Contribution from the Department of Chemistry,
University of Guelph, Guelph, Ontario, Canada N1G 2W1

Kinetic Investigation of the Chromium(II) Reduction of Thiosulfatopentaamminecobalt(III). Refinement of the Crystal Structure of $[(NH_3)_5CoS_2O_3]Cl\cdot H_2O$

RODERIC J. RESTIVO, GEORGE FERGUSON,* and ROBERT J. BALAHURA*

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The structure of $[(NH_3)_5CoS_2O_3]Cl\cdot H_2O$, which contains the octahedral species $[(NH_3)_5Co-S-SO_3]^+$ with S-bonded thiosulfate, has been refined by full-matrix least-squares calculations to a final *R* value of 0.031 for 1065 observed reflections measured by diffractometry. The crystals are orthorhombic, $a = 13.092$ (2), $b = 7.9954$ (9), $c = 10.299$ (3) Å, and $Z = 4$ in space group *Pnma* with molecular symmetry *m*. Any structural trans effect is small; the trans Co–N bond length, 1.986 (4) Å, is significantly longer (0.026 (5) Å, 5.2σ) than one of the cis Co–N bonds 1.960 (3) Å but only 0.013 (5) Å (2.6σ) longer than the other (Co–N = 1.973 (3) Å). Other important dimensions in the cation are S–S = 2.048 (2) Å, mean S–O = 1.463 (1) Å, Co–S–S = 110.20 (6)° and S–S–O = 102.8, 109.7 (1)°. The cation also contains an intramolecular N–H···O hydrogen bond (N···O = 2.923 (4) Å). Reduction of $[(NH_3)_5CoS_2O_3]ClO_4$ by chromium(II) follows the rate law $-d \ln [Co^{3+}]/dt = k[Cr^{2+}]$. At 25 °C and $\mu = 1.0$ M ($LiClO_4$), the second-order rate constant is 850 ± 50 M^{-1} s^{-1} with $\Delta H^\ddagger = 9.4 \pm 0.7$ kcal mol^{-1} and $\Delta S^\ddagger = -14 \pm 3$ eu. The data are discussed in terms of attack of chromium(II) at the uncoordinated oxygens with formation of a chromium(III)–oxygen-bonded thiosulfate complex.

Introduction

Structural studies on metal complexes with the thiosulfate ion have dealt mainly with the ambidentate nature of the ligand. On the basis of infrared evidence both sulfur[1-4] and oxygen[5] bonding have been claimed for the thiosulfatopentaamminecobalt(III) complex. Peters and Fraser[5] also studied the chromium(II) reduction of the thiosulfato complex and reported two rates of reduction. These have been attributed to reduction of the O-bonded species (comprising 90% of the mixture) and the S-bonded complex (comprising the remaining 10% of the mixture). We have reinvestigated the chromium(II) reduction in an attempt to clarify these observations. In addition, there has been a considerable interest in the structural and kinetic trans effects exerted by sulfur-containing ligands,[6-9] and we hoped that the results of this analysis would contribute to the understanding of this phenomenon. With this aim in mind we report herein a redetermination of the single-crystal x-ray analysis of thiosulfatopentaamminecobalt(III) chloride[10] which has been shown to contain the S-bonded cation. The results of this earlier photographic x-ray determination were of low accuracy and there was no distinction between cis and trans Co–N bond distances. Our spectroscopic results prompted us to reexamine this structure and seek improved accuracy in order to answer the question concerning the presence of a structural trans effect for this compound. We also wanted to locate the hydrogen atom positions in order to provide reliable structural data on the OH···S hydrogen bond, which has not been extensively studied.

Experimental Section

Preparation of Thiosulfatopentaamminecobalt(III). $[(NH_3)_5CoS_2O_3]Cl$ was prepared by the method of Ray.[11] The resulting impure crystals were dissolved in water and charged onto a cation-exchange column containing Rexyn 102 in the sodium ion form. Elution with 0.1 M NaCl moved a purple band comprising about 80% of the total complex down the column as a 1+ cation. The remaining pink band was retained at the top of the column and was not isolated. The major band was eluted from the column and concentrated HCl was added to precipitate the anhydrous chloride salt. Anal. Calcd for $[(NH_3)_5CoS_2O_3]Cl$: N, 24.0; H, 5.18. Found: N, 23.7; H, 5.22.

The perchlorate salt was prepared from a separate ion-exchange experiment where the major band was separated physically. The complex was removed from the resin with dilute perchloric acid and precipitated from solution with $NaClO_4$. Anal. Calcd for $[(NH_3)_5CoS_2O_3]ClO_4$: N, 19.7; H, 4.22. Found: N, 19.4; H, 4.33.

Crystals for x-ray analysis were grown from a dilute solution of the purified chloride salt as the monohydrate.

The visible spectrum of the complex in H_2O and 0.1 M $HClO_4$ was identical with λ_{max} 512 nm and extinction coefficient 64 ± 1 M^{-1} cm^{-1}. In the ultraviolet region a peak was observed at 289 nm with ϵ 12800 ± 300 M^{-1} cm^{-1}.

A proton magnetic resonance spectrum in $(Me)_2SO$-d_6 showed the trans NH_3 at τ 6.60 while the cis NH_3's were at τ 6.92 with respect to TMS.

Kinetic Studies. Kinetic studies were carried out on a Durrum stopped-flow spectrophotometer by observing the decrease in absorbance of the Co(III) peak at 512 nm. All solutions were deoxygenated using high-purity argon. The kinetic runs were all carried out under pseudo-first-order conditions using an excess of chromium(II). The rate constants were determined from plots of log $(A_t - A_\infty)$ vs. time where A_t is the absorbance at time *t* and A_∞ is the absorbance after the reaction is complete.

