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Formation of $Co(NH_3)_5X^{+2}$ Complexes by the Reaction of $Co(NH_3)_5N_3^{+2}$ with HNO_2 in the Presence of Various Anions: the Mechanism of Substitution Reactions of Pentaamminecobalt(III) Complexes

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Received June 10, 1963

The reaction between $Co(NH_3)_5N_3^{+2}$ and HNO_2 in a perchlorate medium yields $Co(NH_3)_5OH_3^{+3}$, N_2, and N_2O. At 25° and $\mu = 0.50$, the rate law $9.3 \times 10^4(Co(NH_3)_5N_3^{+2})(HNO_2)(H^+)$ (time in minutes) is obeyed. Addition of Cl^-, Br^-, NO_3^- SCN^-, or SO_4^{-2} increases the reaction rate and results in the formation of $Co(NH_3)_5X^{+2}$ complexes in addition to $Co(NH_3)_5OH_2^{+3}$. It is suggested that the $Co(NH_3)_5N_3^{+2}$–HNO_2 reaction proceeds by way of the intermediate $Co(NH_3)_5N_3NO^{+3}$ which loses N_2 and N_2O to form the pentacoordinated species $Co(NH_3)_5^{+3}$. Competition between the added anions and water for $Co(NH_3)_5^{+3}$ results in the formation of the observed products. The agreement between the product distributions observed in the present system with the distributions expected if the direct anation reaction proceeds *via* the formation of the pentacoordinated intermediate $Co(NH_3)_5^{+3}$ is taken as an indication that the mechanism of reaction 1 is of the SN1 type.

The difficulties involved in the elucidation of the mechanisms of substitution reactions of complex ions have often been referred to.[1] The present paper describes the results of an attempt to generate the pentacoordinated intermediate $Co(NH_3)_5^{+3}$ by the reaction of $Co(NH_3)_5N_3^{+2}$ with HNO_2. There is ample evidence that the reaction of free N_3^- with HNO_2 proceeds by way of the nitrosyl azide intermediate, which rapidly decomposes to yield N_2 and N_2O.[2,3] It was hoped that a similar reaction would occur for the coordinated N_3^- of $Co(NH_3)_5N_3^{+2}$, and that the intermediate $Co(NH_3)_5N_3NO^{+3}$ would lose N_2 and N_2O with formation of $Co(NH_3)_5^{+3}$. If this expectation were fulfilled, it would be possible to study the competition of various anions and water for reaction with $Co(NH_3)_5^{+3}$. Indeed, we have found that $Co(NH_3)_5N_3^{+2}$ rapidly reacts with HNO_2 and that, in the absence of anions other than ClO_4^-, the cobalt-containing species is $Co(NH_3)_5OH_2^{+3}$. In the presence of other anions, complexes of the type $Co(NH_3)_5X^{+2}$ ($X^- = F^-$, Cl^-, Br^-, NO_3^-, SCN^-, $H_2PO_4^-$, SO_4^{-2}) are formed in addition to $Co(NH_3)_5OH_2^{+3}$. Additional insight into the mechanism of the $Co(NH_3)_5N_3^{+2}$–HNO_2 reaction as well as the anation and aquation reactions of pentaamminecobalt(III) complexes has been obtained by comparing the product distributions observed in the present system with the distributions expected if the equilibration represented by eq. 1 proceeded by an SN1 mechanism.

$$Co(NH_3)_5OH_2^{+3} + X^- \rightleftharpoons Co(NH_3)_5X^{+2} + H_2O \quad (1)$$

Experimental

Materials.—$[Co(NH_3)_5N_3](ClO_4)_2$ was prepared as described by Linhard and Flygare.[4] All other chemicals were reagent grade. Solutions of sodium nitrite were standardized as described by Kolthoff and Belcher.[5]

Kinetic Studies.—Solutions of $Co(NH_3)_5N_3^{+2}$, $NaNO_2$, and all other reagents except the $HClO_4$ were pipetted into a volumetric flask which was placed in a constant temperature bath at 25 ± 0.1°. After temperature equilibration had been achieved, the $HClO_4$ was added and the solution was made up to volume and rapidly transferred to a spectrophotometric cell. The cell was placed in the thermostated (25 ± 0.1°) cell holder of a Cary recording spectrophotometer, and a recording of optical density *vs.* time was obtained. Measurements were made at 300 and 515 mμ, where large changes in optical density occur upon reaction, and therefore very precise rate data could be obtained. In all experiments the concentration of $Co(NH_3)_5N_3^{+2}$ was small compared to that of the other reagents and therefore pseudo-first-order rate constants were obtained from the slopes of the linear plots of log $(D_t - D_\infty)$ *vs.* time. D_t and D_∞ are the optical densities of the solution at time t and after reaction is complete, respectively.

