

observable. However, the position of the coordinated water peak was invariant with composition in the ClO_4^- and NO_3^- solution spectra. Assuming all the Cl^- is complexed in the form of monomeric species only, these points and the observation of a solvation number of ~ 3 in the 1:1 Cl^- - UO_2^{2+} solution of Figure 2 are consistent with the presence of roughly equal amounts of $\text{UO}_2(\text{H}_2\text{O})_4$ and $(\text{H}_2\text{O})_2\text{UO}_2\text{Cl}_2$. The tetrahydrate would give rise to the low-field broad peak of Figure 2, and the two isomers of the dichloro complex, if equally stable, would be responsible for the doublet. However, no firm conclusions can be drawn without the support of other types of experimental data.

In the DMSO solutions containing a 1:1 and 1.5:1 mole ratio of Cl^- to UO_2^{2+} , the water contribution to the cation solvation shell decreases. The corresponding decrease in the signal intensity made signal integrations very difficult. In these systems the estimates of the amount of Cl^- complexed are in doubt, perhaps by as much as 0.1–0.2 unit. At higher Cl^- concentrations, when essentially all the water had been replaced in the solvation shell by DMSO and anion, the estimates are more reliable since only the integrations of the sharper DMSO peaks are involved. In all cases, however, it is clear that the presence of DMSO decreases the extent of UO_2^{2+} - Cl^- complex formation. Up to a Cl^- : UO_2^{2+} mole ratio of 4:1, Cl^- is completely complexed in similar solutions containing no DMSO.¹⁹ The data of Table III demonstrate that when DMSO is present, the order of binding to UO_2^{2+} is $\text{DMSO} > \text{Cl}^- > \text{H}_2\text{O} > \text{acetone}$, a trend similar to that observed in the NO_3^-

solutions. This order parallels the relative basic strengths generally quoted for these species.²³

It is interesting that only one signal is observed for bound DMSO in the spectra corresponding to the solutions of Tables I–III. This observation may mean that only one DMSO solvation complex, perhaps $\text{UO}_2(\text{DMSO})_4^{2+}$, is present in each case, intramolecular exchange is very rapid, or the chemical shifts of the DMSO molecules in different environments are the same. The ion-exchange studies of King, *et al.*, demonstrated the presence of mixed solvation complexes in several solvent systems,^{3–7} including water–DMSO solutions of Cr^{3+} ,⁷ and by analogy, one might reasonably assume that species of similar composition are present here. It is not possible to distinguish unambiguously between the remaining two possibilities. Since the multiple signal pattern of Figure 2 may arise either from a combination of complexes such as those previously mentioned or from water molecules in the same complex, the intramolecular exchange rate cannot be estimated. Most likely, however, only small shift variations would result for bound DMSO molecules in different environments, since the methyl groups are far removed from the complexing interaction site in the DMSO molecule, the oxygen atom unshared electron pair.

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Competitive Reductions of Cobalt(III) Complexes by Chromium(II)

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Relative rates of reduction by chromous ion of cobalt(III) complexes containing bridging groups have been determined by a method involving competing reactions. The technique exploits the competition of two potential bridging ligands (either in separate ions or in the same ion) for Cr^{2+} and treats the experimental data by means of a rate expression for competing reactions. For the system $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ - Cr^{2+} , relative rates of 2.75:1.89:1.51:1.00:0.88, at $\mu = \sim 2 \times 10^{-2} M$, are obtained for the iodo, bromo, chloro, fluoro, and azido complexes, respectively; at $\mu = 0.1 M$ the relative rates for the iodo through the fluoro complexes are 4.3:2.6:1.8:1.00. The calculated interrelationships of these relative rates have been confirmed by Cr^{2+} competitive reductions of the requisite pairs of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ ions as well as the reduction of a solution containing the three ions $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$. When two different halides are present in the same complex, as in *cis*- and *trans*- $\text{Co}(\text{en})_2\text{BrCl}^+$, the relative preference of Cr^{2+} for Br^- over Cl^- is reduced from 1.26 (for the pentaammine system) to values of 1.14 and 1.00 for these *cis* and *trans* complexes, respectively. When Cr^{2+} reacts with a mixture of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and *trans*- $\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}^+$, the rate of the reaction with chloride acting as the bridging group becomes greater than the rate of the reaction with bromide acting as the bridging group.

Introduction

Several studies^{1–4} show that in the reactions of chro-

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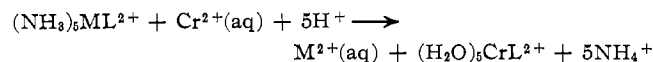
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mous ion with both chromium(III) and cobalt(III) complexes of the general formula $\text{M}(\text{NH}_3)_5\text{L}^{2+}$, where $\text{L}^- = \text{F}^-$, Cl^- , Br^- , I^- , etc., the electron-transfer process proceeds *via* a bridged transition state in which L functions as a bridging group and then appears in the coor-

dination sphere of the oxidized chromium as CrL^{2+}

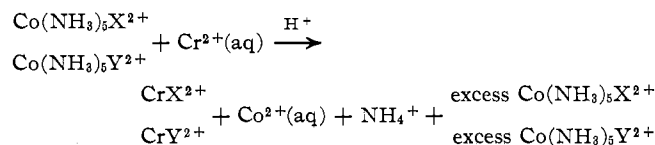


Absolute second-order rate constants have been determined by Ogard and Taube⁴ for the Cr^{2+} -catalyzed dissociation of $\text{Cr}(\text{NH}_3)_5\text{L}^{2+}$. For the corresponding cobalt system, however, the reduction by Cr^{2+} is far more rapid and cannot be followed by conventional kinetic methods. When the present work was initiated, no absolute rate constants had been reported for this latter system; later, however, Candlin and Halpern⁵ were able to adapt a stopped-flow procedure to these reactions and have reported approximate absolute rate constants (Table VIII).

