Contribution from the Department of Chemistry, Faculty of Military Studies, Royal Military College,
University of New South Wales, Duntroon, Canberra, ACT, Australia 2600

Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$. Capture of Sulfur and Nitrogen of the Thiocyanate Ion

W. G. JACKSON* and C. N. HOOKEY

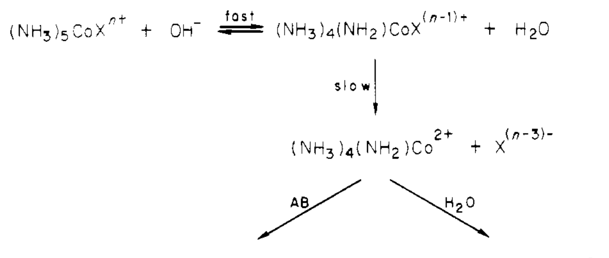
Received May 18, 1983

New syntheses and a method for the accurate determination of the $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$ linkage isomers in solution are described. The base-catalyzed reaction of $[(NH_3)_5CoX]^{n+}$ (X = OSO_3^{2-}, I^-, ONO_2^-, $O_3SCH_3^-$, $O_3SCF_3^-$, $OClO_3^-$, $OS(CH_3)_2$, $OP(OCH_3)_3$, $OC(NH_2)_2$, $OC(NH_2)N(CH_3)_2$) in aqueous 1.0 M NaNCS at 25 °C yields initially[1] both S- and N-bonded $[(NH_3)_5Co(SCN)]^{2+}$ (7–18%), along with $[(NH_3)_5CoOH]^{2+}$. Subsequently the $[(NH_3)_5CoSCN]^{2+}$ isomer rearranges[1] in OH^-, but the initial S/N capture ratio for the primary reaction has been determined accurately and shown to be constant, 2.0 ± 0.1 (i.e., 67.0 ± 1.5% S isomer, 33.0 ± 1.5% N isomer). This result contrasts with the previous[1] and more limited data, S/N = 3.3–6.9. The implied leaving group independence holds for the ten X examined where the reactivity, donor atom, charge, and bonding geometry vary widely. The results are consistent with those of two very recent studies[2,3] for a similar wide range of X and where other ambidentate competitors were used: NO_2^-, O/N = 2.0 ± 0.2 (7); $S_2O_3^{2-}$, S/O = 2.3 ± 0.3 (7); the number of different X used is in parentheses. Also consistent are the data for total anion capture (SCN^-, NO_2^-, $S_2O_3^{2-}$). This increases systematically with the formal charge (*n*) of the $[(NH_3)_5CoX]^{n+}$ complex, yet the total anion capture is independent of X within each set of complexes for a given *n*. For SCN^-: *n* = 1, 6.8% (1); *n* = 2, 13.9 ± 0.6% (5); *n* = 3, 17.5 ± 0.5% (3). The results are interpreted in terms of a common short-lived pentacoordinate intermediate, $[(NH_3)_4(NH_2)Co]^{2+}$, which captures competing nucleophiles from an ion atmosphere inherited from the conjugate base complex $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$.

Introduction

Competition experiments have provided information on the detailed mechanism of base hydrolysis of pentaamminecobalt(III) ions, $[(NH_3)_5CoX]^{n+}$. The thrust of these studies has been the close examination of the leaving group (X) dependence of the product distribution for the reaction of $[(NH_3)_5CoX]^{n+}$ in aqueous OH^- containing competiting Y. The state of this work was reviewed recently.[4]

In two more recent articles,[2,3] it was demonstrated that anion competition by an ambidentate ligand (AB) can provide a means of determining the leaving group dependence of anion competition in the base hydrolysis reaction (eq 1), devoid of the complication of an inherited ion atmosphere.[4] For this limiting dissociative S_N1cb mechanism, the relative efficiency of capture of the A and B termini will be independent of X, since, although the inherited ion atmosphere of the short-lived $[(NH_3)_4(NH_2)Co]^{2+}$ intermediate could depend detectably upon X,[1,2] the alternative termini arise from a *common* atmosphere *that does not contain X*. On the other hand, if there is no pentacoordinate intermediate, then both the total A and B capture and the A/B linkage isomer ratio will depend upon X, since this is contained in the direct precursor of the products, $[(NH_3)_4(NH_2)CoX]^{(n-1)+}$. Obviously the distinction in mechanism on this basis rests with the accuracy of the linkage isomer product ratio.



(1)

The first competition experiments involving an ambidentate competitor were performed with the thiocyanate ion, NCS^-.[1,4] These results allegedly revealed an appreciable variation in the S/N product ratio for different leaving groups. Only a few leaving groups were examined, and the S/N isomer product ratio[1] ranged from 3.3 for X = NO_3^- and 4.3 for X = I^- to 6.9 for X = Me_2SO.[4] The variation evident in the latter result appeared to be outside experimental error.

When the ambidentate $S_2O_3^{2-}$ ion is used as a competitor in the base hydrolysis reaction of $[(NH_3)_5CoX]$ the prospect exists for either S or O bonding. The product distribution for $[(NH_3)_5Co(S_2O_3)]^+$ has been found to be a constant 70 ± 2% S isomer and 30 ± 2% O isomer, irrespective of the leaving group.[3] Similarly, when the ambidentate ion NO_2^- (N or O bonded) is the competitor, 67 ± 3% O and 33 ± 3% N isomer product is observed.[2] Thus for both NO_2^- and $S_2O_3^{2-}$ a constant isomer product ratio is formed, even though the total anion competition varies with the charge of X.[2-4]

The seemingly anomalous NCS^- system initiated the present investigation on the precise product distribution for the base hydrolysis of $[(NH_3)_5CoX]^{n+}$ in 1.0 M NaNCS, using a wide range (11) of leaving groups X. Also, the reliability of the previous analyses[1,4] for the linkage isomeric products $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$ required scrutiny, and this problem is addressed.

A particular difficulty with product analyses for all these systems (AB = NO_2^-, $S_2O_3^{2-}$, NCS^-) is the subsequent base-catalyzed rearrangement reaction[1,3,5] of the less stable linkage isomer (eq 2). This reaction occurs with a rate not

$$\begin{aligned}(NH_3)_5Co{-}AB &\xrightarrow{OH^-} (NH_3)_5Co{-}BA\\ &\xrightarrow{OH^-} (NH_3)_5CoOH^{2+} + AB\end{aligned} \tag{2}$$

too different from that for the generating base hydrolysis process (eq 1), and the relative rates are independent of $[OH^-]$. For the NCS^- system, the rearrangement of $[(NH_3)_5CoSCN]^{2+}$ is especially rapid (k_{OH} = 0.14 M^{-1} s^{-1},

---

[*] To whom correspondence should be addressed at the Institut de Chemie, Universitê de Neuchâtel, Neuchâtel, Switzerland CH-2000.

