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Contribution from the Department of Chemistry,
University of Cincinnati, Cincinnati, Ohio 45221

A Rational Synthesis of Coordinated Disulfides from Coordinated Thiols. Crystal Structure of $[(en)_2Co(S(SC_2H_5)CH_2CH_2NH_2)](ClO_4)_3 \cdot H_2O$

DENNIS L. NOSCO, R. C. ELDER, and EDWARD DEUTSCH*

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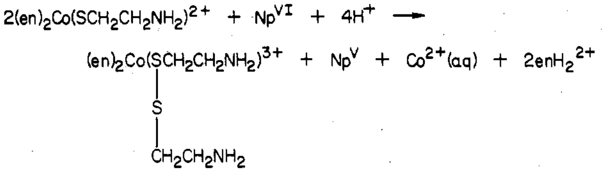
The synthesis of coordinated disulfides from coordinated thiols and *N*-thiophthalimides in *N,N*-dimethylformamide is described. The thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is utilized as a prototype, and the series of disulfide derivatives $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$, with R = methyl, ethyl, isopropyl, *tert*-butyl, and phenyl, are prepared and characterized. All disulfide complexes exhibit a characteristic absorption band at ca. 340 nm which is not present in the spectra of other cobalt(III) complexes containing coordinated sulfur. These complexes are decomposed by aqueous alkali to regenerate the parent thiolato complex, the rate of decomposition being strongly dependent on the nature of the R group. A single-crystal X-ray structure analysis of ((S^1-ethyl S^2-(2-aminoethyl) disulfide)-*N*,S^2)bis(ethylenediamine)cobalt(III) perchlorate monohydrate, refined to a conventional *R* value of 0.063, is reported. The cobalt(III) center is approximately octahedrally coordinated with one coordination site occupied by a disulfide sulfur atom. The sulfur–sulfur bond length is 2.033 (3) Å, and the C–S–S–C torsion angle is 103°. The coordinated disulfide does not induce a significant structural trans effect, consistent with the lack of a formal negative charge on the coordinated sulfur atom and the relatively long Co–S bond (2.272 (2) Å).

Introduction

A few years ago we reported[1] the unusual oxidation of a coordinated thiol to a coordinated disulfide by induced electron transfer (eq 1). The identity of this coordinated disulfide



$$2(\text{en})_2\text{Co}(\text{SCH}_2\text{CH}_2\text{NH}_2)^{2+} + \text{Np}^{\text{VI}} + 4\text{H}^+ \longrightarrow (\text{en})_2\text{Co}(\underset{\substack{|\\ \text{S}\\ |\\ \text{CH}_2\text{CH}_2\text{NH}_2}}{\text{S}}\text{CH}_2\text{CH}_2\text{NH}_2)^{3+} + \text{Np}^{\text{V}} + \text{Co}^{2+}(\text{aq}) + 2\text{enH}_2{}^{2+} \quad (1)$$

product was established by indirect means since all attempts to grow single crystals of this particular material proved fruitless. Therefore, in order to conclusively establish the nature of the product complex, we sought to develop a synthetic route to analogous unsymmetrical disulfide complexes, $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$, which might be more readily crystallized and hence characterized by X-ray diffraction techniques. Also, because of the established importance of the multitudinous interactions among thiols, disulfides, and metal ions in biological systems,[2–9] we sought a general route which would allow the relatively unrestricted conversion of coordinated thiols into a variety of coordinated disulfides.

Extant synthetic routes to coordinated disulfides are few in number and usually yield only the symmetric disulfide. The most prevalent routes involve direct combination of metal ions with chelating disulfides[9–11] or ligand substitution by simple alkyl or aryl disulfides.[12,13] In a more specific synthesis Stein and Taube[14] have recently prepared coordinated cyclic disulfides by chemical or electrochemical oxidation or coordinated dithiols. Finally, the reaction of $(CH_3)_3SiSR$ (R = CH_3, CH_2CH_3) with WCl_6 has been reported to yield a disulfide-bridged dimer.[15]

In this paper we present a new synthetic route for the conversion of coordinated thiols to coordinated unsymmetrical disulfides. The thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is utilized as a prototype, and a variety of disulfide complexes of the general formula $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ are prepared. The complex with R = CH_2CH_3 is characterized by single-crystal X-ray structural analysis.

Experimental Section

General Data. All common laboratory chemicals were of reagent grade. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. SP-Sephadex C-25 strong-acid cation exchanger (sodium form) was prepared and stored as recommended by the manufacturer (Pharmacia). The ion-exchange matrix was cleaned between uses by layering solid NaCl on the moist, contaminated resin in a large fritted funnel; this mixture was then washed with distilled water until the washings were free from chloride.

(2-Mercaptoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III) Perchlorate. This compound was prepared as previously described.[16]

***N*-(Alkylthio- or Arylthio)phthalimides.** These sulfenimides were synthesized by standard procedures[17] with only minor modifications. In the synthesis of the phenylthio derivative, thionyl chloride can be used in place of molecular chlorine. Since free phthalimide proved difficult to separate from the final product, in all preparations an excess of disulfide over phthalimide was used in order to ensure that all the phthalimide was consumed in the condensation step. In a typical preparation of the methyl derivative, 12.5 g (0.133 mol, 0.266 equiv) of dimethyl disulfide was dissolved in 125 mL of dry pentane stirred at −10 °C. Molecular chlorine was bubbled through the initially clear solution producing an orange color within 5 min. Chlorine addition was continued until a white solid (CH_3SCl_3)[18] just began to form on the gas-dispersion tube. At this time chlorination was stopped and 2 or 3 drops of disulfide was added to cause the white solid to dissolve.

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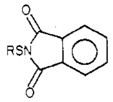
Table I. ^{1}H NMR Spectral Parameters for Selected *N*-(Alkyl- or Arylthio)phthalimides[a] and $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$

R	protons	δ	character	solvent
				
CH_3	CH_3	2.5	singlet	acetone-d_6
	C_6H_4	8.0	singlet	
CH_2CH_3	CH_3	1.2	triplet	acetone-d_6
	CH_2	3.0	quartet	
	C_6H_4	7.9	singlet	
C_6H_5	C_6H_5	7.4	singlet	dimethyl-d_6 sulfoxide
	C_6H_4	8.0	singlet	
		$[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$		
CH_3	CH_3	2.9	singlet	acetone-d_6
	NH_2	4.5-5.9	broad	
	CH_2	3.4-3.9	multiplet	
CH_2CH_3	CH_3	1.6	triplet	acetone-d_6
	NH_2	4.3-6.0	broad	
	CH_2	2.8-4.2	multiplet	
C_6H_5	C_6H_5	7.2-8.2	multiplet	acetone-d_6
	NH_2	4.2-5.2	broad	
	CH_2	2.7-3.6	multiplet	

[a] Me_4Si used as an internal standard.

