may very well be that an outer-sphere redox reaction is a major contribution here.

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The Mechanism of Substitution Reactions of Pentaamminecobalt(III) Complexes. Product Distributions in the Induced Aquation of Some $[Co(NH_3)_5X]^{2+}$ Ions in the Presence of Added Anions

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The competition ratios of added anions for the proposed intermediate $(NH_3)_5Co^{3+}$ have been measured or remeasured in aqueous solution. The intermediate was generated by the reaction of $(NH_3)_5CoN_3^{2+}$ or $(NH_3)_5CoOCONH_2^{2+}$ with NO^+ and $(NH_3)_5CoX^{2+}$ (X = Cl, Br, I) with Hg^{2+}; constant competition ratios were observed for each anion Y^- ($Y^- = Cl^-$, Br^-, NO_3^-, HSO_4^-, F^-) despite the fact that the leaving groups were widely different in each reaction. The common competition ratios do not agree, however, with those calculated for the spontaneous anation reaction of $(NH_3)_5CoOH_2^{3+}$ with the anions Cl^-, Br^-, and NO_3^- assuming the reaction takes place *via* the $(NH_3)_5Co^{3+}$ intermediate.

Introduction

For the elucidation of the mechanism of substitution reactions at the cobalt atom for cobalt(III) complexes it is important initially to establish the characteristics of two extremes for the process, one where bond making is the important act between substrate and reactant (SN2) leading to a seven-coordinate activated complex or intermediate and the other where bond breaking is important (SN1) and leads to a five-coordinate intermediate. In this paper we are concerned with the work devoted to characterizing the $Co(NH_3)_5^{3+}$ intermediate. Two principal methods have been used,[1,2] one by the evaluation of the H_2O^{18}/H_2O^{16} ratio in the common aquopentaammine product when the $[Co(NH_3)_5]^{3+}$ species is generated in water from a variety of sources, the other by competition of species other than H_2O for $Co(NH_3)_5^{3+}$. For example, the induced aquation of $[A_5CoX]^{2+}$ complexes by Hg^{2+} ion (A = NH_3; X = Cl, Br, I)

$$A_5CoX^{2+} + Hg_{aq}^{2+} \longrightarrow A_5CoOH_2^{3+} + HgX_{aq}^{+} \qquad (1)$$

gave a constant fractionation factor for H_2O^{18}/H_2O^{16} in the aquopentaammine products[1] which was interpreted as evidence for a common intermediate since the induced aquation of the halide ions by other metal ions such as Tl^{3+} and Ag^+ gave substantially different O^{18}/O^{16} fractionation factors in the common product from the different halide complexes. Also, Haim and Taube[2] obtained evidence for the same intermediate formed by the reaction of the $A_5CoN_3^{2+}$ ion

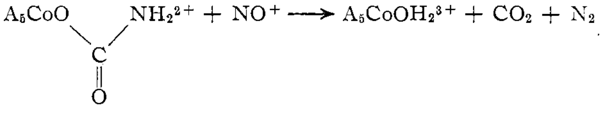
$$A_5CoN_3^{2+} + NO^+ \longrightarrow A_5Co^{3+} + N_2 + N_2O \qquad (2)$$

The rate law was of the form

$$R = k[Co][HNO_2][H^+] + k'[Co][HNO_2][H^+][X]$$
$$(X = Cl^-, Br^-, SCN^-, NO_3^-, SO_4^{2-})$$

and it was suggested that the intermediate A_5Co-$NNNNO^{3+}$ was formed which spontaneously decomposed to A_5Co^{3+} and N_2 and N_2O. Both of the gaseous products are excellent leaving groups conducive to the formation of the reactive cobalt(III) intermediate, which was characterized by allowing it to compete for other anions and solvent water molecules. The term in the rate law which is dependent on the anion concentration leads to an enhancement in the rate with an increase in $[X^-]$ but does not lead to a parallel increase in the formation of A_5CoX^{2+} as compared with $A_5CoOH_2^{3+}$. The product distributions for various anions were compared with the distributions expected if the direct anation reactions proceed *via* the same pentacoordinated intermediate and were found to agree. However, a later experiment by Pearson and Moore[3] showed that the nitrosation of the azido complex and the spontaneous aquation of the $A_5CoNO_3^+$ ion do not proceed by the same intermediate since the latter reaction gives first the aquo complex which then anates, so the apparent agreement is fortuitous.

More recently the carbamatopentaamminecobalt(III) ion was shown to react with NO^+ (eq 3) to give



$$A_5CoO{-}C({=}O){-}NH_2^{2+} + NO^+ \longrightarrow A_5CoOH_2^{3+} + CO_2 + N_2 \qquad (3)$$

80% Co–O bond rupture, and in this instance the leaving group is either CO_2 or $\overset{O}{\underset{O}{}}{>}CN{=}N$, both poor

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

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

[3] R. G. Pearson and J. W. Moore, *ibid.*, **3**, 1334 (1964).

coordinating agents.[4] The degree of bond rupture was independent of HCl or $HClO_4$, and it was shown also that nitrosation in 1.0 *M* HCl gave the A_5CoCl^{2+} ion immediately. All of these factors implied that the A_5Co^{3+} ion was being formed.

