

derivative 6¹⁰ (only one compound detectable because of the fast hydrogen exchange between the two nitrogen atoms) (Scheme II).

Registry No. 1a, 122271-86-7; 2a, 24261-90-3; 2b, 117357-77-4; 2d, 122271-81-2; 2f, 117357-84-3; 2g, 122271-82-3; 3a, 122271-68-5; 3b, 122271-70-9; 3c, 122271-72-1; 3d, 122271-74-3; 3e, 122271-76-5; 3f, 122271-78-7; 5 (isomer 1), 122271-84-5; 5 (isomer 2), 122271-85-6; 6, 122271-80-1; *i*-Pr₂NPCl₂, 921-26-6; Et₂NPCl₂, 1069-08-5; (2,2,6,6-tetramethyl-1-piperidinyl)phosphonous dichloride, 64945-24-0; chlorodiphenylphosphine, 1079-66-9; (trimethylsilyl)trifluoromethanesulfonate, 27607-77-8.

Supplementary Material Available: Tables listing bond lengths, bond angles, positional and anisotropic thermal parameters, and derived H

- (10) 6: ³¹P NMR (C₆D₆) δ 54.1, 49.9 (¹J_{PP} = 308.8 Hz); ¹H NMR (CDCl₃) δ 1.30 (d, ³J_{HH} = 6.5 Hz, 12 H, Me₂CH), 3.01 (m, 2 H, Me₂CH), 7.61 (m, 15 H, C₆H₅), 10.36 (t, ²J_{HP} = ³J_{HP} = 10.36 Hz, 1 H, >NH); ¹³C NMR (CDCl₃) δ 24.20 (s, Me₂CH), 47.91 (s, Me₂CH), 120.73 (q, ¹J_{CF} = 319.9 Hz, CF₃SO₃), 128 (m, C₆H₅), 176.06 (dd, ²J_{CP} = 8.36 Hz, ²J_{CP} = 8.31 Hz, C-C₆H₅); IR (CDCl₃) 1670 cm⁻¹ (νC=N).

atom coordinates for 3a (13 pages); a table of calculated and observed structure factors (15 pages). Ordering information is given on any current masthead page.

- (11) Roques, C.; Mazières, M. R.; Majoral, J. P.; Sanchez, M. Unpublished results.

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Articles

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Reduction of Oxygen- and Sulfur-Bonded (Thiocarbamato)pentaamminecobalt(III) Complexes by Chromium(II)

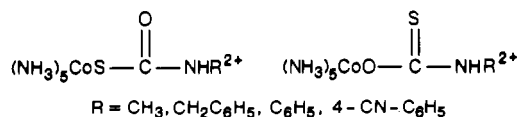
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The chromium(II) reduction of several S- and O-bonded (thiocarbamato)pentaamminecobalt(III) complexes has been studied. For (NH₃)₅CoSCONHR²⁺ (R = CH₃, C₆H₅, CH₂C₆H₅, 4-CN-C₆H₄) the reductant attacks at the remote oxygen atom, giving the rate constants 6.5 × 10⁴, 3.5 × 10⁴, 4.0 × 10⁴, and 2.2 × 10⁴ M⁻¹ s⁻¹, respectively, at T = 25 °C and I = 1.0 M (LiClO₄). The O-bonded chromium(III) product formed in the reduction step isomerizes with k_{obs} = k[H⁺], where k = 41 M⁻¹ s⁻¹ for R = CH₃ and k = 14 M⁻¹ s⁻¹ for R = C₆H₅ and CH₂C₆H₅. The O-bonded complexes (NH₃)₅CoOCSNHR²⁺ (R = CH₃, CH₂C₆H₅) are reduced by attack at the remote S with the rate constants 68 and 55 M⁻¹ s⁻¹ at 25 °C and I = 1.0 M (LiClO₄). The facile electron transfer in the S-bonded cobalt(III) complexes is attributed to a structural trans effect.

Introduction

Redox reactions between Co(III) complexes containing low-valent coordinated sulfur and Cr(II) are "unusually" facile.^{1,2} For example, thiolate complexes are reduced 100–1000 times more rapidly than the corresponding alkoxy species. The nature of this rate enhancement is not well-understood, although it has been suggested that it arises from a sulfur-induced structural trans effect (STE).³ This explanation has been supported by X-ray data, which show a lengthening of the bond trans to the coordinated sulfur atom.^{3–5} In an attempt to probe the electron-mediating ability of sulfur, both coordinated and remote, we report here the reduction of several S- and O-bonded thiocarbamato complexes of pentaamminecobalt(III) by Cr(II):



Experimental Section

Organic starting materials and solvents were of reagent grade and were used without further purification (Eastman Kodak, Aldrich). Purification of complexes was carried out by chromatography on CM-Sephadex C-25 or SP Sephadex in the Na⁺ form (Sigma) in a cold room held at 5 °C.