[1] Buckingham, D. A.; Creaser, I. I.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 655–661.

[2] Jackson, W. G.; Randall, M. L.; Sargeson, A. M.; Marty, W. *Inorg. Chem.* **1983**, *22*, 1013–1016.

[3] Jackson, W. G.; Fairlie, D. P.; Randall, M. L. *Inorg. Chim. Acta*, **1983**, *70*, 197–205.

[4] Dixon, N. E.; Jackson, W. G.; Marty, W.; Sargeson, A. M. *Inorg. Chem.* **1982**, *21*, 688–697.

[5] Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *Inorg. Chem.* **1980**, *19*, 904–910.

0020-1669/84/1323-0668$01.50/0

μ = 1 M, 25 °C),[1] such that significant secondary reaction (eq 2) occurs in the time required to completely base hydrolyze (eq 1) most $[(NH_3)_5CoX]^{n+}$ complexes. In general corrections for subsequent rearrangement are required, and clearly the initial S/N isomer distribution (eq 1) can be determined accurately only if these corrections are not severe. The successful circumvention of this problem, in part by using new and especially good leaving groups, has been described for the systems AB = NO_2^-, $S_2O_3^{2-}$,[2,3] and this article deals with its extension to the NCS^- system.

Experimental Section

Visible absorption spectra were recorded in duplicate with use of either a Cary 118C or Cary 210 spectrophotometer at 25 °C. Matched 1-cm or 1-dm silica cells were employed. All ^1H NMR spectra were measured on a Varian T60 spectrometer; Me_2SO-d_6 (Merck) was the solvent and tetramethylsilane (Aldrich) the reference. Ion-exchange chromatography was performed with the use of Bio-Rad 50WX2 (200–400 mesh, H^+ or Na^+ form) or Pharmacia SP-Sephadex C25 (Na^+ form) cation-exchange resins. For kinetic experiments, temperature control (±0.05 °C) was maintained by using water circulated from a Lauda thermostat bath. The absolute temperature of the bath (±0.05 °C) was monitored by a Hewlett-Packard digital quartz crystal thermometer, standardized by using the usual water triple point method. Cell temperatures were monitored with a calibrated thermistor or platinum resistance probes coupled to a Leeds-Northrup bridge or "house" digital thermometer.

Syntheses. The complex salts $[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3 \cdot H_2O$,[6] $[(NH_3)_5CoI](ClO_4)_2$,[7] $[(NH_3)_5CoOH_2](ClO_4)_3$,[8] $[(NH_3)_5CoONO_2](ClO_4)_2$,[9] $[(NH_3)_5CoOS(O)_2CH_3](ClO_4)_2$,[6,8] $[(NH_3)_5CoOS(O)_2CF_3](ClO_4)_2$, $[(NH_3)_5CoOClO_3](ClO_4)_2$,[8] $[(NH_3)_5CoOP(OCH_3)_3](ClO_4)_3 \cdot H_2O$, $[(NH_3)_5CoOC(NH_2)_2]_2(S_2O_6)_3 \cdot H_2O$,[4,6] $[(NH_3)_5CoOSO_3]ClO_4 \cdot H_2O$,[4] and $[(NH_3)_5CoOC(NH_2)N(CH_3)_2]_2(S_2O_6)_3 \cdot H_2O$[10] were made by the cited procedures or minor modifications thereof. The $[(NH_3)_5CoOSO_3]ClO_4 \cdot H_2O$ complex was obtained also as follows: $[(NH_3)_5CoOH_2](ClO_4)_3$ (11 g) was suspended in a mixture (70 mL) of Na_2SO_4 (5 M) and $NaHSO_4$ (0.5 M) and heated (100 °C, 2.5 h). The resultant solution was cooled (5 °C, 1 h) and then filtered to remove some precipitated $[(NH_3)_5CoOH_2](ClO_4)_3$. Addition of $HClO_4$ (10 M, 15 mL) and further cooling (5 °C, 1 h) precipitated any residual aqua complex. The filtrate on standing slowly deposited crystals of the pure sulfato complex (5 °C, 24 h). The product was recrystallized twice from $H_2O/HClO_4$. The crystals were washed with ethanol (2 × 50 mL) and ether (2 × 50 mL) and air-dried ($\epsilon_{516}{}^{max}$ 63.9, H_2O).

The complexes $[(NH_3)_5CoSCN]Cl_2 \cdot 1.5H_2O$, $[(NH_3)_5CoSCN](ClO_4)_2$, $[(NH_3)_5CoNCS]Cl_2$, and $[(NH_3)_5CoNCS](ClO_4)_2$ were synthesized by a new method,[11,12] as follows. (All manipulations involving the azido and the thiocyanato complexes were carried out in reduced light.[13]) The complex $[(NH_3)_5CoN_3](ClO_4)_2$[8] (30 g) was dissolved in NaSCN (10 M, 300 mL) with stirring. (Some of the NCS^- salt of the azido complex precipitates, but this is immaterial as it redissolves on reaction.) $NaNO_2$ (8.28 g, 1.5 equiv) was then dissolved in the solution with stirring, after which acid (CF_3COOH, 19.5 mL) was added *very* slowly with constant stirring. Copious quantities of N_2 and N_2O are liberated. The solution stood for 5 min at 25 °C to allow complete reaction and then was filtered to remove a quantity of intense yellow insoluble side product, presumably $(SCN)_n$. The filtrate was diluted to 3 L with water and then sorbed on a 20 × 10 cm column of Dowex (50W-X2, H^+ form), and the first band ($[(NH_3)_5CoSCN]^{2+}$ + $[(NH_3)_5CoNCS]^{2+}$) was eluted with HCl (2 M),[1] well separated from the orange $[(NH_3)_5CoOH_2]^{3+}$ band. After cooling (0 °C) overnight, most of the N isomer had precipitated as the orange-red $[(NH_3)_5CoNCS]Cl_2$ salt, and this was removed by filtration. The remaining (now violet) solution (4 L) was then rotary-evaporated (<30 °C) separately in small portions of ~200 mL to minimize the S to N isomer conversion,[1] to a final total volume of ~400 mL. This was then diluted carefully to 2.5 L with acetone. A fine mauve crystalline precipitate formed, essentially quantitatively (~5 g). This was filtered, washed with acetone (3 × 50 mL) and ether (3 × 50 mL), and then air-dried.