A problem has now arisen concerning the meaning of the O^{18}/O^{16} fractionation factors in these induced aquations.[5] While the nitrosation of the azido complex gave the same factor as for the $A_5CoX^{2+} + Hg^{2+}$ reactions, this factor was also obtained for the spontaneous aquation of $A_5CoNO_3^{2+}$, A_5CoBr^{2+}, and A_5CoCl^{2+}, which suggests that for the aquation reactions the constant fractionation factor (1 part per 1000) is not necessarily a reliable criterion to identify a common intermediate. However, it should be constant if there is a common intermediate. This places a large burden of proof for the existence of the intermediate on the competition ratios of A_5Co^{3+} for H_2O and X^-, and the accuracy of these values becomes important. In the study of the nitrosation of the azido complex, the competition ratios[2] were measured spectrophotometrically and the spread in the observed values was quite large (a factor of $\sim$2) owing to the insensitivity of the method. This present paper is concerned with the remeasurement of these competition ratios by a more sensitive procedure and with the competition ratios for the nitrosation of the carbamato complex in the presence of the same anions. Also the comparison of these results with the remeasured values for the anation of the $A_5CoOH_2^{3+}$ ion with Cl^-, Br^- and NO_3^- is significant.

Experimental Section

Analar reagents were used throughout without further purification.

$[Co(NH_3)_5Cl](ClO_4)_2$,[6] $[Co(NH_3)_5Br](ClO_4)_2$,[7] and $[Co(NH_3)_5I](ClO_4)_2$[8] were prepared from the chloride, bromide, and iodide salts, respectively, by treating them with concentrated $HClO_4$ and cooling the solution in ice. $[Co(NH_3)_5F](ClO_4)_2$ was prepared by the method of Linhard and Weigel.[9a] The perchlorates were then recrystallized from water with $NaClO_4$ until pure. $[Co(NH_3)_5OCONH_2](ClO_4)_2$ and $[Co(NH_3)_5N_3](ClO_4)_2$[9b] were prepared as described. The carbamato complex was purified by converting it to the iodide and then to the acetate with silver acetate, and the complex perchlorate was precipitated finally with $NaClO_4$.

Anal. Calcd for $[CO(NH_3)_5Cl](ClO_4)_2$: N, 18.50; H, 3.99. Found: N, 18.51; H, 4.16. Calcd for $[Co(NH_3)_5Br](ClO_4)_2$: N, 16.56; H, 3.57. Found: N, 16.25; H, 3.55. Calcd for $[Co(NH_3)_5I](ClO_4)_2$: N, 14.91; H, 3.22. Found: N, 15.25; H, 3.31. Calcd for $[Co(NH_3)_5OCONH_2](ClO_4)_2$: N, 20.85; H, 4.25; C, 2.98. Found: N, 20.65; H, 4.41; C, 3.02.

Kinetic Studies. Hydrolysis of $[Co(NH_3)_5OCONH_2](ClO_4)_2$.—The complex was dissolved in water and mixed with solutions of $HClO_4$ and $NaClO_4$ at 25°. The mixture was transferred to a spectrophotometric cell thermostated at 25° in a Cary 14 recording spectrophotometer, and a recording of optical density *vs.* time was made at 510 mμ.

Nitrosation of $[Co(NH_3)_5OCONH_2](ClO_4)_2$.—A solution of a weighed sample of complex, $NaNO_2$, and $NaClO_4$ was made up and quickly mixed with an equal volume of the acid at 25° using a stopped-flow reactor similar to that described by Chance.[10]

Stoichiometric Studies.—The complex (10^{-3} mole) was dissolved in dilute acid (40 ml) at 25° where this was possible (the carbamato complex was soluble in all acids, the azido complex, only in H_2SO_4 solutions). Solid $NaNO_2$ (2×10^{-3} mole) was added under stirring and the solution was left at 25° for 10 min. When the azido complex was not soluble in the acids, it was dissolved in 50 ml of water at pH 3 at 25°. A 50-ml sample of the acid at 25° was added rapidly under stirring, and, immediately after mixing, solid $NaNO_2$ (2×10^{-3} mole) was added. After reaction, the solutions were diluted with water and adsorbed on an ion-exchange column (Bio-Rad analytical resin, Dowex (H^+) 50W-X2, 200–400 mesh, 15 × 120 mm). The column was eluted first with 1 *M* $NaClO_4$ at pH 3 (1 *M* KCl for the sulfato complex) to remove the +1 and +2 charged complex ions and then wth 3 *M* HCl to recover the aquopentaammine complex. Optical densities of the solutions were measured immediately after recovery from the column. In every instance the total recovery was better than 98%. The molar absorptivity of the individual products was measured in 1 *M* $NaClO_4$ (the sulfato complex, in 1 *M* KCl), and the molar absorptivity of $[Co(NH_3)_5OH_2](ClO_4)_3$ was measured in 3 *M* HCl in order to calculate the concentrations of the species isolated from the column. The measured molar absorptivities were: in 1 *M* KCl for $[Co(NH_3)_5SO_4]ClO_4$, ϵ_{515} 61; in 1 *M* $NaClO_4$ for $[Co(NH_3)_5Cl](ClO_4)_2$, ϵ_{532} 50.5; $[Co(NH_3)_5Br](ClO_4)_2$, ϵ_{550} 55.5; $[Co(NH_3)_5NO_3](ClO_4)_2$; ϵ_{502} 56.3; $[Co(NH_3)_5F](ClO_4)_2$, ϵ_{514} 46.8; in 3 *M* HCl for $[Co(NH_3)_5OH_2](ClO_4)_3$, ϵ_{492} 47.7.

