{expt.} - (A_\infty-A_t)_{ext}$, *vs* t, the rate constant for the faster reacting isomer (β-isomer) can be obtained. This method is known to give greater accuracy[6] for mixtures having relatively large ratios of rate constants. Also, as the ratio of $[A]_0$ $[B]_0$ becomes closer to 1, the accuracy is increased.

After separating the two rates, the plots all gave straight lines for at least 3 half lives, and consecutive runs usually agreed to within 4%. The reaction was also followed at 410.0 nm, 456.5 nm, 620.0 nm, 650.0 nm at which the disappearance of the reactants was observed) and at 535.0 nm, 545.0 nm (at which the appearance of the products was observed) to confirm that no other unexpected side reactions were complicating the system. The results at different

wavelengths are all in good agreement with one another. At 456.5 nm, there is no absorbance change corresponding to the second reaction. Only the first reaction (β-isomer $\xrightarrow{k_\beta}$ $Co(tren)H_2OCl^{2+}$ has been observed, even though the spectrum of the pure $Co(tren)ClBr^+$ has not been obtained. Presumably, the α-isomer in the chloro-bromo complex has the same molar absorptivity as $Co(tren)H_2OBr^{2+}$ at this wavelength and hence no absorbance occurs during this step.

Analytical methods: (1) Determination of the uncoordinated free chloride ion. The concentration of the free chloride ion was measured by using a titration technique after the primary acid hydrolysis of $Co(tren)ClBr^+$. A weighed amount of [Co(tren)ClBr] Br in H_2O was allowed to react for 20 minutes at room temperature. The solution was then cooled in an ice bath. All cationic Co(III) species were removed by passing the solution through an ice-cooled cation-exchange column (Dowex 50W-X, Na^+ form). To the effluent from the column, iodate-nitric acid solution was added to oxidize Br^- to Br_2. The chloride ion content was then determined by a mercurimetric method.[7a,b]

(2) *Bromide ion electrode method*: A bromide ion activity electrode (Model 94-35, Orion Research, Inc.) was used for a qualitative confirmation that, during the latter part of the reaction, the hydrolysis reaction being measured does not involve the loss of bromide ion from the complex [i.e., the only reaction involved is α-$Co(tren)ClBr^+$ + H_2O → α-$Co(tren)H_2OBr^{2+}$ + Cl^-]. This observation demonstrates that two parallel reactions are occuring at different rates, and that the two initial species are not in equilibrium with each other. A chloride ion electrode was also
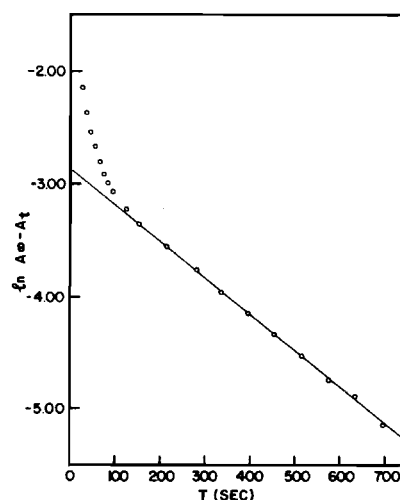

Figure 1. Plot of ln $(A_\infty-A_t)$vs t for the acid hydrolysis of chlorobromo(triaminotriethylamine) cobalt(III) ion at 25°, in 0.1 M $HClO_4$.

(6) H.S. Mark, Jr. and G.A. Rechnitz, « Kinetics in Analytical Chemistry », Interscience Publishers, 1968, Chapt. 7.
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in an attempt to detect the release of chloride in the slow stage. Unfortunately, due to the interference of the bromide ion, the chloride ion electrode does not function effectively.

Results and Discussion

A typical plot of ln $(A_\infty - A_t)$ vs t for the acid hydrolysis of Co(tren)ClBr$^+$ at pH = 1 and 25.0°C is illustrated in Figure 1. The initial curvature is believed to be due to the presence of two parallel reactions. Similar behavior was also found in the acid hydrolysis reaction of Co(tren)H$_2$OCl^{2+}.[2d]

In this study, chlorobromo(triaminotriethylamine) cobalt(III), Co(tren)ClBr$^+$, was prepared from Co(tren)H$_2$OCl^{2+}. Since it is believed there are isomers present in the Co(tren)H$_2$OCl^{2+} system, it is reasonable to expect that isomers will also be present in the chlorobromo complex. The possible geometrical isomers are shown in Figure 2.

α-isomer   β-isomer

Figure 2. Possible geometrical isomers of Co(tren)ClBr$^+$.