Stoichiometric Studies.—Solutions of $Co(NH_3)_5N_3^{+2}$, $NaNO_2$, the sodium salt of the anion under study, and $HClO_4$ were pipetted into a volumetric flask and any volume defect was made up by adding solvent. After the reaction had proceeded to completion (25°) the solutions were examined spectrophotometrically to establish the reaction products and appropriate wave lengths were chosen to provide maximum accuracy in the determination of the $Co(NH_3)_5OH_2^{+3}$ and $Co(NH_3)_5X^{+2}$ species.

Results

The stoichiometry of the reaction between $Co(NH_3)_5N_3^{+2}$ and HNO_2 in the absence of anions other than ClO_4^- was studied only to the extent of establishing the nature of the Co(III) product. Under the conditions studied the only cobalt-containing species produced is $Co(NH_3)_5OH_2^{+3}$, the identification being done spectrophotometrically between 580 and 380 mμ. As reaction occurs gas evolution is observed and by comparison with the corresponding reaction between free N_3^- and HNO_2[2,3] it was assumed that N_2 and N_2O were formed, the stoichiometry being represented by the equation

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

The experiments performed to establish the kinetics of the above reaction are summarized in Table I. The

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[1] For a recent review see R. G. Wilkins, *Quart. Rev.* (London), **16**, 316 (1962).

[2] K. Clusius and E. Effenberger, *Helv. Chim. Acta*, **38**, 1843 (1955).

[3] G. Stedman, *J. Chem. Soc.*, 1702 (1960), and preceding papers.

[4] M. Linhard and H. Flygare, *Z. anorg. allgem. Chem.*, **262**, 328 (1950).

[5] I. M. Kolthoff and R. Belcher, "Volumetric Analysis," Vol. 3, Interscience Publishers, New York, N.Y., 1957, p. 526.

measured pseudo-first-order rate constants k are listed in column 6. Column 7 gives the calculated third-order rate constants k' assuming a rate law of the form $k'(Co(NH_3)_5N_3^{+2})(HNO_2)(H^+)$. The values of (HNO_2) and (H^+) necessary to compute k' were obtained from the known concentrations of added $HClO_4$ and $NaNO_2$ and using a value of 5×10^{-4} for the dissociation constant of HNO_2.[6] The constancy of k' upon reasonable variations in the concentrations of the reactants indicates that the form of the rate law adopted adequately represents the kinetics of the reaction. The increase in k' at higher ionic strengths (expt. 7) is consistent with the form of the rate law.

TABLE I

KINETICS OF THE $Co(NH_3)_5N_3^{+2}$–HNO_2 REACTION AT 25° AND $\mu = 0.50$

Expt.	$(Co(NH_3)_5N_3^{+2})$, $M \times 10^5$	$\Sigma(NO_2^-)$, $M \times 10^{4a}$	$\Sigma(H^+)$, $M \times 10^{4b}$	(H^+), $M \times 10^{4c}$	k, min.$^{-1}$ $\times 10^2$	k', M^{-2} min.$^{-1}$ $\times 10^{-4d}$
1	1.08	4.48	9.35	6.77	1.64^e	9.4
2	1.08	4.48	18.7	15.3	4.62^e	8.9
3	1.08	8.96	18.7	12.4	7.59^e	9.7
4	1.18	22.4	28.1	12.1	10.2^e	10.5
5	9.67	11.2	9.25	4.21	2.09^f	9.6
6	9.67	11.2	28.1	19.2	15.1^f	8.8
7	1.18	11.2	9.35	4.21	5.1^{e,g}	24

[a] Concentration of added $NaNO_2$; $\Sigma(NO_2^-) = (NO_2^-) + (HNO_2)$. [b] Concentration of added $HClO_4$; $\Sigma(H^+) = (H^+) + (HNO_2)$. [c] Calculated from $\Sigma(NO_2^-)$, $\Sigma(H^+)$, and the dissociation constant of HNO_2, 5×10^{-4}. [d] Calculated from the expression $k' = k/(H^+)(HNO_2)$. [e] Measured at 300 mμ. [f] Measured at 515 mμ. [g] Ionic strength 1.0.

A series of kinetic experiments was performed in the presence of added anions, and the results are summarized in Table II. The measured pseudo-first-order rate constants k'' are listed in column 7. Column 8 gives $k'' - k$, the increase in rate caused by addition of the anion, and it is apparent that all anions studied accelerate the reaction. Furthermore, the values of $k''' = (k'' - k)/(HNO_2)(H^+)(X^-)$ listed in column 9 indicate that the dependence of the reaction rate upon anion concentration becomes less than first order as the anion concentration increases.

