When potassium thiocyanate is added to a solution containing equimolar $Cd(NO_3)_2$ and glycine at pH 5.0, the thiocyanate yields a spectrum characteristic of coordinated SCN^-. At lower thiocyanate concentrations, the C≡N stretching frequency appears at 2100 cm^{-1} and, as the thiocyanate concentration is increased, this line moves down to 2095 cm^{-1}, indicating, as in the case of the Zn(II) system, the presence of mixed thiocyanato-glycine complexes with Cd(II). If thiocyanate is added to an equimolar solution of $CdCl_2$ and glycine, at pH 5, for small amounts of added thiocyanate, the Cd–Cl stretching frequency moves down to 215 cm^{-1}. When more thiocyanate is added, this line disappears completely. The C≡N stretching frequency in all of these solutions is located at 2095 cm^{-1}. These results are very similar to those obtained for the $ZnCl_2$–glycine–thiocyanate system, and accordingly we conclude that the ternary complex $Cd(NH_2CH_2COO)SCNCl^-$ probably exists in these solutions. The C–S stretching frequency of the coordinated thiocyanate is located at 775 cm^{-1} in all of these solutions, indicating bonding of the SCN^- group to the metal through the nitrogen atom.[19]

Beryllium Chloride–Glycine System.—Spectra of $BeCl_2$–glycine solutions exhibited behavior very different from those of the Zn(II)- and the Cd(II)-glycine systems. At pH near 2.0, the Raman spectrum of $BeCl_2$–glycine solutions shows the C–C stretching frequency around 915 cm^{-1}. The NH_2 stretching frequencies could not be detected, and the C–H stretching frequencies for these solutions are at 2975 and 3010 cm^{-1}, indicating that the amino group is protonated. The large shift of the C–C stretching fequency indicates strong coordination of the ligand to the metal, and, because the amino group is protonated, glycine seems to bind only through the oxygen atom of the carboxyl group. The solution containing a mole ratio of glycine to $BeCl_2$ of 1 shows the C–C stretching frequency at 920 cm^{-1}; the solution containing a mole ratio of glycine to $BeCl_2$ of 2 shows this line at 915 cm^{-1}. However, when the ratio of glycine to the metal is increased, the line moves down toward 896 cm^{-1}, which corresponds to the free glycine frequency. These results seem to suggest that the Be(II) coordinates only two glycine molecules. All of these solutions show a weak, broad Raman line at 440 cm^{-1}, which probably arises from a Be–O stretching vibration. When the pH of an equimolar solution of glycine is lowered below 1, the complex begins to dissociate, showing a Raman line at 869 cm^{-1}, characteristic of the C–C stretching vibration of the $NH_3^+CH_2COOH$ ion, in addition to the line at 920 cm^{-1}.

As the pH of the above solution is increased progressively, the C–C stretching frequency shifts down, and, at pH 6.5, it moves down to 896 cm^{-1}. The rest of the glycine spectrum is still characteristic of the protonated amino group, and the entire spectrum resembles very closely the spectrum of the free glycine dipolar ion, $NH_3^+CH_2COO^-$. These changes can only be taken to mean that, as the pH is increased, the Be(II) ion is hydrolyzed with the consequent dissociation of the glycine from the metal. Thus, at no stage in the pH range between 1.0 and 6.5 does the glycine seem to form a bidentate complex with the Be(II) ion.

The $BeCl_2$–glycine solutions at higher pH show a very weak, broad Raman line at 430 cm^{-1}. Probably this line may be characteristic of some hydrolyzed Be(II) ion.

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Product Competition Ratios in Substitution Reactions of Pentaamminecobalt (III) Complexes

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Studies of the competition between water and other species as entering groups in the replacement of L from $Co^{III}(NH_3)_5L$ have been extended. The oxygen isotopic fractionation effect has been found to be the same within experimental error (±0.001) for $HgCl^+$, $HgBr^+$, N_3^-, NO^+, Cl^-, Br^-, and NO_3^- as leaving groups. Trimethyl phosphate has been investigated as a leaving group. It is found that the competition ratios are different from those reported by Haim and Taube for two other systems involving neutral leaving groups.