The products of the reaction were separated by cation-exchange chromatography on Dowex 50W-X8 in the lithium ion form. The chromium(III) complexes were characterized by their visible spectra with chromium being determined as chromate, ϵ 4815 M^{-1} cm^{-1} at 372 nm.[12]

Crystal Structure Analysis of Thiosulfatopentaamminecobalt(III) Chloride Monohydrate. From a batch of dark red parallelepiped crystals of $[Co(NH_3)_5S_2O_3]Cl\cdot H_2O$ a crystal with dimensions 0.13 × 0.14 × 0.26 mm was chosen for x-ray analysis. Precession and Weissenberg photographs taken with Cu Kα radiation indicated an orthorhombic space group with systematic absences of $0kl$ when $k + l$ is odd and of $hk0$ when $h = 2n + 1$; these conditions determine the space group as either *Pnma* (D_{2h}^{16}, No. 62) or $Pn2_1a$ (C_{2v}^{9}, No. 33). The unit cell parameters $a = 13.092$ (2), $b = 7.9954$ (9), and $c = 10.299$ (2) Å were obtained by a least-squares refinement of the setting angles of 12 general reflections with $\pm 2\theta$ in the range 18–21°, measured on a Hilger and Watts Y290 four-circle diffractometer using graphite-monochromated Mo Kα radiation ($\bar{\lambda}$ 0.71069 Å). The unit cell volume *V*, based on these dimensions, is 1078 Å^3. A density of 1.90 g cm^{-3} was calculated for $Z = 4$, and this agreed with that of 1.86 g cm^{-3} measured by flotation of several crystals in carbon tetrachloride–ethylene bromide.

Data were collected on the same crystal used for the preliminary investigation at room temperature (22 °C) using the Hilger and Watts diffractometer (and graphite-monochromated Mo Kα radiation, $\bar{\lambda}$ 0.71069 Å). The crystal was aligned so that the *c* axis was approximately 15° from being coincident with ϕ. A θ–2θ scanning technique was used to collect a unique data set to a maximum of $\theta = 25°$; a rate of 60 steps of 0.01° with a 1-s count at each step was used and stationary-background measurements (b_1, b_2) of 15-s duration were made at both sides of the peak. Zirconium-foil attenuators were automatically inserted if the intensity of the diffracted beam exceeded 10000 counts/s. The intensity of two standard reflections, which were monitored at 100-reflection intervals, varied by less than 1.8% over the period of data collection and this was corrected for by application of linear-scale factors.

Table I. $|E|$ Statistics and Distribution

Mean	Found	Calcd Centric	Calcd Acentric
$\|E\|$	0.806	0.798	0.886
$\|E^2\|$	1.024	1.000	1.000
$\|E^2 - 1\|$	0.965	0.968	0.736
$\|(E^2 - 1)\|^2$	1.914	2.000	1.000
$\|(E^2 - 1)\|^3$	7.524	8.000	2.000

A total of 1401 intensity maxima were collected and corrected for Lorentz and polarization effects $[1/Lp = (\sin 2\theta_s)(\cos^2 2\theta_m + 1)/(\cos^2 2\theta_m + \cos^2 2\theta_s)$, where $2\theta_s$ and $2\theta_m$ are the diffraction angles at the sample crystal and monochromator, respectively]. With an absorption coefficient $\mu = 22.6$ cm^{-1} for Mo Kα radiation, transmission coefficients of the order 73–75% would arise for a crystal of the size used to collect the octant measured, and absorption corrections were not applied. Standard deviations were assigned to intensity values according to $\sigma(I) = (S + B)^{1/2}$ where S is the scan count and $B = 4(b_1 + b_2)$. Of the 1401 measured reflections, 1065 with $I > 3\sigma(I)$ were employed in the elucidation and refinement of the structure.

An analysis of intensity distribution and E statistics (Table I) gave a clear indication that the space group was the centrosymmetric *Pnma* rather than the noncentrosymmetric $Pn2_1a$. We chose to reexamine the Patterson map in order to verify the crystallographic mirror plane imposed on the molecular structure. Choice of space group *Pnma* demands that the cobalt, chlorine, both sulfurs, one nitrogen, and two oxygen atoms (one each from the thiosulfate and water moieties) lie on a crystallographic mirror plane with their y coordinates fixed. An estimate of the overall scale factor was obtained using Wilson's method. An analysis of the vector set obtained from a three-dimensional sharpened Patterson was consistent with the molecule having m symmetry. Approximate coordinates for the cobalt and sulfur atoms were obtained from the Patterson map, and a Fourier synthesis based on these atoms revealed the positions of all chlorine, oxygen, and nitrogen atoms.

The structure was refined initially by full-matrix least-squares calculations with anisotropic thermal parameters for the cobalt atom and isotropic parameters for the other nonhydrogen atoms, using unit weights and the atomic scattering functions[13] for the chlorine ion and the neutral species for the rest of the nonhydrogen atoms. Three cycles of refinement reduced $R = \sum\|F_o| - |F_c\|/\sum|F_o|$ to 0.068. A weighting scheme of the form $w^{1/2} = 1/[\sigma^2(F) + 0.003F^2]^{1/2}$ was then applied and an analysis of variance indicated that $\sum w\Delta^2$ was independent of $|F_o|$ and $(\sin\theta)/\lambda$. Two further cycles of refinement, using anisotropic thermal parameters for all atoms and both the real and imaginary parts of the anomalous dispersion correction[14] applied to cobalt, reduced R to 0.048 and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, the function minimized, to 0.070. A final difference Fourier map revealed electron density maxima (~0.6 e Å^{-3}) only in positions which were chemically reasonable for all of the hydrogen atoms; these were then included in observed positions (with isotropic U values of 0.063 Å^2 and scattering factors from ref 15) but not refined in subsequent calculations. A further verification of the correct choice of centrosymmetric space group is the observation that all the hydrogen atom positions were obtained as well-defined peaks in the final difference Fourier map. Two additional refinement cycles converged to $R = 0.031$ and $R_w = 0.064$ for 1065 observed reflections; the overall R for the entire set of 1401 reflections is 0.036. The standard deviation of an observation of unit weight is 1.07. In the last refinement cycle, the ratio of the largest shift to standard deviation is 0.54 for the x coordinate of atom O(3). A list of observed and calculated structure factors is available.[16]

Final positional and thermal parameters for the nonhydrogen atoms are in Table II; the hydrogen positions obtained from the final difference Fourier map are in Table III. The principal interatomic distances and angles are in Table IV. Details of the hydrogen-bond network in the crystal structure are in Table V.