This solution of sulfenyl chloride was added dropwise from an airtight constant-pressure dropping funnel to a stirred solution of 29.8 g (0.100 mol) of phthalimide and 27 g (0.2 mol) of triethylamine in 100 mL of *N,N*-dimethylformamide (DMF). A slurry of white crystals formed almost immediately. After addition was complete, the mixture was stirred for 1 h and then added to 1.5 L of cold (10–15 °C) distilled water. The resulting mixture was filtered, and 29.7 g (77% yield) of white crystals was collected. This product was recrystallized twice from toluene to give a solid with mp 176–179 °C (lit.[19] mp 180–182 °C) and an R_f = 0.91 (Eastman Kodak Silica Gel 6060 Chromagram TLC sheets, chloroform development, fluorescent indicator). ^{1}H NMR chemical shift data for *N*-(methylthio)phthalimide is given in Table I; Anal. Calcd for $C_9H_7O_2NS$: C, 55.94; H, 3.65; O, 16.56; N, 7.25; S, 16.59. Found: C, 56.02; H, 3.73; O, 16.31; N, 7.32; S, 16.78. The identities of the other sulfenimides prepared in this work were similarly established by using melting points[17] and ^{1}H NMR (Table I).

Preparation of ((S^1-Alkyl or -Aryl S^2-(2-aminoethyl) disulfide)-*N*,S^2)bis(ethylenediamine)cobalt(III)) Perchlorate, $[(en)_2Co(S(SR)CH_2CH_2NH_2)](ClO_4)_3$. In a typical preparation of the methyl derivative 4.5 g (10 mmol) of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ was dissolved in 50 mL of DMF. A 10-fold excess (on the basis of sulfenimide) of either $HClO_4$ (as a 6 M aqueous solution) or boron trifluoride (as the diethyl ether adduct) was then added with stirring. To the resulting brown solution was added 1.8 g (9.3 mmol) of *N*-(methylthio)phthalimide dissolved in 50 mL of DMF. The solution turned from brown to cherry red within 30 s. After being stirred for 10 min, the solution was diluted with about 1500 mL of ethyl ether and refrigerated for 30 min at −10 °C. When $HClO_4$ was used in place of BF_3, addition of 100 mL of 2-butanol aided in separation of the inorganic phase. The ether layer was decanted and the red oil diluted with 150 mL of 0.10 M $HClO_4$. The aqueous solution was then loaded on an SP-Sephadex C-25 column (ca. 4 × 15 cm i.d.) in the Na^+ form equilibrated at 4 °C. The excess brown $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ was eluted with 0.15 M $NaClO_4$ (0.05 M $HClO_4$). The remaining orange product was displaced from the column by using 0.5 M $Ba(ClO_4)_2$. Then 0.5 M potassium sulfate was added to the orange eluant until tests showed no further $BaSO_4$ was produced. The mixture was refrigerated at −10 °C for 30 min to ensure complete precipitation of $BaSO_4$ and $KClO_4$, and the cold mixture was then filtered. Ten milliliters of 70% $HClO_4$ was added to the cooled supernatant, and within 6 h red-orange crystals began to form. After 24 h, the product crystals were collected and washed successively with cold 95% EtOH and diethyl ether. A second crop of product crystals can be obtained by evaporation and cooling of the supernatant. The product was then recrystallized from dilute $HClO_4$. To ensure complete removal of phthalimide, we dissolved the purified product in 5:1 acetone/$CHCl_3$ and sorbed it onto silica gel.[20] This plug of silica gel was placed on top of a previously packed silica gel column, and then $CHCl_3$ was passed through the column until all the phthalimide was removed. The inorganic product was leached from the silica gel by using DMF; subsequent workup and recrystallization as above yielded dark orange-red crystals. Anal. Calcd for $[(en)_2Co(S(SCH_3)CH_2CH_2NH_2)](ClO_4)_3$: Co, 9.81; C, 14.00; H, 4.19; N, 11.66; S, 10.68. Found: Co, 9.52; C, 13.74; H, 4.25; N, 11.41; S, 10.57. Elemental analysis of the title complex (R = CH_2CH_3) yielded the following results. Anal. Calcd for $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)](ClO_4)_3 \cdot H_2O$: Co, 9.31; C, 15.18; H, 4.62; N, 11.07; S, 10.13. Found: Co, 9.67; C, 15.25; H, 4.70; N, 11.15; S, 9.93. The ^{1}H NMR and visible–UV spectra of several disulfide complexes are given in Tables I and II, respectively.

Equipment. Visible–UV spectra were recorded on a Cary Model 14 spectrophotometer at ambient temperature. ^{1}H NMR spectra were recorded on a Varian T-60 spectrometer. Melting points (Thomas-Hoover apparatus) were determined in open-end capillaries and are uncorrected. The laser Raman spectrum was obtained in the solid state through the courtesy of Dr. Glen Tolman, Union Carbide Corp., Tarrytown, NY.

X-ray Characterization of $[(en)_2CoS(SCH_2CH_3)CH_2CH_2NH_2](ClO_4)_3$. A large orange-red crystal (long dimension = 0.75 mm, short dimension = 0.50 mm) with a truncated octahedral morphology was mounted on a glass fiber and precession photographs of the *hk*0, *h*0*l*, *hk*1, *hk*2, and *h*1*l* layers were taken by using Cu Kα radiation. The systematic absences indicated were for 0*kl* *k* = odd, for *h*0*l* *l* = odd, and for *hk*0 *h* = odd. These suggested the space group[21] *Pbca* for the orthorhombic cell. The approximate cell constants were *a* = 12.5 (2), *b* = 13.2 (2), *c* = 28.0 (2) Å. After the precession work, a number of crystals of the same morphology and approximately the same size were ground in a crystal grinder. An approximately spherical (long dimension = 0.450 mm, short dimension = 0.375 mm) crystal was mounted on a glass fiber and optically centered on a Syntex P$\bar{1}$ diffractometer. Precise cell constants were determined by least-squares refinement using 2θ values of 15 pairs of reflections measured at ±2θ values in the range 23–27 °C. These are *a* = 12.554 (4), *b* = 13.212 (6), and *c* = 28.346 (16) Å. Partial oscillation photographs (±14°) were taken about each of the crystal axes to check crystal quality and correctness of indexing. With *Z* = 8 the calculated density is 1.82 g cm^{-3}; the measured density is 1.78 (3) g cm^{-3} (neutral buoyancy in $CCl_4/CHBr_3$). All measurements were made at room temperature.

