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Mechanism of Base Hydrolysis for $[Co(pentaamine)X]^{2+}$ Ions. Hydrolysis and Rearrangement for the Sulfur-Bonded *trans*-$[(en)_2NH_3CoSCN]^{2+}$ Ion

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Base hydrolysis of *trans*-$[(en)_2NH_3CoSCN]^{2+}$ shows two reaction paths: one an intramolecular rearrangement to give *cis*- and *trans*-$[(en)_2NH_3CoNCS]^{2+}$ (7%) and the other the normal dissociative reaction of the conjugate base to yield *cis*- and *trans*-$[Co(en)_2NH_3(OH)]^{2+}$ (92%). The intermediate generated by the latter path scavenges both water and NCS^- (1%) to give the same stereochemistry for the products and the same competition ratios as other leaving groups. The intramolecular S → N rearrangement appears to occur with trans → cis isomer rearrangement which implies rupture of the Co–(SCN) bond in the process.

Introduction

In a study of the base hydrolysis of $[(NH_3)_5Co-SCN]^{2+}$ ion

$$[(NH_3)_5CoSCN]^{2+} + OH^- \longrightarrow [(NH_3)_5CoOH]^{2+} + SCN^-$$

some Co–SCN → Co–NCS isomerization (26%) was observed although little exchange of bound NCS^- with a trace of $N^{14}CS^-$ in solution was detected.[1] Two possibilities were entertained to explain these results: one was that NCS^- was bonded through the π system to cobalt in a reactive intermediate which either lost NCS^- altogether or rearranged to the more stable N-bonded form; the other was that the reaction proceeded through the formation of an "intimate ion pair" which was not in equilibrium with solvent NCS^- and which either lost NCS^- to solvent or recombined to the N-bonded isomer. There was no clear evidence for either proposal but the possibility of resolving the problem was presented by using a closely related complex, *trans*-$[(en)_2NH_3CoSCN]^{2+}$, which has more stereochemical detail. If trans to cis rearrangement is observed during the Co–SCN → Co–NCS rearrangement then the inference is that somewhere along the reaction path the Co–SCN link is severed. However, if no rearrangement is observed either the ion pair reacts with retention or the Co–SCN link remains intact. This paper records the preparation and characterization of *trans*-$[(en)_2NH_3CoSCN]Cl_2 \cdot 2.5H_2O$ and the course of the base hydrolysis reaction.

Experimental Section

***trans*-$[(en)_2NH_3CoSCN]Cl_2 \cdot 2.5H_2O$.**—*trans*-$[Co(en)_2NH_3N_3]Cl_2$[2] (7 g) dissolved in NaSCN solution (100 ml, 10 *M*) was treated with $NaNO_2$ (100% excess). $HClO_4$ (6 *M*) was then added slowly until all the azido complex had reacted. The solution was diluted with H_2O (1.5 l.) and the complex sorbed on a cation-exchange resin (Dowex 50W-X2, 200–400 mesh, H^+ form, 7 × 20 cm). On elution with HCl (1 *M*) the 3+ and 2+ products separated. The purple-red fraction containing largely the thiocyanato complex was collected, 1.5 l., and evaporated under reduced pressure at ~20°. On cooling and addition of ethanol, lustrous purple crystals of *trans*-$[(en)_2NH_3CoSCN]Cl_2$ formed. The salt was recrystallized twice from water (pH 3) by adding HCl and ethanol, dried *in vacuo* and analyzed. *Anal.* Calcd for $[(C_4H_{16}N_4)NH_3CoSCN]Cl_2 \cdot 2.5H_2O$: C, 16.22; H, 6.53; N, 22.70. Found: C, 16.25; H, 6.59; N, 22.60. The isomeric purity of the complex was tested in several ways: (1) by elution on the ion-exchange column with 1 *M* $NaClO_4$ (pH 3 HCl) which separated the cis and trans S-bonded and N-bonded isomers but not cis isothiocyanate from trans thiocyanate and (2) by mixing *cis*-$[(en)_2NH_3CoN^{14}CS]Cl_2$[3a] (0.01 g) with *trans*-$[(en)_2NH_3CoSCN]Cl_2$ (0.5 g) in water (5 ml, pH 4) and recrystallizing the S-bonded isomer using HCl (2 ml, 10 *N*) and ethanol. The radioactive samples were prepared and counted as follows. (a) Cis isothiocyanato (0.002 g) was dissolved in water (1 ml) and a sample (0.050 ml) sorbed on ion-exchange paper (Amberlite SA-2, 2 × 4 cm). (b) The solution of trans thiocyanato and cis isothiocyanato was sampled (0.050 ml) and also sorbed on an ion-exchange paper. (c) The recrystallized sample (0.4 g) dissolved in 4 ml of water was sampled (0.050 ml) and also sorbed on an ion-exchange paper. (d) The filtrate from the recrystallization was redissolved in water (5 ml) and sampled (0.050 ml) and the sample sorbed on the ion-exchange paper. The samples of paper were dried in air at ~20° and were then immersed in the dioxane scintillating fluid[1] and counted in a Beckman LS-150 liquid scintillation counter to a standard deviation of 0.5% or for 20 min, whichever was least.

A similar experiment was performed using *trans*-$[(en)_2NH_3CoSCN]Cl_2$ (0.5 g) and *trans*-$[(en)_2NH_3CoN^{14}CS]Cl_2$ (0.005 g) in water (5 ml, pH 4). The same standard concentrations were used and the samples were treated in the same way.

