Synthesis and Study of Monomeric and Sulfur-Bridged Dimeric Cobalt(III) Thioxanthate Complexes and Their Relationship to Sulfur-Bridged Iron(III) Dimers

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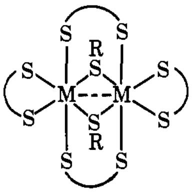
Abstract: The synthesis of the compounds $[Co(S_2CSR)_2(SR)]_2$, R = C_2H_5, *n*-C_3H_7, and $Co(S_2CSR)_3$, R = CH_3, C_2H_5, *n*-C_3H_7, *tert*-C_4H_9, and $C_6H_5CH_2$, is reported. The elimination of carbon disulfide from tris(ethyl thioxanthato)cobalt(III) to form tetrakis(ethyl thioxanthato)-μ-bis(ethylthio)-dicobalt(III) has been directly confirmed and is shown to be a first-order reaction. The molecular structure of the latter compound was revealed in a single-crystal X-ray diffraction study. The molecule is a centrosymmetric dimer with two bridging ethyl mercaptide ligands [distances: Co–S, 2.242 (2), 2.250 (2) Å; nonbonded Co · · · Co, 3.321 (2) Å; angles: S–Co–S, 84.54 (5)°; Co–S–Co, 95.34 (3)°] and four terminal thioxanthate groups [Co–S distances: 2.261 (2), 2.264 (2), 2.282 (2), and 2.290 (2) Å; S–Co–S chelate ring angles: 75.68 (7)°, 76.05 (7)°]. The relationship between metal-metal bonding and the choice of stereoisomer for $[M(S_2CSR)_2(SR)]_2$ complexes, M = Fe, Co, is discussed. The pmr spectra of solutions of the cobalt dimers are consistent with the structure found in the solid for the ethyl derivative. The methylenic protons attached to the bridging sulfur atoms exhibit large upfield shifts which may result from paramagnetic anisotropy effects. Voltammetric studies of the dimers indicate irreversible one-electron reduction and oxidation waves. The monomers exhibit reversible one-electron reduction waves. Electronic and selected infrared spectral absorptions are reported and assigned. A rationale is suggested for the low and varying redox potentials in nonheme proteins containing the Fe_2S_2 core.

Previous reports from this laboratory[2,3] describe the synthesis and characterization of the binuclear complexes $[Fe(S_2CSR)_2(SR)]_2$, where R is a straight chain alkyl group, and monomeric $Fe(S_2CSR)_3$, where R is the *tert*-butyl group. Both in the solid state and in solution, the sulfur-bridged dimeric iron(III) complexes were shown to have structure I (M = Fe), and substantial evidence for direct iron–iron bonding was presented. In addition, the redox properties of both the mono- and binuclear iron(III) thioxanthate complexes were studied in view of their possible relationship to the oligonuclear iron–sulfur chromophores thought to comprise the active sites in the ferredoxins, an important class of non-heme iron electron-transfer protein having low redox potentials.[4] Although the monomeric tris(*tert*-butyl thioxanthato)iron(III) complex could be reversibly reduced with a half-wave potential of −0.36 V (*vs.* Ag|AgI in methylene chloride), the sulfur-bridged dimers exhibited irreversible two-electron reduction waves at −0.7 V. Despite the fact that the potential is substantially lowered in the dimeric complexes compared to the monomer (*cf.* the E_0' value of mononuclear rubredoxin, −0.057 V, with that of the binuclear ferredoxins, −0.43 V),[4] no firm conclusions could be drawn in view of the irreversibility.



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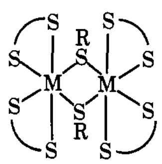

II

As indicated previously,[2] one possible explanation for the irreversibility of the two-electron reduction process is that the energetically lowest lying empty orbital is the metal–metal antibonding orbital, $\sigma^*(xy)$ (Figure 1), which becomes populated in a rapid two-electron transfer step that is then followed by a slow, intramolecular rearrangement (*e.g.*, I → II) or by cleavage to monomers. Since $[Fe(S_2CSR)_2(SR)]_n^{n-}$ (*n* = 1 or 2) could not be isolated, we were led to extend our studies to the cobalt(III) analogs, $[Co(S_2CSR)_2(SR)]_2$ being isoelectronic with the hypothetical binuclear iron(III) dianion. The decision to investigate the cobalt(III) system was also influenced by the recent analysis of Dahl, de Gil, and Feltham,[5] detailing the stereochemical consequences of metal–metal bonding in ligand-bridged complexes. In particular, it appeared from a straightforward application of their analysis that a structural rearrangement might well occur in going from $[Fe(S_2CSR)_2(SR)]_2$ to $[Co(S_2CSR)_2(SR)]_2$. Finally, we were aware of previous work by Coucouvanis[6] in which the prototype molecule $[Co(S_2CSR)_2(SR)]_2$, R = benzyl, had been prepared but not studied in connection with more extensive work on the nickel thioxanthate complexes $Ni(S_2CSR)_2$ and $[Ni(S_2CSR)(SR)]_2$.[7] The cobalt(III) analogs therefore appeared to be amenable to synthesis and of ob-

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[1] National Institutes of Health Predoctoral Fellow, 1967–1971.

[2] D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, **92**, 3342 (1970).

[3] D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **9**, 2775 (1970).

[4] For reviews, see (a) J. C. M. Tsibris and R. W., Woody, *Coord. Chem. Rev.*, **5**, 417 (1970); (b) D. O. Hall and M. C. W. Evans, *Nature (London)*, 223, 1342 (1969); (c) T. Kimura, *Struct. Bonding*, **5**, 1 (1968); (d) R. Malkin and J. C. Rabinowitz, *Annu. Rev. Biochem.*, 36, 11 (1967).

[5] L. F. Dahl, E. R. de Gil, and R. D. Feltham, *J. Amer. Chem. Soc.*, **91**, 1653 (1969).

[6] D. Coucouvanis, Ph.D. Thesis, Case Institute of Technology, 1967.

[7] (a) J. Mayhew, D. Coucouvanis, and J. P. Fackler, Jr., *Inorg. Chem.*, in press; (b) J. P. Fackler, Jr., and J. M. Andrews, 160th National Meeting of the American Chemical Society, Chicago, Ill., 1970, Abstract INOR-49.

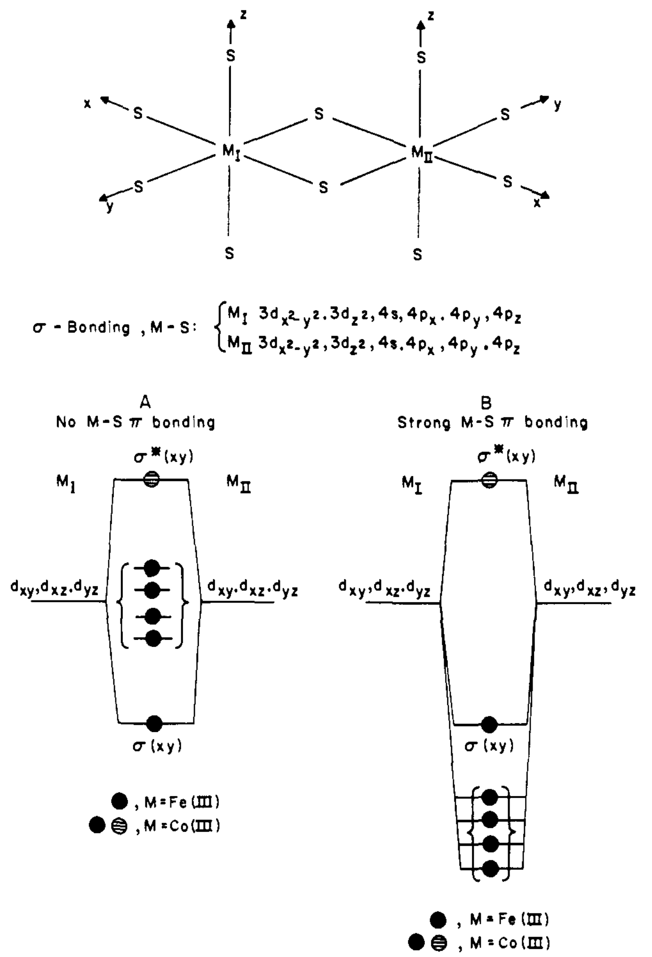

Figure 1. Schematic representation of the bonding in $[M(S_2CSR)_2(SR)]_2$ complexes (filled circles designate electron pairs). For discussion, see ref 2 and 3.

vious interest to compare to the more fully investigated iron(III)[2,3] and nickel(II)[7-9] systems.

Experimental Section

Preparations. All compounds were prepared from commercially available starting materials in a well-ventilated hood. The complex $[Ni(S_2CSC_2H_5)(SC_2H_5)]_2$ was synthesized as described in ref 6 and identified by its melting point and proton nmr spectrum. Microchemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Melting points were obtained using a Thomas-Hoover melting point apparatus and are uncorrected. Molecular weights were determined at 37° using a Mechrolab vapor pressure osmometer calibrated with benzil and are reliable to ±2%. Solution concentrations were approximately 10^{-2} *M*.