The crude $[(NH_3)_5CoSCN]Cl_2$ salt was extracted with a minimum volume of water (30 × 20 mL, ~22 °C), leaving the N isomer largely undissolved, and filtered. The filtrate was treated with HCl (2.5 M, 5 mL) and crystallization allowed to proceed slowly at 5 °C. Fractions were collected at regular intervals, and more HCl (2.5 M, 5 mL) was added to the filtrate each time. All fractions were filtered and easily separated into two visually distinct crystalline forms by flotation in ether. The combined S and N fractions were separately recrystallized twice from water/HCl. The S isomer crystallized as large violet-maroon chunky needles, the N isomer as smaller orange-red blocks. The purified isomers were washed with ethanol (3 × 20 mL) followed by ether (3 × 20 mL) and briefly air-dried before storing at −10 °C. Small samples of $[(NH_3)_5CoSCN]Cl_2 \cdot 1.5H_2O$ and $[(NH_3)_5CoNCS]Cl_2$ were recrystallized from $H_2O/HClO_4$ to give the respective perchlorate salts.[14] ^1H NMR spectra (Me_2SO-d_6): S isomer, δ 3.45 (12 H, cis NH_3), 3.45 (3 H, trans NH_3); N isomer, δ 3.45 (12 H, cis NH_3), 3.40 (3 H, trans NH_3). Visible spectra (H_2O): S isomer, $\epsilon_{288}{}^{max}$ 15700, $\epsilon_{514}{}^{max}$ 74.8; N isomer, $\epsilon_{306}{}^{max}$ 1598, $\epsilon_{498}{}^{max}$ 169.

A sample of the N isomer was also prepared from $[(NH_3)_5CoOH_2](ClO_4)_3$ by heating a saturated aqueous solution (pH 2, $HClO_4$) with a fivefold molar excess of NaNCS (60 °C, 30 min). On cooling, the product was precipitated with HCl (10 M) and twice recrystallized from H_2O/HCl. It is noted that this more conventional synthesis gives some S isomer,[11] removed in the recrystallization, and also, unless the pH is kept below 3, some NH_3 loss results and an $[(NH_3)_4Co(NCS)_2]Cl$ impurity (established chromatographically) is incurred. This is not readily removed by recrystallization.

Characterization. All the complex salts analyzed satisfactorily for at least four elements. Ion-exchange chromatography was the major tool used to establish the absence of trace impurities, in particular $[(NH_3)_5CoOH_2]^{3+}$.[8] The complexes were individually absorbed onto either Dowex or Sephadex cation-exchange resins and were eluted as single bands with the appropriate eluents. For example, $[(NH_3)_5CoCl]^{2+}$ is a common impurity in $[(NH_3)_5CoI]^{2+}$,[7] but none was observed by either the chromatography technique or the alternative method,[8] ^1H NMR spectroscopy. For the ^1H NMR spectroscopic method of analysis, the spectra of *all* the individual complexes in concentrated Me_2SO-d_6 solution were recorded. None showed the characteristic[8] Co-OH_2 signal (δ 5.62), and the spectra were identical with those of authentic specimens. Also the molar extinction coefficients (ϵ) for the complex ions in water (pH 3) agreed well with the published data.

Particular attention was given to the purity of the $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$ salts. This item was crucial to the accuracy of the S/N isomer product distributions for the base hydrolysis reaction. Recrystallization to a constant (ϵ, ±0.5%) visible and UV spectrum was considered good evidence of purity, along with agreement between the different salts of the same cation. Also, the S and N isomers partly separate on long ion-exchange columns,[1,11] the S isomer being faster running (Dowex 50W-X2, H^+ form, 1 M HCl). The purified NCS^- complex isomers eluted as single bands of uniform and characteristic color. Also, the ^1H NMR spectra (Me_2SO-d_6) are characteristic (vide supra).

Thiocyanate Ion Competition. Method. Samples (~300 mg) of the $[(NH_3)_5CoX]^{n+}$ complex salts were reacted with 1.00 M NaNCS (0.100 M in OH^-, 40–60 mL), by one or more of the techniques described below, for 8 or 30 s or 30 min at 25.0 °C, and the reactions were quenched by reducing the pH to ~9 with NH_4ClO_4 (1 g). The solution was diluted with water to about 500 mL (4 L for the 30-s

---

[6] Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Dixon, N. E.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 470–476.

[7] Jackson, W. G.; Begbie, C. M.; Randall, M. L. *Inorg. Chim. Acta* **1983**, *70*, 7–12.

[8] Buckingham, D. A.; Cresswell, P. J.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.* **1981**, *20*, 1647–1653.

[9] Buckingham, D. A.; Olsen, I. I.; Sargeson, A. M. *J. Am. Chem. Soc.* **1966**, *88*, 5443–5447.

[10] Dixon, N. E.; Fairlie, D. P.; Jackson, W. G.; Sargeson, A. M. *Inorg. Chem.*, in press.

[11] McGregor, B. C.; B.Sc. Thesis, University of New South Wales, 1982.

[12] Creaser, I. I., unpublished work; ref 24, cited in ref 1; no details have been since published.

[13] These complexes are appreciably photosensitive.

[14] The ClO_4^- salt of the S isomer undergoes striking and unusual color changes from brown to mauve and vice versa, depending upon the degree of solvation. This phenomnenon was also seen in the crystallization process, depending upon the temperature. Vacuum drying yields the mauve form, which is unsolvated. The two forms have identical visible and UV spectra.

reaction of $[(NH_3)_5CoOSO_3]^+$) and sorbed onto a cation-exchange resin of Sephadex, and the cations were eluted with NaCl (pH 3). The eluent was acidified to convert the $[(NH_3)_5CoOH]^{2+}$ to $[(NH_3)_5CoOH_2]^{3+}$. The bands were cleanly separated in the order $[(NH_3)_5CoOSO_3]^+$ (recovered; 0.25 M NaCl), $[(NH_3)_5Co(SCN)]^{2+}$ (0.25 M), and $[(NH_3)_5CoOH_2]^{3+}$ (0.5 M). The [Co] in the eluates were determined by using ϵ_{516} 63.9 for $[(NH_3)_5CoOSO_3]^+$ and ϵ_{492} 47.7 for $[(NH_3)_5CoOH_2]^{3+}$ (for $[(NH_3)_5Co(SCN)]^{2+}$—see Analysis). Experiments were performed in triplicate; cobalt recoveries were routinely >98.5% (100 ± 1.5%). Results were normalized to 100% recovery and averaged.

Three different reaction techniques were used for specific types of compounds, depending upon their solubility, reactivity, and rate of dissolution; the exact reaction time was the important item.

(i) The complex was placed in a Quickfit tube (60 mL), the NCS^-/OH^- solution (25.0 °C) added rapidly in one lot, and the tube sealed. The compound dissolved on shaking in <1 s, and the reaction was quenched after 30.0 s (30 min for one set of experiments on the sulfato complex).

