Table II. Nmr Spectra of Solutions of 2,4-Dinitroaniline in Liquid Ammonia Containing Various Bases

Base (B^-)	$-\delta$, ppm from external TMS					J_{AB}, cps	J_{BC}, cps
	NH	H_c	H_b	H_a	HB/B^- [a]		
None[b]	...	8.83	8.08	7.09	...	9.64	2.87
OH^-, 1 equiv	...	8.63	7.25	6.56	...	9.7	2.9
OH^-, >2 equiv	11.22	5.24	6.95	5.59	4.55	10.22	0.75
OMe^-, >2 equiv	11.25	5.23[c]	7.02	5.59	3.10	10.29	...
NH_2^-, >2 equiv	~11.0	5.19	6.94	5.52	...	10.22	0.69

[a] Time-averaged signal of rapidly exchanging proton. [b] These are the nmr, parameters for a solution of this acid in plain liquid ammonia and not of the un-ionized acid. [c] Slow OMe^- exchange results in broadened H_c peak.

solution is shown in Figure 5 and is assigned to a complex having structure V. The AB quartet of H_a and H_b is retained, but shifted to higher magnetic field as a result of the extra negative charge, and H_c is now found to resonate at a higher magnetic field than H_a. This shift is ten times the shift undergone by H_b and is best explained by a rehybridization at the 3 carbon from sp^2 to sp^3. This change is accompanied by a reduction in the spin–spin coupling between H_b and H_c. The new broad peak observed at lowest field is assigned to the NH proton internally hydrogen bonded to the 2-nitro group; this peak is present when OCH_3^- or NH_2^- are used instead of OH^-. The areas of the peaks due to NH, H_b, H_a, and H_c are in the expected 1:1:1:1 ratio. Water produced in the ionization of the aniline gives rise to the peak at −4.55 ppm, and this peak presumably also includes the signal from the proton of the OH group at the 3 position, proton exchange causing a merging of these two types of hydrogen.

Proton removal occurs when 4-nitroaniline is treated with base in liquid ammonia; but, whereas sodium hydroxide produces no further interaction, excess amide does. A collapse in the spectrum of the ring protons occurs, implying attack of one or more ring positions by amide ion.

These phenomena illustrate the stronger basicity of liquid ammonia compared to the solvents used by other investigators[9,13] who observed addition of base to aromatic systems only with trinitro compounds. It is clear that addition occurs to dinitro and probably even mononitro compounds in liquid ammonia.

Other Acids. Recent interest in the acidities of carbon compounds[2,4] has led us to examine a few of these, in a preliminary manner, in the hope that we will be able to obtain good data for both nitrogen and carbon acids in the same solvent. We have examined solutions of the following acids in liquid ammonia in the presence of sodium amide: indene, fluorene, triphenylmethane, diphenylmethane, and toluene. With the exception of toluene all of these acids can be completely ionized with excess amide ion. Literature data[4] indicate that diphenylmethane is ~11 p*K* units weaker than fluorene, and it appears that fluorene is at the more acidic end of our aniline scale.[1,2] It follows that we should be able to extend our scale by at least another 5 p*K* units, since diphenylmethane can be completely ionized in liquid ammonia. Toluene cannot be detectably ionized, even with high concentrations of potassium amide, so it appears that the limit to our scale lies somewhere between toluene and diphenylmethane.

Acknowledgments. The authors wish to thank Drs. R. Stewart and D. Dolman for making their data available to us in advance of publication. This work was supported by the United States Atomic Energy Commission.

Mechanism of Base Hydrolysis of Some Acidopentaamminecobalt(III) Complexes

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Abstract: Base hydrolysis of $[Co(NH_3)_5X](ClO_4)_2$ ($X = Cl^-, Br^-, I^-, NO_3^-$) in aqueous solution in the presence of added anions Y ($Y = N_3^-, SCN^-, NO_2^-, OAc^-, SO_4^{2-}, PO_4^{3-}$) leads to formation of some $[Co(NH_3)_5Y]^{n+}$. The competition ratio for monovalent ions, $[Co(NH_3)_5Y]^{2+}/[Co(NH_3)_5OH]^{2+}$, determined by ion-exchange chromatography, shows little dependence on the leaving group, is independent of $[OH^-]$, but depends on the concentration of Y, and varies slightly from one Y ion to the next. These results suggest the formation of a common intermediate formed by an SN1CB mechanism and appear to exclude an SN2 mechanism.