Tetrakis(ethyl thioxanthato)-μ-bis(ethylthio)-dicobalt(III), $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$. (a) Sodium hydride (2.4 g, 0.1 mol) was suspended in 50 ml of THF and cooled in an ice bath. An excess (12 ml) of ethanethiol was added and the solution cooled to 0°. When the reaction subsided, 15 ml of carbon disulfide (again an excess) was added to form a clear yellow solution.[2,10] Added to this solution was 8.7 g (0.03 mol) of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 50 ml of water. The mixture was stirred vigorously and allowed to stand for about 5 min before filtering. The filtrate was extracted several times with methylene chloride (total volume, 150 ml). Removal of THF from the filtrate was found on occasion to facilitate this extraction procedure. The extracts were combined and the brown-black solution was dried over anhydrous magnesium sulfate. Addition of 250 ml of methanol followed by cooling at ice bath temperature for several hours resulted in the formation of a fine, microcrystalline brown precipitate which was recrystallized from CS_2–pentane, washed with methanol and then ether, and dried *in vacuo*. The yield was 4.2 g, or 36% based on cobalt nitrate; mp 161–163° dec.

Anal. Calcd for $C_{16}H_{30}S_{14}Co_2$: C, 24.4; H, 3.81; S, 56.9; mol wt, 789. Found: C, 25.2; H, 4.10; S, 57.0; mol. wt, 787.

Ir (KBr pellet): 3093 (w), 3073 (w), 3041, 2981, 2937, 2878 (w), 1503, 1459, 1419 (w, mult), 1381, 1270, 1256 (sh), 1051 (w, mult), 986 (s), 959 (s), 764 (sh), 757, 702, 655 (w, br), 514, 464, 407 (w), 375, 360 (w), 335, 318 cm^{-1}.

(b) A 65-ml chloroform solution of 0.85 g of tris(ethyl thioxanthato)cobalt(III), prepared as described below, was refluxed for 7 hr on the steam bath. Methanol was added to the resultant brown solution, and the mixture was cooled overnight at 0°. Crystals of a brown complex (0.70 g, 98% yield) having a pmr spectrum identical with that of the dimer prepared in (a) were collected the next day.

Tetrakis(*n*-propyl thioxanthato)-μ-bis(*n*-propylthio)-dicobalt(III), $[Co(S_2CSC_3H_7)_2(SC_3H_7)]_2$. This compound was prepared by a procedure analogous to that for the ethyl dimer except that the crude product was recrystallized from chloroform–ethanol, mp 142–144.5° dec.

Anal. Calcd for $C_{22}H_{42}S_{14}Co_2$: C, 30.3; H, 4.85; S, 51.4; mol wt, 873. Found: C, 30.6; H, 4.88; S, 50.8; mol wt, 870.

Ir (KBr pellet): 1456, 1424, 1410, 1380, 1339, 1298, 1285 (sh), 1242, 1230, 1083, 1045, 979 (s), 951 (s), 899, 880 (w, sh), 844 (w), 824, 779, 734, 525, 511, 456, 416 (w), 370 (br), 341, 321 cm^{-1}.

The compound was also prepared by refluxing a solution of tris(*n*-propyl thioxanthato)cobalt(III) for 7 hr in chloroform and identified by its pmr spectrum.

Tris(ethyl thioxanthato)cobalt(III), $Co(S_2CSC_2H_5)_3$. Sodium hydride (4.6 g, 0.2 mol) was suspended in 100 ml of THF and cooled in an ice bath. Ethanethiol (23 g) was added slowly and the resulting solution allowed to cool. Carbon disulfide (30 ml) was then added dropwise. To this yellow thioxanthate solution were added 4.9 g of anhydrous ferric chloride (0.03 mol) and 8.7 g of $Co(NO_3)_2 \cdot 6H_2O$ (0.03 mol) dissolved in 50 ml of water. The resultant green-brown solution which formed was filtered to remove some insoluble material, and the concentrated filtrate extracted with 75 ml of chloroform as in the preparation of the dimers. To the chloroform extract was added 75–100 ml of methanol and the solution was allowed to stand overnight at ice bath temperature. Brown-green crystals were collected which proved to be impure by pmr spectroscopy and thin layer chromatography with CS_2 as the solvent, the latter revealing both green and brown components. Separation of the mixture was accomplished by silica gel chromatography using carbon disulfide as the eluent. The first band off the column was green which, when treated with 75 ml of pentane, produced green crystals of monomeric $Co(S_2CSC_2H_5)_3$, which were dried in air. The yield was 4.1 g, or 29% based on cobalt, mp 110.5–112° dec.

Anal. Calcd for $C_9H_{15}S_9Co$: C, 23.0; H, 3.21; S, 61.3; mol wt, 471. Found: C, 23.3; H, 3.17; S, 61.3; mol wt, 484.

Ir (KBr pellet): 1444, 1407, 1369, 1259, 1236 (w), 1047, 978 (s), 949 (s), 879 (w), 746, 693 (w), 549 (w), 506, 458, 361 (sh), 341, 335 (sh), 316 (w) cm^{-1}.

Further elution of material from the column produced a brown solution which contained (pmr criteria) the cobalt ethyl dimer with some $[Fe(S_2CSC_2H_5)_2(SC_2C_5)]_2$[2] as impurity. Partial separation of this mixture was achieved by passing the brown CS_2 solution through a second silica column. Pentane was added to this solution, and the resulting brown-green material recrystallized from 20 ml of CS_2 to which 10 ml of pentane had been added. Cooling to 0° yielded 1.5 g of $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$.

The red solution which finally came off the second column yielded, upon addition of pentane and cooling, a very small amount (~0.2 g) of $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$.

Tris(*n*-propyl thioxanthato)cobalt(III), $[Co(S_2CSC_3H_7)_3]$. This compound was prepared by a procedure analogous to that for the ethyl monomer. From 2.3 g of NaH in 50 ml of THF, 10 ml of *n*-propanethiol, 15 ml of CS_2, and a mixture of 2.4 g of $FeCl_3$ and 4.3 g of $Co(NO_3)_2 \cdot 6H_2O$ in 25 ml of distilled water was isolated 3.2 g (41.5%) of crystalline, green $[Co(S_2CSC_3H_7)_3]$, mp 60–61°.

Anal. Calcd for $C_{12}H_{21}S_9Co$: C, 28.1; H, 4.10; S, 56.3; mol wt, 513. Found: C, 27.8; H, 4.19; S, 56.7; mol wt, 522.

Ir (KBr pellet): 1448, 1417 (w, sh), 1400, 1373, 1332, 1284, 1235, 975 (s), 948 (s), 833 (w), 770 (w), 719 (w), 693 (w), 520, 507, 461, 415 (w), 389 (w), 349, 323 cm^{-1}.

No attempt was made to separate the brownish solution which

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(8) P. Bladon, R. Bruce, and G. R. Knox, *Chem. Commun.*, 557 (1965).

(9) A. C. Villa, A. G. Manfredotti, M. Nardelli, and C. Pelizzi, *ibid.*, 1322 (1970).

(10) A. H. Ewald and E. Sinn, *Aust. J. Chem.*, 21, 927 (1968).

came off the column afterward. This solution presumably contains the mercaptide-bridged iron and cobalt dimers.

Tris(methyl thioxanthato)cobalt(III), $Co(S_2CSCH_3)_3$. This complex was prepared by allowing sodium methyl thioxanthate (from 0.92 g of NaH in 25 ml of THF, 5 ml of CH_3SH, and 7 ml of CS_2 at 0°) to react with 1.2 g of $FeCl_3$ and 2.0 g of $Co(NO_3)_2 \cdot 6H_2O$ in 25 ml of H_2O. The resulting green solution was concentrated and extracted with 50–75 ml of methanol. The crude material was dried in air for 24–36 hr and recrystallized in a large test tube by dissolving it in 15 ml of chloroform, carefully adding a layer of methanol, and allowing the two layers to diffuse together slowly over a period of 24 hr. Large green-black crystals of pure product formed in 1.9-g (65.5%) yield, mp 150–152.5° dec.

Anal. Calcd for $C_6H_9S_9Co$: C, 16.8; H, 2.10; S, 67.3; mol wt, 429. Found: C, 16.7; H, 2.12; S, 68.3; mol wt, 434.

Ir (KBr pellet): 1412, 1308, 1004, 981 (s), 920 (s), 694 (w), 508, 455, 353, 341 (sh), 334, 321 cm^{-1}.

