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Synthesis and Characterization of Coordinated Disulfides. Single-Crystal Structural Analysis of $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2 \cdot H_2O$[1]

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A series of cobalt(III) complexes containing symmetrical disulfides bonded to cobalt through one sulfur atom, i.e., $[(en)_2Co(S(SCH_2COOH)CH_2COO)]^{2+}$, $[(en)_2Co(S(SCH(CH_3)COOH)CH(CH_3)COO)]^{2+}$, and $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+}$, have been prepared via induced electron transfer initiated by 1-equiv oxidation of the respective thiolato complexes, $[(en)_2Co(SCH_2COO)]^+$, $[(en)_2Co(SCH(CH_3)COO)]^+$, and $[(en)_2Co(SC(CH_3)_2COO)]^+$, with $[Co(aq)]^{3+}$. Analogous complexes containing unsymmetrical disulfides, e.g., $[(en)_2Co(S(SR)C(CH_3)_2COO)]^{2+}$, have been prepared by reaction of the parent thiolato complexes with $[RS]^+$ donors such as sulfenyl iodides (RSI) or methoxycarbonyl alkyl disulfides (CH_3O–C(O)–S–SR). Characterization of the disulfide complexes by physical and chemical techniques is reported. All the disulfide complexes exhibit a characteristic, intense, absorption maximum at ca. 340 nm which is not observed in the spectra of the parent thiolato complexes. The possible origins of this absorption are discussed in terms of similar absorptions reported for a wide variety of related compounds. The single-crystal X-ray structural analysis of $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2 \cdot 2H_2O$, refined to a conventional *R* factor of 0.062, is reported. The cobalt(III) center is approximately octahedrally coordinated with the composition of the primary coordination sphere (4 N, O, S) being identical with that of the parent thiolato complex. Oxidation of a coordinated thiolato ligand to a coordinated disulfide causes a lengthening of the Co–S bond and a concomitant reduction of the trans Co–N bond length. There is no detectable structural trans effect in the title compound.

Introduction

Interest in the chemistry of the thiol–disulfide couple has accelerated markedly over the last 50 years, largely because of the importance of this couple in biological systems. Our interest in this area stems from our studies on the chemistry of sulfur–metal interactions and in particular on the redox chemistry of thiolates and thiolate derivatives that are coordinated to robust metal centers. Recently we reported on a facile method for converting coordinated thiols to coordinated unsymmetrical disulfides using *N*-thiophthalimides as potent RS^+ donors.[2] Previous to this we had reported on the unusual oxidation of a specific thiolato–cobalt(III) complex to a cobalt(III) complex containing the coordinated symmetrical disulfide (eq 1).[3,4] This reaction presumably proceeds via

$$2[(en)_2Co(SCH_2CH_2NH_2)]^{2+} + Np^{VI} + 4H^+ \rightarrow [(en)Co(S(SCH_2CH_2NH_2)CH_2CH_2NH_2)]^{3+} + Np^{V} + [Co(aq)]^{3+} + 2[enH_2]^{2+} \quad (1)$$

induced electron transfer and a radical ion dimer intermediate.[3,4] The evidence establishing the nature of this singular oxidation was thorough but indirect due to our lack of success in growing single crystals of the product complex that were suitable for X-ray structure determination. The potential importance of the induced electron-transfer mechanism to an overall understanding of the chemistry of the coordinated thiol–disulfide couple has led us to extend our studies of this reaction. In addition, we have been interested in expanding our basic knowledge of coordinated disulfides in the hope of mapping some correlations between structure and physical–chemical properties. Therefore, we also wished to extend our arsenal of synthetic methods applicable to the preparation of coordinated disulfides and to use these methods, along with the induced electron-transfer reaction, to prepare series of disulfide complexes of varying structural characteristics. Reported herein are our studies on disulfide complexes derived from the prototype mercaptoacetato complex $[(en)_2Co(SCH_2COO)]^+$ and its analogues $[(en)_2Co(SCH(CH_3)COO)]^+$ and $[(en)_2Co(SC(CH_3)_2COO)]^+$.

Experimental Section

General Considerations. All common laboratory chemicals were of reagent grade. Dowex 50W-X2 (200–400 mesh) cation-exchange resin was cleaned as previously described.[5] Sephadex SP-C25 (sodium form) cation exchanger was generated and stored as recommended by the manufacturer (Pharmacia). Some batches required treatment with excess aqueous bromine (0.0375 M Br_2, 0.01 M HCl) for 10 h to eliminate a reducing capacity which caused decomposition of coordinated disulfides. This treatment was followed by copious washing with water.

Procedures. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. Total cobalt analyses were performed by a modified Kitson procedure.[6,7] Formal charges on complexes were inferred from elution characteristics on Dowex 50W-X2 (H^+ or Na^+ forms) and Sephadex SP-C25 (Na^+ form) ion-exchange columns. IR spectra were recorded for KBr pellets. ^1H NMR spectra were run in D_2O with sodium 3-(trimethylsilyl)-1-propanesulfonate as an internal reference. pD was adjusted with DCl.

Equipment. Visible–UV and infrared spectra were recorded respectively on Cary 14 and Perkin-Elmer 599 spectrophotometers at ambient temperature. Electrolysis of solutions of Co(II) was performed with a Sargent coulometric current source. X-ray data were collected with a Syntex $P\bar{1}$ diffractometer, equipped with a graphite monochromator and molybdenum target tube (Mo Kα, λ = 0.710 69 Å), at ambient temperature. Computer calculations were performed on an AMDAHL 470/V6 located at the University of Cincinnati. ^1H NMR spectra were obtained on a Varian T-60 instrument. pH measurements were made with a Beckman Research pH meter. Melting points (Thomas-Hoover apparatus) were determined in open-end capillaries.

Materials. Co(III)–HCO_3^- stock solutions were prepared by the method of Hofman-Bang and Wulff.[8] For the stoichiometry studies, $[Co(aq)]^{3+}$ was generated in situ from this solution by following the literature procedure.[8] For preparative work, where high concentrations were desirable, $[Co(aq)]^{3+}$ was generated electrolytically following a general literature procedure.[9]

2-Mercapto-2-methylpropionic acid, $HSC(CH_3)_2COOH$. This compound was prepared by a literature method reported for the general synthesis of tertiary thiols.[10] In a typical preparation 166.9 g (1 mol) of 2-bromo-2-methylpropionic acid and 76.12 g (1 mol) of thiourea were dissolved in 50 mL of water and heated, with stirring, at 90–95 °C for ca. 1.5 h. The mixture was then cooled to ca. 5 °C, and 120

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g (3 mol) of sodium hydroxide was added, with stirring, under a blanket of nitrogen. This mixture was then heated (under nitrogen) at 90–95 °C for 2 h. The product mixture was cooled in an ice-water bath to ca. 5 °C, and 196 g (ca. 2 mol) of sulfuric acid was added dropwise. The crude product separated as a waxy white solid, which was recovered by filtration and then washed with cold 4 M H_2SO_4, followed by a small amount of cold water. A second crop was obtained by further acidification of the combined reaction solution and washings with H_2SO_4 and then extraction with ethyl ether. Drying the ether layer over anhydrous $CaCl_2$ followed by evaporation yielded a yellow oil which solidified to a crystalline mass on standing. The combined product was dissolved in a minimum volume of deaerated water at ca. 50 °C. Upon slow addition of H_2SO_4 and subsequent cooling, the product separated as a white crystalline solid, which was recovered by filtration and dried over $CaSO_4$: yield 66 g (55%); ^1H NMR (neutral D_2O) δ 1.57 (s); IR (KBr) ν_{CO} 1695, 1290 cm^{-1}. Subsequent oxidation with hydrogen peroxide yields the corresponding disulfide, $(HOOCC(CH_3)_2S-)_2$: mp 196–198 °C (lit.[11] mp 197–198 °C); ^1H NMR (acetone-d_6) δ 1.50 (s); IR (KBr) ν_{CO} 1685, 1280 cm^{-1}.

Chlorocarbonylsulfenyl chloride, ClC(O)SCl,[12] and **methoxycarbonylsulfenyl chloride, $H_3COC(O)SCl$,**[13] were prepared by literature procedures. **Methoxycarbonyl 2-hydroxyethyl disulfide, $H_3COC(O)SSCH_2CH_2OH$,** and **methyl methoxycarbonyl dithioacetate, $H_3COC(O)SSCH_2C(O)OCH_3$,** were prepared from methoxycarbonylsulfenyl chloride and the corresponding thiol by a literature procedure[14] and purified by fractional distillation. ^1H NMR ($CDCl_3$): for $H_3COC(O)SSCH_2CH_2OH$ δ 3.93 (3 H, s), 3.80 (2 H, t, J = 5 Hz), 3.35 (1 H, s), 2.93 (2 H, t, J = 5 Hz); for $H_3COC(O)SSCH_2C(O)OCH_3$ δ 3.92 (3 H, s), 3.77 (3 H, s), 3.57 (2 H, s).

(2-Mercaptoethylamine-*N*,*S*)bis(ethylenediamine)cobalt(III) perchlorate was prepared as previously described.[15] The perchlorate salts of **(mercaptoacetato-*O*,*S*)bis(ethylenediamine)cobalt(III)**[16] and its analogues **(2-mercaptopropionato-*O*,*S*)bis(ethylenediamine)cobalt(III)**[16] and **(2-mercapto-2-methylpropionato-*O*,*S*)bis(ethylenediamine)cobalt(III)**[17] were prepared by literature procedures. The PF_6^- salt of (mercaptoacetato-*O*,*S*)bis(ethylenediamine)cobalt(III) was prepared by metathesis from the ClO_4^- salt in water with NH_4PF_6. The chloride salts of this complex and (2-mercaptopropionato-*O*,*S*)bis(ethylenediamine)cobalt(III) were available from a previous study.[18]

(2,2′-Dithiobis(2-methylpropionato)-*O*,*S*²)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2\cdot 2H_2O$. In a typical preparation 0.25 g (0.63 mmol) of $[(en)_2Co(SC(CH_3)_2COO)]ClO_4$ was dissolved in 40 mL of water, and 1.37 mL (0.63 mmol) of fresh, electrolytically prepared $[Co(aq)]^{3+}$ was added rapidly with vigorous stirring. The solution changed from a purple to a cherry red color within 5 s. The reaction mixture was then diluted to ca. 100 mL with cold water and sorbed onto a column (2.5 cm i.d. × 15 cm) of Sephadex SP-C25 (Na^+) cationic exchanger at ca. 5 °C. The column was then eluted with cold 0.10 M $NaClO_4$ (0.01 M $HClO_4$) until a clear separation of products was obtained. Under these conditions the desired compound is the major component and has the smallest R_f of all the reaction products. The band containing cobaltous ion smeared badly, and eventually the cobalt bound irreversibly to the resin; a very minor, high-charged (≥3+) product was not pursued. The $NaClO_4$–$HClO_4$ eluent containing the desired complex was rotoevaporated (<35 °C) until incipient crystallization and then cooled to ca. 0 °C over 30 min to yield cherry red crystals (yield 0.37 g, 84%). Attempts to recrystallize the product, or to grow crystals containing other anions, resulted in partial decomposition of the coordinated disulfide. Therefore, all characterizations were carried out on material obtained as above. Anal. Calcd for $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2\cdot 2H_2O$: Co, 9.05; C, 22.11; H, 5.07; N, 8.06; S, 9.85; Cl, 10.89. Found: Co, 8.87; C, 22.22; H, 5.49; N, 8.62; S, 9.56; Cl, 10.87.