Intensity measurements were made as previously[22] described for the 3943 reflections with $2\theta \leq 45°$. From these data 3107 unique reflections were obtained. The θ–2θ scan for these measurements, using Mo K$\bar{\alpha}$ radiation (λ 0.71069 Å) and a graphite monochromator, was from 1.0° below to 1.0° above the reflection in 2θ. Scan rates varied from 1.0 to 4.0°/min depending on the intensity of the reflection. Four standard reflections were monitored to check stability and to account for long-term drift. The drift correction varied from 1.000 to 1.050. Although μ, the linear absorption coefficient was 13.65 cm^{-1}, no absorption corrections were applied since the small deviations from sphericity of the crystal would result in a maximum correction of only 1.8%. Of the set of 3107 unique, normalized structure factors 2569 had $F_o^2 \geq 2\sigma(F_o^2)$, where a value of 0.04 was used for *p*, the ignorance factor,[22] in calculating $\sigma(F_o^2)$.

A Patterson map[23] was computed, and the positions of the cobalt atom and coordinated sulfur atom were determined. An electron density synthesis based on the phases derived from these two atom positions revealed the remaining 29 nonhydrogen atoms. Least-squares refinement of atom positions, general scale factor, and isotropic thermal parameters gave R_1 = 0.102.[24,25] Refinement of the model was continued with anisotropic thermal parameters and fixed hydrogen

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(24) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.

(25) $R_2 = [\sum w(|F_o| - |F_c|)^2/w(F_o)^2]^{1/2}$.

Table II. Visible–UV Spectrophotometric Parameters for $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and Selected Derivatives[a]

complex	λ_{max} (ϵ)	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)	λ_{max} (ϵ)	λ_{min} (ϵ)
$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ [b]	482 (142), 600 (44) sh	423 (95)			282 (13 800)	250 (1550)
$[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ [b]	487 (177)	405 (18)			282 (8380)	257 (4140)
$[(en)_2Co(S(Ag)CH_2CH_2NH_2)]^{3+}$ [c]	495 (150)				285 (13 000)	
$[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ [d]	470 (500)		365 (6700)		284 (3700)	
$[(en)_2Co(S(H)CH_2CH_2NH_2)]^{3+}$ [e]	485		345 (540)		272 (7800)	
$[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$						
$R = CH_3$	489 (149)	429 (60)	343 (1710)	319 (1340)	278 (7550)	261 (6460)
$R = CH_2CH_3$	490 (150)	429 (60)	340 (1840)	327 (1620)	280 (7410)	260 (5640)
$R = CH(CH_3)_2$	491 (161)	430 (59)	337 (1660)	330 (1600)	283 (6100)	261 (4350)
$R = C(CH_3)_3$	490 (167)	425	332 (2280) sh		287 (7900)	263
$R = C_6H_5$ [g]	491 (200)	442 (123)	*h*		285 (31 000)	253 (15 500)
$R = CH_2CH_2NH_3^+$ [f]	492 (175)	430 (56)	330 (2000) sh		275 (8300)	265 (6300)

[a] Wavelengths, λ, of maxima (max), minima (min), and shoulders (sh) in nm; molar extinction coefficients, ε, given in parentheses, are in $M^{-1}\ cm^{-1}$. Spectra are recorded in dilute aqueous perchloric acid. [b] Reference 31. [c] Reference 33. [d] Reference 32. [e] Reference 34. [f] Reference 1. [g] Spectral parameters determined in 20/1 DMF/H_2O which is 0.05 M in $HClO_4$. [h] The 340-nm band is obscured by the unusually intense CT at 285 nm.

atoms at their calculated positions (C–H = 0.97 Å, N–H = 0.87 Å) (all hydrogen atoms were assigned isotropic thermal parameters[26] of $B = 4.0$ Å^2). Full-matrix refinement using weights based on $p = 0.04$ behaved badly, giving $R_1 \approx 0.07$ and $R_2 \approx 0.16$. Examination of reflections grouped on $\sin \theta$ or $|F_o|$ indicated that a value of $p = 0.02$ was better. Refinement on this basis converged to $R_1 = 0.062$ and $R_2 = 0.092$. The 3107 values of F_o were used to refine 289 variables. In the final cycle of least squares the maximum shift per error was 0.06 and the average shift per error was 0.008. A final difference map was essentially featureless with only one peak larger than 0.8 e Å^{-3}. This unique peak of magnitude 2.1 e Å^{-3} is in the region of one of the perchlorate anions. Scattering curves were taken from standard tabulations[27,28] for S, Co, O, N, Cl, C and H. Corrections for anomalous dispersion[29] were made by using $\Delta f'$ and $\Delta f''$ values of 0.299 and 0.973 for Co, 0.1 and 0.1 for S, and 0.1 and 0.2 for Cl. The values of $|F_o|$ and F_c are listed in Table A.[30]

Results

Characterization. In addition to the X-ray structure analysis described below, the title complexes are characterized by (1) the synthetic route employed for their preparation, (2) elemental analyses of isolated perchlorate salts (methyl and ethyl derivatives) which give empirical compositions in agreement with those predicted, (3) cation-exchange elution characteristics which are consistent with the assigned formal charge, (4) IR and Raman spectral data, and (5) the ^1H NMR and visible–UV spectral parameters listed in Tables I and II, respectively.

The ^1H NMR spectral parameters confirm the presence and identity of the organic moieties bonded to the noncoordinated sulfur atom of $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$. The infrared spectrum of the complex with $R = CH_2CH_3$ exhibits a broad band at ca. 3440 cm^{-1} arising from the water of hydration (confirmed by the X-ray structure analysis). The Raman spectrum of this complex exhibits a band at 508 cm^{-1} attributable to the S–S linkage of the coordinated disulfide.