The results on the formation of $Co(NH_3)_5X^{+2}$ ($X^- = F^-, Cl^-, Br^-, NO_3^-, SCN^-, H_2PO_4^-, SO_4^{-2}$) when the reaction of $Co(NH_3)_5N_3^{+2}$ with HNO_2 is carried out in the presence of added anions are summarized in Table III. In column 6 are listed the values of F, the per cent of $Co(NH_3)_5N_3^{+2}$ converted to $Co(NH_3)_5X^{+2}$ on reaction. Since the values of F are obtained from small differences in optical density measurements, they are good to only ±5% for F values larger than 10, and the errors may be as large as 10% for smaller F values, except for the SCN^- system where, because of the larger differences in the extinction coefficients of $Co(NH_3)_5NCS^{+2}$ and $Co(NH_3)_5OH_2^{+3}$, the values of F are believed to be good to ±2%. The dependence of F upon concentrations of NO_2^-, H^+, and $Co(NH_3)_5N_3^{+2}$ has not been tested except for experiments 3 and 4, where (H^+) is changed by a factor of *ca.* 500 without appreciably altering the value of F. The variation of F with anion concentration has been tested in a few cases and within experimental error the quantity $R = F/(100 - F)(X^-) = (Co(NH_3)_5X^{+2})/(Co(NH_3)_5OH_2^{+3})(X^-)$ listed in column 7 is independent of (X^-), except for SCN^- where R decreases with increasing (SCN^-).

Discussion

The form of the rate law for the reaction of $Co(NH_3)_5N_3^{+2}$ with HNO_2 in a perchlorate medium is consistent with the mechanism represented by eq. 2, 3, 4, and 5. There is ample evidence[2,3] that the reaction of N_3^- with HNO_2 involves the formation of a nitrosyl azide intermediate, and this formulation is adopted in eq. 4. Equation 5 has only stoichiometric significance at this point and the mechanism of this reaction will be discussed in a subsequent section.

$$H^+ + HNO_2 \overset{K'}{\rightleftharpoons} H_2NO_2^+ \qquad (2)$$

$$H_2NO_2^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO^+ + H_2O \qquad (3)$$

$$Co(NH_3)_5N_3^{+2} + NO^+ \xrightarrow{k_3} Co(NH_3)_5N_3NO^{+3} \qquad (4)$$

$$Co(NH_3)_5N_3NO^{+3} + H_2O \xrightarrow{\text{rapid}} Co(NH_3)_5OH_2^{+3} + N_2 + N_2O \qquad (5)$$

On the basis of eq. 2–5, the following rate law is derived

$$-\frac{d(Co(NH_3)_5N_3^{+2})}{dt} = \frac{k_1K'(H^+)(HNO_2)(Co(NH_3)_5N_3^{+2})}{(k_2/k_3) + (Co(NH_3)_5N_3^{+2})} \qquad (6)$$

The third-order rate constant k' listed in column 7 of Table I has, therefore, the following significance

$$k' = \frac{k_1K'}{(k_2/k_3) + (Co(NH_3)_5N_3^{+2})} \qquad (7)$$

At the low concentrations of $Co(NH_3)_5N_3^{+2}$ used in the kinetic experiments k' was found to be independent of $(Co(NH_3)_5N_3^{+2})$. Therefore, it must be concluded that $(k_2/k_3) >> (Co(NH_3)_5N_3^{+2})$ and $k' = k_1k_3K'/k_2$. Reaction 3 provides a path for oxygen exchange between nitrite and water and it is possible therefore to verify the adequacy of the approximation indicated above. Anbar and Taube[7] reported that the rate of exchange at 25° and ionic strength 1.0 is given by the expression $2.6 \times 10^8(NO_2^-)(H^+)^2$ (time in minutes). Using the value 5×10^{-4} for the dissociation constant of nitrous acid and assuming that the mechanism of exchange involves the slow dissociation of $H_2NO_2^+$,[7] k_1K' is calculated as 13×10^4 min.$^{-1}$ at 25°. Combining this value with that of k' measured in the present investigation, it is concluded that $k_2/k_3 = 1.4$. Since the highest $Co(NH_3)_5N_3^{+2}$ concentration used in the kinetic experi-

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[6] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, "Stability Constants of Metal Ion Complexes, Part II: Inorganic Ligands," Special Publication No. 7, The Chemical Society, London, 1958, p. 53.

[7] M. Anbar and H. Taube, *J. Am. Chem. Soc.*, **76**, 6243 (1954).

