Inorg. Chem. **1992**, *31*, 2909–2914 **2909**

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Importance of Ion Association in the Substitution Reactions of Cobalt(III)–Acido Complexes. 8.[2] Spontaneous Isomerization of $[Co(NH_3)_5SCN]^{2+}$ in Aqueous Solution

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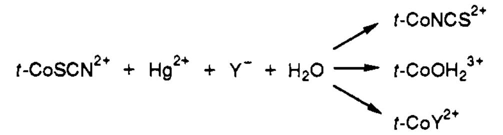
Received November 20, 1991

The spontaneous isomerization of $[Co(NH_3)_5SCN]^{2+}$ (abbreviated $CoSCN^{2+}$) in aqueous 0.15 M $NaS^{14}CN$ at 25 °C (pH 5.6) results in the *direct* incorporation of ionic $S^{14}CN^-$ and $N^{14}CS^-$ into the $CoSCN^{2+}$ reactant and $CoNCS^{2+}$ product, respectively. This occurs prior to subsequent $S^{14}CN^-/N^{14}CS^-$ anation of the small amount of $CoOH_2^{3+}$, also produced in the isomerization reaction (9.1%). These direct incorporations are interpreted as occurring via an ion-paired $CoSCN^{2+}{\cdot}N^{14}CS^-$ reactant, and their amounts, when compared to the $CoSCN^{2+}/CoNCS^{2+}$ products formed in the spontaneous aquation of other CoX^{2+} ions in the presence of added NCS^-, are similar. This leads to the conclusion that all such spontaneous hydrolyses occur in a similar fashion; viz., the CoY^{2+} products are formed via tight regiospecific reactant ion pairs, $CoX^{2+}{\cdot}Y^-$, with entry of Y^- and H_2O being largely independent of the leaving group X^-. The major requirement appears to be the presence of entering groups *adjacent* to the leaving group at the instant of Co–X bond rupture. This view differs from that recently expressed by Jackson and co-workers (ref 23).

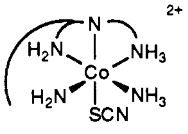
Introduction

The present experiments arose out of an earlier study of the reaction between t-$[Co(tren)(NH_3)SCN]^{2+}$ (abbreviated t-$CoSCN^{2+}$ (**1**) below) and Hg^{2+} (or Ag^+).[1] It was found that the presence of added Y^- anions ($Y^- = NO_3^-$, ClO_4^-, $CF_3SO_3^-$, $N^{14}CS^-$) resulted in the formation of some t-CoY^{2+} and that this product competed directly for the two other major reaction products, the isomerized t-$CoNCS^{2+}$ ion and t-$CoOH_2^{3+}$, eq 1; i.e., increasing $[Y^-]$ resulted in decreasing amounts of t-$CoNCS^{2+}$ and t-$CoOH_2^{3+}$. The rate law also showed a substantial $[Y^-]$ dependence.



(1)

These observations led to the proposal of transition state **2** for reactant decay in which all entering groups, as well as the leaving group (which is also an entering group), are in close proximity.



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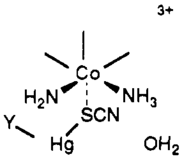

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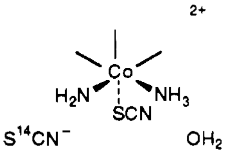
The ability of Y^- to gain direct entry to the metal ($Y^- = NO_3^- > CF_3SO_3^- \approx ClO_4^- \geq N^{14}CS^-, Cl^-$) appears to be largely controlled by its affinity for Hg^{2+}.[1] For example, the 57% entry of NO_3^- in t-$CoSCN{\cdot}Hg{\cdot}NO_3^{3+}$ can be attributed to its weak bonding to Hg^{2+} (and possibly to its poor solvation by surrounding water molecules), whereas the diminished entry of $N^{14}CS^-$ (0.7%) can be attributed to the much stronger attachment of S (compared to O) to Hg^{2+}. A similar situation exists with Cl^-.[2] From the viewpoint of the present paper the $Y^- = N^{14}CS^-$ example is significant since 40% of coordinated SCN^- reenters to form unlabeled t-$CoNCS^{2+}$ compared to 0.7% t-$CoN^{14}CS^{2+}$ from ionic $N^{14}CS^-$ (the remaining 59% of the product being t-$CoOH_2^{3+}$). The different incorporations mean that the two thiocyanates in **2** ($Y^- = N^{14}CS^-$) never become equivalent during the substitution process, and this implies a restricted lifetime for the reaction intermediate if a purely dissociative Co–S bond cleavage process occurs prior to the formation of new bonds.[3]

To further investigate this idea, we decided to see if it were possible to observe *direct* entry of ionic $N^{14}CS^-$ from an ion-paired species such as **3** using the spontaneous (uncatalyzed) reaction of the pentaammine thiocyanate ion $[Co(NH_3)_5SCN]^{2+}$ (hereafter abbreviated $CoSCN^{2+}$). This reaction[4] is very much slower than the Hg^{2+}-induced reaction,[5] and it was expected from previous studies[4,6] that only a $CoNCS^{2+}$ product (perhaps containing $N^{14}CS^-$) would result, i.e., that solvent entry to form $CoOH_2^{3+}$ would not occur. However, more careful experiments established that a small but significant amount of $CoOH_2^{3+}$ was indeed formed in the spontaneous reaction, and subsequent $S^{14}CN^-/N^{14}CS^-$ anation of this product proved a complicating factor in the analysis.



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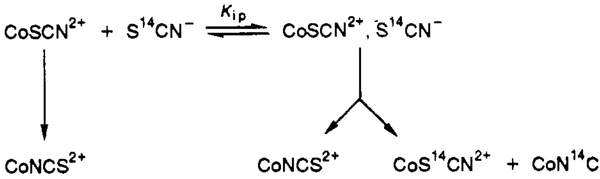
The aim of this investigation was then to see if it were possible to observe *direct* entry of ionic $N^{14}CS^-$ in competition with the intramolecular rearrangement process, eq 2, and if so, to see if the two thiocyanates in the ion pair became equivalent at any stage.



(2)

Experimental Section

Materials. The following complexes were prepared by literature methods: $[Co(NH_3)_5SCN]Cl_2{\cdot}H_2O$,[4] $[Co(NH_3)_5NCS]Cl_2$,[4] [Co(N-

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[1] Buckingham, D. A.; Clark, C. R.; Gaudin, M. J. *Inorg. Chem.* **1988**, *27*, 293.

[2] Part 7 in this series: Buckingham, D. A.; Clark, C. R.; Webley, W. S. *Inorg. Chem.* **1991**, *30*, 466. Entry of Y^- occurs via a HgY^+ term in the rate law, and transition state **2** is proposed in this paper.