Tris(*tert*-butyl thioxanthato)cobalt(III), $[Co(S_2CSC_4H_9)_3]$. The yellow *tert*-butyl thioxanthate solution was formed from 2.3 g of NaH in 100 ml of THF, 12 ml of *tert*-C_4H_9SH, and 15 ml of CS_2. Addition of 8.7 g of $Co(NO_3)_2 \cdot 6H_2O$ in 50 ml of H_2O produced a green precipitate and a brown solution. The filtered precipitate was washed with 20 ml of carbon disulfide, then dissolved in a large amount of CS_2, and crystallized by addition of pentane at 0°. Large green crystals were obtained (mp 181.5° dec). The filtered brown solution was, in turn, extracted with 50–75 ml of chloroform and the combined extracts were dried with 2 g of anhydrous magnesium sulfate (only oils could be obtained unless this drying procedure was employed). The chloroform solution was filtered, diluted with 75 ml of methanol, and cooled at ice bath temperature to give crude green solid material. Recrystallization from CS_2–pentane overnight at 0° gave a further crop of large green crystals (mp 181.5° dec).

Anal. Calcd for $C_{15}H_{27}S_9Co$: C, 32.5; H, 4.87; S, 52.0; mol wt, 555. Found: C, 32.3; H, 4.81; S, 51.6; mol wt, 554.

Tris(benzyl thioxanthato)cobalt(III), $Co(S_2CSCH_2C_6H_5)_3$. Addition of a mixture of 4.9 g of $FeCl_3$ and 8.7 g of $Co(NO_3)_2 \cdot 6H_2O$ dissolved in 50 ml of water to the yellow solution of sodium benzyl thioxanthate in THF, prepared as for the ethyl analog, resulted in a green solution. Extraction of this solution with 75 ml of chloroform gave immediate precipitation of a green solid which was recrystallized from CS_2–pentane to give 3.5 g of green, microcrystalline product (mp 126–127° dec).

Anal. Calcd for $C_{24}H_{21}S_9Co$: C, 43.9; H, 3.22; mol wt, 657. Found: C, 44.2; H, 3.20; mol wt, 649, 664 (two determinations).

Tris(ethyl thioxanthato)chromium(III), $Cr(S_2CSC_2H_5)_3$. Sodium hydride (2.3 g) was suspended in 100 ml of THF and cooled in an ice bath. To the suspension were added 15 ml of carbon disulfide and the resulting yellow solution was allowed to react with 8.1 g of $CrCl_3 \cdot 6H_2O$ in 50 ml of H_2O. Extraction of the complex by 75 ml of chloroform followed by addition of 75 ml of methanol and cooling at 0° for several hours gave crude material. Green crystals formed after recrystallization from CS_2–pentane, mp 105–107° dec.

Anal. Calcd for $C_9H_{15}S_9Cr$: C, 23.3; H, 3.24; S, 62.2; mol wt, 464. Found: C, 23.3, H, 3.27, S, 59.3; mol wt, 463.

Although the sulfur analysis for this complex is not satisfactory, it is believed to be pure based upon the analytical data for C, H, and molecular weight. The complex was found to have a magnetic moment ($\mu_{\text{eff}}^{\text{corr}}$) of 3.84 BM at room temperature, a result consistent with a d^3 metal ion having a $^4A_{2g}$ ground state.

Magnetic, Spectroscopic, and Electrochemical Measurements. The gram magnetic susceptibilities of dried crystalline solids were measured at room temperature (*ca.* 23°) by the Gouy technique as described by Figgis and Lewis.[11] The temperature dependence of the magnetic susceptibilities was studied by the Faraday method over the range $85°K < T < 295°K$ using an Alpha Scientific Model 1402 magnetic susceptibility system equipped with a Model 1424 variable temperature accessory. The Gouy tubes and Teflon Faraday buckets were calibrated with $Hg[Co(NCS)_4]$. Each sample was run at three field strengths and the results averaged to give the final value.

Proton nuclear magnetic resonance (pmr) spectra were recorded on a Varian Associates A-60A or HA-100 spectrometer, both equipped with a variable temperature probe. Relative intensities were determined in triplicate with the Varian integrator. A spectrum of $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ at 220 MHz was obtained at The Bell Telephone Laboratories, Murray Hill, N. J.[12] The complexes were dissolved in CS_2, $CDCl_3$, or $CHCl_3$. Tetramethylsilane was added as an internal chemical shift calibrant. Calculated pmr spectra were obtained on an IBM 360-91 computer using the program LAOCN3 by A. A. Bothner-By and S. Castellano, which was made available through the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind. 47401 (QCPE 111). Electronic spectra of chloroform solutions were recorded on a Cary 14 spectrophotometer at concentrations of 10^{-3}–10^{-6} M using 1-cm matched quartz cells. Visible spectra of solids were taken on a Beckman Model DU spectrophotometer equipped with a reflectance attachment. Powdered magnesium carbonate was used as a reference and diluent. Infrared spectroscopic data were obtained with a Perkin-Elmer 621 grating instrument in the range 4000–250 cm^{-1} using polystyrene as the calibrant. Spectra were taken on KBr pellets containing 5% of the sample by weight.

Conventional voltammetry was performed with a modified Heath Model EUW-401 polarograph in the three-electrode configuration. A rotating platinum working electrode and silver–silver iodide reference electrode were used. Triangular wave stationary electrode cyclic voltammetric data were obtained using a Chemtrix Model SSP-2 polarograph equipped with Tektronix storage oscilloscopic readout. The working electrode was a 1.5-mm diameter stationary platinum sphere. Half-wave potentials were obtained from the voltammograms and have an estimated precision of ±25 mV. As before,[2] the one-electron oxidations of $[CrS_6C_6(CN)_6]^{3-}$ and $[NiS_4C_4(CN)_4]^{2-}$ were used to monitor and calibrate the system. The measured potentials for the first one-electron oxidation of $[NiS_4C_4(CN)_4]^{2-}$ were corrected to agree with those previously reported by other workers[13] (the correction was approximately +0.1 V). All values subsequently obtained for the cobalt(III) complexes were corrected in the same manner. The internal consistency of results was maintained, and values which can be compared to other studies in the literature are thus presented. Note that the values previously quoted (Table IV, ref 2) for the half-wave potentials of $[CrS_6C_6(CN)_6]^{3-}$ are in error; the corrected values for this complex on our apparatus are +0.33 and +0.89 V for the $(-3 \rightarrow -2)$ and $(-2 \rightarrow -1)$ oxidations, respectively (lit.[13] +0.29, +0.83 V). Solutions were 10^{-3} M in complex dissolved in methylene chloride which had been doubly distilled over calcium hydride. Tetra-*n*-butylammonium perchlorate, recrystallized from ethyl acetate, in 0.1 M concentration was used as supporting electrolyte. The useful working range was −1.4 to +1.6 V. Further experimental details including cell design and preparation of reference electrode may be found in ref 14.

Kinetic Study. Kinetic data at 62.5° were obtained in the following manner. A solution of 1.316 g (2.8×10^{-3} mol) of $Co(S_2CSC_2H_5)_3$ in 100 ml of chloroform was prepared. Ethanol preservative had been removed from the spectrograde $CHCl_3$ by passing the solvent through an activated alumina column. The solution was refluxed under nitrogen and the reaction quenched for 3 or 4 min at ice temperature at appropriate intervals. The pmr spectra of aliquots were taken and integrated, after which the sample was returned to the mother solution and refluxing continued. No correction was made for the time lag in heating and cooling the large solution volume, and the data obtained at this temperature are judged to be inherently less accurate. Kinetic data at 57 and 52° were obtained by preparing a solution of the ethyl monomer, 2.48×10^{-2} M in chloroform, and sealing two aliquots under vacuum in nmr tubes. These were then immersed for fixed intervals in a constant temperature bath, quenched for 2 min in an ice bath, and allowed to warm to ambient temperature for 5 min, following which the pmr spectra were recorded.

X-Ray Diffraction Measurements. Collection and Reduction of Data. The complex $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ crystallizes as small black needles or prisms, several of which were mounted for study on glass fibers. Precession photographs of these crystals taken with Cu Kα radiation showed them to be monoclinic with extinctions for $h0l$, $l \neq 2n$ and $0k0$, $k \neq 2n$, requiring the space group to be $P2_1/c$.[15] Using the approximate cell dimensions obtained by film

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(11) B. N. Figgis and J. Lewis in "Modern Coordination Chemistry," J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N. Y., 1960, Chapter 6.

(12) We are grateful to Dr. Kurt Wüthrich for providing this spectrum.

(13) F. Röhrscheid, A. L. Balch, and R. H. Holm, *Inorg. Chem.*, **5**, 1542 (1966).

(14) J. A. Zubieta, Ph.D. Thesis, Columbia University, 1971, Appendix I.

(15) "International Tables for X-Ray Crystallography," Vol. I, 2nd ed, Kynoch Press, Birmingham, England, 1965, p 99.

measurement, 20 reflections were accurately centered in the counter window of a Picker full-circle automated X-ray diffractometer. A least-squares procedure was used to obtain a best fit between the observed and calculated values of χ, ϕ, and 2θ for these reflections. The results show that $a = 8.622 \pm 0.003$ Å, $b = 21.616 \pm 0.008$ Å, $c = 9.978 \pm 0.003$ Å, and $\beta = 118.89 \pm 0.03°$. The calculated density of 1.609 g cm^{-3} for four formula units of $Co(S_2CSC_2H_5)_2(SC_2H_5)$ ($M = 394.5$) per unit cell is in excellent agreement with the value of 1.60 ± 0.02 g cm^{-3}, obtained by flotation in an aqueous solution of potassium iodide. The linear absorption coefficient is 157.0 cm^{-1}.