TABLE II

KINETICS OF THE $Co(NH_3)_5N_3^{+2}$–HNO_2 REACTION IN THE PRESENCE OF ADDED ANIONS AT 25°, $\mu = 0.50$, $\lambda = 300$ mμ

Expt.	Anion, M	$(Co(NH_3)_5N_3^{+2})$, $M \times 10^5$	$\Sigma(NO_2^-)$, $M \times 10^4$	$\Sigma(H^+)$, $M \times 10^4$	(H^+), $M \times 10^4$	k'', min.$^{-1}$	$(k'' - k)$,[a] min.$^{-1}$	k''',[b] M^{-3} min.$^{-1}$
1	Cl^-, 0.10	1.08	4.48	9.35	6.77	0.163	0.147	8.48×10^6
2	Cl^-, .30	1.08	4.48	9.35	6.77	.422	.406	7.80×10^6
3	Cl^-, .50	1.08	4.48	9.35	6.77	.640	.624	7.15×10^6
4	Br^-, .10	1.08	4.48	9.35	6.77	.440	.424	2.42×10^7
5	Br^-, .30	1.08	4.48	9.35	6.77	1.07	1.05	2.00×10^7
6	Br^-, .50	1.08	4.48	9.35	6.77	1.69	1.67	1.91×10^7
7	SCN^-, .10	1.08	4.48	9.35	6.77	0.360	0.344	1.93×10^7
8	SCN^-, .30	1.08	4.48	9.35	6.77	.690	.674	1.29×10^7
9	SCN^-, .50	1.08	4.48	9.35	6.77	.750	.734	0.84×10^7
10	NO_3^-, .50	9.7	11.2	28.1	19.2	.226[c]	.075	8.80×10^4
11	SO_4^{-2}, .17	1.08	22.4	28.1	3.91[d]	.132	.096	1.44×10^6
12	SO_4^{-2}, .50	1.08	22.4	28.1	2.30[e]	.092[f]	.050	0.58×10^6

[a] k is the pseudo-first-order rate constant in the absence of added anion. [b] Calculated from the expression $k''' = (k'' - k)/(H^+)\cdot(HNO_2)(X^-)$. [c] Measured at 515 m$\mu$. [d] Calculated using 0.047 for the dissociation constant of HSO_4^-: W. L. Reynolds and S. Fukushima, *Inorg. Chem.*, **2**, 176 (1963). [e] Calculated using 0.063 for the dissociation constant of HSO_4^-, ref. *d*. [f] Ionic strength 1.0.

TABLE III

PRODUCT DISTRIBUTIONS IN THE $Co(NH_3)_5N_3^{+2}$–HNO_2 REACTION WITH ADDED ANIONS (25°, $\mu = 0.50$)

Expt.	$(Co(NH_3)_5N_3^{+2})$, $M \times 10^3$	$\Sigma(NO_2^-)$, $M \times 10^3$	$\Sigma(H^+)$, $M \times 10^3$	Anion, M	F[a]	R[b]	R_{calcd}[c]
1	0.95	1.12	0.94	Cl^-, 0.30	6.45	0.23	
2	.95	1.12	.94	Cl^-, .40	9.20	.25	
3	.95	1.12	.94	Cl^-, .50	17.2	.42	
4	1.42	1.96	480	Cl^-, .48	14.6	.36	
						.32	0.35
5	0.95	2.24	2.80	Br^-, .20	8.1	.44	
6	.95	2.24	2.80	Br^-, .40	11.6	.33	
7	.95	2.24	2.80	Br^-, .50	14.5	.34	
						.37	0.43
8	1.10	2.24	4.68	NO_3^-, .30	7.1	.25	
9	1.10	2.24	4.68	NO_3^-, .40	15.1	.44	
10	1.10	2.24	4.68	NO_3^-, .50	19.1	.47	
11	1.04	2.24	2.80	NO_3^-, .50	22.7	.59	
						.44	0.38
12	0.55	1.12	1.87	SCN^-, .10	5.4	.57	
13	.55	1.12	1.87	SCN^-, .30	11.4	.43	
14	.55	1.12	1.87	SCN^-, .50	14.5	.34	
15	1.04	2.24	220	F^-, 1.0	4.1	.053	
16	1.48	2.24	4.68	SO_4^{-2}, 0.50	12.2[d]	.28	0.37
17	1.09	1.12	[e]	$H_2PO_4^-$, 0.50	6.95	.15	0.14

