Inorg. Chem. **1985**, *24*, 1788–1790

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Simple Thiocyanate Ion Substitution Reactions: Not So Simple?

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Received August 9, 1984

The SCN^- anation reaction of $(NH_3)_5CoOH_2^{3+}$ involves the hitherto unrecognized formation of the unstable S-bonded $(NH_3)_5CoSCN^{2+}$ ion (26%), produced in parallel with the stable N-bonded complex $(NH_3)_5CoNCS^{2+}$ (74%). The kinetic S isomer/N isomer ratio (0.36 ± 0.01) at 25 °C is the same for 0.5, 1.0, and 3.1 M NaSCN. Second-order total (k_{NCS}) and individual anation rate constants have been determined, by ion-exchange analyses at early reaction times, without interference from the ensuing S- to N-linkage isomerization process ($k = 8.2 \times 10^{-7}$ s^{-1}):[12] for I = 0.5, 1.0, and 3.1 M, $10^7 k_{NCS}$ = 11.0, 8.7, and 8.4 M^{-1} s^{-1}, respectively. Reasons for the formation and subsequent decay of the S isomer going undetected in the several previous studies are considered.

The thiocyanate ion is a widely used[1-8] anion in kinetic studies of substitution reactions, e.g.:

$$Fe(OH_2)_6^{3+} + SCN^- \rightarrow Fe(OH_2)_5NCS^{2+}$$

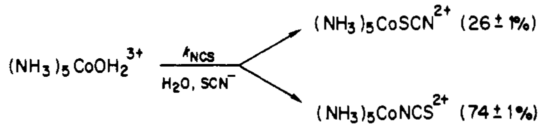
$$Mo(OH_2)_6^{3+} + SCN^- \rightarrow Mo(OH_2)_5NCS^{2+} \qquad (1)$$

$$(NH_3)_5CoOH_2^{3+} + SCN^- \rightarrow (NH_3)_5CoNCS^{2+}$$

The major reasons for the choice of SCN^- appear to be the following: (i) reactions are fairly readily forced to completion because it strongly complexes most metal ions. (ii) Large absorbance changes amenable to spectrophotometric study are usual. (iii) It is relatively stable and feebly basic;[9] thus, it can be used in acidic and basic solution. While certainly the alternative N- and S-bonding modes are well recognized,[10] it is practice to consider one or the other, rather than both, as prospects in *simple* substitution reactions. The less stable linkage isomer in Co(III) chemistry,[10] the S-bonded form, was thought to arise as a product only under special circumstances, e.g., in inner-sphere electron-transfer reactions involving the migration of SCN^- from one metal ion to another[11] and in the induced and base-catalyzed reactions[12-14] of (amine)$_5$CoX^{n+} in aqueous SCN^-. However, herein we demonstrate that the *simple* and classical[2] SCN^- substitution reaction of $(NH_3)_5CoOH_2^{3+}$ involves the hitherto unrecognized formation of *both* $(NH_3)_5CoSCN^{2+}$ and $(NH_3)_5CoNCS^{2+}$. This result emphasizes the generality of this possibility for SCN^- substitution reactions of other[4-8] metal ion complexes. Reasons why this prospect may have gone undetected (rather than overlooked) are considered.

Results and Discussion

The aqua complex $(NH_3)_5CoOH_2^{3+}$ in 1.00 M NaSCN (pH ~3) was reacted for 5.0 h at 25.0 °C. Recovered $(NH_3)_5CoOH_2^{3+}$ was separated from $(NH_3)_5Co(SCN)^{2+}$ product by ion-exchange chromatography. The cobalt concentrations and S isomer/N isomer ratio for $(NH_3)_5Co(SCN)^{2+}$ were determined by an accurate spectrophotometric method recently described.[14] Although the SCN^- anation reaction has proceeded only a few percent, the amount of $(NH_3)_5Co(SCN)^{2+}$ (1.53 ± 0.06 (3)%)[15] and the S/N ratio ($0.35_9 \pm 0.00_9$ (3))[15] are nonetheless well-defined. Also, S to N rearrangement of $(NH_3)_5CoSCN^{2+}$ is insignificant in this time (5 h; $t_{1/2}$ = 9.5 days, 25 °C).[12] Thus, both linkage isomers are formed in parallel, the S isomer in a hitherto unrecognized proportion:



(2)

