$(glyglyOEt)^{3+}$ [26] and β-Co(trien)(Cl)(OH$_2$)$^{2+}$,[6] has that configuration at N(2) in which the proton is directed toward the apical chelate ring of trien. These structures support the conclusion that in general this configuration is the more stable for β-trien.[27,28]

The coordination of (S)-proline, with O(2) *trans* to N(4) of trien (referred to as β_2),[3] is in agreement with the prediction that large nonbonded interactions would occur in the alternative β_1 configuration. Steric considerations further imply that for the coordination of (S)-proline the most stable configuration at cobalt would be L$(-)_{589}$, which is the situation realized in this structure. As mentioned earlier, a species containing (S)-proline but having the opposite configuration at cobalt has been found in almost equal abundance.[5] This contradicts the stereospecificity predicted for this system. A crystal-structure analysis of the D$(+)_{589}$Co-(trien)((S)-Pro)$^{2+}$ complex has been completed, and a detailed discussion of the relative stabilities of the two diastereoisomers will be included in a subsequent paper.

The absolute configuration as determined by the anomalous dispersion method confirms the assignment of confiurgation to (S)-proline.[29] More importantly, the absolute configuration of the complex confirms the assignment made by Douglas.[30] It also supports the suggestion by Sargeson and Searle[31] that in β-Co(trien)-X$_2$$^{2+}$ complexes, a negative dominant circular dichroism coinciding with the first ligand field band is indicative of an L configuration about the cobalt center.

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The Mechanism of Base Hydrolysis for $Co^{III}(NH_3)_5X^{2+}$ Ions. Hydrolysis and Rearrangement for the Sulfur-Bonded $Co(NH_3)_5SCN^{2+}$ Ion

BY D. A. BUCKINGHAM, I. I. CREASER, AND A. M. SARGESON

The base hydrolysis of a set of $(NH_3)_5CoX^{2+}$ ions (X = Cl, Br, I, NO$_3$) in the presence of anions such as N$_3$$^-$ and NCS$^-$ shows that the rate of entry of the extraneous anion is coincident with the rate of loss of X$^-$. The preparation of the S-bonded isomer $[(NH_3)_5CoSCN]Cl_2 \cdot 1.5H_2O$ is also described. The base hydrolysis of this isomer follows two paths, one leading to the N-bonded isomer (24%) and the other to the hydroxo complex. The former path occurs without exchange with N^{14}CS$^-$ in solution. The latter path shows the same competition characteristics as observed for the chloro, bromo, iodo, and nitrato complexes. The results in this study complement those in support of the SN1CB mechanism for base hydrolysis in pentaamminecobalt(III) complexes. Some results for the rearrangement of CoSCN → CoNCS in dilute acid and in the solid state are also given.

Several recent publications have described competition studies[1-3] which support the proposal for an SN1CB mechanism in the base hydrolysis of acidocobalt(III)–pentaammine complexes. The present study was instituted to test this proposal further by measuring the rate of entry of competing anion.

If the following mechanism obtains

$$(NH_3)_5CoX^{2+} + OH^- \underset{}{\overset{fast}{\rightleftharpoons}} (NH_3)_4NH_2CoX^+ + H_2O$$

$$\downarrow slow$$

$$\left.\begin{array}{c}(NH_3)_5CoY^{2+} \\ (NH_3)_5CoOH^{2+}\end{array}\right\} \overset{H_2O \text{ or } Y^-}{\underset{fast}{\longleftarrow}} (NH_3)_4NH_2Co^{2+} + X^-$$
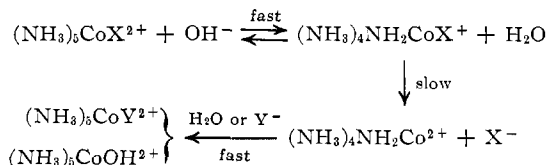
the rate of entry of the competing anion (Y$^-$) should coincide with the rate of loss of X$^-$ if the intermediate is as reactive as has been suggested.[2-4] Experiments of this nature can be performed using anions such as N$_3$$^-$

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

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(4) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd. ed, John Wiley & Sons, Inc., New York, N. Y., p 182.
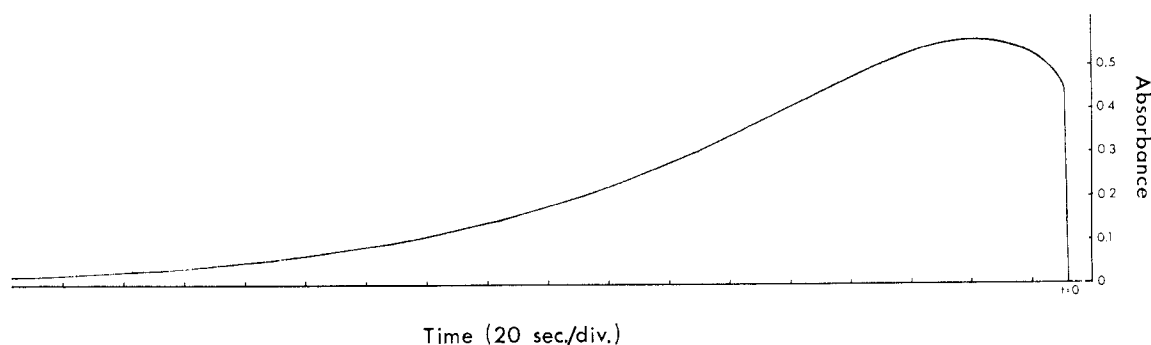
Time (20 sec./div.)

Figure 1.—Change in optical density *vs.* time for the base hydrolysis of $[Co(NH_3)_5Cl](ClO_4)_2$ (10^{-3} M) in 0.1 M NaOH and 1 M NaSCN at 290 nm. The abscissa is the infinite-time reading for the reaction.

and NCS^- where the competition product hydrolyzes in base slowly compared with the reactant. The rates may be measured accurately despite the small quantity of competition product (7–10%) primarily because of the large intensity of the second ligand field absorption band for the competition product ($\epsilon \geqslant 1500$) relative to that for the substrate ($\epsilon \sim 50$).