Stock solutions of lithium perchlorate prepared from the anhydrous material (G. Frederick Smith) were filtered by using a 0.6 μm Millipore filter. Triplicate portions of this solution were standardized by titration of hydrogen ions released from the strong-acid ion-exchange resin Amberlite IR 120(H). Perchloric acid solutions were prepared from doubly distilled HClO₄ (G. Frederick Smith) and standardized with NaOH. Chromium(II) solutions were prepared and analyzed by standard methods. Water used in this study was from a Millipore ion-exchange system.

UV-visible spectra were obtained with a Beckman Acta (III) spectrophotometer. NMR spectra were recorded with a Varian HA 100 or Bruker WH-400 spectrometer. Chemical shifts are given relative to tetramethylsilane (TMS).

Preparation of Complexes. The S-bonded complexes were synthesized by the general procedure described previously.⁶ All analyses were performed by Guelph Chemical Laboratories, Guelph, Ontario, Canada.

Pentaammine(N-methylthiocarbamato-S)cobalt(III) Perchlorate. Anal. Calcd for [Co(NH₃)₅SCONH(CH₃)](ClO₄)₂: C, 5.55; H, 4.42; N, 19.41. Found: C, 5.50; H, 4.38; N, 18.89.

- (1) Balahura, R. J.; Lewis, N. A. *Inorg. Chem.* 1977, 16, 2213.
(2) (a) Lane, R. H.; Bennett, L. E. *J. Am. Chem. Soc.* 1970, 92, 1089. (b) Lane, R. H.; Sedor, F. A.; Gilroy, M. J.; Eisenhardt, P. F.; Bennett, J. P.; Ewall, R. X.; Bennett, L. E. *Inorg. Chem.* 1977, 16, 93.
(3) Elder, R. C.; Florian, L. R.; Lake, R. E.; Yacynych, A. M. *Inorg. Chem.* 1973, 17, 2690.
(4) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* 1976, 15, 139.
(5) Elder, R. C.; Kennard, G. J.; Payne, M. D.; Deutsch, E. *Inorg. Chem.* 1978, 17, 1296.

- (6) Balahura, R. J.; Ferguson, G.; Ecott, L.; Siew, P. Y. *J. Chem. Soc., Dalton Trans.* 1982, 747.

Table I. ^1H NMR Data for Thiocarbamato and Related Complexes of $(\text{NH}_3)_5\text{Co}^{\text{III}}$ ^a

ligand	cis NH_3	trans NH_3	NH	other
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—S—C—NH(CH}_3\text{)} \end{array}$	3.16	3.36	8.03–8.06 (q)	CH_3 ; ^b 2.56, 2.57 (d)
$\begin{array}{c} \text{S} \\ \parallel \\ \text{—O—C—NH(CH}_3\text{)} \end{array}$	4.19	2.89	7.76–7.79 (q)	CH_3 ; ^b 2.48–2.50 ^c
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—S—C—NH(CH}_2\text{C}_6\text{H}_5\text{)} \end{array}$	3.19	3.38	8.65 ^c	C_6H_5 ; 7.21–7.32
$\begin{array}{c} \text{S} \\ \parallel \\ \text{—O—C—NH(CH}_2\text{C}_6\text{H}_5\text{)} \end{array}$	4.22	3.06	8.32 ^c	CH_2 ; 4.21, 4.23 (d) C_6H_5 ; 7.20–7.31
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—S—C—NH(C}_6\text{H}_5\text{)} \end{array}$	3.24	3.44	10.1	CH_2 ; 4.13, 4.15 (d) C_6H_5 ; 6.98–7.58
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—S—C—NH(4—CN—C}_6\text{H}_4\text{)} \end{array}$	2.97	3.55	<i>d</i>	C_6H_4 ; 7.35–7.73
$\begin{array}{c} \text{O} \\ \parallel \\ \text{—O—C—NH(C}_6\text{H}_5\text{)} \end{array}$	3.92	2.78	8.36	C_6H_5 ; 6.88–7.04, 7.22–7.56

^aSolvent $\text{DMSO-}d_6$; chemical shifts in ppm with respect to TMS at 0 ppm. q = quartet; d = doublet. ^bIn ref 7 the CH_3 group is reported at 3.35 and 3.30 ppm for the S- and O-bonded isomers, respectively. Our observation at 400 MHz of a doublet, resulting from coupling with the NH proton, allows an unambiguous assignment for this peak. We have confirmed that the peaks at 3.35 and 3.30 ppm are due to water in $\text{DMSO-}d_6$. In addition we disagree on the cis- and trans- NH_3 peak assignments for the S-bonded isomer; however, since the cis- NH_3 assignments are essentially the same for both studies, the value reported in ref 7 may be a misprint. ^cCenter of triplet. ^dBroadened by exchange. ^eSuperimposed on DMSO peak.

Pentaammine(*N*-benzylthiocarbamato-*S*)cobalt(III) Perchlorate. Anal. Calcd for $[\text{Co}(\text{NH}_3)_5\text{SCONH}(\text{CH}_2\text{C}_6\text{H}_5)](\text{ClO}_4)_2$: C, 18.87; H, 4.56; N, 16.51. Found: C, 18.55; H, 4.50; N, 16.30.