***trans*-$[(en)_2ClCoNCS]ClO_4$.**[3a,b]—*trans*-$[Co(en)_2Cl_2]Cl$ (4 g in 15 ml of H_2O) was treated with KNCS (1.16 g containing 0.01 mCi of $KN^{14}CS$). The green crystals of *trans*-$[Co(en)_2Cl_2]SCN$ were collected and washed with cold water and methanol and dried in air. The thiocyanate salt was mixed to a paste with water (6 ml) and heated to boiling with vigorous stirring. Ice (2 g) was added at the moment of boiling and the red solution was left standing in ice for 2 hr. *cis*-$[(en)_2ClCoNCS]Cl$ crystallized and was collected. The filtrate was treated with $HClO_4$ (3 ml, 70%) and cooled in ice. The red-violet crystalline product *trans*-$[(en)_2ClCoNCS]ClO_4$ was collected, washed with ethanol, and dried in air (1.8 g) (ϵ_{556} 102 in 10^{-3} *M* $HClO_4$).

***cis*- and *trans*-$[(en)_2NH_3CoNCS](NCS)_2$.**—*trans*-$[(en)_2ClCoNCS]ClO_4$ (1.5 g) was dissolved in liquid NH_3 (50 ml) containing NH_4Cl (0.1 g). The purple solution changed slowly to bright orange and the ammonia was allowed to evaporate. The residual orange product was dissolved in the minimum amount of water and precipitated with NaNCS. The red isothiocyanate salt was then recrystallized into two fractions of which the first was pure *trans*-$[(en)_2NH_3CoNCS](NCS)_2$ (ϵ_{490} 164).[2] The second fraction (ϵ_{490} 206) largely contained the cis isomer and was recrystallized to the pure cis form (ϵ_{490} 220).[2]

***trans*-$[Co(en)_2NH_3Cl]Cl_2 \cdot 1.5H_2O$** was prepared by a modified method of Werner.[3a] The reaction mixture obtained after hydrogen peroxide oxidation of *trans*-$[(en)_2ClCoNCS]Cl$ was sorbed directly on a cation-exchange column. Elution with HCl (1 *M*) gave a fast moving complex fraction which was discarded. HCl (2 *M*) eluted the main fraction which was evaporated to small volume under reduced pressure. Addition of ethanol to this concentrate led to deposition of crystals of the product. The substance was recrystallized twice from a small

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(1) D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, *Inorg. Chem.*, **9**, 655 (1970).

(2) D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *J. Amer. Chem. Soc.*, **90**, 6654 (1968).

(3) (a) A. Werner, *Justus Liebigs Ann. Chem.*, **386**, 1 (1912). (b) A reviewer recommends that attention be drawn to the potentially explosive nature of nitrate and perchlorate salts of Co(III) amines (W. R. Tomlinson, K. G. Ottoson, and L. F. Audrieth, *J. Amer. Chem. Soc.*, **71**, 375 (1949)).

TABLE I

HYDROLYSIS OF *trans*-$[(en)_2NH_3CoSCN]Cl_2\cdot 2.5H_2O$ AND OF *trans*-$[Co(en)_2NH_3NO_3](NO_3)_2\cdot H_2O$ AT 25° AND $\mu = 1.0$ ($NaClO_4$) IN 0.1 *M* AMINE BUFFERS

Reactant	[Co], *M*	pH	k_{obsd}, sec^{-1}	k_{OH},[f] M^{-1} sec^{-1}
trans-$[(en)_2NH_3CoSCN]Cl_2\cdot 2.5H_2O$	2.8×10^{-4}	10.83[a]	9.6×10^{-2}	1.4×10^2
		10.16[b]	2.1×10^{-2}	1.4×10^2
		9.13[c]	1.7×10^{-3}	1.3×10^2
trans-$[Co(en)_2NH_3NO_3](NO_3)_2\cdot H_2O$	5×10^{-3}	9.15[d]	2.05×10^{-2}	1.5×10^3
		8.19[e]	2.4×10^{-3}	1.8×10^3

[a] Et_3N, $HClO_4$. [b] Me_3N, $HClO_4$. [c] Me_2NH, $HClO_4$. [d] Triethanolamine, $HClO_4$. [e] $H_2NC(CH_2OH)_3$, $HClO_4$. [f] Calculated assuming $K_w = 10^{-14}$.

TABLE II

PRODUCT ANALYSIS FOR BASE HYDROLYSIS EXPERIMENTS AT 25°

							Products		
							$[(en)_2NH_3CoNCS]^{2+}$		$[Co(en)_2NH_3H_2O]^{3+}$
Expt no.	Complex	[Co], *M*	[OH$^-$], *M*	Reaction medium	Total volume, ml	Reaction time, sec	% *trans*	% *cis*	% *trans* + *cis*
1	*trans*-$[(en)_2NH_3CoSCN]Cl_2\cdot 2.5H_2O$	0.031	0.1	H_2O	10	180	6.7	1.2	92 (59 cis, 33 trans)
2	*a*	0.041	0.1	H_2O	10	180	6.8	1.2	92 (61c, 31t)
3	*a*	0.029	0.1	1 *M* $NaClO_4$	10	90	7.2	1.0	93
4	*a*	0.0069	0.2	1 *M* NaSCN	10	60	13.2	7.7	77 (51c, 26t)
5	*trans*-$[Co(en)_2NH_3NO_3](NO_3)_2\cdot H_2O$	0.011	0.2	1 *M* NaSCN	10	60	5.3	6.7	86
6	*b*	0.058	0.136	0.12 *M* NaSCN	5.5	60	1.1	1.3	97
7	*b*	0.058	0.136	0.12 *M* NaSCN 1 *M* $NaClO_4$	7.7	60	0.55	0.60	97
8	*trans*-$[Co(en)_2NH_3Cl]Cl_2\cdot 1.5H_2O$[b]	0.06	0.136	0.12 *M* NaSCN	5.5	60	1.5	1.6	97
9	*trans*-$[Co(en)_2NH_3NO_3](NO_3)_2\cdot H_2O$[b]	0.058	0.136	0.06 *M* NaSCN	5.5	60	0.54	0.62	97
10	*b*	0.058	0.136	0.03 *M* NaSCN	5.5	60	0.24	0.27	99
							cis- + *trans*-$(en)_2NH_3CoNCS^{2+}$ + $(en)_2NH_3CoSCN^{2+}$		
11		0.011	1.25×10^{-5}[c]	1 *M* NaSCN	20	168	27.2		73