The crystal used for data collection was a fragment of approximate dimensions 0.21 × 0.10 × 0.27 mm and was mounted along the longest of the three dimensions, which corresponded to b^*. Intensity data were collected on the Picker diffractometer using Cu Kα radiation (λ 1.5418 Å) filtered through nickel foil and a take-off angle of 2.0°. Each reflection was measured by the moving crystal–moving counter technique with a scan range in 2θ of 1.25° (or 1.5° when $2\theta > 90°$) plus an allowance for the splitting of the Kα_1 and Kα_2 radiation. A scan speed of 1°/min was employed. The background for each reflection was determined by 10-sec stationary counts at both ends of the scan range. In order to ensure a linear counter response, copper foil attenuators were inserted into the diffracted beam whenever the count rate exceeded $\sim 10^4$ cps. A total of 2434 unique reflections were collected in the limits $0° < 2\theta < 120°$. At regular intervals, four "standard" reflections were measured in order to monitor the crystal and instrument stability. In no case did the intensity of a standard vary by more than 1.5% of its mean, and no systematic trend was observed. Since the integrated intensity of the weakest standard was $\sim 10^4$ counts, the variation is seen to be that expected from counting statistics.

The observed intensities were corrected for background, use of attenuators, Lorentz, polarization, and absorption effects using ACAC-3.[16] The transmission factors ranged from 0.04 to 0.15. As a check on the absorption correction, the variation with ϕ of the intensity of two axial reflections at $\chi = 90°$ was measured and found to correlate well with the variation in the calculated transmission factors. A Wilson plot subsequently yielded an approximate absolute scale factor. Scattering factors for the zerovalent cobalt, sulfur, carbon, and hydrogen atoms were obtained from the International Tables.[17] The calculated structure factors were corrected for the effects of anomalous dispersion of the cobalt and sulfur atoms.[18] The integrated intensity corrected for background and attenuators is given by I, the standard deviation of which, $\sigma(I)$, was obtained from the expression $\sigma(I) = [E + (T_E/2T_B)^2 \cdot (B_1 + B_2) + (\epsilon I)^2]^{1/2}$ where E is the total counts in the peak plus background observed for time T_E, B_1 and B_2 are the background counts observed at time T_B at each end of the scan, and ϵ is an "ignorance factor"[19] assumed in this case to be 0.04. Smaller values of ϵ would tend to overweight the strongest reflections. Weights used in the refinement, w, were assigned according to $4F^2/\sigma^2(F^2)$, where $\sigma(F^2)$ is the standard deviation of F^2 obtained from $\sigma(I)$ after absorption, Lorentz, and polarization corrections were applied. Only reflections which satisfied the condition $I > 3\sigma(I)$ were included in the refinement, a total of 2019 data points. Although during the final stages of refinement five intense reflections (100, $\bar{3}23$, 011, 020, 060) were excluded as they appeared to be seriously affected by secondary extinction, no systematic attempt was made to correct the data for extinction effects.

Determination of the Structure. A set of normalized structure factors (E values) was obtained using FAME (FMLS package[16]) from the intensity data corrected for background, attenuators, and Lorentz and polarization effects.[20] Repetitive application of the Sayre equation to the 500 reflections having the highest $|E|$ values using the program MAGIC[16] led to the determination of phases for 300 reflections in terms of six symbols, each of which represented a positive or negative phase assignment. An E map, calculated for the most probable combination of the signs, clearly showed the cobalt and seven sulfur atoms. A difference Fourier synthesis phased on these eight atoms revealed the remaining part of the structure. Refinement of the positional parameters and individual isotropic temperature factors for the 16 iron, sulfur, and carbon atoms in the asymmetric unit converged at values of 0.116 and 0.144 for the indices $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_c|^2)^{1/2}$, respectively. At this stage a difference Fourier map showed residual peaks around the atoms, indicative of some anisotropic thermal motion. Refinement was continued with each atom assigned an anisotropic temperature factor of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Several cycles of refinement reduced the residuals to 0.059 and 0.074 for R_1 and R_2, respectively. A difference Fourier map now showed several peaks ~ 0.5 e/Å^3 (on a scale where the average value for a carbon atom is ~ 3–5 e/Å^3) at chemically reasonable positions for hydrogen atoms. In this manner, 13 of the 15 hydrogen atoms were located. When these were introduced into the structure with fixed isotropic temperature factors of 6.0 (the average value for the isotropic temperature factors of the methyl and methylene carbon atoms) and refined, the residuals were further reduced to $R_1 = 0.058$ and $R_2 = 0.068$. No attempt was made to vary the thermal parameters of the hydrogen atoms. A final difference Fourier map showed no anomalies.

Results

Preparations. The syntheses of the cobalt(III) dimers, $[Co(S_2CSR)_2(SR)]_2$ ($R = C_2H_5$, n-C_3H_7), and *tert*-butyl monomer $[Co(S_2CSR)_3]$ ($R = tert$-C_4H_9) proceed in a manner analogous to the preparation of the related iron(III) compounds.[2,21] Addition of carbon disulfide to a suspension of the sodium alkyl mercaptides produces the bright yellow color of the thioxanthates,[6,10] according to eq 1. The resulting

$$Na^+SR^- + CS_2 \xrightleftharpoons{THF-CS_2} Na^+(S_2CSR)^- \quad (1)$$

$$3Na^+(S_2CSR)^- + Co(NO_3)_2 \xrightarrow[air-H_2O]{THF-CS_2} Co(S_2CSR)_3 + \text{other products} \quad (2)$$

$$2Co(S_2CSR)_3 \xrightarrow{\Delta} [Co(S_2CSR)_2(SR)]_2 + 2CS_2 \quad (3)$$

solution is then allowed to react with aqueous cobaltous nitrate in air to yield, after work-up, the tris(*tert*-butyl thioxanthato)cobalt(III) complex (eq 2), or the ethyl or n-propyl dimers (eq 2, 3). Reaction of cobaltous nitrate with sodium n-butyl thioxanthate gave only an intractable oil upon work-up.

As with the iron(III) system,[2] it was not possible to isolate the *tert*-butyl dimer under the conditions and work-up of the reaction, and only the monomeric tris(*tert*-butyl thioxanthato)cobalt(III) complex was obtained. A solution of this monomer in chloroform was allowed to reflux for 5 days, after which time the absorbance of the band at 25.6×10^3 cm^{-1} decreased by 37%. A loss of intensity of the same band was also observed for a solution allowed to stand at room temperature for several days in a sealed tube. The pmr spectra of these solutions did not indicate any obvious

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(16) Programs for the IBM 360-91 computer used in this work include local versions of MODE-1, the Brookhaven diffractometer setting and cell constant and orientation refinement program, GSET, the Prewitt diffractometer setting program, ACAC-3, a revised version of the Prewitt absorption correction and data reduction program, XDATA, the Brookhaven Wilson plot and scaling program, FMLS, the Dewar and Stone symbolic addition program package, FORDAP, the Zalkin Fourier program, CULS, a local version of the Busing–Martin–Levy structure factor calculation and least-squares refinement program (ORFLS), ORFFE, the Busing–Martin–Levy molecular geometry and error function program, and ORTEP, the Johnson thermal ellipsoid plotting program.

(17) See ref 15, Vol. III, pp 202, 204.

(18) See ref 15, Vol. III, p 213 ff.

(19) (a) G. M. Brown and H. A. Levy, *J. Phys.* (*Paris*), 25, 497 (1964); (b) R. D. Ellison and H. A. Levy, *Acta Crystallogr.*, 19, 260 (1965); (c) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, 6, 197 (1967).

(20) For discussions of and further references to the symbolic addition method, *cf.* (a) H. Hauptman and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal," A.C.A. Monograph No. 3, Polycrystal Book Service, Pittsburgh, Pa., 1953; (b) G. H. Stout and L. H. Jensen, "X-ray Structure Determination," Macmillan, New York, N. Y., 1968, Chapter 13.

(21) Tris(*tert*-butyl thioxanthato)cobalt(III) has been previously postulated to exist in solution, but no attempt was made to isolate it.[10]

new species and exhibited the resonance at τ 8.32 which is characteristic of the $Co(S_2CSC(CH_3)_3)_3$ complex. A yellow insoluble material appeared on the walls of the reaction vessel, however, suggesting that some decomposition had occurred.