Pentaammine(*N*-phenylthiocarbamato-*S*)cobalt(III) Perchlorate. Anal. Calcd for $[\text{Co}(\text{NH}_3)_5\text{SCONH}(\text{C}_6\text{H}_5)](\text{ClO}_4)_2$: C, 16.97; H, 4.24; N, 16.97. Found: C, 16.71; H, 4.13; N, 16.78.

Pentaammine(*N*-(4-cyanophenyl)thiocarbamato-*S*)cobalt(III) Perchlorate. Anal. Calcd for $[\text{Co}(\text{NH}_3)_5\text{SCONH}(\text{C}_6\text{H}_4\text{-CN})](\text{ClO}_4)_2$: C, 18.47; H, 3.88; N, 18.85. Found: C, 18.71; H, 4.18; N, 18.94.

The O-bonded *N*-methylthiocarbamato and *N*-benzylthiocarbamato complexes were synthesized according to Jackson and Jurisson,⁷ purified by cation-exchange chromatography on CM-Sephadex, and isolated directly as their perchlorate salts. The complexes were characterized by their electronic spectra and by ^1H NMR spectroscopy.

Pentaammine(*N*-phenylthiocarbamato)cobalt(III) Perchlorate. The complex was prepared by adding phenyl isocyanate (11 mmol) to a solution of aquapentaamminecobalt(III) perchlorate (22 mmol) and dimethylbenzylamine in dimethylformamide.⁶ The solution was stirred for 60 h at room temperature. The pure product was obtained via chromatography on CM-Sephadex as the perchlorate salt. The complex was photosensitive and was stored in the dark. Anal. Calcd for $[\text{Co}(\text{NH}_3)_5\text{OCONH}(\text{C}_6\text{H}_5)](\text{ClO}_4)_2$: C, 17.54; H, 4.43; N, 17.54. Found: C, 17.35; H, 4.45; N, 17.74.

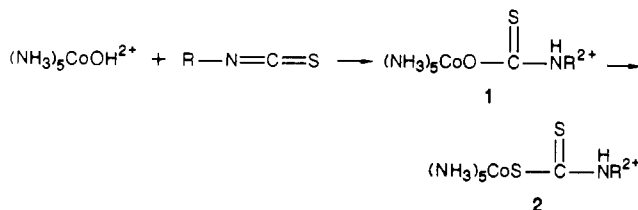
Kinetic Measurements. Kinetic experiments utilized a Durrum Model D-110 stopped-flow spectrophotometer interfaced with a DASAR digital data collection module. Observed rate constants were obtained directly from the exponential traces by curve matching with a calibrated decay generator. In all cases, pseudo-first-order conditions were maintained with chromium(II) in at least 10-fold excess over the cobalt(III) complex concentration. Rate constants are the average of three to five runs and are precise to at least 10%. The rapid-scan spectrophotometer was a Harrick rapid-scan monochromator interfaced with a Durrum stopped-flow instrument as designed by Dr. R. DeSa (Olis, Jefferson, GA). The temperature of the water bath in the stopped-flow spectrophotometer was regulated by a Colora constant-temperature bath in conjunction with a peristaltic pump. Data were fit to the various rate laws by using a standard linear regression.

Product Analyses. Reaction mixtures were subjected to ion-exchange chromatography with Dowex 50W-X8 200 resin. Elution was carried out with a standard 0.5 M NaClO_4 /0.1 M HClO_4 stock solution. The eluting solution was initially added in one-fourth strength and the concentration gradually increased as separation was achieved.

Chromium(III) products were characterized by their UV-visible absorption spectra. Extinction coefficients were calculated on the basis of the chromium concentration, which was determined spectrophotometrically as chromate, where the extinction coefficient at 372 nm is $4.185 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$.⁸

Results and Discussion

Preparation and Characterization of Complexes. The complexes were prepared by utilizing the nucleophilic character of coordinated hydroxide^{6,9} in adding to isothiocyanates:



The resulting thiocarbamates are stabilized by coordination to cobalt(III). The synthesis initially produces the thermodynamically unstable species **1**, and whether **1** or **2** is isolated depends on the electronic characteristics of R,¹⁰ the polarity of the solvent,¹¹ and the temperature.⁷ Production of O-bonded thiocarbamates is favored for electron-donating R groups, solvents of low polarity, and low temperatures. In this work we were successful in preparing the S-bonded complexes for R = methyl, benzyl, phenyl, and 4-cyanophenyl and the O-bonded complexes for R = methyl and benzyl. It is also important to note that the isomerization of **1** to **2** is accelerated by acid (vide infra).

The complexes can be unambiguously assigned as O-bonded or S-bonded by their ^1H NMR spectra. The chemical shift difference between the cis- and trans- NH_3 signals is diagnostic of the bonding atom: $\Delta\delta = 1.0$ – 1.5 ppm for oxygen donors, -0.1 to $+0.5$ ppm for nitrogen donors, and -0.1 to -1.0 ppm for sulfur donors.¹² The NMR data given in Table I follow these predictions. Furthermore, the S-bonded phenyl complex has also been structurally characterized by X-ray methods and verifies the NMR assignments.⁶ The carbamate ligands are also clearly identified by the observed splitting patterns of the NH proton and the R protons. For example, the linkage isomers with R = methyl both show a clearly defined quartet for the NH proton and a doublet for the CH_3 protons as predicted.