The controversy over the mechanism of aqueous base hydrolysis for complexes of the type $[Co(NH_3)_5X]^{2+}$ is expounded elsewhere and will not be dealt with in detail. Briefly, three proposals have been discussed, all of which appear to be kinetically indistinguishable. One mechanism, supported by Ingold and associates,[1] requires the OH^- ion to displace the X group in a bimolecular process (SN2)

$$OH^- + [Co(NH_3)_5X]^{2+} \xrightarrow{k} [Co(NH_3)_5OH]^{2+} + X^-$$

Another, originally proposed by Garrick,[2] requires the formation of a deprotonated intermediate which subsequently loses X^- by a rate-determining unimolecular mechanism (SN1CB)

$$[Co(NH_3)_5X]^{2+} + OH^- \underset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2X]^+ + H_2O$$

$$[Co(NH_3)_4NH_2X]^+ \xrightarrow{k} [Co(NH_3)_4NH_2]^{2+} + X^-$$

$$[Co(NH_3)_4NH_2]^{2+} + H_2O \xrightarrow{\text{fast}} [Co(NH_3)_5OH]^{2+}$$

Basolo and Pearson[3] have extensively developed the latter approach and have amplified Garrick's suggestion to include a bimolecular path for the reaction of the conjugate base intermediate (SN2CB)

$$[Co(NH_3)_5X]^{2+} + OH^- \overset{\text{fast}}{\rightleftharpoons} [Co(NH_3)_4NH_2X]^+ + H_2O$$

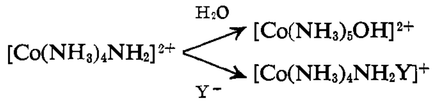
$$[Co(NH_3)_4NH_2X]^+ + H_2O \xrightarrow{k} [Co(NH_3)_5OH]^{2+} + X^-$$

More recently strong support for Garrick's mechanism was obtained by the ingenious use of the large isotope effect in the equilibrium

$$H_2O^{16} + O^{18}H^- \rightleftharpoons H_2O^{18} + O^{16}H^-$$

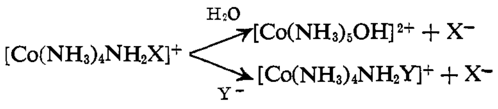
Green and Taube[4] found that the O^{18}/O^{16} isotope fractionation factor was constant for the base hydrolysis of the complexes $[Co(NH_3)_5X]^{2+}$ where X = Cl, Br, NO_3 and was of a magnitude consistent with an SN1CB mechanism and inconsistent with an SN2 process. They asserted that if a common intermediate were produced then the fractionation factor should be independent of X, whereas if the SN2 or SN2CB mechanism obtained then the fractionation factor should be related to X since X is contained in the activated complex.

The present paper concerns another method of distinguishing between these processes by allowing the possible intermediates to compete for species (Y^-) other than a water molecule in solution, *i.e.*



$$[Co(NH_3)_4NH_2]^{2+} \begin{cases} \xrightarrow{H_2O} [Co(NH_3)_5OH]^{2+} \\ \xrightarrow[Y^-]{} [Co(NH_3)_4NH_2Y]^+ \end{cases}$$

or



$$[Co(NH_3)_4NH_2X]^+ \begin{cases} \xrightarrow{H_2O} [Co(NH_3)_5OH]^{2+} + X^- \\ \xrightarrow[Y^-]{} [Co(NH_3)_4NH_2Y]^+ + X^- \end{cases}$$

It is apparent that if a common intermediate is produced (SN1CB) a constant competition ratio of $[Co(NH_3)_5Y]^{2+}/[Co(NH_3)_5OH]^{2+}$ should appear for each species of Y^-, whereas if the SN2CB mechanism obtains, the ratio should be dependent on the nature of both Y and X. The SN2 mechanism, of course, leads exclusively to the hydroxo complex.