Introduction

The question as to whether an intermediate of reduced coordination number is formed in substitution reactions can in principle be settled by investigating the relative reactivity of the intermediate to a variety of incoming groups. Using this approach and comparing the results of chemical competition studies for the nitrous acid assisted removal of azide ion from $Co(NH_3)_5N_3^{2+}$ on the one hand with those derivable from measurements of the rates of anation of $Co(NH_3)_5H_2O^{3+}$, Haim and Taube[1] concluded that a common intermediate is formed in the two kinds of reactions. By extending this kind of measurement to reactions in

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[1] A. Haim and H. Taube, *Inorg. Chem.*, **2**, 1199 (1963).

which NO_3^- is the leaving group, Pearson and Moore[2] showed that the product distributions are sensitive to the nature of the leaving group. Thus the agreement recorded by Haim and Taube for two different leaving groups, which formed the basis for their conclusion, must be regarded as fortuitous, or to have an explanation other than that advanced.

We have undertaken to investigate the subject further and have, in particular, extended the range of the competition studies. Oxygen isotopic frationation factors have been determined, similar to those described by Posey and Taube,[3] but not limited to the metal ion assisted reactions. We have also done chemical competition studies with nitrate ion and trimethyl phosphate as the leaving groups and with chloride, bromide, nitrate, or thiocyanate ions competing against water as the entering group. Trimethyl phosphate was chosen as the leaving group because it is a neutral species, thus affording a significant comparison with the earlier studies by Haim and Taube. The trimethyl phosphate complex is well suited to the experiments because its aquation is so rapid that the competition studies can be carried out with only minor complications caused by further reaction of the initial product of the aquation reactions.

Experimental Section

Reagents and Preparations.—All chemicals were reagent grade, used as supplied by the manufacturers except as noted.

Water for the fractionation experiments was doubly distilled, the second time from alkaline permanganate, and stored in a carboy fitted with a trap to exclude carbon dioxide. Water thus prepared was used in all of the fractionation experiments.

The carbon dioxide used in the fractionation experiments was prepared by the action of concentrated sulfuric acid upon sodium carbonate and was repeatedly sublimed *in vacuo* from a Dry Ice bath to ensure freedom from water and air. The same sample of CO_2 provided the gas used in all of the equilibrations.

Perchloric acid for the preparation of all solutions in the fractionation experiments was from the same bottle.

Sodium nitrite was recrystallized twice from the water used in the fractionation experiments so that the oxygen in the nitrite would be in isotopic equilibrium with the solvent.

In the preparations of all of the compounds for the fractionation studies, methanol was the only solvent used to wash the solids. Use of ethanol, acetone, or ether interferes with the isotopic analysis of the carbon dioxide.

The compound $Co(NH_3)_5CO_3NO_3 \cdot 0.5H_2O$ used as an intermediate in the preparation of the various complexes was obtained following the method of Basolo and Murmann.[4] The compounds $Co(NH_3)_5Cl_3$,[5] $Co(NH_3)_5Br_3$,[6] and $Co(NH_3)_5N_3Cl_2$[7] were obtained by the methods described in the references cited. The halide salts were converted to the corresponding perchlorates by dropwise addition of two equivalents of $AgClO_4$ solution to a well-stirred suspension of the sparingly soluble halide salts. After filtering to remove the silver halides, concentrated perchloric acid was added until precipitation began, and the solutions were then cooled in ice. The salts were recrystallized from a minimum of room-temperature water and analyzed spectrophotometrically.

The salt $Co(NH_3)_5NO_3(ClO_4)_2$ was prepared using $NaClO_4$ to precipitate it from a solution of $Co(NH_3)_5CO_3NO_3 \cdot 0.5H_2O$ in 3 *M* H_2SO_4, as described by Green and Taube.[8] The perchlorate salt was recrystallized from the minimum of room-temperature water using concentrated perchloric acid.