(7) Jackson, W. G.; Jurisson, S. S. *Inorg. Chem.* **1987**, *26*, 1060.
(8) Haupt, G. *J. Res. Natl. Bur. Stand. (U.S.)* **1952**, *48*, 414.

(9) van Eldik, R. *Adv. Inorg. Bioinorg. Mech.* **1984**, *3*, 275.
(10) The O-bonded linkage isomers are favored by electron-donating R groups. For the electron-withdrawing R groups, isomerization appears to be rapid on the preparative time scale.
(11) Jackman, L. M.; Dormish, J. F.; Scott, R. M.; Portman, R. H.; Minard, R. D. *Inorg. Chem.* **1979**, *18*, 1503.
(12) Balahura, R. J.; Jordan, R. B. *Inorg. Chem.* **1970**, *9*, 1567.

Table II. Electronic Absorption Parameters for Thiocarbamate and Related Complexes of $(\text{NH}_3)_5\text{Co}^{\text{III}a}$

ligand	λ_{max} , nm (ϵ_{max} , $\text{M}^{-1} \text{cm}^{-1}$)
$-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_3)$	510 (84.7), 334 (sh), 294 (6710), 253 (7640)
$-\text{O}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_3)$	518 (108.5), 227 (16 800) ^b
$-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_2\text{C}_6\text{H}_5)$	510 (90.1), 292 (8521), 255 (9876)
$-\text{O}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_2\text{C}_6\text{H}_5)$	517 (115), 235
$-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{C}_6\text{H}_5)$	510 (98.6), 302 (sh), 262 (24 200)
$-\text{S}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(4-\text{CN}-\text{C}_6\text{H}_4)$	510 (104), 331 (sh), 288 (29 400)
$-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{C}_6\text{H}_5)$	508 (76.1), 270 (sh), 237 (29 600)

^a 0.10 M HClO_4 . ^b Reference 7.

Table III. Kinetic Data for the Isomerization of $(\text{NH}_3)_5\text{CoOCSNH}(\text{CH}_3)^{2+}$ to $(\text{NH}_3)_5\text{SCONH}(\text{CH}_3)^{2+}$ ^a

$[\text{H}^+]$, M	$10^5 k_{\text{obs}}$, s^{-1}	$[\text{H}^+]$, M	$10^5 k_{\text{obs}}$, s^{-1}	$[\text{H}^+]$, M	$10^5 k_{\text{obs}}$, s^{-1}
<i>b</i>	7.03	0.250	8.90	0.750	15.0
0.100	8.41	0.500	11.9	1.00	16.6
0.100	8.25				

^a Concentrations are initial values; $T = 25^\circ\text{C}$, $I = 1.0 \text{ M}$ (LiClO_4), $\lambda = 295 \text{ nm}$, and $[\text{cobalt(III) complex}] = 10^{-4} \text{ M}$. ^b 1.0 M LiClO_4 .

The electronic absorption spectra are summarized in Table II. The S-bonded complexes all show the typical ligand-to-metal charge-transfer absorption in the near-ultraviolet region that is characteristic of the cobalt(III)-sulfur bond.¹³ The O-bonded linkage isomers do not give strong bands in this region of the spectrum.

The possibility of isomerization of the O-bonded (methylthiocarbamate)cobalt(III) complex in an acidic medium was also investigated. In 0.10 M HClO_4 ($I = 1.0 \text{ M}$ (LiClO_4)), both isomerization and aquation are observed, with the products $(\text{NH}_3)_5\text{CoSCONH}(\text{CH}_3)^{2+}$ ($60 \pm 10\%$) and $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ ($40 \pm 10\%$) as determined by cation-exchange chromatography. The kinetics of the isomerization reaction were investigated at 295 nm, where the $(\text{NH}_3)_5\text{CoSCONH}(\text{CH}_3)^{2+}$ complex makes the major contribution to the absorbance. The isomerization follows the rate law

$$k_{\text{obsd}} = k_i + k[\text{H}^+]$$

The kinetic data are given in Table III. At 25°C and $I = 1.0 \text{ M}$ (LiClO_4) $k_i = (7.10 \pm 0.30) \times 10^{-5} \text{ s}^{-1}$ and $k = (9.77 \pm 0.50) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$. The value of k_i determined in this work compares favorably with values determined for a neutral aqueous solution in a base-catalyzed study:⁷ $k_i = 8.81 \times 10^{-5} \text{ s}^{-1}$ ($I = 0.1 \text{ M}$ (NaClO_4)) and $9.60 \times 10^{-5} \text{ s}^{-1}$ (H_2O). The spontaneous reaction lacks dissociative labilization, and the driving force for the reaction appears to be the nucleophilicity of the nearby sulfur atom.¹⁴ In a base-catalyzed pathway, dissociative labilization is undoubtedly provided by the amido group in an $\text{S}_{\text{N}}1\text{cb}$ mechanism. For the cobalt complex, the addition of a proton to sulfur could weaken the Co-O bond, thus promoting a dissociatively assisted isomerization. The fact that more $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ is produced as the $[\text{H}^+]$ is increased is consistent with competition for the vacant site by the S atom and solvent water.