(Dithiobis(acetato)-*O*,*S*²)bis(ethylenediamine)cobalt(III), $[(en)_2Co_2(S(SCH_2COOH)CH_2COO)]^{2+}$, and **(2,2′-dithiobis(propionato)-*O*,*S*²)bis(ethylenediamine)cobalt(III), $[(en)_2Co(S(SCH(CH_3)COOH)CH(CH_3)COO]^{2+}$,** were prepared by the preceding method but were much more susceptible to hydrolytic decomposition and were not isolable as solid salts. Therefore, all characterizations of these complexes were carried out on solutions freshly derived from reaction mixtures by ion-exchange chromatography. For separations performed on Sephadex SP-C25 (Na^+) the eluent was 0.05 M $NaClO_4$–0.05 M $HClO_4$. For separations on Dowex 50W-X2 (H^+) solutions of $HClO_4$, $NaClO_4$ (pH 1) or NaCl (pH 1) were used. All ion-exchange separations were conducted at ca. 5 °C. An analysis for a solution of the dithiodiacetato product eluted from Dowex 50W-X2 with 3 M NaCl (0.1 M HCl) determined S:Co = 2.08:1. The calculated value for $[(en)_2Co(S(SCH_2COOH)CH_2COO)]^{2+}$ is S:Co = 2.0:1.

(((2-Methyl-2-propyl)dithio)acetato-*O*,*S*²)bis(ethylenediamine)cobalt(III) Perchlorate, $[(en)_2Co(S(SC(CH_3)_3)CH_2COO)](ClO_4)_2$. In a typical preparation 1.0 g (2.41 mmol) of $[(en)_2Co(SCH_2COO)]PF_6$ was dissolved in 200 mL of dimethylformamide, and then 30 mL (ca. 2.3 mmol) of freshly prepared *tert*-butylsulfenyl iodide solution[19] was added with stirring. This reaction mixture was stirred in the dark for ca. 5 min, and the product was precipitated as an oil by the addition of 2 L of ethyl ether and 5 mL of 0.01 M $HClO_4$ (cooling the mixture to ca. −20 °C aided the separation). The ether layer was then decanted, and the remaining oil was dissolved in 25 mL of 0.01 M $HClO_4$ and loaded onto a Sephadex SP-C25 column (2 cm i.d. × 20 cm) at ca. 5 °C. The excess $[(en)_2Co(SCH_2COO)]^+$ was eluted with 0.1 M $NaClO_4$ (0.01 M $HClO_4$), and the remaining cherry red product was displaced from the resin with 0.25 M $Ba(ClO_4)_2$ (0.01 M $HClO_4$). Cooling of this eluent to ca. 0 °C resulted in the slow formation of long, fanlike crystals (yield 0.77 g, 60%). The product was recrystallized by dissolving it in 0.05 M $HClO_4$ at ambient temperature, adding saturated $NaClO_4$ to ca. 2 M, and cooling to 0 °C. The chloride salt was prepared by eluting the product from Sephadex-C25 with 0.25 M $BaCl_2$ (0.01 M HCl), rotoevaporating to ca. 20% the original volume, and cooling to 0 °C. Anal. Calcd for $[(en)_2Co(S(SC(CH_3)_3)CH_2COO)](ClO_4)_2$: Co, 10.65; C, 21.45; H, 4.80; N, 9.93; S, 11.47; Cl, 12.74. Found: Co, 10.58; C, 21.55; H, 4.85; N, 10.06; S, 11.51; Cl, 12.72.

(2-((2-Methyl-2-propyl)dithio)propionato-*O*,*S*²)bis(ethylenediamine)cobalt(III) perchlorate, $[(en)_2Co(S(SC(CH_3)_3)CH(CH_3)COO)](ClO_4)_2$, and **(2-((2-methyl-2-propyl)dithio)(2-methylpropionato)-*O*,*S*²)bis(ethylenediamine)cobalt(III) perchlorate, $[(en)_2Co(S(SC(CH_3)_3)C(CH_3)_2COO)](ClO_4)_2$,** were prepared by the preceding method and were isolated as the perchlorate salts in the same manner.

(1-((2-Methyl-2-propyl)dithio)-2-aminoethane-*N*,*S*²)bis(ethylenediamine)cobalt(III) perchlorate, $[(en)_2Co(S(SC(CH_3)_3)CH_2CH_2NH_2)](ClO_4)_3$, was prepared by a modification of the preceding method. Because of the excellent solubility of the precursor thiolato complex, $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$, in DMF, much less reaction solvent was needed (10 mL of DMF per 1 g of starting thiolato complex). Separation of the product on Sephadex SP-C25 required elution with 0.25 M $NaClO_4$ (0.01 M $HClO_4$), and the orange product was displaced from the resin with 0.25 M $Ba(ClO_4)_2$ (0.01 M $HClO_4$). Rotoevaporation of the eluent and cooling to ca. 5 °C yielded an orange oil. Attempts at producing a solid, crystalline product failed (despite the use of a variety of anions), and this oil of the perchlorate salt was used for compound characterization.

(2-((Carboxymethyl)dithio)-2-methylpropionato-*O*,*S*²)bis(ethylenediamine)cobalt(III) perchlorate, $[(en)_2Co(S(SC(CH_3)_2COOH)CH_2COO)](ClO_4)_2$, was prepared by a procedure analogous to that used above for the 2-methylpropane derivatives. Preparation of the intermediate (2-methylpropionato)sulfenyl iodide, $HOOCC(CH_3)_2SI$, was accomplished with use of the method of Danehy.[20] In a typical preparation 0.372 g (3.10 mmol) of 2-mercapto-2-methylpropionic acid in 10 mL of methanol at ca. −20 °C was rapidly added to 98.4 mL (3.10 mmol) of a 3.15 × 10^{-2} M solution of iodine in methanol, also cooled to ca. −20 °C. The resulting mixture was stirred in the

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absence of light for 10 s and then rapidly added to a stirred solution of 1.0 g (3.10 mmol) of $[(en)_2Co(SCH_2COO)]Cl\cdot H_2O$ in 50 mL of 0.03 M HCl. This solution was stirred for 5 min and subsequently adsorbed onto a plug of Sephadex SP-C25 (Na^+) resin, which was then washed with 0.01 M HCl to remove methanol and any excess iodine. This plug was then placed on top of a column of Sephadex SP-C25 preequilibrated at ca. 5 °C and eluted with cold 0.1 M $NaClO_4$ (0.02 M $HClO_4$) until a clear separation of bands was obtained. The excess cobalt-containing starting material was removed with this eluent, and the red product band was displaced from the resin with 0.25 M $Ba(ClO_4)_2$ (0.02 M $HClO_4$). This eluent was rotoevaporated to ca. 20% the initial volume and upon cooling to 0 °C yielded a red crystalline product. This was filtered, washed with cold 1 M $HClO_4$ and then with ethanol, and dried in vacuo over P_2O_5 (yield 0.87 g, 45%).

(2-((1-Carboxyethyl)dithio)-2-methylpropionato-*O*,*S*²)bis(ethylenediamine)cobalt(III) tetrachlorozincate, $[(en)_2Co(S(SC(CH_3)_2COOH)CH(CH_3)COO)]ZnCl_4$, and **(2-((2-aminoethyl)dithio)-2-methylpropionato-*N*,*S*²)bis(ethylenediamine)cobalt(III) perchlorate, $[(en)_2Co(S(SC(CH_3)_2COOH)CH_2CH_2NH_2)](ClO_4)_3$,** were prepared in the same general manner as outlined for $[(en)_2Co(S(SC(CH_3)_2COOH)CH_2COO)](ClO_4)_2$. The $ZnCl_4^{2-}$ salt of the first complex was prepared by addition of a saturated solution of $ZnCl_2$ in 6 M HCl to the concentrated eluent containing the cation which had been displaced from Sephadex SP-C25 with 0.25 M $BaCl_2$ (0.02 M HCl).

(1-((2-Hydroxyethyl)dithio)-2-aminoethane-*N*,*S*²)bis(ethylenediamine)cobalt(III), $[(en)_2Co(S(SCH_2CH_2OH)CH_2CH_2NH_2)]^{3+}$. In a typical preparation 1.0 g (2.21 mmol) of $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$ and 1.10 mL (4.4 mmol) of 4 M $HClO_4$ were dissolved in 25 mL of DMF. To this solution was added an excess of $H_3COC(O)SSCH_2CH_2OH$ (0.743 g, 4.42 mmol). This was stirred for 10 min whereupon the crude product was precipitated as an oil by addition of a large excess of ethyl ether and subsequent cooling. After decantation of the ether layer, the oil was taken up in 50 mL of 0.01 M $HClO_4$, loaded on a cold (ca. 5 °C) column of Sephadex SP-C25 (2.0 cm i.d. × 20 cm), and eluted with 0.1 M NaCl (0.01 M HCl) until a clean separation of bands was obtained. The brown starting material was removed with 0.2 M NaCl (0.01 M HCl), and the higher charged orange product was displaced with 0.25 M $BaCl_2$ (0.01 M HCl). This eluent was then rotoevaporated (<35 °C) until a heavy orange oil separated (yield 0.44 g, 45%). No crystalline solid could be isolated. Therefore, this oil was used for characterization of the product.

(Methyl ((2-aminoethyl)dithio)acetate-*N*,*S*²)bis(ethylenediamine)cobalt(III), $[(en)_2Co(S(SCH_2C(O)OCH_3)CH_2CH_2NH_2)]^{3+}$. This preparation was conducted exactly as the preceding one, but with substitution of $H_3COC(O)SSCH_2C(O)OCH_3$ as the $[RS]^+$ donor. However, due to the increased tendency of this complex to undergo hydrolytic decomposition, it was not isolable in a pure state as either a solid or an oil. Characterizations were, therefore, performed on freshly eluted, cold solutions.

X-ray Characterization of $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2\cdot 2H_2O$. A large, cherry red crystal with parellelepiped morphology was mounted on a glass fiber, and precession photographs of the *hk*0, *hk*1, 0*kl*, and 1*kl* layers were taken with use of Cu Kα radiation. The systematic absences indicated were for *h*0*l* $h + l$ = odd and for 0*k*0 k = odd. These suggested the space group $P2_1/n$ for the monoclinic cell.[21] A second, smaller crystal of the same morphology with mean dimensions of 0.27 × 0.20 × 0.22 mm was mounted on the diffractometer, and our usual procedures[18] were followed to check the crystal quality (three axial rotation photographs and mosaic-scan measurements). Cell constants were determined by least-squares refinement using 2θ values for 15 pairs of reflections. These are a = 13.272 (7) Å, b = 12.714 (8) Å, c = 16.031 (8) Å, and β = 103.02 (3)°. With Z = 4, d_{calcd} = 1.64 g cm^{-3} and d_{measd} = 1.64 (2) g cm^{-3} (neutral buoyancy in CCl_4–$CHBr_3$). The rate for the θ–2θ scan varied between 1.0 and 4.0° min^{-1}, depending on the intensity of the reflection being measured. The scan ranged from 0.7° in 2θ below the calculated Kα_1 peak position to 0.7° above that calculated for Kα_2. Four standard reflections were monitored to check crystal stability and to account for long-term drift; the drift correction varied randomly from 1.043 to 0.993. The linear absorption coefficient (μ) was 10.96 cm^{-1}, and absorption corrections were not applied. A trial calculation of transmission coefficients yielded values that varied from 0.835 to 0.792. Within the sphere 2θ < 45°, 4233 reflections were measured; from these, 3392 unique reflections were obtained by averaging.[22] Of these, 2578 had $I > 2\sigma(I)$, where p, the ignorance factor used to calculate[18] $\sigma(I)$, was set equal to 0.04.