The species $Co(NH_3)_5OP(OCH_3)_3^{3+}$ was originally prepared by Schmidt and Taube,[9] who were not able to isolate it as a solid. Using an approach suggested by Sargeson,[10] the compound $Co(NH_3)_5OP(OCH_3)_3(ClO_4)_3$ was prepared in solution by the reaction

$$Co(NH_3)_5N_3^{2+} + NO^+ + OP(OCH_3)_3 = Co(NH_3)_5OP(OCH_3)_3^{3+} + N_2 + N_2O$$

in trimethyl phosphate as the solvent. The detailed method is as follows. Seven grams of carefully dried $Co(NH_3)_5N_3(ClO_4)_2$ was added with stirring to 50 ml of $OP(OCH_3)_3$ which had been distilled from calcium sulfate at 192–194° (760 mm). Small amounts of $NOClO_4$, prepared by the method of Schmeisser,[11] were added until gas evolution ceased, 4.1 g being used. The resulting solution was repeatedly extracted with anhydrous ether until a dark red oil remained. This oil was alternately triturated with a few drops of anhydrous ethanol and extracted with ether until a mass of finely divided pink crystals remained. These were collected by filtration, washed with ether, and dried under vacuum. Attempts at recrystallization failed owing to the extreme solubility of the salt.[9] All operations were performed as rapidly as possible (about 15 min being taken in the preparation) to minimize the formation of $Co(NH_3)_5OH_2(ClO_4)_3$ by reaction with water from the air.

Characterization by spectrophotometric analysis[9] and by determining the amount of $Co(NH_3)_5OH_2^{3+}$ resulting from hydrolysis in water showed that the compound had an effective molecular weight of 750 ± 20. The difference between this and the formula weight (582.5) corresponds almost to the weight of 1 mole of $OP(OCH_3)_3$. After the preparation was kept 2 months under vacuum in a desiccator, the impurity had been removed and the compound gave the spectrum as reported in the literature.[9] *Anal.* Calcd for $Co(NH_3)_5OP(OCH_3)_3(ClO_4)_3$: C, 6.2; H, 4.12; N, 12.0. Found: C, 6.23; H, 4.10; N, 11.0. The pure salt was used in the chemical competition experiments.

The compound $Co(NH_3)_5NCS(NO_3)_2$ was prepared by the method of Werner and Muller[12] and was analyzed spectrophotometrically.

Sodium perchlorate solutions used to make up the ionic strength were prepared by adding reagent $HClO_4$ to a weighed amount of Na_2CO_3 and heating to expel CO_2.

Fractionation Studies.—Symbols and terms are defined as: $R = {}^{46}(CO_2)/[{}^{44}(CO_2) + {}^{45}(CO_2)]$, the observed isotopic ratio; $N = {}^{16}O/{}^{18}O$, the isotopic content of the analyzed samples, calculated using the equation of Dostrovsky and Klein[13]

$$= \frac{N_{\text{product}}}{N_{\text{solvent}}} = \frac{\text{d ln }({}^{16}O)}{\text{d ln }({}^{18}O)}$$

where f is the isotopic fractionation factor.

Fractionation experiments were performed in the following way. A solution of the reactant salt and perchloric acid was made up in an amber bottle with 25° water, stoppered, and placed in a thermostated bath. After a predetermined time had elapsed, an aliquot of the solution was taken for solvent analysis and the bulk of the solids precipitated by the addition of ice-cold, concentrated hydrobromic acid. After cooling to *ca.* 5°, the sample was filtered to collect the solid $Co(NH_3)_5OH_2Br_3$ which was promptly recrystallized from a minimum of room-temperature water. These crystals were washed with methanol and dried several hours in a vacuum desiccator.

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(2) R. G. Pearson and J. W. Moore, *Inorg. Chem.*, **3**, 1334 (1964).

(3) F. A. Posey and H. Taube, *J. Am. Chem. Soc.*, **79**, 255 (1957).