$[Co(NH_3)_5OH_2](ClO_4)_3$ (10^{-3} mole) was dissolved in HX (0.25 *M*) and $HClO_4$ (0.75 *M*) (except for the HNO_3–$HClO_4$ mixture which was 0.5 *M* in each), and the mixtures were equilibrated at 25° for 14 days. At the end of this time the components were separated using the ion-exchange column and measured spectrophotometrically.

Representative examples of recovery of the products from the reactions above are: reaction of $[Co(NH_3)_5OCONH_2](ClO_4)_2$ with $NaNO_2$ in 0.5 *M* H_2SO_4 gave 11.8% $[Co(NH_3)_5SO_4]^+$ + 88.4% $[Co(NH_3)_5H_2O]^{3+}$; in 1 *M* HCl 16.9% $[Co(NH_3)_5Cl]^{2+}$ + 83.8% $[Co(NH_3)_5H_2O]^{3-}$; in 1 *M* HNO_3 26.4% $[Co(NH_3)_5NO_3]^{2+}$ + 73.0% $[Co(NH_3)_5H_2O]^{3+}$; reaction of $[Co(NH_3)_5N_3](ClO_4)_2$ in 1 *M* HBr gave 19.6% $[Co(NH_3)_5Br]^{2+}$ + 80.1% $[Co(NH_3)_5H_2O]^{3+}$. Samples of the pure pentaammine products treated in the same manner gave better than 99.2% recovery unchanged.

The proton association constant of $[Co(NH_3)_5OCONH_2](ClO_4)_2$ (0.76×10^{-3} *M*)

$$Co(NH_3)_5OCONH_2^{2+} + H^+ \rightleftharpoons Co(NH_3)_5OCONH_3^{3+}$$

was measured spectrophotometrically at constant Cl^- concentration and $\mu = 1$ using mixtures of NaCl and HCl. The optical density of the parent complex perchlorate in 1 *M* NaCl, pH 3.8, was 0.681, and the extrapolated value for the protonated complex was 0.035. Using the added acid concentration as a measure of H^+, the association constant was calculated as 6.7 ± 0.3.

Results

Kinetics.—The rate of the nitrosation of the $A_5CoOCONH_2^{2+}$ ion was measured under a variety of conditions. Linear plots of log $(D_t - D_\infty)$ *vs.* time were obtained, and the observed pseudo-first-order rate constants k_{obsd} are listed in column 4, Table I. Column 5 gives the calculated third-order rate constants k', assuming a rate law[11] of the form

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[4] A. M. Sargeson and H. Taube, *Inorg. Chem.*, **5**, 1094 (1966).

[5] G. Dolbear and H. Taube, *ibid.*, **6**, 60 (1967).

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

[7] H. Diehl, H. Clark, and H. H. Willard, *Inorg. Syn.*, **1**, 186 (1939).

[8] R. G. Yalman, *J. Am. Chem. Soc.*, **77**, 3219 (1955).

[9] (a) M. Linhard and M. Weigel, *Z. Anorg. Allgem. Chem.*, **266**, 82 (1951); (b) M. Linhard and H. Flygare, *ibid.*, **262**, 328 (1950).

[10] B. Chance in "Technique of Organic Chemistry," Vol. VIII, S. L. Friess, E. S. Lewis, and A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1953, p 690.

[11] This rate law was described incorrectly in a previous communication.[4]

$$\text{rate} = \frac{k'[\text{carbamate}][\text{H}^+][\text{HNO}_2]}{1 + K_{\text{H}^+}[\text{H}^+]}$$

where

$$K_{\text{H}^+} = \frac{[\text{A}_5\text{CoOCONH}_3{}^{3+}]}{[\text{A}_5\text{CoOCONH}_2{}^{2+}][\text{H}^+]}$$

and [carbamate] = total carbamato complex. The values of $[\text{HNO}_2]$ and $[\text{H}^+]$ were calculated from the known concentrations of added HClO_4 and NaNO_2 using a value of 5×10^{-4} for the dissociation constant of HNO_2.[12] The third-order rate constant k' appears to describe the kinetics of the reaction reasonably and it can be seen (Table I, footnote *f*) that there is no great dependence of the rate on the presence of halide ion nor on the concentration of the reactant complex (Table I, footnote *e*).