Structure Solution and Refinement of $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2\cdot 2H_2O$. A Patterson vector map was computed, and positions of the cobalt atom and coordinated sulfur atom were determined. However, solution of an electron density map on the basis of these positions proved difficult. Treatment of the data in the acentric space group *Pn* yielded a new Patterson solution which, with succeeding electron density maps, led to location of all 70 atoms (2 formula units). Subsequently, a center of symmetry relating two sets of atoms was located, and further refinement was carried out in $P2_1/n$. Anisotropic thermal parameters were used for all atoms. Hydrogen atoms were not included. In the final cycles of least-squares refinement, 421 parameters were varied, including the scale factor, the positional parameters, and anisotropic thermal parameters for all atoms. Convergence was achieved with R_1 = 0.062 and R_2 = 0.071.[23] In the last cycle of refinement, the maximum shift per error was 0.316, and the average shift per error was 0.024. A final difference map was essentially featureless with the largest peak being less than 0.75 Å^{-3}. Neutral-atom scattering curves as given by Cromer[24] were used for Co, S, Cl, N, C, and O. Corrections for anomalous dispersion[25] were made by using $\Delta f'$ and $\Delta f''$ values of 0.299 and 0.973 for Co, 0.132 and 0.159 for Cl, and 0.110 and 0.124 for S. The values of $|F_o|$ and F_c are listed in Table A.[26]

Results

Characterization. In addition to the single-crystal X-ray structural determination of the title complex, the disulfide–cobalt(III) complexes introduced in this report are characterized by (1) the chemistry and stoichiometry of their synthesis from thiolato–cobalt(III) precursors, (2) elemental analyses of representative compounds, the results of which are in agreement with the proposed formulations, (3) the visible–UV, ^{1}H NMR, and IR spectral parameters given in Tables I, II, and III, (4) cation-exchange elution characteristics that are consistent with the assigned formal charges, and (5) regeneration of the precursor thiolato complexes by chemical reduction of the S–S linkage.

The $[Co(aq)]^{3+}$ oxidation of $[(en)_2Co(SC(CH_3)_2COO)]^+$ to yield the title complex (eq 2) generates 1.9 ± 0.1 mol of $[Co(aq)]^{2+}$/mol of $[Co(aq)]^{3+}$ consumed in accord with the stoichiometry required by induced electron transfer and in agreement with earlier results for the analogous oxidation of $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ by Np(VI) (eq 1).[3,4]

$$2[(en)_2Co(SC(CH_3)_2COO)]^+ + [Co(aq)]^{3+} + 5H^+ \rightarrow [(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+} + 2[Co(aq)]^{2+} + 2[enH_2]^{2+} \quad (2)$$

The visible–UV spectrophotometric parameters for the new complexes reported in this study (Table I) are consistent with parameters observed for previously prepared disulfide–cobalt(III) complexes.[2] Upon conversion of a coordinated thiolate to a coordinated disulfide there is a shift in the low-energy d–d transition to shorter wavelength, while the ligand-to-metal charge-transfer (LTMCT) band at ca. 280 nm, characteristic of the Co–S bond, is preserved.[27] In addition, a new band appears at approximately 340 nm, which is assigned to the Co–S(SR)R chromophore.[2] The position of this near-UV band

(21) "International Tables for X-Ray Crystallography", 2nd ed.; Kynoch Press: Birmingham, England, 1965; Vol. 1, p 99.

(22) All computations were performed by using a local version of XRAY 67: J. M. Stewart, University of Maryland, crystallographic computer system.

(23) $R_1 = \sum||F_o| - |F_c||/|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$.

(24) Cromer, D. T.; Mann, J. B. *Acta Crystallogr., Sect. A* **1968**, *A24*, 321.

(25) "International Tables for X-Ray Crystallography", 3rd ed.; Kynoch Press: Birmingham, England, 1974; Vol. 4.

(26) Supplementary material. This includes all tables designated by alphabetic characters.

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

Table I. Visible-UV Spectrophotometric Parameters for Coordinated Disulfides, Their Precursors, and Related Complexes[a]

complex	λ (ε) max	min	max	min	max	min
$[(en)_2Co(SCH_2COO)]^{+}$ [b]	518 (152)	430 (73)	360 sh (340)		282 (11 700)	255 (4270)
$[(en)_2Co(SCH(CH_3)COO)]^{+}$ [b]	515 (150)	428 (75)	360 sh (340)		280 (12 600)	254 (5350)
$[(en)_2Co(SC(CH_3)_2COO)]^{+}$ [b]	514 (153)	427 (56)	360 sh (340)		282 (10 900)	258 (5090)
$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ [b]	600 sh (44) 482 (142)	423 (95)	360 sh (315)		282 (13 800)	250 (1550)
$[(en)_2Co(S(CH_3)CH_2COO)]^{2+}$ [d]	499 (168)	420 (34)	350 sh (280)		280 (7300)	270 (7210)
$[(en)_2Co(S(CH_3)CH_2CH_2NH_2)]^{3+}$ [d]	487 (177)	405 (18)	340 sh (260)		282 (8380)	257 (4140)
$[(en)_2Co(S(O)CH_2COO)]^{+}$ [b]	493 (350)		360 (6000)		285 (3100)	
$[(en)_2Co(S(O)CH_2CH_2NH_2)]^{2+}$ [b]	470 (500)		365 (6700)		284 (3700)	
$[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$						
R = CH_3 [c]	489 (149)	429 (60)	343 (1710)	319 (1340)	278 (7550)	261 (6460)
R = CH_2CH_3 [c]	490 (150)	429 (60)	340 (1840)	327 (1620)	280 (7410)	260 (5640)
R = $CH(CH_3)_2$ [c]	491 (161)	430 (59)	337 (1660)	330 (1600)	283 (6100)	261 (4350)
R = $C(CH_3)_3$	490 (167)	425 (49)	332 sh (2280)		287 (7900)	263 (4420)
R = $CH_2CH_2NH_3^{+}$ [c]	492 (175)	430 (56)	330 sh (2000)		275 (8300)	265 (6300)
R = CH_2CH_2OH	489 (167)	428 (59)	339 (3150)	313 (2080)	277 (5850)	266 (5490)
R = $CH_2C(O)OCH_3$	488 (154)	421 (50)	324 (3350)	312 (3160)	277 (6180)	264 (5710)
R = $C(CH_3)_2COOH$ pH 1	489 (168)	427 (54)	331 (3460)	311 (2970)	281 (6420)	267 (5460)
pH 4.5	489 (185)	337 (91)	348 (3300)	319 (2410)	284 (4650)	272 (4470)
$[(en)_2Co(S(SR)CH_2COO)]^{2+}$						
R = $C(CH_3)_3$	501 (161)	429 (37)	340 sh (1640)		285 (7680)	270 (6740)
R = CH_2COOH	502 (144)	431 (48)	326 sh (2150)		275 sh (6110)	
R = $C(CH_3)_2COOH$ pH 1	401 (138)	431 (40)	322 sh (1960)		279 sh (5180)	
pH 4.5	501 (172)	440 (66)	346 (2820)	322 (1570)	282 sh (4510)	
$[(en)_2Co(S(SR)CH(CH_3)COO)]^{2+}$						
R = $C(CH_3)_3$	500 (189)	431 (50)	334 (3230)	320 (3100)	285 (5970)	275 (5700)
R = $CH(CH_3)COOH$	501 (176)	431 (56)	329 (2910)	315 (2480)	275 sh (5770)	
R = $C(CH_3)_2COOH$ pH 1	500 (185)	431 (49)	330 (4030)	309 (3420)	280 sh (5290)	
pH 4.5	499 (197)	437 (69)	346 (3870)	314 (2450)	280 sh (4750)	
$[(en)_2Co(S(SR)C(CH_3)_2COO)]^{2+}$						
R = $C(CH_3)_3$	504 (228)	446 (124)	340 sh (2480)		287 (7600)	268 (6410)
R = $C(CH_3)_2COOH$ pH 1	504 (192)	429 (41)	325 sh (3550)		288 (5210)	280 (5200)
pH 4.5	504 (219)	435 (60)	343 (3680)	322 (3160)	285 sh (4810)	

[a] Wavelengths, λ, of maxima (max), minima (min), and shoulders (sh) are 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 17. [c] Reference 2. [d] Reference 40.

Table II. Infrared Carbonyl Stretching Frequencies (cm^{-1}) for Products and Precursors[a]

complex	COO–Co ν_{as}	COO–Co ν_s	COOH ν_{as}	COOH ν_s
$[(en)_2Co(SCH_2COO)]ClO_4$	1630	1330		
$[(en)_2Co(SCH(CH_3)COO)]ClO_4$	1615	1370		
$[(en)_2Co(S(CH_3)_2COO)]ClO_4$	1625	1380		
$[(en)_2Co(S(SC(CH_3)_3)CH_2COO)](ClO_4)_2$	1640	1330		
$[(en)_2Co(S(SC(CH_3)_3)CH(CH_3)COO)](ClO_4)_2$	1640	1335		
$[(en)_2Co(S(SC(CH_3)_3)C(CH_3)_2COO)](ClO_4)_2$	1655	1320		
$[(en)_2Co(S(SC(CH_3)_2COOH)CH_2COO)](ClO_4)_2$	1630	1350	1720	1465
$[(en)_2Co(S(SC(CH_3)_2COOH)CH(CH_3)COO)]ZnCl_4$	1660	1325	1715	1460
$[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2$	1625	1380	1700	1450

[a] ν_s = symmetric; ν_{as} = asymmetric.

is dependent on the steric and electronic nature of the pendant segment of the disulfide. This dependence is especially pronounced in the spectra of the acid and conjugate base forms of those complexes containing the $-SC(CH_3)_2COOH$ pendant group.

In Table II are presented the carbonyl region IR bands for the coordinated disulfides, the corresponding precursor thiolato complexes, and some related compounds. Bands have been assigned to be consistent with literature assignments for similar functional groups.[28,29] The spectra of those complexes containing the noncoordinated carboxylic acid group show increased complexity in the carbonyl region. When the precursor thiolato complex contains a chelated carboxylate, the bands associated with this functionality are preserved in the spectrum of the disulfide product.