Using a bromide ion activity electrode for a qualitative study during the acid hydrolysis reaction of Co(tren)ClBr$^+$, we found that the bromide ion was released during the initial part of the reaction, but no further bromide release can be detected in the reaction. However, from titration of the free chloride at the end of the primary acid hydrolysis of Co(tren)-ClBr$^+$, it was found that 22.4% of the Cl$^-$ originally contained in the [Co(tren)ClBr]Br sample had been released as Cl$^-$.
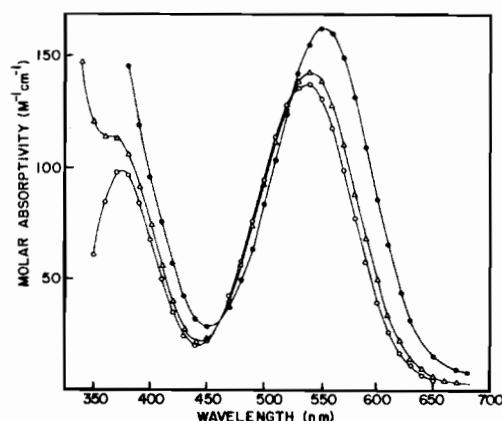

Figure 3. The visible spectra of Co(tren)H$_2$OCl^{2+} (O) and Co(tren)H$_2$OBr^{2+} (●) and that of the final spectrum of the product of the primary acid hydrolysis for Co(tren)ClBr$^+$ (△) in 0.1 M HClO$_4$ at 25°.

The visible spectra of Co(tren)H$_2$OCl^{2+} and Co-(tren)H$_2$OBr^{2+} and those of the products of the primary acid hydrolysis of Co(tren)ClBr$^+$ are shown in Figure 3. The content of Co(tren)H$_2$OBr^{2+} produced in the acid hydrolysis of Co(tren)ClBr$^+$ was calculated by using the molar absorptivities (ε) of the bromoaquo and the chloroaquo species by the equation:

$\varepsilon_{ClBr\ product}$ = (1−x) of the Co(tren)H$_2$OCl^{2+} in the product × ε_{ClH_2O} + x of Co(tren)H$_2$OBr^{2+} in the product × ε_{BrH_2O}

where x is the percent content of Co(tren)H$_2$OBr^{2+} in the final primary acid hydrolysis product of Co-(tren)ClBr$^+$. The content was found to be 21.6%, 22.8%, and 21.1% at 600.0 nm, 570.0 nm, and 490.0 nm, respectively. The results are in good agreement with the titration data. [The amounts of Co(tren)-H$_2$OBr^{2+} and Cl$^-$ are the same in the primary acid hydrolysis products of Co(tren)ClBr$^+$].

Furthermore, if we make a model for the system, we find that the position *cis* to the tertiary nitrogen of the tren ligand is very crowded. Also, from the results of a detailed X-ray study for the complex Ni-(tren)(SCN)$_2$, reported by Rasmussen,[8] it was noticed that the metal-ligand bond *trans* to the tertiary nitrogen of the tren ligand is shorter than the metal-ligand bond *cis* to it. It seems logical to assume that the same situation prevails in the cobalt-tren system. This effect would, therefore, cause the metal-ligand bond *cis* to the tertiary nitrogen to be much more reactive than the *trans* one and is evident if we compare the kinetic rate data for some related tren and ethylenediamine (en) complexes. The rate data are summarized in Table I.

Table I. Rate Constants for some Related tren and (en) Cobalt(III) Complexes.

Compound	Rate constant for acid hydrolysis (sec^{-1})	Ref.
Co(tren)Br$_2$$^+$	2.82×10^{-2}	2b
Co(tren)Cl$_2$	2.96×10^{-3}	2a
Co(tren)F$_2$$^+$	9.0×10^{-6}	2c
Co(tren)H$_2$OBr^{2+}	3.29×10^{-6}	2e
Co(tren)H$_2$OCl^{2+}	2.38×10^{-6}	2d
cis-Co(en)$_2$Br$_2$$^+$	9.33×10^{-4}	9
cis-Co(en)$_2$Cl$_2$$^+$	2.5×10^{-4}	10
cis-Co(en)$_2$F$_2$$^+$	3.06×10^{-6}	11
cis-Co(en)$_2$H$_2$OCl^{2+}	1.6×10^{-6}	12

The rate of acid hydrolysis of Co(tren)Br$_2$$^+$ is 3000% faster than that of Co(en)$_2$Br$_2$$^+$, but those of Co(tren)-Cl$_2$$^+$ and Co(tren)F$_2$$^+$ are only 1200% and 300% faster, respectively, than in the corresponding ethylenediamine system. It is reasonable to assume that this decrease in the rate ratio Co(tren)X$_2$$^+$/Co(en)$_2X_2$$^+$ from 30 for the dibromo system to 12 for the dichloro and 3 for the difluoro system is largely due to the

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Table II. Rates [a] of Acid Hydrolysis of Chlorobromo(triaminotriethylamine) Cobalt(III) Ion in MClO₄ Under Various Conditions at 529.4 nm.