This research was undertaken with the view of obtaining information of two types regarding the reactions of cobalt(III) complexes with Cr^{2+} : (1) accurate *relative* rates for reactions involving a series of L bridging ligands and (2) effect on relative rates of incorporating two bridging ligands in the same ion, *e.g.*, $\text{Co}(\text{en})_2\text{XY}^+$. The general technique exploits the competition of two potential bridging ligands (either in separate ions as $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ or in the same ion as $\text{Co}(\text{en})_2\text{ClBr}^+$) for Cr^{2+} and treats the experimental data by means of a rate expression for competing reactions. The method proved admirably suited to the above systems.

Experimental Section

Method and Treatment of Data.—In the determination of relative rates of reactions when the bridging ligands are in ions of the type $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$, chromous ions are added to a solution containing two different ions, $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Y}^{2+}$ (whose total concentration is of the order $2.5 \times 10^{-3} M$). The reaction taking place can be visualized as a competition between two similar complex ions, A and B, for the chromous ion, where the latter is always less than the stoichiometric amount (*i.e.*, neither of the starting ions A or B can be totally consumed). The overall reaction may be represented in abbreviated form as



The reaction, which is very rapid, is carried out with slow addition of Cr^{2+} , with stirring, and with sufficient H^+ ions present to maintain a slightly acid solution after all ammonia molecules have been converted to ammonium ions. By the use of a cation-exchange resin the CrX^{2+} and CrY^{2+} species are isolated and a quantitative determination of X^- and Y^- is carried out. From the amounts of X^- and Y^- obtained, the fraction of complex A ($\text{Co}(\text{NH}_3)_5\text{X}^{2+}$) and the fraction of complex B ($\text{Co}(\text{NH}_3)_5\text{Y}^{2+}$) remaining after the reaction is complete can be calculated. Since the reactions are homocompetitive (kinetically analogous), the *ratio* of specific rate constants (r) can be calculated from the relation⁶

$$r = \frac{k_1}{k_2} = \frac{\text{logarithm of fraction of A remaining}}{\text{logarithm of fraction of B remaining}}$$

The results obtained by this method, in which r can be determined from the results of just one run, were verified by the use

of a graphical method. Analyses of products were made at various stages of reaction and the logarithm of the fraction of A remaining was plotted against the logarithm of the fraction of B remaining. The slope of the straight line obtained is equal to r , thus confirming the homocompetitive nature of the reactions.⁶

In the cases where Cr^{2+} reacts with ions of the type $\text{Co}(\text{en})_2\text{XY}^+$, there is no change in the *relative* amounts of X and Y remaining at any stage in the reaction. Once Cr^{2+} has selected X (or Y) and reduced Co(III) to Co^{2+} , the latter ion is labile and the other potential bridging ligand Y (or X) is liberated into the solution as the free ion. For these reactions, excess Cr^{2+} is always used. In these systems r can be calculated simply from the relationships

$$\frac{C_X}{C_Y} = \frac{C_{\text{CrX}^{2+}}}{C_{\text{CrY}^{2+}}} = \frac{k_X}{k_Y} = r$$

Preparation of Cobalt(III) Complexes.—All of the following complexes were prepared according to previously reported methods: $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$,⁷ $[\text{Co}(\text{NH}_3)_5\text{NO}_3](\text{NO}_3)_2$,⁷ $[\text{Co}(\text{NH}_3)_5\text{F}](\text{NO}_3)_3$,⁷ $[\text{Co}(\text{NH}_3)_5\text{NCS}](\text{ClO}_4)_2$,⁸ $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$,⁹ $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Br}_2$,¹⁰ $[\text{Co}(\text{NH}_3)_5\text{I}](\text{NO}_3)_3$,¹¹ *cis*- and *trans*- $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$,^{12,13} *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$,¹⁴ *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{BrCl}]\text{Br}$,¹⁵ *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{NH}_3\text{Cl}]\text{Cl}_2$,¹⁶ *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{Cl}(\text{NCS})]\text{ClO}_4$,^{17,18} *trans*- $[\text{Co}(\text{en})_2(\text{OH})\text{Cl}]\text{Cl}$,¹⁹ *cis*- and *trans*- $[\text{Co}(\text{en})_2(\text{NO}_2)\text{Cl}]\text{NO}_3$,^{20a} and *trans*- $[\text{Co}(\text{en})_2\text{Br}_2]\text{Br}$.^{20b}

The complex $[\text{Co}(\text{NH}_3)_5\text{N}_3](\text{ClO}_4)_2$ was prepared by the addition of 10 g of solid $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}](\text{NO}_3)_3$ to a solution of 10 g of NaN_3 and 10 drops of glacial acetic acid in 90 ml of water; the resulting solution was heated on a steam bath for 15 min, 40 g of NaClO_4 was added, and the heating was continued for another 15 min. The rose red azido complex was removed by filtration and washed with alcohol and ether. The original procedure²¹ called for $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ as the starting material and the use of hydrochloric acid instead of NaClO_4 ; these were not used here because when they were employed, a mixture of the chloro- and azidopentaammine complexes was obtained. The perchlorate salt of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ was obtained by the addition of solid NaClO_4 to a warm solution of the chloride, followed by rapid cooling in an ice bath. Similarly, aqueous solutions of *cis*- and *trans*- $[\text{Co}(\text{en})_2\text{BrCl}]\text{Br}$ were treated with solid NaClO_4 to obtain the solid perchlorates. These isomers and $[\text{Co}(\text{NH}_3)_5\text{I}](\text{NO}_3)_3$ were prepared in the dark to prevent any possible photodecomposition. The ions *cis*- $\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}^{2+}$ and *cis*- $\text{Co}(\text{en})_2(\text{H}_2\text{O})\text{Cl}^{2+}$ were isolated as the sulfate salts;²² however, in order to eliminate possible interference by the sulfate ion in subsequent reactions, these complexes were converted to solutions of the nitrates by the addition of $\text{Ba}(\text{NO}_3)_2$ and removal of BaSO_4 just prior to their use.

The compound *trans*- $[\text{Co}(\text{en})_2\text{N}_3\text{Cl}]\text{ClO}_4$ was prepared by the method of Staples and Tobe.²³ We were not able, however, to prepare the corresponding *cis* isomer by following the directions given by these authors. Neither were we able to obtain *trans*- $[\text{Co}(\text{en})_2\text{NH}_3\text{Br}]\text{Br}_2$ by the procedure outlined in the literature;²⁴ the substance obtained presumably as the *trans* isomer had the same absorption spectrum as that of the *cis* form.