In an attempt to synthesize a mixed metal dimer of the kind $[FeCo(S_2CSR)_4(SR)_2]$, reactions 1 and 2 were carried out using ferric chloride, cobaltous nitrate, and alkyl thioxanthate in molar ratio 0.5:0.5:3.0. Although the desired mixed metal dimer was not obtained, the cobalt monomers $Co(S_2CSR)_3$, R = CH_3, C_2H_5, n-C_3H_7, and $C_6H_5CH_2$, could be crystallized after chromatography of the reaction medium.[22] Small quantities of both the iron(III) and cobalt(III) dimers were also isolated for the ethyl derivative. The synthesis of the monomeric cobalt(III) thioxanthate complexes with straight-chain hydrocarbon R groups by the addition of iron(III) to the reaction was unexpected. Although chromatography was not generally employed in the preparation of the cobalt ethyl and propyl dimers, a check on the composition of the crude reaction mixture by chromatography and pmr spectroscopy revealed the presence of a small amount of the monomeric $[Co(S_2CSR)_3]$ complex for R = C_2H_5, which could be isolated along with the $[Co(S_2CSR)_2(SR)]_2$ dimer.

Since the iron(III) monomers, $Fe(S_2CSR)_3$, could not be obtained for R = C_2H_5, n-C_3H_7, n-C_4H_9, and $C_6H_5CH_2$, and since the *tert*-butyl dimer could not be isolated, the analog of reaction 3 was not studied for the iron system, although postulated to exist.[2,24] With the availability of the $Co(S_2CSR)_3$ compounds, however, eq 3 could be directly confirmed. In particular, when samples of $Co(S_2CSR)_3$, R = C_2H_5 and n-C_3H_7, were refluxed in chloroform for 5 hr, the solutions turned color from the characteristic green of concentrated monomer to the brown solutions characteristic of the dimers. The pmr spectra of these samples (discussed below) indicated that they had indeed undergone CS_2 elimination[25] according to eq 3.

In order to examine the possibility that reactions 1–3 might produce a binuclear sulfur-bridged analog of chromium(III), sodium ethyl thioxanthate was allowed to react with chromic chloride. Only green, monomeric $Cr(S_2CSC_2H_5)_3$ was isolated. Analogous blue trisxanthate complexes of chromium(III) have been characterized,[22] and $Cr(S_2CSR)_3$, R = CH_3, C_2H_5, compounds have been mentioned.[23,26] Refluxing a chloroform solution of tris(ethyl thioxanthato)chromium for 16 hr did not lead to the formation of any isolable dimeric complex.

Kinetic Analysis. The kinetics of reaction 3 were investigated for the ethyl complex by heating a known concentration of monomeric $Co(S_2CSC_2H_5)_3$, $[M_0]$, in chloroform at three different temperatures. After quenching the reaction at 0°, the relative concentrations of dimer, [D], and monomer, [M], in aliquots of the solution were determined by pmr spectroscopy, according to eq 4 and 5. The symbol α in eq 4 represents the ratio of the relative integrated intensities, multiplet/triplet, where the multiplet refers to the methylene and methyl resonances (τ 9.00) of the bridging ethyl mercaptide groups in the dimer (10 protons) and the triplet refers to the methyl resonances (τ 8.55) of the ethyl thioxanthate ligands in both the monomer (9 protons) and dimer (12 protons). The results are summarized in Figure 2, from which it is apparent that the reaction is first order in monomer. An Arrhenius plot, and application of the Eyring equations, yielded the following activation parameters: E_a = 23 ± 1 kcal mol^{-1}, log A = 11 ± 1, $\Delta H^{\ddagger}(298°)$ = 21 ± 1 kcal mol^{-1}, and $\Delta S^{\ddagger}(298°)$ = −7 ± 2 eu, where the error

$$[D] = \frac{9\alpha[M_0]}{10 + 6\alpha} \tag{4}$$

$$[M] = [M_0] - 2[D] \tag{5}$$

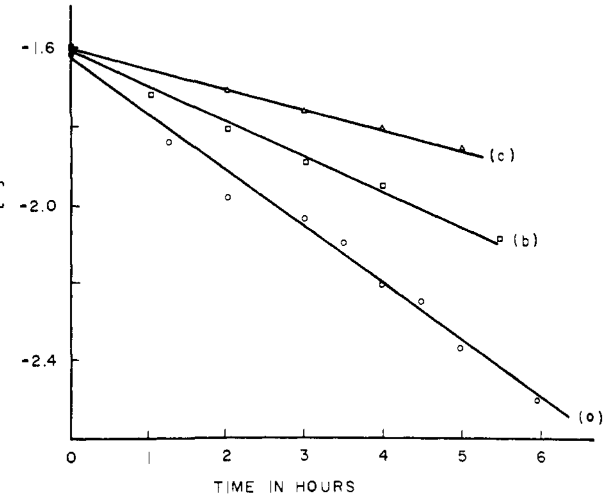

Figure 2. Kinetic results for the elimination of carbon disulfide from $Co(S_2CSC_2H_5)_3$, reaction 3, at temperatures of (a) 62.5°, (b) 57°, and (c) 52°. The first-order rate constants (×10^5) and their estimated standard deviations are 9 ± 1, 6.0 ± 0.3, and 2.9 ± 0.2 sec^{-1}, respectively.

Table I. Proton Nmr Data for Cobalt(III) Thioxanthate Complexes[a]

Compd	Chemical shifts (τ), ppm[b]			Rel intensities
$Co(S_2CSR)_3$				
R = CH_3	7.31 (s)			
R = C_2H_5	6.71 (q)	8.56 (t)		2:3
	J = 7.3	J = 7.3		
R = n-C_3H_7	6.73 (t)	8.18 (m)	8.91 (t)	2:2:3
	J = 7.5	J = 7.5	J = 7.0	
R = *tert*-C_4H_9		8.32 (s)		
R = $CH_2C_6H_5$	2.76 (s)	5.49 (s)		2:5
$[Co(S_2CSR)_2(SR)]_2$				
R = C_2H_5	6.68 (q)	8.54 (t)	~9.00 (m)	4:6:5
	J = 7.5	J = 7.5		
R = C_2H_5[c]	6.61 (q)	8.55 (t)	~9.00 (m)	4:6:5
	J = 7.5	J = 7.5		
R = n-C_3H_7	6.72 (t)	8.19 (m)	~9.00 (m)[d]	1:1:3.2
	J = 7.0	J = 7.0		

[a] Data taken at 60 MHz on carbon disulfide solutions unless otherwise noted. [b] Abbreviations: s = singlet, t = triplet, m = multiplet, J = coupling constant in Hz. [c] In $CDCl_3$. [d] Broad peak with at least five well-defined resonances.

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[22] A more direct route to the $Co(S_2CSR)_3$ complexes, R = CH_3, C_2H_5, has been described.[23]

[23] F. Galsbøl and C. E. Schäffer, *Inorg. Syn.*, 10, 42 (1967).

[24] D. Coucouvanis, S. J. Lippard, and J. A. Zubieta, *J. Amer. Chem. Soc.*, 91, 761 (1969).

[25] D. Coucouvanis, *Progr. Inorg. Chem.*, 11, 233 (1970), and references cited therein.

[26] C. K. Jørgensen, "Inorganic Complexes," Academic Press, New York, N. Y., 1963, p 137.

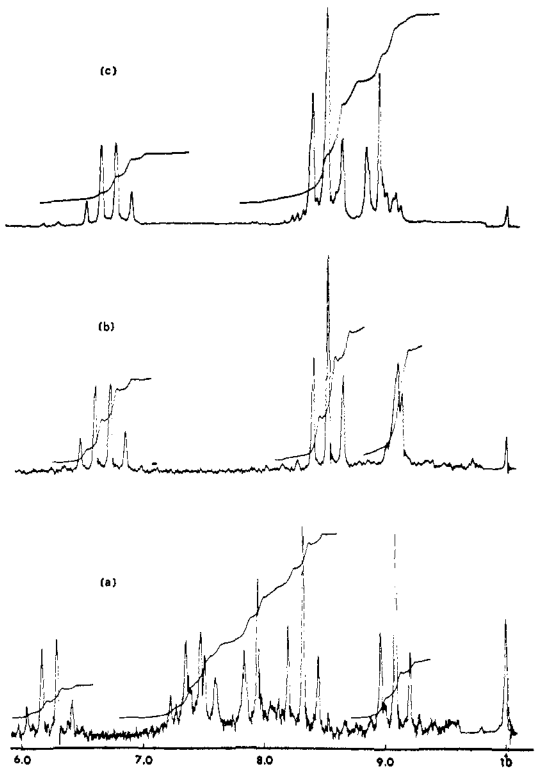

Figure 3. Proton nmr spectra of (a) $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$, (b) $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$, and (c) $[Ni(S_2CSC_2H_5)(SC_2H_5)]_2$ in carbon disulfide solution at 60 MHz.

limits on these activation parameters are graphically estimated standard deviations.

Proton Magnetic Resonance Spectra and Assignments. Proton nuclear magnetic resonance (pmr) spectral data for the cobalt(III) thioxanthate complexes are summarized in Table I. The chemical shift values and spin–spin splitting patterns for the tris(alkyl thioxanthato)cobalt(III) compounds are unexceptional and may be readily identified.