Reduction Studies. For each complex, the stoichiometry was shown to involve one Cr(II) per Co(III) complex by determining

Table IV. Spectral Characteristics of Cr(III) Products from the Reduction of (Thiocarbamate)- and (Carbamate)pentaamminecobalt(III) by Chromium(II)^a

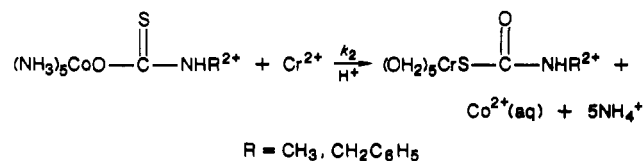
oxidant	Cr(III) product λ_{max} , nm (ϵ_{max} , $\text{M}^{-1} \text{cm}^{-1}$)	% recovery of Cr(III) product
$(\text{NH}_3)_5\text{CoSCONH}(\text{CH}_3)^{2+}$	563 (36), 423 (31), 255 (2.1×10^3)	84 ± 10
$(\text{NH}_3)_5\text{CoOCSNH}(\text{CH}_3)^{2+}$	562 (35), 420 (38), 255 (2.7×10^3)	80 ± 10
$(\text{NH}_3)_5\text{CoSCONH}(\text{CH}_2\text{C}_6\text{H}_5)^{2+}$ ^b	567, 408 (sh), 284	
$(\text{NH}_3)_5\text{CoOCSNH}(\text{CH}_2\text{C}_6\text{H}_5)^{2+}$ ^b	566, 410 (sh), 284	
$(\text{NH}_3)_5\text{CoSCONH}(\text{C}_6\text{H}_5)^{2+}$	568 (36), 421 (35), 255 (1.0×10^4)	94 ± 5
$(\text{NH}_3)_5\text{CoSCONH}(4-\text{CN}-\text{C}_6\text{H}_4)^{2+}$ ^b	566, 422, 256	
$(\text{NH}_3)_5\text{CoOCONH}(\text{C}_6\text{H}_5)^{2+}$ ^c	582 (21), 415 (22)	

^a Analyses were carried out at $[\text{H}^+] = 0.10$ and 0.20 M . The data were the result of at least four separate determinations. ^b λ_{max} values were obtained from spectral scans of 1:1 mixtures of the Cr(II) and Co(III) complexes. Hydrolysis and precipitation precluded the accurate determination of extinction coefficients by this method. Attempted chromatography of the reaction mixtures was also unsuccessful. ^c λ_{max} values were obtained from spectral scans of 1:1 mixtures of the Cr(II) and Co(III) complexes. For this complex, slow decomposition to CO_2 and aniline is a complication.

Table V. Kinetic Data for the Reduction of the O-Bonded (Methylthiocarbamate)- and (Benzylthiocarbamate)pentaamminecobalt(III) Ions by Chromium(II)^a

complex ^b	$10^3[\text{Cr}^{2+}]$, M	$[\text{H}^+]$, M	k_2 , $\text{M}^{-1} \text{s}^{-1}$ ^c
methyl	6.25	0.10	70.4
	12.4	0.10	62.4
	18.75	0.10	68.3
	25.0	0.10	66.8
	12.5	0.20	66.4
benzyl	25.0	0.20	68.0
	1.25	0.10	52.0
	6.12	0.10	51.1
	12.5	0.10	54.8
	1.25	0.20	46.4
	12.5	0.20	54.4

^a Concentrations are initial values; $T = 25^\circ\text{C}$ and $I = 1.0 \text{ M}$ (LiClO_4). ^b $[\text{Cobalt(III) complex}] = 10^{-4} \text{ M}$. ^c $k_{\text{obs}}/[\text{Cr}^{2+}]$.

Scheme I

excess Cr(II) for several initial ratios of $[\text{Cr(II)}]:[\text{Co(III)}]$. Furthermore, in a few cases, the products of the reaction were isolated by cation-exchange chromatography and the percent ligand transfer determined. The spectral characteristics and percent recovery of the chromium(III) products for the Cr^{2+} reductions are given in Table IV. Some hydrolysis of the Cr(III) products was observed on the column, and the isolated percentages are somewhat less than 100%. Nevertheless, the data indicate that the reactions are all inner sphere with virtually no outer-sphere component. For all of the thiocarbamate complexes studied, the spectral characteristics of the chromium(III) products indicate the presence of a Cr-S bond. Particularly diagnostic in this regard is the presence of a ligand-to-metal charge-transfer band in the ultraviolet region of the spectrum.¹³ The reduction of both linkage isomers by Cr^{2+} ($\text{R} = \text{CH}_3$ and $\text{CH}_2\text{C}_6\text{H}_5$) gave the same final chromium(III) product.

The reduction of the O-bonded methyl and benzyl complexes follows the simple rate law

$$-\frac{d[\text{Co(III) complex}]}{dt} = k_2[\text{Cr(II)}][\text{Co(III) complex}] \quad (1)$$

The kinetic data are given in Table V. The reaction was mon-

(13) Weschler, C. J.; Deutsch, E. *Inorg. Chem.* **1973**, *12*, 2682.