The wide variety of rates of base hydrolysis of cobalt(III) pentaammine complexes allows the competition experiments to be carried out and we have chosen to treat $[Co(NH_3)_5X]^{2+}$ (where X = Cl, Br, I, NO_3 and the rates of base hydrolysis are rapid) in aqueous solution with OH^- in the presence of Y (where Y = NO_2^-, N_3^-, NCS^-, $OOCCH_3^-$, PO_4^{3-}, SO_4^{2-}). The rates of base hydrolysis for the $[Co(NH_3)_5Y]$ complexes are considerably slower than those for the former species and no measurable amount of base hydrolysis of these compounds occurs in the time required for reaction of the $[Co(NH_3)_5X]^{2+}$ complexes (~4 min). Also it is known that the rate of $O^{18}H_2$ exchange with $[Co(NH_3)_5OH]^{2+}$ is very slow[5] and that Y^- does not react to any measurable extent with $[Co(NH_3)_5OH]^{2+}$ or with $[Co(NH_3)_5X]^{2+}$ [6] in the time required for base hydrolysis to be essentially complete (~4 min).

Experimental Section

"Analar" reagents were used throughout without further purification. $[Co(NH_3)_5Cl](ClO_4)_2$, $[Co(NH_3)_5Br](ClO_4)_2$, and $[Co(NH_3)_5I](ClO_4)_2$ were prepared from the chloride,[7] bromide,[8] and chloride[9] salts, respectively, by treating them with concentrated $HClO_4$ and cooling the solution in ice. The perchlorates were then recrystallized from water with $NaClO_4$ until pure. $[Co(NH_3)_5(NO_3)](ClO_4)_2$ was prepared by heating $[Co(NH_3)_5(H_2O)](NO_3)_3$ at 80° for 2 days and treating the formed $[Co(NH_3)_5(NO_3)](NO_3)_2$ with perchloric acid. *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 $[Co(NH_3)_5(NO_3)](ClO_4)_2$: N, 20.75; H, 3.73. Found: N, 20.73; H, 3.69. The complexes were further tested for purity on an ion-exchange column (Bio-Rad analytical Resin Dowex (H^+) 50 W-X 2, 200–400 mesh, dimension: 15 × 120 mm). In some of the crude preparations aquopentaammine, hexaammine, and nitropentaammine complexes were detected as impurities. For the pure complexes the molar absorptivities were measured on a Cary 14 spectrophotometer in 10^{-3} *M* $HClO_4$: iodo ϵ_{582} 78.0, bromo ϵ_{550} 54.2, chloro ϵ_{530} 50.1, and nitrato ϵ_{502} 56.3.

Base Hydrolysis. The complex (1.00 mmole) was dissolved in water (10 ml at pH 4) at 25° and then added to a solution of the sodium salt of the anion in base (10 ml) also at 25° (see Table I). In most instances $HClO_4$ (11.7 *M*) was added to the mixture after 4.0 min to pH 5. The solution was diluted with water and the complexes adsorbed on the column. Once the complexes were adsorbed the column was washed with water to remove extraneous ions. These procedures were not possible with the nitrite solution, and here the reaction mixture was adsorbed directly on the ion-exchange column in the Na form, then washed with water thoroughly, and finally acidified with dilute acetic acid. The column was eluted first with aqueous KCl (1 *M* at pH 3) to remove the +1 and +2 charged complex ions and then with 3 *M* HCl to recover the $[Co(NH_3)_5(H_2O)]^{3+}$. In every instance the total recovery was greater than 98%, and representative results are given below. $[Co(NH_3)_5(NO_3)](ClO_4)_2$ in 0.5 *M* $NaNO_2$ and 0.125 *M* NaOH gave 3.2% $[Co(NH_3)_5(NO_2)]^{2+}$ and 96.7% $[Co(NH_3)_5(H_2O)]^{3+}$. $[Co(NH_3)_5I](ClO_4)_2$ in 1 *M* NaN_3 and 0.125 *M* NaOH gave 10.0% $[Co(NH_3)_5(N_3)]^{2+}$ and 88.5% $[Co(NH_3)_5(H_2O)]^{3+}$. $[Co(NH_3)_5I](ClO_4)_2$ in 1 *M* KSCN and 0.125 *M* NaOH gave 6.4% $[Co(NH_3)_5(SCN)]^{2+}$ and 93.9% $[Co(NH_3)_5(H_2O)]^{3+}$.