(4) F. Basolo and R. K. Murmann, *Inorg. Syn.*, **4**, 171 (1953).

(5) W. A. Hynes, L. K. Yanowski, and M. Shiller, *J. Am. Chem. Soc.*, **60**, 3053 (1938).

(6) H. Diehl, H. Clark, and H. H. Willard, *Inorg. Syn.*, **1**, 186 (1937).

(7) M. Linhard and S. Flygare, *Z. Anorg. Chem.*, **262**, 328 (1950).

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

(9) W. Schmidt and H. Taube, *ibid.*, **2**, 698 (1963).

(10) A. M. Sargeson, private communication.

(11) M. Schmeisser in "Handbook of Preparative Inorganic Chemistry," Vol. 1, G. Braun, Ed., 2nd ed, Academic Press Inc., New York, N. Y., 1963, p 320.

(12) A. Werner and H. Muller, *Z. Anorg. Chem.*, **22**, 91 (1900).

(13) I. Dostrovsky and F. S. Klein, *Anal. Chem.*, **24**, 415 (1952).

The mercuric ion and nitrous acid assisted reactions were carried out at approximately 25° by addition of mercuric perchlorate or nitrous acid solutions (from $NaNO_2 + HClO_4$) to rapidly stirred solutions of the reactant complexes. Solid samples were collected as above.

The collection of water and equilibration with CO_2 for isotopic analysis were performed by the methods developed by earlier workers[3,9,14] using standard vacuum techniques.[15] Analyses were made on an Atlas M-86 mass spectrometer, which is a double-collecting instrument. All measurements were made relative to a sample of standard CO_2 taken from the same gas used in the equilibrations and adjusted to the value $R = 0.00400$ for the standard.

The internal consistency of the isotopic analysis is shown by the constancy of R found for the solvent water which had a standard deviation of 4 parts in 10,000 on over 40 samples taken over a period of 8 months. The much higher average deviations (15 to 20 parts in 10,000) in the values of f are attributed to impurities in the reactant compounds, to small amounts of water occluded in the precipitated $Co(NH_3)_5OH_2Br_3$, and other random errors which were not recognized in the course of the analysis. In the studies of $Co(NH_3)_5NO_3^{2+}$ aquation, fractionation values ranging from 1.001 to 1.006 were observed in the earliest series of experiments. The higher values as reported were observed in all later samples in which the precaution was taken of recrystallizing the salt to be analyzed in order to remove all traces of the nitrato complex. It should be noted that as little as 2 ppm of NO_2 in the CO_2 would lead to a difference of the magnitude (and direction) observed.

Chemical Competition Studies.—Chemical competition measurements were performed two in different ways. In the first, the absorption of a reacting solution was followed as a function of time at two or more wavelengths. Using extinction coefficients measured under the same conditions of temperature and ionic strength, it was possible to determine the composition of the solution at any time. Results on product composition at various time intervals were averaged to yield the reported values of competition ratios.

The measurments conducted in this fashion lead to values for the specific rates of disappearance of the aquating species. Our results on this point are incidental to our main purpose, but, since comparison with literature values may be of some interest, they are reported here (temperature 25.0°; all solutions contained 0.01 M $HClO_4$): k governing the total rate of disappearance of $Co(NH_3)_5OP(OCH_3)_3^{3+}$ in 0.2 M NaBr was found to be $(0.25 \pm 0.01) \times 10^{-3}$ sec^{-1} to be compared with 0.245×10^{-3} in 0.4 M $NaClO_4$ reported by Schmidt and Taube;[9] k for the disappearance of $Co(NH_3)_5Br^{2+}$ in 0.2 M NaBr and in 0.2 M $NaClO_4$, respectively, was found to be $(0.33 \pm 0.02) \times 10^{-4}$ and $(0.30 \pm 0.1) \times 10^{-4}$ sec^{-1} which may be compared to 0.27×10^{-4} sec^{-1} as reported by Pearson and Moore[2] for 0.5 M NaSCN.