[a] As above, sample twice more recrystallized. [b] Concentrations of complex and base as applied to the tracer experiments. [c] Diethanolamine–$HClO_4$ buffer (0.1 *M*) in 1 *M* NaSCN.

amount of water (pH 3) by addition of ethanol. *Anal.* Calcd for $[Co(C_4H_{16}N_4)NH_3Cl]Cl_2\cdot 1.5H_2O$: N, 21.23; H, 6.74; C, 14.61. Found: N, 21.19; H, 6.46; C, 14.58.

trans-$[Co(en)_2NH_3NO_3](NO_3)_2\cdot H_2O$.[3b]—*trans*-$[Co(en)_2NH_3Cl]Cl_2$ was treated with $Hg(NO_3)_2$ in concentrated HNO_3 as described.[2] The crude product precipitated with ethanol was recrystallized three times from dilute nitric acid by adding ethanol. After elution with 1 *M* $NaClO_4$ no aquo complex was detected. The molar absorptivity ϵ_{497} was 56 (H_2O, pH 3 ($HClO_4$)). *Anal.* Calcd for $[Co(C_4H_{16}N_4)NH_3NO_3](NO_3)_2\cdot H_2O$: C, 12.01; H, 5.29; N, 28.00. Found: C, 12.10; H, 5.23; N, 28.01.

Kinetics.—The hydrolyses of the thiocyanato and the nitrato complexes were followed spectrophotometrically (Cary 14) at 305 and 416 nm, respectively, using a stopped flow reactor[4] thermostated to 25°. The buffers and other conditions are described in Table I.

Base Hydrolysis and Competition Experiments.—The reaction mixture at 25° was composed of solutions of the complex in water (pH 5) or in the appropriate electrolyte and NaOH containing if necessary inert electrolyte or salt of the competing ion to give the conditions described in Table II. The reaction mixture was quenched with glacial acetic acid to pH <5 and sorbed on a cation-exchange column (Bio-Rad AG 50W-X2, 200–400 mesh, H^+ form, 30 × 1 cm).

The products were eluted with $NaClO_4$ (1 *M*) until the first fraction was close to the bottom of the column. Then the column was washed with NaCl (1 *M*) and the 2+ fractions were collected using NH_4Cl (1 *M*) as eluent (~50 ml); *trans*- and *cis*-$[(en)_2NH_3CoNCS]^{2+}$ gave two red bands with ϵ_{302} 1590 (eluted first) and ϵ_{302} 1660, respectively.[2] The two fractions were not completely separated but a minimum was observed and the concentration of the two species was established by matching the elution profile with that of a known composition. *cis*- and *trans*-$[Co(en)_2NH_3H_2O]^{3+}$ were eluted together using 3 *M* HCl[2] or 2 *M* H_2SO_4 (ϵ_{472} 62, ~50 ml). The cobalt concentrations in the fractions were determined spectrophotometrically on a Cary 14 recording spectrophotometer using the above extinction coefficients. The values obtained by this method were in good agreement with the values obtained by atomic absorption spectrophotometry (Techtron AA-4, high-intensity Co lamp), which are listed in Table II.

$N^{14}CS^-$ Tracer Experiments.—*trans*-$[(en)_2NH_3CoSCN]Cl_2\cdot 2.5H_2O$ (0.031 g) in water (0.6 ml) containing 10^{-2} mCi of $KS^{14}CN$ (16.5 mCi/mmol) was treated with NaOH (0.2 *M*, 0.5 ml) for 60 sec at 25° and then acidified with acetic acid (17 *M*, 0.1 ml). Samples (0.05 ml) of the reaction mixture were sorbed on ion-exchange paper Amberlite SA-2 and the products were eluted with $La(NO_3)_3$ solution (0.25 *M*, 18–24 hr). The spots corresponding to the products were detected in uv light. Portions of the paper (4 × 2.5 cm) centered around the spots were counted at least three times in scintillation fluid. Samples of the reaction mixture and paper blanks (both untreated and eluted) were counted in the same manner.

trans-$[Co(en)_2NH_3NO_3](NO_3)_2\cdot H_2O$ (0.032 g) was dissolved in water (0.6 ml) containing NaSCN (6.55 mg) and $KN^{14}CS$ (10^{-2} mCi; 41 mCi/mmol) and treated with NaOH (0.2 *M*, 0.5 ml) at 25° for 1 min. The solution was then acidified with acetic acid (17 *M*, 0.1 ml) and samples of the reaction mixture were sorbed on ion-exchange paper and eluted and counted as described above.

trans-$[(en)_2NH_3CoSCN]Cl_2\cdot 2.5H_2O$ (0.019 g) dissolved in water (0.7 ml) containing 10^{-2} mCi of $KN^{14}CS$ (41 mCi/mmol) was treated with NaOH (0.1 *M*, 0.25 ml) and held at 25° for 30 sec. The solution was acidified with acetic acid (17 *M*, 0.1 ml) and samples of the reaction mixture (0.05 ml) sorbed on ion-exchange paper. The products were eluted with a solution of $La(NO_3)_3$ (0.25 *M*) for 14–24 hr. Samples of the paper were taken and counted as described.