Experimental Section

Preparation of $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$.—A solution of supersaturated NaSCN (500 ml, ~10 M) at pH 4 was saturated with $[Co(NH_3)_5NO_3](ClO_4)_2^2$ (~40 g) at 25°. To this mixture was added a solution of NaOH (250 ml, 0.5 M) in NaSCN (5 M) under stirring. After 0.5 min the solution was acidified with concentrated HCl and cooled. The precipitated $[Co(NH_3)_5$-NCS]Cl_2$ was filtered off and the filtrate was diluted with water (~8 l.). This solution was then sorbed on an ion-exchange column (Bio-Rad analytical resin Dowex (H^+) 50 WX2 200–400 mesh). The column was eluted first with 1 M HCl to separate the 2+ ions from $Co(NH_3)_5OH_2^{3+}$ on the column. The 2+ ions were then eluted from the column with 2 M HCl and the eluate was reduced to a small volume on a vacuum evaporator. The precipitated thiocyanato complexes were taken out in fractions, $[Co(NH_3)_5NCS]Cl_2$ being the least soluble compound. Purple $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ was purified by fractional crystallization (yield 4 g). *Anal.* Calcd for $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$: N, 28.00; H, 6.05; C, 4.00. Found: N, 28.06; H, 5.93; C, 4.06.

Partial separation of $Co(NH_3)_5NCS^{2+}$ and $Co(NH_3)_5SCN^{2+}$ was obtained on a long ion-exchange column (~25 cm) using 1 M NaClO_4 as eluent. This procedure was inefficient for preparative purposes but it was useful to test the isolated $Co(NH_3)_5$-SCN^{2+} complex for an impurity of isothiocyanato complex. $Co(NH_3)_5NCS^{2+}$ was eluted before $Co(NH_3)_5SCN^{2+}$. $[Co(NH_3)_5$-NCS](ClO_4)_2$ was prepared as described previously[5] (ϵ_{498} 179, 1 M NaClO_4$).

Kinetics of the Base Hydrolysis of $Co(NH_3)_5X^{2+}$ Complexes.—Each of the complexes $[Co(NH_3)_5Cl](ClO_4)_2$,[2] $[Co(NH_3)_5Br]$-$(ClO_4)_2$,[2] and $[Co(NH_3)_5NO_3](ClO_4)_2^2$ was dissolved in water (pH ~3) and mixed rapidly at 25° in a stopped-flow reactor with the NaOH solutions containing NaClO_4, NaSCN, or NaN_3 using the conditions described in Table I. The change in absorbancy with time was followed using a Cary 14 spectrophotometer. The rate of base hydrolysis of $[Co(NH_3)_5I](ClO_4)_2$ was also followed using a Radiometer recording titrator (TTT_1, ABU_1, SBR_2, TTA_3).

Base Hydrolysis of $Co(NH_3)_5X^{2+}$ Complexes in the Presence of NaSCN.—Each of the complexes $[Co(NH_3)_5I](ClO_4)_2$ and $[Co(NH_3)_5NO_3](ClO_4)_2$ (0.1 g) was dissolved in an NaSCN solution at pH 4 (10 ml, 1 M). A solution of NaOH in 1 M NaSCN (10 ml, 0.1 M) was quickly added and the reactions were quenched after $10t_{1/2}$ by the addition of 70% HClO_4. The 2+ and 3+ ions were separated on an ion-exchange column

using 1 M NH_4Cl as eluent. The 3+ ion was then eluted with 3 M HCl. The concentrations of the products were determined spectrophotometrically and by atomic absorption spectroscopy (Techtron AA-4).

Base Hydrolysis of $Co(NH_3)_5SCN^{2+}$ in the Presence of Added N_3^- and NO_2^-.—The above procedure was applied using 0.2 M NaOH in 2 M NaY ($Y^- = N_3^-$, NO_2^-) solution. The formed $Co(NH_3)_5Y^{2+}$ and $Co(NH_3)_5NCS^{2+}$ were eluted together from the column and their concentrations were determined from the absorption spectra of the mixture and atomic absorption measurements for cobalt. $Co(NH_3)_5OH_2^{3+}$ was determined as before.

Rearrangement in the Base Hydrolysis of $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$.—The complex (0.025 g) was dissolved in water (pH ~3) (5 or 10 ml) at 25° and mixed with an equal volume of NaOH solutions in 2 M NaClO_4. After completion of the reactions (~$10t_{1/2}$) at 25°, the solutions were acidified with glacial HOAc, diluted with water (two times), and sorbed on an ion-exchange column. The column was eluted with 1 M NaClO_4 to remove $Co(NH_3)_5$-NCS^{2+}$ and then with 3 M HCl to remove $Co(NH_3)_5OH_2^{3+}$. The concentrations of these solutions were determined spectrophotometrically.

Rearrangement in Acid Aqueous Solution of $[Co(NH_3)_5SCN]$-$Cl_2 \cdot 1.5H_2O$.—The complex (6 × 10^{-6} and 2.4 × 10^{-5} M) was dissolved in 1 M NaClO_4 at pH ~3 and the change in absorbancy with time was followed at 290 nm at 25°. One solution ([Co] = 1.6 × 10^{-2} M in 1 M NaClO_4, pH ~3) was left at 40° for 7 days then sorbed on an ion-exchange column and eluted with 1 M KOAc at pH ~5. The product was almost completely (NH_3)_5-CoNCS^{2+}$ (<2% (NH_3)_5CoOH_2^{3+}$).