Results and Discussion

Kinetic Results. The reduction of $[(NH_3)_5CoS_2O_3]^+$ follows the rate law

$$-d \ln [\text{Co(III) complex}]/dt = k[\text{Cr(II)}]$$

The kinetic data are given in Table VI. At 25 °C, $k = 850 \pm 50$ M^{-1} s^{-1} with $\Delta H^{\ddagger} = 9.4 \pm 0.7$ kcal mol^{-1} and $\Delta S^{\ddagger} = -14 \pm 3$ eu. The chromium(III) product of the reduction was isolated by cation-exchange chromatography of reaction mixtures containing a 1:1 ratio of Cr(II):Co(III). The initial rapid reduction produced a bright green solution, which underwent subsequent reactions (vide infra). A white colloidal precipitate was formed in the solution after a time and this was dependent on the acid concentration in the solution. In 0.15 M $HClO_4$, the precipitate formed almost immediately after reduction, but in 0.30 M $HClO_4$ the first appearance of precipitate was after approximately 20 min. The solutions were filtered but the clear green filtrate also became cloudy after a short time. It appears that the green complex contains coordinated thiosulfate which aquates to give free thiosulfate and Cr(III) in acid media and that it is this latter mixture which produces the white precipitate (see eq 1–3). Reaction

$$(NH_3)_5CoS_2O_3^{+} + Cr^{2+} \xrightarrow{H^+} \underset{\text{green}}{(OH_2)_5CrS_2O_3^{+}} + Co^{2+}(aq) + 5NH_4^{+} \quad (1)$$

$$\underset{\substack{\text{(initial product}\\ \text{of redn)}}}{(OH_2)_5CrS_2O_3^{+}} + \xrightarrow{H^+} Cr(OH_2)_6^{3+} + S_2O_3^{2-} \quad (2)$$

$$S_2O_3^{2-} + H^+ \rightleftarrows HS_2O_3^{-} \rightleftarrows HSO_3^{-} + S\downarrow \quad (3)$$

Table II. Positional[a] and Thermal[b] Parameters for Nonhydrogen Atoms of $[(NH_3)_5CoS_2O_3]Cl\cdot H_2O$

Atom	x	y	z	Atom	x	y	z
Co	0.162 94 (4)	0.25[c]	0.253 02 (5)	O(2)	0.398 3 (2)	0.0998 (3)	0.441 7 (3)
Cl	0.398 23 (11)	0.25[c]	−0.015 56 (13)	O(3)	0.081 9 (5)	0.25[c]	0.763 5 (6)
S(1)	0.198 75 (9)	0.25[c]	0.470 39 (10)	N(1)	0.129 1 (3)	0.25[c]	0.065 1 (4)
S(2)	0.353 53 (9)	0.25[c]	0.499 34 (10)	N(2)	0.058 8 (2)	0.0774 (4)	0.288 0 (3)
O(1)	0.362 2 (3)	0.25[c]	0.641 1 (3)	N(3)	0.262 7 (2)	0.0730 (4)	0.217 3 (3)

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	2.29 (4)	2.11 (4)	1.96 (4)	0.0[d]	−0.35 (2)	0.0[d]
Cl	5.23 (8)	3.38 (7)	2.72 (6)	0.0[d]	0.65 (5)	0.0[d]
S(1)	2.28 (6)	3.51 (7)	1.97 (6)	0.0[d]	−0.19 (4)	0.0[d]
S(2)	2.34 (5)	2.25 (6)	2.11 (7)	0.0[d]	−0.37 (4)	0.0[d]
O(1)	3.99 (18)	3.92 (20)	2.23 (17)	0.0[d]	−0.93 (14)	0.0[d]
O(2)	3.60 (12)	3.35 (14)	4.02 (14)	1.01 (10)	−0.57 (10)	−0.96 (12)
O(3)	7.97 (45)	9.70 (58)	7.80 (42)	0.0[d]	1.53 (27)	0.0[d]
N(1)	4.37 (23)	2.66 (21)	2.50 (19)	0.0[d]	−0.70 (17)	0.0[d]
N(2)	2.76 (12)	3.12 (15)	3.23 (14)	−0.55 (12)	−0.42 (12)	0.27 (12)
N(3)	3.73 (14)	2.69 (13)	2.27 (12)	0.49 (12)	−0.21 (11)	−0.31 (11)

[a] The estimated standard deviations of the last digit are in parentheses. [b] Anisotropic temperature factors of the form $\exp[-2\pi^2\cdot(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ were used for the nonhydrogen atoms; the resulting thermal coefficients U_{ij} ($\times 10^2$ Å^2), with standard deviations of the last significant figure given in parentheses, are tabulated above. [c] Special symmetry position. [d] Held constant.