Temp. (°C)	Added Electrolyte	pH	Ionic Strength	$k_\alpha \times 10^3 sec^{-1}$	$k_\beta \times 10^2 sec^{-1}$
14.0	None	1	0.10	1.05	1.16
20.0	None	1	0.10	1.93	2.07
25.0	None	1	0.10	3.21	3.38
31.0	None	1	0.10	5.76	6.23
35.5	None	1	0.10	9.81	7.96
25.0	0.05 M NaCl	1	0.15	3.37	3.45
25.0	0.05 M NaBr	1	0.15	3.11	3.40
25.0	0.05 M Na₂SO₄	1	0.25	4.08	3.73
25.0	0.1 M Na₂SO₄	1	0.40	5.05	4.23
25.0	0.5 M Na₂SO₄	1	1.60	7.61	7.36
25.0	None	2 [b]	0.01	3.25	3.44
25.0	None	4	—	3.19	3.32
25.0	None	6	—	3.24	3.36

[a] All rate constants are from least squares treatment of data and are the mean values of at least three determinations. [b] in HNO₃.

fact that the position *cis* to the tertiary nitrogen in the tren ligand is quite crowded. The rate decrease therefore parellels the decreasing ionic radii of the halogens, $Br^- > Cl^- > F^-$.

A comparison of the rate of acid hydrolysis of Co(tren)Cl₂⁺ with that of the corresponding ethylenediamine complexes shows that at 25.0°C, the tren complex reacts about 1200% faster, while the acid hydrolysis of Co(tren)H₂OCl²⁺ (the cloride is *trans* to the tertiary nitrogen of the tren ligand) proceeds at a rate only 150% faster than that of cis-Co(en)₂H₂OCl²⁺ under similar conditions. This abrupt decrease in the rate ratio from Co(tren)Cl₂⁺/Co(en)₂Cl₂⁺ = 12 to Co(tren)H₂OCl²⁺/Co(en)₂H₂OCl²⁺ = 1.50 is due to the fact that after the prlimary aquation step, the remaining chloride ion in the tren complex is *trans* to the tertiary nitrogen and is in a much less crowded environment.

A similar comparison of acid hydrolysis rates shows that Co(tren)Br₂⁺/Co(tren)Cl₂⁺ ≈ 10, but the acid hydrolysis rate of Co(tren)H₂OBr²⁺/Co(tren)H₂OCl²⁺ ≈ 1.4 under similar conditions. Likewise, the rate of aquation for Co(tren)Br⁺ is 100 times faster than that of cis-Co(en)₂Cl₂⁺ but Co(tren)H₂OBr²⁺ aquates at a rate only 2 times faster than cis-Co(en)H₂OCl²⁺.

All the above comparisons strongly support conclusion that the much greater aquation rate for the primary acid hydrolysis in the tren system cannot be explained by the strain of the system alone, but must also be due to the peculiar geometric arrangement of the tren, which causes steric crowding at the halide position *cis* to the tertiary nitrogen of the tren. As a result of this steric crowding, the ligand in the *cis*-posiion is very labile, so that the actual reactions observed are reactions 1 and 3 of the theoretically four possible hydrolysis reactions shown in Figure 4. The final spectrum for the aquation product of Co(tren)ClBr⁺ has two isosbestic points with the spectra of Co(tren)H₂OCl⁺ and Co(tren)H₂OBr⁺ as shown in Figure 3. Although these two isobestic points do not by themselves exclude the presence of reactions 2 and/or 4, they are consistent with the presence of reactions 1 and 3.

The rate constants for the acid hydrolysis reactions of Co(tren)ClBr⁺ were obtained in HClO₄ under various conditions of temperature, ionic strength and

pH. Data obtained are summarized in Table II.