Tracer Experiments with $S^{14}CN^-$.—$[Co(NH_3)_5SCN]Cl \cdot 1.5H_2O$ (0.025 g) was dissolved in water (0.6 ml) containing ~10^{-2} mCi of $KS^{14}CN$ (16.5 mCi/mM) and 0.5 M NaOH (0.5 ml) was added. After 4 min the solution was neutralized by addition of 1 drop of glacial HOAc. Samples of 0.05 ml of the reaction mixture were transferred to strips of cation-exchange paper (Amberlite, SA-2). It was not possible effectively to remove excess $KS^{14}CN$ from ion-exchange paper by eluting with water. Instead 1 M HCl was used as eluent to remove the excess $KS^{14}CN$ and to separate $Co(NH_3)_5NCS^{2+}$ from $Co(NH_3)_5OH_2^{3+}$. After drying, the ion-exchange paper was cut into equal-sized pieces (4 × 2 cm) containing the two complexes and also a piece of ion-exchange paper was taken from below the $Co(NH_3)_5NCS^{2+}$ spot as a blank. The activity of the samples was measured on the ion-exchange paper in vials containing a mixture of 0.5% 2,5-diphenyloxazole and 10% naphthalene in dioxane using a Beckman LS-150 liquid scintillation counter. The counts obtained were compared with the counts observed from a sample of 0.05 ml of the reaction mixture on a sample of ion-exchange paper (untreated).

$[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ (0.050 g) was dissolved in 1 M NaClO_4, pH 3 (5 ml), containing 10^{-2} mCi of $KS^{14}CN$. The solution was left at 40° for 8 days when $[Co(NH_3)_5NCS](ClO_4)_2$ had precipitated (>95%) and 0.05 ml of the solvent was transferred to a strip of cation-exchange paper. The precipitated $[Co(NH_3)_5NCS](ClO_4)_2$ was removed from the solvent by decant-

(5)   R. L. Carlin and J. O. Edwards, *J. Inorg. Nucl. Chem.*, **6**, 217 (1958).

ing and washed with 1 M NaClO$_4$ and water. The complex was then dissolved in 10 ml of hot water and 0.05 ml of this solution was transferred to ion-exchange paper. This part was eluted with 1 M HCl for 2 days. The activity of the samples was measured as above.

Results

Kinetics.—When the hydrolysis of [Co(NH$_3$)$_5$Cl]-(ClO$_4$)$_2$ was measured spectrophotometrically (~300 nm) in 1 M NaSCN at [OH$^-$] = 0.01 M, two rate processes were evident, Figure 1. Both reactions obeyed the rate law v = k[substrate][OH$^-$], and the pseudo-first-order rate constants (Table I) at each OH$^-$ concentration were separated using a computer[6] program. The second-order rate constants at 25° were calculated as 0.21 and 0.14 M^{-1} sec^{-1}. When [(NH$_3$)$_5$CoBr](ClO$_4$)$_2$, [(NH$_3$)$_5$CoI](ClO$_4$)$_2$, and [(NH$_3$)$_5$CoNO$_3$](ClO$_4$)$_2$ were hydrolyzed under the same conditions again, two rates were observed: the first varied with the substrate and was faster than for the chloro complex; the second rate was the same as the second rate seen for the chloro complex. However, when the hydrolysis rate was followed at 500 nm using the chloro complex in the presence of 1 M NaSCN, only one process was observed with a rate constant of 0.22 M^{-1} sec^{-1} at 25°. At this wavelength only a small change in absorption occurs for the second process. The initial rate coincided with the base hydrolysis rate for loss of anion at μ = 1.0 and 25° for the chloro, iodo, and nitrato ions (Table I).[7] The initial rate for the bromo complex was not sought. The constant second rate implied the presence of a common product formed in the course of these reactions presumably either (NH$_3$)$_5$CoSCN^{2+} or (NH$_3$)$_5$CoNCS^{2+}. It is known that the latter reacts very slowly under these conditions[8] and we presumed the product was the S-bonded complex which subsequently hydrolyzed in the basic solution.

The preliminary kinetics suggested a method of preparation for (NH$_3$)$_5$CoSCN^{2+} by treating (NH$_3$)$_5$CoNO$_3$$^{2+}$ with OH$^-$ in the presence of a large excess of SCN$^-$. The nitrato ion hydrolyzed rapidly relative to (NH$_3$)$_5$CoSCN^{2+} and the reaction was quenched with acid before appreciable hydrolysis of the competition product occurred. The aquo and thiocyanato plus isothiocyanato complexes were separated by ion-exchange chromatography and the recovered violet complex [(NH$_3$)$_5$CoSCN]Cl$_2$·1.5H$_2$O crystallized to purity.

The rate constant for base hydrolysis of (NH$_3$)$_5$CoSCN^{2+} was 0.14 M^{-1} sec^{-1} at 25° in 1 M NaSCN and 0.16 M^{-1} sec^{-1} in 1 M NaClO$_4$. The rate in 1 M NaSCN was identical with the second rate found when the chloro complex was hydrolyzed in 1 M NaSCN (Table I). The hydrolysis rate constant found in 1 M NaSCN is slightly smaller than that found in 1 M NaClO$_4$ since (NH$_3$)$_5$CoSCN^{2+} is also formed by competition of SCN$^-$ for the intermediate.

(NH$_3$)$_5$CoSCN^{2+} slowly rearranged to the N-bonded

(6) M. Osborne and N. Day, *Biometrica*, in press.

(7) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Inorg. Chem.*, **7**, 174 (1968).