TABLE I

KINETICS OF THE $\text{Co(NH}_3)_5\text{OCONH}_2{}^{2+}$–$\text{HNO}_2$ REACTION AT 25° AND $\mu = 1.0$ ($C_{\text{Co}} = 10^{-3}\ M$)

$\Sigma 10^3[\text{NO}_2{}^-]$,[a] M	$\Sigma 10^3[\text{H}^+]$,[b] M	$10^3[\text{H}^+]$,[c] M	10^3k_{obsd}, sec^{-1}	$10^{-1}k'$,[d] $M^{-2}\ \text{sec}^{-1}$
5.0	50.0	45.0	4.26	2.5
5.0	100.0	95.0	7.7	2.7
10.0	25.0	15.3	4.12	3.0
10.0	50.0	40.0	8.77	2.8
10.0	100.0	90.0	14.7	2.6
20.0	100.0	80.0	28.3	2.7
20.0	200.0	180.0	48.6	3.0
40.0	100.0	60.0	49.5	2.9
50.0	100.0	50.5	55.4	2.9
20.0	100.0	80.0	26.3	2.5[e]
10.0	100.0	90.0	14.0	2.5[f]
10.0	100.0	90.0	13.9	2.5[f]

[a] Concentration of added NaNO_2; $\Sigma[\text{NO}_2{}^-] = [\text{NO}_2{}^-] + [\text{HNO}_2]$. [b] Concentration of added HClO_4; $\Sigma[\text{H}^+] = [\text{H}^+] + [\text{HNO}_2]$. [c] Calculated from $\Sigma[\text{NO}_2{}^-]$, $\Sigma[\text{H}^+]$, and the dissociation constant of HNO_2, 5×10^{-4}.[12] [d] Calculated from $k' = k_{\text{obsd}}(1 + K_{\text{H}^+}[\text{H}^+])/[\text{H}^+][\text{HNO}_2]$ and $K_{\text{H}^+} = 6.7$. [e] $C_{\text{Co}} = 2 \times 10^{-3}\ M$. [f] $\mu = 1.0$ with NaCl.

The rate law is substantially the same as that obtained for the azido complex[2] except that there is no term involving extraneous anion and it should be noted that the denominator, $1 + [\text{H}^+]K_{\text{H}^+}$, merely takes account of that portion of $\text{A}_5\text{CoOCONH}_2{}^{2+}$ which is protonated and is therefore impervious to the addition of NO^+. The proton association constant K_{H^+} for $\text{A}_5\text{CoOCONH}_2{}^{2+}$ was measured spectrophotometrically as 6.7 ± 0.3 at 25° and this agrees with that calculated from the rate data (7 ± 1).

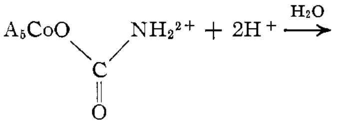
TABLE II

ACID HYDROLYSIS OF $[\text{Co(NH}_3)_5\text{OCONH}_2](\text{ClO}_4)_2$ ($C_{\text{Co}} = 10^{-3}\ M$)

Temp, °C	C_{HClO_4}, M	10^5k,[a] sec^{-1}	$k_{\text{H}} = k(1 + k_{\text{H}^+}[\text{H}^+])/K_{\text{H}^+}[\text{H}^+]$, $\text{sec}^{-1} \times 10^5$
		$\mu = 1$	
25	0.10	1.04 ± 0.05	2.6
25	0.25	1.34 ± 0.05	2.1
25	0.50	1.63 ± 0.03	2.1
25	0.75	1.72 ± 0.01	2.1
25	1.00	1.98 ± 0.01	2.3
15	1.00	0.44	
35	0.10	4.45	
35	0.25	6.48	
35	0.50	8.25	
35	1.00	8.88	
45	0.10	13.3	
45	0.25	26.3	
45	0.50	30.3	
45	1.00	31.2	
		$\mu = 3$	
25	1.0	2.52	
25	2.0	2.52	
25	3.0	2.57	

[a] Average of two values.

The results of experiments on the rate of acid hydrolysis of the $\text{A}_5\text{CoOCONH}_2{}^{2+}$ ion (eq 4) are given in



$$\text{A}_5\text{CoOC(=O)NH}_2{}^{2+} + 2\text{H}^+ \xrightarrow{\text{H}_2\text{O}} \text{A}_5\text{CoOH}_2{}^{3+} + \text{CO}_2 + \text{NH}_4{}^+ \quad (4)$$

Table II. The acid hydrolysis rate does not show a simple first-order dependence on H^+, and from the results at $\mu = 3$, Table II, the rate is independent of H^+ from 1 to 3 M H^+. The kinetics are accounted for adequately by a rate law of the form

$$\text{rate} = \frac{k_{\text{H}}[\text{carbamate}][\text{H}^+]K_{\text{H}^+}}{1 + K_{\text{H}^+}[\text{H}^+]}$$

from which K_{H^+} is calculated to be ~7 in agreement with that for the nitrosation reaction. The observed rate constants show that the acid hydrolysis rate is not significant in the time required to complete the nitrosation reactions.