From Table II, it can be seen that the reaction was acid-independent below pH value 6, and is ionic strength-independent. The fact that the rate is independent of ionic strength was as expected, since this behavior is typical for the reaction between a univalent cation and a neutral molecule in dilute solutions. The pseudo-first-order rate constant was found to be independent of the initial concentration of the complex.
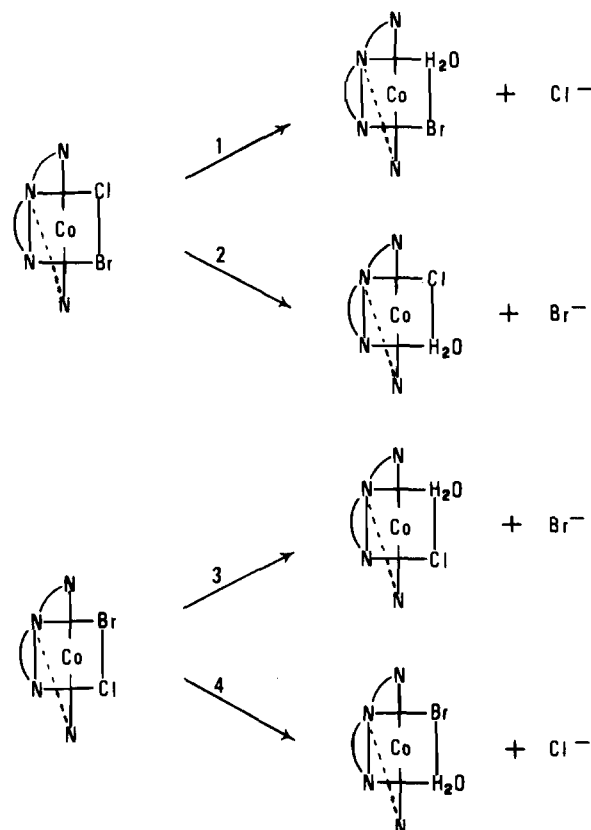

Figure 4. Possible theoretical isomres of Co(tren)ClBr⁺.

The acceleration of the acid hydrolysis rate by added sulfate ion can be understood by assuming that

the Co(tren)ClBr$^+$ forms ion pairs with the sulfate anion, Co(tren)ClBr$^+$SO$_4^{2-}$, which induces the removal of the coordinated halide ions by an S$_N$2 dissociation type mechanism.[13]

The pseudo-first-order rate constants (k$_\alpha$ and k$_\beta$), for the chlorobromo species are quite close to those of the dichloro (k$_1$ = 2.96 × 10^{-3} sec^{-1}) and of the dibromo species (k$_1$ = 2.82 × 10^{-2} sec^{-1}), respectively.

The Arrhenius plots for both k$_\alpha$ and k$_\beta$ in the temperature range 14.0 - 35.5°C gave straight lines. From these the activation enthalpies ΔH_α^* = 18.3 ± 0.8 kcal mol^{-1} and ΔH_β^* = 16.2 ± 0.2 kcal mol^{-1} were obtained. The free energies of activation, ΔG_α^* = 20.7 kcal mol^{-1} and ΔG_β^* ± 18.7 kcal mol^{-1}; and the entropies of activation, ΔS_α^* = −13.5 ± 2.7 cal mol^{-1} deg^{-1} and ΔS_β^* = −9.0 ± 0.7 cal mol^{-1} deg^{-1}, were calculated from ΔH^* values at 25.0°C. The activation enthalpies for the primary acid hydrolysis of Co(tren)Cl$_2^+$ and Co(tren)Br$_2^+$, which are 17.8 and 15.0 kcal mol^{-1}, respectively, are quite close to 18.3 and 16.2 kcal mol^{-1} for the α and β isomers respectively in the chlorobromo system.

From the above information it can be concluded that, during the primary aquation of the chlorobromo species, the halide ligand which is *trans* to the tertiary nitrogen of the tren has very little effect on the leaving group, which is *cis* to the tertiary nitrogen of the tren ligand. The ratio of rate constants, k$_\beta$/k$_\alpha$ ≈ 10, for the hydrolysis of Co(tren)ClBr$^+$ is an indication of the relative bond strengths in the complex and is in the same order as that found in all other cobalt(III) complexes. However, the fact that the ratio of k$_\alpha$/k$_\beta$ ≈ 10, while the ratio of k$_{Br}$/k$_{Cl}$ ≈ 4 for both [Co(en)$_2$ClBr]$^+$ [14] and [Co(NH$_3$)$_5$X]$^{2+}$ [15] (X = Cl, Br) indicates that the strength of the Co-Br bond is more sensitive to steric crowding than that of the Co-Cl bond which is reasonable on the basis of ionic radii considerations.

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