The visible spectra are typical for derivatives of the parent (thiolato-*N*,*S*)cobalt(III) complex (see Table II); specifically the 600-nm shoulder characteristic of $[(en)_2C(SCH_2CH_2NH_2)]^{2+}$ disappears upon chemical modification of the coordinated sulfur.[1,31-34] The UV spectra of the disulfide complexes retain the intense ligand-to-metal charge-transfer (LTMCT) band which characteristically arises when sulfur is coordinated to a potentially oxidizing metal center.[35] Figure 1 compares the visible–UV spectrum of $[(en)_2Co(S(SCH_3)CH_2CH_2NH_2)]^{3+}$ to that of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. The visible–UV spectrum of the methyl derivative is very similar to that reported for the analogous disulfide complex $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]^{4+}$ prepared by an indirect redox route (eq 1).[1] The spectra of all of the disulfide complexes $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ prepared to date exhibit a band at ca. 340 nm which is *not* present in the spectrum of the parent

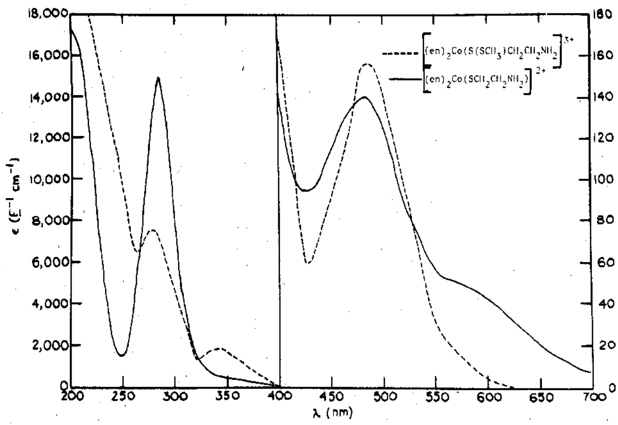

Figure 1. Visible and ultraviolet absorption spectra of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and $[(en)_2Co(S(SCH_3)CH_2CH_2NH_2)]^{3+}$ in 1.0 M $HClO_4$.

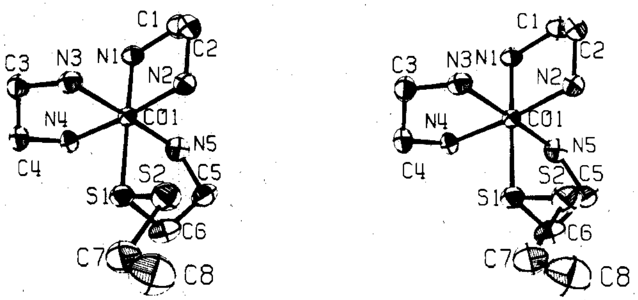

Figure 2. Perspective view of the cation $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)]^{3+}$ with 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

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[26] Isotropic thermal parameters were of the form $\exp(-B(\sin^2 \theta)/\lambda^2)$.

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Table III. Fractional Atomic Positional Parameters[a, b] for $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)](ClO_4)_3\cdot H_2O$

atom	*x*	*y*	*z*
Co(1)	−0.00678 (6)	0.19882 (6)	0.10655 (3)
Cl(1)	0.2292 (2)	0.3499 (2)	0.2514 (1)
Cl(2)	0.2104 (1)	−0.0630 (1)	0.0363 (1)
Cl(3)	−0.0765 (1)	−0.2544 (1)	0.0718 (1)
S(1)	0.0345 (1)	0.3661 (1)	0.1100 (1)
S(2)	−0.0586 (1)	0.4387 (1)	0.1579 (1)
O(11)[b]	0.3066 (6)	0.2738 (6)	0.2549 (3)
O(12)	0.1336 (7)	0.3276 (6)	0.2284 (4)
O(13)	0.2608 (7)	0.4516 (5)	0.2522 (4)
O(14)	0.1993 (9)	0.3568 (9)	0.3007 (3)
O(21)	0.2392 (4)	−0.1634 (4)	0.0244 (2)
O(22)	0.1196 (5)	−0.0300 (5)	0.0116 (3)
O(23)	0.1832 (7)	−0.0642 (6)	0.0868 (3)
O(24)	0.2945 (6)	0.0053 (5)	0.0339 (3)
O(31)	−0.0322 (9)	−0.1986 (6)	0.1085 (3)
O(32)	−0.1727 (6)	−0.2929 (9)	0.0827 (3)
O(33)	−0.0037 (7)	−0.3337 (7)	0.0646 (4)
O(34)	−0.0830 (6)	−0.1952 (5)	0.0295 (2)
O(99)	0.4742 (5)	0.4516 (4)	0.1895 (2)
N(1)	−0.0426 (4)	0.0538 (4)	0.0982 (2)
N(2)	−0.1395 (4)	0.2070 (4)	0.1432 (2)
N(3)	0.0751 (4)	0.1676 (4)	0.1645 (2)
N(4)	0.1322 (4)	0.1825 (4)	0.0745 (2)
N(5)	−0.0823 (5)	0.2294 (4)	0.0476 (2)
C(1)	−0.1539 (6)	0.0362 (5)	0.1143 (3)
C(2)	−0.1760 (5)	0.1013 (6)	0.1553 (3)
C(3)	0.1835 (5)	0.1345 (5)	0.1538 (3)
C(4)	0.2188 (5)	0.1904 (5)	0.1102 (3)
C(5)	−0.1146 (6)	0.3383 (6)	0.0418 (3)
C(6)	−0.0207 (7)	0.4024 (6)	0.0529 (3)
C(7)	0.0331 (7)	0.5429 (6)	0.1736 (3)
C(8)	−0.0176 (9)	0.6124 (8)	0.2058 (4)

[a] The estimated error in the last digit is shown in parentheses. This form is used throughout. [b] O(*n*1), O(*n*2), O(*n*3), O(*n*4) are bonded to Cl(*n*); O(99) is from the water of hydration; the rest of the numbering scheme is as shown in Figure 2.