Table III. Positional Parameters for Hydrogen Atoms of $[(NH_3)_5CoS_2O_3]Cl{\cdot}H_2O$

Atom	x	y	z
H(11)	0.100	0.153	0.038
H(12)	0.189	0.250	0.015
H(21)	0.075	0.000	0.329
H(22)	0.020	0.052	0.228
H(23)	0.018	0.109	0.360
H(31)	0.241	−0.022	0.189
H(32)	0.301	0.045	0.280
H(33)	0.299	0.093	0.150
H(41)	0.106	0.250	0.650
H(42)	0.000	0.250	0.813

Table IV. Principal Intermolecular Bond Distances (Å)[a] and Interatomic Bond Angles (deg)[a] for $[(NH_3)_5CoS_2O_3]Cl{\cdot}H_2O$

(a) Distances from Cobalt			
Co-S(1)	2.287 (1)	Co-N(2)	1.973 (3)
Co-N(1)	1.986 (4)	Co-N(3)	1.960 (3)
(b) Distances in Thiosulfate Group			
S(1)-S(2)	2.048 (2)	S(2)-O(2)	1.462 (3)
S(2)-O(1)	1.464 (3)		
(c) Ammine N-H Distances			
N(1)-H(11)	0.91	N(2)-H(23)	0.94
N(1)-H(12)	0.94	N(3)-H(31)	0.86
N(2)-H(21)	0.78	N(3)-H(32)	0.85
N(2)-H(22)	0.83	N(3)-H(33)	0.85
(d) Water O-H Distances			
O(3)-H(41)	1.21	O(3)-H(42)	1.18
(e) Bond Angles			
S(1)-Co-N(1)	178.9 (5)	N(2)-Co-N(3′)	178.1 (2)
S(1)-Co-N(2)	87.9 (1)	N(3)-Co-N(3′)	92.4 (1)
S(1)-Co-N(3)	92.7 (1)	Co-S(1)-S(2)	110.20 (6)
N(1)-Co-N(2)	91.4 (1)	S(1)-S(2)-O(1)	102.8 (1)
N(1)-Co-N(3)	88.0 (1)	S(1)-S(2)-O(2)	109.7 (1)
N(2)-Co-N(3)	89.4 (1)	O(1)-S(2)-O(2)	112.0 (1)
N(2)-Co-N(2′)[b]	88.8 (1)	O(2)-S(2)-O(2′)	110.4 (2)

[a] The esd's shown in parentheses are right adjusted. [b] The coordinates of atoms marked with a prime are obtained from those of Table I by applying the mirror symmetry axis transformation $x, {}^1/_2 - y, z$.

Table V. Possible Hydrogen-Bonding Contacts for $[(NH_3)_5CoS_2O_3]Cl{\cdot}H_2O$

X-H· · ·Y	X-H, Å	H· · ·Y, Å	X· · ·Y, Å	X-H· · ·Y, deg
O(3)-H(41)· · ·S(1)^{I} [a]	1.21	2.21	3.385 (7)	161.7
N(3)-H(33)· · ·Cl^{I}	0.85	2.49	3.302 (3)	160.2
N(2)-H(23)· · ·Cl^{II}	0.94	2.51	3.437 (3)	166.4
N(2)-H(21)· · ·Cl^{III}	0.78	2.58	3.356 (3)	170.6
N(1)-H(11)· · ·O(2)^{IV}	0.91	2.25	3.092 (3)	153.8
N(2)-H(22)· · ·O(2)^{V}	0.83	2.39	3.168 (4)	156.1
N(3)-H(32)· · ·O(2)^{I}	0.85	2.14	2.923 (4)	153.2
N(3)-H(31)· · ·O(1)^{VI}	0.86	2.32	3.155 (3)	163.0
O(3)-H(42)· · ·O(1)^{VII}	1.18	1.87	3.040 (7)	169.6

[a] The superscripts refer to the following equivalent positions: I, x, y, z; II, $x - {}^1/_2, {}^1/_2 - y, {}^1/_2 - z$; III, ${}^1/_2 - x, y - {}^1/_2, {}^1/_2 + z$, IV, ${}^1/_2 - x, -y, z - {}^1/_2$; V, $x - {}^1/_2, y, {}^1/_2 - z$; VI, ${}^1/_2 - x, y - {}^1/_2, z - {}^1/_2$; VII, $x - {}^1/_2, {}^1/_2 - y, {}^3/_2 - z$.

Table VI. Kinetic Data for the Reduction of $[(NH_3)_5CoS_2O_3]^+$ by Cr^{2+} [a]

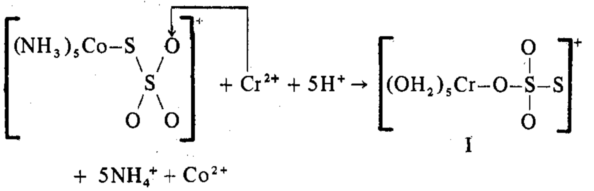
T, °C	$10^2[Cr^{2+}]$, M	$10^3[Co^{3+}]$, M	$[H^+]$, M	k, M^{-1} s^{-1}
25.4	1.1	2.0	0.20	840
	1.1	2.5	0.61	850
	1.1	2.0	0.20	867
	2.3	2.0	0.20	884
	2.3	2.0	0.20	861
	4.6	2.0	0.20	884
	0.57	0.059	0.20	867[b]
34.4	2.3	3.0	0.20	1260
	2.3	3.0	0.20	1370
	2.3	2.5	0.61	1370
	2.3	2.5	0.61	1590
43.8	2.3	3.0	0.20	2230
	2.3	3.0	0.20	2410
	2.3	3.0	0.20	2230
	2.3	3.0	0.20	2230
	2.3	3.0	0.61	2230
	2.3	3.0	0.61	2410

[a] Ionic strength maintained at 1.0 M with $LiClO_4$. All runs monitored at λ 512 nm unless otherwise noted. [b] λ 289 nm.

3 is catalyzed by Cr(III). The solution produced upon reduction was charged onto the cation-exchange resin and a diffuse green band was eluted from the column with a solution which was 0.125 M in $NaClO_4$ and 0.0125 M in $HClO_4$. Under these conditions, the Co^{2+}(aq) produced in the reaction remains at the top of the column implying that the green complex has a 1+ charge. Also, under these conditions, there is less than 5% Cr^{3+}(aq) detected and thus the stoichiometry involved 1 mol of Cr(II)/mol of cobalt(III) complex. The green solution gave a uv–visible spectrum with peaks at 582 (26 ± 1), 422 (26 ± 1), and 258 nm (2800 ± 100 M^{-1} cm^{-1}). If the solution was allowed to stand, a white precipitate was formed, thus substantiating the previous comments. The green complex is thus formulated as $[(OH_2)_5CrS_2O_3]^+$. The same product was isolated from product studies carried out with excess Cr^{2+}(aq).