The ^1H NMR data presented in Table III show that upon conversion of a coordinated thiolate to a coordinated disulfide the shapes of the ethylenediamine CH_2 resonances change in a manner indicative of a more symmetrical ligand field,[30] an effect also seen for the conversion of coordinated thiols to coordinated thioethers. The characteristic signals of the pendant groups are observed upfield of those of the ethylenediamine protons and in all cases yield correct integration ratios with respect to the ethylenediamine CH_2 protons. The amine NH_2 resonances are not recorded due to their broad character and tendency to overlap with the rather large HOD signal. The methyl resonances of the title complex, which normally generate an overlapping three-peak pattern (approximate integration ratio of 1:1:2), are shifted upfield and are resolved into two pseudodoublets (Figure 1) when an excess of hydrated europium(III) perchlorate is added to the test

(28) Nakamoto, K. "Infrared and Raman Spectra of Inorganic and Coordination Compounds"; Wiley-Interscience: New York, 1978.
(29) Kothari, V. M.; Busch, D. H. *Inorg. Chem.* **1969**, *8*, 2276–80.
(30) Lydon, J. D.; Mulligan, K. J.; Elder, R. C.; Deutsch, E. *Inorg. Chem.* **1980**, *19*, 2083–7.

Table III. ^{1}H NMR Spectral Parameters for Some Coordinated Disulfides and Related Compounds[a]

complex	protons	δ	character
$[(en)_2Co(SCH_2COO)]^+$	$enCH_2$	2.60; 2.93	br mults[b]
	SCH_2	3.18	s
$[(en)_2Co(SCH(CH_3)COO)]^+$	$enCH_2$	2.60; 2.97	br mults[b]
	SCH	3.58	q (J = 7 Hz)
	$SC(CH_3)$	1.40	d (J = 7 Hz)
$[(en)_2Co(SC(CH_3)_2COO)]^+$	$enCH_2$	2.55; 2.95	br mults[b]
	$SC(CH_3)_2$	1.45	s
$[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$	NCH_2	2.70; 2.83	br mults
	SCH_2	2.23	mult
$[(en)_2Co(S(SC(CH_3)_3)CH_2COO)]^{2+}$	$enCH_2$	2.90	br mult
	SCH_2	4.23	AB mult
	$SC(CH_3)_3$	1.53	s
$[(en)_2Co(S(SC(CH_3)_3)CH(CH_3)COO)]^{2+}$	$enCH_2$	2.87	br mult
	SCH	4.32	sh mult
	$SC(CH_3)$	1.55, 1.67, 1.70, 1.78	sh mult
	$SC(CH_3)_3$	1.58	s
$[(en)_2Co(S(SC(CH_3)_3)C(CH_3)_2COO)]^{2+}$	$enCH_2$	2.83	br mult
	$SC(CH_3)_2$	1.65; 1.70	2 s
	$SC(CH_3)_3$	1.57	s
$[(en)_2Co(S(SC(CH_3)_3)CH_2CH_2NH_2)]^{3+}$	CH_2CH_2	2.88	br mult
	$SC(CH_3)_3$	1.55	s
$[(en)_2Co(S(SC(CH_3)_2COOH)CH_2COO)]^{2+}$	$enCH_2$	2.90	br mult
	SCH_2	4.23	AB mult
	$SC(CH_3)_2$	1.73; 1.85	2 s
$[(en)_2Co(S(SC(CH_3)_2COOH)CH(CH_3)COO)]^{2+}$	$enCH_2$	2.88	br mult
	SCH	4.30	q (J = 7 Hz)
	$SC(CH_3)$	1.65	d (J = 7 Hz)
	$SC(CH_3)_2$	1.72; 1.92	2 s
$[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+}$	$enCH_2$	2.83	br mult
	$SC(CH_3)_2$	1.65	s
	$SC(CH_3)_2COOH$	1.70; 1.80	2 s
$[(en)_2Co(S(SC(CH_3)_2COOH)CH_2CH_2NH_2)]^{3+}$	CH_2CH_2	2.92; 3.30	br mults
	$SC(CH_3)_2$	1.70; 1.85	2 s
$[(en)_2Co(S(SCH_2CH_2OH)CH_2CH_2NH_2)]^{3+}$	$enCH_2$, SCH_2CH_2N	2.95	br mult
	CH_2O	3.98	t (J = 6 Hz)
	SCH_2	3.45	t (J = 6 Hz)
$DSCH_2CH_2OD$	SCH_2	2.68	t (J = 6 Hz)
	CH_2O	3.69	t (J = 6 Hz)
$DSC(CH_3)_2COOD$	$SC(CH_3)_2$	1.57	s
$DSCH(CH_3)COOD$	SCH	3.62	q (J = 8 Hz)
	$SC(CH_3)$	1.47	d (J = 8 Hz)

[a] Spectra determined in D_2O (pD ≈2) with sodium 3-(trimethylsilyl)-1-propanesulfonate as internal standard. NH_2 protons are not reported. Abbreviations: mult = multiplet; br = broad; sh = sharp; s = singlet; d = doublet; t = triplet; q = quartet. [b] These $enCH_2$ protons are split into two multiplets of approximate relative intensity 1:3, the higher field resonance being the larger.

solution. Subsequent analysis of the test solution by ion-exchange chromatography and visible–UV spectrophotometry shows no apparent decomposition of the disulfide complex. The other complexes containing pendant $-SC(CH_3)_2COOH$ moieties also show upfield shifts when $[Eu(aq)]^{3+}$ is added but none as dramatic as with the title compound. Acidification of the ^{1}H NMR test solution with DCl negates the effect of added $[Eu(aq)]^{3+}$, thereby implicating coordination of the pendant carboxylate to $[Eu(aq)]^{3+}$ as the source of the effect.

All of the disulfide complexes reported herein can be reduced to the corresponding thiolato compounds by excess thiol (e.g., 2-mercaptoethanol) or by stannous chloride in HCl. These reactions are quite rapid (1–30 s), and the rate qualitatively decreases with increasing steric bulk of the pendant group. The coordinated disulfides are also susceptible to base hydrolysis, which yields the precursor thiolato complex and, presumably, a noncoordinated sulfenic acid (which is a transient species)[31] derived from the pendant segment of the disulfide (eq 3). However, when the pendant group contains

a tertiary carbon atom bonded to the pendant sulfur atom, the reaction with OH^- is complicated by concurrent Co–S bond fission, which generates the aquation product $[(en)_2Co(OH_2)(X—S–SR)]^{n+}$. Potentiometric pH titration of the pendant carboxylate group of the title complex with OH^- yields an equivalent weight of ca. 635 (theory: 651 g equiv^{-1}) and a pK_a of ca. 2.9 although the accuracy of this determination is limited by base-promoted hydrolysis reactions at pH >7. The comparable pK_a of noncoordinated $HOOCC(CH_3)_2SH$ is 3.9,[32] and that of the corresponding disulfide is expected to be slightly smaller.[33] The increase in acidity of a pendant group upon association with a positively charged metal center is a well-established phenomenon;[34] for example, the pK_a values of $HSCH_2COOH$ and $[(en)_2Co(S(CH_2COOH)CH_2CH_2NH_2)]^{3+}$ are 3.3 and 2.1, respectively.[32,35]

Decomposition of the title complex in 1 M HCl yields $[(en)_2Co(OH_2)(OOCC(CH_3)_2SSC(CH_3)_2COOH)]^{2+}$ and, as a minor product, the precursor thiolato complex. The former is identified by its chemical and physical characteristics: (1) ion-exchange analysis shows it to have a 2+ formal charge; (2) upon standing, the ion-exchange eluents containing this

(31) Hogg, D. R. *Compr. Org. Chem.* **1979**, *4*, 261.

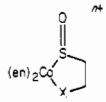
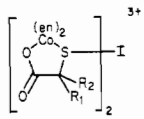
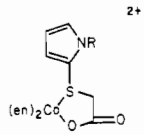
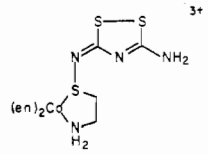
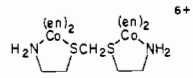
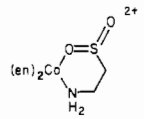
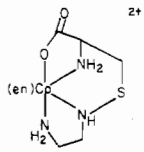
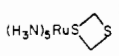
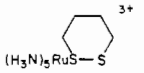
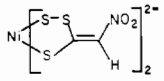
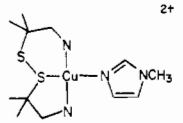
(32) Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.: New York, 1958; Vol. I, p 470.

(33) Reid, E. E. "Organic Chemistry of Bivalent Sulfur"; Chemical Publishing Co.: New York, 1958; Vol. III, p 382.

(34) Basolo, F.; Pearson, R. G. "Mechanisms of Inorganic Reactions", 2nd ed.; Wiley: New York, 1967; pp 31–3.

(35) Kennard, G. J.; Deutsch, E. *Inorg. Chem.* **1978**, *17*, 2226.

Table IV. Selected Chalcogen-Containing Complexes That Exhibit Anomalous Charge-Transfer Spectra

no.	complex	λ_{max} (ϵ), nm	ref
1		ca. 340 (2000)	this work
2		ca. 365 (6000)	17
3			
	$R_1 = R_2 = H$	325 (ca. 4000)	49
	$R_1 = H, R_2 = CH_3$	320 (ca. 5000)	
	$R_1 = R_2 = CH_3$	330 sh (ca. 4500)	
4			
	R = H	410 (6820)	49
	R = CH_3	412 (6870)	
4		399 (7210)	49
5		333 sh (3160)	50
6		325 (4100)	51
6	$(H_3N)_5CoOSO_2^+$	330 (ca. 2100)	52
7		345 (2590)	56
8		425 (130), 545 (40)	57
9		618 (171), 360 (110)	57
10	$[(H_3N)_5CoO]_2^{4+}$	360 (ca. 290)	60
10	$[(CN)_5CoX]_2^{6-}$		
	X = S	370 (3160), 312 (8710),	61
	X = Se	380 (3715)	
10	$[(H_2O)_5CrS]_2^{4+}$	397 (ca. 2640)	61
10	$[(H_3N)_5RuS]_2^{4+}$	720 (1730)	63
11		392 (16 000), 353 (23 000)	64
12		445 (ca. 510), 335 (ca. 1150)	65

red product eventually yield the free disulfide, $HOOCC(CH_3)_2SSC(CH_3)_2COOH$, which is identified by comparison to an authentic sample; (3) the visible–UV spectrum is similar to that of *cis*-$[(en)_2Co(OH_2)(OOCCH_3)]^{2+}$ [36] and likewise

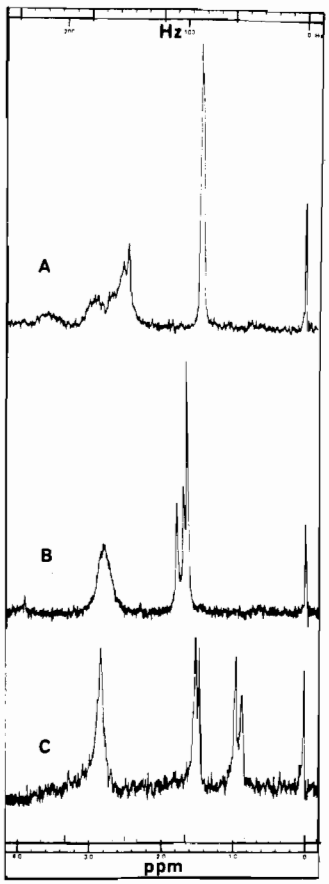


Figure 1. ^1H NMR spectra (in D_2O, with sodium 3-(trimethylsilyl)-1-propanesulfonate as reference): (A) $[(en)_2Co(SC(CH_3)_2COO)]^+$; (B) $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+}$; (C) $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+}$–$[Eu(aq)]^{3+}$.