Table IV. Root-Mean-Square Displacements (Å) of $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)](ClO_4)_3\cdot H_2O$

atom	min	mean	max
Co	0.153	0.155	0.163
Cl(1)	0.219	0.226	0.239
Cl(2)	0.166	0.208	0.268
Cl(3)	0.196	0.205	0.211
S(1)	0.164	0.189	0.204
S(2)	0.189	0.215	0.233
O(11)	0.288	0.304	0.395
O(12)	0.303	0.329	0.507
O(13)	0.255	0.340	0.487
O(14)	0.316	0.378	0.477
O(21)	0.174	0.252	0.304
O(22)	0.234	0.286	0.347
O(23)	0.258	0.314	0.386
O(24)	0.239	0.286	0.497
O(31)	0.268	0.322	0.464
O(32)	0.229	0.345	0.568
O(33)	0.304	0.363	0.439
O(34)	0.220	0.328	0.345
O(99)	0.224	0.253	0.297
N(1)	0.162	0.189	0.197
N(2)	0.174	0.179	0.204
N(3)	0.170	0.179	0.208
N(4)	0.147	0.186	0.200
N(5)	0.199	0.203	0.209
C(1)	0.174	0.212	0.258
C(2)	0.172	0.203	0.257
C(3)	0.172	0.196	0.227
C(4)	0.156	0.209	0.224
C(5)	0.174	0.229	0.235
C(6)	0.183	0.220	0.265
C(7)	0.207	0.248	0.273
C(8)	0.237	0.296	0.316

Table V. Bond Lengths (Å) in $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)](ClO_4)_3\cdot H_2O$

Co–S(1)	2.272 (2)	Co–N(3)	1.980 (6)
Co–N(1)	1.982 (5)	Co–N(4)	1.980 (5)
Co–N(2)	1.967 (5)	Co–N(5)	1.962 (6)
N(1)–C(1)	1.489 (9)	C(7)–C(8)	1.442 (14)
N(2)–C(2)	1.510 (9)	C(1)–C(2)	1.473 (11)
N(3)–C(3)	1.462 (9)	C(3)–C(4)	1.506 (10)
N(4)–C(4)	1.489 (9)	C(5)–C(6)	1.486 (11)
N(5)–C(5)	1.504 (9)	S(1)–C(6)	1.824 (8)
S(1)–S(2)	2.033 (3)	S(2)–C(7)	1.849 (9)
Cl(1)–O(11)	1.402 (8)	Cl(2)–O(21)	1.415 (6)
Cl(1)–O(12)	1.397 (10)	Cl(2)–O(22)	1.406 (7)
Cl(1)–O(13)	1.401 (7)	Cl(2)–O(23)	1.472 (8)
Cl(1)–O(14)	1.451 (7)	Cl(2)–O(24)	1.391 (7)
Cl(3)–O(33)	1.405 (9)	Cl(3)–O(31)	1.391 (9)
Cl(3)–O(34)	1.435 (7)	Cl(3)–O(32)	1.347 (9)

thiolato complex (Table II, Figure 1).

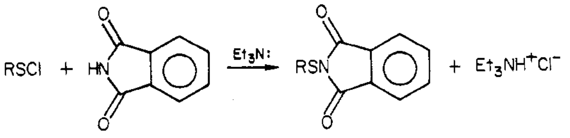
Crystal Structure. Final fractional atomic coordinates, with associated estimated standard deviations, for nonhydrogen atoms are listed in Table III. Anisotropic thermal parameters are listed in Table B,[30] and the associated root-mean-square displacements are presented in Table IV. A perspective view of the cation is shown in Figure 2. Bond lengths and angles not involving hydrogen atoms are given in Tables V and VI. The hydrogen fractional atomic coordinates are given in Table C.[30] Possible hydrogen bonds are listed in Table VII.

The structure consists of discrete $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)]^{3+}$ cations, three perchlorate anions, and a single water molecule which is weakly hydrogen bonded to ammine hydrogen atoms (Table VII). The cobalt(III) center is six-coordinate (five nitrogen atoms and the sulfur atom of the derivatized cysteamine ligand) in an approximately octahedral configuration. The three perchlorate anions undergo librational motion as shown by their large root-mean-square displacements. The majority of the residual electron density is located in the region of the perchlorate anions.

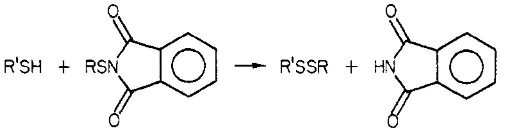
Discussion

Synthesis and Properties. *N*-Thiophthalimides are relatively stable compounds which are readily prepared by literature procedures[17] (eq 2 and 3).

$$RSSR + Cl_2 \rightarrow 2RSCl \qquad (2)$$


(3)

These sulfenimide reagents are known to react with thiols to yield either symmetrical or unsymmetrical disulfides[36] (eq 4).


(4)

Similarly, the coordinated thiolato moiety of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ also reacts with *N*-thiophthalimides to form the corresponding coordinated disulfide (eq 5). However, this reaction requires the presence of a Lewis acid to scavange the phthalimide anion product; we have utilized the "hard" acids BF_3 or H_3O^+ in order to minimize binding to the "soft" sulfur atom of the coordinated thiol. As in the alkylation of coordinated thiols,[36] *N*,*N*-dimethylformamide appears to be the solvent of choice for this reaction—both the inorganic perchlorate salt and the organic

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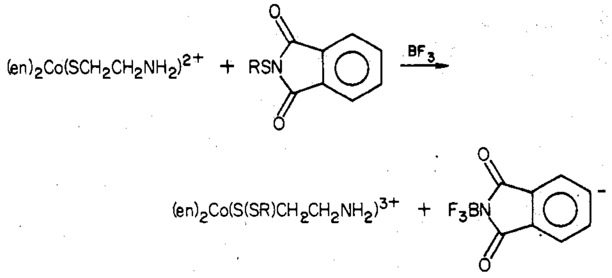
[36] (a) Boustany, K. S.; Sullivan, A. S. *Tetrahedron Lett.* **1970**, *41*, 3547–9. (b) Harpp, D. N.; Ash, D. K.; Back, T. G.; Gleason, J. G.; Orwig, B. A.; Van Horn, W. F. *Ibid.* **1970**, *41*, 3551–4.



(5)

N-thiophthalimide reagents are very soluble in this medium, thus permitting the reaction be conducted homogeneously. Chromatographic purification of the $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ product is necessary, due to the presence of excess $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ and due to the slow decomposition of the coordinated disulfides in aqueous solution. The phenyl derivative is so unstable that it cannot be dissolved in even cold aqueous solution without rapid decomposition.

While reaction 5 is indeed a redox process involving net conversion of a thiol to a disulfide, it is more usefully viewed as a substitution reaction in which the coordinated thiol acts as a nucleophile and the *N*-thiophthalimide acts as an RS^+ donor. The thiolato sulfur atom of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ is known to be a potent nucleophile, e.g., readily reacting with alkyl halides to yield coordinated thioethers[31] and with hydrogen peroxide to yield the coordinated sulfenic acid,[32] and *N*-thiophthalimides are well-known to function as RS^+ donors.[17] Thus reaction 5 involves transfer of RS^+ from phthalimide to the coordinated thiol, and a large portion of the driving force for the reaction is derived from the formation of the adduct between BF_3 and the phthalimide anion. The disulfide product $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ can itself act as an RS^+ donor, e.g., in the reaction with OH^- to yield the parent thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ (and presumably the transient free sulfenic acid RSOH).