Since thiosulfate is an ambidentate ligand, all mechanistic conclusions must be based on the identity of the cobalt(III) complex as well as on the resultant mode of coordination in the chromium(III) product. In the cobalt(III) complex, bonding through the sulfur atom is clearly established in the solid state by the x-ray structural analysis. Furthermore, infrared studies on $K_4[(CN)_5CoS_2O_3]$ indicate that the thiosulfate group retains an identical bonding mode and stereochemistry both in the solid state and in aqueous solution.[4] In addition, the ^1H NMR spectrum of $[(NH_3)_5CoS_2O_3]^+$ indicates sulfur bonding since the trans NH_3 resonance is 0.32 τ unit downfield of the cis NH_3 resonance. For oxygen bonding the trans NH_3 resonance would be expected about 1–1.5 τ units upfield of the cis NH_3 resonance.[17] Thus, we feel that the thiosulfate ligand is coordinated to cobalt through the sulfur atom in aqueous solution.

The kinetic and ion-exchange results are consistent with the production of either I or II via the pathways outlined in eq 4 and 5. Models of the cobalt(III) complex indicate that both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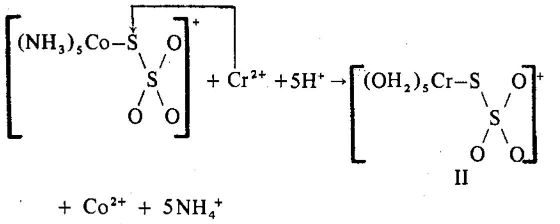
(5)

coordinated sulfur and remote oxygen are potential sites for attack of reductant. When the reduction was studied in the ultraviolet region, no evidence for the formation of intermediates was observed; thus, the bonding mode in the chromium(III) product likely indicates the position of attack by the reductant. Unfortunately, the bonding mode in the Cr(III) product cannot be unambiguously assigned. However,

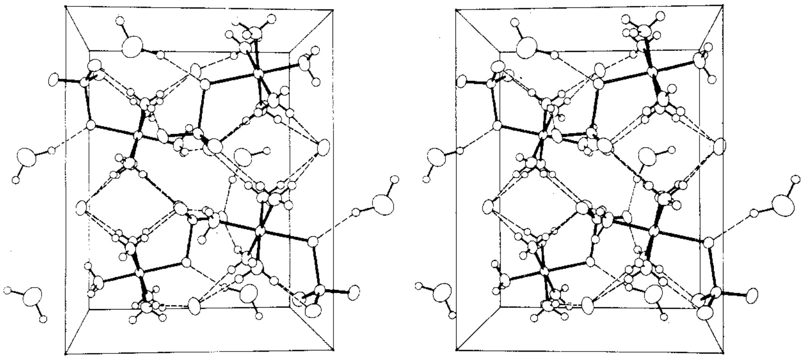

Figure 1. Stereoview of the unit cell contents of $[(NH_3)_5CoS_2O_3]Cl \cdot H_2O$

we favor oxygen coordination (I) on the basis of the arguments presented below. Since Cr(III) is a hard acid, a chromium–oxygen bond with the thiosulfate ligand would be expected to be more stable than a corresponding chromium–sulfur bond. The spectrum of the product of the reaction (λ_{max} at 582 and 422 nm) is very similar to that found for sulfatopentaaquochromium(III), $[(OH_2)_5CrOSO_3]^+$, with λ_{max} at 586 and 417 nm.[18] If the product of the reduction was $[(OH_2)_5CrS{-}SO_3]^+$, the λ_{max} would be expected at a much lower energy. (Compare, for example, $[(OH_2)_5CrSCN]^{2+}$, λ_{max} at 435 nm, with $[(OH_2)_5CrNCS]^{2+}$, λ_{max} at 410 nm.[19])

The reduction of $[(NH_3)_5CoSCN]^{2+}$ by Cr(II) has been shown to occur both by adjacent attack at coordinated sulfur and by remote attack at nitrogen.[20] The two rates obtained were similar, with k(adjacent) = 0.8×10^5 M^{-1} s^{-1} and k(remote) = 1.9×10^5 M^{-1} s^{-1}. It appears that the coordinated sulfur is exposed to attack by virtue of the angular coordination to cobalt. In $[(NH_3)_5CoSCN]^{2+}$ and $[(NH_3)_5CoS{-}SO_3]^+$, the Co–S–C[21] and Co–S–S bond angles are 104.9 (11) and 110.20 (6)°, respectively. For the adjacent path in $[(NH_3)_5CoSCN]^{2+}$, the unfavorable stability of a chromium–sulfur bond with respect to chromium–nitrogen bond appears to be offset by the unusually high electron-mediating ability of the sulfur atom. When $[Co(CN)_5]^{3-}$ is the reductant,[22] attack takes place exclusively at coordinated sulfur at a very much faster rate than for Cr(II) reduction. In this case, the $[(CN)_5CoSCN]^{3-}$ complex formed is favored thermodynamically and, along with the effective electron-mediating ability of sulfur, contributes to the high rate estimated. The rates of reduction for attack at coordinated sulfur are all $>10^5$ M^{-1} s^{-1} and the rate for the thiosulfato complex (850 M^{-1} s^{-1}) thus indicates attack at the remote oxygens rather than coordinated sulfur (eq 4).