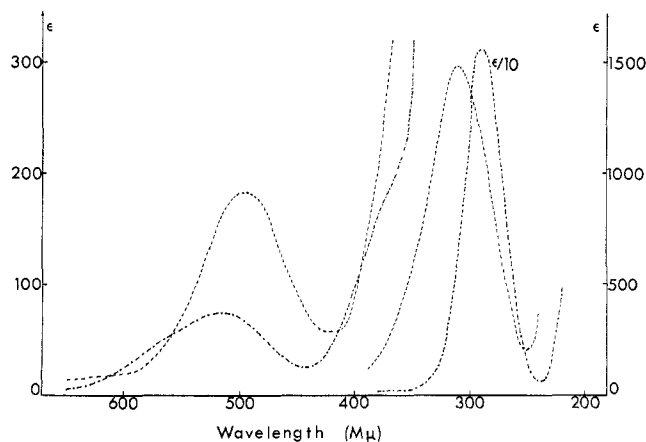(8) D. L. Gay and G. C. Lalor, *J. Chem. Soc., A*, 1179 (1966).

Figure 2.—Absorption spectra of [Co(NH$_3$)$_5$NCS](ClO$_4$)$_2$ (- - - - -) and [Co(NH$_3$)$_5$SCN]Cl$_2$·1.5H$_2$O (-·-·-·-) in 1 M NaClO$_4$.

isomer in dilute acid (0.01 M HClO$_4$). Only a trace of (NH$_3$)$_5$CoOH^{2+} (<2%) was obtained when the final solution (after 7 days at 40°) was sorbed on a cation-exchange resin and eluted with 1 M KOAc at pH 5. The half-life for the rearrangement at 25° was ~9 days (Table I).

Heating the solid [(NH$_3$)$_5$CoSCN]Cl$_2$·1.5H$_2$O for 1 day at 80° changed the color of the complex from violet to orange. The spectrum of the orange complex had maxima at 498 nm (ϵ 179) and 306 nm (ϵ 1486) in 1 M NaClO$_4$. These values compare with those for the authentic isothiocyanato complex.[2] Heating the complex for another 2 days did not alter the spectrum. This isomerization was also observed to occur slowly in the infrared spectrometer over 1 hr. However at 0° in the absence of light [(NH$_3$)$_5$CoSCN]Cl$_2$·1.5H$_2$O was unchanged over 6 months.

Spectra.—The visible and uv absorption spectra of [Co(NH$_3$)$_5$SCN]Cl$_2$·1.5H$_2$O and [Co(NH$_3$)$_5$NCS]-(ClO$_4$)$_2$ are given in Figure 2. In 1 M NaClO$_4$ for the thiocyanato complex the molar absorptivities at the maxima were ϵ_{512} 74 and ϵ_{288} 15,600 compared with those for the isothiocyanato ion, ϵ_{498} 179 and ϵ_{306} 1490. The spectrum of the thiocyanate ion also shows the presence of the two transitions in the first ligand field band, i.e., ^{1}A$_{1g}$ → ^{1}E$_g$ and ^{1}A$_{1g}$ → ^{1}A$_{2g}$, whereas the isothiocyanate shows little or no sign of the splitting. This is attributed to the difference in ligand field strengths between the S- and N-bonded NCS$^-$ relative to NH$_3$. The results are at least qualitatively in accord with Yamatera's proposals[9] in that a shift to longer wavelength is predicted for the ^{1}A$_{1g}$ → ^{1}E$_g$ transition whereas the ^{1}A$_{1g}$ → ^{1}A$_{2g}$ transition should occur at ~490 nm, the absorption maximum for (NH$_3$)$_6$Co^{3+}. The results indicate that the S-bonded thiocyanate ion correlates with halide in the spectrochemical series whereas the N-bonded isomer has a ligand field strength near ammonia. These results are consistent with other investigations of the same nature which are summarized by Jørgensen.[10]

(9) H. Yamatera, *Bull. Chem. Soc. Japan*, **31**, 95 (1958).

(10) C. K. Jørgensen, *Inorg. Chim. Acta Rev.*, **2**, 76 (1968).

TABLE I

BASE HYDROLYSIS RATE CONSTANTS AT 25.0° AND $\mu = 1.1$

Co(NH3)5X2+ species	10^3[Co], M	Reaction medium, Na+Y-	[OH-], M	k_{obsd},[a,b] sec-1 Loss of X- or entry of Y-	k_{obsd} Loss of SCN-	k_{OH}-, M-1 sec-1 Loss of X- or entry of Y-	k_{OH} Loss of SCN-	λ_{obsd}, nm
[Co(NH3)5Cl](ClO4)2	1.0	1 M NaSCN	0.10	0.021^b	0.014	0.23	0.14	230
	2.2		0.075	0.017^b	0.011	0.23	0.15	305
			0.050	0.012^b	0.0070	0.24	0.14	305
			0.025	0.0063^b	0.0035	0.25	0.14	305
	10.0		0.10	0.022^a		0.22		500
	1.7	1 M NaClO4	0.10	0.023^a		0.23		280
	1.7	1 M NaN3	0.10	0.022^b		0.22		320
	1.7	1 M NaNO2	0.05	0.011^a		0.22		550
[Co(CH3)5NO3](ClO4)2	2.0	1 M NaSCN	0.05	0.27^b	0.0072	5.4	0.14	305
	2.0	1 M NaClO4	0.050	0.28^a		5.6		250
[Co(NH3)5Br](ClO4)2	2.0	1 M NaSCN	0.10		0.014		0.14	305
		1 M NaClO4				1.4		310
[Co(NH3)5I](ClO4)2	2.0	1 M NaSCN	0.1 (pH 10.9c)	$2.6 \times 10^{-3\,c}$	0.014	3.3	0.14	305
	2.0	1 M NaClO4	0.050	0.016^a		3.2		420
[Co(NH3)5SCN]Cl2·1.5H2O	0.20	1 M NaSCN	0.10		0.014		0.14	305
	0.10	1 M NaClO4	0.10		0.016		0.16	305
	0.30		0.10		0.016		0.16	305
	5.0		0.10		0.016		0.16	510
	5.0	1 M NaClO4	0.10		0.016		0.16	550
	0.024	1 M NaClO4	[pH 3 (HClO4)]	$8.0 \times 10^{-7\,d}$				290
	0.0058			$8.2 \times 10^{-7\,d}$				290
[Co(NH3)5NCS](ClO4)2						$8 \times 10^{-4\,e}$		

[a] Loss of X-. [b] Entry of Y-. [c] Measured with Radiometer pH stat; $C_{Co} = 8.5 \times 10^{-3}$ M and follows consumption of OH-. [d] Rearrangement CoSCN → CoNCS. [e] $\mu \approx 0$: D. L. Gay and G. C. Lalor, *J. Chem. Soc.*, A, 1179 (1966).