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Table VI. Kinetic Data for the Reduction of S-Bonded $(\text{NH}_3)_5\text{CoSCONHR}^{2+}$ by Chromium(II)^{a,b}

R	$10^3[\text{Cr}^{2+}]$, M	$[\text{H}^+]$, M	10^4k_2 , $\text{M}^{-1} \text{s}^{-1}$ ^c
C_6H_5	10.6	0.10	3.4
	12.0	0.10	3.5
	7.98	0.060	3.5
	10.2	0.060	3.5
	6.80	0.11	3.4
	10.2	0.12	3.5
	7.98	0.16	3.5
	6.90	0.21	3.5
	6.90	0.40	3.5
	6.80	0.40	3.5
	5.30	0.10	3.4
	6.00	0.10	3.5
	CH_3	5.10	0.10
10.1		0.10	6.5
4.05		0.053	6.5
4.03		0.10	6.5
6.90		0.10	6.5
5.18		0.21	6.5
4.04		0.30	6.4
4.04		0.40	6.5
4-CN- C_6H_4	10.8	0.10	2.2
	7.50	0.10	2.2
	10.1	0.10	2.2
	7.98	0.055	2.2
	7.98	0.10	2.2
	7.98	0.26	2.1
	7.98	0.51	2.1
$\text{CH}_2\text{C}_6\text{H}_5$	2.50	0.10	4.0
	5.00	0.10	4.0
	2.50	0.20	4.0

^aConcentrations are initial values; $T = 25^\circ\text{C}$, $I = 1.0 \text{ M}$ (LiClO_4), and $\lambda = 510 \text{ nm}$ (first reaction, absorbance decrease). ^b[Cobalt(III) complex] = 10^{-3} – 10^{-4} M . ^cEach determination was the average of 8–12 runs.

itored by following both the disappearance of cobalt(III) ($\lambda = 518 \text{ nm}$) and the appearance of the chromium(III) product ($\lambda = 560 \text{ nm}$). In both cases only one reaction was observed with the production of a single chromium(III) product. Both the kinetic results and the product analyses strongly suggest direct attack of chromium(II) at the remote sulfur to produce a S-bonded chromium(III) complex (Scheme I).

The reduction of the S-bonded cobalt(III) complexes also follows the simple rate law given by (1) with a first-order dependence on chromium(II) concentration. The data are collected in Table VI. However, in addition to the reduction step, a subsequent chromium(II)-independent reaction was observed with

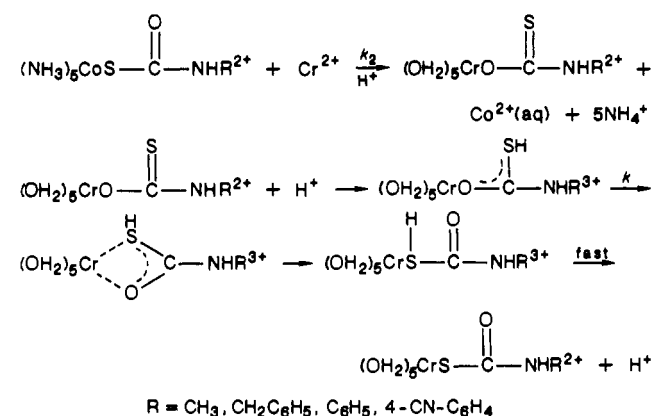
$$k_{\text{obsd}} = k[\text{H}^+] \quad (2)$$

The kinetic data for this second step are given in Table VII. For $\text{R} = \text{CH}_3$, $k = 41 \pm 2 \text{ M}^{-1} \text{ s}^{-1}$, and for $\text{R} = \text{C}_6\text{H}_5$ and $\text{CH}_2\text{C}_6\text{H}_5$, $k = 14 \pm 1 \text{ M}^{-1} \text{ s}^{-1}$, at 25°C and $I = 1.0 \text{ M}$. The final product of the reaction (two separate steps) was identical with that produced directly by reduction of the O-bonded linkage isomers, i.e. the pentaquachromium(III) S-bonded thiocarbamate species. A mechanism consistent with these facts is given in Scheme II. Although we have proposed a mechanism involving only remote attack at oxygen, it is not possible to rule out an adjacent attack component since the proposed intermediate cannot be isolated and characterized. However, rapid-scan spectra of the initial product of reduction and its subsequent isomerization to the final Cr(III)-S-bonded species give no indication that two species are initially produced. Furthermore, the increase in absorbance for this second reaction observed in the 550–600-nm region for the production of the Cr(III)-S-bonded complex is consistent with known extinction coefficients of Cr-S and Cr-O complexes.¹⁵ An unexpected feature of the Cr-O to Cr-S isomerization reaction

Table VII. Kinetic Data for the Isomerization of $(\text{OH}_2)_5\text{CrOCSNHR}^{2+}$ Complexes^{a,b}