The rates of reduction by chromium(II) of $[(NH_3)_5CoOSO_3]^+$,[5] $[(NH_3)_5CoSO_3]^+$,[5] and $[(NH_3)_5CoSSO_3]^+$ are 18, 18.6, and 850 M^{-1} s^{-1} at 25 °C. It appears that coordinated sulfur is about 50 times more effective than coordinated oxygen as a mediator in electron transfer when comparing the sulfato (O–S–O path) and thiosulfato complexes (O–S–S path). However, on this basis the sulfite complex (O–S path) would be expected to react much faster. Since, in all three cases, the stability of the precursor complex formed by attack at the remote oxygens must be about the same, it appears that electron mediation through oxygen is rate limiting. The unusually facile electron mediation for sulfur is apparently restricted to attack at coordinated sulfur and direct mediation of the electron to the metal. For remote attack paths, sulfur appears to be an unusually effective mediator only when oxygen is not in the electron-transfer path.

The results obtained by Peters and Fraser[5] conflict with those reported here. First, the only cobalt(III) isomer isolated has been shown to be S bonded and not a mixture of O- (90%) and S-bonded (10%) isomers. Second, the kinetic studies reported by Peters and Fraser also seem invalid due to the fact that a mixture of impure compounds was probably used in the rate studies. If the complex studied was actually the Co–$S_2O_3^+$ isomer, the previous authors no doubt were observing aquation of Cr–$S_2O_3^+$ and the subsequent reactions that follow.

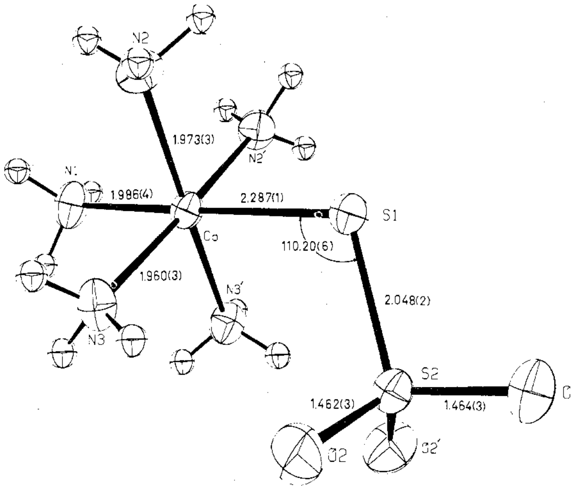

Figure 2. Perspective view with 50% probability ellipsoids of the $[(NH_3)_5CoS_2O_3]^+$ cation.

Structural Results. The crystal structure (Figure 1) consists of discrete $[(NH_3)_5CoS_2O_3]^+$ cations with m symmetry, Cl^- ions, and water of hydration. The constituent ions and water molecules are held together by a three-dimensional network of hydrogen-bonding and electrostatic interactions. Our analysis agrees, in general, with the previous determination[10] but is much more precise.

The $[(NH_3)_5CoS_2O_3]^+$ cation (Figure 2) is composed of an octahedrally coordinated cobalt atom bonded to five ammonia ligands with cis N–Co–N angles of 88.0–92.4 (1)° and a thiosulfate ligand with cis N–Co–S angles of 87.9 and 92.7 (1)°. The attachment of the thiosulfate group to the cobalt atom through the sulfur atom is clearly established, with Co–S = 2.287 (1) Å. This Co–S distance is longer than the value of 2.218 Å[6] reported for the sulfur-bound sulfito complex $[(NH_3)_5CoSO_3]^+$, which has been shown to possess an extremely large kinetic[8] as well as sulfur structural[6] trans effect.

The original structural analysis[10] had relatively large estimated standard deviations (0.011–0.017 Å) associated with the Co–N bond lengths and the results of that analysis will not be discussed here. The Co–N distances for those ammonia ligands cis to sulfur in $[(NH_3)_5CoS_2O_3]^+$ are 1.960 (3) and 1.973 (3) Å; these compare favorably with the mean cis Co–N value of 1.963 (4) Å found[23] in $[(NH_3)_5CoNHCOCH_3]^{2+}$ and the mean Co–N length of 1.968 (11) Å[24] in $[Co(NH_3)_6]^{3+}$.

Table VII. Sulfur Structural Trans Effect[a]

	M–S, Å	M–N(trans), Å	Mean M–N(cis), Å	Trans lengthening, Å	Ref
$[(NH_3)_5CoNHCONH_3]^{2+}$			1.963 (4)[b]		23
$Co(en)_2(SO_3)(NCS)$	2.203 (6)	1.974 (18)	1.963 (4)[b]	0.011 (18)[c]	7
$[(NH_3)_5CoS_2O_3]^+$	2.287 (1)	1.986 (4)	1.967 (7)[b]	0.019 (8)	This work
$[Cr(en)_2(SCH_2CO_2]^+$	2.337 (2)	2.112 (4)	2.090 (13)[d]	0.022 (14)	25
$[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$	2.226 (2)	2.001 (5)	1.960 (9)[d]	0.041 (10)	25
$[Co(en)_2(SCH_2CO_2)]^+$	2.243 (2)	2.005 (4)	1.965 (7)[d]	0.040 (8)	25
$[(NH_3)_5CoSO_3]^+$	2.218	2.055 (2)	1.966 (4)[d]	0.089 (4)	6

[a] The structural analysis of $[(NH_3)_5Co(SCN)]Cl_2\cdot H_2O$[21] is not included in this table since it is of lower resolution than those present. The authors stated that, at the final level of precision, they could not ascertain whether there was any structural trans effect present. [b] The estimate of the standard deviation of the mean value has been computed according to the formula $\sigma = \{\Sigma_i(x_i - \bar{x})^2/[n(n-1)]\}^{1/2}$. [c] $\sigma(\Delta) = (\sigma_1{}^2 + \sigma_2{}^2)^{1/2}$. [d] These standard deviations were calculated by Elder et al. using the formula $\sigma = [\Sigma_i(x_i - \bar{x})^2/(n-1)]^{1/2}$. Recalculation of the standard deviation using the more usual formula[26] $\sigma = \{\Sigma_i(x_i - \bar{x})^2/[n(n-1)]\}^{1/2}$ leads to values which are smaller by a factor $n^{-1/2}$. This results in a lowering of the standard deviation of the trans lengthening value. [E.g., for the cobalt thiolato complex $[Co(en)_2(SCH_2CO_2)]^+$, the trans lengthening 0.040 (8) Å reported in ref 25 becomes 0.040 (6) Å, which is the value quoted by Elder et al. in a later paper.[27]]