In the infrared spectrum (NH3)5CoSCN2+ shows a very strong band at 835 cm-1 ascribed to a rocking mode of NH3; cf. [Co(NH3)5Cl]Cl2 at 849 cm-1, [Co(NH3)5Br]Br2 at 830 cm-1, and [Co(NH3)5I]I2 at 810 cm-1. However (NH3)5CoNCS2+ shows two strong bands in this region at 840 cm-1 (s) (with a shoulder or peak at 850 cm-1) and 806 cm-1. The latter is probably ν(C-S) for N-bonded NCS. For Rh(NH3)5-NCS2+ and Ir(NH3)5NCS2+ ν(C-S) has similarly been reported at 815 and 825 cm-1, respectively.[11] In general ν(C-S) appears in the range 780-860 cm-1 in M-NCS and at ~700 cm-1 in M-SCN.[12] Care has to be exercised in the assignment, however, because the first overtone of δ(NCS) has comparable intensity with that of ν(C-S), and in M-SCN the first overtone is at 800-880 cm-1.[12-14] (NH3)5CoSCN2+ shows a very weak band at ~710 cm-1 which is probably ν(C-S), since it is absent from the spectrum of (NH3)5CoNCS2+. Schmidtke[11] gives ν(C-S) as 730 cm-1 (w, br) for Rh(NH3)5SCN2+ and 700 cm-1 (m) for Ir(NH3)5SCN2+.

In general δ(NCS) appears as one band at ~475 cm-1 in M-NCS and as more than one band in the range 400-480 cm-1 in M-SCN; the most characteristic of the latter is a medium strong band at ~420 cm-1.[15,16] (NH3)5CoNCS2+ shows two medium weak bands at 490 and 460 cm-1, whereas (NH3)5CoSCN2+ shows three bands at 480 (w), 459 (w), and 426 cm-1 (m). The appearance of the band at 426 cm-1 provides further evidence for M-SCN. The other bands cannot be simply assigned without further work, because ν(M-NH3) bands also appear in the same region, e.g., [Co(NH3)5Cl]Cl2 at 498, 490, and 466 cm-1.[17] Indeed, δ(NCS) and ν(M-NH3) may well be coupled.

In Cr(NCS)6^3- ν(M-N) appears at 364 cm-1, while in Au(SCN)4- ν(M-S) is at 310-290 cm-1. Thus in principle it should be possible to distinguish between (NH3)5CoNCS2+ and (NH3)5CoSCN2+ by locating ν(M-NCS) and ν(M-SCN), respectively. (NH3)5CoSCN2+ shows a strong band centered at about 330 cm-1 which is probably due to δ(NMN); cf. [Co(NH3)5Cl]2 at 331 cm-1. (NH3)5CoNCS2+ shows an enormous band (H3H3) in this region with numerous shoulders probably because ν(M-NCS) and δ(NH3-M-NH3) overlap. (NH3)5CoSCN2+ shows a strong band at 265 cm-1 which may be ν(M-S) but unfortunately (NH3)5CoNCS2+ shows a broad absorption in the same region.

In (NH3)5CoNCS2+ ν(CN) appears as a rather broad peak at 2125 cm-1 with several shoulders on the low-frequency side whereas in (NH3)5CoSCN2+ ν(CN) is sharp at 2100 cm-1. This corresponds with results from accurate band-width measurements on N- and S-bonded thiocyanates.[18] Although it has been stated that ν(CN) is generally higher for M-SCN than for M-NCS,[14] this appears to be true only for isomers in the series of square-planar Pd(CNS)2(ligand)2 compounds,[19]

(11) H. H. Schmidtke, *Inorg. Chem.*, **5**, 1682 (1966).
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(13) M. M. Chamberlain and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **81**, 6412 (1959).
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(15) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 715 (1965).
(16) A. Sabatini and I. Bertini, *ibid.*, **4**, 959 (1965).
(17) L. Sacconi, A. Sabatini, and P. Gans, *ibid.*, **3**, 1772 (1964).
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(19) I. Bertini and A. Sabatini, *ibid.*, **5**, 1025 (1966).