[3] Palmer, Van Eldik, and Kelm (*Inorg. Chim. Acta* **1978**, *30*, 83) report ΔV^{*}_{obs} for the spontaneous isomerization of $CoSCN^{2+}$ in aqueous 0.1 M $NaClO_4$ at 50 °C as -5.3 ± 0.8 cm^3 mol^{-1} (-1.0 ± 1.2 cm^3 mol^{-1} in DMSO). On the basis of this value and estimated ΔV° values for the dissociated ion pair of a five-coordinate intermediate and the $CoNCS^{2+}$ product (+2.7 ● 1.8, −0.5 ● 1.7 cm^3 mol^{-1} respectively), these researchers support a π-bonded (such as **2**) rather than an intimate ion pair transition state for the overall reaction.

[4] Buckingham, D. A.; Creaser, I. I.; Sargeson, A. M. *Inorg. Chem.* **1970**, *9*, 655. In this first report of a Co(III)-coordinated S-bound thiocyanate complex, it was reported that $[Co(NH_3)_5SCN]^{2+}$ isomerizes without aquation (<2% $CoOH_2^{3+}$) in 0.01 M $HClO_4$ at 40 °C.

[5] Adegite, A.; Orhanovic, M.; Sutin, N. *Inorg. Chem. Acta* **1975**, *15*, 185.

[6] Jackson, W. G.; Hookey, C. N. *Inorg. Chem.* **1984**, *23*, 668. These researchers report that $[Co(NH_3)_5SCN]^{2+}$ isomerizes "essentially quantitatively" to the N-bound isomer at 95 °C, but also note some "competitive hydrolyses". Palmer, Van Eldik, and Kelm (ref 3) report some (unspecified) aquation at 50 °C.

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$H_3)_5OH_2](ClO_4)_3$,[7] $[Co(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$,[8] Λ-$[Co(en)_2$(*S*)-Val]$(ClO_4)_2$, (Val = valine).[9] $KS^{14}CN$ (250 μCi) was purchased from Amersham.

Chromatographic Separations. RP-HPIPC separations were carried out using a μ-Bondapak C-18 Radial Pak column (Waters Associates) and a Varian 5000 HPLC system equipped with Waters Z-module, Waters U6-K injector, and a Varian UV-50 detector (cell maintained at 25.0 °C). Peak areas (230, 500 nm) were quantified using a Hewlett-Packard 3390A integrator and were referenced against an internal Λ-$[Co(en)_2$(*S*)-Val$]^{2+}$ standard. Elution of $[Co(NH_3)_5X]^{2+/3+}$ ions was carried out using 65:35 or 55:45 mixtures of aqueous sodium hexanesulfonate (25 mM) and triethylamine (25 mM) adjusted to pH 3.5 (HCl), and a similar solution made up in 67.5% methanol-water. Each eluting reagent was filtered through a Whatman GF/F glass fiber filter, and then through a Nucleopore (0.4 μm) membrane filter, immediately prior to use.

Ion exchange separations were usually carried out on Sephadex SP-C25 cation exchange resin. Columns were loaded and eluted in an Isco refrigerated cabinet maintained at 4 °C.

Rate and Product Studies. Isomerization of $[Co(NH_3)_5SCN]Br_2$. A solution of $[Co(NH_3)_5SCN]Br_2$ (3 mg) and Λ-$[Co(en)_2$(*S*)-Val]$(ClO_4)_2$ (1 mg) in either 0.01 M CF_3SO_3H with 0.14 M $NaClO_4$ (1 cm^3) or in 0.15 M KSCN buffered to pH 5.59 (MES, 0.05 M, 1 cm^3) was thermostated at 25 °C. Samples (25 μL) were withdrawn daily and analyzed by HPLC (230 nm, AUFS = 0.5) for $[Co(NH_3)_5SCN]^{2+}$ and Λ-[Co-$(en)_2$(*S*)-Val$]^{2+}$ over a period of 20 days. Plots of log (area of $CoSCN^{2+}$/area of $CoVal^{2+}$) versus time were linear in both cases, giving first-order rate constants of 1.29×10^{-6} s^{-1} (pH 5.59) and 1.24×10^{-6} s^{-1} (0.01 M CF_3SO_3H) at 25 °C. Attempts to monitor the formation of $[Co(NH_3)_5NCS]^{2+}$ in these solutions were prevented by its crystallization as the bromide salt.

The formation of $[Co(NH_3)_5OH_2]^{3+}$ at pH 5.59 (MES, 0.05 M, 1 cm^3) and 25 °C in the absence of KSCN was also monitored over long reaction times (1–20 days) by separate injections (25 μL) using a higher detector sensitivity (AUFS = 0.1).

Anation of $[Co(NH_3)_5OH_2]^{3+}$ by NCS^-/SCN^-. A solution of $[Co(NH_3)_5OH_2](ClO_4)_3$ (10.54 mg) in 0.15 M KSCN (4.0 cm^3) containing 0.05 M MES buffer (pH 5.59) was maintained at 25 °C. The solution was sampled periodically (2–4-day intervals) and analyzed for $[Co(NH_3)_5NCS]^{2+}$ and $[Co(NH_3)_5OH_2]^{3+}$ by HPLC (230 nm). In a second experiment aimed at determining the immediate products of anation, 470 mg of $[Co(NH_3)_5OH_2](ClO_4)_3$ was dissolved in 5.0 cm^3 of 1.0 M NaSCN solution at 25.0 °C. After 4.0 h the solution was diluted with ice–water and loaded onto a column of Sephadex SP-C25 ion exchange resin maintained at 4 °C. The column was eluted with water (200 cm^3) and then with HCl (0.2 M) to remove the 2+ band. This was collected and rapidly reduced to dryness (rotary evaporator, 25 °C, ~0.5 mmHg). The residue was dissolved in H_2O (1.0 cm^3), and aliquots (70 μL) were immediately analyzed by HPLC (500 nm) to determine the distribution of $[Co(NH_3)_5SCN]^{2+}$ (23.4%) and $[Co(NH_3)_5NCS]^{2+}$ (76.6%).

Tracer Studies. Isomerization of $[Co(NH_3)_5SCN]^{2+}$ in the Presence of $N^{14}CS^-$. In a typical experiment $[Co(NH_3)_5SCN]Br_2$ (10 mg) was dissolved in 4 cm^3 of 0.15 M KSCN containing 0.05 M MES buffer (pH 5.59) and ~100 μCi of $KS^{14}CN$. Samples of this solution (2 × 15 μL) were diluted into water (50, 100 cm^3) for determination of the $S^{14}CN^-$ content. The remaining solution was sealed into five 2 cm^3 ampules, which were foil-wrapped and maintained at 25 °C. At appropriate time intervals an ampule was opened and 25 μL of its contents analyzed by HPLC for its $[Co(NH_3)_5SCN]^{2+}$ content. The remaining solution was then diluted with ice–water (~5 cm^3) and sorbed onto a column (1 × 5 cm) of Sephadex SP-C25 resin maintained at 4 °C. Washing with NaSCN solution (0.025 M, ~500 cm^3, 4 °C) removed most of the ionic $S^{14}CN^-$. The 2+ band was then eluted with HCl (0.1–0.4 M). This was rapidly reduced to dryness (rotary evaporator, ~0.1 mmHg) and the residue resorbed onto a second column of ion exchange resin. This was washed with HCl (0.05 M, 50 cm^3, 4 °C) and the 2+ fraction eluted and recovered as before. Sampling of the eluate immediately before emergence of this band showed the presence of negligible amounts of $S^{14}CN^-$ (0–10 cpm/cm^3 above background (40 ± 4 cpm)). The residue obtained following evaporation of the 2+ fraction was taken up in water (400 or 600 μL) and a quantity (50 or 100 μL) immediately injected into the HPLC. The separate $[Co(NH_3)_5SCN]^{2+}$ and $[Co(NH_3)_5NCS]^{2+}$ peaks were estimated by integration (500 nm), the complexes collected at the detector exit, and their volumes recorded. Samples of each fraction (1.0 cm^3) were counted to determine incorporation of ^{14}C label.