(ii) The iodo and nitrato complexes do not dissolve sufficiently quickly in 1 M [NaNCS], so a Y-tube method[15] was utilized. The complex was placed in one arm of the tube and dissolved in a 10.00-mL (pipet) aliquot of water. A 10.00-mL (pipet) aliquot of 2.00 M NaNCS was added to the same arm of the tube and quickly mixed in. A 20.00-mL (pipet) portion of 1.00 M NaNCS in 0.20 M OH^- was contained in the other arm of the Y-tube (all at 25.0 °C). The tube was inverted, and the solutions were mixed (<< 1 s) by rapid shaking. No significant reaction occurs in the time of mixing. The reaction was quenched after 30.0 s.

(iii) A modification of the above Y-tube method was employed for the very labile complexes, in order to ensure homogeneity and an accurately known reaction time. The solid complex was placed in one arm of the tube and the 1.00 M NaNCS (0.1 M in $[OH^-]$) in the other arm, and the entire assembly was thermally equilibrated at 25.0 °C (10 min). The tube was inverted and shaken rapidly to dissolve (<1 s) the solid. The reaction was quenched, as before, after the desired 8.0-s reaction time.

The oxygen-bonded urea and dimethylurea complexes rearrange in base by minor pathways (7% and 3%, respectively) to give some N-bonded urea species.[16] The N-bonded urea products were determined as described elsewhere.[3,16] The NCS^- competition data are corrected for these intramolecular paths, which do not involve net substitution at Co^{III}. The $[(NH_3)_5CoOC(NH_2)_2]^{3+}$ ion also reacts by a path (2.5%) involving C–O rather than Co–O cleavage and yielding $[(NH_3)_5CoOH]^{2+}$ and free urea, as shown by ^{18}O-tracer work.[4] The NCS^- competition data are also corrected for this.

Attempts were made to detect $[(NH_3)_5CoO_2P(OCH_3)_2]^{2+}$ as a possible product in the reactions of the $[(NH_3)_5CoOP(OCH_3)_3]^{3+}$ ion. In acid solution, the trimethyl phosphate complex is readily demethylated to give CH_3SCN and the dimethyl phosphato complex.[11,17] However, we did not observe this reaction in 0.1 M OH^-/1.0 M NCS^-: normal base hydrolysis (k_{OH} 79 $M^{-1}\ s^{-1}$, 25 °C, μ = 1 M; $k_{obsd} = 7.9\ s^{-1}$)[4] is ~10^5-fold faster than the demethylation reaction ($k_{obsd} = 1.0 \times 10^{-4}\ s^{-1}$, 25 °C, μ = 1 M)[11,16] under the same conditions. The $[(NH_3)_5CoO_2P(OCH_3)_2]^{2+}$ ion elutes in front of and well separated from $[(NH_3)_5Co(SCN)]^{2+}$ on Sephadex; it was not observed.

Analysis. Attempts to completely separate the N and S isomers of $[(NH_3)_5Co(NCS)]^{2+}$ using various ion-exchange and eluting media were unsuccessful. However, a method was formulated for indirectly, although accurately, estimating the S/N ratio and the total amount of S and N isomers in the mixture.

In the thiocyanate ion competition experiments the first (2+) band eluted from the ion-exchange column (with NaCl; 0.25 M, pH 3) contains a mixture of the S and N isomers of the thiocyanato complex. The absorbance (A^{287}) of this band was obtained immediately while another (sealed) sample of the same band was heated (95 °C, 1.0 h) on a steam bath to effect (primarily) the S to N isomerization (see Discussion). The absorbance (A^{303}) for this heated sample was then obtained after the solution had cooled to room temperature. The S and N isomer concentrations and the S/N ratio were calculated by using the molar absorptivities determined for the pure $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$ ions, for the solutions untreated, and after the above treatment. The results follow from the solution to the two simultaneous equations

Table I. Analytical Results for $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$

	expt 1		expt 2	
	known[a]	exptl[b]	known[a]	exptl[b]
$10^5[(NH_3)_5CoSCN^{2+}]$, M	6.38	6.41	6.64	6.83
$10^5[(NH_3)_5CoNCS^{2+}]$, M	7.16	7.71	6.94	7.32
$10^5\Sigma(S + N)$, M	13.54	14.12	13.58	14.15
S/N ratio	0.89	0.83	0.96	0.93

[a] Synthetically constructed mixtures, by weight. [b] Spectrophotometrically determined; see text.

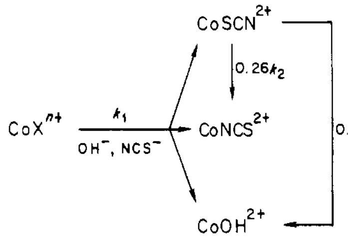
$$A^{287} = \epsilon_S^{287}[S] + \epsilon_N^{287}[N] = 15676[S] + 1284[N] \quad (3)$$

$$A^{303} = \epsilon_S^{303}[S] + \epsilon_N^{303}[N] = 1274[S] + 1514[N] \quad (4)$$

Note that the absorbance and molar absorptivities at 303 nm refer to the heated samples, whereas [S] and [N] in both equations are the same—the *initial* $[(NH_3)_5Co(SCN)]^{2+}$ concentrations.

The reliability of the method was checked on synthetic S/N isomer mixtures, using [Co] similar to those of the column eluates (0.25 M NaCl, pH ~2–3). The calculated values are in excellent agreement with the known values (Table I) and indicate the accuracy of the analytical technique for obtaining both the total and individual S- and N-bonded isomer concentrations.

The amounts of $[(NH_3)_5CoSCN]^{2+}$ (% S_0) and $[(NH_3)_5CoNCS]^{2+}$ (% N_0) formed as direct products of the base hydrolysis reaction (eq 1) on its completion were computed from the observed values (% S_{obsd}, % N_{obsd}) by correcting for the subsequent rearrangement/hydrolysis reaction of $[(NH_3)_5CoSCN]^{2+}$ (eq 2), using published specific first-order rate (k_1, k_2) and product distribution data and the known total reaction time, as follows:



(5)

For this scheme, it is readily shown that

$$\%\ S_0 = [(k_2 - k_1)(1 - e^{-k_1 t})/k_1(e^{-k_1 t} - e^{-k_2 t})]\ \%\ S_{obsd} \quad (6)$$

and

$$\%\ N_0 = \%\ N_{obsd} - 0.26(\%\ S_0 - \%\ S_{obsd}) \quad (7)$$

where $k_2 = k_{OH}[OH^-] = 0.014\ s^{-1}$.