The data allow a convenient determination of the *total* anation rate constant k_{NCS}. The reaction is pseudo-first-order since $[SCN^-] \gg [Co]$, and thus

$$1 - [Co(SCN)^{2+}]/[\text{total Co}] = \exp[-k_{NCS}[SCN^-]t] \qquad (3)$$

where Co(SCN)$^{2+}$ refers to CoSCN^{2+} plus CoNCS^{2+}. The result, $k_{NCS} = (8.6 \pm 0.4) \times 10^{-7}$ M^{-1} s^{-1}, was confirmed by reacting the aqua complex in 1.00 M NaSCN for both shorter (~2 h; 0.63% Co(SCN)$^{2+}$) and longer (~7 h; 2.1_2% Co(SCN)$^{2+}$) periods. The constant k_{NCS} value ($10^7 k$ = 8.8 and 8.5 M^{-1} s^{-1}, respectively) and, in addition, the invariance of the S/N ratio (0.35 (1) and 0.38 (1), respectively) are consistent with the analysis according to eq 2.

Experiments were carried out also for 0.5 and 3.1 M NaSCN (pH ~3–4). The former conditions correspond to those used by Pearson and Moore[3] in work including the $(NH_3)_5CoOH_2^{3+}/SCN^-$ reaction, and the latter (together with 1.0 M NaSCN) are conditions employed in our concurrent studies on SCN^- competition in the spontaneous, base-catalyzed and induced aquation reactions of a wide range of $(NH_3)_5CoX^{n+}$ complexes.[14,16] Again, both $(NH_3)_5CoSCN^{2+}$ and $(NH_3)_5CoNCS^{2+}$ were found as the immediate products, in precisely the same ratio (0.5 M SCN^-, S/N = $0.35_4 \pm 0.01_0$(4); 3.1 M SCN^-, S/N = $0.36_8 \pm 0.01_0$(2); cf. 1.0 M SCN^-, S/N = 0.36). The magnitudes of the anation rate constants (0.5 M SCN^-, $k_{NCS} = 11.0 \times 10^{-7}$ M^{-1} s^{-1}; 3.1 M SCN^-, $k_{NCS} = 8.4 \times 10^{-7}$ M^{-1} s^{-1}; cf. 1.0 M SCN^-, $k_{NCS} = 8.6 \times 10^{-7}$ M^{-1} s^{-1}) are consistent with the assumed linear dependence of the rate on $[SCN^-]$. The slight reduction in the second-order rate constant, more apparent on going from 0.5 to 1.0 M than from 1.0 to 3.1 M SCN^-, is a usual consequence of increased ionic strength for cation/anion reactions (irrespective of mechanism).

We did not perform experiments in which $[SCN^-]$ was varied (at constant ionic strength), to confirm the assumed (eq 3) linear dependence of the rate on $[SCN^-]$. This rate law is clear from

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Table I. Comparison of Actual[a] and Derived[b] First-Order Rate Constants for the SCN^- Anation Reaction of $(NH_3)_5CoOH_2{}^{3+}$ (25 °C, I = 1.0 M)

$[SCN^-]$, M	10^8k,[a] s^{-1}				$-10^8 \times$ slope,[b,c] s^{-1}				
	$k_1 = k_1'' + k_1'$	k_1''	k_1'	k_2	$t = 0$	$t_{1/2}$	$2t_{1/2}$	$3t_{1/2}$	$t \to \infty$
0.1	8.6	2.24	6.36	82	6.63	8.6	8.6	8.6	8.6
0.25	21.5	5.59	15.9	82	16.6	20.8	21.4	21.5	21.5
0.5	43.0	11.2	31.8	82	33.2	38.3	40.6	41.8	43.0
0.75	64.5	16.8	47.7	82	49.7	53.8	56.5	58.3	64.5
0.9	77.4	20.1	57.3	82	59.7	62.7	64.9	66.6	77.4
1.0	86.0	22.4	63.6	82	66.3	68.5	70.2	71.6	82.0

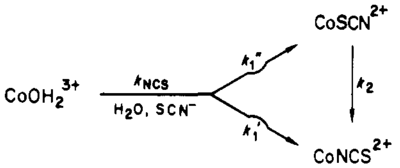
[a] First-order rate constants defined in eq 4 (text). [b] First-order rate constants (=−(slope)) derived conventionally from plots of ln $|\epsilon - \epsilon_C|$ vs. t; times refer to half-lives of the primary ($k_1' + k_1'' = k_1$) reaction. [c] Slopes calculated from the expression for d(ln $|\epsilon - \epsilon_C|$)/dt.[28]

the several earlier studies[1] and is expected when ion pairing is weak (i.e., $K_{IP}[SCN^-] \ll 1$[4,19]) and/or a poorly discriminating $Co(NH_3)_5{}^{3+}$ intermediate is involved.