Competition Studies.—The results of the competition experiments for the nitrosation of $\text{A}_5\text{CoN}_3{}^{2+}$ and $\text{A}_5\text{CoOCONH}_2{}^{2+}$ in the presence of added anion X^- (Cl^-, Br^-, $\text{NO}_3{}^-$, F^-, $\text{HSO}_4{}^-$) are given in Tables III and IV. The reactions with the azido complex are more or less a repetition of Haim and Taube's work[2] at $\mu = 0.5$ and also at $\mu = 1.0$, but modified to fit the ion-exchange technique used to analyze the reaction mixture. The slow acid hydrolysis of the $\text{A}_5\text{CoX}^{2+\text{ or }+}$ complexes[13] formed and the slow anation of the aquopentaammine complex (by water exchange)[3,14] allow the separation of $\text{A}_5\text{CoX}^{2+\text{ or }+}$ from $\text{A}_5\text{CoOH}_2{}^{3+}$ on the ion-exchange column without significant change. By this procedure all of the complex species were recovered to better than 98% and the individual species were analyzed spectrophotometrically. The method is more accurate than the spectrophotometric analysis of the reaction mixture which contains species often with no great spectral differences from the predominant aquo product.

The nitrosation reactions in the presence of NCS^- could not be carried out because of reaction between

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[12] 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.

[13] D. R. Stranks in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience Publishers, Inc., New York, N. Y., p 128.

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

TABLE III

PRODUCT DISTRIBUTION FROM THE $Co(NH_3)_5N_3^{2+}$–HNO_2 REACTION IN THE PRESENCE OF ADDED ANIONS AT 25°

($C_{NaNO_2} = 2C_{complex}$)

$C_{Co(NH_3)_5N_3^{2+}}$, M	Reaction medium	μ	F^a	R^b
0.01	0.5 M HCl	0.5	9.6	0.19
			9.5	0.19
0.01	1 M HCl	1.0	19.6	0.24
0.01	1 M HBr	1.0	19.6	0.24
0.01	1 M HNO_3	1.0	33.2	0.49
0.01	0.88 M HF	~1.0	9.7	0.12
0.025	0.5 M H_2SO_4	0.5	15.7	0.37
0.025	1 M H_2SO_4	1.0	22.1	0.28
0.01	0.5 M HCl	2.0[c]	8.1	0.18
0.01	1.0 M HCl	2.0[c]	15.9	0.19
0.01	1.5 M HCl	2.0[c]	21.8	0.19
0.01	2.0 M HCl	2.0[c]	28.3	0.20

[a] Per cent $Co(NH_3)_5N_3^{2+}$ converted to $Co(NH_3)_5X^{2+}$. [b] $R = F/(100 - F)[X^-]$. [c] $HClO_4$ added.

TABLE IV

PRODUCT DISTRIBUTION FROM THE $Co(NH_3)_5OCONH_2^{2+}$–HNO_2 REACTION IN THE PRESENCE OF ADDED ANIONS AT 25°

($C_{Co} = 0.025\ M$, $C_{NaNO_2} = 0.05\ M$)

Reaction medium	μ	F_{exptl}^a	F_{calcd}^b	R^c
1 M HCl	1.0	17.0	21.2	0.27
	1.0	16.2	20.2	0.25
1 M HBr	1.0	16.4	20.5	0.26
	1.0	17.2	21.5	0.27
1 M HNO_3	1.0	26.4	33.0	0.49
0.88 M HF	~1.0	9.1	11.3	0.14
0.5 M H_2SO_4	1.0	11.7	14.6	0.34
	1.0	11.8	14.7	0.34
	1.0	12.2	15.2	0.36
1 M H_2SO_4	2.0	16.6	20.7	0.26
	2.0	17.2	21.5	0.27
0.5 M HCl	2.0[d]	7.2	9.0	0.20
1.0 M HCl	2.0[d]	14.0	17.5	0.21
1.5 M HCl	2.0[d]	20.4	25.5	0.23
2.0 M HCl	2.0[d]	25.1	31.4	0.23

[a] Per cent of $Co(NH_3)_5OCONH_2^{2+}$ converted to $Co(NH_3)_5X^{2+}$. [b] Per cent of $Co(NH_3)_5OCONH^{2+}$ converted to $Co(NH_3)_5X^{2+}$ assuming that 80% of the $Co(NH_3)_5^{3+}$ intermediate is formed in the reaction. [c] $R = F_{calcd}/(100 - F_{calcd})[X^-]$. [d] $HClO_4$ added.

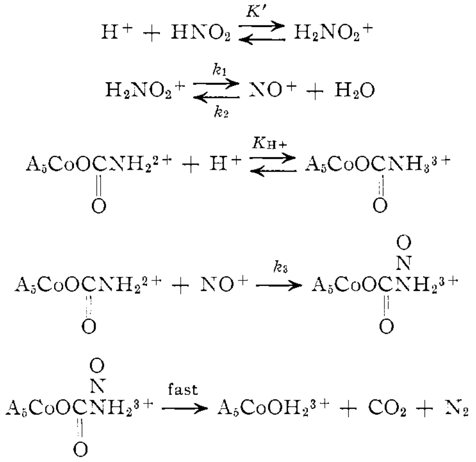
NCS^- and NO_2^- in the acid solution. This reaction may account for some of the unusual behavior which Haim and Taube[2] observed for this system.