Results

Synthesis and Properties.—*trans*-$[(en)_2NH_3CoSCN]Cl_2$ was obtained from *trans*-$[Co(en)_2NH_3N_3]^{2+}$ using NO^+ to remove N_3^- in the presence of NCS^-. Some N-bonded isomer was also formed and was removed by recrystallization. Both the N- and S-bonded isomers absorbed at 2100 cm^{-1} but the absorption band for the violet S-bonded isomer was considerably sharper (half-width ~20 cm^{-1}) than that for the orange N-bonded form (~100 cm^{-1}) in Nujol mulls. The S-bonded isomer slowly rearranged in the ir beam to the N-bonded form so that ir spectra in the mulls were

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(4) Y. Inoue and D. D. Perrin, *J. Phys. Chem.*, **66**, 1689 (1962).

measured under almost identical conditions. The rearrangement also occurred thermally at 80° in a few hours. These results are analogous to the observations made using the isomeric species of $[(NH_3)_5CoSCN]Cl_2$.[1] Similarly the S-bonded isomer was characterized by a ligand field absorption band at 510 nm (ϵ 65.7 in 10^{-3} M $HClO_4$) which showed signs of a shoulder around 550 nm. The most characteristic feature, however, was the intense absorption at 286 nm (ϵ 13,450, 10^{-4} M HCl). These values should be compared with those for $[(NH_3)_5CoSCN]Cl_2$[1] (ϵ_{512} 74, ϵ_{288} 15,600) and for *trans*-$[(en)_2NH_3CoNCS](NCS)_2$ (ϵ_{490} 168, ϵ_{303} 1590; 1 M KCl).[2]

Kinetics.—The rates of hydrolysis of *trans*-$[(en)_2NH_3CoSCN]Cl_2 \cdot 2.5H_2O$ and *trans*-$[Co(en)_2NH_3NO_3](NO_3)_2 \cdot H_2O$ were followed in buffer solutions at 25° and $\mu = 1.0$. Linear plots of log $(D - D_\infty)$ against time were obtained for at least 4 half-lives and the rate constants from these plots are given in Table I along with the derived second-order rate constants. The results show a rate law of the form

$$v_{trans\text{-}[(en)_2NH_3CoSCN]^{2+}} = k[trans\text{-}[(en)_2NH_3CoSCN]^{2+}][OH^-]$$

which is in keeping with that observed for the $[(NH_3)_5CoSCN]^{2+}$ ion.[1]

Proton exchange at the N centers was followed by pmr spectroscopy at pD 5.0[5] in 0.1 M acetate buffer (34°). Under these conditions the trans NH_3 group was completely deuterated in 5 min while the NH_2 protons were appreciably diminished after 30 min.

Product Analysis.—*trans*-$[(en)_2NH_3CoSCN]Cl_2 \cdot 2.5H_2O$ was hydrolyzed in base at 25° under the conditions given in Table II which also records the reaction products. These were identified by their elution rates on the ion-exchange resin and by spectral comparison with authentic samples of the compounds concerned. The ratio *trans*- (7%) to *cis*-$[(en)_2NH_3CoNCS]^{2+}$ (1%) (Table II, experiment 1) was essentially unchanged when the starting material was twice more recrystallized (experiment 2) or if the reaction was carried out in 1 M $NaClO_4$ (experiment 3). The reason for the two sets of reaction conditions (experiments 1 and 2) arose from the small fraction of cis isothiocyanato isomer observed in the reaction mixture. One possibility was that this fraction arose from either cis isothiocyanato or cis thiocyanato impurities in the starting material. However, recrystallization of the parent compound (twice) did not alter the product ratio. Alternatively the possibility of recrystallization to constant impurity (~1%) could not be excluded by these two results and the purity question was examined more closely.

cis-$[(en)_2NH_3CoSCN]Cl_2$ was prepared by treating *cis*-$[Co(en)_2NH_3N_3]^{2+}$ with NO^+ in the presence of a large excess of NCS^-. The isolated cis S-bonded isomer was then mixed with an equal amount of the trans S-bonded isomer and sorbed on the cation-exchange column. On elution with 1 M $NaClO_4$ the two isomers separated and the trans complex moved ahead of the cis. This experiment allowed a test of the purity of the trans thiocyanato complex by absorbing 0.5 g of the complex chloride on the ion-exchange column. *cis*-$[(en)_2NH_3CoSCN]^{2+}$ ($\ll$1%) would have been detected after elution with 1 M $NaClO_4$. It should also be noted, however, that *trans*-$[(en)_2NH_3CoSCN]^{2+}$ and *cis*-$[(en)_2NH_3CoNCS]^{2+}$ were not separated on the ion-exchange column and an alternative method of detecting small amounts of cis isothiocyanato impurity was required.