In order to assign the resonances for the ethyl dimer, it is necessary to make the rather interesting assumption that the multiplet at τ 9.0 contains the overlapping methylene and methyl resonances of a bridging ethyl mercaptide group (the remaining two multiplets ($\Delta\tau$ 1.86 ppm) result from two equivalent terminal ethyl thioxanthate ligands). Verification of this assumption was achieved by (1) running the spectrum of $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ in $CDCl_3$ and observing a significant change in the general appearance of the multiplet at τ 9.0 and (2) spreading out the spectrum of the complex in CS_2 at 220 MHz and computing a nearly identical spectrum of A_2B_3 type using LAOCN3 and the parameters τ (CH_3) 9.123 ppm, τ (CH_2) 9.014 ppm, and J = 7.5 Hz. As indicated in Figure 3, the pmr spectra of the bridging ethyl mercaptide groups in the binuclear complexes $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$,[2] $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$, and $[Ni(S_2CSC_2H_5)(SC_2H_5)]_2$ are not first order at 60 MHz, with $J/\Delta\nu \geq 0.24$.[27] The spectrum of $[Co(S_2CSC_3H_7)_2(SC_3H_7)]_2$ at 60 MHz (Table I) is somewhat more complex than that of the ethyl analog, but the methylene protons of the *n*-propyl

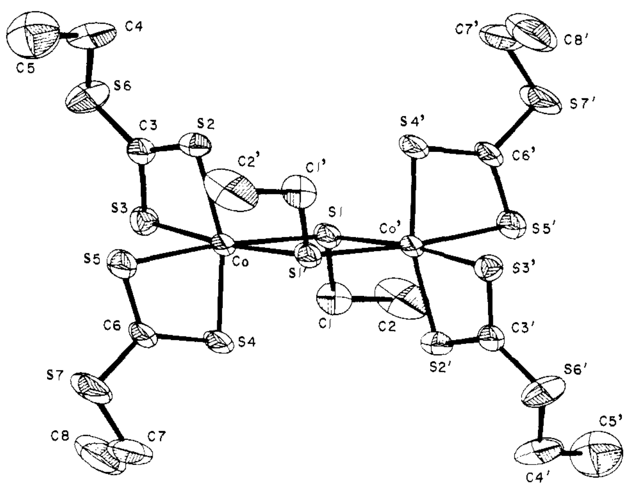

Figure 4. The molecular structure of tetrakis(ethylthioxanthato)-μ-bis(ethylthio)-dicobalt(III) showing the 50% probability ellipsoids and the atom-labeling scheme. The primed and unprimed atoms are related by a center of symmetry. Hydrogen atoms are omitted for clarity.

thioxanthate groups may be readily distinguished at τ 6.72 and 8.19. As with the ethyl dimer, the methylene protons of the bridging *n*-propyl mercaptide groups have been shifted upfield and appear as part of the broad multiplet centered around τ 9.0. Because of the small $\Delta\tau$ values for the bridging mercaptide ligands in the ethyl and *n*-propyl dimers, the possibility of syn–anti isomerism[28] could not be investigated.

Crystallographic Results for $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$. Atomic positional and thermal parameters with their standard deviations as derived from the inverse matrix of the final least-squares refinement are collected in Table II.[29] Root-mean-square amplitudes of thermal vibration are given in Table III. Figure 4 shows the atom labeling scheme and the relative orientations of the thermal ellipsoids. The packing of dimeric molecules in the unit cell is shown in a stereoscopic view (Figure 5). Intramolecular bond distances and angles are summarized in Tables IV and V. The C–H bond distances ranged from 0.78 (11) to 1.18 (10) Å, with a mean value of 0.95 ± 0.15 Å, and the H–C–H angles from 87 (7) to 122 (13)°, with a mean value of 109 ± 11°.

Electrochemical and Magnetic Susceptibility Studies. Electrochemical data are summarized in Table VI. The cobalt(III) dimers exhibit a one-electron reduction wave and, near the positive limit of the range, a one-electron oxidation wave, both of which are irreversible at scan rates of 1 V/sec. The monomeric tris(alkyl thioxanthato)cobalt(III) complexes were observed to undergo reversible or nearly reversible one-electron reductions in all cases, judging by cyclic voltammetry at 0.1, 0.5, and 1.0 V/sec. Plots of peak current, i_p, *vs.* $v^{1/2}$

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(27) K. B. Wiberg and B. J. Nist, "The Interpretation of Nmr Spectra," W. A. Benjamin, New York, N. Y., 1962, pp 579–593.

(28) (a) E. W. Abel, R. P. Bush, F. J. Hopton, and C. R. Jenkins, *Chem. Commun.*, 58 (1966); (b) M. Dekker, G. R. Knox, and C. G. Robertson, *J. Organometal. Chem.*, **18**, 161 (1969), and references cited therein.

(29) A compilation of observed and calculated structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to author, title of article, volume, and page number. Remit check or money order for $3.00 for photocopy of $2.00 for microfiche.

Table II. Final Positional and Thermal Parameters of the Atoms[a,b]

Atom	x	y	z	β_{11} or B^c	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	−0.0263 (1)	0.0695 (1)	0.4209 (1)	11.5 (2)	0.8 (1)	9.8 (1)	0.2 (1)	6.1 (1)	0.1 (1)
S1	−0.1529 (2)	−0.0245 (1)	0.3541 (2)	12.2 (3)	0.9 (1)	8.0 (2)	−0.2 (1)	4.5 (2)	−0.2 (1)
S2	0.1408 (2)	0.0534 (1)	0.3055 (2)	12.5 (3)	1.5 (1)	9.9 (2)	0.5 (1)	6.4 (2)	0.3 (1)
S3	−0.1996 (2)	0.1043 (1)	0.1769 (2)	12.5 (3)	1.5 (1)	12.4 (3)	0.9 (1)	6.5 (2)	1.5 (1)
S4	−0.1983 (2)	0.1084 (1)	0.5152 (2)	16.5 (3)	0.9 (1)	15.6 (3)	−0.1 (1)	10.8 (3)	−0.5 (1)
S5	0.0872 (2)	0.1661 (1)	0.5069 (2)	16.6 (4)	1.0 (1)	16.3 (3)	−0.7 (1)	10.0 (3)	−0.3 (1)
S6	−0.0384 (3)	0.0967 (1)	−0.0254 (2)	16.1 (4)	3.5 (1)	9.6 (3)	−0.8 (1)	5.9 (3)	1.0 (1)
S7	−0.0885 (3)	0.2386 (1)	0.6455 (3)	26.5 (5)	1.3 (1)	25.1 (4)	−1.0 (1)	16.4 (4)	−2.6 (1)
C1	−0.3770 (9)	−0.0166 (4)	0.3261 (8)	9.1 (12)	1.8 (2)	9.9 (11)	−0.5 (4)	0.7 (9)	0.4 (4)
C2	−0.4774 (12)	−0.0763 (5)	0.2856 (15)	13.6 (18)	2.8 (3)	33.5 (25)	−3.4 (6)	8.0 (18)	−3.8 (6)
C3	−0.0277 (9)	0.0850 (3)	0.1485 (8)	14.4 (14)	1.0 (2)	12.0 (10)	−0.3 (4)	7.6 (10)	−0.1 (3)
C4	0.1841 (12)	0.0799 (5)	0.0116 (10)	19.2 (18)	3.3 (3)	12.2 (12)	−0.8 (6)	10.4 (13)	−0.4 (5)
C5	0.2996 (17)	0.1336 (7)	0.0698 (19)	20.7 (26)	4.3 (5)	42.3 (37)	1.2 (9)	16.8 (27)	−2.2 (9)
C6	−0.0717 (10)	0.1730 (3)	0.5586 (8)	18.1 (15)	0.7 (2)	16.2 (12)	0.2 (4)	11.1 (12)	−0.3 (3)
C7	−0.2875 (14)	0.2250 (4)	0.6594 (13)	27.7 (24)	2.0 (2)	28.5 (21)	−0.6 (6)	21.6 (21)	−2.0 (6)
C8	−0.4518 (19)	0.2366 (6)	0.5134 (21)	28.6 (30)	2.4 (3)	45.1 (44)	1.5 (8)	23.0 (31)	−1.4 (9)
HC1A	−0.451 (14)	0.014 (5)	0.237 (12)	6.0					
HC1B	−0.367 (14)	−0.001 (5)	0.409 (13)	6.0					
HC2A	−0.453 (14)	−0.105 (5)	0.221 (13)	6.0					
HC2C	−0.571 (15)	−0.069 (6)	0.256 (14)	6.0					
HC4A	0.219 (13)	0.039 (5)	0.098 (12)	6.0					
HC4B	0.153 (15)	0.065 (5)	−0.082 (13)	6.0					
HC5A	0.323 (15)	0.149 (6)	0.183 (12)	6.0					
HC5B	0.253 (17)	0.161 (6)	0.008 (14)	6.0					
HC5C	0.398 (15)	0.123 (6)	0.069 (13)	6.0					
HC7A	−0.280 (15)	0.183 (5)	0.709 (12)	6.0					
HC8A	−0.463 (15)	0.274 (5)	0.453 (12)	6.0					
HC8B	−0.490 (15)	0.215 (6)	0.427 (12)	6.0					
HC8C	−0.490 (17)	0.236 (6)	0.570 (14)	6.0					

[a] Atoms are labeled as indicated in Figure 3. Hydrogen atoms are labeled to correspond to the carbon atoms to which they are attached. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] β's are defined in the text; values reported here are $\times 10^3$. For hydrogen atoms only, $\beta_{11} = B$, the isotropic thermal parameter, in Å^2.