In the second approach, the primary reaction was allowed to proceed essentially to completion and the spectra of the product solutions were analyzed. Shortly before product analysis, solutions of sodium perchlorate and other salts and distilled water were added to make the anionic compositions of the various solutions the same. This was necessary to eliminate variations in the charge-transfer spectra, which are very sensitive to ion atmosphere effects. When both techniques were employed with the same system, the results agreed satisfactorily.

Extinction coefficients for the species involved in these studies are collected in Table I. All measurements were made using a Cary 14 spectrophotometer with cell compartment thermostated at 25.0 ± 0.05°. Ionic strengths were 0.50 with hydrogen ion concentrations *ca.* 5×10^{-3} M.

Results and Discussion

Isotopic Fractionation Experiments.—Values determined for the value of f in the assisted reactions are collected in Table II. The reactions studied are

$$Co(NH_3)_5X^{2+} + Hg^{2+} + H_2O = Co(NH_3)_5OH_2^{3+} + HgX^+$$

where $X^- = Cl^-$ or Br^-, and

$$Co(NH_3)_5N_3^{2+} + H^+ + HNO_2 = Co(NH_3)_5OH_2^{3+} + N_2 + N_2O$$

The values reported by Posey and Taube[3] for the mercuric-assisted reactions are listed for comparison; agreement is excellent.

TABLE I

ABSORPTION SPECTRA OF VARIOUS SPECIES

Species	Wave-length, mμ	Extinction coeff
$Co(NH_3)_5OH_2^{3+}$	491.0	48.0
	345.0	45.0
$Co(NH_3)_5Cl^{2+}$ (0.1 M)	290.0	311 ± 5
	285.0	412 ± 6
	280.0	533 ± 10
$Co(NH_3)_5Br^{2+}$ (0.1 M Br^-)	310.0	740 ± 10
	305.0	790 ± 10
	300.0	870 ± 10
$Co(NH_3)_5NO_3^{2+}$	262.0	$(1.17 \pm 0.03) \times 10^3$
(0.1 M NO_3^-)	260.0	$(1.29 \pm 0.03) \times 10^3$
$Co(NH_3)_5NCS^{2+}$	495	175 ± 3
(0.1 M SCN^-)	360	420 ± 5
	355	480 ± 5
	350	560 ± 5
	305	$(1.56 \pm 0.03) \times 10^3$
$Co(NH_3)_5OP(OCH_3)_3^{3+}$	530	44.8
	515	46.3
	345	39.2
	320	32.5

TABLE II

FRACTIONATION DATA FOR ASSISTED REACTIONS[a]

Reaction	f	Source
$Co(NH_3)_5Br^{2+} + Hg^{2+}$	1.012 ± 0.0014	This work
$Co(NH_3)_5Br^{2+} + Hg^{2+}$	1.012 ± 0.001	Ref 3
$Co(NH_3)_5Cl^{2+} + Hg^{2+}$	1.011 ± 0.001	This work
$Co(NH_3)_5Cl^{2+} + Hg^{2+}$	1.012 ± 0.001	Ref 3
$Co(NH_3)_5N_3^{2+} + HNO_2 + H^+$	1.0115 ± 0.0012	This work

[a] [Co(III)] ~ 0.03M.

Results for the spontaneous aquations of the various complexes are shown in Table III, which gives the values of f corrected for the exchange reaction

$$Co(NH_3)_5{}^{18}OH_2^{3+} + {}^{16}OH_2 \rightleftharpoons Co(NH_3)_5{}^{16}OH_2^{3+} + {}^{18}OH_2$$

as described in detail by Dolbear.[15] The value of f at exchange equilibrium is 0.9808.[16]

TABLE III

FRACTIONATION DATA FOR SPONTANEOUS REACTIONS[a]

Reactant	No. of determinations	f^b
$Co(NH_3)_5Cl^{2+}$	4	1.0105 ± 0.0013
$Co(NH_3)_5Br^{2+}$	7	1.0117 ± 0.0019
$Co(NH_3)_5NO_3^{2+}$	5	1.0041[c]
$Co(NH_3)_5NO_3^{2+}$	6	1.0124 ± 0.0016

[a] [Co(III)] ~0.03 M. [b] Deviations are average deviations. [c] For samples probably containing NO_2, see text.