R	$10^3[\text{Cr}^{2+}]$, M	$[\text{H}^+]$, M	k_{obsd} , s^{-1}
CH_3	2.50	0.0010	0.10
	2.50	0.050	1.90
	2.50	0.10	4.10
	12.5	0.10	4.10
	2.50	0.20	8.20
	12.5	0.20	8.20
C_6H_5	2.50	0.10	1.40
	5.00	0.10	1.43
	2.50	0.20	2.81
$\text{CH}_2\text{C}_6\text{H}_5$	2.50	0.10	1.39
	5.00	0.10	1.43
	2.50	0.20	2.81

^aConcentrations are initial values; $T = 25^\circ\text{C}$, $I = 1.0 \text{ M}$ (LiClO_4), and $\lambda = 560 \text{ nm}$ (second reaction, absorbance increase). ^bChromium(III) complex generated by reduction of the corresponding $(\text{NH}_3)_5\text{CoSCONHR}^{2+}$ cation by chromium (II).

Scheme II

is the first-order hydrogen ion term. As noted above, similar behavior was observed for the Co-O to Co-S isomerization. However, in the case of the chromium(III) reaction, the isomerization is totally dominated by the hydrogen ion assisted pathway. Presumably, protonation at the remote sulfur weakens the Cr-oxygen bond, providing the driving force for attack by the more nucleophilic sulfur atom. Although we have no direct evidence for the 7-coordinate intermediate proposed in this intramolecular isomerization, a similar proposal is favored for the isomerization of $(\text{NH}_3)_5\text{Co}^{18}\text{OCOCH}_3^{2+}$ in polar solvents.¹¹

For comparative purposes, the reaction of the (*N*-phenylcarbamato)cobalt(III) complex with chromium(II) was briefly investigated. At low acid concentrations (0.010–0.10 M) the observed rate constant was first order in both cobalt(III) and chromium(II) concentration and independent of hydrogen ion. The second-order rate constant was $0.646 \text{ M}^{-1} \text{ s}^{-1}$ at 25°C and $I = 1.0 \text{ M}$ (LiClO_4). The chromium(III) product of the reduction behaved as a 2+ ion on a cation-exchange column and displayed absorption maxima at 582 nm ($21 \text{ M}^{-1} \text{ cm}^{-1}$), 415 (22), and 233. These values are consistent with those expected for the O-bonded complex $(\text{OH}_2)_5\text{CrOCONH}(\text{C}_6\text{H}_5)^{2+}$. At hydrogen ion concentrations $>0.10 \text{ M}$ good kinetic data for the reduction could not be obtained due to competing decomposition of the cobalt(III) complex. Scans of the visible region of the spectrum as a function of time at $[\text{H}^+] = 0.20 \text{ M}$ for the Co(III) complex alone showed that the band at 508 nm due to the (phenylcarbamato)pentaamminecobalt(III) ion decreased and shifted to 492 nm. The final cobalt(III) product of the reaction was isolated by cation-exchange chromatography and shown to be the aquapentaamminecobalt(III) complex by its visible spectrum (λ_{max} (ϵ_{max}) 492 nm ($49 \text{ M}^{-1} \text{ cm}^{-1}$) and 345 (46)) and ¹H NMR spectrum (cis NH_3 , 3.93 ppm; trans NH_3 , 2.93 ppm; OH_2 , 5.8 ppm). The nature of the organic product of the decomposition was probed by obtaining ¹H NMR spectra as a function of time in $\text{D}_2\text{O}/\text{D}_2\text{SO}_4$ and also in tri-

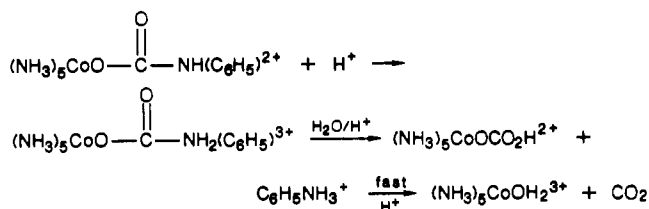
(15) Sedor, F. A. Ph.D. Thesis University of Florida, 1971. See also Table IV.

Table VIII. Rate Constants for the Reduction of Cobalt(III) Complexes by Chromium(II)

entry no.	complex	$k,^a \text{ M}^{-1} \text{ s}^{-1}$	pathway	ref
1	$(\text{NH}_3)_5\text{CoS}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_3)^{2+}$	6.5×10^4	→ O-C-S	this work
2	$(\text{NH}_3)_5\text{CoS}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{C}_6\text{H}_5)^{2+}$	3.5×10^4	→ O-C-S	this work
3	$(\text{NH}_3)_5\text{CoS}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_2\text{C}_6\text{H}_5)^{2+}$	4.0×10^4	→ O-C-S	this work
4	$(\text{NH}_3)_5\text{CoS}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(4-\text{CN}-\text{C}_6\text{H}_4)^{2+}$	2.2×10^4	→ O-C-S	this work
5	$(\text{NH}_3)_5\text{CoO}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_3)^{2+}$	68	→ S-C-O	this work
6	$(\text{NH}_3)_5\text{CoO}-\overset{\text{S}}{\parallel}{\text{C}}-\text{NH}(\text{CH}_2\text{C}_6\text{H}_5)^{2+}$	55	→ S-C-O	this work
7	$(\text{NH}_3)_5\text{CoO}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}(\text{C}_6\text{H}_5)^{2+}$	0.64	→ O-C-O	this work
8	$(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$	3.3×10^4	→ S	2b
9	$(\text{en})_2\text{Co}(\text{OCH}_2\text{CH}_2\text{NH}_2)^{2+}$	9.4×10^2	→ O	2b
10	$(\text{en})_2\text{Co}(\text{S}(\text{CH}_3)\text{CH}_2\text{CH}_2\text{NH}_2)^{3+}$	0.337	→ S	17
11	$(\text{en})_2\text{Co}(\text{S}(\text{O})_2\text{CH}_2\text{CH}(\text{COOH})\text{NH}_2)^{2+}$	1.46×10^3	→ O-S	18