^{14}C Counting. Samples (1.0 cm^3) were added to Bray's scintillation fluid (9.0 cm^3) in Wheaton scintillation vials, and counted (5 or 10 min) using an LKB 1217 Rackbeta liquid scintillation counter. Quenching of $N^{14}CS^-/S^{14}CN^-$ activity was not observed for samples of [Co] < 10^{-4} M, and matrix effects were absent; identical activities were recorded in water, 0.1 M HCl, and the HPLC eluant (25 mM sodium *n*-hexanesulfonate in aqueous methanol). A quenching factor of 0.70 was found for coordinated $N^{14}CS^-$ by using $[Co(NH_3)_5N^{14}CS]Cl_2$ prepared from $NaS^{14}CN$ of known activity (1.05×10^{11} cpm/mol). Solutions of the labeled complex in water (9.4×10^{-5} and 4.7×10^{-5} M, 1.0 cm^3) gave measured activities (6910 and 3462 cpm/cm^3, respectively) which correspond to a specific activity of 7.35×10^{10} cpm/mol. A similar factor (0.68 ± 0.02) had previously been found for quenching of $N^{14}CS^-$ in the *t*-[Co(tren)$(NH_3)N^{14}CS]^{2+}$ system.[1]

Rate Equations and Mathematical Treatment. Schemes II and III give the reaction models on which the $N^{14}CS^-/S^{14}CN^-$ tracer results are based. The relevant rate equations are

$$d[CoSCN^{2+}]/dt = -(k_1 + k_{SCN(ip)} + k_2 + k_{NCS(ip)})[CoSCN^{2+}]$$

$$d[CoNCS^{2+}]/dt = k_1[CoSCN^{2+}]$$

$$d[CoOH_2{}^{3+}]/dt = k_2[CoSCN^{2+}] + k_2[CoS^{14}CN^{2+}] - (k_{SCN} + k_{NCS})[CoOH_2{}^{3+}]$$

$$d[CoS^{14}CN^{2+}]/dt = k_{SCN}[CoOH_2{}^{3+}] + k_{SCN(ip)}[CoSCN^{2+}] - (k_1 + k_2 + k_{NCS(ip)})[CoS^{14}CN^{2+}]$$

$$d[CoN^{14}CS^{2+}]/dt = k_{NCS}[CoOH_2{}^{3+}] + k_{NCS(ip)}[CoSCN^{2+}] + (k_1 + k_{NCS(ip)})[CoS^{14}CN^{2+}]$$

with $k_{NCS(ip)} = k_{SCN(ip)} = 0$ for Scheme II (cf. eq 3 with $N^{14}CS^-/S^{14}CN^-$ incorporation via $CoOH_2{}^{3+}$ only) and $k_{NCS(ip)}$ and $k_{SCN(ip)}$ to be determined for Scheme III. Rate constants k_1, k_2, k_{SCN}, and k_{NCS} are available from separate experiments under reaction conditions identical, or very similar, to those used in the tracer study. These rate constants are listed in Table II.

The above rate equations comprise a cascade of simple linear systems of matrix form $\vec{x}' = M\vec{x}$, and the solution is

$$\vec{x} = e^{tm}\vec{x}_0 \text{ for } \vec{x} = \begin{bmatrix} CoSCN^{2+} \\ CoNCS^{2+} \\ CoOH_2{}^{3+} \\ CoS^{14}CN^{2+} \\ CoN^{14}CS^{2+} \end{bmatrix}$$

Solutions for Scheme II are given by the dashed lines in Figure 3 (model without direct pathways for exchange; $k_{SCN(ip)} = k_{NCS(ip)} = 0$). For Scheme III the observed incorporations as a function of time led to estimates for the ratios $CoS^{14}CN^{2+}/(CoSCN^{2+} + CoS^{14}CN^{2+})$ and $CoN^{14}CS^{2+}/(CoNCS^{2+} + CoN^{14}CS^{2+})$, and parameters $k_{SCN(ip)}$ and $k_{NCS(ip)}$ were varied to achieve a least-squares fit to these data. Details of the method used in the derivation of these estimates, their distribution as a function of time, and the weights used in the fitting routine are available as supplementary material. It was assumed that the main source of experimental error occurred in the counts of the recovered $CoS^{14}CN^{2+}$ and $CoN^{14}CS^{2+}$ fractions, and these have been allowed for in the derivation of these estimated ratios. Likewise (in two cases) allowance was made in the error analysis for a small amount of isomerization of $CoS^{14}CN^{2+}$ to $CoN^{14}CS^{2+}$ on the ion exchange column used for their separation. All such details and their treatment are available on request.

The final least-squares fits lead to the full curves given in Figure 3 and to the $k_{SCN(ip)}$ and $k_{NCS(ip)}$ values listed in Table II. The contribution of errors to the experimental points is shown by the vertical error bars in the figures, and the significance of the $k_{SCN(ip)}$ and $k_{NCS(ip)}$ values at the 50%, 90%, 95%, and 99% levels (using Baysian probabilities) are shown by the contours given in Figure 1. This figure shows that the constants are reliable estimates.

Results

Terminology and Stereochemistry. In what follows $CoX^{2+/3+}$ abbreviations are used for the appropriate $[Co(NH_3)_5X]^{2+/3+}$ complex ions. Stereochemical retention is difficult to establish in this system, but no stereochemical change was found in the spontaneous aquation of trans-^{15}N-labeled $CoBr^{2+}$,[10] and very little,

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

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

[9] Buckingham, D. A.; Marzilli, L. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1967**, *89*, 5133.

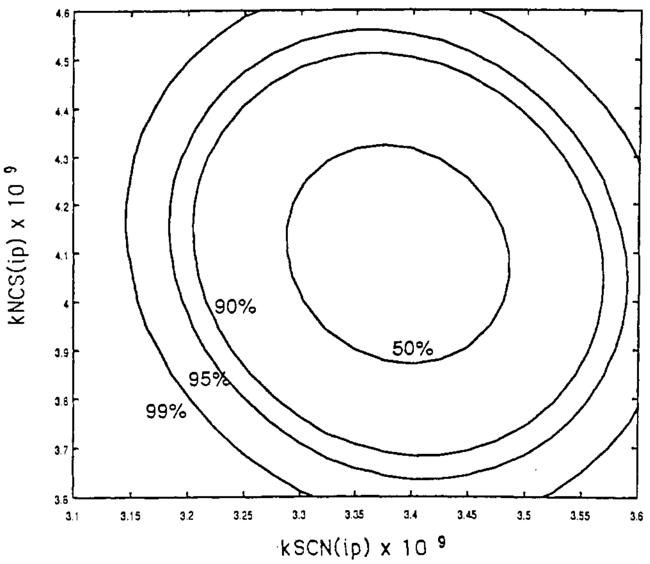


Figure 1. Significance contours for the $k_{NCS(ip)}$ and $k_{SCN(ip)}$ rate constants for the $CoSCN^{2+}$ system obtained using the experimental counting errors and Baysian probabilities (cf. supplementary material).