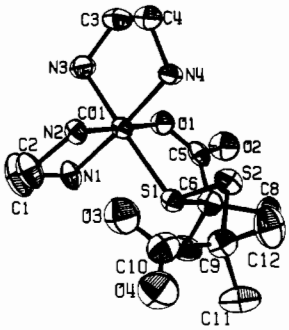


Figure 2. Perspective view of $\Lambda S(-)\delta\delta$-$[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+}$. The ellipsoids represent 50% probability.

shows a pH dependence corresponding to the deprotonation of the coordinated water molecule. Monitoring the progress of the acid decomposition reaction by ^1H NMR in D_2O (1 M DCl) shows two new, equally intense, single resonances appearing at 1.52 and 1.43 ppm. As these new signals appear there is a concomitant decrease in the intensity of the methyl resonances of the starting material. Throughout the course of the reaction the total integrated intensity of the old and new methyl resonances remains the same (relative to the intensity of the ethylenediamine CH_2 resonance).

Crystal Structure. Final fractional atomic positional parameters, and their estimated standard deviations, are given in Table V. The corresponding anisotropic thermal parameters may be found in Table B,[26] the root-mean-square dis-

(36) Carunchio, V.; Illuminati, G.; Ortaggi, G. *Inorg. Chem.* **1967**, *6*, 2168.

Table V. Fractional Atomic Positional Parameters[a,b] of $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2\cdot 2H_2O$

atom	x	y	z
Co	0.1692 (1)	0.1490 (1)	0.2448 (1)
S(1)	0.0247 (2)	0.1425 (2)	0.2972 (1)
S(2)	0.0576 (2)	0.2023 (2)	0.4194 (1)
N(1)	0.0804 (6)	0.1395 (6)	0.1275 (4)
N(2)	0.1623 (5)	0.3017 (5)	0.2279 (4)
N(3)	0.2948 (5)	0.1381 (6)	0.1983 (4)
N(4)	0.2647 (5)	0.1654 (6)	0.3573 (4)
O(1)	0.1770 (4)	0.0005 (4)	0.2597 (4)
O(2)	0.1270 (5)	−0.1488 (4)	0.3073 (4)
O(3)	0.0063 (6)	0.3906 (5)	0.3062 (5)
O(4)	−0.1208 (6)	−0.4534 (6)	0.3588 (5)
C(1)	0.0891 (10)	0.2412 (9)	0.0839 (7)
C(2)	0.0932 (9)	0.3288 (8)	0.1423 (6)
C(3)	0.3848 (7)	0.1107 (8)	0.2706 (6)
C(4)	0.3750 (7)	0.1776 (8)	0.3468 (6)
C(5)	0.1136 (6)	−0.0549 (6)	0.2911 (5)
C(6)	0.0126 (6)	−0.0046 (6)	0.3048 (6)
C(7)	−0.0768 (7)	−0.0366 (8)	0.2280 (7)
C(8)	−0.0106 (8)	−0.0381 (7)	0.3905 (6)
C(9)	−0.0502 (7)	0.2944 (7)	0.4186 (6)
C(10)	−0.0505 (7)	0.3838 (7)	0.3550 (6)
C(11)	−0.1555 (8)	0.2366 (9)	0.3998 (8)
C(12)	−0.0228 (10)	0.3392 (9)	0.5110 (6)
Cl(1)	0.6752 (2)	0.0016 (2)	0.4467 (2)
Cl(2)	0.1936 (2)	−0.0683 (2)	0.0164 (2)
O(11)	0.7492 (6)	0.0211 (7)	0.5231 (5)
O(12)	0.7275 (8)	−0.0148 (8)	0.3793 (6)
O(13)	0.6136 (8)	0.0892 (10)	0.4227 (6)
O(14)	0.6223 (9)	−0.0885 (11)	0.4581 (6)
O(21)	0.2017 (11)	0.0380 (7)	0.0079 (7)
O(22)	0.2551 (10)	−0.1029 (10)	0.0877 (7)
O(23)	0.1836 (17)	−0.1250 (11)	−0.0531 (9)
O(24)	0.0955 (11)	−0.0788 (12)	0.0411 (12)
O(31)	−0.1272 (5)	−0.3742 (6)	0.2696 (4)
O(32)	0.2465 (9)	0.2367 (7)	−0.3353 (6)

[a] The estimated error in the last digit is given in parentheses. This form is used throughout. [b] The numbering scheme is shown in Figure 2.

Table VI. Bond Lengths (Å) of $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2\cdot 2H_2O$

Co–S(1)	2.260 (3)	N(1)–C(1)	1.484 (13)
Co–N(1)	1.984 (6)	C(1)–C(2)	1.446 (15)
Co–N(2)	1.955 (7)	C(2)–N(2)	1.507 (11)
Co–N(3)	1.976 (8)	N(3)–C(3)	1.506 (11)
Co–N(4)	1.966 (6)	C(3)–C(4)	1.516 (14)
Co–O(1)	1.899 (6)	C(4)–N(4)	1.517 (12)
S(1)–C(6)	1.878 (9)	S(1)–S(2)	2.052 (3)
C(6)–C(7)	1.557 (12)	S(2)–C(9)	1.844 (9)
C(6)–C(8)	1.532 (14)	C(9)–C(11)	1.546 (13)
C(6)–C(5)	1.544 (12)	C(9)–C(12)	1.550 (14)
C(5)–O(1)	1.282 (11)	C(9)–C(10)	1.524 (13)
C(5)–O(2)	1.223 (10)	C(10)–O(3)	1.204 (14)
Cl(1)–O(11)	1.408 (8)	C(10)–O(4)	1.296 (13)
Cl(1)–O(12)	1.423 (11)	Cl(2)–O(21)	1.362 (10)
Cl(1)–O(13)	1.381 (12)	Cl(2)–O(22)	1.321 (11)
Cl(1)–O(14)	1.375 (14)	Cl(2)–O(23)	1.306 (14)
		Cl(2)–O(24)	1.448 (17)

placements calculated therefrom are collected in Table C,[26] and the associated ellipsoids for the complex cation are shown in Figure 2. Bond lengths and bond angles are found in Tables VI and VII and Table D.[26]

The structure consists of discrete cationic complexes, anions, and waters of hydration. As shown in Figure 2, the cationic complex is octahedrally coordinated by two bidentate ethylenediamine ligands and a bidentate dithiobis(2-methylpropionato) ligand. The disulfide is coordinated to cobalt by a carboxylate oxygen atom and a sulfur atom to form a five-membered ring. The pendant half of the disulfide is in the protonated form. The crystal is centrosymmetric and

Table VII. Bond Angles (Deg) of $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2\cdot 2H_2O$

Metal Coordination Sphere			
S(1)–Co–O(1)	86.8 (2)	O(1)–Co–N(4)	89.1 (3)
S(1)–Co–N(1)	88.6 (2)	N(1)–Co–N(2)	86.0 (3)
S(1)–Co–N(2)	94.0 (2)	N(1)–Co–N(3)	90.6 (3)
S(1)–Co–N(3)	173.9 (3)	N(1)–Co–N(4)	175.5 (3)
S(1)–Co–N(4)	95.2 (2)	N(2)–Co–N(3)	92.0 (3)
O(1)–Co–N(1)	93.6 (3)	N(2)–Co–N(4)	91.3 (3)
O(1)–Co–N(2)	179.1 (3)	N(3)–Co–N(4)	85.9 (3)
O(1)–Co–N(3)	87.2 (3)		
Ligands			
Co–N(1)–C(1)	107.5 (6)	C(5)–C(6)–C(8)	111.6 (7)
N(1)–C(1)–C(2)	111.0 (9)	C(5)–C(6)–C(7)	108.2 (7)
C(1)–C(2)–N(2)	109.8 (8)	S(1)–C(6)–C(7)	105.3 (6)
C(2)–N(2)–Co	110.6 (5)	S(1)–C(6)–C(8)	111.8 (6)
Co–N(3)–C(3)	108.5 (6)	Co–S(1)–S(2)	108.9 (1)
N(3)–C(3)–C(4)	107.0 (7)	C(6)–S(1)–S(2)	108.0 (3)
C(3)–C(4)–N(4)	106.9 (7)	C(7)–C(6)–C(8)	111.5 (8)
C(4)–N(4)–Co	110.4 (5)	S(1)–S(2)–C(9)	103.2 (3)
Co–S(1)–C(6)	98.8 (3)	S(2)–C(9)–C(10)	111.1 (7)
S(1)–C(6)–C(5)	108.2 (6)	S(2)–C(9)–C(11)	111.5 (6)
C(6)–C(5)–O(1)	119.7 (7)	S(2)–C(9)–C(12)	102.2 (6)
C(5)–O(1)–Co	124.8 (6)	C(10)–C(9)–C(11)	110.9 (6)
C(6)–C(5)–O(2)	117.5 (8)	C(10)–C(9)–C(12)	109.2 (8)
O(1)–C(5)–O(2)	122.7 (8)	C(11)–C(9)–C(12)	111.6 (9)
C(5)–C(6)–C(7)	108.2 (7)	C(9)–C(10)–O(3)	125.4 (9)
		C(9)–C(10)–O(4)	111.7 (9)
		O(3)–C(10)–O(4)	122.9 (9)

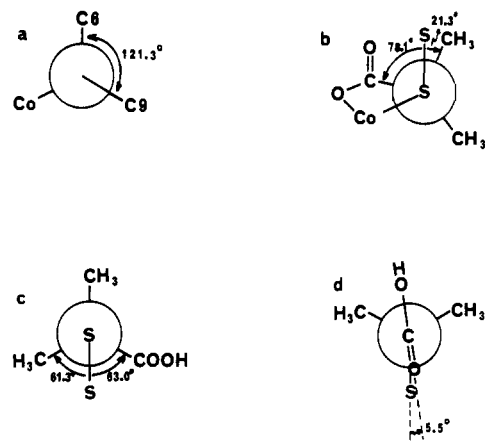


Figure 3. Newman projections showing selected orientations and torsional angles of $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+}$: (a) S(2) to S(1); (b) S(1) to C(6); (c) S(2) to C(9); (d) C(10) to C(9).

contains molecules of the $\Lambda S(-)\delta\delta$ and $\Delta R(+)\lambda\lambda$ configurations, where the chirality at S(1) is represented by R/S and the screw sense of the disulfide is designated by (+)/(−).[37] The dihedral angle, Φ, i.e., the angle subtended by the two C–S bonds when the S–S bond is viewed end on (Figure 3a), is 121.3°, and the two torsional angles that involve the carboxylate carbon atoms, i.e., S(2), S(1), C(6), C(5), and S(1), S(2), C(9), C(10), are 78.1 and 63.0°, respectively (Figure 3b,c).

There is no discernible structural trans effect. The Co–N bond trans to S is 1.976 (8) Å as compared to 1.975 (6) Å for the average of the Co–N bonds cis to S.[38] The two perchlorate anions undergo librational motion as shown by their large root-mean-square displacements.