Within the errors of the determinations, the isotopic fractionation measurements yield the same values for

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(14) H. Feder, Ph.D. Thesis, University of Chicago, 1954.

(15) These procedures are discussed in greater detail in the Ph.D. Thesis of G. E. D., Stanford University, 1966.

(16) H. R. Hunt and H. Taube, *J. Am. Chem. Soc.*, **80**, 2642 (1958).

all systems studied in this work. This is in contrast to to the sizable variations found by Posey and Taube[3] within the Ag^+- and Tl^{3+}-assisted reactions.

Chemical Competition Experiments.—In Table IV are listed the experimentally determined values of F, where

$$F = \frac{[Co(NH_3)_5X^{2+}]}{[Co(NH_3)_5OH_2^{3+}][X^-]}$$

F is thus defined as the ratio of the rate constants, k_x/k_w, for the formal reactions

$$Co(NH_3)_5Y^{n+} + X^- \xrightarrow{k_x} Co(NH_3)_5X^{2+} + Y^{m+}$$

$$Co(NH_3)_5Y^{n+} + H_2O \xrightarrow{k_w} Co(NH_3)_5OH_2^{3+} + Y^{m+}$$

TABLE IV

PRODUCT DISTRIBUTION DATA FOR AQUATION REACTIONS OF $Co^{III}(NH_3)_5L$[a]

Leaving group	Anion	Concn, M	% anion[b] product		F
$(CH_3O)_3PO$	Cl^-	0.1	0.51		0.051
		0.2	1.49		0.076
		0.5	2.60		0.053
				Av	0.061 ± 0.01
$(CH_3O)_3PO$	NO_3^-	0.1	2.5		0.252
		0.2	5.53		0.292
		0.5	11.5		0.260
$(CH_3O)_3PO$	NO_3^-	0.1	2.6		0.266
		0.2	5.3		0.282
		0.5	11.2		0.251
				Av	0.266 ± 0.013
	Br^-	0.1	0.58		0.058
		0.2	1.30		0.066
		0.5	3.3		0.068
				Av	0.064 ± 0.003
AgBr[c]	NO_3^-	0.1	20.3		2.5
		0.2	42		3.6
		0.3	59		4.8
			$F = 1.4 + 11.2(NO_3^-)$		
NO_3^-	Br^-	0.2	2.8 ± 0.2		0.144 ± 0.01
$(CH_3O)_3PO$[d]	SCN^-	0.05	0.50		0.101
		0.10	0.85 ± 0.05		0.085
		0.20	1.16 ± 0.20		0.058
		0.50	3.0 ± 0.2		0.063

[a] Approximate concentration of Co(III) 10^{-3} M; $\mu = 0.5$; 25°. [b] When $(CH_3O)_3PO$ is the leaving group, the values in this column are corrected for the fact that only 80% of the aquation reaction proceeds by Co–O bond fission. [c] For the reaction $Co(NH_3)_5Br^{2+} + Ag^+$. [d] Averages of two series of determinations are listed; because of the presence of an impurity (see text) little importance should be attached to these numbers.

Although F has the form of an equilibrium quotient, the values are not equilibrium values but were measured as concentrations of reaction products of the original reaction, correcting[17] where necessary for the effect of the reaction

$$Co(NH_3)_5OH_2^{3+} + X^- = Co(NH_3)_5X^{2+} + H_2O$$

The values of F are independent of the concentration of the entering group for all reactions studied except those in which silver ion was involved. In this case, the variation of F with NO_3^- can be expressed by the equation

$$F = 1.4 + 11(NO_3^-)$$

Table V lists the results of product analysis measurements involving nitrate ion as an entering group.