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Stock Solutions.—A chromium(III) perchlorate stock solution was prepared by the addition of 98 ml of concentrated HClO_4 to 29.81 g of $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ in 500 ml of water, followed by dropwise addition of 75 ml of 30% H_2O_2 ; the resulting solution was heated to incipient boiling for about 45 min to remove all of the oxygen. This solution was approximately 0.2 M in chromium(III) and 0.5 M in HClO_4 . The original preparation²⁵ called for either hydrochloric acid or sulfuric acid, but since the anions of these acids would interfere in the subsequent analytical results and kinetic studies, respectively, they were not used in our synthesis.

A chromium(II) perchlorate solution was prepared from the chromium(III) solution as outlined by Lingane and Pecsok.²⁵ The sky blue chromium(II) solution was stored under a slight pressure of CO_2 in a storage bottle; the solution was subsequently withdrawn by means of a syringe introduced into the bottle through a self-sealing rubber diaphragm lid.

Analysis and Identification of Compounds.—Each of the cobalt(III) complexes used as an oxidant was checked spectrophotometrically against the spectral characteristics cited in the literature and then analyzed quantitatively for the halides or pseudohalides present both inside and outside of the coordination sphere of the cobalt(III). For the monohalopentaamminecobalt(III), the dihalobis(ethylenediamine)cobalt(III), and the dihalotetraamminecobalt(III) complexes, a slight excess of Cr^{2+} was added to a cold acidic solution of the complex. The CrL^{2+} species was isolated by a column technique as outlined below. The amount of L in the CrL^{2+} corresponded to the amount of L within the coordination sphere of the cobalt(III) complex; the first eluate contained the halides, if any, outside the coordination sphere.

For the complexes of the type $\text{Co}(\text{en})_2\text{XY}^+$, a very slight excess of Cr^{2+} was added to an acidic solution of the complex, and the first and second eluates from the ion-exchange column were used for analyses. Since all of the complexes of this type were in the form of the perchlorate salts, the first eluate was analyzed directly for both X^- and Y^- . For each reduction which took place through an X^- group acting as a bridge to produce a CrX^{2+} species, a Y^- was produced, and *vice versa*. The second eluate was analyzed for X^- and Y^- present as CrX^{2+} and CrY^{2+} . The ratio between the total X^- and Y^- found in both eluates was 1:1.

In the analysis of complexes of the type $\text{Co}(\text{en})_2\text{QL}^{n+}$, where L is a bridging group and Q is not, equimolar amounts of Cr^{2+} were added to the cobalt(III) solutions and essentially all of the Cr^{2+} added was recovered as CrL^{2+} from the halide analysis. This observation indicates that bridging takes place solely through L in complexes of this type.

Rates of aquation are available for most of the complexes used in this study (see ref 26, for example). Since most of these aquation reactions are very slow at 25°, and even slower at 0°, in comparison with the rates of reduction of these complexes by Cr^{2+} , no correction had to be made for any possible side reactions. Although CrCl^{2+} , CrBr^{2+} , and CrI^{2+} are unstable with respect to hexaaquochromium(III) and the free halide ion, with CrCl^{2+} being the most stable, the rates of aquation of CrCl^{2+} and CrBr^{2+} are slow enough so that their molar absorptivities can be measured satisfactorily² in a cell compartment at room temperature. Since the rate of aquation of CrI^{2+} is greater²⁷ than for the analogous chloro or bromo ions, a cooled ion-exchange column is advisable when working with this ion. Consequently, for uniformity in the interpretation of results, all separations in this study were made using a jacketed column cooled to about 2°.

Chloride, bromide, iodide, and thiocyanate ions were determined by following the change in potential²⁸ of a silver electrode

vs. a mercury-mercurous sulfate electrode²⁹ as the solution containing these species was titrated with a standard silver nitrate solution. This method was carefully checked and was found to give accurate, reliable, and reproducible results. Halide analyses on synthetic samples and mixtures which simulated our experimental conditions were accurate to within about $\pm 1\%$ of the theoretical values. Reinvestigation of results reported in an earlier study³⁰ indicated some of these to be in error due to the method used in analyzing for halide ions in mixtures. The method, while theoretically sound, was unreliable at the concentrations of halides encountered in the actual experiments.

Analysis for fluoride was made³¹ by following the change in pH of a solution when titrated with a standard $\text{La}(\text{NO}_3)_3$ solution. Both chromous³² and azide³³ ions were determined by the addition of an excess of standard ceric sulfate solution and the excess cerium(IV) was back-titrated with standard ferrous solution with ferroin as indicator.

Potentiometric titration was used for determining the components in mixtures of Cl^- and Br^- , Br^- and I^- , Cl^- and I^- , Cl^- and NCS^- , and Cl^- , Br^- , and I^- . In mixtures containing either F^- or N_3^- , analysis was first made for these ions and then the other members of the mixtures were determined by potentiometric titration. In the cases where F^- and N_3^- were both present in the same solution, the fluoride analysis was carried out first.

Procedure.—The description of the following procedure will serve to illustrate the general experimental approach employed in this work. A variable, but known, volume (150–200 ml) of 10^{-2} M acidic solution was added to a 250-ml filter flask. Perchloric acid was normally used, but in several cases because of solubility complications nitric acid was found more satisfactory. In each case there was more than enough acid present to convert all of the released ammonia or ethylenediamine to the protonated form; the acid concentration was kept low however so that the reaction solutions could be subsequently placed rapidly on the ion-exchange resin. The water used to make the reaction solutions was deaerated with carbon dioxide just prior to its use. The filter flask containing the acid solution and pieces of Dry Ice to maintain a carbon dioxide atmosphere was then placed in an ice bath on a magnetic stirrer, $1.5\text{--}2.5 \times 10^{-4}$ mol each of the solid complexes was added, and the mixture was stirred until solution was complete. For those reactions run at $\mu = 0.1$ M, the requisite amount of solid NaClO_4 was added at this point. Less than a stoichiometric amount of chromous ion (40–70% $\text{Cr}^{2+}/\text{Co}^{\text{III}}$) was then introduced into the rapidly stirred reaction mixture with a hypodermic syringe. The reaction was essentially complete as soon as all of the chromous solution had been added. Experiments involving quite different ratios of Cr^{2+} to Co^{III} were carried out when the graphical method for determining the relative rate values was to be employed. Also in those experiments where excess chromous ions needed to be used the reaction flask was opened to the air, after the reduction had proceeded to completion, to allow oxidation of the chromous ions.