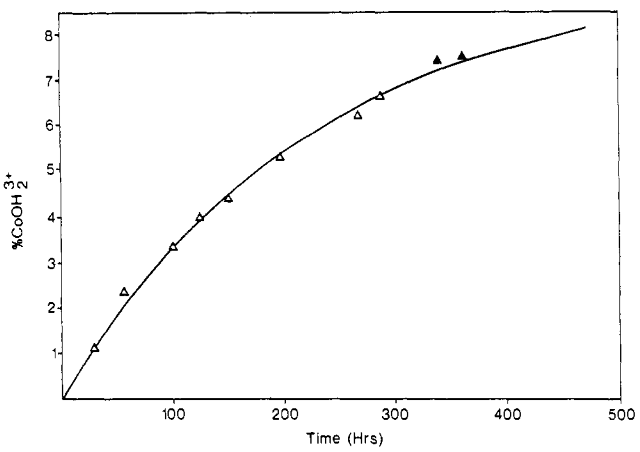
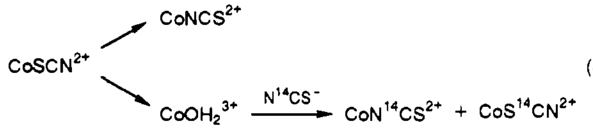


Figure 2. Percent $CoOH_2^{3+}$ production vs time results (Table S1) for the isomerization of $CoSCN^{2+}$ in 0.10 M (pH 5.59) MES buffer (△) and in 0.01 M CF_3SO_3H (▲) at 25.0 °C. The solid curve is the computed first-order fit using a rate constant of 1.29×10^{-6} s^{-1} (infinite time 9.1%).

if any, occurred in the reverse anation of trans-^{15}N-labeled $CoOH_2^{3+}$.[10] The similar chemistry reported here suggests that stereochemical retention will be maintained in the spontaneous isomerization of $CoSCN^{2+}$, and for the incorporations of ionic $N^{14}CS^-$ and $S^{14}CN^-$.

Reaction Products. At the outset it was important to quantify the products of the spontaneous reaction. In particular it was important to establish whether or not any aquation occurred since if so this would give $N^{14}CS^-$ incorporations via subsequent anation of $CoOH_2^{3+}$, eq 3. It would then be necessary to distinguish this process from any direct incorporation (eq 2).



$$CoSCN^{2+} \rightarrow CoNCS^{2+}; \quad CoSCN^{2+} \rightarrow CoOH_2^{3+} \xrightarrow{N^{14}CS^-} CoN^{14}CS^{2+} + CoS^{14}CN^{2+} \qquad (3)$$

When an aqueous solution of chromatographically pure $CoSCN^{2+}$ in 0.10 M MES buffer (pH 5.59) was allowed to react for several days at 25.0 °C, HPLC analysis showed large amounts of $CoNCS^{2+}$ product, some $CoOH_2^{3+}$, and a small amount of unreacted starting material. The gradual formation of $CoOH_2^{3+}$ was confirmed by the experiments described below in which its production as a function of time was followed. These data (Table S1 in the supplementary material and Figure 2) extrapolate to 9.1 ± 0.3% $CoOH_2^{3+}$ at $10t_{1/2}$. They include measurements in 0.01 M CF_3SO_3H, as well as at pH 5.59, and this demonstrates that $CoOH_2^{3+}$ does not arise by an OH^--catalyzed process (which certainly leads to some hydrolysis[4]). Although not specifically analyzed for, small amounts of $CoOH_2^{3+}$ consistent with the expected result (cf. Figure 3c) were also observed in HPLC chromatograms in the experiment using 0.15 M NaNCS. Also, control experiments were carried out to show that $CoOH_2^{3+}$ does not result from subsequent aquation of the major $CoNCS^{2+}$ product.