There is no doubt that accurate rate studies, contingent upon the correct identification of the products, can be crucial to subtle distinctions in mechanism. The recent results[17] for the $(NC)_5CoOH_2{}^{2-}/N_3{}^-,SCN^-$ systems bear convincing testimony to this fact—the long-believed case for a genuine reduced coordination number intermediate $(NC)_5Co^{2-}$ in the substitution reactions of $(NC)_5CoX^{n-}$ has now all but dissolved. Similar tales, for different reasons, apply to the substitution reactions of $(NH_3)_4Co(SO_3)X$ and $(en)_2Co(SO_3)X$.[18] It is therefore appropriate to review the $(NH_3)_5CoOH_2{}^{3+}$/Y anation reactions and, in particular, the Y = SCN^- substitution process. We note that at least two of the earliest studies[2,3] of this reaction (eq 2) predated the synthesis of the S-bonded (thiocyanato) complex $[(NH_3)_5CoSCN]Cl_2 \cdot 1.5H_2O$.

In hindsight, there is no obvious reason to suspect that the anation reaction could involve both S- and N-bonded SCN^- (eq 2). Standard pseudo-first-order rate plots are reported to be linear over several half-lives, and this is consistent with the assumption of irreversible formation of the N-bonded (isothiocyanato) complex. Also, the final visible and UV spectra closely match those of authentic $(NH_3)_5CoNCS^{2+}$. Yet, clearly our new data invalidate the earlier work,[1-3] and it is now reasonable to inquire why the simple first-order rate plots of $|\epsilon - \epsilon_\infty|$ vs. t were apparently linear[1,2] and what their slopes represent.

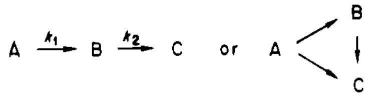
The reaction scheme in eq 4 completely defines the $(NH_3)_5CoOH_2{}^{3+}/SCN^-$ system ($k_{NCS}[SCN^-] = k_1' + k_1'' = k_1$).



(4)

The large[20] formation constant for $(NH_3)_5CoNCS^{2+}$ and complete isomerization[12] of $(NH_3)_5CoSCN^{2+}$ to $(NH_3)_5CoNCS^{2+}$ under equilibrium conditions ensures the irreversibility of the reactions as shown (eq 4), under all practical circumstances. The constant k_2 is known[12] (8.2×10^{-7} s^{-1}), and we have determined k_{NCS} ($=k_1' + k_1''$ for 1.0 M SCN^-; 8.6×10^{-7} s^{-1}). The ratio k_1''/k_1' is defined by the S/N product ratio at early reaction times that we now know also (0.36). Thus, $k_1' = 6.3 \times 10^{-7}$ s^{-1} and $k_1'' = 2.3 \times 10^{-7}$ s^{-1} for 1.00 M SCN^- at 25 °C.

A biphasic reaction is expected[22] since k_1 and k_2 are not very different. Why has it not been observed previously? The usual analysis of the spectrophotometric data (ϵ, t) involves plotting ln $|\epsilon - \epsilon_\infty|$ vs. t; ϵ_∞ is the molar absorptivity of $(NH_3)_5CoNCS^{2+}$. For simple consecutive reactions of the kind



applicable here (eq 4) (but which is analytically equivalent[22] to

$$A \xrightarrow{k_{NCS}[SCN]} B' \xrightarrow{k_2} C$$

where B′ is the *initial* S isomer/N isomer mixture), plots of ln $|\epsilon - \epsilon_\infty|$ vs. t are typically curved. They usually[22] show a later time linear section, from which always the *smaller* of the two rate constants is obtained (k_2 in this case, the S to N isomerization constant, and *not* that for the anation reaction). However, it has been emphasized more than once[22,26] that such plots can be accidentally linear, and this appears to be the case for the $(NH_3)_5CoOH_2{}^{3+}/SCN^-$ system, from what can be gauged from the literature data.[1-3,23]