TABLE II

PRODUCT DISTRIBUTION IN THE HYDROLYSIS REACTIONS OF $Co(NH_3)_5X^{2+}$ COMPLEXES AT $25°$

Complex	$C_{complex}$, M	Reaction medium	Products
$[Co(NH_3)_5NO_3](ClO_4)_2$	0.01	1 M NaSCN, 0.05 M NaOH	13% $Co(NH_3)_5SCN^{2+}$ + 4% $Co(NH_3)_5NCS^{2+}$ + 83% $Co(NH_3)_5OH^{2+}$
$[Co(NH_3)_5I](ClO_4)_2$	0.01	1 M NaSCN, 0.05 M NaOH	13% $Co(NH_3)_5SCN^{2+}$ + 3% $Co(NH_3)_5NCS^{2+}$ + 84% $Co(NH_3)_5OH^{2+}$
$[Co(NH_3)_5SCN](ClO_4)_2 \cdot 1.5H_2O$	4.2×10^{-3}	1 M NaClO₄, 0.025 M NaOH	26% $Co(NH_3)_5NCS^{2+}$ + 74% $Co(NH_3)_5OH^{2+}$
	4.2×10^{-3}	1 M NaClO₄, 0.050 M NaOH	26% $Co(NH_3)_5NCS^{2+}$ + 74% $Co(NH_3)_5OH^{2+}$
	4.2×10^{-3}	1 M NaClO₄, 0.10 M NaOH	26% $Co(NH_3)_5NCS^{2+}$ + 74% $Co(NH_3)_5OH^{2+}$
	8.4×10^{-3}	1 M NaClO₄, 0.10 M NaOH	25% $Co(NH_3)_5NCS^{2+}$ + 75% $Co(NH_3)_5OH^{2+}$
	8.4×10^{-3}	0.1 M NaOH	27% $Co(NH_3)_5NCS^{2+}$ + 73% $Co(NH_3)_5OH^{2+}$
	4.2×10^{-3}	1 M NaN₃, 0.10 M NaOH	26% $Co(NH_3)_5NCS^{2+}$ + 7% $Co(NH_3)_5N_3^{2+}$ + 67% $Co(NH_3)_5OH^{2+}$
	8.4×10^{-3}	1 M NaNO₂, 0.10 M NaOH	27% $Co(NH_3)_5NCS^{2+}$ + 4% $Co(NH_3)_5NO_2^{2+}$ + 69% $Co(NH_3)_5OH^{2+}$
	1.4×10^{-3}	1 M NaClO₄, pH 3	~100% $Co(NH_3)_5NCS^{2+}$

and for these cobalt compounds as well as the analogous Rh and Ir compounds the reverse is the case.

Products and Competition Products.—The products from the base hydrolysis of the thiocyanate complex in 1 *M* NaClO₄ were 26 ± 1% $(NH_3)_5CoNCS^{2+}$ and 74 ± 1% $(NH_3)_5CoOH^{2+}$ over a wide range of conditions (Table II) which includes a factor of 4 in the base concentration and a factor of 2 in the cobalt concentration. The appearance of $(NH_3)_5CoOH^{2+}$ was monitored at 550 nm as well as the appearance of $(NH_3)_5CoNCS^{2+}$ at 510 nm. At these wavelengths $(NH_3)_5CoSCN^{2+}$, $(NH_3)_5CoNCS^{2+}$ and $(NH_3)_5CoSCN^{2+}$, $(NH_3)_5CoOH^{2+}$, respectively, have isosbestic points. The rate constant in both instances was 0.16 M^{-1} sec⁻¹ at 25° (Table I).

When the hydrolysis was performed in the presence of 1 *M* NaN₃, 26% $(NH_3)_5CoNCS^{2+}$, 7% $(NH_3)_5CoN_3^{2+}$, and 67% $(NH_3)_5CoOH^{2+}$ were obtained. The same experiment in 1 *M* NaNO₂ gave 27% $(NH_3)_5CoNCS^{2+}$, 4% $(NH_3)_5CoNO_2^{2+}$, and 69% $(NH_3)_5CoOH^{2+}$ (Table II).

The competition behavior of NCS⁻ during the base hydrolysis of the nitrato and iodo complexes was also examined. These substrates were chosen because they hydrolyze much faster (nitrato, 5.6 M^{-1} sec⁻¹; iodo, 3.3 M^{-1} sec⁻¹ at 25°, μ = 1.0) than both the thiocyanato (0.16 M^{-1} sec⁻¹) and the isothiocyanato products ($<10^{-3}$ M^{-1} sec⁻¹). Making allowance for a trace of hydrolysis of $(NH_3)_5CoSCN^{2+}$ the product ratios in 1 *M* NaSCN were 13% thiocyanato, 4% isothiocyanato, and 83% hydroxo from the nitrato complex and 13, 3, and 84%, respectively, from the iodo complex ion (Table II).

Tracer Experiments.—The base hydrolysis of $(NH_3)_5CoSCN^{2+}$ was performed in the presence of a trace of $S^{14}CN^-$ (~1% of total NCS⁻). The products were separated on ion-exchange paper and the activity of the $(NH_3)_5CoNCS^{2+}$ was compared with the activity of the reaction mixture. The aquo sample value of 960 counts/min is to be compared with a background of 53 counts/min and the value of the blank paper sample after elution (1149 counts/min). The $(NH_3)_5CoNCS^{2+}$ sample gave 7555 counts/min relative to 558, 535 counts/min for the uneluted reaction mixture sample.

The radioactive enrichment in the isothiocyanato complex which arises from competition by released NCS⁻ during the reaction was calculated as ~1500 counts/min. This value was estimated by assuming a constant NCS⁻ concentration of half the total NCS⁻ available. Using this value and the background from the paper the activity in the isothiocyanato complex unaccounted for by competition is ~5000 counts/min. If all of the S to N bonded rearrangement took place by exchange with $N^{14}CS^-$ in solution, ~150,000 counts/min would be expected for the isothiocyanato product, *i.e.*, about one-fourth the initial counts. The result shows there is only ~3% exchange with $N^{14}CS^-$ in solution.

A similar experiment for the rearrangement in acid solution (0.01 *M* HClO₄) gave 120,032 counts/min for the reaction mixture, 75 counts/min for the background, and 223 counts/min for the eluted ion-exchange paper. The isothiocyanate complex precipitated in this experiment as it formed so it was necessary to redissolve it in water and sorb the solution on ion-exchange paper and elute the sample in the same manner as for the reaction mixture. For half the concentration of $(NH_3)_5CoNCS^{2+}$ originally contained in the reaction mixture 542 counts/min was measured. Subtracting the background we ascribe 319 counts/min to the complex which needs to be doubled before being compared with the initial activity ~120,000 counts/min. If complete exchange had occurred, practically all the initial solution activity (less 1%) should have appeared in the complex. Clearly the experiment shows that <1% exchange has occurred.