[a] Per cent of $Co(NH_3)_5N_3^{+2}$ converted to $Co(NH_3)_5X^{+2}$. [b] Calculated from $R = F/(100 - F)(X^-)$. [c] Calculated from $R = K(k_a + k_a')/k_e[1 + K_0(X^-)]$. [d] Ionic strength 1.0. [e] 0.5 M H_3PO_4.

ments was 9.67×10^{-5} M, it is apparent that $(k_2/k_3) >> (Co(NH_3)_5N_3^{+2})$.[8]

An alternate formulation features nucleophilic attack of $Co(NH_3)_5N_3^{+2}$ on $H_2NO_2^+$, as has been suggested for the corresponding reactions of N_3^- and HNO_2.[3] On the basis of the available evidence, it is not possible to distinguish between the two mechanisms in the present system and we have chosen the formulation involving NO^+ arbitrarily.

The kinetic results in the presence of added anions (Table II) together with the results on product proportions (Table III) are sufficient to demonstrate that the increase in rate caused by addition of the anions is not accompanied by a parallel increase in the formation of $Co(NH_3)_5X^{+2}$ as compared to $Co(NH_3)_5OH_2^{+3}$. For example at $(X^-) = 0.50$ M, the contributions of the anion dependent paths are 98, 99, 33, and 98% for Cl^-, Br^-, NO_3^-, and SCN^-, respectively, whereas the values of $F/(100 - F) = (Co(NH_3)_5X^{+2})/(Co(NH_3)_5OH_2^{+3})$ are, at $(X^-) = 0.50$ M, 0.21, 0.17, 0.25, and 0.17, respectively. The immediate conclusion is that addition of the anions under study results in a new reaction path which leads not only to the formation of $Co(NH_3)_5X^{+2}$ but also to an increased production of $Co(NH_3)_5OH_2^{+3}$.

Some comments on the way that X^- affects the rate of consumption of $Co(NH_3)_5N_3^{+2}$ seem to be in order, even though the complete kinetic analysis of the reactions is incidental to the main theme of this paper. An additional SN2 path would account for the increase in rate but would not account for the saturation of rate with respect to (X^-). Nor can X^- act by providing an additional path for the formation of NO^+ since on the basis of reactions 2, 3, and 4, NO^+ is in equilibrium with $H^+ + HNO_2$. A possible role for X^- is that it converts NO^+ to NOX, with NOX acting as an agent to transfer NO^+ to $Co(NH_3)_5N_3^{+2}$.

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[8] C. A. Bunton and G. Stedman, *J. Chem. Soc.*, 3466 (1959), have also reported a rate law of the form $k_{ex}(HNO_2)(H^+)$ for the oxygen exchange between nitrite and water, with $k_{ex} = 1.5 \times 10^4$ min.$^{-1}$ at 0°.

$$\mathrm{NOX} + \mathrm{Co(NH_3)_5N_3^{+2}} \rightleftarrows \mathrm{Co(NH_3)_5N_3NO^{+3}} + \mathrm{X^-} \qquad (8)$$

If the reverse of reaction 8 competes with 5, the saturation of rate with respect to $(\mathrm{X^-})$ can be accounted for. At sufficiently high $(\mathrm{X^-})$, the intermediate $\mathrm{Co(NH_3)_5N_3NO^{+3}}$ is in equilibrium with the reactants, and a limiting rate is reached. This conclusion from the mechanism has the corollary that if no new paths are introduced by changing to a new substance X, the same limiting rate at constant $(\mathrm{H^+})$, $(\mathrm{HNO_2})$, and $\mathrm{Co(NH_3)_5M_3^{+2}}$ should be reached whatever be the choice of X. This corollary conclusion has not been tested thoroughly but the data of Table II suggest that the mechanism we propose may be in difficulty on this point. Finally, we must consider the possibility that the rate saturation arises from conversion of $\mathrm{Co(NH_3)_5N_3^{+2}}$ to the outer-sphere complex $\mathrm{Co(NH_3)_5N_3^{+2}\cdot X^-}$. This possibility cannot be rejected categorically, but it is rendered unlikely by the work of Phipps and Plane[9] on the association of $\mathrm{SCN^-}$ with $\mathrm{Cr(H_2O)_6^{+3}}$, $\mathrm{Cr(NH_3)_6^{+3}}$, and $\mathrm{Cr(NH_3)_5Cl^{+2}}$ and of King, *et al.*,[10] on the association of $\mathrm{Co(NH_3)_6^{+3}}$ with halide ions. If outer-sphere association is indeed the explanation of the kinetic effects under discussion, it points to some special interaction of $\mathrm{X^-}$ with bound $\mathrm{N_3^-}$.