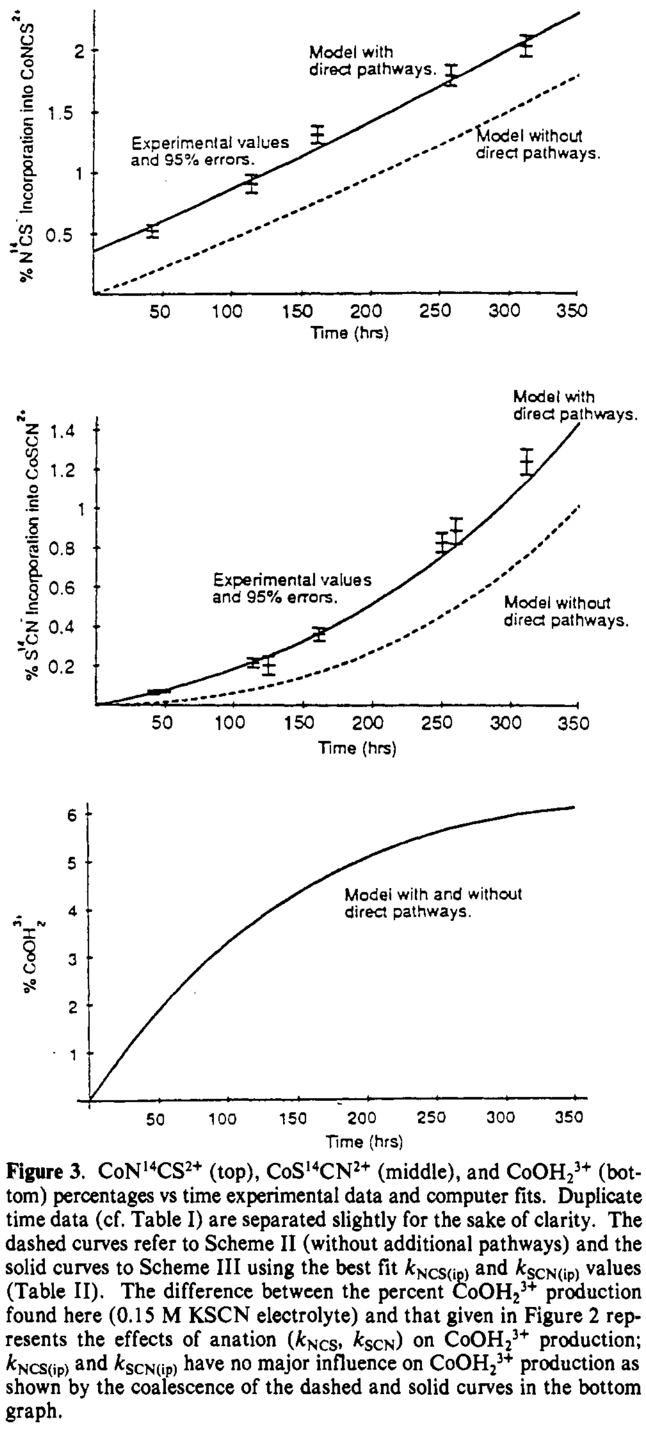


Figure 3. $CoN^{14}CS^{2+}$ (top), $CoS^{14}CN^{2+}$ (middle), and $CoOH_2^{3+}$ (bottom) percentages vs time experimental data and computer fits. Duplicate time data (cf. Table I) are separated slightly for the sake of clarity. The dashed curves refer to Scheme II (without additional pathways) and the solid curves to Scheme III using the best fit $k_{NCS(ip)}$ and $k_{SCN(ip)}$ values (Table II). The difference between the percent $CoOH_2^{3+}$ production found here (0.15 M KSCN electrolyte) and that given in Figure 2 represents the effects of anation (k_{NCS}, k_{SCN}) on $CoOH_2^{3+}$ production; $k_{NCS(ip)}$ and $k_{SCN(ip)}$ have no major influence on $CoOH_2^{3+}$ production as shown by the coalescence of the dashed and solid curves in the bottom graph.

The 9.1% result is substantially more than was suggested by the qualitative ion exchange experiment reported previously (<2% in 0.01 M $HClO_4$ at 40 °C;[4] ~0% at 95 °C[6]). Since the reactant gave some $CoOH_2^{3+}$ (in addition to major amounts of the $CoNCS^{2+}$), it became necessary to establish the rate of the

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(10) Brasch, N. E.; Buckingham, D. A.; Clark, C. R.; Finnie, K. S. *Inorg. Chem.* **1989**, *28*, 3386.

Table I. Incorporation of $S^{14}CN^-/N^{14}CS^-$ into $[Co(NH_3)_5SCN]^{2+}$ and Its Isomerized Product $[Co(NH_3)_5NCS]^{2+}$, pH 5.59, 25 °C, $[SCN^-]$ = 0.15 M

	time (h)	$CoSCN^{2+}$ + $CoS^{14}CN^{2+}$ (10^7 mol)	vol (cm^3)	cpm/ cm^3 [a]	cpm (total)	$CoS^{14}CN^{2+}$ [b] (10^9 mol)	mol % $CoS^{14}CN^{2+}$ [c]	σ [f]
$CoSCN^{2+}$	42	19.0	5.0	45.0	225	1.13	0.060	0.005
	48.5	5.28	3.6	112.4	405	0.363[d]	0.069	0.003
	48.5	7.44	3.9	144.6	564	0.505[d]	0.068	0.003
	114	6.68	4.0	70.1	280	1.41	0.21	0.012
	125	1.50	2.5	133.3	333	2.99[d]	0.20	0.008
	161	6.36	4.2	107.6	452	2.27	0.36	0.017
	252	6.20	4.4	230.1	1012	5.08	0.82	0.025
	257	3.82	4.2	159.4	670	3.37	0.88	0.033
	311	5.08	4.2	296.4	1245	6.26	1.23	0.033
$CoNCS^{2+}$	42	3.70	3.9	84.6	330	1.66	0.45 (0.52)[e]	0.026
	114	3.94	5.1	138.3	705	3.54	0.90 (0.90)[e]	0.038
	161	5.40	4.8	277.2	1331	6.69	1.24 (1.36)[e]	0.035
	257	7.00	6.0	410.2	2461	12.4	1.77 (1.78)[e]	0.041
	311	6.08	5.1	474.7	2421	12.2	2.00 (2.03)[e]	0.043

[a] Obtained using a 5-min count time and corrected for a background of 40 ± 4 cpm. [b] Corrected for 30% quenching by coordination to Co(III), and compared to a reaction medium which contained 2.84×10^{11} cpm/mol of labeled $N^{14}CS^-$. [c] Column 6 of table divided by column 2 and multiplied by 100. [d] For these experiments the reaction medium contained $N^{14}CS^-$ equivalent to 1.595×10^{12} cpm/mol. [e] The values in parentheses are the observed values corrected for dilution due to isomerization of $CoS^{14}CN^{2+}$ during workup. These corrected values are the ones plotted in Figure 3. [f] Standard deviation at the 95% significance level.

isomerization reaction, as well as the rate of anation of $CoOH_2^{3+}$ by NCS^- under the same conditions.

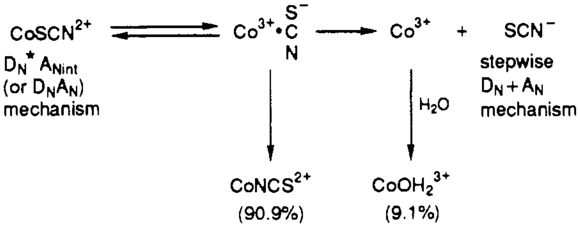
Rates of the Isomerization Reaction. HPLC monitoring of $CoSCN^{2+}$ dissolved in 0.01 M CF_3SO_3H, and in a separate experiment dissolved in pH 5.59 buffer containing 0.15 M KSCN, led to essentially identical rate constants for its decay (viz., 1.24×10^{-6} and 1.29×10^{-6} s^{-1}, respectively, at 25 °C). Similar monitoring of $CoOH_2^{3+}$ production from $CoSCN^{2+}$ in the presence of 0.10 M MES buffer (pH 5.50), 25 °C, gave a rate constant of 1.29×10^{-6} s^{-1} (cf. Figure 2 and Table S1). These data compare with an earlier spectrophotometric value of $(8.1 \pm 0.1) \times 10^{-7}$ s^{-1} at pH 3 in 1 M $NaClO_4$.[4]

Rate and Products of Anation by NCS^-. Rate data, as well as the distribution of the two products $CoNCS^{2+}$ and $CoSCN^{2+}$, have previously been reported by Jackson, Jurisson, and McGregor.[11] However, we felt it important to obtain this data under our experimental conditions using the direct HPLC method for analysis. In 0.15 M KSCN (0.05 M MES buffer, pH 5.59) HPLC monitoring of $CoOH_2^{3+}$ gave a linear plot of log $[CoOH_2^{3+}]$ vs time, $k_{obs} = 2.9 \times 10^{-7}$ s^{-1}, corresponding to a half-time for anation of 27.4 days. Initial production of $CoNCS^{2+}$ followed this same rate, and although some $CoSCN^{2+}$ was also produced (see below), its near absence in the chromatograms at long times is in agreement with its more rapid isomerization under the conditions (see above). The value of k_{An} $(=k_{obs}/[NCS^-])$ $(2.0 \times 10^{-6}\ M^{-1}\ s^{-1})$ compares favorably with the values 2.2×10^{-6} and 8.6×10^{-7} M^{-1} s^{-1} found by Jackson et al.[11] in 0.5 and 1.0 M NaSCN, respectively. The direct HPLC measurement of the $CoNCS^{2+}/CoSCN^{2+}$ distribution after 4 h in 1.0 M NaSCN solution gave 76.6% $CoNCS^{2+}$ and 23.4% $CoSCN^{2+}$. This also compares favorably with 74 ± 1% and 26 ± 1%, respectively, found by Jackson et al. using an indirect analytical method.[11]