TABLE V

RESULTS OF PRODUCT ANALYSIS EXPERIMENTS INVOLVING NITRATE ION AS ENTERING GROUP

Reacting system	F	μ	Source
$Co(NH_3)_5OP(OCH_3)_3^{3+}$	0.26 ± 0.015	0.50	This work
$Co(NH_3)_5I^{2+} + Hg^{2+}$	0.22	1.0	Ref 3
$Co(NH_3)_5Br^{2+} + Hg^{2+}$	0.22	1.04	Ref 3
$Co(NH_3)_5Cl^{2+} + Hg^{2+}$	0.85 ± 0.15	1.1, 1.3	Ref 3
$Co(NH_3)_5N_3^{2+} + HNO_2 + H^+$	0.44 ± 0.09	0.50	Ref 1
$Co(NH_3)_5Br^{2+} + Ag^+$	$1.4 + 11(NO_3^-)$	0.50	This work

The data show that the attack of an anion on a reacting complex ion is sensitive to the nature of the leaving group. It is noteworthy that nitrate ion can compete with water much more effectively than either bromide or chloride; rate studies have shown that nitrate is also a much better leaving group than the halides.

It was hoped that the studies of thiocyanate as an entering group might resolve the questions arising from the anomalous behavior of this anion in earlier studies.[1] Anomalies were again observed and were traced to the presence of an unknown species having an intense light absorption with a peak in the region around 300 mμ. This species could conceivably be $(SCN)_2$ produced by the oxidation of the thiocyanate by thiocyanate complexes, analogous to the oxidation of iodide by iodopentaamminecobalt(III) studied by Yalman.[18] Long[19] reports that $(SCN)_2$ in water absorbs at 302 mμ (ε 840 ± 160). The concentration necessary to account for the absorptions observed in this study are thus on the order of 10^{-4} M.

Comments.—A limitation of the general approach used is illustrated by the isotopic fractionation data: similarities of competition ratios can never prove that a common intermediate is involved—although, of course, the greater the number of similarities and the more exact the comparison, the greater is the likelihood that such a conclusion is justified. Within experimental error, the oxygen isotopic fractionation effects are the same for the mercury-assisted removal of Br^- and Cl^-, for the nitrous acid assisted removal of N_3^-, and for the spontaneous aquations of the chloro, bromo, and nitrato complexes. As already noted, other evidence shows that the reactions do not all involve a common intermediate. It must be concluded therefore that the differences which exist are within the limits of the present experimental error. The accuracy of the method can in principle be improved, but this would be a laborious undertaking, and there is no assurance that the differences would appear even if the accuracy were pushed to the present limit of the mass spectrometer, which is at about 2 parts in 10,000.

The present work tends to confirm the general interpretation advanced of the earlier fractionation results[3] which is that the large differences in fractionation observed in the reactions with Ag^+ and Tl^{3+} as the inducing agents are ascribable to specific effects of these metal ions. The fact that the values of f are so nearly alike for the variety of leaving groups studied in the course of the present work is consistent with the view that the metal ion leaving group separation is

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(17) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 1st ed, John Wiley and Sons, Inc., New York, N. Y., 1953, p 154.

(18) R. G. Yalman, *J. Am. Chem. Soc.*, **75**, 1843 (1953).

(19) C. H. Long, Ph.D. Thesis, Stanford University, 1964.

large when the bond to water is formed. This interpretation of the data is however by no means unique, for, if the water attacked at a coordination site remote from the leaving group, only a small difference between different leaving groups would be expected. A specific effect of Ag^+ is to be noted also for the present series of experiments: NO_3^- is peculiarly efficient as an entering group in the Ag^+-assisted removal of Br^- and furthermore becomes relatively more efficient as its concentration increases. This may be a consequence of some surface effect (AgBr is formed and the reaction may take place at the surface), but the general behavior has precedent also in homogeneous solution—*cf.* the formation[3] of $Co(NH_3)_5SO_4^+$ in the Hg^{2+}-assisted removal of Cl^- from $Co(NH_3)_5Cl^{2+}$.