Discussion

The hydrolysis of $(NH_3)_5CoCl^{2+}$ in the presence of SCN⁻ at ~300 nm shows at first an increase in optical density followed by a decay, Figure 1. This procedure measures the entry of the anion followed by its hydrolysis. Also the kinetics results for the hydrolysis of $(NH_3)_5CoCl^{2+}$ in the presence of 1 *M* solutions of NaClO₄, NaN₃, NaNO₂, and NaSCN clearly are constant and the entry of the anions N₃⁻ (320 nm) and SCN⁻ (305 nm) coincides with the loss of Cl⁻ (500 nm), Table I. These results are consistent with the proposal
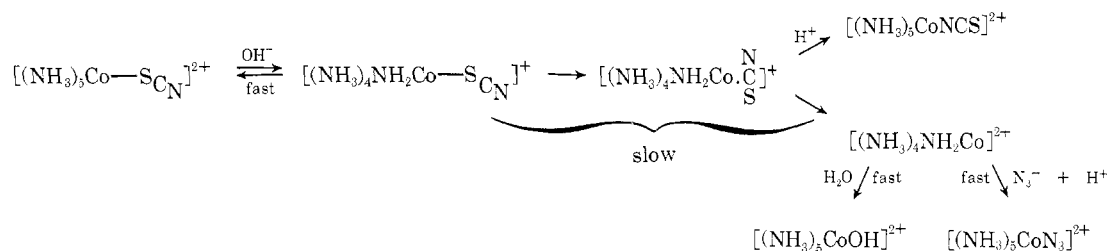
Figure 3.—Mechanism proposed for the base hydrolysis of $(NH_3)_5CoSCN^{2+}$ ion.

for an Sn1CB mechanism where the five-coordinate intermediate rapidly scavenges species in solution.

Probably the most interesting feature of this part of the study was the behavior of NCS^- as a competitor during base hydrolysis. Both N and S ends of the NCS^- ion are captured and after the subsequent hydrolysis of the thiocyanato product is accounted for, the rate of entry of the NCS^- ion coincides with the hydrolysis of Cl^-, I^-, and NO_3^- from the reactant. All these data are consistent with the Sn1CB proposal. The deprotonated five-coordinate intermediate abstracts species in its vicinity and possibly the rate-determining factor for this part of the process is the removal of the competitor from its solvent sheath. If the intermediate is common to all the substrates used $[(NH_3)_5CoX^{2+}$ (X = I, Cl, Br, NO_3], then the ratio of the products $(NH_3)_5CoNCS^{2+}$, $(NH_3)_5CoSCN^{2+}$, and $(NH_3)_5CoOH^{2+}$ should be constant for the constant NCS^- concentration. This was established at least for the nitrato and iodo complexes (Table II). In the other instances rearrangement and loss of NCS^- from the product $Co(NH_3)_5SCN^{2+}$ complicated the evaluation of the competition results.

It should be noted in this context that the competition values of NCS^- reported earlier[2] for these substrates were constant at $7 \pm 1\%$ $(NH_3)_5CoNCS^{2+}$ and $93 \pm 1\%$ $(NH_3)_5CoOH^{2+}$ for 1 M NaSCN. Under these earlier conditions all the preliminary product $(NH_3)_5CoSCN^{2+}$ would have either rearranged or hydrolyzed. Using the present results to calculate the expected final concentration of $(NH_3)_5CoNCS^{2+}$ we can predict it as $[(3.5 \pm 0.5) + (13 \times 0.26)]\%$, i.e., $7 \pm 0.5\%$ for the hydrolysis in 1 M NaSCN. Clearly this duplicates the previous observation and the present conclusions supplement those reached earlier.

The fact that the sulfur atom of the ion competes more effectively than the N atom might be attributed to the relative basic strength of the two atoms in this environment. It seems likely that N is more effectively H bonded to a water molecule than S since the parent acid exists as HNCS, leaving the S orbitals exposed for capture. The present results do not alter the general picture that there is little discrimination between the entering nucleophiles on a molar basis, implying that the intermediate is very reactive and scavenges the nearest molecules or ions, that activation enthalpies are low, and that the entering groups do not get to exert their nucleophilic character.

The second aspect of the study is the behavior of SCN^- as a leaving group in $(NH_3)_5CoSCN^{2+}$. The

base hydrolysis rate constant 0.16 M^{-1} sec^{-1} at $\mu = 1.0$ and 25° is close to that for the chloro complex and the course of reaction differs only in the production of the isomer $(NH_3)_5CoNCS^{2+}$ as well as the hydroxo complex. The question which immediately arises is whether the rearrangement is intra- or intermolecular and the tracer experiment shows that the NCS^- retained in the complex does not exchange with $N^{14}CS^-$ in the solvent ($\sim 3\%$). A tentative mechanism is proposed in Figure 3.

Deprotonation at the ammonia *trans* to the SCN group labilizes the S-bonded moiety and allows it to rearrange to a labile intermediate where the cobalt is bonded to both N and S. It is conceivable that cobalt could bond to the filled π molecular orbital over all three atoms of the NCS^- ion
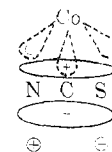
It is also conceivable that some overlap could occur with the filled xz or yz orbitals on cobalt and the empty π^* orbitals on NCS^- of suitable symmetry. This type of bonding is analogous to that described for some ethylene complexes.