Incorporation of $N^{14}CS^-$ during Isomerization. This experiment was carried out using a buffered (pH 5.59) aqueous solution of $CoSCN^{2+}$ in the presence of 0.15 M KSCN and added $KS^{14}CN$. The solution was sampled periodically, and $CoNCS^{2+}$ and $CoSCN^{2+}$ were separated and analyzed for by HPLC. Their separate ^{14}C activities were then measured. Results are given in Table I.[1]

This data shows that $N^{14}CS^-$ is incorporated into both the $CoSCN^{2+}$ reactant and the $CoNCS^{2+}$ product, and that these amounts increase with time. However, the incorporations are not large. For example, after 311 h ($2t_{1/2}$ for isomerization) the remaining $CoSCN^{2+}$ contained only 1.23% of label while the $CoNCS^{2+}$ product contained 2.03%. Particularly at early times the low incorporations (e.g., 0.06% into $CoSCN^{2+}$ after 42-h reaction) were such that extreme care was necessary to remove all residual $S^{14}CN^-$ activity from the sample prior to ^{14}C counting. This was achieved by extensive washing on an ion exchange column at 4 °C, followed by HPLC separation of $CoSCN^{2+}$ from $CoNCS^{2+}$. In one or two samples partial isomerization of $CoSCN^{2+}$ had occurred during ion exchange chromatography and subsequent workup, and this resulted in dilution of the ^{14}C label in the $CoNCS^{2+}$ product. This was allowed for in the final result by comparing the $CoSCN^{2+}/CoNCS^{2+}$ ratio obtained immediately from the reaction mixture with that obtained following workup. Such corrections were never large (maximum 14% of $CoNCS^{2+}$ activity, 42-h sample), and were taken care of in the error analysis (cf. Experimental Section). Control experiments (carried out on the similar *t*-$[Co(tren)(NH_3)NCS]^{2+}$ complex ion)[12] showed that no significant ^{14}C tracer is incorporated into the $CoNCS^{2+}$ product over the time course of the isomerization.

Scheme I



Discussion

Interpretation of Experimental Results. Our first aim was to establish whether or not the spontaneous reaction gave only a $CoNCS^{2+}$ product (eq 2), or whether some $CoOH_2^{3+}$ was also formed, eq 3. The latter was found to be true. The $CoNCS^{2+}$ product must arise from an intramolecular switch since its amount is Co(III) concentration independent and the reaction occurs in the absence of added NCS^-.[3,4] The $CoOH_2^{3+}$ product (9.1 ± 0.3%) must arise from some sort of competitive entry of solvent. This could occur via a $D_N{}^*A_{Nint}$ or D_NA_N mechanism[13] without the formation of a discrete, solvent-equilibrated five-coordinate Co^{3+} intermediate, or it could arise from mixed mechanisms (of similar energies), with H_2O entry occurring via a stepwise $D_N + A_N$ process[13] and a liberated Co^{3+} intermediate, Scheme I.

The former interpretation is favored in view of the fact that ion-paired, rather than bulk solvent, $S^{14}CN^-/N^{14}CS^-$ is thought to enter the coordination sphere (see below), but the alternative mechanism involving a completely dissociative pathway for

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(11) Jackson, W. G.; Jurisson, S. S.; McGregor, B. C. *Inorg. Chem.* **1985**, *24*, 1788.

(12) Information available as supplementary material.

(13) Cf. IUPAC recommendations for reaction mechanism: *Pure Appl. Chem.* **1989**, *61*, 23-56.

Scheme II

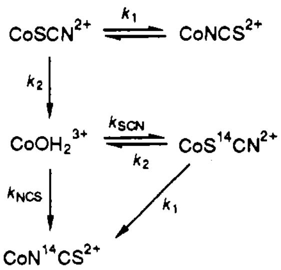


Table II. Observed and Derived First-Order Rate Constants (s^{-1}) for Isomerization (k_I, k_1), Aquation (k_2), Anation (k_{An}, k_{NCS}, k_{SCN}), and Exchange ($k_{NCS(ip)}$, $k_{SCN(ip)}$) in the $CoSCN^{2+}/CoOH_2^{3+}$ System at 25.0 °C, $I = 0.15$ (KSCN)

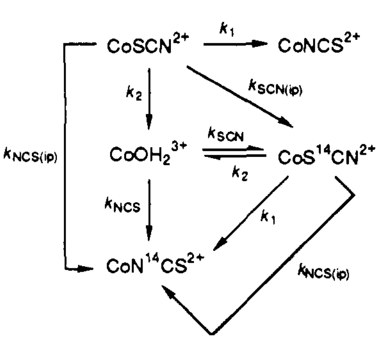
	(a) Observed Rate Constants[a]
k_I	1.26×10^{-6}
k_{an}	2.9×10^{-7} (2.0×10^{-6})
	(b) Derived Rate Constants[a]
k_1[b]	1.14×10^{-6}
k_2[b]	1.2×10^{-7}
k_{SCN}[c]	6.8×10^{-8} (4.5×10^{-7})
k_{NCS}[c]	2.22×10^{-7} (1.48×10^{-6})
$k_{SCN(ip)}$[d]	$(3.39 \pm 0.22) \times 10^{-9}$ (2.31×10^{-8})
$k_{NCN(ip)}$[d]	$(4.10 \pm 0.41) \times 10^{-9}$ (2.7×10^{-8})

[a] Values in parentheses are second-order rate constants, obtained using the relationship $k = k_{obs}/0.15$ ($M^{-1}\ s^{-1}$). [b] Derived from the observed division of products $CoNCS^{2+}/CoOH_2^{3+}$ found for the spontaneous reaction (see Results); $k_I = k_1 + k_2$. [c] Derived from the observed division of products $CoNCS^{2+}/CoSCN^{2+}$ found for anation of $CoOH_2^{3+}$ by NCS^-; $k_{An} = k_{NCS} + k_{SCN}$. [d] Obtained from the excess $CoN^{14}CS^{2+}$ and $CoS^{14}CN^{2+}$ incorporations into the product and reactant, respectively. Errors are at the 95% significance level (cf. Figure 1).