For the iodo ($k_1 = k_{OH}[OH^-] = 0.37\ s^{-1}$), nitrato ($k_1 = 0.56\ s^{-1}$), and dimethyl sulfoxide ($k_1 = 0.54\ s^{-1}$) complexes, $e^{-k_1 t} << 1$ for reaction times $t \geq 8$ s, and the reduced form (eq 8) of eq 7 suffices.

$$\%\ S_0 = [(k_1 - k_2)e^{k_2 t}/k_1]\ \%\ S_{obsd} \quad (8)$$

For all other complexes k_1 is so much greater than k_2 that the first reaction (eq 1) is >99% complete in <1 s and before any significant subsequent reaction. Equation 9 is an excellent approximation in these cases. The sulfato complex base hydrolyzes so slowly (k_1 = 0.0049 s^{-1})[18] that the exact eq 6 was required. The % S_{obsd} used here is that commensurate with the amount of sulfato complex reacted; i.e., % S_{obsd} = % S(obsd)/[1 − (fraction of total Co which is recovered, $[(NH_3)_5CoOSO_3]^+$)].

$$\%\ S_0 = [e^{k_2 t}]\ \%\ S_{obsd} \quad (9)$$

It is noted that the accuracy of the corrections for secondary reaction do not hinge upon the accuracy of k_1, except for the sulfato complex. However, since there is only an 11% loss of the first-formed $[(NH_3)_5CoSCN]^{2+}$ ion in 8 s but a 34% loss in 30 s, it is clear that

---

[15] Jackson, W. G.; Lawrance, G. A.; Lay, P. A.; Sargeson, A. M. *J. Chem. Educ.* **1981**, *58*, 734–738.

[16] Fairlie, D. P.; Jackson, W. G. *Inorg. Chem.*, to be submitted for publication.

[17] Jackson, W. G.; McGregor, B. C. *Inorg. Chim. Acta*, in press.

[18] Po, L. L.; Jordan, R. B. *Inorg. Chem.* **1968**, *7*, 526–530.

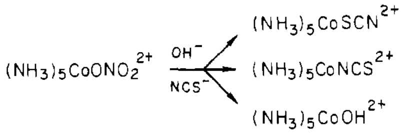
the accuracy does depend upon that for the reported k_2 value (0.014 s^{-1}) and the 74:26 $CoOH^{2+}$–$CoNCS^{2+}$ product distribution (eq 5) and that the $t = 8$ s corrected data should be better.

At infinite reaction time, $[(NH_3)_5CoNCS]^{2+}$ and $[(NH_3)_5CoOH]^{2+}$ are the only observable products. The % N isomer at $t = \infty$ was measured for only the sulfato complex; the calculated % N_∞ for this and all other complexes was deduced (eq 10) from the initial product distribution (eq 6, 7)

$$\%\ N_\infty = \%\ N_0 + 0.26(\%\ S_0) \tag{10}$$

Results and Discussion

Synthesis. The thermodynamically unstable S-bonded SCN^- complex $[(NH_3)_5CoSCN]Cl_2{\cdot}1.5H_2O$ was first prepared by Creaser et al.[1,12] The method involved the base hydrolysis of $[(NH_3)_5CoONO_2]^{2+}$ in aqueous NCS^- solution:

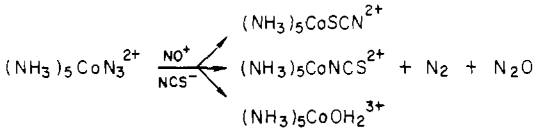


$$(NH_3)_5CoONO_2^{2+} \xrightarrow[NCS^-]{OH^-} \begin{cases} (NH_3)_5CoSCN^{2+} \\ (NH_3)_5CoNCS^{2+} + NO_3^- \\ (NH_3)_5CoOH^{2+} \end{cases} \tag{11}$$

More than 60% of the product is $[(NH_3)_5Co(NCS)]^{2+}$ in strong (10 M) NCS^- solution, and this was easily separated from $[(NH_3)_5CoOH_2]^{3+}$ by ion-exchange chromatography with an acidic (2 M HCl) eluent. The S- and N-bonded NCS^- complex isomers elute together, but they have been separated successfully by fractional crystallization as the chloride salts.[1]

The initial S/N isomer ratio was reported to be 3–4:1, but we find the ratio to be 2.0:1 (vide infra). Moreover, significant base-catalyzed rearrangement of the $[(NH_3)_5CoSCN]^{2+}$ isomer occurs in the time required to completely base hydrolyze the $[(NH_3)_5CoONO_2]^{2+}$ ion; an isomer mixture of predominately the isothiocyanato (N-bonded) form results. Overall, the yield of pure $[(NH_3)_5CoSCN]Cl_2{\cdot}1.5H_2O$ is less than 15%.[1]

We have described an alternative route[12] to the S-bonded complex



$$(NH_3)_5CoN_3^{2+} \xrightarrow[NCS^-]{NO^+} \begin{cases} (NH_3)_5CoSCN^{2+} \\ (NH_3)_5CoNCS^{2+} + N_2 + N_2O \\ (NH_3)_5CoOH_2^{3+} \end{cases} \tag{12}$$

using the well-known "induced" reaction, exploited to synthetic advantage on numerous occasions.[8,19,20] Other work[11] has shown that, while total NCS^- competition is more efficient for this reaction (eq 12) as opposed to the OH^--catalyzed route (eq 11), the S/N isomer ratio (0.6:1) is less favorable. However, the kinetic stability of the $[(NH_3)_5CoSCN]^{2+}$ ion under acidic conditions ($t_{1/2} \sim 9$ days, 25 °C)[1] renders reaction time a less crucial item, and the new procedure is therefore to be preferred (although the overall yield is not significantly better than before). We note that the facile reaction between NO_2^- and free NCS^- in acid solution is not a problem—$[(NH_3)_5CoN_3]^{2+}$ reacts much more rapidly than NCS^-.

The S- and N-bonded $[(NH_3)_5Co(NCS)]^{2+}$ isomers are difficult to separate by fractional crystallization. In our hands, the separation[21] via the perchlorate salts was inefficient and gave low yields of the pure isomers. The separation via the chloride salts[1] is also ineffective unless, as described in the Experimental Section, conditions for slow crystallization are contrived. The S-bonded form, while more soluble, crystallizes more quickly. Nonetheless the slowly cocrystallized isomers are very readily and efficiently separated mechanically (by flotation in ether); the S isomer forms as thick chunky deep purple-maroon needles, the N isomer as smaller orange-red blocks.

Analysis for $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoNCS]^{2+}$ in Isomeric Mixtures. Before discussing the SCN^- competition results, it is necessary to consider the previous and present methods for the analysis of the S and N isomers in the mixtures obtained by chromatography of the base hydrolysis products.

(1) The *total* concentration of S plus N isomer was determined by atomic absorption spectrometry, and the *proportion* of the two isomers was determined spectrophotometrically.[1]

(2) A more recent method[4] involved the measurement of *total* isomer concentration spectrophotometrically at an $[(NH_3)_5CoSCN]^{2+}/[(NH_3)_5CoNCS]^{2+}$ isosbestic point in the visible region. The proportion of the two isomers was then determined by using an absorbance measurement at 300 nm, where the molar absorptivities for the isomers differ greatly, by a factor of about 10.