A comment about the possible structure of the $(NH_3)_5CoSCN^{2+}$ ion is pertinent here. In the structures established for divalent S the bond angle appears to be as close as possible to 90°, and in two recent Cu(II) structures[20,21] $\angle CuSCN$ is $90 \pm 1°$. If this geometry pertains or is approached in the present instance, the rearrangement of the deprotonated reactant is, comparatively, a minor alteration and at least one vibrational mode has the momentum to achieve the intermediate bonding state. The proposal accommodates the intramolecular rearrangement and the loss of NCS^- from the same metastable intermediate and provides an attractive path for the rearrangement. However, the results do not require it. Both processes could occur separately *via* the deprotonated reactant. Clearly the $N^{14}CS^-$ tracer study eliminates an easily dissociable ion pair as the means to accommodate both reaction paths. An "intimate ion pair" akin to that proposed for some organic reactions[22] may be feasible since some exchange

(20) G. Marongiu, E. C. Lingafelter, and P. Paoletti, *Inorg. Chem.*, **8**, 2763 (1969).

(21) M. A. Porai-Koshits, *Acta Cryst.*, *Suppl.*, **16**, A42 (1963).

(22) S. Winstein, B. Appel, R. Baker, and A. Diaz, Special Publication No. 19, The Chemical Society, London, 1965, p 109.

occurs. However the ionic strength effects do not support this proposal since a substantial increase in the ionic strength of the medium did not lead to a decrease in the amount of NCS⁻ retained on the complex ion. If the association were intimate but electrostatic, the increase in salt concentration should help to dissociate the species and should lead to less isothiocyanate product.

The features of the mechanism discussed here are closely related to those proposed by Sutin and co-workers[23] for hydrolysis of CrSCN(aq)²⁺. An interesting possibility in this context is that *trans*-N¹⁵H₃-(NH₃)₄CoSCN²⁺ might give both *cis*- and *trans*-isothiocyanato complexes during the base hydrolysis. Such a result appears to require that Co and SCN⁻ be separate at some time on the reaction path leading to CoNCS. However, if retention of configuration is obtained, then either there is a nondissociable ion pair reacting with retention or Co and SCN never separate. We have not devised an economical method for making, stereospecifically, the isotopically labeled pentaammine ion yet, but experiments to test the possibility of CoSCN → CoNCS rearrangement before loss of NCS⁻ are being carried out with the *trans*-CoNH₃(en)₂SCN²⁺ ion. An alternative possibility that the isothiocyanato product arises from a reaction between the intermediate (NH₃)₄NH₂Co²⁺ and either (NH₃)₅CoSCN²⁺ or (NH₃)₄-NH₂CoSCN⁺ by a bridged intermediate; *e.g.*, (NH₃)₅-CoSCNCoNH₂(NH₃)₄⁴⁺, can be eliminated. If the five-coordinate intermediate competes for reactant or deprotonated reactants as well as for water when the concentration of the reactant is increased, the concentration of (NH₃)₅CoNCS²⁺ product must increase relative to the hydroxo complex. This arises because the concentration of water is essentially constant in the two experiments. In Table II where the complex concentration varies by a factor of 2 the ratio of (NH₃)₅-CoNCS²⁺ to (NH₃)₅CoOH²⁺ remains constant and these competitive bridging paths therefore are negligible.

The path which leads to dissociation of SCN⁻ presumably is the normal base hydrolysis route and should lead to the deprotonated five-coordinate intermediate Co(NH₃)₄NH₂²⁺ which has been characterized previously by its competition ratio for solvent and various anions.[2] This possibility was tested by performing the base hydrolysis of (NH₃)₅CoSCN²⁺ in the presence of 1 *M* solutions of N₃⁻ and NO₂⁻. In both

(23) A. Haim and N. Sutin, *J. Am. Chem. Soc.*, **88**, 434 (1966); M. Orhanović and N. Sutin, *ibid.*, **90**, 4286 (1968).

instances the formation of the azido and nitro complexes coincided with the hydrolysis of (NH₃)₅CoSCN²⁺. Moreover, the competition ratios [CoY²⁺]/[CoOH²⁺]·[Y⁻] of 10.4 (azido) and 5.8 (nitro) for the path which leads to hydroxo complex agree with those measured previously[2] for chloro, bromo, nitrato, and iodo substrates. These new data enhance the evidence in favor of the Sn1CB mechanism for base hydrolysis of cobalt(III)–pentaammine complexes. The leaving groups differ widely in size, shape, and electronic properties and it appears inconceivable that the constant competition data could arise accidentally.

In dilute acid the (NH₃)₅CoSCN²⁺ ion rearranges slowly to (NH₃)₅CoNCS²⁺ and only a trace of (NH₃)₅-CoOH₂³⁺ is produced. The questions which then arise are: Does the NCS⁻ ion dissociate and reanate the complex ion? Does the rearrangement occur intramolecularly or is a bridged intermediate, *e.g.*

$$(NH_3)_5Co \underset{NCS}{\overset{SCN}{\diagup\diagdown}} Co(NH_3)_5{}^{4+}$$
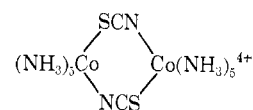
involved? The rates at different cobalt concentrations (Table I) clearly show that the reaction is not second order in complex concentration which eliminates the bridged intermediate. Also the tracer experiment with N¹⁴CS⁻ eliminates the possibility that coordinated NCS⁻ dissociates and recombines. This leaves the possibility of rearrangement of CoSCN to CoNCS by processes similar to those described for the base hydrolysis. Such paths are also consistent with the thermally induced rearrangement in the solid state.

The capture of ambidentate ligands by intermediates of reduced coordination number suggests numerous possibilities for the preparation of isomeric species with ligands such as SO₃²⁻, S₂O₃²⁻, ONO⁻, NCO⁻, SeCN⁻, and NH₂CH₂COO⁻ to mention a few. It is also possible, for example, to treat (NH₃)₅CoN₃²⁺ with NO⁺ in the presence of SCN⁻ to give a good yield of (NH₃)₅CoSCN²⁺.[24] Some of the possibilities described above may be too labile to be observed easily but since competition is feasible in both acid and alkaline solutions a wide choice for the experimental conditions is available.

(24) I. I. Creaser, unpublished work.