The solution was then placed on a 1-cm diameter water-jacketed ion-exchange column containing 15 cm^3 of cation exchange resin in the hydrogen-form (Dowex 50W-X8, 100–200 mesh). A 250-ml reservoir above the resin column was also jacketed and the whole maintained at about 2° by means of ice water forced through the jacket. When the reaction products were on the column, the resin was washed with 0.1 M HClO_4 to remove any anionic, neutral, or unipositive cationic species. The CrL^{2+} band (where L represents any of the negative ions used) was then eluted with 1.0 M HClO_4 . In order to minimize the possibility of aquation reactions, the solutions were placed on the column and the desired species were taken off the resin as rapidly as possible. This was accomplished by fitting a filter

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TABLE I
 RELATIVE RATES FOR THE COMPETITIVE REDUCTION BY Cr^{2+} OF $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ (A) AND $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (B) IONS^a

Mol of A $\times 10^4$	Mol of B $\times 10^4$	Mol of Cr^{2+} $\times 10^4$	Mol of CrBr^{2+} $\times 10^4$	Mol of CrCl^{2+} $\times 10^4$	Log (fraction of A remaining)	Log (fraction of B remaining)	$r(k_A/k_B)$
2.29	2.50	3.18	1.58	1.56	-0.509	-0.425	1.20
1.83	2.50	3.60	1.56	1.98	-0.830	-0.682	1.22 ^b
2.29	2.50	2.92	1.46	1.40	-0.441	-0.357	1.24
2.29	2.50	2.98	1.50	1.42	-0.462	-0.365	1.27 ^b
2.29	2.50	2.88	1.46	1.38	-0.441	-0.349	1.26 ^c
2.29	3.50	3.10	1.34	1.74	-0.382	-0.298	1.28
2.29	2.50	3.27	1.66	1.58	-0.561	-0.434	1.29
3.50	2.50	3.20	1.96	1.20	-0.357	-0.284	1.26

Av 1.26 \pm 0.07

^a All reactions carried out at 0° unless otherwise noted; ionic strength $\sim 2 \times 10^{-2} M$. ^b Reaction carried out at 25°; r value not used in calculating the average. ^c Very slow stirring rate employed.

 TABLE II
 RELATIVE RATES FOR THE COMPETITIVE REDUCTION BY Cr^{2+} OF $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ (A) AND $\text{Co}(\text{NH}_3)_5\text{Y}^{2+}$ (B)^a

A (RX^{2+}) ^b	B (RY^{2+}) ^b	Mol of A $\times 10^4$	Mol of B $\times 10^4$	Mol of $\text{Cr}^{2+} \times 10^4$	No. of runs	$r(k_A/k_B)$
$\mu = \sim 2 \times 10^{-2} M$						
RI^{2+}	RN_3^{2+}	2.50	1.74	2.80	2	3.08 \pm 0.11
RI^{2+}	RF^{2+}	2.50	2.50	3.05	2	2.75 \pm 0.10
RI^{2+}	RCI^{2+}	2.10-2.50	2.28-2.50	2.77-3.47	8	1.87 \pm 0.22
RI^{2+}	RBr^{2+}	2.10-2.50	1.83-2.29	2.47-3.29	5	1.44 \pm 0.07
RBr^{2+}	RN_3^{2+}	2.29	1.55-1.80	2.47-2.70	3	2.29 \pm 0.11
RBr^{2+}	RF^{2+}	2.29	2.50	3.07-3.32	2	1.89 \pm 0.11
RBr^{2+}	RCI^{2+}	2.29-3.50	2.50-3.50	2.88-3.27	6	1.26 \pm 0.07
RCI^{2+}	RN_3^{2+}	2.38-2.50	1.55-1.74	2.60-2.90	4	1.79 \pm 0.06
RCI^{2+}	RF^{2+}	2.50	2.50	3.01-3.08	2	1.51 \pm 0.04
RF^{2+}	RN_3^{2+}	2.50	1.74	2.70-2.88	3	1.14 \pm 0.24
$\mu = 0.1 M^c$						
RI^{2+}	RCI^{2+}	2.50	2.50	2.92-3.04	2	2.40 \pm 0.07
RBr^{2+}	RCI^{2+}	2.29	2.50	2.90-3.10	2	1.44 \pm 0.02
RCI^{2+}	RF^{2+}	2.50	2.50	2.87-2.95	2	1.80 \pm 0.11

^a Both X and Y are potential bridging ligands; all reactions carried out at 0°. ^b R = $\text{Co}(\text{NH}_3)_5$. ^c Ionic strength maintained with NaClO_4 .

flask to the column outlet and creating a partial vacuum in this flask by means of an aspirator pump. The greenish CrL^{2+} band on the column was not as sharp under these conditions as when a slow elution rate was used, but the separation of these species from other ions was just as efficient. The CrL^{2+} complexes were decomposed by the addition of NaOH to the appropriate eluate until the resulting solution was at pH 10; the solution was then made acidic with HNO_3 to about pH 2. This solution was then analyzed for the L components as outlined above.

Results

Chromous Ion Reduction of Mixtures of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ Complexes.—A summary is given in some detail in Table I of the conditions and results obtained when a series of solutions containing mixtures of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ ions are allowed to compete for Cr^{2+} to form CrBr^{2+} and CrCl^{2+} . The eight runs involving these ions include two which were carried out at 25° and a third in which a very slow stirring rate was deliberately employed. As indicated by this table, within the experimental error of our analytical methods, all the Cr^{2+} ion added in the reactions was recovered, *i.e.*, $[\text{Cr}^{2+}]_{\text{added}} \simeq [\text{CrBr}^{2+}] + [\text{CrCl}^{2+}]$. The last column gives the ratio of rate constants, r , for the faster reaction relative to the slower; *i.e.*, the reduction of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ by Cr^{2+} ion is about 1.26 times faster than the reduction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$. The value 1.26 is the average of the values for six runs (see footnote *b*, Table I) and 0.07 represents the standard deviation. This

practice is employed throughout this paper. It is worth noting that variations in the molar ratios of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ in the starting solutions within the limits indicated, a higher temperature, and a deliberately slow rate of mixing of the reactants resulted in no apparent change in the value of r . Although the results are not shown in Table I, experiments were also carried out at higher acidities; no change in the r values was observed.