(v = scan speed) gave straight lines that passed through the origin, and the ratio of cathodic to anodic peak currents was nearly unity.[30] The monomers also show, in general, an ill-defined one-electron oxidation process which looks complex on triangular wave cyclic voltammograms.

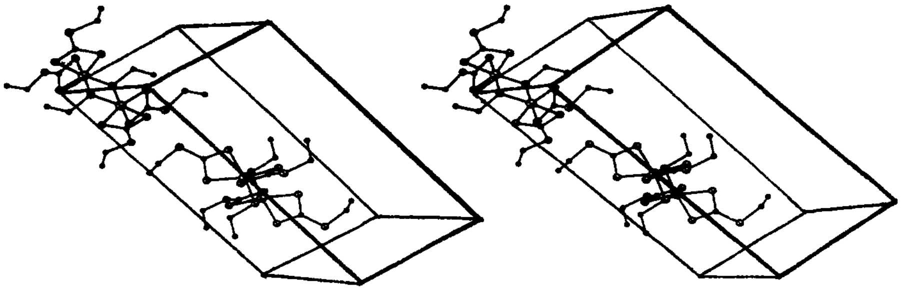

Figure 5. A stereoscopic view of the packing of binuclear $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ molecules in the unit cell.

Room temperature Gouy measurements of the magnetic susceptibilities indicated slight paramagnetism for the complexes $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ ($\chi_M^{corr} = +225 \times 10^{-6}$ cgs/mol), $[Co(S_2CSC_3H_7)_2(SC_3H_7)]_2$ (+171 cgs/mol), and $[Co(S_2CSC_2H_5)_3]$, (+51 $\times 10^{-6}$ cgs/mol). The experimental changes in weight were very close to zero, with the final values for χ_M^{corr} being largely determined by the correction for underlying ligand diamagnetism. No field dependence of the susceptibilities was observed. In addition, the magnetic susceptibility of the ethyl dimer was studied by the Faraday method over the temperature range 88° $< T <$ 300°K. The resultant values of χ_g varied only slightly and in a nonsystematic fashion, indicative of temperature independent paramagnetism (TIP).[11]

Electronic and Infrared Spectra and Assignments. The electronic spectral bands of chloroform solutions containing the various cobalt complexes are presented in Table VII. In addition, reflectance spectra were taken of the solid n-propyl monomer (ν_{max} 16,000, 26,000, and 31,300 cm^{-1}) and ethyl dimer (ν_{max} 16,200, 22,200, 26,700, and 31,800 cm^{-1}). By comparison with results obtained for the corresponding xanthate complexes $Co(S_2COR)_3$[25,31] (*cf.* Table VII for R = ethyl), bands 1 and 2 in the monomers are assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions, respectively. With this assignment, application of eq[31] 6 and

$$\nu_1 = \Delta - 4B + 86B^2/\Delta \qquad (6)$$

$$\nu_2 = \Delta + 12B + 2B^2/\Delta \qquad (7)$$

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(30) R. S. Nicholson and I. Shain, *Anal. Chem.*, 36, 706 (1964).

(31) C. K. Jørgensen, *Inorg. Chim. Acta*, 2, 65 (1968).

Table III. Root-Mean-Square Amplitudes of Vibration in Å[a,b]

Atom	Minimum	Medium	Maximum
Co	0.135 (2)	0.169 (2)	0.197 (1)
S1	0.147 (3)	0.178 (2)	0.192 (3)
S2	0.172 (3)	0.186 (4)	0.205 (3)
S3	0.160 (3)	0.185 (3)	0.240 (2)
S4	0.142 (3)	0.182 (2)	0.251 (2)
S5	0.147 (3)	0.201 (3)	0.253 (2)
S6	0.183 (3)	0.213 (2)	0.298 (3)
S7	0.148 (3)	0.246 (3)	0.327 (3)
Cl	0.15 (1)	0.20 (1)	0.25 (1)
C2	0.16 (1)	0.28 (1)	0.38 (1)
C3	0.15 (1)	0.19 (1)	0.22 (1)
C4	0.18 (1)	0.24 (1)	0.28 (1)
C5	0.21 (1)	0.31 (2)	0.42 (2)
C6	0.13 (1)	0.20 (1)	0.26 (1)
C7	0.18 (1)	0.23 (1)	0.35 (1)
C8	0.20 (2)	0.28 (2)	0.42 (2)

[a] Taken along the principal axes of the thermal ellipsoids. The orientation of these axes may be seen from Figure 4. [b] See footnotes *a* and *b*, Table II.

Table IV. Intramolecular Bond Distances in Å[a]

Co· · ·Co′	3.321 (2)	S5–C6	1.683 (7)
Co–S1	2.250 (2)	S6–C3	1.710 (7)
Co–S1′	2.242 (2)	S6–C4	1.805 (9)
Co–S2	2.261 (2)	S7–C6	1.705 (7)
Co–S3	2.282 (2)	S7–C7	1.809 (9)
Co–S4	2.264 (2)	C1–C2	1.50 (1)
Co–S5	2.290 (2)	C4–C5	1.46 (2)
S1–Cl	1.822 (7)	C7–C8	1.48 (2)
S2–C3	1.684 (7)	S1· · ·S1′	3.022 (3)
S3–C3	1.688 (7)	S2· · ·S3 (bite)	2.798 (3)
S4–C6	1.695 (7)	S4· · ·S5 (bite)	2.795 (3)

[a] See footnotes *a* and *b*, Table II; values reported have not been corrected for thermal motion.

7 gives values of ~16.6 × 10^3 cm^{-1} for the subshell energy differences, Δ, and ~297 cm^{-1} for the interelectronic repulsion parameters, B. The calculated values of ν_1 and ν_2 are 15,870 and 20,180 cm^{-1}, respectively. From their intensity, bands 3, 4, 5, and 6 in the monomers and bands 5 and 6 in the dimers appear to be either charge-transfer or ligand internal-transition absorptions. Bands 1 and 2 in the dimers are probably d → d transitions, similar to those associated with bands 1 and 2 in the monomers. Assignment of bands 3 and 4 in the dimers is difficult, for they may correspond to transitions from an ^1A_g ground state to ^1A_g or ^1B_g excited states, the idealized symmetry of the dimers being reduced from O_h to C_{2h} (structure II).

A summary of selected mid-infrared spectral transitions may be found in Table VIII. Although the infrared spectra of metal xanthate complexes have been reported[32] and analyzed,[32,33] fewer studies have been made of thioxanthate analogs.[2,6] As suggested previously,[2] the two strong absorptions between 900 and 1000 cm^{-1} are assumed to have considerable C⩵S character, and the band ~460 cm^{-1} an appreciable metal–sulfur contribution, by analogy to the normal coordinate analysis of $Co(S_2COC_2H_5)_3$ and related complexes.[33] Similarly, bands in the 330–370-cm^{-1} region are presumed to have considerable M–S character.

Table V. Intramolecular Bond Angles (in Degrees)[a]

S1–Co–S1′	84.54 (5)	Co′–S1–C1	110.8 (2)
S1–Co–S2	92.67 (7)	Co–S2–C3	86.3 (2)
S1–Co–S3	90.43 (8)	Co–S3–C3	85.5 (2)
S1–Co–S4	97.86 (7)	Co–S4–C6	86.6 (2)
S1–Co–S5	173.20 (7)	Co–S5–C6	86.1 (2)
S1′–Co–S2	98.21 (7)	C3–S6–C4	103.6 (5)
S1′–Co–S3	172.47 (8)	C6–S7–C7	102.4 (6)
S1′–Co–S4	90.93 (8)	S1–C1–C2	113.2 (5)
S1′–Co–S5	93.30 (8)	S2–C3–S3	112.2 (4)
S2–Co–S3	76.05 (7)	S2–C3–S6	127.1 (4)
S2–Co–S4	166.63 (8)	S3–C3–S6	120.7 (4)
S2–Co–S5	94.03 (8)	S6–C4–C5	111.3 (7)
S3–Co–S4	95.59 (8)	S4–C6–S5	111.6 (4)
S3–Co–S5	92.33 (8)	S4–C6–S7	127.8 (4)
S4–Co–S5	75.68 (7)	S5–C6–S7	120.6 (4)
Co–S1–Co′	95.34 (3)	S7–C7–C8	112.9 (7)
Co–S1–Cl	107.1 (3)		

[a] See footnotes *a* and *b*, Table II.