The efficiency of the recrystallization procedure in removing *cis*- and *trans*-$[(en)_2NH_3CoNCS]Cl_2$ from *trans*-$[(en)_2NH_3CoSCN]Cl_2$ was evaluated by using the isothiocyanato isomers labeled with $N^{14}CS^-$. *cis*-$[(en)_2NH_3CoN^{14}CS]^{2+}$ was added to the trans thiocyanato complex as a 2% impurity and the complex was then recrystallized in the usual way to recover ~80% of the starting material. The impurity (745 cpm), the mixture (518 cpm), the recrystallized product (46 cpm), and the filtrate (642 cpm) were sampled in an equivalent manner and counted under the same conditions to a standard deviation of 0.5%. The background (50 cpm) has been subtracted from these values. The results show that >90% of the added impurity was removed by one recrystallization of the trans thiocyanato complex and that a 1% impurity of *cis*-$[(en)_2NH_3CoNCS]Cl_2$ is not retained after recrystallization.

A similar experiment was carried out with *trans*-$[(en)_2NH_3CoSCN]^{2+}$ doped with 1% *trans*-$[(en)_2NH_3CoNCS]^{2+}$. Here again the impurity (380 cpm), the mixture (259 cpm), the recrystallized product (49 cpm) and the filtrate (210 cpm) were sampled equivalently and counted under the same conditions (0.5% δ, background subtracted). It is also evident here that the majority of the impurity is removed in one recrystallization. These results show therefore that the 7% trans isothiocyanato isomer and 1% cis isothiocyanato isomer observed after hydrolysis of the trans thiocyanato complex arise in the course of the reaction and not from impurities in the starting material.

The ratio of *cis*- to *trans*-$[Co(en)_2NH_3OH]^{2+}$ found in these experiments (1 and 2) was the same as that for other leaving groups.[2] Also the cis:trans aquo ratio for the experiment carried out in 1 M NaSCN (experiment 4) was the same as above (±1%). It appears therefore that hydrolysis occurs by the conjugate base dissociative mechanism through a five-coordinate intermediate.[6]

However, for hydrolysis carried out in 1 M NaSCN the cis:trans isothiocyanato ratio (7.7/13.2, experiment 4) was substantially different from that observed with nitrate as the leaving group (experiment 5) and for other leaving groups.[2] The difference may come from the substantial amount of cis plus trans Co–NCS product (~8%) which arose in the absence of added NCS^-. It is possible that this path is intramolecular or the products may come from recapture of NCS^- by the intermediate. The possibilities were tested initially by hydrolyzing *trans*-$[Co(en)_2NH_3X]^{2+}$ ($X = Cl, NO_3$) in the presence of 2, 1, and 0.5 equiv of NCS^- (experiments 6–10). Clearly none of these conditions perfectly simulates the build up of NCS^- as it is released from *trans*-$[(en)_2NH_3CoSCN]^{2+}$ since they all approximate to a constant NCS^- concentration during hydrolysis. However experiments such as 9 and 10 where the nitrato complex was hydrolyzed in the presence of 1 equiv of NCS/Co and 0.5 equiv of NCS^-/Co,

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[5] P. K. Glasoe and F. A. Long, *J. Phys. Chem.*, **64**, 188 (1960).

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

respectively, should provide upper and lower limits for competition of the five-coordinate intermediate for NCS^- during hydrolysis of $[(en)_2NH_3CoSCN]^{2+}$. The results indicate that ~0.6% cis and ~6.3% trans Co–NCS products arise from some intramolecular process since only ~0.5% *cis*- and ~0.5% *trans*-$[(en)_2NH_3CoNCS]^{2+}$ can be accounted for by the competition path. Applying this conclusion to the results of the hydrolysis of *trans*-$[(en)_2NH_3CoSCN]^{2+}$ in 1 *M* NaSCN, the 6.7% *cis*- and 6.0% *trans*-$[(en)_2NH_3CoNCS]^{2+}$ which are deduced to arise by the competition process now agree reasonably with those for the nitrate (expt 5) and other leaving groups.[2]

The amount of competition arising for NCS^- (0.12–1 *M*) at $\mu = 1.0$ ($NaClO_4$) substantially agreed with that estimated from the competition ratio $R = [(en)_2NH_3CoNCS^{2+}]/[Co(en)_2NH_3OH^{2+}][NCS^-] = 0.13$.[2] As expected the higher competition ratios found in experiments 6, 8–10 correlate with the lower ionic strengths at which these experiments were performed. The accuracy of the product analyses was impaired ($\leqslant 20\%$ for cis isothiocyanate) by the failure to separate completely the *cis*- and *trans*-$[(en)_2NH_3CoNCS]^{2+}$.