In Table II data are shown for the competitive reduction by Cr^{2+} of other mixtures containing ions of the type $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Y}^{2+}$, where both X and Y are potential bridging ligands. For the sake of brevity, only the range in amounts of the reactants is shown. It is evident from the data of this table that r for a given pair of reactants increases with increasing ionic strength.

Experiments were carried out to confirm the anticipated results when Cr^{2+} reacts with three different ions of the type $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ in the same solution; these results are tabulated in Table III. Here also the total quantity of anions (L^-) in the CrL^{2+} cations recovered is seen to be equal to the quantity of Cr^{2+} used. This implies that in the mixtures containing $\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}^{3+}$ and $\text{Co}(\text{NH}_3)_5\text{NO}_3^{2+}$ virtually no reduction takes place *via* the aquo and nitrate ions.

Chromous Ion Reduction of $\text{Co}(\text{en})_2\text{XY}^+$ Complexes.—A summary is given in Table IV of the data for three

TABLE III

RELATIVE RATES FOR THE COMPETITIVE REDUCTIONS BY Cr²⁺ OF Co(NH₃)₅X²⁺ (A), Co(NH₃)₅Y²⁺ (B), AND Co(NH₃)₅Z²⁺ (C)^a

Expt	A (RX ⁿ⁺)	B (RY ²⁺)	C (RZ ²⁺)	Mol of Cr ²⁺ × 10 ⁴	Mol of CrX ⁿ⁺ × 10 ⁴	Mol of CrY ²⁺ × 10 ⁴	Mol of CrZ ²⁺ × 10 ⁴	No. of runs	k _A /k _B	k _A /k _C	k _B /k _C
1 ^{b,c}	RI ²⁺	RBr ²⁺	RCI ²⁺	4.90	1.95	1.50	1.42-1.44	2	1.42 ± 0	1.78 ± 0.03	1.26 ± 0.02
2 ^{b,c}	RH ₂ O ³⁺	RBr ²⁺	RCI ²⁺	3.20	...	1.66	1.55	1	1.29
3 ^{b,d}	RNO ₃ ²⁺	RBr ²⁺	RCI ²⁺	3.18	...	1.60	1.54	1	1.25

^a Reactions carried out at 0°; $\mu = \sim 2 \times 10^{-2} M$; 2.29×10^{-4} mol of RBr²⁺ and 2.50×10^{-4} mol each of RI²⁺, RCI²⁺, RH₂O³⁺, and RNO₃²⁺ used in reaction solutions (R = Co(NH₃)₅). ^b Reaction mixture made acidic with HClO₄; resin column height 8 cm. ^c Reaction solution volume 200 ml. ^d Reaction solution volume 150 ml.

TABLE IV

RELATIVE RATES FOR THE COMPETITIVE REDUCTIONS BY Cr²⁺ OF Co(en)₂XY⁺ FOR REACTIONS PROCEEDING VIA X- OR Y-BRIDGED INTERMEDIATES^{a,b}

Complex (R'XY ⁺)	No. of runs	r(k _X /k _Y)
cis-R'BrCl ⁺	3	1.14 ± 0
trans-R'BrCl ⁺	3	1.03 ± 0.06
trans-R'(N ₃)Cl ⁺	2	0.9 ^c

^a Reactions carried out at 0°; $\mu = \sim 2 \times 10^{-2} M$; R' = Co(en)₂. ^b Reduction was found to take place exclusively through a halogen-bridged intermediate in the following cases: cis- and trans-R'ClNO₂⁺, cis- and trans-R'ClH₂O²⁺, cis- and trans-R'ClNH₃²⁺, cis-R'BrNH₃²⁺, and cis-Co(NH₃)₄ClH₂O²⁺. The results from the reactions involving cis- and trans-R'(NCS)Cl⁺ were ambiguous (see text for discussion). ^c Corrected for presence of uncoordinated azide in solution.

of the ions investigated which fit into the above category. In each case, excess of the reducing agent (Cr²⁺) was used. The number of compounds of this type which were available for study was limited by experimental preparative difficulties. As will be discussed later, clean-cut results were obtained with only the cis- and trans-Co(en)₂BrCl⁺ ions.

Chromous Ion Reduction of Mixtures of Co(NH₃)₅X²⁺ with Co(en)₂Y²⁺ and with Co(NH₃)₄Y²⁺ Complexes.—The results of these experiments are summarized in

TABLE V

RELATIVE RATES FOR COMPETITIVE REDUCTIONS BY Cr²⁺ OF MIXTURES OF Co(NH₃)₅X²⁺ (A) AND EITHER cis- OR trans-Co(en)₂Y²⁺ (B) OR cis- OR trans-Co(NH₃)₄Cl₂²⁺ (B)^a

A (RX ²⁺) ^b	B ^c	No. of runs	r(k _A /k _B) ^d
RI ²⁺	cis-R'Cl ₂ ⁺	3	2.02 ± 0.08
RI ²⁺ ^e	trans-R'Cl ₂ ⁺ ^e	4	1.24 ± 0.18
RI ²⁺	trans-R'Br ₂ ⁺	2	0.83 ± 0.07
RBr ²⁺	cis-R'Cl ₂ ⁺	2	1.69 ± 0.04
RBr ²⁺ ^f	trans-R'Cl ₂ ⁺ ^f	2	1.05 ± 0.01
RCI ²⁺	trans-R'Br ₂ ⁺	2	0.51 ± 0.07 ^g
RN ₃ ²⁺	cis-R'Cl ₂ ⁺	2	0.81 ± 0.01 ^h
RN ₃ ²⁺ ^f	trans-R'Cl ₂ ⁺ ^f	2	0.45 ± 0.01 ⁱ
RBr ²⁺	cis-R''Cl ₂ ⁺	2	1.22 ± 0.03
RBr ²⁺	trans-R''Cl ₂ ⁺	2	1.15 ± 0.01

