The origin of the remaining five bands at 2150.0, 2045.7, 2041.0, 2011.8, and 2007.0 cm^{-1} is not clear. Unambiguous assignments of these bands must await a rigorous normal-coordinate analysis. The peak observed at 2139.0 cm^{-1} is due to the free ^{12}CO.

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Registry No. $Ni(CO)_4$, 13463-39-3.

Contribution from the Department of Chemistry, State University of New York, Stony Brook, New York 11790

Adjacent Attack in the Redox Reaction between Pentacyanocobaltate(II) and Thiocyanatopentaamminecobalt(III)[1]

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It was reported previously[3] that the reduction of thiocyanatopentaamminecobalt(III) by chromium(II) proceeds *via* parallel adjacent and remote attack mechanisms. Since on the basis of thermodynamic[3,4] and steric[3] considerations a negligible contribution of the adjacent attack pathway would have been anticipated, the occurrence of such a pathway was interpreted as a manifestation of the high electron mediating ability of thiocyanate sulfur in inner-sphere redox reactions.[3] Another example of high redox reactivity when sulfur is bound to cobalt(III) was discovered earlier[5] in the mercaptoacetatobis(ethylenediamine)cobalt(III)-chromium(II) reaction. Since the two cases of sulfur-mediated electron transfer involved chromium(II) as the reductant, it was decided to investigate the reduction of $Co(NH_3)_5SCN^{2+}$ by $Co(CN)_5^{3-}$. This reductant was chosen because examination of the cyanocobalt(III) products can provide direct evidence about the position of attack on the bridging ligand and for comparison with the analogous $Co(NH_3)_5NCS^{2+}$-$Co(CN)_5^{3-}$ reaction which is known to proceed by remote attack.[6,7]

Experimental Section

Argon, used in the manipulation of oxygen-sensitive substances, and water were purified as described previously.[8] $[Co(NH_3)_5NCS](ClO_4)_2$ and $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ were synthesized by recorded procedures.[9,10]

Stoichiometric experiments designed to identify the cobalt(III) products of the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5^{3-}$ reaction were conducted in two ways. The first method involved addition of 5-10 mg of $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ to 15 ml of deaerated 5.0×10^{-3} *M* NaCN, 1.0×10^{-3} *M* NaOH, and 0.10 *M* $NaClO_4$. The second method involved anaerobic mixing in the fast-flow apparatus[11] of a solution of $Co(NH_3)_5SCN^{2+}$, Co^{2+}, and $NaClO_4$ with a solution of NaCN, NaOH, and $NaClO_4$. The resulting solutions were collected and their visible and ultraviolet spectra were recorded with a Cary 14 spectrophotometer.

Table I. Identification of the Product of the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5^{3-}$ Reaction[a]

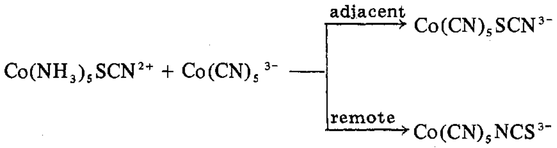
$10^4[Co(NH_3)_5SCN^{2+}]$, *M*	$10^5[Co(CN)_5^{3-}]$, *M*	λ,[b] nm	ε,[c] M^{-1} cm^{-1}
14.0	⩽0.01[d,e]	377, 263	215, 1.90×10^4
2.93	⩽0.01[d,e]	377, 263	201, 1.79×10^4
1.10	⩽0.01[d,f]	377, 263	215, 1.74×10^4
0.66	0.40[f]	377, 263	200, 1.83×10^4
1.08	0.40[f]	377, 263	202, 1.85×10^4
0.75[g]	1.0[f]	377, 263	215, 1.78×10^4
		377, 263[h]	196, 1.84×10^4[h]
		378, 264[i]	195, 1.82×10^4[i]
		378, 265[j]	191, 1.71×10^4[j]
		363, 265[k]	500, 2.34×10^3[k]