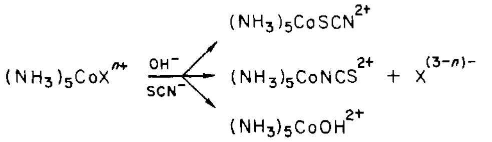
The main problem with these methods for the determination of the isomers is the lack of reproducibility. As can be seen from an inspection of the pure absorption spectra for the two isomers,[1] the crossing (isosbestic) points consist of an overlap of two steep curves, and hence any small error in the wavelength used causes a large error in the absorption (for the ultraviolet isosbestic point(s)), while in the visible region the absorbances are rather weak and subject to inaccuracies arising from fluctuations in background absorption.

A new method for the isomer product determination has been devised, similar to that used to determine the O and N isomers of $[(NH_3)_5Co(NO_2)]^{2+}$.[2] In this method the absorbance of the thiocyanato isomer mixture is measured spectrophotometrically at the absorption maximum of 287 nm, where typically molar absorptivities have a value of about 10 000 M^{-1} cm^{-1}. At this wavelength, the intensely absorbing S isomer (ϵ 15 676 M^{-1} cm^{-1}) dominates the light absorption. The mixture is then thermally equilibrated (1.0 h, 95 °C) to destroy the S isomer. The absorbance is remeasured, this time at the new maximum of 303 nm. This method utilizes the measured molar absorptivities for the pure S and N isomers at 287 and 303 nm, before and after heating, respectively.

In effect, the absorbance measurement at 303 nm determines total $[CoSCN^{2+}] + [CoNCS^{2+}]$, and this, coupled with the absorbance measurement at 287 nm for the freshly generated isomer mixture, defines the S/N isomer ratio. This follows from the fact that the S isomer isomerizes to the N form *essentially* quantitatively in 1.0 h at 95 °C. But it must be noted that the accuracy of the analysis is not contingent upon this fact. Indeed, the S isomer does not isomerize cleanly to the N form at 95 °C (there is some competitive hydrolysis),[11] nor is the N isomer completely stable at 95 °C. This is of no importance, however, provided the aqueous S and N isomers give *reproducible* product distributions when heated under standard conditions. This was found to be the case.

This new spectrophotometric method was tested on synthetically constructed S and N isomer mixtures of accurately known composition. The results (Table I) testify to its accuracy and precision.

Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$—Thiocyanate Ion Competition. The primary purpose of this work was to accurately define the product distribution for NCS^- entry accompanying the base hydrolysis reaction (eq 13). We required the S/N



$$(NH_3)_5CoX^{n+} \xrightarrow[SCN^-]{OH^-} \begin{cases} (NH_3)_5CoSCN^{2+} \\ (NH_3)_5CoNCS^{2+} + X^{(3-n)-} \\ (NH_3)_5CoOH^{2+} \end{cases} \tag{13}$$

---

[19] Jordan, R. B.; Sargeson, A. M.; Taube, H. *Inorg. Chem.* **1966**, *5*, 1091–1094.

[20] Dolbear, G. E.; Taube, H. *Inorg. Chem.* **1967**, *6*, 60–64.

[21] Palmer, D. A.; Van Eldik, R.; Kelm, H. *Inorg. Chim. Acta* **1978**, *30*, 83–86.

Table II. Thiocyanate Ion Competition Results for the Base Hydrolysis of $[(NH_3)_5CoX]^{n+}$ Ions in 1.00 M NaNCS (0.1 M OH^-; $\mu = 1.1$ M; 25 °C)

	obsd^{a,b}				cor^{c}				
X	S/N	% S	% N	Σ(% S + % N)	S/N	% S	% N	Σ(% S + % N)	% N_∞^{g}
$OC(NH_2)_2$	1.19	5.38	4.52	9.9	(2.13	8.11	3.81	11.9)	
					2.13	8.95	4.20	13.2^{d}	6.5
	1.82	7.03	3.87	10.9^{f}	(2.10	7.72	3.68	11.4)	
					2.10	8.51	4.06	12.6^{d}	6.3
$OC(NH_2)N(CH_3)_2$	1.44	8.79	6.11	14.9^{i}	(1.96	10.9	5.57	16.5)	
					1.96	11.3	5.74	17.0^{e}	8.7
	1.23	7.67	6.23	13.9	(2.20	11.5	5.23	16.7)	
					2.20	11.9	5.39	17.3^{e}	8.5
$OP(OCH_3)_3$	1.29	8.11	6.29	14.4	2.38	12.3	5.19	17.5	8.4
	1.54	9.34	6.06	15.4^{i}	2.12	11.62	5.48	17.1	8.5
$OS(CH_3)_2$	1.16	8.22	7.08	15.3	2.01	12.2	6.05	18.2	9.2
	1.82	11.1	6.10	17.2^{f}	2.02	12.0	5.93	17.9	9.0
I^-	1.12	6.08	5.42	11.5	1.90	8.90	4.69	13.6	7.0
ONO_2^-	1.10	6.44	5.86	12.3	1.95	9.56	4.90	14.4	7.4
$OClO_3^-$	1.10	6.60	6.00	12.6	1.96	10.0	5.11	15.1	7.7
	1.19	6.52	5.48	12.0	2.16	9.92	4.60	14.5	7.2
	1.53	7.80	5.10	12.9^{j}	1.79	8.72	4.86	13.6	7.1
$OS(O)_2CF_3^-$	1.67	7.94	4.76	12.7^{j}	1.96	8.88	4.52	13.4	6.8
	1.47	7.44	5.06	12.5^{i}	2.00	9.20	4.60	13.8	7.0
$OS(O)_2CH_3^-$	1.57	7.76	4.94	12.7^{j}	1.85	8.68	4.70	13.4	7.0
	1.44	7.14	4.96	12.1^{i}	1.97	8.89	4.51	13.4	6.8
OSO_3^{2-}	0.9	3.0	3.3	6.3	1.2	3.7	3.1	6.8	4.1
									4.4^{h,k}

av cor S/N: $2.0_3 \pm 0.1_4$ (67.0 ± 1.5% S, 33.0 ± 1.5% N)

[a] Except where noted otherwise: reaction time 30 s; 25 °C. [b] S = $[(NH_3)_5CoSCN]^{2+}$, N = $[(NH_3)_5CoNCS]^{2+}$; the other product is $[(NH_3)_5CoOH]^{2+}$ = 100 − % S − % N). [c] Corrected for subsequent reaction of $[(NH_3)_5CoSCN]^{2+}$ (see Experimental Section). [d] Corrected also for two paths not involving net ligand substitution; C–O cleavage (2.8%) and O to N linkage isomerization (7%). [e] Corrected also for a path not involving net ligand substitution; O to N linkage isomerization (3%). [f] Reaction time 30 s; 16 °C. [g] Calculated amount of $[(NH_3)_5CoNCS]^{2+}$ after complete reaction of first-formed $[(NH_3)_5CoSCN]^{2+}$; % N_∞ = % N(cor) + 0.26% S(cor). [h] Obsd (see footnote *g*). [i] Reaction time 30 s; 20 °C. [j] Reaction time 8 s; 25 °C. [k] Reaction time 30 min; 25 °C.