Also some variation in different experiments may arise from the possibility that the absolute and relative amounts of rearrangement products alter slightly in different ionic strengths. Marked preference for the S end of the SCN^- ion was found in base hydrolysis of $Co(NH_3)_5X^{2+}$ ($X^- = NO_3^-, I^-$) in the presence of thiocyanate.[1] In order to establish whether the same preference also exists in hydrolysis of *trans*-$[Co(en)_2NH_3X]^{2+}$, *trans*-$[Co(en)_2NH_3NO_3]NO_3 \cdot H_2O$ was base hydrolyzed for 5 half-lives (Table I) in the presence of 1 *M* NaSCN. Since no separation was achieved on an ion-exchange column all the 2+ species were collected in one fraction (27.2% of total cobalt) and 73% of aquo complexes were formed. In order to approximate the competition numbers for S and N end of the thiocyanate ion, the amount has to be corrected for the decay of S-bonded species. *cis*- and *trans*-$[Co(en)_2NH_3X]^{2+}$ complexes are known to hydrolyze at very similar rates.[7] Assuming that cis and trans SCN complexes hydrolyze at the same rate, after $5t_{1/2}$ (168 sec) of reaction time, the amount of decayed S-bonded species is calculated (Table I) to be ~18% of the total amount expected. Base hydrolysis of the SCN complex in 1 *M* SCN^- leads to formation of 21% of N-bonded species, from both competition and rearrangement. The loss of 18% of S-bonded species gives 3.8% of rearranged N-bonded species. The competition numbers are roughly calculated the following way: let x be the amount (%) of S-bonded species resulting from scavenging by the reactive intermediate and y the corresponding percentage of N-bonded species. After 5 half-lives of hydrolysis of the nitrato complex, $(x - 0.18x)\%$ of S-bonded species are present, together with $[y + (0.18 \times 0.21)x]\%$ of N-bonded species, and $x - 0.18x + y + 0.038x = 27.2\%$. Also $y + 0.21x = 12\%$ of N-bonded species are present after a longer reaction time ($10t_{1/2}$) of the S-bonded species when all S-bonded species are hydrolyzed. The competition values for the S and N end of the competitor are thereby estimated to be ~25 and ~7%, respectively, which is consistent with previous observations.[1]

Exchange with External $N^{14}CS^-$.—Base hydrolysis experiments were carried out on *trans*-$[(en)_2NH_3CoSCN]^{2+}$ and *trans*-$[Co(en)_2NH_3NO_3]^{2+}$ to test whether the rearrangement was intramolecular or not and to see if the *cis*-$[(en)_2NH_3CoNCS]^{2+}$ ion arose solely from competition. *trans*-$[(en)_2NH_3CoSCN]Cl_2$ was hydrolyzed in base in the presence of a trace (0.7 mol %) of $KS^{14}CN$. Samples of the acidified reaction mixture (668,000 cpm) were sorbed on ion-exchange paper and eluted with $La(NO_3)_3$ solution (0.25 *M*) to separate the aquo (230 cpm), cis (4221 cpm) and trans (4461 cpm) isothiocyanato products. Papers containing the fractions were counted in scintillation fluid along with eluted blanks (382 cpm). From all values a background of 40 cpm has been subtracted. If complete exchange of NCS^- with $N^{14}CS^-$ from solution had occurred in the formation of the Co–NCS complexes ~47,000 cpm for the trans and ~6700 cpm for the cis species would be expected. Clearly the rearrangement is largely intramolecular although measurable exchange (~1%) has occurred.

An analogous experiment with the nitrato complex (671,000 cpm) was carried out to give aquo (550 cpm) and cis (3995 cpm) and trans (3433 cpm) Co–NCS species (paper blank 603 cpm). The enrichment in the Co–NCS species here agrees within the error with that in the thiocyanato hydrolysis. The counting results correspond to ~0.5% cis and ~0.4% trans Co–NCS species which agrees moderately well with the competition experiment 9, Table II. The same computation from the tracer results for the trans Co–SCN complex gives ~0.6% trans and 0.6% cis Co–NCS products. All these results are consistent within the accuracy of the counting experiments and all the activity in the isothiocyanato products therefore can be accommodated by the competition path (Scheme I). It follows that if the intermediate captures the N end of NCS^- it should also capture the S end and lead to *cis*- and *trans*-$[(en)_2NH_3CoSCN]^{2+}$. To test for this possibility *trans*-$[(en)_2NH_3CoSCN]^{2+}$ was hydrolyzed for 1 half-life in the presence of a trace of $N^{14}CS^-$ and the reaction mixture (745,000 cpm) sorbed on ion-exchange paper was separated into aquo (1122 cpm), cis Co–SCN (2300 cpm), trans Co–SCN + cis Co–NCS (3349 cpm) and trans Co–NCS (1506 cpm) fractions (blank 915 cpm). If all the tracer had exchanged with *trans*-$[(en)_2NH_3CoSCN]^{2+}$ 370,000 cpm should appear in this fraction. Clearly this has not occurred. However some exchange has taken place and we can evaluate the enrichment in all the species if the tracer results from the nitrato experiment are used to estimate the relative enrichment in cis and trans Co–NCS species (~ equal). The incorporation of activity is as follows: cis Co–SCN, 0.19%; trans Co–SCN, 0.17%; cis Co–NCS, 0.08%; trans Co–NCS, 0.08%; and there is substantially more activity in the S-bonded species than in the N-bonded species. Clearly the intermediate captures both S and N ends of NCS^- and prefers S to N which is consistent with the conclusion reached from the competition experiments. Some discussion of the accuracy of the tracer experiments is required. All the activity values given are mean values from repetitive counting where deviations up to ±5% were

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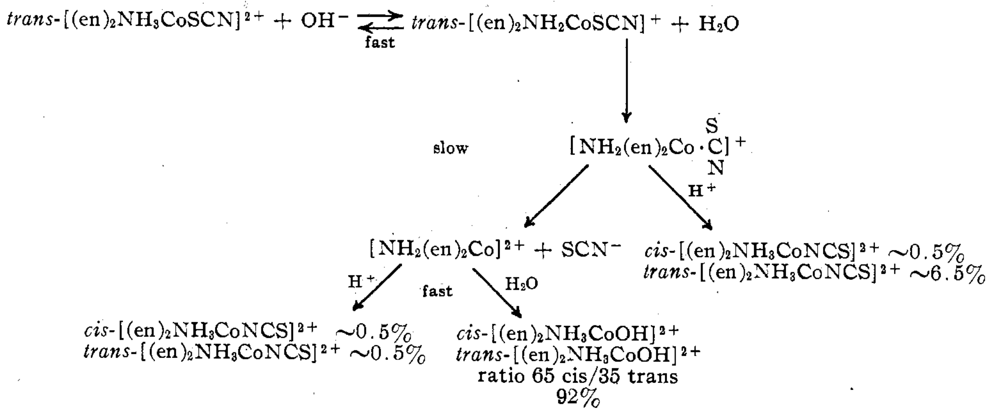
(7) M. L. Tobe, *Accounts Chem. Res.*, **3**, 377 (1970).