For the reactions in NaN_3 and NaSCN solutions, twice the volume of solvent was used to prevent precipitation of the reactant as the azide or thiocyanate during the hydrolysis. The molar absorptivities of the reaction products were measured in 1 *M* KCl, and the molar absorptivity for $[Co(NH_3)_5(H_2O)](ClO_4)_3$ was measured in 3 *M* HCl in order to calculate the concentrations of the species

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[1] C. K. Ingold, Weizmann Memorial Lecture, 1958; M. L. Tobe, *Sci. Progr.*, 48, 483 (1960); also S. C. Chan, K. Y. Hui, J. Miller, and W. S. Tsang, *J. Chem. Soc.*, 3207 (1965).

[2] F. J. Garrick, *Nature*, 139, 507 (1937).

[3] F. Basolo and R. G. Pearson, *Advan. Inorg. Chem. Radiochem.*, 3, 25 (1960).

[4] M. Green and H. Taube, *Inorg. Chem.*, 2, 948 (1963).

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

[6] J. W. Moore and R. G. Pearson, *Inorg. Chem.*, 3, 1334 (1964); also this work.

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

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

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

isolated from the column. The measured molar absorptivities were: in 1 *M* KCl for $[Co(NH_3)_5(NO_2)](ClO_4)_2$, ϵ_{467} 95.5; $[Co(NH_3)_5(N_3)](ClO_4)_2$, ϵ_{518} 272; $[Co(NH_3)_5(SCN)](ClO_4)_2$, ϵ_{498} 183; $[Co(NH_3)_5(OCOCH_3)](ClO_4)_2$, ϵ_{519} 66; $[Co(NH_3)_5(SO_4)](ClO_4)$, ϵ_{515} 61. In 3 *M* HCl the molar absorptivities for $[Co(NH_3)_5(H_2O)](ClO_4)_3$ was ϵ_{492} 47.7.

In order to ensure that azide ions do not replace the halogen ions directly, $[Co(NH_3)_5Cl](ClO_4)_2$ was treated with 1 *M* NaN_3 at pH 5 for 4 min. The solution was poured on the column which was then washed thoroughly with water. The adsorbed complex was hydrolyzed on the column with 1 *M* NaOH, acidified with acetic acid, and eluted with 1 *M* KCl. No azido complex was detected.

Two experiments were carried out by hydrolyzing $[Co(NH_3)_5I](ClO_4)_2$ in diethanolamine buffer at pH 10.5 (0.2 *M*) in the presence of 1 *M* NaN_3 at $\mu = 1.0$ and 25°. The mixture was allowed to stand for 2 hr and then run through the column, washed with water, and eluted as before (Table IIC). A similar experiment was also carried out using a Radiometer pH Stat at pH 10.5 using 2.1 *N* NaOH as titrant (Table IIC). These experiments could not be carried out at $\mu = 2$ (added $NaClO_4$) as the iodo complex precipitated slowly under these conditions.

Results

The results of the competition reactions at 25° are given in Tables I and 2A and B and several correlations emerge.

Table I. Formation of $[A_5CoY]$ in the Base Hydrolysis ($[OH^-] = 0.125$ *M*) of $[A_5CoX]^{2+}$ Complexes in the Presence of Anion $[Y^-]$ at 25°

		% $[A_5CoY]$ from the reactants (0.05 *M*)[a]				
Added anion	$[Y^-]$, *M*	A_5CoI^{2+}	A_5Co-Br^{2+}	A_5CoCl^{2+}	$A_5CoNO_3^{2+}$	μ
$NaNO_2$	1.0	4.5	5.0	4.2	5.1	1.25
	0.5	2.6	3.1	2.4	3.2	0.75
KCNS	1.0	6.3	6.1	5.5, 5.4	7.1, 6.9, 7.2 (5 min)	1.20
NaOAc	1.0	4.8				1.25
	0.5	3.1				0.75
NaN_3	1.0	9.9, 9.8 (1 min), 10.2	8.7	8.5	10.6, 10.2	1.20
	0.5	5.9	5.3	4.9	6.3	0.70
Na_3PO_4	0.25	6.8, 4.7	Trace	4.7, 6.0	Nil	
Na_2SO_4	1.0	8.2[b]				

[a] Reactant concentration in NaN_3 and KNCS experiments 0.025 *M*. [b] May possibly be $[Co(NH_3)_4SO_4]^+$.