Irrespective of the detailed nature of the catalysis by certain anions, a conclusion can be drawn from the observations on product composition which is directly germane to the question of the mechanism of substitution at the metal ion center. Since the ratios $(\mathrm{Co(NH_3)_5X^{+2}})/(\mathrm{Co(NH_3)_5OH_2^{+3}})$ increase with increasing anion concentration, even when substantially all of the reaction proceeds by the $(\mathrm{X^-})$-dependent path, it must be concluded that at least one intermediate is formed as a product of, or after, the rate-determining step and that $\mathrm{X^-}$ and $\mathrm{H_2O}$ compete for reaction with the intermediate.

We suggest that the intermediate for which $\mathrm{X^-}$ and $\mathrm{H_2O}$ compete is the pentacoordinated species $\mathrm{Co(NH_3)_5^{+3}}$. It arises from the decomposition of $\mathrm{Co(NH_3)_5N_3NO^{+3}}$: electronic rearrangement of $\mathrm{N_3NO}$ results in $\mathrm{N_2}$ $(+\mathrm{N_2O})$ as a "good leaving group."

If outer-sphere association of $\mathrm{Co(NH_3)_5^{+3}}$ with $\mathrm{X^-}$ is weak, eq. 9 and 10 suffice to account for the product distribution

$$\mathrm{Co(NH_3)_5^{+3}} + \mathrm{X^-} \xrightarrow{k_\mathrm{x}} \mathrm{Co(NH_3)_5X^{+2}} \qquad (9)$$

$$\mathrm{Co(NH_3)_5^{+3}} + \mathrm{H_2O} \xrightarrow{k_\mathrm{w}} \mathrm{Co(NH_3)_5OH_2^{+3}} \qquad (10)$$

but in the general case, if it is assumed that the intermediate survives long enough to reach equilibrium with respect to ion atmosphere and ion association effects, reactions 11, 12, and 13 must be included.

$$\mathrm{Co(NH_3)_5^{+3}} + \mathrm{X^-} \overset{K_\mathrm{int}}{=\!=} \mathrm{Co(NH_3)_5^{+3}\cdot X^-} \qquad (11)$$

$$\mathrm{Co(NH_3)_5^{+3}\cdot X^-} \xrightarrow{k_\mathrm{x}'} \mathrm{Co(NH_3)_5X^{+2}} \qquad (12)$$

$$\mathrm{Co(NH_3)_5^{+3}\cdot X^-} + \mathrm{H_2O} \xrightarrow{k_\mathrm{w}'} \mathrm{Co(NH_3)_5OH_2^{+3}} + \mathrm{X^-} \qquad (13)$$

On the basis of this mechanism the quantity R (*cf.* Table III) is given by eq. 14, which simplifies to $R = k_\mathrm{x}/k_\mathrm{w}$ when outer-sphere association is negligible.

$$R = \frac{(k_\mathrm{x} + k_\mathrm{x}'K_\mathrm{int})}{k_\mathrm{w} + k_\mathrm{w}'K_\mathrm{int}(\mathrm{X^-})} \qquad (14)$$

The last condition is probably met for $\mathrm{Cl^-}$, $\mathrm{Br^-}$, $\mathrm{NO_3^-}$, and $\mathrm{F^-}$, and the values of $k_\mathrm{x}/k_\mathrm{w}$ are 0.32, 0.37, 0.44, and 0.053, respectively. The decrease of R with increasing $(\mathrm{SCN^-})$ indicates that outer-sphere association is important in this system and from a plot of $1/R$ *vs.* $(\mathrm{SCN^-})$ the following quantities have been obtained: $k_\mathrm{w}/(k_\mathrm{x} + k_\mathrm{x}'K_\mathrm{int}) = 1.44$, $k_\mathrm{w}'K_\mathrm{int}/(k_\mathrm{x} + k_\mathrm{x}'K_\mathrm{int}) = 3.0$, and $k_\mathrm{w}'K_\mathrm{int}/k_\mathrm{w} = 2.1$. When $\mathrm{X} = \mathrm{SO_4^{-2}}$ or $\mathrm{H_2PO_4^-}$, outer-sphere association with $\mathrm{Co(NH_3)_5^{+3}}$ is undoubtedly important, and it is therefore not possible to calculate $k_\mathrm{x}/k_\mathrm{w}$ from our limited data. The data are nevertheless useful for comparisons of the kind which are described below.