There are three conditions for coincidental (or apparent[25]) linearity:[22,32] (i) $\epsilon_B = \epsilon_C$; (ii) $(\epsilon_A - \epsilon_C)/(\epsilon_B - \epsilon_C) = k_1/k_1 - k_2$);[31] (iii) $k_1 \simeq k_2$. Obviously the first two conditions depend upon the wavelength of the study (which has invariably been around 490 nm). The very first can be rejected, since at 490 nm $\epsilon_B(CoSCN^{2+})$ = 62 and $\epsilon_C(CoNCS^{2+})$ = 169, compared with $\epsilon_A(CoOH_2{}^{3+})$ = 47.5 M^{-1} cm^{-1}, and similar large differences are apparent at most[24] other wavelengths. Rather, it is a subtle combination of the second and third conditions that leads to the apparent linearity, at least for $[SCN^-]$ = 1.0 M. This is seen most readily by comparing the calculated initial (t = 0) and final ($t \to \infty$) slopes of the ln $|\epsilon - \epsilon_C|$ bs. t plots. We need to reemphasize[22] that even when later time curvature is expected, it is evident only beyond 3–4 half-lives when $k_1 \simeq k_2$ and, hence, is undetected in practice. The data of Table I (1.0 M SCN^-) illustrate this clearly. Note that the apparent slope obtained from 0–3 half-lives data is not related simply to either k_1 or k_2, and it is wavelength dependent.

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(19) This comment implies little about the mechanism; ion pairing, weak or strong, may be unrelated to the product formation step although in principle it still introduces $[SCN^-]$ terms into the rate law. Similar terms can arise by other mechanisms not involving ion pairing.

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(23) Some of the previous studies[1,2] were for temperatures above 25 °C, but the S/N product ratio (26/74 at 25 °C) is unlikely to be *dramatically* temperature dependent.

(24) Isosbestic points in the spectra of $(NH_3)_5CoSCN^{2+}$ and $(NH_3)_5CoNCS^{2+}$ occur at 613, 559, 413, and 397 nm.[12]

(25) The "linearity" depends upon the percent reaction covered by the (D, t) data. Measurements covering at least 2 half-lives, more often 3, are usual.

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(28) The slope of the ln $|\epsilon - \epsilon_C|$ vs. t plot at any point is given as $d(\ln|\epsilon - \epsilon_C|)/dt = [-(k_1' + k_1'')X + k_2Y]/(X - Y)$, where $X = [(\epsilon_A - \epsilon_C) + Y] \exp(-(k_1' + k_1'')t)$ and $Y = [(\epsilon_B - \epsilon_C)k_1''/[k_2 - (k_1'' + k_1')]] \exp(-k_2t)$. Substituting $t = 0$ gives the zero t slope $-(k_1'' + k_1') + k_1''(\epsilon_B - \epsilon_C)/(\epsilon_A - \epsilon_C)$. Since $k_1''/k_1' = 26/74$, this simplifies to $-(k_1'' + k_1')[1 - 0.26(\epsilon_B - \epsilon_C)/(\epsilon_A - \epsilon_C)]$; $k_1'' + k_1'$ is identified with $k_{NCS}[SCN^-]$ (see text). Note that if $\epsilon_A = \epsilon_B$, the zero t slope is simply $-k_1'$. This is a common although not very accurate way of obtaining individual rate constants for parallel reactions, with or without a subsequent interconversion step.

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(30) Stotz, I.; Wilmarth, W. K.; Haim, A. *Inorg. Chem.* **1968**, *7*, 1250–1253.

(31) For the scheme shown in eq 4, this condition is modified: $(\epsilon_A - \epsilon_C)/(\epsilon_B - \epsilon_C) = k_1''/[(k_1'' + k_1') - k_2] = k_2''(k_1 - k_2)$.

(32) (a) Marty, W.; Espenson, J. H. *Inorg. Chem.* **1979**, *18*, 1246–1250. (b) Pohl, M. C.; Espenson, J. H. *Inorg. Chem.* **1980**, *19*, 235–242.

A remarkable feature peculiar to the present system is that the zero time slope[28] is perchance very close to k_1' ($0.77k_1$), simply because ϵ_A happens to be $\sim\epsilon_B$. The later time slope is k_2, the smaller of k_1 and k_2, which also happens to be very nearly k_1'. Thus, there is very little curvature while these fortuitous relationships between the rate constants and molar absorptivities exist. Ironically, the constant obtained closely represents the rate constant for the formation of the N isomer, as always believed![1-3] This constant is of course some 20% less than the true (total) anation rate number, k_1 ($=k_{NCS}[SCN^-]$; 8.6×10^{-7} s^{-1} at 1.0 M SCN^-, 25 °C).