All of the coordinated disulfides prepared in this work are susceptible to sulfur–sulfur bond fission in aqueous solution, and the mechanism of this process is currently under investigation. The stability of any given $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ complex depends on the nature of the R group. Thus, the methyl derivative is stable for days in aqueous solutions with $[H^+]$ ranging from 0.01 to 4.0 M, whereas the phenyl derivative undergoes significant decomposition within minutes even in 0.1 M H^+.

The changes in the visible spectrum induced upon conversion of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to the coordinated disulfide $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ are very similar to those induced upon conversion to the coordinated thioether $[(en)_2Co(S(R)CH_2CH_2NH_2)]^{3+}$. In both cases the dominant d–d transition shifts from 482 nm toward the red region (489–491 nm for disulfides, 485–490 nm for the thioethers). Also in both cases the 600-nm shoulder characteristic of the $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ starting material disappears, providing a useful diagnostic for monitoring chemical modification of the coordinated sulfur atom. This 600-nm band presumably arises because the asymmetric field provided by five nitrogen atoms and the one weak-field thiolato sulfur atom causes splitting of the $^1T_{1g}$ excited state in $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$. As previously noted for the thioether complexes,[31] the absence of the 600-nm shoulder in the spectra of the product complexes implies that the modified ligands (thioethers and disulfides) provide stronger ligand fields than the parent thiolato ligand. This apparent anomaly may be explained if there is significant π back-bonding in these systems; electron flow from cobalt(III) to sulfur would be much more favorable for the neutral sulfur ligands RSR and RSSR than for the negatively charged RS^- ligand.

Table VI. Bond Angles (Deg) in $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)](ClO_4)_3\cdot H_2O$

	Metal Coordination Sphere		
S(1)–Co–N(1)	175.6 (2)	N(1)–Co–N(5)	89.3 (2)
S(1)–Co–N(2)	96.7 (2)	N(2)–Co–N(3)	90.8 (2)
S(1)–Co–N(3)	92.8 (2)	N(2)–Co–N(4)	174.6 (2)
S(1)–Co–N(4)	85.7 (2)	N(2)–Co–N(5)	91.6 (2)
S(1)–Co–N(5)	86.9 (2)	N(3)–Co–N(4)	84.3 (2)
N(1)–Co–N(2)	85.7 (2)	N(3)–Co–N(5)	177.6 (3)
N(1)–Co–N(3)	90.9 (2)	N(4)–Co–N(5)	93.4 (2)
N(1)–Co–N(4)	92.3 (2)		
	Ligands		
Co–N(5)–C(5)	115.0 (4)	Co–N(1)–C(1)	109.1 (4)
N(5)–C(5)–C(6)	107.9 (6)	N(1)–C(1)–C(2)	109.2 (6)
C(5)–C(6)–S(1)	109.9 (5)	C(1)–C(2)–N(2)	107.7 (6)
C(6)–S(1)–S(2)	104.5 (3)	C(2)–N(2)–Co	109.1 (4)
Co–S(1)–S(2)	110.9 (1)	Co–N(3)–C(3)	112.0 (4)
Co–S(1)–C(6)	97.5 (2)	N(3)–C(3)–C(4)	107.3 (4)
S(1)–S(2)–C(7)	98.8 (3)	C(3)–C(4)–N(4)	107.9 (5)
S(2)–C(7)–C(8)	110.5 (7)	C(4)–N(4)–Co	108.9 (4)
	Anions		
O(11)–Cl(1)–O(12)	118.5 (5)	O(22)–Cl(2)–O(23)	107.4 (4)
O(11)–Cl(1)–O(13)	119.4 (5)	O(22)–Cl(2)–O(24)	113.0 (4)
O(11)–Cl(1)–O(14)	99.0 (6)	O(23)–Cl(2)–O(24)	103.3 (5)
O(12)–Cl(1)–O(13)	117.0 (5)	O(31)–Cl(3)–O(32)	117.8 (6)
O(12)–Cl(1)–O(14)	103.9 (6)	O(31)–Cl(3)–O(33)	104.2 (6)
O(13)–Cl(1)–O(14)	89.9 (7)	O(31)–Cl(3)–O(34)	111.1 (4)
O(21)–Cl(2)–O(22)	112.4 (4)	O(32)–Cl(3)–O(33)	109.6 (6)
O(21)–Cl(2)–O(23)	106.3 (4)	O(32)–Cl(3)–O(34)	110.2 (5)
O(21)–Cl(2)–O(24)	113.7 (4)	O(33)–Cl(3)–O(34)	108.8 (5)

Table VII. Possible Hydrogen Bonding in $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)](ClO_4)_3\cdot H_2O$

A, H, B	H···B, Å	A···B, Å	A–H···B, deg
N(1), H(11), O(99)[b]	2.043 (10)	2.881 (11)	159.1 (4)
N(2), H(21), O(11)[c]	2.198 (7)	3.049 (9)	168.0 (4)
N(2), H(22), O(32)[d]	2.228 (5)	2.962 (8)	141.7 (4)
N(3), H(31), O(12)[a]	2.256 (6)	3.005 (8)	144.0 (4)
N(3), H(32), O(99)[b]	2.300 (6)	3.042 (8)	143.4 (4)
N(4), H(41), O(21)[e]	2.170 (9)	2.917 (10)	143.7 (5)
N(5), H(51), O(34)[f]	2.345 (8)	3.095 (8)	145.8 (4)

[a] Includes H bonding where A···B ≤ 3.1 Å for N, O interactions and A···B ≤ 3.3 Å for N, S and O, S interactions. [b] Transformed to $1/2 - x, y - 1/2, z$. [c] Transformed to $x - 1/2, y, 1/2 - z$. [d] Transformed to $-1/2 - x, y + 1/2, z$. [e] Transformed to $1/2 - x, y + 1/2, z$. [f] Transformed to $-x, -y, -z$.