[a] Measurements at 25°, $[CN^-] = 5.0 \times 10^{-3}$ *M*, $[OH^-] = 1.0 \times 10^{-3}$ *M*, and $[NaClO_4] = 0.10$ *M*. [b] Wavelengths of maximum absorption for product solution. [c] Extinction coefficients at maxima. Calculated on the basis of the initial [Co(III)]. [d] Estimated impurity present in the cobalt(III) preparation. [e] Mixing solid $[Co(NH_3)_5SCN]Cl_2 \cdot 1.5H_2O$ with CN^- solution. See text. [f] Mixed in rapid-flow apparatus. See text. [g] With 0.83×10^{-4} *M* $Co(NH_3)_5NCS^{2+}$ added. [h] Spectrum of $Co(CN)_5SCN^{3-}$ from ref 14. [i] Spectrum of $Co(CN)_5SCN^{3-}$ from S. Nakamura, Ph.D. Dissertation, University of Chicago, 1964. [j] Spectrum of $Co(CN)_5SCN^{3-}$ from ref 15. [k] Spectrum of $Co(CN)_5NCS^{3-}$ from ref 15.

The $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5^{3-}$ reaction was complete within the dead time (5 msec) of the flow apparatus at 10^{-5} *M* $Co(CN)_5^{3-}$. Lower concentrations of $Co(CN)_5^{3-}$ could not be used because of its sensitivity to oxygen and because such small concentrations become comparable to the amount of cobalt(II) usually present as an impurity in preparations of cobalt(III) complexes.[12] In fact, it was found that usable, although poorly reproducible, oscillograms could be obtained by mixing $Co(NH_3)_5SCN^{2+}$ and CN^- solutions in the *absence* of added cobalt(II). An estimate of the $Co(CN)_5^{3-}$ concentration produced on mixing the above solutions was obtained by "spiking" the $Co(NH_3)_5SCN^{2+}$ solutions with a known amount of $Co(NH_3)_5NCS^{2+}$. When such solutions were mixed with CN^- solutions, two distinct absorbance changes were detected at 263 or 288 nm.[13] The first, rapid change (with half-life $t^f_{1/2}$) corresponded to the disappearance of $Co(NH_3)_5SCN^{2+}$ and formation of $Co(CN)_5SCN^{3-}$ and was followed by the slower (half-life $t^s_{1/2}$) cobalt(II)-catalyzed conversion[6,7] of $Co(NH_3)_5NCS^{2+}$ to $Co(CN)_5SCN^{3-}$. The concentration of $Co(CN)_5^{3-}$ during the second reaction was calculated from the measured half-life and the known[7] second-order rate constant ($[Co(CN)_5^{3-}] = 0.693/1.1 \times 10^6 \times t^s_{1/2}$) and was *assumed* to be prevalent during the first reaction in order to calculate its second-order rate constant ($k = 0.693/[Co(CN)_5^{3-}] \times t^f_{1/2}$). The half-lives for the two reactions were estimated from the corresponding ln ($D_t - D_\infty$) *vs.* time plots. D_t and D_∞ are the absorbances at time *t* and when the reaction under consideration is complete, respectively. The difference in rates between the two reactions was sufficiently large to obtain fairly steady D_∞ values for the first reaction.

Results and Discussion

There are two possible pathways for the inner-sphere redox reaction between $Co(NH_3)_5SCN^{2+}$ and $Co(CN)_5^{3-}$



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[1] This work was supported by the National Science Foundation under Grant GP-9669.

[2] Based on the M.S. thesis of C. J. Shea, State University of New York at Stony Brook, Aug 1971.

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[13] Extinction coefficients (in M^{-1} cm^{-1}) at 288 and 263 nm: $Co(NH_3)_5SCN^{2+}$, 15,600 and 5000; $Co(NH_3)_5NCS^{2+}$, 1250 and 512; $Co(CN)_5SCN^{3-}$, 3600 and 18,400.