The situation is different at lower [SCN^-]. As before, curvature is predicted, but it sets in at much earlier reaction times and, hence, should be more readily detected since k_1 and k_2 are separated more in magnitude as the [SCN^-] is lowered (Table I). At 490 nm, the sense of the curvature is always the same, the gradients being $-0.77\ k_1$ at zero time and, below about 0.95 M SCN^- (at which point the relative magnitudes of k_1 and k_2 invert), $-k_1$ at infinite time.[28]

The net kinetic outcome of not recognizing the formation of $CoSCN^{2+}$ in the SCN^- anation of $CoOH_2^{3+}$ is as follows: Depending upon the wavelength of the study and over how many $t_{1/2}$ data are taken for the determination of k_1, the rate constant will be in error. This error decreases at lower [SCN^-], and in this region rate constants should be less underestimated. Thus, plots of k(obsd) vs. [SCN^-], if the data are sufficiently precise, will show artifactual curvature and in the right sense for the (incorrect) conclusion that the results represent an ion-pairing saturation phenomenon. Obviously the debate[1,2,4] over this sort of issue in the past is not only the result of incorrect product identification but also the result of the inappropriate choice of wavelength for the study. Indeed, we have monitored the absorbance vs. t traces for this reaction at 287 nm, the maximum for the intensely absorbing S isomer (ϵ 15 700), and these traces show quite clearly the appearance and subsequent decay of $CoSCN^{2+}$—the absorbance first rises and then falls.

We believe the observations reported herein may be relevant to all metal complex substitution reactions involving SCN^-. Indeed, for the substitution reactions of $(NH_3)_5CoX^{n+}$ in general, in aqueous[16] and nonaqueous[27] SCN^- media, mixtures of S- and N-bonded $(NH_3)_5Co(SCN)^{2+}$ arise in *every* case. In part, the S/N product ratio seems to be determined[12] by the preferred hydration of the more basic N terminus of SCN^-, leaving the S center more exposed and presumably more available for capture by the metal ion.

This rationale might pertain only to dissociative reactions. There could be a decided preference for N or S bonding in associative substitutions, depending upon the metal ion system, because of the M^{n+}--SCN^- bond-making aspect in the activation process. Even so, the kinetically preferred isomer need not be the stable one, and the problem exposed in this work remains relevant.

The often quoted Pearson and Moore experiments[3] are now in need of being revisited. In that work $(NH_3)_5CoONO_2^{2+}$ (and $(NH_3)_5CoBr^{2+}$) were hydrolyzed in 0.5 M NaSCN at 25 °C, and it was claimed that the initial product was >98% $(NH_3)_5CoOH_2^{3+}$; $(NH_3)_5CoNCS^{2+}$ was formed only by subsequent anation. The analysis did not admit the possibility of $(NH_3)_5CoSCN^{2+}$ formation, in either the primary or secondary step; we know now that at least the second step involves $(NH_3)_5CoSCN^{2+}$ formation. Furthermore, elsewhere[16,27] we report product distributions for SCN^- substitution in the first step for these and other $(NH_3)_5CoX^{n+}$ complexes for which SCN^- *does* compete with H_2O, and both $CoSCN^{2+}$ and $CoNCS^{2+}$ are indeed formed. Dolbear and Taube[29] had noted at about the time of the Pearson and Moore publication[3] that the spontaneous aquation of $(NH_3)_5CoOP(OCH_3)_3^{3+}$ in SCN^- yielded some $(NH_3)_5CoNCS^{2+}$ along with the aqua complex, in the primary step, but they also reported a product that was intensely absorbing at ~300 nm. This was attributed to $(SCN)_2$, but in hindsight[16] it was likely $(NH_3)_5CoSCN^{2+}$. Curiously, this same species was not apparently observed in the NO^+-induced aquation of $(NH_3)_5CoN_3^{2+}$,[3,20] although it is now known[14,16] that appreciable $(NH_3)_5CoSCN^{2+}$ is formed. These studies predated the discovery of authentic $(NH_3)_5CoSCN^{2+}$.