Discussion

Synthesis. In an earlier report on the 1-equiv oxidation of a thiolato–cobalt(III) complex to yield a coordinated sym-

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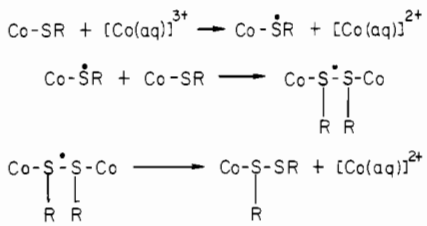
(38) The average was found by using N(1) and N(4), which are trans to each other. N(2) was not included due to a suspected negative trans effect.[17]

Scheme I



metrical disulfide, we proposed the induced electron-transfer mechanism shown in Scheme I. This mechanism is based on the overall reaction stoichiometry, as monitored by total cobalt analysis of ion-exchange-separated products, and on identification of the product complex. Therefore, in the reaction of $[Co(aq)]^{3+}$ with excess $[(en)_2Co(S{-}X)]^{n+}$, the overall reaction stoichiometry is represented by eq 4. The oxidation

$$2[(en)_2Co(S{-}X)]^{n+} + [Co(aq)]^{3+} \rightarrow [(en)_2Co(\overset{S{-}X}{\overset{|}{S}}{-}X)]^{n+1} + 2[Co(aq)]^{2+} + 2en \quad (4)$$

of $[(en)_2Co(SC(CH_3)_2COO)]^+$ conforms to this stoichiometry, and product characterization shows conclusively that the cobalt(III) product contains the coordinated symmetrical disulfide; thus, this reaction proceeds by induced electron transfer. Similarly, by identification of the coordinated symmetrical disulfide product complexes, the same process is shown to occur upon $[Co(aq)]^{3+}$ oxidation of $[(en)_2Co(SCH(CH_3)COO)]^+$ and $[(en)_2Co(SCH_2COO)]^+$. However, in these examples, accurate analysis of the overall reaction stoichiometry is hampered by the lability of the resultant disulfide complexes toward hydrolytic S–S bond cleavage.

In addition to $[Co(aq)]^{3+}$ and $[NpO_2(aq)]^{2+}$,[4] $[Fe(aq)]^{3+}$ is a useful 1-equiv oxidant for these reactions, although it reacts at a much slower rate (ca. 5–30 min compared to <5 s for the former two). Qualitative observations suggest that increased steric hindrance about the coordinated thiolato sulfur atom impedes the $[Fe(aq)]^{3+}$ oxidation, the rate of reaction decreasing along the series $-SCH_2COO- > -SCH(CH_3)COO- > -SC(CH_3)_2COO-$. The other potential oxidants evaluated for this reaction, i.e., $[(en)Co(H_2O)_4]^{3+}$, $[IrCl_6]^{2-}$, $S_2O_8^{2-}$, and Ag^+–$S_2O_8^{2-}$, yielded no detectable amounts of the coordinated disulfide product complexes. The substitution-inert character of $[(en)Co(H_2O)_4]^{3+}$ and $[IrCl_6]^{2-}$ may be the factor that causes these metal ion oxidants to be less effective than $[Co(aq)]^{3+}$, $[NpO_2(aq)]^{2+}$, or $[Fe(aq)]^{3+}$.

The practical synthetic value of oxidizing coordinated thiols with 1-equiv reagents is limited to the preparation of symmetrical disulfides. We have recently reported on a method that allows the preparation of coordinated unsymmetrical disulfides such as $[(en)_2Co(S(SCH_3)CH_2CH_2NH_2)]^{3+}$. This method involves reaction of a thiolato complex with the $[RS]^+$ donor *N*-(alkyl or aryl)thiophthalimide in the presence of acid.[2] While this route provides a nice complement to 1-equiv oxidation, it is also limited in scope by the relative unavailability of the precursor thiophthalimide reagents. Therefore, in this work we have developed two new synthetic strategies for the preparation of disulfide complexes. The first of these methods involves the reaction of coordinated thiolates with a noncoordinated sulfenyl iodide (eq 5). The utility of this method,

$$(en)_2Co(S{-}X)^{n+} + RSI \rightarrow (en)_2Co(\overset{SR}{\overset{|}{S}}{-}X)^{(n+1)+} + I^- \quad (5)$$

however, is limited to the preparation of disulfides that have a tertiary carbon atom attached to the pendant sulfur atom (e.g., $-SC(CH_3)_3$, $-SC(CH_3)_2COOH$, and $-SC(CH_3)_2C(NH_3^+)COOH$) since sulfenyl iodides that have primary or secondary carbon atoms adjacent to sulfur are very unstable.[19,20] The main advantages of this route are that the sulfenyl iodide reagent is easily prepared, that it does not need to be of high purity, and that it reacts with thiolato complexes to give the disulfide products in fairly high yield. The second synthetic technique is much less restricted in terms of steric effects and ancillary functional groups than are the previous tactics. This procedure involves the reaction of a thiolato complex with a methoxycarbonyl alkyl disulfide, $CH_3OC(O)SSR$, another type of potent $[RS]^+$ donor (eq 6). These $CH_3OC(O)SSR$ reagents are easily prepared, and they can incorporate functional groups that often hinder the preparation of other $[RS]^+$ donors;[14] in this work we have utilized reagents with R = CH_2CH_2OH and $CH_2C(O)OCH_3$.

$$(en)_2Co(S{-}X)^{n+} + CH_3O\overset{O}{\overset{\|}{C}}{-}S{-}SR + H^+ \rightarrow (en)_2Co(\overset{SR}{\overset{|}{S}}{-}X)^{(n+1)+} + COS + CH_3OH \quad (6)$$

It should also be noted that alkyl thiosulfonates, $RSS(O)_2R'$, also considered vigorous $[RS]^+$ donors,[39] are not nearly as reactive toward coordinated thiolates as are the previously mentioned reagents. Although the reaction of $CH_3S(O)_2SCH_3$ with $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ does yield the coordinated disulfide $[(en)_2Co(S(SCH_3)CH_2CH_2NH_2)]^{3+}$, the reaction is so slow as to render it impractical.

Characterization. ^{1}H NMR. Some of the specific ^{1}H NMR effects observed upon converting a thiolato complex to a thioether complex (Co–SR → Co–S(R)R) are mimicked upon conversion of a thiolato complex to a disulfide complex (Co–SR → Co–S(SR)R). Thus, transformation of a negatively charged thiolato ligand into a neutral disulfide ligand or a neutral thioether ligand increases the formal charge on the cobalt center by one unit; this increased positive charge causes the resonances resulting from the protons on the chelated portion of the ligand to shift downfield upon conversion to a coordinated disulfide (Table III) or a coordinated thioether.[40] Also, the positive charge of the disulfide complexes causes the chemical shifts of the pendant moieties, e.g., $-SC(CH_3)_3$ and $-SC(CH_3)_2COOH$, to appear downfield of the corresponding signals for the noncoordinated, neutral disulfide, e.g., $[-SC(CH_3)_3]_2$ and $[-SC(CH_3)_2COOH]_2$.

Disulfide complexes containing the pendant $-SC(CH_3)_3$ group exhibit a single CH_3 resonance in the narrow range δ 1.53–1.58 (Table III). However, the CH_3 groups of dangling $-SC(CH_3)_2COOH$ moieties are diastereotopic and for this reason (or possibly also because of sterically induced configuration restrictions) generate two resonances of approximately equal intensity. In the title complex, $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+}$, the situation is even further complicated by the fact that the CH_3 groups of the coordinated $-SC(CH_3)_2COO-$ are also diastereotopic (Figures 1 and 3b). Thus, the assignment of the CH_3 peaks in the ^{1}H NMR spectrum of the title complex is not trivial, but a consistent assignment has been generated through analysis of the less ambiguous ^{1}H NMR spectra of unsymmetrical disulfide complexes containing the $-SC(CH_3)_2COOH$ pendant, or $-SC(CH_3)_2COO^-$ chelated, moiety (Table III). Thus, it appears that in $[(en)_2Co(S(SC(CH_3)_2COOH)CH(CH_3)COO)]^{2+}$ and $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)]^{2+}$ the CH_3 resonances of the pendant moiety appear at *lower* field than do those of the coordinated segment. The use of $[Eu(aq)]^{3+}$ as a shift reagent to preferentially

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displace the CH_3 signals arising from the pendant moiety (Figure 1) is also consistent with this assignment. However, in the analogous complexes $[(en)_2Co(S(SC(CH_3)_3)C(CH_3)_2COO)]^{2+}$ and $[(en)_2Co(S(SC(CH_3)_3)CH(CH_3)COO)]^{2+}$ the effect is countered by the inherently greater shielding of protons within $-C(CH_3)_3$ (relative to that in $-C(CH_3)_2COOH$ or $-CH(CH_3)COOH$), and the net result is that the CH_3 signals of the *tert*-butyl moieties lie at *higher* field than do the CH_3 signals of the coordinated segment.

The methylene protons of the coordinated mercaptoacetato moiety of $[(en)_2Co(SCH_2COO)]^+$ generate a singlet in the ^1H NMR spectrum. Conversion of the coordinated mercaptoacetate to a coordinated disulfide (Table III), a coordinated thioether,[40] or a coordinated sulfenic acid,[17] reduces the symmetry of the sulfur atom; this causes the methylene protons to be diastereotopic and generate an AB multiplet in the ^1H NMR spectrum.

Visible–UV. The visible–UV spectrophotometric data in Table I show three effects which occur upon conversion of a thiolato–cobalt(III) complex to a disulfide–cobalt(III) complex and which help to characterize the resultant coordinated disulfide: (1) an appropriate shift in the low-energy cobalt(III) dd band, (2) preservation of the characteristic Co–S ligand-to-metal charge-transfer (LTMCT) band at ca. 280 nm,[28] and (3) the appearance of a new band of medium intensity in the near-UV region of the spectrum. The first two effects are similar to those observed upon conversion of a thiolato–cobalt(III) complex to a thioether complex,[40] but the near-UV band does not appear in the spectra of thioether complexes.

In the visible region the coordinated disulfides show absorbance maxima very near those observed for the corresponding thioethers[40] (Table I). This is reasonable since thioethers and disulfides are expected to provide similar ligand fields.[41] Given this similarity, the fact that coordinated disulfides provide a stronger ligand field than do coordinated thiolates is in agreement with Jørgensen's prediction for the spectrochemical series: $Cl < RS^- < F < H_2O < R_2S < NH_3$.[42] That the observed wavelength maxima for the complexes derived from $[(en)_2Co(SCH_2CH_2NH_2)]^{2+}$ actually exhibit a positive change (482 to ca. 490 nm) upon conversion of the thiolato complex to the disulfide or thioether complexes has been discussed previously;[2] this apparent anomaly is an artifact arising from the disappearance of the 600-nm shoulder, which is present in the spectrum of the thiolato complex but not in the spectra of the thioether and disulfide derivatives (Table I).

In all the complexes reported in Table I there is an intense band in the 275–288-nm region, which has been previously shown to be diagnostic for the presence of a sulfur atom coordinated to cobalt(III).[28] Observation of this band establishes the presence of a Co–S bond in the disulfide products. Of importance to the ensuing discussion is the fact that this band at ca. 280 nm has been assigned[43] as an S (σ) → Co (e_g^*) LTMCT transition. This assignment as a transition originating in the σ, rather than π electrons of the coordinated sulfur atom stems from the observations that (1) the energy of this transition is very insensitive to the nature of the ancillary groups bonded to the coordinated sulfur atom (RS^+, R^+,[40] O^{2-},[17] $2(O^{2-})$,[43] Ag^+,[44] etc.[30,45,46] and (2) the sulfinic acid complex $[(en)_2Co(S(O)_2CH_2CH_2NH_2)]^{2+}$[64] and the sulfito complex $[(NH_3)_5CoSO_3]^+$[46] exhibit this transition even though there are no nonbonding π electrons associated with the coordinated sulfur atoms.