product isomer ratio as well as the total (S plus N) NCS^- capture in order to assess the leaving group dependence over a wide range of X. Recently such experiments were performed by using the ambidentate nucleophiles $S_2O_3^{2-}$[3] and NO_2^-,[2] where S/O and O/N capture are observed, respectively. For a wide range of X (10), consistent patterns were observed. For the SCN^- system, only three different leaving groups were examined,[1,4] and the results do not conform to these patterns. We believed the problem could be resolved by a scrutiny of the earlier NCS^- work and an extension of that work to include a much wider range of leaving groups.

The $[(NH_3)_5CoNCS]^{2+}$ ion is quite stable in acid and basic solution, but $[(NH_3)_5CoSCN]^{2+}$, while it only slowly isomerizes to the N isomer in acid solution ($t_{1/2}$ ~9 days, 25 °C), rearranges rapidly in base.[1] The specific rate is 0.14 M^{-1} s^{-1} at 25 °C, corresponding to a half-life of only 50 s in 0.1 M OH^-. Moreover, only 26% of this OH^- catalyzed pathway leads to the N isomer; the other 74% results in $[(NH_3)_5CoOH]^{2+}$ (eq 5). Consequently, to obtain an accurate measurement of the initial amounts of N and S isomeric products (eq 13), the conditions needed to be devised such that their rate of formation was much faster than the secondary rearrangement process or, in default, the reaction time was known so that an accurate correction for subsequent reaction could be applied. Since both the generating reaction, base hydrolysis of $[(NH_3)_5CoX]^{n+}$ in 1 M NaNCS, and the subsequent rearrangement process are base catalyzed, i.e., first order in $[OH^-]$, varying $[OH^-]$ has no effect on the relative reaction rates. This constraint limited the choice of leaving groups to those $[(NH_3)_5CoX]^{n+}$ having $k_{OH} > 3$ M^{-1} s^{-1}.

The other experimental variable was reaction time. There were two choices. First, each complex could be allowed to react completely ($10t_{1/2}$). Under these conditions, the reaction times would be different for each complex, and consequently, the correction for subsequent S to N isomer rearrangement would vary with X. Alternatively, all the complexes could be reacted for a common time, determined by the slowest reaction and corresponding to its 10 half-lives. Thus, the (larger) correction for the S to N rearrangement for all complexes would be the same, and so a comparison of even the observed (uncorrected) S/N isomer product distribution results would enable an immediate assessment of the leaving group dependence of the initial total S plus N isomer and S/N isomer ratio. Even so, this correction is not strictly constant; there is a small difference in the correction terms for the very fast and the not-so-fast reactions (see Experimental Section). Nonetheless quite precise corrections for subsequent rearrangement may be made, although these vary with X.

The thiocyanate ion competition results are presented in Table II. Much of the data refer to the common reaction time of 30 s, where a correction for ~34% subsequent rearrangement was required. In separate experiments, the amounts of S and N isomer formed initially were obtained almost directly for the very reactive (X = ClO_4^-, $CF_3SO_3^-$, and $CH_3SO_3^-$) complexes by shortening the reaction time (8 s); here subsequent reaction amounts to only ~11%. While the results for the shorter reaction time should be the more accurate—the extrapolation for the rearrangement is smaller—the close agreement between the corrected results for the *same* complexes reacted for both 8 and 30 s (and under other conditions; refer to Table II) indicates that all these analyses are substantially correct.

There are three important general results to be gleaned from Table II. First, the corrected S/N isomer capture ratio is a remarkably constant 2.0 ± 0.1 for *all* leaving groups; i.e., the initial amounts of NCS^- isomers are 67 ± 1.5% S and 33 ± 1.5% N. Second, the total NCS^- competition depends quite clearly on the formal charge (*n*) of the $[(NH_3)_5CoX]^{n+}$ complex. There is 17.5 ± 0.5% capture for the 3+ complexes (three examples; excluding X = $OC(NH_2)_2$—vide infra) and 13.9 ± 0.6% for the 2+ species (five examples). Third, and implied above, within each charge group the result (S/N and

$\sum(\mathrm{S} + \mathrm{N})$) is independent of the leaving group.

The result for the O-bonded urea complex is clearly anomalous. It is a significantly lower value (12.9%; cf. 17.5%) for total $\mathrm{SCN^-}$ competition, yet the S/N product ratio, 2.1:1, is indistinguishable from the others. For this cation, cleavage by both C–O and Co–O paths has been demonstrated.[4] Even though both routes provide net hydrolysis, $\mathrm{NCS^-}$ competition is possible only via the latter. In 0.1–0.4 M NaOH there is 97.2% Co–O bond cleavage and 2.8% C–O bond cleavage ($^{18}\mathrm{O}$ tracer results)[4] (eq 14). However, there is such a large decrease in the total $\mathrm{NCS^-}$ competition for the urea complex, compared with the other 3+ complexes, it would appear that $\mathrm{NCS^-}$ alters the relative importance of these two bond-cleavage pathways. This phenomenon has been observed also for Y = $\mathrm{SO_4^{2-}}$ and $\mathrm{S_2O_3^{2-}}$ and an explanation advanced.[2,3] Yet for monoanions other than $\mathrm{NCS^-}$ (e.g., $\mathrm{N_3^-}$), the reaction appears to be very largely (97.2%) Co–O cleavage.[4] A definitive explanation of the peculiarity of $\mathrm{SCN^-}$ in this respect awaits the appropriate $^{18}\mathrm{O}$ data.

$$\mathrm{(NH_3)_5CoO{=}C(NH_2)_2} \xrightarrow[\mathrm{^{18}OH_2/^{18}OH^-}]{97.2\%} \mathrm{(NH_3)_5Co^{18}OH^{2+}} + \mathrm{OC(NH_2)_2}$$
$$\xrightarrow[\mathrm{^{18}OH_2/^{18}OH^-}]{2.8\%} \mathrm{(NH_3)_5CoOH^{2+}} + \mathrm{^{18}OC(NH_2)_2} \qquad (14)$$