The competition values for the nitrosation of the carbamato complex in the presence of X^- ions have been corrected for the path which proceeds by Co–O fission (80%).[4] The path which leads to Co–O retention clearly does not allow the anion X^- to enter the coordination sphere except by displacement of water and this is far too slow to influence the competition results.[14]

The results from the competition experiments, Tables III and IV, show that: (1) The competition ratio $R = [A_5CoX^{2+}]/[A_5CoOH_2^{3+}][X^-]$ is constant (± 0.01) for the reactions involving $A_5CoN_3^{2+}$ and $A_5CoOCONH_2^{2+}$ and a common species of X^-. (2) R does not vary widely with different X^- ions. (3) R is constant for $0.5 < [Cl^-] < 2\ M$ at constant ionic strength μ for both complexes within the experimental error. (4) R is slightly dependent on ionic strength, and the greater the ionic strength, the smaller R becomes.

Discussion

The form of the rate law for the reaction $A_5CoOCONH_2^{2+}$ with HNO_2 in dilute $HClO_4$ is consistent with the mechanism proposed in the equations



$$H^+ + HNO_2 \overset{K'}{\rightleftharpoons} H_2NO_2^+$$

$$H_2NO_2^+ \underset{k_2}{\overset{k_1}{\rightleftharpoons}} NO^+ + H_2O$$

$$A_5CoOC(=O)NH_2^{2+} + H^+ \overset{K_{H^+}}{\rightleftharpoons} A_5CoOC(=O)NH_3^{3+}$$

$$A_5CoOC(=O)NH_2^{2+} + NO^+ \xrightarrow{k_3} A_5CoOC(=O)NH_2(NO)^{3+}$$

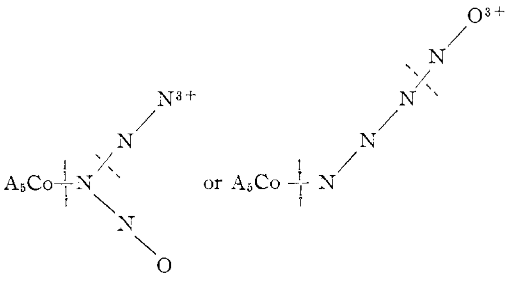
$$A_5CoOC(=O)NH_2(NO)^{3+} \xrightarrow{fast} A_5CoOH_2^{3+} + CO_2 + N_2$$

Assuming a steady-state concentration of NO^+, this mechanism leads to a rate law of the form

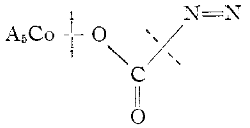
$$\frac{-d[\text{carbamate}]}{dt} = \frac{k_1K'[H^+][HNO_2][\text{carbamate}]}{((k_2/k_3) + [A_5CoOCONH_2^{2+}])(1 + K_{H^+}[H^+])}$$

At the low concentrations of $A_5CoOCONH_2^{2+}$ $(10^{-3}/(1 + K_{H^+}[H^+])$ used in the experiments, k' was found to be independent of the complex concentration. It follows that $k_2/k_3 >> [A_5CoOCONH_2^{2+}]$ and that $k' = k_3k_1K'/k_2$. Using the value of k_1K' estimated by Haim and Taube[2] as $\sim 2 \times 10^3\ sec^{-1}$ along with k' from the present study we evaluate $k_2/k_3 \sim 6 \times 10^3$ which justifies the contention that $k_2/k_3 >> [A_5CoOCONH_2^{2+}]$.

In these respects the nitrosation of the carbamato complex parallels that of $A_5CoN_3^{2+}$ except that the nitrosated azido complex probably decomposes through one of two paths



while the nitrosated carbamato complex



can lose either $\substack{O\\O}{>}CN{=}N$ or first N_2 and then CO_2. In these reactions the leaving groups are poor coordi-

TABLE V

PRODUCT DISTRIBUTIONS FOR Hg^{2+}-INDUCED AQUATION OF $Co(NH_3)_5X^{2+}$ IN THE PRESENCE OF ADDED ANIONS AT 25°

Complex	Reaction medium	Product
0.025 *M* $[Co(NH_3)_5Cl](ClO_4)_2$	0.5 *M* H_2SO_4 + 0.05 *M* $HgSO_4$	21% $[Co(NH_3)_5SO_4]^+$
0.010 *M* $[Co(NH_3)_5Cl](ClO_4)_2$	1 *M* HNO_3 + 0.2 *M* HgO	38% $[Co(NH_3)_5NO_3]^{2+}$
0.025 *M* $[Co(NH_3)_5Br](ClO_4)_2$	0.5 *M* H_2SO_4 + 0.05 *M* $HgSO_4$	19% $[Co(NH_3)_5SO_4]^+$
0.025 *M* $[Co(NH_3)_5Br](ClO_4)_2$	1 *M* HNO_3 + 0.1 *M* HgO	40% $[Co(NH_3)_5NO_3]^{2+}$
0.025 *M* $[Co(NH_3)_5I](ClO_4)_2$	0.5 *M* H_2SO_4 + 0.05 *M* $HgSO_4$	23% $[Co(NH_3)_5SO_4]^+$
0.010 *M* $[Co(NH_3)_5I](ClO_4)_2$	1 *M* HNO_3 + 0.1 *M* HgO	~34% $[Co(NH_3)_5NO_3]^{2+}$