Table II. Dependence of the $[A_5CoN_3]^{2+}$ Concentration on $[N_3^-]$ and $[OH^-]$ for the Reaction $[A_5CoI]^{2+} + OH^-$ at 25°

	(A) NaOH, 0.125 *M*; $\mu = 1.20$			
NaN_3, *M*	1.0	0.75	0.5	0.25
% $[A_5CoN_3]^{2+}$	10.0, 9.8	7.4	5.0	2.5, 2.6
	(B) NaN_3, 1.0 *M*; $\mu = 2.0$			
NaOH, *M*	1.0	0.125	0.025[a]	
% $[A_5CoN_3]^{2+}$	9.1	9.0	8.6	
	(C) NaN_3, 1.0 *M*; $\mu = 1.0$			
Diethanolamine buffer	pH 10.5[a]		pH stat, pH 10.5[a]	
% $[A_5CoN_3]^{2+}$	9.8, 10.3		9.6	

[a] Reaction volume, 100 ml.

(1) The competition ratio $[CoA_5Y]^{2+}/[CoA_5OH]^{2+}$ ($A = NH_3$) shows little dependence on the leaving group for each monovalent competing ion at each $[Y^-]$ concentration, respectively (Table I).

(2) The competition ratio is independent of $[OH^-]$ concentration over a 50-fold change in base concentration even when $[OH^-]$ is present in the same concentration as the competing ion (Table IIA), $\mu = 2$. This independence is extended over ~1000-fold change in OH^- if the per cent $[A_5CoN_3]^{2+}$ values are compared in Tables I and IIC for $NaN_3 = 1.0$ *M* and $\mu = 1.0$.

(3) The competition ratio is dependent on the $[Y^-]$ concentration (Tables I and IIA).

(4) The competition ratio varies from one $[Y^-]$ ion to the next but not greatly (Table I).

Some of the duplicate results in Table I record the concentrations of $[A_5CoY]^{2+}$ when the reaction was taken for different periods of time and it is clear that the products do not undergo further base hydrolysis. The results appear to indicate good accuracy for the amount of $[A_5CoY]^{2+}$ formed, but since the recovery of total complex varies between 98 and 100%, it is difficult to know whether the discrepancies can be attributed to the hydroxo or to the anionic complex or to both. For these reasons the values quoted might be considered less accurate than the duplicate results suggest. The least accurate figure is that obtained for the acetato complex due mainly to the low concentration of this species and its significantly lower ϵ_{max}. For this reason the competition of acetate ion for the remaining substrates was not pursued. The rate of base hydrolysis of $[A_5CoF]^{2+}$ was not sufficiently rapid at 25° to allow a competition study to be made.

Discussion

Neglecting the possibility of a mixed mechanism, the competition results appear to exclude the bimolecular attack by OH^- ion as the rate-determining step since it is known that the added anion does not react with the substrate at least in neutral or acid solutions. We suggest that the added anion competes for an intermediate produced by the SN1CB or SN2CB mechanisms and that the comparatively constant competition ratios for the chloro, bromo, iodo, and nitrato pentaammine ions (Table I) with each anion, respectively, further suggest a common intermediate; the SN1CB mechanism is therefore preferred. For the SN2CB process a dependence of the competition ratio on the leaving group would be expected since the leaving group is still contained in the activated complex for the rate-determining step. It seems unlikely that essentially the same rate for the entry of Y^- would be observed for several $[A_5CoX]^{2+}$ complexes where X varies in size and electronic properties.

The possibility of an SN2 mechanism for the reaction of $[Co(NH_3)_5X]^{2+}$ and Y^- in alkaline solution cannot be entirely excluded by this work since there is always a remote possibility that the ion pair $[Co(NH_3)_5X]^{2+} \cdot OH^-$ could facilitate SN2 attack by Y^-. The narrow range of nucleophilic character observed for the widely differing ions NO_2^-, NCS^-, OAc^-, and N_3^- militates against this possibility. In addition the competition ratios support generally the SN1CB conclusions of Green and Taube[4] derived from the O^{18} isotope fractionation effects and confirm their inference that the iodo complex should behave in the same way as the chloro, bromo, and nitrato compounds.

It is pertinent to add that the nitro complex formed has the nitrite ion N bonded to the cobalt. Normally in aqueous solution nitro complexes form slowly by intramolecular isomerization of the nitrito complexes.[10]

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(10) R. G. Pearson, P. M. Henry, J. G. Bergmann, and F. Basolo, *J. Am. Chem. Soc.*, 76, 5920 (1954).