In a prior report[2] on coordinated disulfides we have noted the appearance of a new absorption of moderate intensity in the 340-nm region and have briefly discussed the possible assignment of this band, hereafter referred to as the "340" band. This "340" band is too intense and too variable in wavelength to be assigned as a high-energy dd transition (in most Co–S complexes the $^1A_{1g} \rightarrow {}^1T_{2g}$ dd transition is either obscured by, or appears as a weak shoulder on, the intense sulfur-to-cobalt LTMCT). It is also unlikely to be a pure intraligand band as its high intensity and low energy are inconsistent with the current perception of the RSSR chromophore.[47] In the present study we have expanded the total number of disulfide complexes available for investigation in the hopes of delineating factors that affect the "340" transition (Table I). Both the pendant and the coordinated segments of the disulfides have been varied in ways that alter steric and electronic interactions among the two sulfur atoms and the cobalt(III) center. For example, in the limited series of coordinated disulfides based on the 5 N, S cobalt(III) center, i.e., $[(en)_2Co(S(SR)CH_2CH_2NH_2)]^{3+}$, prepared in our earlier work,[2] as R is varied along the series of simple alkyl groups CH_3, CH_2CH_3, $CH(CH_3)_2$, and $C(CH_3)_3$ there is a general decrease in the wavelength of the "340" transition from 343 to ca. 332 nm. In this current work we have prepared the related 5 N, S complexes with R = $C(CH_3)_2COO^-$, $C(CH_3)_2COOH$, and CH_2COOCH_3, and the positions of the "340" band observed for these complexes (348, 331, and 324 nm, respectively) span the entire range of values observed for the simple alkyl derivatives (Table I). From comparisons such as this, the data of Table I lead to the following generalizations: (1) variations in the chelating segment of the disulfide do affect the energy of the "340" transition; (2) however, the energy of this band is more sensitive (ca. a factor of 2 in $\Delta\lambda$) to variations in the dangling segment; (3) within the pendant segment, steric effects are less important than are electronic effects; (4) as the groups in the pendant segment become more electron withdrawing, the position of the "340" band moves to higher energy.

In order to develop a framework for understanding the nature of the "340" band, we have surveyed the literature for other examples of complexes that exhibit "anomalous" absorptions in the near-UV region. We have focused on cobalt(III) complexes, especially those with coordinated sulfur atoms, but have also included some other transition-metal centers. The results of this survey are given in Table IV and are discussed by categories below. At the outset it should be noted that a characteristic common to all but one of these examples is the presence of nonbonded, lone electron pairs on two adjacent (or electronically coupled) atoms, only one of which is coordinated to the metal center. To describe this chromophore, we use the designation M–X–Y, where X is the coordinated atom and Y is the pendant atom. The coordinated disulfide complexes obviously fall within this generalization with X = Y = S (Table IV, **1**).

(1) Cobalt(III) complexes containing an S-bonded sulfenato ligand (i.e., Co–S(O)–R, Table IV, **2**; X = S, Y = O) exhibit a characteristic absorption band at ca. 360 nm.[17] While the nature of the "360" transition is unknown, it exhibits properties similar to those of the "340" band of disulfide complexes, it occurs in the same general region of the spectrum, it is intense, and it steals intensity from the sulfur-to-cobalt LTMCT transition at 280 nm. It is noteworthy that the analogous cobalt(III) complexes containing coordinated S-bonded sul-

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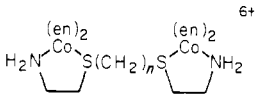
finato ligands[43] (i.e., Co–S(O)$_2$–R) or S-bonded sulfito ligands[46] (i.e., Co–SO$_3$) do *not* contain nonbonding, lone electron pairs on sulfur and also do *not* exhibit an "anomalous" band in the near-UV. These observations imply that the nonbonding electron pair on sulfur is involved in the "360" band of coordinated sulf*e*nates. Also, the relatively low energy of the "360" band eliminates the possibility of it arising from a pure oxygen-to-cobalt LTMCT transition. However, the nonbonding electron pairs on oxygen are implicated in the "360" transition since protonation of the oxygen atom of the coordinated sulf*e*nato ligand[48,49] causes the "360" band to disappear or to be greatly diminished in intensity. Thus, the "360" band appears to be neither a pure S (π) → Co LTMCT nor a pure "outer-sphere" O → Co LTMCT but rather most likely arises from some electronic interaction involving both the oxygen and the sulfur atoms (presumably from a molecular orbital resulting from mixing of localized orbitals containing the nonbonding electron pairs on sulfur and oxygen).

(2) Table IV lists some species related to the S-bonded sulfenato–cobalt(III) complexes. The iodine(I) dimers[49] contain the Co–S–I–S–Co chromophore (Table IV, **3**; X = S, Y = I). The pyrrole and dithiobiuret derivatives (Table IV, **4**) contain a chromophore in which X = S and Y is a carbon or nitrogen atom that is part of a conjugated system. The dimeric dithioether example (Table IV, **5**; X = Y = S) is interesting in that it is one member of the series[50]



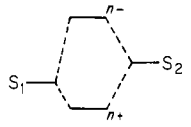
n = 1, 2, 3, ..., 8, 10

Only that complex with n = 1 exhibits an anomalous transition in the near-UV, implying that the X and Y atoms must be electronically coupled for the transition to occur.

(3) Cobalt(III) complexes containing O-bonded sulfito or O-bonded sulf*i*nato ligands (i.e., Co–OSO$_2$ or Co–O–S(O)–R, Table IV, **6**; X = O, Y = S) exhibit anomalous bands in the near-UV, whereas the analogous S-bonded species do not. Again, the possibility of these transitions arising from a pure oxygen-to-cobalt LTMCT transition is eliminated by their low energy. Since the pentaamminecobalt(III) complexes containing –OSO$_3^{2-}$ (O-bonded sulfate[53]), –SSO$_3^{2-}$ (S-bonded thiosulfate[54]), –OS(O)$_2$CF$_3^-$ (O-bonded trifluoromethanesulfonate[55]), and –OS(O)C$_4$H$_8$ (O-bonded sulfolane[55]) do not exhibit such anomalous bands, it would appear that (a) the oxo groups of the pendant moieties are *not* the lone source of the anomalous bands and (b) the presence of a nonbonding pair of electrons on the pendant sulfur atom is a necessary condition. However, this is not a sufficient condition since the O-bonded sulfoxide complexes $[(NH_3)_5Co(O{=}S(CH_3)_2)]^{3+}$ [55] and $[(en)_2Co(OS(CH_3)CH_2CH_2NH_2)]^{3+}$,[49] which also contain a pendant sulfur atom with an associated pair of nonbonding electrons, do not exhibit anomalous bands in the near-UV. With the assumption that the anomalous transitions exhibited by the O-bonded sulfito and sulf*i*nato complexes again arise from electronic interactions between the nonbonded electron pairs on oxygen and sulfur, it is not unreasonable that variations in the nature of the groups bonded to sulfur could either shift this band out of the near-UV region or markedly decrease its intensity.

(4) The cobalt(III) complex containing an N-bonded sulfenamide ligand (Table IV, **7**) is the only example in Table IV that does not contain the M–X–Y chromophore; specifically, the coordinated atom X is a saturated N atom which does *not* have a nonbonded lone pair of electrons. The pendant atom Y is a sulfur atom which does have associated lone electron pairs.

(5) Stein and Taube[57] have reported on the anomalous charge-transfer spectra of pentaammineruthenium(III) complexes of cyclic dithioethers and cyclic disulfides (Table IV, **8** and **9**; X = Y = S). They observe two intense bands, which are both assigned as sulfur-to-ruthenium charge-transfer transitions; these transitions are presumed to arise from two molecular orbitals derived from a mixing of two sulfur atom lone-pair orbitals (S_1 = X, S_2 = Y):



The energies of the charge-transfer bands should thus depend on factors that influence the lone-pair interaction (e.g., ring size in the cyclic ligands, dihedral angles, relative spatial orientations, etc.). The mixing of lone-pair orbitals on adjacent atoms, or the "lone-pair perturbation effect", is well established, there being many spectroscopic reports on this phenomenon in such species as hydrazines, azo compounds, alkyl peroxides, diphosphines, diarsines, and cyclic acetylenes, as well as noncoordinated disulfides and cyclic dithioethers.[58,59]

(6) Many peroxo, persulfido, and perselenido species of the general formula M–A–A–M, where M represents a metal center capable of functioning as a charge-transfer acceptor and A = O, S, or Se (Table IV, **10**; X = Y = A) have been reported to have unusual charge-transfer spectra.[60–63]

(7) Conversion of a M–SR linkage to a M–S–SR linkage by insertion of elemental sulfur into the original M–SR bond (Table IV, **11**; X = Y = S) markedly increases the complexity of the charge-transfer spectrum.

(8) Substantial numbers of copper(II) complexes containing sulfur ligands have been prepared in attempts to model copper-blue proteins. As part of this effort, Bosnich and coworkers[65] recently reported that replacing a coordinated thioether by a coordinated disulfide (Table IV, **12**; X = Y = S) generates a more complex charge-transfer spectrum.

From these several observations culled from the literature, the "340" band of the disulfide–cobalt(III) complexes is seen to be only one example of a more general phenomenon. When Taube's formalism[57] is extended to complexes containing the M–X–Y array, it appears that if orbitals containing the lone

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pairs of electrons on X and Y are of the appropriate energy and orientation to interact (even if X and Y are not bonded to each other) then charge transfers can originate from the molecular orbitals generated by this interaction. A limiting case of this formalism is the situation of zero interaction between X and Y; in this case an "outer-sphere" LTMCT originates solely on the pendant atom Y. This limiting case may account for the anomalous near-UV absorption in the N-bonded sulfenamide complex reported by Sargeson[56] (Table IV, 7); here X is a saturated nitrogen with no nonbonding electron pairs that can interact with the lone pairs of the pendant sulfur atom. This limiting case may also obtain in the O-bonded sulfito and sulfinato complexes (Table IV, **6**) since extensive overlap between lone-pair orbitals of a coordinated oxygen atom and a pendant sulfur atom is unlikely.

Within the disulfide–cobalt(III) complexes, Taube's "lone-pair perturbation" formalism readily explains the previously noted generalizations concerning the position of the "340" band as a function of the coordinated and pendant segments of the disulfide ligand. Since in this model the "340" transition originates in a molecular orbital derived from both the coordinated and the pendant sulfur atoms, the energy of this transition will depend on both the coordinated and pendant segments of the disulfide. However, the pendant sulfur atom contributes more to the character of the originating orbital (since the atomic orbitals on the pendant sulfur atom are higher in energy), and thus the energy of the "340" transition will be more sensitive to the nature of the pendant disulfide segment. Finally, electron-withdrawing groups on the pendant segment will stabilize the atomic orbitals on the pendant sulfur atom, which in turn will lower the energy of the originating molecular orbital and increase the energy of the "340" transition.