The trans Co–N length in the present structure is then 0.013–0.026 Å (2.6–5.2σ) longer than the cis distances. Thus, any sulfur structure trans effect in $[(NH_3)_5CoS_2O_3]^+$ is small. Table VII lists a number of molecules with sulfur atoms trans to ammine ligands for which structural results are available. Some of these show pronounced lengthening of the trans Co–N bond (e.g., $[(NH_3)_5CoSO_3]^+$ 0.089 (4) Å)[6] whereas others show smaller trans effects or the precision of the analysis is such that no definite conclusion could be reached (e.g., $[(NH_3)_5Co(SCN)]Cl_2\cdot H_2O$[21]).

No apparent correlation exists between the sulfur structural trans effect and electron-transfer rate for remote attack. For example, the $[(NH_3)_5CoS_2O_3]^+$ complex is reduced by Cr(II) 50 times faster than the complex $[(NH_3)_5CoSO_3]^+$ [6] even though the latter compound has one of the largest known sulfur structural trans effects. It should be pointed out that in these systems the reductant attacks at a remote oxygen and not at the coordinated sulfur (vide supra). In addition, it appears that, at least for Co(III) complexes, no correlation exists for attack at coordinated sulfur (see ref 28 for another point of view). Thus, the $[(NH_3)_5CoSCN]^{2+}$ [21] complex is reduced by Cr(II) faster than $[Co(en)_2(SCH_2CH_2NH_2)]^{2+}$,[25] both of which are attacked at coordinated sulfur, but while for the latter complex a significant structural trans effect was found, for the former the precision of the analysis was such that no structural trans lengthening was found.

The deviations of the angles S(1)–Co–N(3), 92.7 (1)°, and S(1)–Co–N(2), 87.9 (1)°, are quite clearly caused by intramolecular crowding effects and allow the ammine nitrogen N(3) to be 2.923 (4) Å away from the thiosulfate oxygen O(2). In the absence of such bending, N(3) and O(2) would have been prohibitively close. The N(3)···O(2) distance corresponds to a strong intramolecular hydrogen bond (vide infra; Table V). It is interesting to note at this point that the shorter cis Co–N bond length [Co–N(3) = 1.960 (3) Å compared with Co–N(2) = 1.973 (3) Å] is associated with the intramolecular hydrogen bond. Similar small stereochemical distortions were observed for $[(NH_3)_5CoNHCOCH_3]^{2+}$ [23] and $[(NH_3)_5CoNHCHOCo(NH_3)_5]^{5+}$.[29]

The Co–S–S angle has a nonlinear value of 110.20 (6)° which is similar to the values obtained in other thiosulfate complexes.[30,31]

As expected, the S–S distance in the present cobalt complex is lengthened significantly upon metal coordination compared with the corresponding distance, 2.013 (3) Å, for free $S_2O_3{}^{2-}$ in $MgS_2O_3\cdot 6H_2O$[32] whereas the mean S–O distance shows little change (1.463 (1) Å compared with 1.468 (4) Å in $MgS_2O_3\cdot 6H_2O$[32]). A longer S–S bond length of 2.066 (6) Å (mean) has been reported for $[Pd(en)_2][Pd(en)(S_2O_3)_2]$[30] where the thiosulfate anion acts as a monodentate ligand while a value of 2.046 (3) Å has been obtained for the S–S length in $Na_{4n}[Cu(NH_3)_4]_n[Cu_n(S_2O_3)_{2n}]_2$[31] which contains a bridging thiosulfate ligand. The geometrical arrangement about both sulfur atoms in the present structure corresponds to regular tetrahedral coordination.

The hydrogen-bonding network found in $[(NH_3)_5CoS_2O_3]Cl\cdot H_2O$ is composed of hydrogen bonds of the type OH···S, NH···Cl, NH···O, and OH···O (Table V) linking the chloride ion and the water molecule to the $[(NH_3)_5CoS_2O_3]^+$ cation. All of the hydrogen atoms [except H(12) which has a very weak interionic contact with Cl^- (N(1)–H(12)···Cl = 153.6°; N(1)–H(12) = 0.94, H(12)···Cl = 2.76, and N(1)···Cl = 3.620 (3) Å)] participate in the hydrogen-bonding scheme with essentially normal geometries. The O···S contact distance, 3.385 (7) Å, associated with the O–H···S hydrogen bond is slightly longer than the corresponding distances, 3.255 and 3.263 (5) Å, reported for O–H···S hydrogen bonds in $MgS_2O_3\cdot 6H_2O$.[32]

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Registry No. $[(NH_3)_5CoS_2O_3]Cl\cdot H_2O$, 29158-84-7; $[(NH_3)_5CoS_2O_3]Cl$, 14972-91-9; $[(NH_3)_5CoS_2O_3]ClO_4$, 14972-92-0; Cr^{2+}, 22541-79-3.