The interpretation of the kinetic data for the SCN^- and N_3^- substitution reactions of $(NC)_5CoOH_2^{2-}$ has recently come under fire. For the N_3^- reaction at least, the case for the $(NC)_5Co^{2-}$ intermediate has been withdrawn.[17] In careful experiments, the origin of the otherwise kinetically significant curvature in k(obsd) vs. [N_3^-] plots was identified as spurious; this curvature in the original data was crucial to implying the existence of a pentacoordinate $(NC)_5Co^{2-}$ intermediate that survived for a time sufficient to discriminate significantly between competing nucleophiles. The author noted a remaining anomaly with the $(NC)_5CoOH_2^{2-}/SCN^-$ data where a similar curvature in the k(obsd) vs. [SCN^-] plot was apparent. The system was originally analyzed by assuming only $(NC)_5CoNCS^{3-}$ formation. Now the prospect of both S and N capture by SCN^- is recognized,[17] and the present work emphasizes its likelihood. Both $(NC)_5CoSCN^{3-}$ and $(NC)_5CoNCS^{3-}$ linkage isomers are known.[30]

In conclusion, this work shows that it is generally wise to acquire spectrophotometrically determined substitution rate data at several (well-spaced) wavelengths, to probe the prospect of S- and N-bonded SCN^- complex formation. Additionally, the [SCN^-] dependence of the rate need be scrutinized since at some [SCN^-] it is conceivable that the rate of the S to N rearrangement rather than that of the SCN^- substitution could be measured. Finally, we note that the $(NH_3)_5CoOH_2^{3+}/SCN^-$ kinetics experiment, advanced[1] as an uncommon example of a simple "clean" anation reaction suitable for study by undergraduates, is less deceptively so if the study is confined to a wavelength corresponding to one of the several[12,24] $CoSCN^{2+}/CoNCS^{2+}$ isobestic points. Under this circumstance the true (total) anation rate is measured, and the study is devoid of the problem of absorbance changes due to the subsequent S- to N-linkage isomerization process.

Experimental Section

The fully characterized complexes $[(NH_3)_5CoOH_2](ClO_4)_3$, $[(NH_3)_5CoNCS](ClO_4)_2$, and $[(NH_3)_5CoSCN]Cl_2\cdot 1.5H_2O$ were from the same batches used in concurrent work.[14,16] The reactions of $[(NH_3)_5CoOH_2](ClO_4)_3$ (0.5–1.0 g) in aqueous NaSCN (0.5, 1.0 or 3.1 M, pH 3, 25.0 °C, ~50 mL) were carried out on relatively large scales to permit the ready detection and quantitative analysis of $(NH_3)_5Co(SCN)^{2+}$ (0.5–3% of the total cobalt, for the short reactions times employed).[14] After 2.0-, 5.0-, or 7.0-h reactions times at 25.0 °C in the dark, product mixtures were diluted to ~500 mL (H_2O) and sorbed on and eluted (0.25 M NaCl, pH 2) from SP Sephadex C-25 (Na^+ form) cation-exchange resin. This separated $(NH_3)_5Co(SCN)^{2+}$ (6–65 μmol, in ~500 mL of eluate) cleanly from $(NH_3)_5CoOH_2^{3+}$ (taken rapidly from the column with 1.0 M NaCl, pH 3), but S- and N-bonded thiocyanato complexes eluted together. The aqua complex was determined spectrophotometrically (Cary 210 instrument) with $\epsilon_{492} = 47.7$. The absorbance of the solution containing $CoSCN^{2+} + CoNCS^{2+}$ was measured at 287 nm immediately (A_{287}; 1- or 10-cm cell such that $A > 0.5$), and at 303 nm (10-cm cell) following heating in a sealed flask (95 °C, 1 h). These two measurements precisely define the individual *initial* [$CoSCN^{2+}$] and [$CoNCS^{2+}$][14] as

$$[CoSCN^{2+}] = 10^{-5}(6.85A_{287} - 5.81A_{303})$$

$$[CoNCS^{2+}] = 10^{-5}(70.9A_{303} - 5.76A_{287})$$

where A_{303} and A_{287} are each appropriate to a 1-cm cell. Experiments were performed in triplicate, and cobalt recoveries were better than 98.5%.

Acknowledgment. The authors are grateful for financial support from the Australian Research Grants Scheme. We acknowledge stimulating discussions with Professor W. Marty.

Registry No. SCN^-, 302-04-5; $(NH_3)_5CoOH_2^{3+}$, 14403-82-8.