The latter arise by addition of NO^+ to coordinated oxygen without Co–O cleavage.[11] In the present experiments the direct coordination of N-bonded nitrite ion is also consistent with the production of an intermediate of reduced coordination number.

It appears that OH^- is a poor competitor for the vacant coordination position compared with Y^- (Table IIB) and that water is more efficient in forming the hydroxo complex. A contributing factor to this result must be the much larger concentration of H_2O molecules. The result is also consistent with Green and Taube's observation that the isotope effect is unaffected by the $[OH^-]$ concentration.[4]

Possible reactions which lead to the observed products are as follows.

$$A_4CoNH_2{}^{2+} + Y^- \xrightarrow{k_1} A_5CoY^{2+}$$

$$A_4CoNH_2{}^{2+} + OH^- \xrightarrow{k_2} A_5CoOH^{2+}$$

$$A_4CoNH_2{}^{2+} + H_2O \xrightarrow{k_3} A_5CoOH^{2+}$$

$$A_4CoNH_2{}^{2+} + Y^- \overset{K_Y}{\rightleftarrows} [A_4CoNH_2{}^{2+}\cdot Y^-]$$

$$A_4CoNH_2{}^{2+} + OH^- \overset{K_{OH}}{\rightleftarrows} [A_4CoNH_2{}^{2+}\cdot OH^-]$$

$$[A_4CoNH_2{}^{2+}\cdot Y^-] \xrightarrow{k_4} A_5CoY^{2+}$$

$$[A_4CoNH_2{}^{2+}\cdot Y^-] + OH^- \xrightarrow{k_5} A_5CoOH^{2+} + Y^-$$

$$[A_4CoNH_2{}^{2+}\cdot Y^-] + H_2O \xrightarrow{k_6} A_5CoOH^{2+} + Y^-$$

$$[A_4CoNH_2{}^{2+}\cdot OH^-] \xrightarrow{k_7} A_5CoOH^{2+}$$

$$[A_4CoNH_2{}^{2+}\cdot OH^-] + Y^- \xrightarrow{k_8} A_5CoY^{2+} + OH^-$$

$$[A_4CoNH_2{}^{2+}\cdot OH^-] + H_2O \xrightarrow{k_9} A_5CoOH^{2+} + OH^-$$

In formulating the products the subsequent protonation reactions have been ignored since they do not alter the product ratio. Also $[Y^-]$ and $[OH^-]$ are considered constant for the derivation. The competition ratio then is of the form

$$\frac{A_5CoY^{2+}}{A_5CoOH^{2+}} = \frac{[Y^-][k_1 + k_4K_Y + k_8K_{OH}[OH^-]]}{k_3 + k_6K_Y[Y^-] + [OH^-] \times [k_2 + k_5K_Y[Y^-] + k_7K_{OH} + k_9K_{OH}]} \qquad (1)$$

If the competition ratio is independent of $[OH^-]$ then eq 1 reduces to either

$$\frac{A_5CoY^{2+}}{A_5CoOH^{2+}} = \frac{[Y^-][k_1 + k_4K_Y]}{k_3 + k_6K_Y[Y^-]} \qquad (2)$$

or

$$\frac{A_5CoY^{2+}}{A_5CoOH^{2+}} = \frac{[Y^-]k_8K_{OH}}{k_2 + k_5K_Y[Y^-] + k_7K_{OH} + k_9K_{OH}} \qquad (3)$$

Also the ratios show a first-order dependence of $[Y^-]$ (Table IIA) and therefore $k_6K_Y[Y]^-$ and $k_5K_Y[Y^-]$ must be small compared to the other terms. Thus eqs. 2 and 3 reduced further to

$$\frac{A_5CoY^{2+}}{A_5CoOH^{2+}} = \frac{[Y^-][k_1 + k_4K_Y]}{k_3} \qquad (4)$$

or

$$\frac{A_5CoY^{2+}}{A_5CoOH^{2+}} = \frac{[Y^-]k_8K_{OH}}{k_2 + k_7K_{OH} + k_9K_{OH}} \qquad (5)$$

The most efficient processes appear to be, from eq 4, the reaction of $A_4CoNH_2{}^{2+}$ with Y^-, the collapse of the ion pair $A_4CoNH_2{}^{2+}\cdot Y^-$ and the reaction of $A_4CoNH_2{}^{2+}$ with H_2O. From eq 5, the reaction of $A_4CoNH_2{}^{2+}\cdot OH^-$ with Y^- and of $A_4CoNH_2{}^{2+}\cdot OH^-$ with H_2O as well as collapse of the ion pair should be the most efficient.