Table II. Kinetics of the Reduction of $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ by $Co(CN)_5{}^{3-}$ [a]

$10^5[Co(NH_3)_5SCN^{2+}]$, M	$10^5[Co(NH_3)_5NCS^{2+}]$, M	$10^5[Co(CN)_5{}^{3-}]$, M	$t^f_{1/2}$, msec	$t^s_{1/2}$, sec	$10^{-9}k_{SCN}$,[b] M^{-1}, sec^{-1}	$10^{-6}k_{NCS}$,[c] M^{-1} sec^{-1}
	6.8	2.0		0.035 ± 0.007		1.0 ± 0.2
	11.3	1.0		0.063 ± 0.006		1.1 ± 0.1
	13.0	0.050		35 ± 10		0.04 ± 0.01
7.20	8.1	1.0	*d*	0.069 ± 0.021	>0.1	1.0 ± 0.3
4.88	3.47	0.10	20 ± 4	40 ± 20	2.2 ± 0.5	0.017 ± 0.008
7.84	3.15	0.0010	6 ± 2	45 ± 20	8 ± 3	1.5 ± 0.6
8.65	3.24	*e*	60 ± 10	100 ± 40	1.8 ± 0.3	

[a] Measurements at 25°, $[CN^-] = 5.0 \times 10^{-3}\,M$, $[OH^-] = 1.0 \times 10^{-3}\,M$, and $[NaClO_4] = 0.10\,M$. Each entry for $t_{1/2}$ is the average of three to six replicate measurements at 288 and 263 nm with the same pair of solutions. [b] Second-order constant for the $Co(NH_3)_5SCN^{2+}$–$Co(CN)_5{}^{3-}$ reaction. Calculated from $0.693/t^f_{1/2}[Co(CN)_5{}^{3-}]$ where $[Co(CN)_5{}^{3-}]$ is $0.693/t^s_{1/2} \times 1.1 \times 10^6$. [c] Second-order constant for the $Co(NH_3)_5NCS^{2+}$–$Co(CN)_5{}^{3-}$ reaction calculated from $0.693/t^s_{1/2}[Co(CN)_5{}^{3-}]$. [d] Complete in less than 2 msec. [e] None added; reaction catalyzed by Co(II) impurity.

Since the rate of interconversion between the two linkage isomers in the pentacyanocobaltate(III) series is slow,[6,14,15] a knowledge of the isomeric composition of the reaction product serves to establish whether adjacent and/or remote attacks are operative. It will be seen from Table I that the product has absorption maxima at 377 and 263 nm with extinction coefficients 208 ± 7 and 18,200 ± 500 M^{-1} cm^{-1}, respectively. Comparison of these values with those of $Co(CN)_5SCN^{3-}$ and $Co(CN)_5NCS^{3-}$ (last four entries in Table I) shows that $Co(CN)_5SCN^{3-}$ is produced essentially in quantitative yield and therefore that the reaction proceeds predominantly (>95%) by the adjacent attack mechanism.

At $1.0 \times 10^{-5}\,M$ $Co(CN)_5{}^{3-}$, the disappearance of $Co(NH_3)_5SCN^{2+}$ is complete within the 5-msec dead time of the fast-flow apparatus. Therefore, a lower limit of the second-order rate constant for the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction is $10^8\,M^{-1}$ sec^{-1}. Reliable measurements with lower concentrations of added cobalt(II) could not be performed. Thus, as shown by entries 1 and 2 of Table II, the rate constants $(1.0 \pm 0.2) \times 10^6$ and $(1.1 \pm 0.1) \times 10^6\,M^{-1}$ sec^{-1} measured in this work are in excellent agreement with the reported[7] value $1.1 \times 10^6\,M^{-1}$ sec^{-1}. However, with $[Co(CN)_5{}^{3-}] = 5.0 \times 10^{-7}\,M$ (entry 3 of Table II), our value of $4.0 \times 10^4\,M^{-1}$ sec^{-1} is considerably smaller. The reasons for these difficulties have not been elucidated, but it is likely that oxidation of the very low $Co(CN)_5{}^{3-}$ concentrations by trace oxidizing impurities (*e.g.*, oxygen) is responsible for the low observed rates.