^a Reactions carried out at 0°; $\mu = \sim 2 \times 10^{-2} M$; X and Y are potential bridging ligands. ^b R = Co(NH₃)₅. ^c R' = Co(en)₂; R'' = Co(NH₃)₄. ^d Values corrected for statistics. ^e Made acidic with HCl since [Co(NH₃)₅I](NO₃)₂ and trans-[Co(en)₂-Cl₂]ClO₄ are insoluble in HNO₃ and HClO₄, respectively. ^f Made acidic with HNO₃ since trans-[Co(en)₂Cl₂]Cl is insoluble in HClO₄. ^g r(k_{Br}/k_{Cl}) = 1.99 ± 0.26. ^h r(k_{Cl}/k_{N₃}) = 1.24 ± 0.02. ⁱ r(k_{Cl}/k_{N₃}) = 2.22 ± 0.07.

Table V. It is evident that four of the values for r given in the last column are less than 1.00. Three of these (see footnotes to this table) arise because the form

of the table imposes the inverse of the usual significance on r, i.e., $r = k_{\text{slower}}/k_{\text{faster}}$. In the fourth case (the reduction by Cr²⁺ of a mixture of RI²⁺ and trans-R'Br₂⁺) a bromide ion which is trans to another bromide ion in Co(en)₂Br₂⁺ actually results in a faster reaction with Cr²⁺ than does an iodide ion in Co(NH₃)₅I²⁺ (see Table II).

Chromous Ion Reduction of Mixtures of Co(NH₃)₅X²⁺ with Co(en)₂QYⁿ⁺ and with Co(NH₃)₄QYⁿ⁺.—A summary of the results of these experiments is given in Table VI. In three cases, as can be seen from the

TABLE VI

RELATIVE RATES FOR COMPETITIVE REDUCTIONS BY Cr²⁺ OF MIXTURES OF Co(NH₃)₅X²⁺ (A) AND EITHER cis- OR trans-Co(en)₂QYⁿ⁺ (B) OR cis-Co(NH₃)₄(H₂O)Cl₂²⁺ (B)^a

A (RX ²⁺) ^b	B ^c	No. of runs	r(k _A /k _B)
RBr ²⁺	cis-R'(NO ₂)Cl ⁺	2	1.50 ± 0.07
RBr ²⁺	trans-R'(NO ₂)Cl ⁺	2	0.87 ± 0.03
RBr ²⁺	cis-R'(NH ₃)Cl ²⁺	2	1.82 ± 0.09
RBr ²⁺	trans-R'(NH ₃)Cl ²⁺	2	1.22 ± 0.01
RBr ²⁺	cis-R'(H ₂ O)Cl ²⁺	2	1.61 ± 0.03
RBr ²⁺	trans-R'(H ₂ O)Cl ²⁺ ^d	2	0.88 ± 0.04
RCI ²⁺	cis-R'(NH ₃)Br ²⁺	2	1.11 ± 0.07 ^e
RBr ²⁺	cis-R'(NCS)Cl ⁺	1	1.6 ^f
RBr ²⁺	trans-R'(NCS)Cl ⁺	2	1.14 ± 0.13 ^f
RBr ²⁺	cis-R''(H ₂ O)Cl ²⁺	2	1.22 ± 0.01

^a Reactions carried out at 0°; $\mu = \sim 2 \times 10^{-2} M$; X and Y are potential bridging ligands; Q is not. ^b R = Co(NH₃)₅. ^c R' = Co(en)₂; R'' = Co(NH₃)₄. ^d Starting complex was trans-Co(en)₂(OH)Cl⁺ which in acidic solution was rapidly converted to trans-Co(en)₂(H₂O)Cl²⁺. ^e r(k_{Br}/k_{Cl}) = 0.90 ± 0.06. ^f The results with these compounds were not without ambiguity; an attempt has been made to correct for the uncoordinated thiocyanate ions in solution.

respective r values, the rate of reduction with chloride ion acting as a bridging atom becomes greater than with bromide acting as a bridging atom (see Table II).

Miscellaneous Reductions with Chromous Ion.—The results of several experiments fitting into no specific category are shown in Table VII. Since there is no

TABLE VII

RELATIVE RATES OF COMPETITIVE REDUCTIONS BY Cr²⁺ OF SELECTED MIXTURES OF COBALT(III) COMPLEXES^a

Compd A ^b	Compd B ^b	No. of runs	r(k _A /k _B)
RI ²⁺	trans-R'BrCl ⁺	3	0.49 ± 0.15
RBr ²⁺	trans-R'(N ₃)Cl ⁺	1	1.09 ^c
cis-R'(NH ₃)Br ²⁺	cis-R'(NH ₃)Cl ²⁺	2	1.28 ± 0.01
trans-R'Br ₂ ⁺	trans-R'Cl ₂ ⁺ ^d	2	1.89 ± 0.10

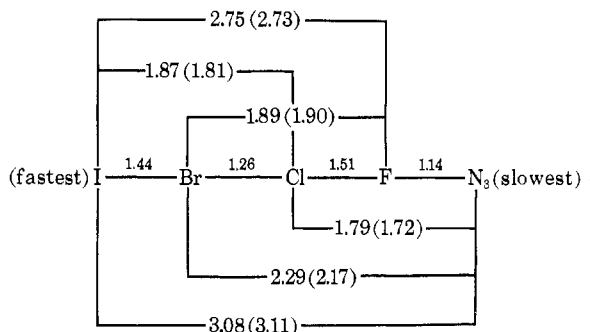
^a Reactions carried out at 0°; $\mu = \sim 2 \times 10^{-2} M$. ^b R = Co(NH₃)₅; R' = Co(en)₂. ^c See text for discussion. ^d Reaction mixture made acidic with HNO₃.

way to correct for statistics in the case of the ion $\text{Co(en)}_2\text{BrCl}^+$, the r value for the experiment involving this species contains a rate for the ion which results from the combined effects of the bridging due to both Br and Cl.