In an effort to determine if the pattern[4] of anion capture for complexes of varying charge applied (3+ > 2+ > 1+), X = $\mathrm{SO_4^{2-}}$ was used as an additional leaving group. Previously, data on the pattern of anion capture, with respect to the variation in complex charge, had been obtained for only Y = $\mathrm{N_3^-}$.[4] For the $[(\mathrm{NH_3})_5\mathrm{CoOSO_3}]^+$ complex $k_{\mathrm{OH}} = 0.049\ \mathrm{M^{-1}\,s^{-1}}$,[18] and so this ion has a half-life in 0.1 M $[\mathrm{OH^-}]$ at 25 °C of 141 s. Even though our standard common reaction time of 30 s did not encompass even one half-life for the sulfato complex, the reaction was examined, and, as expected, only about 11% of the $[(\mathrm{NH_3})_5\mathrm{CoOSO_3}]^+$ was found to have reacted. Thus the absolute value for the total anion capture in this case was low, less than 1% of the initial [complex], and hence accurate measurements were difficult. A single result was obtained, 55% S and 45% N isomer, corrected to zero reaction time, and 6.4% total anion competition for reacted $[(\mathrm{NH_3})_5\mathrm{CoOSO_3}]^+$. Although the S/N ratio is not in very close agreement with the other results, the total competition is reasonable for a 1+ complex. The S/N ratio discrepancy is, however, probably within experimental error, necessarily large for the sulfato complex.

Further studies were conducted on the $[(\mathrm{NH_3})_5\mathrm{CoOSO_3}]^+$ complex, using a 30-min reaction time (ten half-lives, under the experimental conditions, is 24 min). This reaction time is sufficient to have converted *all* the S isomer to the thermodynamically more stable N isomer and $[(\mathrm{NH_3})_5\mathrm{CoOH}]^{2+}$. The amount of N isomer found was 4.4%. To facilitate a comparison of this result with the corresponding results for all the other complexes, the "zero" reaction time S/N and total anion capture data for these other complexes were converted to results giving the total N present at infinite reaction time (see Experimental Section). The relative amounts of N isomer found for these conditions were 8.7 ± 0.4% for the 3+ ions (X = $\mathrm{OC(NH_2)_2}$ excepted, for the reason noted), 7.1 ± 0.3% for the 2+ ions, and 4.1% for the 1+ complex. The last result agrees nicely with that directly observed, 4.4% (Table II). There is a consistency now for *both* $\mathrm{N_3^-}$ and $\mathrm{NCS^-}$ as the competing anions—total anion capture increases systematically with the charge of the substrate (3+ > 2+ > 1+). Also it is worthy of emphasis that these results show the percentage anion capture to be remarkably constant within each group of $[(\mathrm{NH_3})_5\mathrm{CoX}]^{n+}$ complexes having the same charge.

Undoubtedly the most important result is the constant initial S/N isomer ratio, 2.0 ± 0.1. It is significant because the isomer product distribution does *not* depend upon a change in the charge of the leaving group, a factor that clearly affects the total amount of anion capture. Furthermore, this constant result is significant because the leaving groups vary appreciably in charge, steric bulk, bonding geometry, and reactivity.

An especially important observation is the parallel in the constancy of the results for the capture of $\mathrm{NCS^-}$ (67:33, S:N), $\mathrm{S_2O_3^{2-}}$ (70:30, S:O),[3] and $\mathrm{NO_2^-}$ (67:33, O:N)[2] for a very wide range of leaving groups. In particular, it is difficult to consider the constancy of the S/N isomer ratio found for the base hydrolysis reaction to be coincidental; this constancy is highlighted by the quite marked variation in the ratio of S and N capture for the induced and spontaneous aquation of $[(\mathrm{NH_3})_5\mathrm{CoX}]^{n+}$ in 1 M NaNCS (S/N 0.5–1.3).[11]

Earlier work found the S/N ratio for $\mathrm{NCS^-}$ capture in the base hydrolysis reaction to vary significantly with X,[1,4] and the isomer ratios (~3–4:1) were higher than the present ones. It now appears that these previous results are in error, the actual ratio of capture being not only much nearer 2.0:1 but also leaving group independent. It is suggested that the apparent difference between the previous and present results is due to a significantly more reliable method for determining the relative amounts of the S and N isomers. However, it remains true that the more poorly solvated S terminus of $\mathrm{SCN^-}$ is captured in preference to the better hydrated N terminus although not to the degree thought previously. In HNCS, it is the nitrogen center that is selectively protonated, indicating that N is more basic than S, and the parallel with the $\mathrm{NCS^-}$ competition data is retained.

In conclusion, the absolute constancy of the isomer ratio for the capture of the ambidentate $\mathrm{NCS^-}$ ligand, despite variations in the total (S plus N) capture, indicates that the leaving group is not involved in the step leading to final products. The mechanism consistent with this fact, and which provides a satisfactory explanation of all the results (including the systematic charge dependence of total competition), is the limiting $\mathrm{S_N1cb}$ mechanism. The collective results for the capture of $\mathrm{NCS^-}$ (S/N), $\mathrm{NO_2^-}$ (O/N), and $\mathrm{S_2O_3^{2-}}$ (S/O) now strongly testify to this, and the short-lived reduced coordination number intermediate $[(\mathrm{NH_3})_4(\mathrm{NH_2})\mathrm{Co}]^{2+}$ (eq 1) is clearly implicated.

Registry No. $[(\mathrm{NH_3})_5\mathrm{CoOC(NH_2)_2}]_2(\mathrm{S_2O_6})_3$, 75522-61-1; $[(\mathrm{NH_3})_5\mathrm{CoOC(NH_2)N(CH_3)_2}]_2(\mathrm{S_2O_6})_3$, 84623-22-3; $[(\mathrm{NH_3})_5\mathrm{CoOP(OCH_3)_3}](\mathrm{ClO_4})_3$, 15041-41-5; $[(\mathrm{NH_3})_5\mathrm{CoOS(CH_3)_2}](\mathrm{ClO_4})_3$, 51667-94-8; $[(\mathrm{NH_3})_5\mathrm{CoI}](\mathrm{ClO_4})_2$, 14972-83-9; $[(\mathrm{NH_3})_5\mathrm{CoONO_2}](\mathrm{ClO_4})_2$, 15156-24-8; $[(\mathrm{NH_3})_5\mathrm{CoOClO_3}](\mathrm{ClO_4})_2$, 18042-14-3; $[(\mathrm{NH_3})_5\mathrm{CoOS(O)_2CF_3}](\mathrm{ClO_4})_2$, 76024-69-6; $[(\mathrm{NH_3})_5\mathrm{CoOS(O)_2CH_3}](\mathrm{ClO_4})_2$, 76024-71-0; $[(\mathrm{NH_3})_5\mathrm{CoOSO_3}]\mathrm{ClO_4}$, 15156-23-7; $[(\mathrm{NH_3})_5\mathrm{CoSCN}]^{2+}$, 15005-69-3; $[(\mathrm{NH_3})_5\mathrm{CoNCS}]^{2+}$, 14970-18-4.