In an attempt to circumvent these difficulties, solutions of $Co(NH_3)_5SCN^{2+}$ were "spiked" with $Co(NH_3)_5NCS^{2+}$, the hope being that the known[7] rate of the $Co(NH_3)_5NCS^{2+}$-$Co(CN)_5{}^{3-}$ reaction would provide an estimate of the $Co(CN)_5{}^{3-}$ concentration in the reacting solution. As shown by the last three entries of Table II, this hope has been fulfilled since fast and slow absorbance changes are observed for the "spiked" solutions.[16] Using the slow-rate component to calculate the actual (rather than nominal) $Co(CN)_5{}^{3-}$ concentration, we obtain rate constants for the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction in the range $(2\text{-}8) \times 10^9\,M^{-1}$ sec^{-1}. Since the concentration of $Co(CN)_5{}^{3-}$ titrated kinetically with $Co(NH_3)_5NCS^{2+}$ is the minimum value prevalent during the $Co(NH_3)_5SCN^{2+}$ -$Co(CN)_5{}^{3-}$ reaction,[17] the above values represent upper limits to the actual rate constant. Therefore, $10^8 < k_{SCN} < 2 \times 10^9$ (M^{-1} sec^{-1}).

Table III. Rate Constants for Redox Reactions of Thiocyanate Complexes (25°, Variable μ)

Reaction	k, M^{-1} sec^{-1}	Mode of attack	Ref
$(NH_3)_5CoSCN^{2+} + Co(CN)_5{}^{3-}$	$>10^8$, $<2 \times 10^9$	Adjacent	*a*
$(NH_3)_5CoNCS^{2+} + Co(CN)_5{}^{3-}$	1.1×10^6	Remote	*b*
$(NH_3)_5CoSCN^{2+} + Cr^{2+}$	8.0×10^4	Adjacent	*c*
$(NH_3)_5CoSCN^{2+} + Cr^{2+}$	1.9×10^5	Remote	*c*
$(NH_3)_5CoNCS^{2+} + Cr^{2+}$	19	Remote	*c, d*

[a] This work. [b] References 6 and 7. [c] Reference 3. [d] J. P. Candlin, J. Halpern, and D. L. Trimm, *J. Amer. Chem. Soc.*, **86**, 1019 (1964).

The results of the present investigation and of previous, related work are summarized in Table III. It is seen that the isothiocyanatopentaamminecobalt(III) complex reacts with Cr^{2+} and $Co(CN)_5{}^{3-}$ by the remote attack mechanism. Since a necessary condition for precursor, binuclear complex formation is a lone pair of electrons on the atom attacked by the reducing agent[18] and such a pair is not available on the N atom of $Co(NH_3)_5NCS^{2+}$, adjacent attack is precluded. Consequently, the reactions proceed *via* remote attack on the S atom. In the case of Cr^{2+} the reaction is relatively slow because it produces the thermodynamically unstable isomer $CrSCN^{2+}$,[19] but for $Co(CN)_5{}^{3-}$ the reaction proceeds rapidly and yields the stable[6,14,15] linkage isomer $Co(CN)_5SCN^{3-}$.

For $Co(NH_3)_5SCN^{2+}$ both remote and adjacent attack pathways are feasible since the S and N atoms have lone pairs available for precursor complex formation. In the case of Cr^{2+}, both pathways obtain, and we commented previously[3] about the high rate for the reaction proceeding *via* the transition state $[(NH_3)_5CoS(CN)Cr(H_2O)_5{}^{4+}]^{\ddagger}$. For $Co(CN)_5{}^{3-}$ as reductant, only adjacent attack is detected, and, therefore, the ratio of the rate constant for adjacent (k_S) attack to that for remote (k_N) attack is >20.[20] On the basis of the simplest free energy consideration,[4] we would expect k_S/k_N to be equal to $Q^{1/2}$, where Q is the equilibrium constant for isom-