Discussion

Our comparative rate studies show that the rates of reduction by Cr^{2+} of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ ions (on the basis of the bridging ligand L) decrease in the order $\text{I}^- > \text{Br}^- > \text{Cl}^- > \text{F}^-$. This order is the same as that previously found by Ogard and Taube⁴ for the chromous ion reduction of the analogous chromium(III) complexes. However, while in the latter system the range in relative rates is very great (approximately 7100), in the cobalt(III) system this range is compressed to a factor of only about 3. This lack of discrimination is probably a consequence of the extreme reactivity of the cobalt(III) system toward chromous ion.^{34,35}

While the differences in relative rates of reduction of the $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes by Cr^{2+} are unusually small, these differences appear real and can be ascribed to differences in the bridging capabilities of the halogens. Furthermore, as can be verified from the data of Table II, interrelationships exist between the relative rates for the various couples. This point is illustrated very well by the following diagram which shows the experimentally determined relative rate values (at $\mu = \sim 2 \times 10^{-2} M$), along with certain calculated values (in parentheses). (Our experimental error in these values is estimated to be between 2 and 5%, depending upon the specific analytical problem involved.) For example, once the relative rates between the iodo and bromo,



the bromo and chloro, and the chloro and fluoro complexes have been determined experimentally, then the relative rate for the competition reaction between the iodo and fluoro complexes for Cr^{2+} can be predicted to be 2.73 [*i.e.*, $(k_{\text{I}}/k_{\text{Br}})(k_{\text{Br}}/k_{\text{Cl}})(k_{\text{Cl}}/k_{\text{F}}) = (1.44)(1.26) \cdot (1.51)$]; the experimental value actually found for this pair is 2.75. Furthermore, relative rates consistent with those shown in the above diagram were obtained when excess Cr^{2+} was allowed to interact with a solution containing the three ions $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$, $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$, and $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ (Table III).

(34) R. C. Patel, R. E. Ball, J. F. Endicott, and R. G. Hughes, *Inorg. Chem.*, **9**, 23 (1970).

(35) The results of recent work by Patel, *et al.*,³⁴ suggest that for the conditions of their experiments the chromous reduction of $\text{Co}(\text{en})_2\text{QL}^{2+}$ complexes may vary as much as 30-fold in their specific reactivities.

In 1965 Candlin and Halpern⁵ employed a fast-flow technique to obtain absolute rate constants for the reduction of $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ complexes by Cr^{2+} . These constants are listed in the second column of Table VIII and relative rates based upon them are indicated in the third column. As in our work, Candlin and Halpern also found that the rates increase with ionic strength. The rates given in Table VIII are for an ionic strength of 0.1 M ; at an ionic strength of 1.0 M the rates for the bromo and iodo complexes were too fast to measure by their method. In the fourth column of the table are

TABLE VIII
ABSOLUTE AND RELATIVE RATES FOR THE REDUCTION
OF $\text{Co}(\text{NH}_3)_5\text{L}^{2+}$ IONS BY Cr^{2+} ^a

Compd	$10^{-5}k$, ^b $M^{-1} \text{sec}^{-1}$	—Rel rates—		$10^{-5}k$, ^e $M^{-1} \text{sec}^{-1}$
		Halpern, <i>et al.</i> ^c	This work ^d	
$\text{Co}(\text{NH}_3)_5\text{F}^{2+}$	2.5 ± 0.05	0.42 ± 0.008	0.56	2.5
$\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$	6 ± 1	1.00	1.00	4.5
$\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$	14 ± 4	2.3 ± 0.7	1.44	6.5
$\text{Co}(\text{NH}_3)_5\text{I}^{2+}$	30 ± 10	5.0 ± 1.7	2.4	10.8

^a Ionic strength of reaction mixtures is 0.1 M . ^b Data from ref 5. ^c Based upon the absolute rate constants in column 2. ^d These numbers arise from ratios of rates; see Table II for values of standard deviations and the discussion of errors in the text. ^e Absolute rates calculated from the relative rates in column 4 by using $k = 2.5 \times 10^5 M^{-1} \text{sec}^{-1}$ for the reaction $\text{Co}(\text{NH}_3)_5\text{F}^{2+} + \text{Cr}^{2+}$ at 25° as the reference point.

listed our relative rates for solutions of 0.1 M ionic strength. It is evident that a wider spread in relative rates is indicated by Candlin and Halpern's data than by ours; however, considerable uncertainty appears to be associated with their constants, especially those for the reactions involving the bromo and iodo compounds.

To facilitate the discussion which follows, a composite list of the relative rates for interrelated competitive reductions by Cr^{2+} has been compiled (Table IX); this list includes most of the systems we examined. These rates are all relative to a value of 1.00 for the $\text{Co}(\text{NH}_3)_5\text{F}^{2+}$ complex. They have been calculated from the experimentally determined r values and carry the uncertainties associated with these numbers (see discussion of errors). While the exact order of two complexes lying adjacent to each other with quite similar relative rates may be subject to question, nevertheless the overall trend is meaningful.

Our work in this area was initiated partly to answer the intriguing question of whether or not in reduction reactions involving bridging ligands X^- and Y^- the relative preference by Cr^{2+} for one of these over the other is the same when these groups are in separate complexes (*e.g.*, $\text{Co}(\text{NH}_3)_5\text{X}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{Y}^{2+}$) as when they are in the same complex (*e.g.*, $\text{Co}(\text{NH}_3)_4\text{XY}^{2+}$). Although synthetic difficulties unfortunately limited the variety of compounds available for study, nonetheless an examination of our data clearly indicates that the relative preference by Cr^{2+} for one bridging ligand over another is not a unique function but can be varied drastically and even reversed. For example, when Cr^{2+} reacts with a mixture of $\text{Co}(\text{NH}_3)_5\text{Br}^{2+}$ and $\text{Co}(\text{NH}_3)_5\text{I}^{2+}$