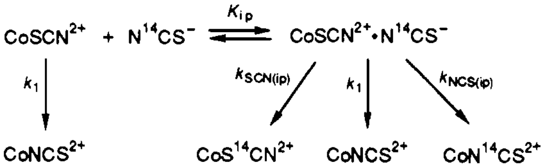
$CoSCN^{2+}$ would roughly correlate the expected number of collisions between Co^{3+} and NCS^- in the lifetime of the encounter ion pair (~10–100) to the 9.1% $CoOH_2^{3+}$ production.[14] Furthermore, production of $CoOH_2^{3+}$ and $CoNCS^{2+}$ appears to be associated with, on the one hand, the ease of breaking the Co–S bond, and on the other to the nucleophilicity of the N end of the departing thiocyanate ligand. Thus, for the related *t*-$[Co(tren)(NH_3)SCN]^{2+}$ system the 5.2 ± 0.1% *t*-$CoOH_2^{3+}$ formed in the spontaneous reaction[12] (analogous to that described here) is to be compared with the 20% and 42% *t*-$CoOH_2^{3+}$ formed in the Ag^+ and Hg^{2+} catalyzed processes,[1] and with the 100% *t*-$CoOH_2^{3+}$ formed by that part of the silver-catalyzed reaction which is second-order in $[Ag^+]$.[1] These increasing amounts of $CoOH_2^{3+}$ correlate with larger rate constants, spontaneous < Ag^+ < Hg^{2+} ≤ $[Ag^+]^2$,[2] and with the decreasing basicity of the N end of the departing ligand (presumably the $[Ag^+]^2$ term arises from attachment of silver to both S and N).[1]

The formation of $CoOH_2^{3+}$ provides an important route for $N^{14}CS^-$ and $S^{14}CN^-$ entry, eq 3, and this must be allowed for in the tracer analysis. Scheme II gives the reaction model used for doing this, and by using the derived rate constants k_1, k_2, k_{NCS}, and k_{SCN} listed in Table II (which allow for the various products of isomerization and anation), the amounts of $CoS^{14}CN^{2+}$, $CoN^{14}CS^{2+}$, and $CoOH_2^{3+}$ as a function of time can be evaluated (cf. Experimental Section).[15] These are given by the dashed curves in Figure 3. Comparison with the experimental data also given in the figures (cf. Table I) shows excess $N^{14}CS^-$ and $S^{14}CN^-$ incorporations *over and above* those possible via anation of $CoOH_2^{3+}$. This is especially so at the shorter reaction times.

Scheme III



Scheme IV



It is these excesses which are important. They can be allowed for by including *direct paths* for exchange of $S^{14}CN^-$ into the reactant ($k_{SCN(ip)}$), and for the incorporation of $N^{14}CS^-$ into the product ($k_{NCS(ip)}$). The revised model, given by Scheme III, has solutions (cf. Experimental Section) represented by the full curves of Figure 3. These curves use best fit $k_{SCN(ip)}$ and $k_{NCS(ip)}$ values (given in Table II). Agreement with experiment is now excellent.

Reaction Mechanism. It is now appropriate to consider what this model (Scheme III) means in terms of reaction mechanism. The excess $CoN^{14}CS^{2+}$ formed as a result of direct $N^{14}CS^-$ entry during isomerization in 0.15 M KSCN amounts to 0.36% ($k_{NCS(ip)}/k_1$, Table II). In terms of Figure 3 this represents the difference between the full and dashed curves. Its constancy as a function of time is in agreement with the requirements of the model (this constancy is only slightly modified by that part of k_1 from $CoS^{14}CN^{2+}$ which arises from the direct $k_{SCN(ip)}$ process), and this means that out of every approximately 300 acts of internal isomerization only one of them leads to *direct* $N^{14}CS^-$ entry. Such entry must occur via an associated species which precedes the formation of $CoOH_2^{3+}$, and this is taken to be the ion-paired reactant. If an ion pair constant (K_{ip}, Scheme IV) of 1.0 M^{-1} is chosen for this species,[16] then some 2.8 acts of $N^{14}CS^-$ entry per 100 acts of NCS^- entry (i.e., $k_{NCS(ip)}/k_1 = 2.85 \times 10^{-2}$) arise from within this species. This calculation assumes equal reactivities of the ion-paired and non-ion-paired complexes, which is in agreement with the absence of a NCS^- concentration effect on the isomerization rate, and with current thinking.[17] If NCS^- entry from within the ion pair had resulted at any stage in equivalence of the two thiocyanates, then this result would necessarily have been 50:50 ($k_{NCS(ip)}/k_1 = 1.00$, Scheme IV).[18] Thus, the two thiocyanates remain distinct throughout the substitution process. Likewise, $k_{SCN(ip)}/k_1 = 0.30\%$ (Table II), and using $K_{ip} = 1.0\ M^{-1}$ gives some 2.3 acts of $S^{14}CN^-$ entry to give $CoS^{14}CN^{2+}$ per 100 acts of isomerization within the ion pair. It is not known how this compares with the return of unlabeled SCN^- since this process is not observable, but we feel that incorporation of the sulfur atom is also unlikely to represent a complete scrambling process.

If, on the other hand, a *specific* ion pair was chosen such that only $N^{14}CS^-$ adjacent to the leaving group enters the coordination sphere (such as in 3), and if interchange occurred such that at some stage the two thiocyanates of this ion pair became equivalent,

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(14) Another argument against OH_2 entry occurring via a separate dissociative $D_N + A_N$ process is that in the Hg^{2+}-catalyzed reaction in the presence of added NO_3^- the $CoONO_2^{2+}$ production is competitive with the formation of *both* $CoNCS^{2+}$ and $CoOH_2^{3+}$.[1]

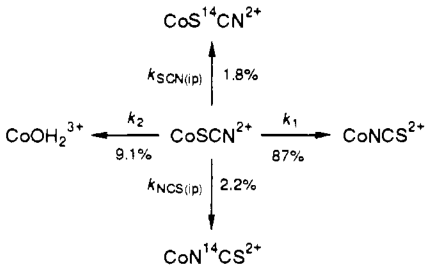
(15) Use of the derived rate constants k_1 and k_2 assumes that the 9.1% $CoOH_2^{3+}$ is formed in both the presence and absence of added NaNCS. This was only qualitatively established.

(16) K_{ip} values for 2+ complexes with 1− anions at $I = 0.1$ M are in the vicinity of 1–10 M^{-1}; cf. Archer, D. W.; East, D. A.; Monk, C. B. *J. Chem. Soc.* **1965**, 720.

(17) Burnett, M. G. *J. Chem. Soc. A* **1970**, 2486 and 2490.

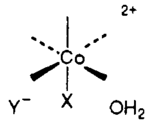
(18) If an ion pair constant (K_{ip}) of 10 M^{-1} were chosen, then $k_{NCS(ip)}/k_1 = 6.0 \times 10^{-3}$, and each act of $N^{14}CS^-$ entry from within the ion pair would be associated with 170 acts of internal isomerization. The conclusions following in the text remain.

Scheme V



then the present results would require $K_{ip(specific)}$ to be about 0.025 M^{-1}. It is likely that the experimental K_{ip} value (of 1–10 M^{-1})[16] represents the average of several stereo ion pairs, and we would expect those ion pairs on the front face adjacent to the anionic leaving group to be less favored than those on the more positively charged back face. However, we are inclined to believe that a specific ion pair constant of 0.025 M^{-1} is just too small, and that equivalence between the two thiocyanates in a transition state such as **3**, or in a subsequent intermediate, does not occur. Certainly our result requires that if complete severance of the Co–S bond occurs prior to $N^{14}CS^-$ entry (and NCS^- reentry) the various stereochemically distinct ion-paired $Co^{3+}{\cdot}NCS^-{\cdot}N^{14}CS^-$ intermediates do not equilibrate in their lifetime; i.e., rotation within the intermediate must be slow compared to bond formation.