If this interpretation is accepted, the values of R measured in the present work can be used to identify $\mathrm{Co(NH_3)_5^{+3}}$ in other systems. The mechanism for the equilibration reactions represented by eq. 1 has not been established, and therefore it is of interest to compare the values of R measured in the present work with the values calculated assuming that reaction 1 proceeds by an SN1 mechanism. In the absence of outer-sphere interaction the SN1 mechanism is represented by eq. 15 and 16.

$$\mathrm{Co(NH_3)_5OH_2^{+3}} \underset{k_\mathrm{w}}{\overset{k_\mathrm{e}}{\rightleftharpoons}} \mathrm{Co(NH_3)_5^{+3}} + \mathrm{H_2O} \qquad (15)$$

$$\mathrm{Co(NH_3)_5^{+3}} + \mathrm{X^-} \underset{k_\mathrm{a}}{\overset{k_\mathrm{x}}{\rightleftharpoons}} \mathrm{Co(NH_3)_5X^{+3}} \qquad (16)$$

On the basis of this mechanism the equilibrium constant for reaction 1 is $K = k_\mathrm{e}k_\mathrm{x}/k_\mathrm{w}k_\mathrm{a}$. k_e, the rate of oxygen exchange between $\mathrm{Co(NH_3)_5OH_2^{+3}}$ and water, is known.[11] k_a, the rate of aquation of $\mathrm{Co(NH_3)_5X^{+2}}$, and K are known for some anions. Therefore, it is possible to calculate the values of $k_\mathrm{x}/k_\mathrm{w}$. When there is outer-sphere interaction, eq. 17 and 18 need to be included.

$$\mathrm{Co(NH_3)_5OH_2^{+3}\cdot X^-} \underset{k_\mathrm{w}'}{\overset{k_\mathrm{e}'}{\rightleftharpoons}} \mathrm{Co(NH_3)_5^{+3}\cdot X^-} + \mathrm{H_2O} \qquad (17)$$

$$\mathrm{Co(NH_3)_5^{+3}\cdot X^-} \underset{k_\mathrm{a}'}{\overset{k_\mathrm{x}'}{\rightleftharpoons}} \mathrm{Co(NH_3)_5X^{+2}} \qquad (18)$$

From eq. 15–18, R is given by the expression

$$R = \frac{K(k_\mathrm{a} + k_\mathrm{a}')}{k_\mathrm{e}[1 + (k_\mathrm{e}'/k_\mathrm{e})K_0(\mathrm{X^-})]} \qquad (19)$$

where K_0 is the outer-sphere association constant for the reaction

$$\mathrm{Co(NH_3)_5OH_2^{+3}} + \mathrm{X^-} \rightleftarrows \mathrm{Co(NH_3)_5OH_2^{+3}\cdot X^-} \qquad (20)$$

In order to calculate R from eq. 19, it is necessary to have a value of k_e', the rate of water exchange for the

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(9) A. L. Phipps and R. A. Plane, *J. Am. Chem. Soc.*, **79**, 2458 (1957).

(10) E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1599).

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

outer-sphere complex. It has been demonstrated that SO_4^{-2} has little effect on the rate of water exchange of $Co(NH_3)_5OH_2^{+3}$,[12] and on this basis it will be assumed that $(k_e'/k_e) = 1$.

The values of the various constants used to calculate R are listed in Table IV. In view of the uncertainties in some of them, the agreement between R and R_{calcd} (columns 7 and 8 of Table III) is considered to be satisfactory and provides strong support to the view that the $Co(NH_3)_5^{+3}$ intermediate is generated in the two systems being compared. For the SCN^- system, using eq. 19 and the values of R measured in the present work, the following quantities have been obtained: $K = 1460$, $k_e' = 1.64 \times 10^{-4}$ min.$^{-1}$, and $k_x/k_w < 0.69$. Independent evidence for the formation of the $Co(NH_3)_5^{+3}$ intermediate in the Hg^{+2}-induced aquation of $Co(NH_3)_5Br^{+2}$ and $Co(NH_3)_5Cl^{+2}$ has been presented elsewhere.[13] The measured values of R for 1.0 M NO_3^- when the intermediate was generated from $Co(NH_3)_5Br^{+2}$ or $Co(NH_3)_5I^{+2}$ were 0.22 and 0.24, respectively, in good agreement with the value 0.30 calculated from the relation $k_x/k_w = R = Kk_a/k_e$. The measurements of the oxygen isotopic fractionation in the induced aquation of $Co(NH_3)_5X^{+2}$ by Ag^+ or Tl^{+3} led Posey and Taube[13] to conclude that these reactions do not proceed solely by the formation of $Co(NH_3)_5^{+3}$. Since reactions in which the removal of X^- is assisted by Ag^+ or Tl^{+3} involve H_2O–Co(III) bond formation before the X^-–Co(III) bond is broken, it was argued that the spontaneous aquation of the complex ions would all the more call for H_2O–Co(III) bond formation to assist in the removal of X^-. We find this argument to be invalid because it does not take account of the possibility of concerted H_2O–X^- interchange (X^- moving from Co(III) to Tl^{+3}, for example, and H_2O from Tl^{+3} to Co(III)), and in fact evidence for such a concerted process was presented by Posey and Taube. In any case, indirect evidence of the kind adduced by Posey and Taube is not as convincing as the evidence presented here which is based on relative reactivities which suggest the same intermediate in systems of radically different chemistry.