TABLE IX
COMPOSITE RATE VALUES FOR
INTERRELATED COMPETITIVE REDUCTIONS BY Cr²⁺ ^a

No.	Oxidant	Bridging ligand	Rel rate ^b
1	Co(NH ₃) ₅ N ₃ ²⁺	N ₃	0.88
2	Co(NH ₃) ₅ F ²⁺	F	1.00
3	<i>cis</i> -Co(en) ₂ (NH ₃)Cl ²⁺	Cl	1.05
4	<i>cis</i> -Co(en) ₂ Cl ₂ ⁺	Cl	1.15
5	<i>cis</i> -Co(en) ₂ (NCS)Cl ⁺	Cl	1.17
6	<i>cis</i> -Co(en) ₂ (H ₂ O)Cl ²⁺	Cl	1.18
7	<i>cis</i> -Co(en) ₂ (NO ₂)Cl ⁺	Cl	1.28
8	<i>cis</i> -Co(en) ₂ (NH ₃)Br ²⁺	Br	1.34
9	Co(NH ₃) ₅ Cl ²⁺	Cl	1.51
10	<i>trans</i> -Co(en) ₂ (NH ₃)Cl ²⁺	Cl	1.57
11	<i>cis</i> -Co(NH ₃) ₄ (H ₂ O)Cl ²⁺	Cl	1.57
12	<i>cis</i> -Co(NH ₃) ₄ Cl ₂ ⁺	Cl	1.57
13	<i>trans</i> -Co(NH ₃) ₄ Cl ₂ ⁺	Cl	1.66
14	<i>trans</i> -Co(en) ₂ (NCS)Cl ⁺	Cl	1.68
15	<i>trans</i> -Co(en) ₂ Cl ₂ ⁺	Cl	1.83
16	Co(NH ₃) ₅ Br ²⁺	Br	1.89
17	<i>trans</i> -Co(en) ₂ (H ₂ O)Cl ²⁺	Cl	2.17
18	<i>trans</i> -Co(en) ₂ (NO ₂)Cl ⁺	Cl	2.19
19	<i>trans</i> -Co(en) ₂ BrCl ⁺	Cl	2.58
20	<i>trans</i> -Co(en) ₂ BrCl ⁺	Br	2.58
21	Co(NH ₃) ₅ I ²⁺	I	2.75
22	<i>trans</i> -Co(en) ₂ Br ₂ ⁺	Br	3.03

^a Ionic strength $\sim 2 \times 10^{-2} M$. ^b These numbers arise from ratios; see discussion of errors in text and the accompanying tables for values of standard deviations.

Cl²⁺, $k_{Br}/k_{Cl} = 1.26$ (Table IV); with a mixture of Co(NH₃)₅Br²⁺ and *trans*-Co(en)₂(NO₂)Cl⁺, $k_{Br}/k_{Cl} = 0.87$ (Table VI) (*i.e.*, the rate of the reaction with chloride acting as the bridging group is now greater than the rate of the reaction with bromide acting as the bridging group).

As already stated, the reductions of cobalt(III) complexes by Cr²⁺ ions are characterized by rates which are only slightly different. It is perhaps presumptuous then to attempt to draw inferences from these small differences in rates. However, our method appears to differentiate between these closely bunched rates and our data are self-consistent. In the following discussion, rate effects which appear to be related to structural features of the oxidizing agent will be emphasized.

The above examples, and others, appear to support the view that for a series of *trans*-substituted chlorobis(ethylenediamine)cobalt(III) complexes the activating effect of the group *trans* to the bridging ligand is Br⁻ > NO₂⁻ > H₂O > Cl⁻ > NCS⁻ > NH₃. A possible *cis* effect also appears discernible. For a series of *cis*-substituted chlorobis(ethylenediamine)cobalt(III) complexes the order of "deactivating" effect of the *cis* substituent seems to be NH₃ > Cl⁻ > NCS⁻ > H₂O >

NO₂⁻. All of these chloro complexes react more slowly than Co(NH₃)₅Cl²⁺ with Cr²⁺ ion. However, when H₂O is *cis* to chloride in *cis*-Co(NH₃)₄(H₂O)Cl²⁺, a slight enhancement in rate of reduction with Cr²⁺ is observed (Table IX).

There is probably no simple relation between the structure of a complex cobalt(III) ion containing a bridging ligand and the rate at which this ion is reduced. Orgel³⁶ has suggested that in the reduction of cobalt(III) complexes the electron gained by the oxidant is accepted into the d_{z²} orbital (which is assumed to be coincident with the metal-bridging ligand axis); the process may be accompanied by an outward movement³⁷ of the group *trans* to the bridging group. This is perhaps why³⁸ the rates for *trans*-Co(en)₂NH₃L²⁺ ions are in general greater than those for *cis*-Co(en)₂NH₃L²⁺ ions, those for Co(NH₃)₅L²⁺ greater than those for *cis*-Co(en)₂NH₃L²⁺, those for *cis*-Co(NH₃)₄L₂⁺ greater than those for *cis*-Co(en)₂L₂⁺, etc. In the latter complexes, the more rigid chelated structure may restrict the outward movement of the *trans* nitrogen atom. (In Table IX compare the values of the relative rates for compounds 3 and 10, 4 and 12, 6 and 11, 3 and 9, and 8 and 16.)

More compounds will have to be investigated before a definite answer can be given to the question of whether or not the relative bridging abilities of groups can be changed. For the comparatively few compounds we examined containing similar ligand atmospheres except for the bridging groups, the relative bridging abilities of any two bridging groups are not constant, but neither are the differences large. (For comparing the relative bridging abilities of bromide *vs.* chloride, use compounds 16 and 9, 8 and 3, 20 and 15, and 22 and 19 in Table IX.)

Finally, it is worth noting that clear-cut results were not obtained in the competitive reductions by Cr²⁺ of the complex ions Co(en)₂(NCS)Cl⁺ and Co(en)₂(N₃)Cl⁺. Apparently once the NCS⁻ and N₃⁻ ions are liberated into solution, they can give rise to a so-called free-ligand effect.³ Competitive reductions were also carried out in the presence of other ions of this type. In these reduction reactions the ligand effect of the free anions appears to decrease in the order P₂O₇⁴⁻ > N₃⁻ > NCS⁻ > SO₄²⁻ > Cl⁻.

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