The small contribution of the terms $k_6K_Y[Y^-]$ and $k_5K_Y[Y^-]$ suggests that ion-pair formation between $A_4CoNH_2{}^{2+}$ and Y^- is not important. This is consistent with independent ion association studies which have been carried out on similar ions. For example the association constants between $Co(NH_3)_6{}^{3+}$ and Cl^-, Br^-, I^-, are <0.2 at $\mu = 0.9$, 35.1°.[12] A study of the association of $[Co(NH_3)_6]^{3+}$ and OH^- proposes that $K_A = 2.3$ at 25°, $\mu = 1.0$.[13] K_A, for $A_4CoNH_2{}^{2+}$ and OH^-, therefore might be expected to something less than this value, and little of the ion pair $[A_4CoNH_2{}^{2+}\cdot OH^-]$ should be present except for the highest OH^- concentrations. Certainly the experiments are not carried out in the concentration regions where the ion pairs are saturated.

There is some preference for eq 4 as the governing relationship since the more abundant $A_4CoNH_2{}^{2+}$ ion should be more efficient in capturing Y^- than the less abundant and lower charged ion pair $[A_4CoNH_2{}^{2+}\cdot OH^-]$.

Solubility problems either for the anionic salt or the complex did not allow a detailed study of all the systems, but from the constant ratio of the competition values at 1.0 *M* $[Y^-]$ ($\mu = 1.2$) and at 0.5 *M* $[Y^-]$ ($\mu = 0.7$) (Table I) a slight decrease in the concentration of $[A_5CoY)^{2+}$ at 0.5 *M* $[Y^-]$ should occur if the ionic strength is maintained constant ($\mu = 1.2$) as for the example in Table IIA. Some slight additional support for a SN1CB mechanism might also be deduced from this dependence of competition ratio on ionic atmosphere. If competition for a common intermediate is dependent on the surrounding ionic atmosphere, then the competition ratio should be even more sensitive to X^-, the leaving ion, when H_2O or $[Y^-]$ with $[X^-]$ are incorporated in the activated complex as for the SN2CB mechanism.[4]

If the competition ratio is redefined as $R = [A_5CoY^{2+}]/([A_5CoOH^{2+}][Y^-])$ to make it independent of $[Y^-]$, then approximate values of R appear as 0.09 for N_3^-, 0.06 for NCS^-, 0.05 for NO_2^-, and 0.05 for acetate ion. These values are lower than those obtained in competition studies between $[Co(NH_3)_5]^{3+}$ and similar ions in aqueous solution ($R \sim 0.3$–0.5),[14] and this may be due in part to the fact that the intermediate in the base hydrolysis experiments has a lower charge, $[Co(NH_3)_4NH_2]^{2+}$. Also the variation in the competition ratio from one anion to the next is not great which suggests that there is not a large difference in the nucleophilic character of the anions for the inter-

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[11] R. K. Murmann and H. Taube, *J. Am. Chem. Soc.*, **78**, 4886 (1956).

[12] E. L. King, J. H. Espenson, and R. E. Visco, *J. Phys. Chem.*, **63**, 755 (1959).

[13] J. A. Caton and J. E. Prue, *J. Chem. Soc.*, 671 (1956).

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

mediate. A similar observation was made also for the competition studies with $[Co(NH_3)_5]^{3+}$.[14]

Surprisingly the PO_4^{3-} and SO_4^{2-} ions do not appear to be much more efficient than Y^- in scavenging the intermediate. Also the failure to observe measurable amounts of phosphate complex from the base hydrolysis of the bromo and nitrato complexes when it does appear from the chloro and iodo reactions is a puzzling feature of the results. However, other species appeared on the column which were not recovered. Also the sulfato complex absorbed maximally at 535 mμ instead of the expected 515 mμ and it is conceivable that $[Co(NH_3)_4SO_4]^+$ was the isolated product. In general the reactions with the multivalent ions appeared to be more complicated than those with the monovalent ions and they were not investigated further.