SCHEME I

PROPOSED MECHANISM FOR THE BASE HYDROLYSIS OF THE *trans*-$[(en)_2NH_3CoSCN]^{2+}$ Ion



found. Parallel experiments were reproducible relatively to a maximum deviation of 15% and the complexes showed little if any ability to quench the counting rate. It would appear therefore that a maximum error of ±20% is a conservative estimate of the error in the tracer experiments.

Discussion

Synthesis and Structure.—The thiocyanato complex was prepared by treating *trans*-$[Co(en)_2NH_3N_3]^{2+}$ with NO^+ in the presence of excess NCS^-. The reaction occurs by addition of NO^+ to N_3^-[8] with the rapid release of N_2 and N_2O. The resulting complex intermediate then competes for NCS^- and water but in the presence of the large excess of NCS^- substantial amounts of the thiocyanato complex form. Reactions of this type occur with retention of configuration with *trans*-$[CoND_3(NH_3)_4N_3]^{2+}$[9] and *cis*- and *trans*-$[Co(en)_2NH_3N_3]^{2+}$[2] ions so that the trans assignment above is supported by the reaction route. Another feature of the preparative process is the intermediate's substantial preference for the S end of NCS^-. This feature was also observed in the study of the base hydrolysis of $[(NH_3)_5CoX]^{2+}$ ions in the presence of NCS^-.[1] It was argued that the preference arose from the lesser ability of S to H bond to the solvent. If abstraction of the NCS^- ion from the solvent is a rate-determining factor for reaction of the intermediate, then S is preferred as the nucleophile since it is more exposed.

The pmr spectrum of the thiocyanato complex is is given in Figure 1. The assignments for the signals are also included in the caption and the spectrum is consistent with the isomer having the trans configuration. The two NH signals arise from the nonequivalence of the protons on the NH_2 groups in relation to their disposition relative to NH_3 or SCN^-. Cis isomers in this type of complex have several signals (>3) in the NH region consistent with the lower symmetry of these ions.[10]

Finally, the supposed *trans*-$[(en)_2NH_3CoSCN]^{2+}$ ion eluted before the cis isomer from the ion-exchange column and this pattern has also been observed for a series of complexes of this nature.[2,11]

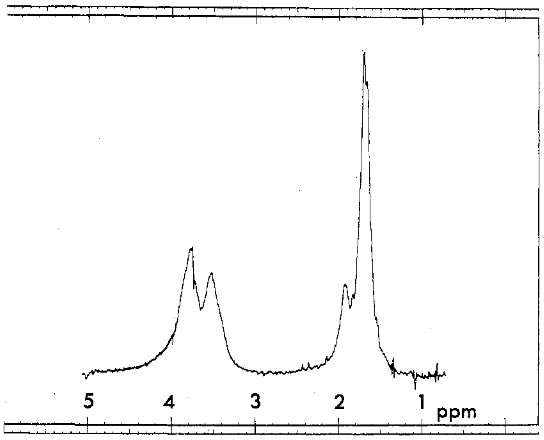


Figure 1.—The pmr spectrum of *trans*-$[(en)_2NH_3CoSCN]Cl_2\cdot 2.5H_2O$ in D_2SO_4 (10^{-3} *M*, 34°) relative to *tert*-butyl alcohol. The signal at 1.7 ppm is attributed to the methylene protons of the ethylenediamine chelate. The signal at 1.95 ppm is attributed to the ammonia protons, and the two signals at 3.5 and 3.8 ppm are assigned to the NH_2 protons of the chelate rings.

Base Hydrolysis.—The rate law

$$v_{[(en)_2NH_3CoSCN]^{2+}} = k[(en)_2NH_3CoSCN^{2+}][OH^-]$$

is consistent with previous examples in the cobalt(III)–pentaamine type complexes and the paths for reaction are analogous to those observed for $[(NH_3)_5CoSCN]^{2+} + OH^-$.[1] Both hydroxo and isothiocyanato complexes are observed as products even though the amount of isothiocyanate (8%) is considerably less than for the pentaammine example. This implies that the reactions of the two complexes proceed by the same route which includes the dissociative mechanism proposed for base hydrolysis of cobalt(III) primary and secondary amine complexes denoted as SN1CB.[6] The suggested mechanism is given in Scheme I.