nating agents and dissociate rapidly. We suggest that the intermediate $[Co(NH_3)_5]^{3+}$ is common to both systems and that this species is characterized by its common competition ratio for each species of X^- in Tables III and IV ($X^- = Cl^-, Br^-, NO_3^-, F^-, HSO_4^-$). The common competition ratios have an enhanced significance when it is realized that the leaving groups are different in the two reactions and the rate laws differ in their anion and H^+ dependence.

Using Haim and Taube's notation[2] the reactions competing for the intermediate in solution are

$$A_5Co^{3+} + X^- \xrightarrow{k_x} A_5CoX^{2+}$$

$$A_5Co^{3+} + H_2O \xrightarrow{k_w} A_5CoOH_2^{3+}$$

$$A_5Co^{3+} + X^- \underset{}{\overset{K_{int}}{\rightleftarrows}} A_5Co^{3+}\cdot X^-$$

$$A_5Co^{3+}\cdot X^- \xrightarrow{k_x'} A_5CoX^{2+}$$

$$A_5Co^{3+}\cdot X^- + H_2O \xrightarrow{k_w'} A_5CoOH_2^{3+} + X^-$$

The competition ratio then becomes

$$R = \frac{[A_5CoX]}{[A_5CoOH_2][X^-]} = \frac{k_x + k_x'K_{int}}{k_w + k_w'K_{int}[X^-]}$$

It is clear from the competition results in both systems that R is independent of $[X^-]$ within experimental error and therefore $k_w'K_{int}[X^-]$ must be small relative to k_w. Also it is known that the association constant for $Co(NH_3)_6^{3+}$ and Cl^- is <1 at $\mu = 0.9$ and 35.1°[15] so it seems likely that the ion-pair concentration $[A_5Co^{3+}\cdot X^-]$ will be small. Some documentation of the ion association constants at 25° is relevant since there are some conflicting reports on their magnitude. The work of Phipps and Plane[16] for similar systems to those considered here, namely, the association of SCN^- with $Cr(H_2O)_6^{3+}$, $Cr(NH_3)_6^{3+}$, and $Cr(NH_3)_5Cl^{2+}$, shows that $K_{int} << 1$. Some of the disagreement probably arises from the large ionic strength dependence of K_{int};[17] for example, for $Co(NH_3)_5OH_2^{3+}$ and SO_4^{2-} log K_{int} is 3.276 at $\mu = 0$ and 1.05 at $\mu = 1$,[18] and for $Co(NH_3)_6^{3+}$ in association with Cl^- log K_{int} is -0.31 at $\mu = 1$ and 0.6 at $\mu = 0$.[19] Even for the $Pt(en)_3^{4+}$ and Cl^- system, log K_{int} is only 1.04 at $\mu = 0$.[20] Thus, if ion association is negligible, the ratio expression reduces to $R = k_x/k_w$ and it seems likely that this condition is met for $X^- = Cl^-, Br^-, NO_3^-, F^-$, and HSO_4^-.

The intermediate is highly reactive and shows little discrimination for the nucleophiles X^- in aqueous solution (a factor of ~4). In this context it is interesting to note that Cl^- and Br^- are less effective than NO_3^-. This might be explained by the ability of the intermediate to extract the anion from its hydration sheath in which case the poorly solvated NO_3^- ion would be captured in preference to the more solvated Cl^- and Br^- ions.[21] The argument is also consistent with the strongly solvated F^- ion being the poorest competitor for A_5Co^{3+}.

Some preliminary results for the competition of NO_3^- and HSO_4^- for the intermediate generated by the reaction $A_5CoX^{2+} + Hg^{2+}$ (X = Cl, Br, I)[1] are given in Table V. The competition values for the three complexes are approximately constant in each case but differ somewhat from the azido and carbamato values. However, the rate laws in these reactions complicate the issue since for the SO_4^{2-} ion, at least, the rate law is of the form[1]

$$R = k[Co][Hg^{2+}] + k_2[Co][SO_4^{2-}][Hg^{2+}] + k_3[Co][Hg^{2+}][SO_4^{2-}]^2$$

and the terms in the rate law have different efficiencies in forming the sulfatopentaammine product. Strictly, the competition ratios for the term independent of SO_4^{2-} should be compared with those for the nitrosation reactions. A similar situation probably exists for NO_3^-, and both reactions are being reexamined at present using the ion-exchange technique. The competition ratios reported here differ from Posey and Taube's values[1] for the same reason as described for the azido system. Despite these problems, it seems unlikely that the relative efficiencies for each path will vary for the chloro, bromo, and iodo complexes, so that the approximately constant competition ratios observed for NO_3^- and HSO_4^- with these ions in their reactions with Hg^{2+} are probably meaningful in terms of a common intermediate and are certainly consistent with the constant O^{18}/O^{16} fractionation factors.