^a $T = 25^\circ \text{C}$, $I = 1.0 \text{ M}$.

Scheme III



fluoroacetic acid. In both solvents, the multiplet due to the phenyl protons of the cobalt(III) complex collapsed to a singlet at 7.2–7.5 ppm. The observed ^1H NMR spectrum for the organic product is identical with a spectrum of an authentic sample of aniline hydrochloride. It was also observed that a gas was evolved during the decomposition reaction. A reasonable mechanism for the reaction is given in Scheme III.

Rate constants for the electron-transfer reactions obtained in this study as well as related reactions are collected in Table VIII. In the absence of steric constraints it has been shown that coordinated sulfur mediates electron transfer between chromium(II) and cobalt(III) more efficiently than coordinated oxygen.^{16,17} For example, the chromium(II) reductions of $(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+}$ and $(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{OH})^{2+}$ occur 35 and 830 times faster than for their alcoholate analogues. This rate enhancement has been attributed to a sulfur-induced structural trans effect (STE), where less activation is then required to lengthen the trans N–Co bond in achieving the transition state. For these reactions the reductant attacks the coordinated S or O directly in an inner-sphere process. The sulfur-bonded thiocarbamate complexes studied herein are all expected to exert a STE since negatively charged sulfur is capable of charge donation to the cobalt(III) oxidizing center.¹³ Although the X-ray structure⁶ of the phenylthiocarbamate complex was not sufficiently precise to determine a STE, we have observed a kinetic trans effect whereby the trans NH_3 is labilized in DMSO. Since the kinetic

trans effect has been shown to be related to the STE, it seems reasonable to expect a STE for the S-bonded complexes. The chromium(II) reductions of the S-bonded thiocarbamate complexes occur approximately 10^4 times more rapidly than for the O-bonded analogues (compare entries 1–4 with entry 7 in Table VIII). Since we have shown that the S-bonded complexes are reduced by attack at the remote oxygen (as opposed to coordinated sulfur), it seems reasonable to ascribe the 10^4 rate enhancement as due to a STE rather than to some intrinsic facility of coordinated sulfur to directly mediate electrons. The comparison seems particularly reasonable since the complexes are structurally and electronically similar. The important result of this study is that unusually facile electron transfer can result for a remote attack pathway for complexes containing a coordinated sulfur capable of charge donation. Where such possibilities exist, it is crucial to determine the initial product of the electron-transfer reaction. A brief reexamination of the reduction of $(\text{NH}_3)_5\text{CoS}_2\text{O}_3^+$ by Cr^{2+} ¹⁹ gave spectral changes consistent with the production of an initial O-bonded Cr(III) complex that subsequently isomerized to the stable S-bonded form. In light of the above we suspect that the Cr^{2+} reduction of coordinated sulfinic and sulfenic acids (see entry 11 in Table VIII, for example) occurs via attack at oxygen rather than sulfur.¹⁸

It is also apparent that sulfur is a more effective remote lead-in group than oxygen by a factor of 100 (compare entries 5 and 6 with entry 7 in Table VIII). For these oxygen-bonded complexes, no STE is expected.

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Registry No. $(\text{NH}_3)_5\text{CoOCSNHCH}_3^{2+}$, 106782-10-9; $(\text{NH}_3)_5\text{CoOCSNHCH}_2\text{Ph}^{2+}$, 122648-05-9; $(\text{NH}_3)_5\text{CoSCONHC}_6\text{H}_5$, 82292-89-5; $(\text{NH}_3)_5\text{CoSCONHCH}_3$, 106782-08-5; $(\text{NH}_3)_5\text{CoSCONHC}_6\text{H}_4-4-\text{CN}$, 122676-10-2; $(\text{NH}_3)_5\text{CoSCONHCH}_2\text{C}_6\text{H}_4$, 122648-04-8; $(\text{OH})_2\text{CrOCSNHCH}_3$, 122648-06-0; $(\text{OH})_2\text{CrOCSNHCH}_2\text{C}_6\text{H}_5$, 122648-07-1; $(\text{OH})_2\text{CrOCSNHCH}_2\text{C}_6\text{H}_5$, 122648-08-2; Cr^{2+} , 22541-79-3.

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