Supplementary Material Available: Listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

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Synthesis and Crystal Structure Analysis of Bis(η^5-cyclopentadienyl)-μ-[trifluoromethyl(oxodiphenylphosphino)acetylene]-dinickel(0)

RODERIC J. RESTIVO,[1] GEORGE FERGUSON,*[1] TAI WING NG,[2] and ARTHUR J. CARTY[2]

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Upon reaction of nickelocene with the phosphinoacetylene $Ph_2PC{\equiv}CCF_3$ six products were isolated, one of which is a deep green solid whose formulation is $[(\eta^5\text{-}C_5H_5)Ni]_2\text{-}\mu\text{-}(Ph_2P(O)C{\equiv}CCF_3)$. The crystal and molecular structure of this complex has been determined from three-dimensional x-ray data collected by counter methods. The crystals are orthorhombic, space group *Pbca*, with eight molecules in a unit cell of dimensions $a = 25.286$ (2), $b = 10.427$ (2), and $c = 17.021$ (2) Å. Full-matrix least-squares refinement on F of the structure has led to a conventional R value of 0.040 for 1796 observed reflections. The binuclear complex contains two nickel atoms asymmetrically bridged by an acetylide moiety in π-bonding fashion with Ni–C distances falling into two distinct sets, 1.873, 1.896 (6) Å and 1.909, 1.920 (6) Å, and a Ni–Ni bond length of 2.365 (1) Å. Both nickel atoms are π bonded to the η^5-cyclopentadienyl groups with mean Ni–C and C–C lengths of 2.096 (8) and 1.402 (13) Å, respectively. The phosphinoacetylide has bond distances P═O = 1.473 (5), P—C(phenyl)(mean) = 1.802 (8), P—C(acetylide) = 1.774 (6), C—C(acetylide) = 1.472 (10), C≡C = 1.353 (9), C—F(mean) = 1.311 (12), and C—C(phenyl)(mean) = 1.386 (11) Å. The angles C≡C—CF_3 [140.7 (6)°] and P—C≡C [150.2 (5)°] are characteristic of a cis-bent geometry for the coordinated phosphinoacetylide.

Cyclopentadienylnickel carbonyl dimer, $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$, and nickelocene, $(\eta^5\text{-}C_5H_5)_2Ni$, react with acetylenes yielding the acetylene-bridged dimer $[(\eta^5\text{-}C_5H_5)Ni]_2(RC{\equiv}CR')$ (I) as major products.[3-5] However, with highly electrophilic acetylenes, cycloaddition of the alkyne to one cyclopentadienyl ring of nickelocene may occur leading to σ,π-norbornyl complexes (II).[6-10] While compounds of formulation I and II are quite stable and examples have been characterized structurally,[11,12] one could intuitively predict that both types should be susceptible to further reaction with acetylenes. For example, acetylene trimers and oligomers as well as organocobalt complexes result from reactions of the isoelectronic and isostructural cobalt analogues of I, $Co_2(CO)_6(RC{\equiv}CR')$, with additional alkyne[13] while acetylene insertion into M—C σ bonds (cf. II) is a well-established organometallic reaction. These predictions are substantiated by results[15] of a reexamination of the hexafluorobut-2-yne/nickelocene system where the new complexes $(\eta^5\text{-}C_5H_5)Ni[C_5H_5(CF_3C_2CF_3)_2]$, $[(\eta^5\text{-}C_5H_5)Ni(CF_3C_2CF_3)]_4$, and $(\eta^5\text{-}C_5H_5)_2Ni_3(CF_3C_2CF_3)_2$ appear to relate to the initial products of formulation I and II. Among several features of these interesting reactions which warrant attention are the role of the metal atom in the cycloaddition process and the fate of the displaced cyclopentadienyl ligand in the formation of the products I from $(\eta^5\text{-}C_5H_5)_2Ni$. In an attempt to gain insight into these processes, we have investigated the reactions of $(\eta^5\text{-}C_5H_5)_2Ni$ and $[(\eta^5\text{-}C_5H_5)Ni(CO)]_2$ with the phosphinoalkynes $Ph_2PC{\equiv}CR$ (R = CF_3, Ph, *t*-Bu). Previous work[16] has demonstrated the utility of these ligands in allowing the isolation and characterization of model intermediate π complexes prior to oligomerization of the alkyne by metal carbonyls. With the less activated alkynes $Ph_2PC{\equiv}CR$ (R = Ph, *t*-Bu) evidence for –C≡C– and phosphorus coordination was found but cycloaddition was suppressed.[17] By contrast, six products have been isolated from the reaction of $Ph_2PC{\equiv}CCF_3$ with $(\eta^5\text{-}C_5H_5)_2Ni$ at room temperature including a derivative with a $\eta^1\text{-}C_5H_5$ ring[15] and a dinickel complex $[(\eta^5\text{-}C_5H_5)Ni]_2[Ph_2PCH{=}C(CF_3)C(PPh_2){=}C(CF_3)C_5H_5]_2$[18] containing a dimer derived from two displaced $C_5H_5^-$ ligands, which will be described in a subsequent publication.[19] In this paper we describe the synthesis and structural characterization of a species obtained on oxidation of one of the reaction products, namely, $[(\eta^5\text{-}C_5H_5)Ni]_2(Ph_2P(O)C{\equiv}CCF_3)$. This is the first acetylenic phosphine oxide π complex to be characterized structurally. Furthermore, our x-ray analysis provides precise details of molecular geometry for a complex of formulation I. Such information is highly relevant to an assessment of the influence of steric and electronic factors on the activation of the coordinated triple bond.

Experimental Section

Preparation. $(\eta^5\text{-}C_5H_5)_2Ni$ (1.9 g) was introduced into a Schlenk tube followed by 1.4 g of freshly distilled phosphine ligand.[20] Degassed benzene (~20 ml) was added and the dissolved components were allowed to react under N_2 for 2 h. The green mixture turned red, maroon, purple, and finally brown. At the end of the reaction, 5 ml of benzene was added and insolubles were filtered off with a filter stick. The solution was chromatographed on alumina giving eight bands. The first two bands were nickelocene and a free ligand. The next five bands, eluted with petroleum ether/benzene mixtures, contained products to be described in a subsequent publication.[15] The last green band, eluted with diethyl ether gave, after removal of solvent,