An analysis of the anation reactions has been carried out[2] assuming they occur by a five-coordinate intermediate also. From the reactions

$$A_5CoOH_2^{3+} \underset{k_w}{\overset{k_e}{\rightleftarrows}} A_5Co^{3+} + H_2O$$

$$A_5Co^{3+} + X^- \underset{k_a}{\overset{k_x}{\rightleftarrows}} A_5CoX^{2+}$$

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the equilibrium constant for the over-all reaction

$$A_5CoOH_2^{3+} + X^- \overset{K}{\rightleftarrows} A_5CoX^{2+} + H_2O$$

has the form $K = k_e k_x / k_w k_a$ assuming there is no significant ion pairing.[15]

The rate of oxygen exchange between $A_5CoOH_2^{3+}$ and water, k_e, is known and the rates of aquation of A_5CoX^{2+} (X = Cl, Br, NO_3) and the equilibrium constant K are known also, whence k_x/k_w was calculated, Table VI. The equilibrium constants have now been remeasured at $\mu = 1$ by the ion-exchange method and they agree substantially with the values quoted by Haim and Taube.[2] The improved precision of the present work removes the apparent agreement between the values of k_x/k_w for the induced aquation reactions (Tables III–V) on the one hand and for the spontaneous (Table VI) on the other, which was indicated by the earlier work,[2] so there is no longer conflict between the competition experiments and the conclusions of Pearson and Moore.[3] This requires either a different intermediate for the anation reactions from that proposed here or a different mechanism.

TABLE VI

RATE AND EQUILIBRIUM CONSTANTS FOR THE REACTION

$$(NH_3)_5CoOH_2^{3+} + X^- \overset{k_a}{\rightleftarrows} (NH_3)_5CoX^{2+} + H_2O$$

(25°, $\mu = 0.5$)[a]

	k_a, sec^{-1}	K	k_x/k_w
Cl^-	1.7×10^{-6}	1.25 (1.11)[b]	0.35 (0.31)
Br^-	6.5×10^{-6}	0.39 (0.35)	0.43 (0.39)
NO_3^-	2.9×10^{-5}	0.077 (0.08)	0.38 (0.40)

[a] From Table IV of ref 2. [b] Measured using the ion-exchange technique at $\mu = 1.0$.

In summary, the competition ratios for the nitrosation reactions are constant and may well agree with those for the anion-independent path for the Hg^{2+}-induced aquations[1] and are different from those for the normal aquation reactions.[2] The O^{18}/O^{16} fractionation factors for the azido reaction[5] and the Hg^{2+}-induced aquations of A_5CoX^{2+} (X = Cl, Br, I)[1,5] are constant, and both the competition ratios and fractionation factors agree with the formation of a common $[(NH_3)_5Co^{3+}]$ intermediate for the induced aquations. Finally the nature of the proposed intermediate involved in reactions 1–3 has been established by selectively deuterating the ammonia *trans* to the substituent.[22] The intermediate reacts with retention of the isotopic distribution imparted into the initial reactants for all three of reactions 1-3 in agreement with the conclusions derived from the anion competition and O^{18}/O^{16} fractionational values. The result suggests that the intermediate has the form substantially of a square pyramid and excludes the possibility of a symmetrical trigonal bipyramid.

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Stereochemistry and Rearrangement in Some Triethylenetetramine Disubstituted Cobalt(III) Ions

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The preparation, stereochemistry, and aquation of the optically active *trans*-$[Co(trien)Cl_2]^+$ ion is discussed. It is shown that $(+)_{589}$-*trans*-$[Co(trien)Cl_2]^+$ aquates stereospecifically to the optically pure $(+)_{589}$-β-$[Co(trien)ClOH_2]^{2+}$ ion which is identical with that obtained from $(+)_{589}$-β-$[Co(trien)Cl_2]^+$. The preparation of the active *trans*-$[Co(trien)Cl_2]^+$ ion allows some ring conformations to be assigned to this ion and the β-chloroaquo and some other β complexes. The two internal diastereoisomers of β-$[Co(trien)(OH_2)_2]^{3+}$ are reported and the mutarotation of the less stable form is observed. The stereochemistry and rearrangements are discussed in the light of the properties of the optically active *sec*-NH centers of the coordinated quadridentate.

Introduction

One of the recent developments in the chemistry of cobalt(III) complexes has been the resolution and racemization and proton-exchange reactions of coordinated asymmetric nitrogen atoms. The $[Co(NH_3)_4(sar)]^{2+}$ [1] (sar = N-methylglycinate), $[Co(NH_3)_4N\text{-}Meen]^{3+}$ [2] (N-Meen = N-methylethylenediamine), *trans*-$[Co(N\text{-}Meen)_2(NO_2)_2]^+$,[3] and *trans*-$[Co(N\text{-}EtOHen)_2(NO_2)_2]^+$ [3] (N-EtOHen = N-(2-hydroxyethyl)ethylenediamine) ions have been resolved, and the rates of racemization, k_R, and proton exchange, k_H,

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