The values of k_x/k_w obtained in the present work vary only by a factor of 8 (from 0.053 for F^- to 0.43 for Br^-), showing that the intermediate $Co(NH_3)_5^{+3}$ is very reactive and does not display much discrimination toward reaction with various nucleophiles.[14] A narrow range of reactivities has also been observed for the reactions of $Co(CN)_5^{-2}$ with Br^-, SCN^-, and N_3^-, where the values of k_x/k_w are 0.1, 0.34, and 0.52, respectively, at 40° and $\mu = 1.0$.[15] Calculations similar to the ones described above may also be carried out for the reaction of Cl^- and SCN^- with the postulated intermediate $Cr(OH_2)_5^{+3}$. Using known values for the rate of water exchange between $Cr(OH_2)_6^{+3}$ and solvent,[16] the equilibrium constant, and the rate of aquation in the thiocyanate[17] and chloride[18,19] systems, the values of k_x/k_w are 0.43 and ~0.2, respectively, at 25° and $\mu = 0.5$. These values are close to the ones obtained in the Co(III) systems, indicating that if an SN1 mechanism applies to the Cr(III) system, the intermediate $Cr(OH_2)_5^{+3}$ is also a very reactive one.

TABLE IV

RATE AND EQUILIBRIUM CONSTANTS PERTAINING TO REACTION 1

($t = 25°$, $\mu = 0.50$)

Anion	$(k_a + k_a')$, min.$^{-1}$[a]	K	K_0	k_x/k_w
Cl^-	1.0×10^{-4}[b]	1.25[c]	...	0.35
Br^-	3.9×10^{-4}[d]	0.39[e]	...	.43
NO_3^-	1.75×10^{-3}[d]	0.077[f]	...	.38
SCN^-	1.7×10^{-7}[g]	...	4.5[h]	...
SO_4^{-2}	7.0×10^{-5}[i]	12.4[j]	11.2[j]	< .24[k]
$H_2PO_4^-$	1.65×10^{-5}[l]	7.4[l]	2.75[l]	< .34[k]

[a] $k_a' = 0$ when there is no outer-sphere association. [b] F. J. Garrick, *Trans. Faraday Soc.*, **33**, 487 (1937). [c] Calculated from the data of H. Taube, *J. Am. Chem. Soc.*, **82**, 524 (1960). [d] A. W. Lamb and J. W. Marsden, *ibid.*, **33**, 1873 (1911). [e] Calculated from the value 0.48 at 45° and $\mu = 1.0$ (R. G. Yalman, *Inorg. Chem.*, **1**, 16 (1962)) using the temperature and ionic strength dependence measured in the Cl^- system (ref. *c*). [f] Calculated from the measured spectrophotometric value 0.65 at $\mu = 1.0$ and the ionic strength dependence measured in the Cl^- system (ref. *c*). [g] A. W. Adamson and R. G. Wilkins, *J. Am. Chem. Soc.*, **76**, 3379 (1954). [h] Measured spectrophotometrically from instantaneous changes in the optical density of $Co(NH_3)_5OH_2^{+3}$ solutions (290–310 mμ) upon addition of SCN^-. [i] H. Taube and F. A. Posey, *J. Am. Chem. Soc.*, **75**, 1463 (1953). [j] F. A. Posey and H. Taube, *ibid.*, **78**, 15 (1956). [k] Upper limit obtained from the relation $k_x/k_w < K(k_a + k_a')/k_e$. [l] W. G. Schmidt and H. Taube, *Inorg. Chem.*, **2**, 698 (1963).

Acknowledgments.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. Funds for purchase of the spectrophotometer were made available by the National Science Foundation under Grant No. 22611.

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(14) Since k_w is a pseudo-first-order rate constant, it is perhaps useful to refer to the discrimination of the $Co(NH_3)_5^{+3}$ intermediate by considering values of k_x/k_w', where $k_w' = k_w/(H_2O)$. Using the value of 55 for the formal concentration of water, k_x/k_w' for F^- and Br^- are 2.9 and 23.6, respectively, showing again a rather narrow range of reactivities for $Co(NH_3)_5^{+3}$.

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