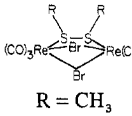
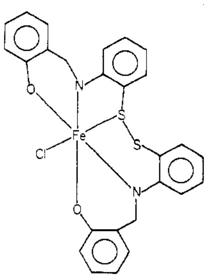
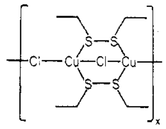
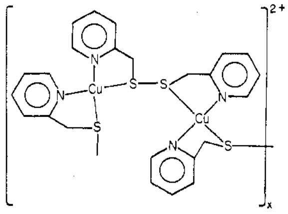
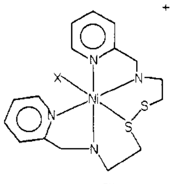
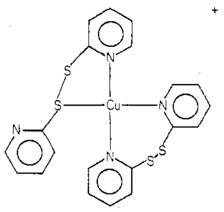
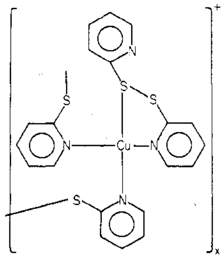
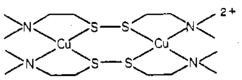
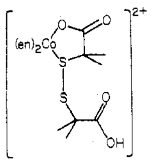
The UV spectra of the coordinated disulfide complexes $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$ are dominated by the intense ligand-to-metal charge-transfer (LTMCT) characteristic of chalcogen–metal complexes[35] (Table I). While the position of this band is not very sensitive to the nature of the R group, a coarse pattern can be discerned in the data of Table I. When R is a primary alkyl group (CH_3, CH_2CH_3, or $CH_2CH_2NH_3^+$), the LTMCT band is at a higher energy than the LTMCT band of the parent thiolato complex; this is as expected since a coordinated disulfide should be a poorer electron donor than a coordinated thiol. However, when R is $CH(CH_3)_2$, $C(CH_3)_3$, or C_6H_5, the LTMCT band is at a lower energy than the LTMCT band of the parent thiolato complex; this could result from the greater electron-donating effect of the secondary and tertiary alkyl groups or from the greater steric requirements of these groups causing an increase in the disulfide torsion angle (vide infra).

All of the coordinated disulfide complexes exhibit a band at ca. 340 nm which is *not* observed in any of the other complexes containing coordinated sulfur (Table I). This 340-nm band is too intense to be assigned as the expected $^1A_{1g} \rightarrow {}^1T_{2g}$ d–d transition which is almost always hidden beneath the tail of the LTMCT band in cobalt–sulfur complexes.[31] In the one known case where the $^1A_{1g} \rightarrow {}^1T_{2g}$ band is observable at 345 nm, i.e., in $[(en)_2Co(S(H)CH_2CH_2NH_2)]^{3+}$,[34] its intensity is only 25–30% that of the 340-nm band observed in the disulfide complexes. Therefore the 340-nm band is most likely associated with the coordinated disulfide ligand, and it is probably a charge-transfer transition. However, the origin(s) of this transition is (are) not at all clear. Stein and Taube[14] have observed a similar band in disulfide–ruthenium(II) complexes and have ascribed it to a second ligand-to-metal charge transfer; the pair of LTMCT transitions originate from disulfide ligand energy levels that in turn arise from a splitting of the previously degenerate sulfur atom lone-pair orbitals. However, it is also possible that the 340-nm band is an intraligand charge-transfer transition, again resulting from the nondegeneracy of the sulfur atom lone-pair orbitals.[37,38] In both of these possibilities, the splitting of the lone-pair orbitals is dependent on the torsion angle of the disulfide ligand; we are currently undertaking experiments designed to distinguish between these and other possibilities.

Structural Characterization. The structure of $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)]^{3+}$ (Figure 2) is as expected from the known structure[22] of the parent thiolato complex, the primary coordination sphere remaining intact during conversion of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ to the disulfide. The structural analysis firmly establishes the presence of a coordinated disulfide; taken in conjunction with the spectrophotometric evidence of Table II, this confirms the structure of the electron-transfer product $[(en)_2Co(S(SCH_2CH_2NH_3)CH_2CH_2NH_2)]^{4+}$ which was previously assigned[1] on the basis of indirect evidence. The sulfur–sulfur bond length in $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)]^{3+}$, 2.033 (3) Å, falls within the range reported for other metal–disulfide complexes (Table VIII) and is equivalent to the S–S bond length of 2.032 (4) Å observed in the noncoordinated disulfide L-cystine.[39] The torsion angle encompassing the sulfur–sulfur bond (i.e., the angle between the projections of the C6–S1 and C7–S2 bonds onto a plane perpendicular to the S1–S2 bond) is 103°, again equivalent to the 106° torsion angle observed in noncoordinated L-cystine.[39] Hordvik[40] has suggested that a noncoordinated disulfide with a bond length of 2.04 Å should exhibit a torsion angle of about 105°, and Seff[41] has stated that coordination of a disulfide should have no discernible effect on the sulfur–sulfur bond length. Our observations are consistent with these generalizations.

There is no discernible structural trans effect (STE) in $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)]^{3+}$: average cis Co–N = 1.972 (9) Å, trans Co–N = 1.982 (5) Å. This result is consistent with our previous suggestion[31] that it is necessary for the coordinated sulfur atom to carry a formal negative charge in order for it to induce a STE. Thus, the coordinated sulfur atoms of the parent thiolato complex $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$,[22] the sulfenato derivative $[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$,[32], and the sulfinato derivative $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$[42] exert significant structural trans effects, but the sulfur atoms of the thioether derivative $[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$,[31] and now the disulfide derivative, do not. Inspection of the structural data for these five related complexes reveals that the presence of the STE is also correlated with the length of the Co–S bond. Thus, the thiolato, sulfenato, and sulfinato complexes which do exhibit a STE have Co–S bond lengths of 2.226 (6), 2.253 (1)

Table VIII. Selected Bond Parameters for Disulfide-Metal Complexes

compd	M-S, Å	S-S, Å	ref
			
R = CH_3	2.492 (9)	2.113 (13)	12a
R = C_6H_5	2.487 (6)	2.140 (9)	12b
	2.536 (4)	2.046 (5)	11
	2.34 (1), 2.40 (1)	2.04 (2)	13a
	2.318 (1), 2.325 (1)	2.0807 (9)	10c
			
X = Cl	2.456 (2)	2.040 (3)	10e
X = Br	2.472 (5)	2.039 (7)	10a
	2.396 (3)	2.032 (4), 2.047 (5)	10d
	2.439 (3)	2.025 (4), 2.026 (4)	10d
	2.288 (6), 2.302 (7) 2.283 (7), 2.326 (6)	2.084 (9), 2.068 (8)	10b
	2.260 (3)	2.052 (3)	45