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[16] It is noteworthy that the rate constant for the $Co(NH_3)_5NCS^{2+}$-$Co(CN)_5{}^{3-}$ reaction, calculated from the nominal concentration of $Co(CN)_5{}^{3-}$ when the amount of added cobalt(II) is very small, can be *larger* than the accepted value. This provides some evidence for the contention that small amounts of cobalt(II) impurities are present in the samples of cobalt(III) complexes. For example, the concentration of $Co(CN)_5{}^{3-}$ calculated for the last experiment in Table II is $7 \times 10^{-9}\,M$.

[17] Some $Co(CN)_5{}^{3-}$ may be oxidized during the time between the very fast $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction and the somewhat slower $Co(NH_3)_5NCS^{2+}$-$Co(CN)_5{}^{3-}$ reaction.

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erization of $Co(CN)_5NCS^{3-}$ to $Co(CN)_5SCN^{3-}$. Unfortunately, the value of Q is not known, and consequently it is not possible on the basis of the comparison between adjacent and remote attacks of $Co(CN)_5{}^{3-}$ on $Co(NH_3)_5SCN^{2+}$ to ascertain the electron-mediating ability of sulfur attached to cobalt(III). Another comparison involves the reaction of $Co(NH_3)_5SCN^{2+}$ *via* adjacent attack with the reaction of $Co(NH_3)_5NCS^{2+}$ *via* remote attack. On the basis of the simplest thermodynamic argument,[4] we would expect the former reaction to be faster than the latter reaction by a factor of $\sim 6 \times 10^2$.[21] Additional considerations based on steric hindrance for adjacent attack[3] can be invoked to reduce this factor to a value of $\sim 10^2$. The observed factor has a value of 4×10^3 for Cr^{2+} and lies in the range 10^2-2×10^3 for $Co(CN)_5{}^{3-}$. If the lower limit obtained, we would conclude that the high reactivity for attack at S in the $Co(NH_3)_5SCN^{2+}$-Cr^{2+} reaction is absent in the corresponding reaction of $Co(CN)_5{}^{3-}$. Alternatively, if the upper limit were applicable, then the remarkable ability of S bound to Co(III) for mediating the transfer of an electron would be operative. Unfortunately, only a range of rate constants could be established for the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction, and the question of the electron-mediating ability of sulfur bound to cobalt(III) cannot be answered. However, it is noteworthy that the ratio of reactivities for Cr^{2+} attack on S in $Co(NH_3)_5SCN^{2+}$ and $Co(NH_3)_5NCS^{2+}$ is remarkably close to the upper limit for the corresponding ratio in the $Co(CN)_5{}^{3-}$ reactions, and this might be taken to indicate that the actual rate constant for the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction is near the upper limit indicated by the measurements. The agreement between these values may, however, be fortuitous. It must be recognized that the $Co(NH_3)_5SCN^{2+}$-$Co(CN)_5{}^{3-}$ reaction is extremely fast and may, in fact, be controlled by the rate of ligand addition to $Co(CN)_5{}^{3-}$. Under these circumstances, the Co(II) center cannot exhibit any kinetic discrimination toward various redox reagents and it becomes impossible to ascertain the relative mediating ability of various ligands for electron transfer.

Registry No. $Co(NH_3)_5SCN^{2+}$, 15005-69-3; $Co(CN)_5{}^{3-}$, 14971-18-7; $Co(NH_3)_5NCS^{2+}$, 14970-18-4.

[21] This value is $(3 \times 10^5)^{1/2}$, where 3×10^5 is the equilibrium constant for S to N linkage isomerization.[4]

Contribution from the Laboratory of Inorganic Chemistry, University of Thessaloniki, Thessaloniki, Greece

Tris(dialkyldiselenocarbamates) of Arsenic, Antimony, and Bismuth

G. E. Manoussakis,* C. A. Tsipis, and A. G. Christophides

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In previous papers we have reported the synthesis and spectroscopic study of some arsenic, antimony, and bismuth tris(dithiocarbamate) (tdtc) complexes.[1,2] The interpretation of the spectroscopic results of all those complexes indicated a distorted octahedral stereochemistry.