In more detail the pmr study shows that proton exchange at the NH centers is faster than base hydrolysis which is consistent with the SN1CB mechanism, and evidence for the presence of an intermediate of reduced coordination number arises directly from the ratio of *cis*- and *trans*-$[Co(en)_2NH_3H_2O]^{3+}$ product, namely 65 ± 1% and 35 ± 1%, respectively. These values agree with those obtained from the hydrolysis of other *trans*-$[Co(en)_2NH_3X]^{2+}$ ions (X = Cl, NO_3) at 25°.[2] This ratio was also kept when *trans*-$[(en)_2NH_3CoSCN]^{2+}$ was hydrolyzed in 1 *M* NaSCN. In addi-

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

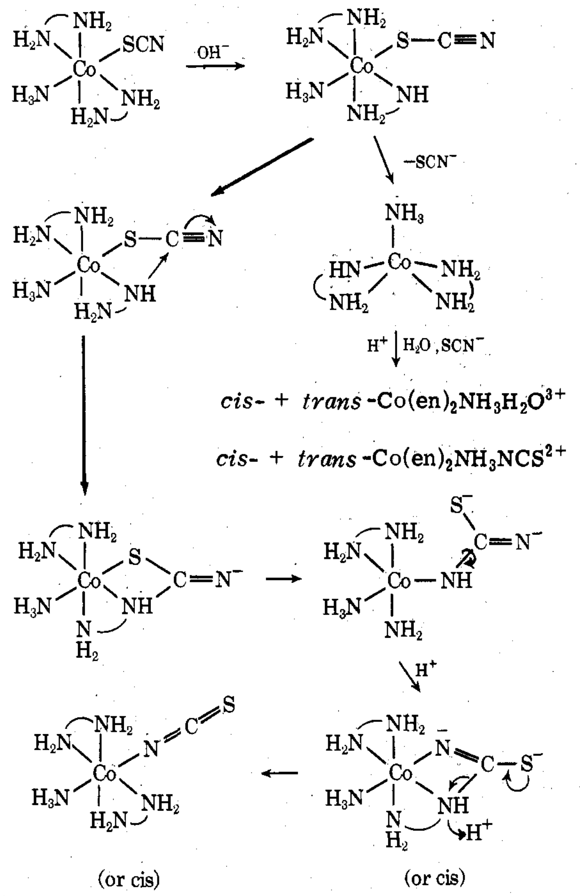
[9] D. A. Buckingham, I. I. Olsen, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 597 (1967).

[10] D. A. Buckingham, L. Durham, and A. M. Sargeson, *ibid.*, **20**, 257 (1967).

[11] L. F. Druding and G. B. Kauffman, *Coord. Chem. Rev.*, **3**, 419 (1968).

SCHEME II

ALTERNATIVE PROPOSAL FOR THE BASE HYDROLYSIS AND REARRANGEMENT OF THE *trans*-[(en)$_2$NH$_3$CoSCN]$^{2+}$ ION



tion the competition ratio of CoNCS to aquo product was essentially the same as for other leaving groups[2] after correction for a base catalyzed path which leads to an intramolecular rearrangement from thiocyanato to isothiocyanato product. It should also be noted that the stereochemistry of the competition product was the same as previously observed.[2] It appears therefore that S-bonded thiocyanate ion is a good leaving group ($\sim$Cl$^-$) and exhibits the regular conjugate base dissociative mechanism for base hydrolysis. Moreover the five-coordinate intermediate captures NCS$^-$ in solution and substantially prefers the S atom over N ($\sim$3-fold). This behavior is in keeping with that observed in the (NH$_3$)$_5$CoSCN^{2+} study[1] and with the argument[1] that S is less H bonded to the solvent than N and is therefore more exposed.

When the S end of NCS$^-$ is captured both *cis*- and *trans*-[(en)$_2$NH$_3$CoSCN]$^{2+}$ ions arise and continue to hydrolyze. There is no detailed information about the fate of the cis thiocyanato ion but it is likely that the product ratios are not greatly different from that for the trans species.[2] This lack of information however does not disturb the conclusions which can be drawn from the competition results since the reactions of the five-coördinate intermediate are common to all leaving groups in the presence of NCS$^-$ ion. The competition paths therefore are not detailed in Scheme I and only the final products are noted.

Where this base hydrolysis reaction differs from that for other cobalt(III) pentaamines is in the rearrangement path S → N. The tracer experiments show that no activity occurs in either thiocyanato or isothiocyanato species which cannot be accounted for by competition. Therefore, the rearrangement is an intramolecular process. One of the questions which the results raise is, "How far along the reaction path does rearrangement occur? Does the deprotonated reactant divide along two paths or is rearrangement a product from an 'intimate ion pair' which is not in equilibrium with NCS$^-$ in solution and which leads on directly to the five-coordinate intermediate.?" No clear answer is adduced but some support for the latter choice comes from the fact that CoSCN → CoNCS rearrangement appears to be accompanied by some trans → cis rearrangement also. We might infer therefore that the Co–SCN bond is broken in the process and that the rearrangement is tied intimately to the hydrolysis mechanism. The thermal rearrangement of Co–SCN → Co–NCS is several orders of magnitude too slow to be considered in this context. An alternative mechanism for the rearrangement (Scheme II) should be considered, where an adjacent deprotonated amino group attacks the electrophilic C of the SCN ligand to give a short-lived five-coordinate intermediate which leads to reentry of the N atom after rotation. Such an intermediate accommodates trans to cis rearrangement without exchange with N^{14}CS$^-$ from solution.

This proposal might be tested with [(^{15}NH$_3$)$_5$CoSCN]$^{2+}$ since if the rearrangement occurs this way one atom of the ^{15}N label must appear in the NCS$^-$ ion of the isothiocyanato product. These intramolecular rearrangements are being examined in more detail.

Acknowledgment.—We are indebted to H. Satrapa for assistance with the preparation of some of the compounds and to the Microanalytical Unit for C, H, N, and Co estimations.