Before we undertook the present work, it seemed possible that the agreement in values of competition rates recorded by Haim and Taube[1] was a consequence of the fact that neutral leaving groups were involved in the reactions which they investigated. The present results obtained with $(CH_3O)_3PO$ as leaving group show that the subject is more complicated—as it is in fact expected to be if the incoming groups make bonds before the leaving group has left the scene of reaction. At the present time, the data are too sparse to reveal a pattern in the way the leaving group influences the competition between entering groups. At one extreme, when N_2 or CO_2 is the leaving group, a genuine intermediate may be formed, and in this extreme the leaving group will not influence the product composition. In the other, when a poor leaving group such as NCS^- is in question, its effect may be profound. Data for the systems involving poor leaving groups will however be hard to obtain because the replacement of the group may be slow compared to the rate at which the immediate products reequilibrate. In the intermediate range of leaving group tenacity, there are a variety of systems which can be studied, among them those in which sulfolane, alcohols, or other moderately good leaving groups are used.[20] Further experiments in this direction are planned.

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[20] R. B. Jordan, A. M. Sargeson, and H. Taube, *Inorg. Chem.*, **5**, 1091 (1966).

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Relative Bond Dissociation Energies and Heats of Formation of Two Series of Five-Coordinated Metal Complexes from Manganese(II) to Zinc(II). A Calorimetric Study

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The enthalpy changes for the formation of five-coordinated high-spin complexes have been obtained. The compounds are of the type $[M(Me_6tren)Br]Br$ and $M(Me_5dien)Br_2$—where M = Mn, Fe, Co, Ni, Cu, Zn; $Me_6tren = N[CH_2CH_2N(CH_3)_2]_3$ and $Me_5dien = CH_3N[CH_2CH_2N(CH_3)_2]_2$. Measurements of heats of solution have been made on the simple metal bromides, ligands, and complexes in hydrochloric acid and on the ligands in water. Using these data, the enthalpy changes relative to that of the manganese compound are obtained for the processes $M^{2+} + Br^- + Me_6tren = [M(Me_6tren)Br]^+$ and $M^{2+} + 2Br^- + Me_5dien = M(Me_5dien)Br_2$ both in the gaesous state (bond dissociation enthalpies) and in aqueous solution. The results are discussed in terms of crystal field stabilization energies of the five-coordinated species and of the aquo ions. The stability of these five-coordinated complexes in aqueous solution increases in the order: $Mn < Fe \approx Ni < Co < Zn < Cu$. The enthalpy changes for the reaction of formation: $MBr_2(s) + \text{ligand}(l) = MBr_2\cdot\text{ligand}(s)$ are also obtained. For both series the order of increasing heat evolved is: Mn < (Fe, Ni) < (Co, Cu, Zn). Throughout, a comparison is made with complexes of octahedral and tetrahedral stereochemistry.

Introduction

Complexes of the bivalent ions of the first transition series with a coordination number of five are relatively little known in comparison with those having a coordination number of four or six. Recently renewed interest has been devoted to this type of complex, and a number of five-coordinated complexes of $3d^{5-10}$ metals have been prepared.[1-3]

The present calorimetric study investigates the tendency of the bivalent transition metal ions from manganese to zinc to form five-coordinated complexes

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[1] L. M. Venanzi, *Angew. Chem. Intern. Ed. Engl.*, **3**, 453 (1964), and previous references therein; L. Sacconi, M. Ciampolini, and G. P. Speroni, *J. Am. Chem. Soc.*, **87**, 3102 (1965); L. Sacconi, P. Nanelli, N. Nardi, and U. Campigli, *Inorg. Chem.*, **4**, 943 (1965); G. S. Benner, W. E. Hatfield, and D. W. Meek, *ibid.*, **3**, 1544 (1964); J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, **207**, 72 (1965). For updated references see also L. Sacconi and I. Bertini, *J. Am. Chem. Soc.*, **88**, 5180 (1966).

[2] (a) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (b) M. Ciampolini and N. Nardi, *ibid.*, **5**, 1150 (1966).

[3] M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966).