Reactivity. The susceptibility of coordinated disulfides to nucleophilic cleavage of the S–S bond is an obstacle to the preparation and isolation of many of the complexes reported in this study and is likely to be a difficulty inherent to the synthesis of most disulfide–metal complexes (e.g., Bosnich and co-workers[65] report this problem in the preparation of disulfide–copper(II) complexes). This susceptibility to nucleophilic attack is readily understood since it is well established that electrophiles such as H^+, Ag^+, or R^+ can assist in the nucleophilic cleavage of the disulfide bond.[66] The electrophile, E^+, enhances the heterolytic bond cleavage by interaction with one of the sulfur atoms; this interaction concomitantly distorts the S–S bond polarity so as to favor nucleophilic attack at the other sulfur atom (eq 7 and 8). A practical application of

$$E^+ + RSSR' = RS\text{–}S(E)R'^+ \quad (7)$$

$$Nuc^- + RS\text{–}S(E)R'^+ \rightarrow RS\text{–}Nuc + R'S\text{–}E \quad (8)$$

the phenomenon is the silver(I)- or mercury(II)-assisted preparation of sulfenamide from disulfides and amines[66b] (eq 9). In the disulfide–cobalt(III) complexes the coordinated

$$2RNH_2 + R'SSR' + Ag^+ \rightarrow R'S\text{–}NHR + RNH_3^+ + AgSR' \quad (9)$$

disulfide ligand is inherently activated toward nucleophilic attack by being robustly bonded to the highly electrophilic cobalt(III) center. Cleavage of the S–S bond by nucleophiles such as OH^- or RSH is therefore very rapid unless the S–S linkage is protected by sterically bulky groups.[19,67] Thus, coordinated disulfides containing $-SC(CH_3)_3$ or $-SC(CH_3)_2COOH$ pendant moieties are resistant to nucleophilic attack, even to the point that S_N1cB base hydrolysis of the Co–S bond becomes competitive with OH^- cleavage of the S–S bond. In acid media the S–S bond is relatively stable and Co–S bond fission predominates.

Structural Characterization. The structure of the title complex (Figure 2) is as expected from the known structure of the homologous parent thiolato complex $[(en)_2Co(SCH_2COO)]^+$.[18] The atom composition of the primary coordination spheres are identical (4 N, O, S), but in the title complex the coordinated sulfur atom is part of a coordinated symmetrical disulfide ligand. This molecular structure confirms that oxidation of $[(en)_2Co(SC(CH_3)_2COO)]^+$ with 1 equiv of $[Co(aq)]^{3+}$ leads to the net 2-equiv oxidation product containing a coordinated symmetrical disulfide.

The CSSC dihedral angle observed in the title complex (121.3°) is consistent with values observed in noncoordinated disulfides which also have tertiary carbon atoms bonded to the sulfur; these disulfides are known to exhibit dihedral angles larger than those observed in disulfides with primary or secondary carbon atoms bonded to sulfur.[68] This effect is probably due to steric interactions between the groups on the α-carbon atoms, which induce expansion of the dihedral angle from the optimum 90° (a dihedral angle of 90° minimizes interactions between the lone-pair electrons on the adjacent sulfur atoms). For neutral penicillamine disulfide,[69] which crystallizes as the dizwitterion, and for penicillamine disulfide dihydrochloride,[70] the CSSC dihedral angles are 119.4 and 115°, respectively. A dihedral angle of 114° has been predicted for *tert*-butyl disulfide[68] on the basis of a force field calculation of the minimum-energy configuration.

The S–S bond length observed in the title complex (2.052 (3) Å) is in accord with Hordvik's correlation of bond lengths and dihedral angles[71] and with Seff's generalization that coordination of a disulfide should not significantly affect the S–S bond length.[72] This S–S bond length is also in good agreement with that reported for the dihydrochloride salt of penicillamine disulfide (2.049 (3) Å)[70] but not with that reported for the neutral penicillamine disulfide (2.032 (3) Å).

The two SSCC torsional angles observed in the title complex (63.0 and 78.1°) are consistent with those reported for the two penicillamine disulfide structures (70 and 67° for the neutral form[69] and 81.8 and 67.1° for the dihydrochloride[70]). In the pendant arm of the coordinated disulfide, the configuration observed by sighting down the S(2)–C(9) bond is staggered (Figure 3c) with the C(12) methyl group being trans to S(1) (torsional angle 179.4°). The pendant carboxylate group is oriented such that the C=O oxygen atom points toward one of the ethylenediamine ligands, and the C–OH linkage is directed away from the cobalt center. The C=O oxygen atom (O(3)) is only 2.88 (1) Å from N(2), suggesting a possible hydrogen-bonding interaction between the carbonyl and amine groups. The plane of the carboxylate moiety nearly bisects the angle between the pendant methyl carbon atoms C(11) and C(12), falling 5.5° from an eclipse with the S(2)–C(9) bond (Figure 3d). The coordinated segment of the disulfide is conformationally restricted by chelation to cobalt; C(6) is bent down out of the S(1), C(5), O(1), Co plane and away from the S–S bond, thus rotating the C(8) methyl group out of an eclipsed arrangement with S(2) (Figure 3b). This results

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in pseudoequatorial and pseudoaxial orientations, respectively, for the C(8) and C(9) methyl groups.

The absence of a significant structural trans effect (STE) in the title compound is consistent with the lack of a formal negative charge on the coordinated sulfur atom. It has been postulated[2,40] that in these types of complexes neutral S-bonded ligands such as thioethers and disulfides generate minimal STE's, whereas anionic S-bonded ligands such as thiolates, sulfenates, and sulfinates generate marked STE's, because the anionic ligands are stronger σ donors and form stronger, shorter Co–S bonds. The hypothesis is supported by the relatively long Co–S distance in the title complex (2.260 (3) Å), which may be compared to the shorter Co–S distance (2.243 (2) Å) in the analogous thiolato complex $[(en)_2Co(SCH_2COO)]^+$.[18]

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Registry No. $[(en)_2Co(S(SC(CH_3)_2COOH)C(CH_3)_2COO)](ClO_4)_2\cdot 2H_2O$, 81898-13-7; $[(en)_2Co(S(SCH_2COOH)CH_2COO)]^{2+}$, 81898-17-1; $[(en)_2Co(S(SCH(CH_3)COOH)CH(CH_3)COO)]^{2+}$, 81898-14-8; $[(en)_2Co(S(SC(CH_3)_3)CH_2COO)](ClO_4)_2$, 81898-16-0; $[(en)_2Co(S(SC(CH_3)_3)CH_2COO)]Cl_2$, 81898-18-2; $[(en)_2Co(S(SC(CH_3)_3)CH(CH_3)COO)](ClO_4)_2$, 81898-20-6; $[(en)_2Co(S(SC(CH_3)_3)C(CH_3)_2COO)](ClO_4)_2$, 81898-22-8; $[(en)_2Co(S(SC(CH_3)_3)CH_2CH_2NH_2)](ClO_4)_3$, 81898-23-9; $[(en)_2Co(S(SC(CH_3)_2COOH)CH_2COO)](ClO_4)_2$, 81898-25-1; $[(en)_2Co(S(SC(CH_3)_2COOH)CH(CH_3)COO)]ZnCl_4$, 81915-54-0; $[(en)_2Co(S(SC(CH_3)_2COOH)CH_2CH_2NH_2)](ClO_4)_3$, 81915-56-2; $[(en)_2Co(S(SCH_2CH_2OH)CH_2CH_2NH_2)]^{3+}$, 81898-26-2; $[(en)_2Co(S(SCH_2C(O)OCH_3)CH_2CH_2NH_2)]^{3+}$, 81898-27-3; $[(en)_2Co(SCH_2COO)]ClO_4$, 26743-67-9; $[(en)_2Co(SCH(CH_3)COO)]ClO_4$, 60828-75-3; $[(en)_2Co(SC(CH_3)_2COO)]ClO_4$, 68645-87-4; $[(en)_2Co(SCH_2COO)]PF_6$, 81898-28-4; $[(en)_2Co(SCH_2CH_2NH_2)](ClO_4)_2$, 40330-50-5; $[(en)_2Co(SCH_2COO)]Cl$, 54453-35-9; $HSC(CH_3)_2COOH$, 4695-31-2; $H_3COC(O)SSCH_2CH_2OH$, 30453-26-0; $H_3COC(O)SSCH_2C(O)OCH_3$, 81897-82-7; $HSCH_2CH_2OH$, 60-24-2; $HSCH(CH_3)COOH$, 79-42-5; *tert*-butylsulfenyl iodide, 25558-08-1.

Supplementary Material Available: Listings of $|F_o|$ and $|F_c|$ values (Table A), anisotropic thermal parameters (Table B), root-mean-square displacements (Table C), and perchlorate bond angles (Table D) (17 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Radiation Laboratory, University of Notre Dame, Notre Dame, Indiana 46556

Effects of Bridging Hydrogens on Metal–Metal Bonds. 1. Geometrical Comparison of $Fe_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_3)$, $Co_3(CO)_9(\mu_3\text{-}CCH_3)$, and Model Compounds

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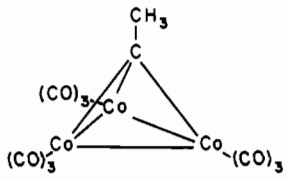
Received March 9, 1982

The solid-state structure of $Fe_3(\mu\text{-}H)_3(CO)_9(\mu_3\text{-}CCH_3)$ (II) consists of a triangular M_3 base constructed of three $Fe(CO)_3$ fragments with hydrogens symmetrically bridging the M–M edges and with a $C\text{–}CH_3$ fragment symmetrically capping the metal triangle. The molecule has C_{3v} symmetry, each iron being six-coordinate (three carbonyl ligands, two bridging hydrogens, and the methylidyne carbon) and the capping carbon four-coordinate (three irons and the methyl carbon). The comparison of the geometry of II with that of isoelectronic $Co_3(CO)_9(\mu_3\text{-}CCH_3)$ (I) reveals several changes that are interpreted in terms of the bridging hydrogens acting as hydride-like ligands. It is demonstrated that the geometries of main-group model compounds for I and II ($CH_3CC_3H_3$ and $CH_3CB_3H_6$) as generated by ab initio calculations reproduce the structural differences of I and II. Hence, in I and II the representation of the $Co(CO)_3$ and $Fe(CO)_3$ fragments with CH and BH provides much more than a simple, descriptive analogy of the cluster bonding. Crystals of II form in the triclinic space group $P\bar{1}$ with the following unit cell parameters: a = 7.979 (2), b = 9.478 (3), c = 12.714 (4) Å; α = 93.45 (3), β = 106.94 (3), γ = 60.79 (3)°; V = 799 Å^3; Z = 2. The X-ray structure was solved as described in the text and refined to R_1 = 0.076 and R_2 = 0.075 for 2496 independent reflections.

Alkylidynetrimetal systems such as I constitute the first



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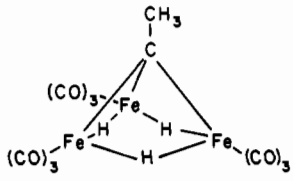

II

cluster systems to be studied systematically.[2] The geometrical structure of this cluster has been defined,[3] and synthetic routes to derivatives with a significant variation in the methylidyne carbon substituent have been developed.[4] The chemistry of the methylidyne carbon has also been elucidated, and spectroscopic and theoretical techniques have been used to define the bonding of this capping carbon to the trimetal fragment.[5] Recently, added impetus to such studies arose from the hypothesis that the μ_3-CR bonding is representative of a possible mode of binding of the CR fragment to a metal surface.[6]

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