This work was undertaken to prepare and study the following octahedral complexes containing arsenic, antimony, and bismuth as central atoms and several diselenocarbamates as bidentate ligands: tris(diethyldiselenocarbamato)arsine, $As[SeC(Se)N(C_2H_5)_2]_3$, -stibine, $Sb[SeC(Se)N(C_2H_5)_2]_3$, and -bismuthine, $Bi[SeC(Se)N(C_2H_5)_2]_3$; tris(diisobutyldiselenocarbamato)arsine, $As[SeC(Se)N(C_4H_9)_2]_3$, -stibine, $Sb[SeC(Se)N(C_4H_9)_2]_3$, and -bismuthine, $Bi[SeC(Se)N(C_4H_9)_2]_3$; tris(dibenzyldiselenocarbamato)arsine, $As[SeC(Se)N(CH_2C_6H_5)_2]_3$, -stibine, $Sb[SeC(Se)N(CH_2C_6H_5)_2]_3$, and -bismuthine, $Bi[SeC(Se)N(CH_2C_6H_5)_2]_3$.

Dithiocarbamate complexes of transition and nontransition metals have been extensively studied by many authors. However, the study of diselenocarbamate complexes has been almost limited to those of the transition metals.[3-10] As far as we know nothing is known about the diselenocarbamate complexes of the elements of group Va.

The donor properties and the spectroscopic behavior of the prepared diselenocarbamate compounds are compared to those of analogous sulfur compounds. The $-NR_2$ groups in diselenocarbamates have been selected according to their electron-donating capacity.

Experimental Section

Preparation. The dialkyldiselenocarbamate complexes studied were prepared according to the following general method. In a three-necked flask equipped with a reflux condenser, a mechanical stirrer, and a droping funnel, metal trichloride, MCl_3 (M = As, Sb, or Bi), in a quantity of approximately 10 mmol was mixed with carbon diselenide ($\simeq$30 mmol). Carbon tetrachloride ($\simeq$150 ml) was used as the solvent. To this mixture a solution of dialkylamine ($\simeq$60 mmol) in 50 ml of carbon tetrachloride was added dropwise over a period of 30 min. The mixtures were continuously stirred for 30 min at room temperature and afterward heated for 2 hr at 60-70°. After being cooled, the mixtures were filtered. The precipitates were washed with warm carbon tetrachloride and identified as amine hydrochlorides. The identification was done by comparison of their properties with those of authentic samples. The filtrates were concentrated under vacuum to a small volume (50 ml) and, after the addition of methanol or petroleum ether, tris(dialkyldiselenocarbamates) were obtained. The compounds were then recrystallized from a mixture of chloroform and methanol or from acetone. The recrystallized compounds were quite stable in air and were soluble in carbon tetrachloride, chloroform, acetone, benzene, and dichloromethane. All were practically insoluble in methanol, ethanol, petroleum ether, and water. Analytical data of the prepared compounds are shown in Table I. Carbon diselenide was prepared according to Ives, *et al.*[11]

Measurements. The infrared spectra, for Nujol mulls, chloroform solutions, and KBr disks, were obtained on a Beckman-IR 5A spectrophotometer. Proton nmr spectra were recorded on a Varian A-60A (60 Mc/sec) instrument in deuteriochloroform solutions and benzene solutions, using TMS as an internal standard. The uv-vis spectra were recorded on a Beckman DB-GT spectrophotometer with freshly prepared $CHCl_3$ solutions. The color of these solutions (concentration $\simeq 10^{-5}$ M) in ordinary daylight when freshly prepared was yellow. The yellow color of the solutions progressively decolorized

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