Acknowledgment. The authors wish to thank the Microanalytical Unit of the John Curtin School of Medical Research, Australian National University, for the N and H analyses.

The Stereochemistry of Complex Inorganic Compounds. XXXIII.[1] Reactions of Optically Active α-Dichlorotriethylenetetraminecobalt(III) Cation with Optically Active Propylenediamine

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Abstract: The reaction of optically active α$[CoCl_2(trien)]^+$ with racemic or optically active propylenediamine in aqueous solution leads to the formation of β-$[Co(pn)(trien)]^{3+}$ with an inversion of configuration about the cobalt atom. Several of the possible optical isomers have been prepared and their ORD curves measured. There seems to be only a minor stereospecific effect in the reaction which produces the complex, $[Co(pn)(trien)]^{3+}$. Complexes in which the chelate rings are in the same positions show almost the same rotatory dispersion curves, irrespective of the sign of rotation of the propylenediamine. It is believed that the inversion of configuration which is produced by the reaction of α-$[CoCl_2(trien)]^+$ with propylenediamine in aqueous solution, like that with other bases, proceeds by a base hydrolysis through the formation of β-$[Co(OH)_2(trien)]^+$ as an inverted intermediate.

In a previous paper,[1a] it was reported that under certain conditions optically active α-$[CoCl_2(trien)]^+$ reacts with ethylenediamine with almost complete inversion to the β configuration. The analogous reaction with 1,2-propanediamine (propylenediamine) would be expected to follow the same course, but the dissymmetry of the propylenediamine molecule may introduce stereospecific effects which will determine the ease of formation and the stabilities of the several possible isomers of the product. The reaction is of particular interest because the formation of a complex of this type, containing one optically active ligand, provides a simple example of the influence of stereospecific factors in optical inversions in the reactions of complexes.

Figure 1 shows the structures of the possible isomers of $[Co(pn)(trien)]^{3+}$. Several studies on the preparation of optically active complexes containing optically active ligands have been reported.[2-4] Studies by Dwyer and his co-workers on stereospecific effects in mixed ethylenediamine–propylenediamine complexes have shown that the stereoselectivity is relatively small energetically, but still sufficient to influence greatly the relative yields of the isomers formed.[5-7] Conformational analyses of complexes of ethylenediamine and propylenediamine,[8] based on X-ray measurements of bond lengths and bond angles,[9] has given a rational explanation for the differences in stability between the various isomers of complexes containing propylenediamine.

In the reaction of α- or β-$[CoCl_2(trien)]^+$ with propylenediamine, one might expect the formation of strain-free rings, with the cobalt–propylenediamine ring in a staggered, or *gauche*, form as it is in $[Co(pn)(en)_2]^{3+}$.[8] However, the presence of an additional chelate ring (between the two secondary nitrogen atoms and the cobalt atom) introduces stereochemical effects of unknown magnitude. Supposedly, the most stable structure will be that in which there is the least repulsion between the four chelate rings, taken as a whole. If stereospecific influences pay little or no part in the reaction, the optical activity of the product should be essentially the same, whether *d*- or *l*-propylenediamine is used. On the other hand, if the incoming propylenediamine molecule subjects the complex to strong stereospecific influences, certain isomers of the complex

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(1) (a) Paper XXXI: E. Kyuno and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **88**, 1125 (1966); (b) paper XXXII: T. Habu and J. C. Bailar, Jr., *ibid.*, **88**, 1128 (1966).

(2) I. Lifschitz, *Z. Physik. Chem.*, **114**, 493 (1925).

(3) F. M. Jaeger and H. B. Blumendal, *Z. Anorg. Allgem. Chem.*, **175**, 161 (1928).

(4) J. C. Bailar, Jr., and J. P. McReynolds, *J. Am. Chem. Soc.*, **61**, 3199 (1939).

(5) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 1043 (1959).

(6) F. P. Dwyer, F. L. Garvan, and A. Schulman, *ibid.*, **81**, 290 (1959).

(7) F. P. Dwyer and A. M. Sargeson, *ibid.*, **81**, 5269 (1959).

(8) E. J. Corey and J. C. Bailar, Jr., *ibid.*, **81**, 2620 (1959).

(9) K. Nakatsu, M. Shiro, Y. Saito, and H. Kuroya, *Bull. Chem. Soc. Japan*, 30, 158 (1957).