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and 2.191 (3) Å, respectively, while the thioether and disulfide complexes which do not exhibit a STE have Co–S bond lengths of 2.267 (10) and 2.272 (2), respectively. This correlation is as expected in terms of the classical σ trans effect described by Langford and Gray;[43] a shorter, stronger Co–S bond induces a longer, weaker trans Co–N bond. A more extended analysis of this correlation, incorporating all available STE data for cobalt(III) complexes containing coordinated sulfur, will be published separately.[44]

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Registry No. $[(en)_2Co(S(SCH_3)CH_2CH_2NH_2)](ClO_4)_3$, 74037-06-2; $[(en)_2Co(S(SCH_2CH_3)CH_2CH_2NH_2)](ClO_4)_3{\cdot}H_2O$, 74037-04-0; $[(en)_2Co(S(SC_6H_5)CH_2CH_2NH_2)]^{3+}$, 74037-01-7; $[(en)_2Co(S(SCH(CH_3)_2)CH_2CH_2NH_2)]^{3+}$, 74037-00-6; $[(en)_2Co(S(SC(CH_3)_3)CH_2CH_2NH_2)]^{3+}$, 74036-99-0; *N*-(methylthio)phthalimide, 40167-20-2; *N*-(ethylthio)phthalimide, 17796-70-2; *N*-(phenylthio)phthalimide, 14204-27-4; $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$, 40330-50-5.

Supplementary Material Available: Table A, $|F_o|$ and $|F_c|$ values, Table B, anisotropic thermal parameters, and Table C, hydrogen fractional atomic coordinates (13 pages). Ordering information is given on any current masthead page.

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Contribution from the Center for Materials Science,
National Bureau of Standards, Washington, D.C. 20234

Crystal Structure of Tritin(II) Hydroxide Oxide Phosphate, $Sn_3O(OH)PO_4$

T. H. JORDAN,* B. DICKENS, L. W. SCHROEDER, and W. E. BROWN

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$Sn_3O(OH)PO_4$ crystallizes in the monoclinic cell $a = 4.8851$ (7) Å, $b = 11.465$ (2) Å, $c = 12.362$ (2) Å, and $\beta = 105.81$ (1)° at 25 °C with space group $P2_1/c$ and $Z = 4$. The structure has been solved and refined to $R_w = 0.047$ and $R = 0.055$ by using 1938 observed X-ray diffraction data collected from a single crystal by a counter method (θ–2θ scans). Corrections for absorption and secondary extinction were not applied. The structure crystallizes in (010) layers. A lone pair of electrons on each Sn^{II} atom is directed into the interlayer space. Each Sn atom is coordinated to three oxygen atoms at ~2.1 Å and to other more distant ones at 2.5–3.3 Å, with all the coordinated oxygen atoms in the same hemisphere about Sn. The hydrogen bond in the structure appears to be between the hydroxide and oxide ions, forming an (O–H···O) grouping with O···O = 2.602 (9) Å.

Introduction

We showed in a previous paper[1] that one of the products of the reaction between stannous fluoride and hydroxyapatite is $Sn_2(OH)PO_4$. $Sn_2(OH)PO_4$ can also be prepared by the aqueous hydrolysis of a mixture of $Sn_3F_3PO_4$ and $Sn_3(PO_4)_2$ at reflux temperature. While searching through this reflux product for a suitable crystal of $Sn_2(OH)PO_4$ for the single-crystal investigation previously mentioned, we first discovered the title compound of this paper. We eventually found a total of three crystals of this compound. A comparison of the powder diagram of the reflux product with that calculated from the crystal structure of $Sn_3O(OH)PO_4$ indicates that $Sn_3O(OH)PO_4$ was a very minor product of the hydrolysis.

The crystal structure analysis of $Sn_3O(OH)PO_4$ was undertaken to determine its formula and to augment the meager knowledge of the structural chemistry of tin phosphates. The X-ray powder pattern diagram as calculated from the cell dimensions was unlike any pattern reported for a tin phosphate. After completion of the data collection, the crystal used was subjected to electron microprobe analysis. No evidence for a mixed F,OH salt that might have resulted from incomplete hydrolysis was found.

Data Collection and Structure Refinement

The crystal used in the data collection was an irregular fragment with minimum dimensions 0.045 × 0.052 × 0.026 mm. It was mounted on an automated Picker[2a] four-circle diffractometer using a procedure described previously.[2b] Crystal data: formula (ideal) $Sn_3O(OH)PO_4$; cell at 25 °C monoclinic; $a = 4.8851$ (7) Å, $b = 11.465$ (2) Å, $c = 12.362$ (2) Å, $\beta = 105.81$ (1)°; vol = 666.2 Å^3, λ(Mo Kα) = 0.7093 Å; space group $P2_1/c$; cell contents 4 ($Sn_3O(OH)PO_4$; reciprocal lattice extinctions $l = 2n + 1$ for $h0l$, $k = 2n + 1$ for $0k0$; density calculated from unit cell = 4.825 g/cm^3; μ(Mo) = 105.7 cm^{-1}.

The experimental procedure was similar to that[1] used for $Sn_2(OH)PO_4$. The X-ray data were collected by using θ–2θ scans carried out at 1°/min for 2θ. Each peak intensity was surveyed before being scanned. If the stationary count rate was not equal to or greater than 0.7 counts/s, the scan was omitted. In this manner 4171 reflections in the $k \geq 0$ hemisphere were measured up to a maximum 2θ of 80°. These were then merged into a unique set of 2224, of which 1938 have $I > 2\sigma(I)$. Equivalent reflections agreed within 6.7% on average based on F. This divergence probably reflects differences in absorption ($\mu r \approx 0.3$).

The positions of the tin atoms in the structure were determined from a sharpened Patterson synthesis. Examination of a difference electron density synthesis then revealed the positions of all the oxygen and phosphorus atoms in the structure. These atoms were refined with isotropic temperature factors to $R_w = 0.066$ and $R = 0.092$. R_w is defined as $[\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|^2)]^{1/2}$ and R is defined as $\sum||F_o| - |F_c||/\sum|F_o|$. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Scattering factors were taken from Cromer and Mann[3] and Cromer and Liberman.[4] Least-squares refinements were carried out with the program RFINE.[5]

The weighting function (w) was altered to include a contribution from the magnitude of F according to the equation $w = (\sigma^2 + 10^{-4}F^2)^{-1}$,

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* To whom correspondence should be addressed at the Department of Chemistry, Cornell College, Mt. Vernon, Iowa 52314.

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