Comparison with Related Systems. It is instructive to compare our results with those of Jackson, McGregor, and Jurisson who studied the direct entry of NCS^-/SCN^- during the spontaneous aquation of other $[Co(NH_3)_5X]^{2+}$ complexes.[19] For anionic leaving groups such as $CH_3SO_3^-$, $CF_3SO_3^-$, and ClO_4^- where direct measurement was possible, they found 1.6–2.6% of both $CoNCS^{2+}$ and $CoSCN^{2+}$ (total 3–5%) were formed in 1.0 M NaNCS.[20] If the direct exchange paths found here increase proportionally with increasing NCS^-/SCN^- concentration, then our results in 1.0 M NaNCS would be similar to these; cf. Scheme V (2.2% $CoN^{14}CS^{2+}$, 1.8% $CoS^{14}CN^{2+}$).[21] This correspondence is, we believe, significant. It suggests similar transition states, with entry of NCS^-/SCN^- not being very sensitive to the leaving group, nor to its eventual fate. Just as much NCS^-/SCN^- enters from ion pair **3** (where the leaving group itself reenters to a major extent) as from ion pair **4** ($Y^- = NCS^-$). The single most important feature appears to be the presence of Y^- adjacent to the reaction site. It then enters, probably exclusively from a particular stereochemical location.[22]



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If Y^- is not present at that site, then the site will be occupied by the solvent OH_2, which gains entry. For $CoSCN^{2+}$ the N end of the leaving group must occupy a site otherwise taken up by OH_2 or Y^-, and N gains entry instead. In this case, because the leaving group is presumably in an excited vibrational state, it is probably not solvated to the same extent as ion-paired Y^-, so that a larger preference for its reentry over Y^- and OH_2 is likely. This can be seen in the $CoSCN^{2+}$ system, but for most CoX^{2+} immediate reentry of the same X^- cannot be detected.

Summary. The main result of this study is clear. Added NCS^- and SCN^- enters the coordination sphere during the intermolecular isomerization of $CoSCN^{2+}$ in aqueous solution. Some OH_2 also becomes coordinated. It appears that the amount of NCS^-/SCN^- entry is similar to that found for other CoX^{2+} ions under similar circumstances. This suggests similar transition states, with entry occurring from sites immediately adjacent to the leaving group with little or no additional activation. A $D_N{*}A_{Nint}$ or D_NA_N mechanism is implied. This view differs from that arrived at by Jackson et al. in a recent mixed anion competition study.[23]

Registry No. $Co(NH_3)_5SCN^{2+}$, 15005-69-3; $Co(NH_3)_5OH_2^{3+}$, 14403-82-8.

Supplementary Material Available: Table S1 giving mol % t-$CoOH_2^{3+}$ and $CoOH_2^{3+}$ produced in the spontaneous isomerization of t-$CoSCN^{2+}$ and $CoSCN^{2+}$ in MES buffer (0.05 and 0.10 M, respectively, pH 5.70 and 5.59, respectively) at 25.0 °C, as a function of time (h), Table S2 giving production of t-$CoSCN^{2+}$ and t-$CoNCS^{2+}$ on the anation of t-$CoOH_2^{3+}$ at 25 °C and in 1.0 M NaSCN, pH 3.0, Table S3 giving incorporation of $N^{14}CS^-$ into t-$[Co(tren)(NH_3)NCS]^{2+}$ for $[NCS^-]$ = 0.15 M solutions, at 25.0 °C and pH 5.62 (0.05 M MES buffer), Table S4 giving incorporations of $S^{14}CN^-$ and $N^{14}CS^-$ into t-$[Co(tren)(NH_3)SCN]^{2+}$ and its isomerized product t-$[Co(tren)(NH_3)NCS]^{2+}$ in $[NCS^-]$ = 0.15 M solutions, at 25.0 °C and pH 5.62, Table S5 giving observed and derived first-order rate constants (s^{-1}) for isomerization (k_I, k_1), aquation (k_2), anation (k_{an}, k_{NCS}, k_{SCN}), and exchange ($k_{NCS(ip)}$, $k_{SCN(ip)}$) for the t-$[Co(tren)(NH_3)SCN]^{2+}$ reaction and a comparison with the similar rate constants listed in Table II for the $[Co(NH_3)_5SCN]^{2+}$ system, textual description of the analytical method used to follow $CoN^{14}CS^{2+}$/t-$CoN^{14}CS^{2+}$ and $CoS^{14}CN^{2+}$/t-$CoS^{14}CN^{2+}$ production as a function of time, according to the reaction models given by Schemes II and III (this includes an analysis of the experimental errors leading to the Baysian probability distributions of Figures 1 (text) and S1), Figure S1 showing significance contours for $k_{NCS(ip)}$ and $k_{SCN(ip)}$ for the t-$CoSCN^{2+}$ isomerization reaction, obtained using counting errors and the Baysian probability distribution mentioned above, Figure S2 showing production vs time curves for the data listed in Table S1 (includes both $CoOH_2^{3+}$ and t-$CoOH_2^{3+}$ data), and Figure S3 showing t-$CoN^{14}CS^{2+}$ (top), t-$CoS^{14}CN^{2+}$ (middle), and t-$CoOH_2^{3+}$ (bottom) percentage vs time experimental data and computer fits [duplicate time data (cf. Table S4) are slightly separated for the state of clarity; the dashed curves refer to Scheme II (with no direct exchange pathways) and the solid curves to Scheme III where the best fit $k_{NCS(ip)}$ and $k_{SCN(ip)}$ values (Table S5) in addition to k_{NCS} and k_{SCN} are used; clearly $k_{SCN(ip)} \simeq 0$ (coalescence of dashed and solid curves for middle graph), and $k_{NCS(ip)}$ has no obvious influence on t-$CoOH_2^{3+}$ production; the difference between the % $CoOH_2^{3+}$ production given here and in Figure S2 (bottom curve) represents the effects of subsequent anation of t-$CoOH_2^{3+}$ (k_{NCS}, k_{SCN}), and this is seen to be appreciable for this system] (12 pages). Ordering information is given on any current masthead page.

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(19) Jackson, W. G.; McGregor, B. C.; Jurisson, S. S. *Inorg. Chem.* **1987**, *26*, 1286.

(20) For neutral leaving groups somewhat more $CoNCS^{2+}$ (compared to $CoSCN^{2+}$) was found, with the total being somewhat larger (5–13%); cf. ref 19.

(21) A similar calculation based on Scheme IV, with entry of $N^{14}CS^-$/$S^{14}CN^-$ occurring only through the ion pair, would lead to somewhat smaller amounts of $CoN^{14}CS^{2+}$ (1.4%) and $CoS^{14}CN^{2+}$ (1.2%) in 1 M $N^{14}CS^-$.

(22) At least four stereochemical locations are possible for entering groups about the site of the leaving group, so that competitive entry of Y^- and OH_2 is still possible within a specific ion pair.

(23) Jackson, W. G.; McGregor, B. C.; Jurisson, S. S. *Inorg. Chem.* **1990**, *29*, 4677.