Table VI. Electrochemical Data for $[Co(S_2CSR)_2(SR)]_2$ and $[Co(S_2CSR)_3]$ in Dichloromethane Solution[a]

Complex	$E_{1/2}$, V[b]	i_d/C, μA/mmol[c]	Rev (r) or irrev (i)[d]
$[Co(S_2CSR)_2(SR)]_2$			
R = C_2H_5	−1.01	+98	i
	+1.23	−96	i
R = C_3H_7	−0.95	+97	i
	+1.36	−101	i
$[Co(S_2CSR)_3]$			
R = CH_3	−0.98	+89	r
	+1.6	−108	i
R = C_2H_5	−0.80	+108	r
	+1.43	−92	i
R = *n*-C_3H_7	−0.95	+100	r
R = *tert*-C_4H_9	−1.00	+99	r
R = $C_6H_5CH_2$	−0.93	+95	r
	+1.6	−93	i
$[NiS_4C_4(CN)_4]^{2-}$	+0.30	−90	r
	+1.37	−71	r

[a] Using 0.1 *M* tetra-*n*-butylammonium perchlorate as supporting electrolyte and a rotating platinum electrode. [b] *Vs.* Ag|AgI reference electrode. [c] Concentration calculated on the basis of formulas given in the first column; positive current indicates a reduction and negative current, an oxidation. Comparison of current densities with those for the known[13] one-electron oxidations of the $[Ni(mnt)_2]^{2-}$ ion (last entry in table) indicates all processes to be one-electron transfers. [d] i = irreversible as judged by cyclic voltammetry, r = reversible (see text).

Discussion

Synthesis and Mechanism. The synthesis of sulfur-bridged binuclear complexes of general formula $[Co(S_2CSR)_2(SR)]_2$ proceeds in a manner similar to that previously described[2] for the iron(III) analogs (eq 1–3). Monomeric $Co(S_2CSR)_3$ can also be isolated in small quantities from the reaction mixture, however, in contrast to the iron(III) system.[2] Although eq 3 has been experimentally verified in the present work, monomeric $Co(S_2CSR)_3$ is not necessarily an intermediate in the direct synthesis of the dimers from cobaltous nitrate and sodium alkyl thioxanthate, since an equilibrium concentration of mercaptide for sulfur-bridging is potentially available through eq 1. The kinetic study shows eq 3 to be first order in monomer for R = ethyl. This result together with the activation parameters are in close agreement with the findings of Fackler and Andrews on the carbon disulfide elimination from Ni-

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(32) G. M. Watt and B. J. McCormick, *Spectrochim. Acta*, 21, 753 (1965), and references cited therein.

(33) U. Agarwala, Lakshmi, and P. B. Rao, *Inorg. Chim. Acta*, 2, 337 (1968).

Table VII. Electronic Spectral Bands of Cobalt(III) Thioxanthate Complexes in Chloroform[a]

	Absorption maxima, cm^{-1} × 10^{-3}					
Compd	Band 1	Band 2	Band 3	Band 4	Band 5	Band 6
$Co(S_2CSR)_3$						
R = CH_3	15.9 (2.54)	20.5 (sh)	25.8 (4.25)	31.3 (4.88)	33.5 (sh)	38.5 (4.06)
R = C_2H_5	15.9 (2.97)	20.0 (sh)	25.8 (4.56)	31.3 (5.02)	33.3 (sh)	38.5 (4.53)
R = *n*-C_3H_7	15.8 (3.12)	20.2 (sh)	25.6 (4.74)	31.3 (5.12)	33.3 (sh)	38.5 (4.77)
R = *tert*-C_4H_9	16.0 (2.91)[b]	20.1 (sh)	25.6 (4.58)	30.9 (5.10)	33.3 (sh)	38.5 (4.51)
$[Co(S_2CSR)_2(SR)]_2$						
R = C_2H_5	16.7 (3.43)	22.3 (sh)	26.4 (sh)	29.7 (sh)	32.1 (5.25)	39.6 (4.91)
R = *n*-C_3H_7	16.4 (3.44)	22.3 (sh)	26.6 (sh)	29.4 (sh)	31.9 (5.16)	39.2 (4.83)
$Co(S_2COC_2H_5)_3$[c]	16.2 (2.43)	20.8 (2.56)		28.3 (4.11)		35.2 (4.51)

[a] Values in parentheses are molar extinction coefficients (log ϵ_{max}); sh = shoulder. [b] Beer's law was experimentally verified for this absorption band. [c] Data from Table XXIII, ref 25.

Table VIII. Selected Mid-Infrared Spectral Frequencies (cm^{-1}) of Cobalt(III) Thioxanthate Complexes in KBr Pellets[a,b]

$[Co(S_2CSR)_2(SR)]_2$		$Co(S_2CSR)_3$			
R = C_2H_5	R = *n*-C_3H_7	R = CH_3	R = C_2H_5	R = *n*-C_3H_7	Assignment[c]
986 (s)	979 (s)	981 (s)	978 (s)	975 (s)	$\nu_{(C=S)}$
959 (s)	951 (s)	920 (s)	949 (s)	948 (s)	
464	456	455	458	461	$\nu_{(M-S)}$[d]
407 (w)	416 (w)			413	
375	370 (br)			389	$\nu_{(M-S)}$
360 (w)		353	361 (sh)	349	
335	341	341 (sh)	341		
		334	335 (sh)		
318	317	321	316 (w)	323	

[a] Abbreviations: s, strong; br, broad; sh, shoulder; w, weak. [b] A more complete list of frequencies is included for each compound in the Experimental Section. [c] Substantial contributions (>40%) from group oscillators are indicated (see text). [d] Although two sharp bands have sometimes been resolved at 482 and 474 cm^{-1} in this region for Nujol mulls on polyethylene strips,[2] only one band was observed in KBr.

$(S_2CSR)_2$ complexes, eq 8.[7b] The rate-determining step in the mechanism for both reactions 3 and 8 most likely involves cleavage of the $MS_2C{-}SR$ bond. This step is then followed by rapid loss of carbon disulfide and by dimer formation utilizing the available mercaptide ligands. In view of the agreement between the present results and those for the nickel system, no further kinetic studies of eq 1 (*e.g.*, variation of R group or solvent) were undertaken.

$$2Ni(S_2CSR)_2 \longrightarrow [Ni(S_2CSR)(SR)]_2 + 2CS_2 \qquad (8)$$
$$R = C_2H_5,\ tert\text{-}C_4H_9,\ C_6H_5CH_2$$

In both the iron and cobalt systems, it has not been possible to isolate a sulfur-bridged dimer for R = *tert*-butyl. A sulfur-bridged *tert*-butyl dimer has been obtained by CS_2 elimination in the nickel system, however,[7b] which led us to investigate the thermal stability of solutions of $Co(S_2CSR)_3$ for R = *tert*-C_4H_9. The results of heating solutions of tris(*tert*-butyl thioxanthato)cobalt(III) indicate decomposition, probably through carbon disulfide elimination, but there was no positive evidence of dimer formation. Although *tert*-butyl mercaptide can bridge nickel in $[Ni(S_2CSR)(SR)]_2$[7b] and iron in $[Fe(CO)_3(SR)]_2$ or $Fe_3(CO)_9H(SR)$,[34] the steric requirements are presumably too severe to accommodate such bridging for structures I or II.

The synthesis of the cobalt(III) monomers was achieved by using cobaltous nitrate and ferric chloride. Preferential formation of the cobalt over the iron monomers is consistent with the more inert character and greater ligand field stabilization of cobalt(III) complexes. The increased yield of monomers from this mixed-metal reaction was unexpected, however, since in the absence of iron(III) the main product is $[Co(S_2CSR)_2(SR)]_2$.

Solid State Structure Determination and the Relationship between Metal–Metal Bonding and Isomerism in $[M(S_2CSR)_2(SR)]_2$ Compounds for M = Fe, Co. The structure consists of sulfur-bridged cobalt dimers that are required by the space group symmetry to be centrosymmetric. The ethyl thioxanthate ligands are terminal (structure II), and the ethyl groups of the bridging mercaptide ligands are restricted to the anti configuration.[28] The anti isomer was also found to occur in the crystal structure of $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$.[3] The coordination polyhedron about each of the cobalt atoms is essentially an octahedron with distortions arising, at least in part, from the geometrical constraints of the four-membered thioxanthate chelate rings. Further structural information about the coordination geometry may be found in Tables IV and V and by reference to Figure 4. Examination of the shortest intermolecular contact distances revealed no unusual features, and packing of the dimeric molecules in the unit cell is determined by the normal van der Waals interactions (Figure 5).

A collection of structural parameters for the M_2X_2 rhombus in selected bridged, binuclear iron, cobalt, and nickel compounds is presented in Table IX. As discussed previously,[2,3] there is substantial evidence for metal–metal bonding in $[Fe(S_2CSR)_2(SR)]_2$. In the cobalt(III) analog, however, the metal–metal antibonding orbital, $\sigma^*(xy)$, is populated (Figure 1), the geometric consequences of which include (1) a 27% increase in the metal–metal distance over the value found for the iron dimer, (2) substantial relief of strain

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(34) J. A. de Beer and R. J. Haines, *J. Organometal. Chem.*, 24, 757 (1970).

Table IX. Some Correlations for the M_2X_2 Rhombus in Bridged Binuclear Complexes

Complex	Distance, Å			Angle, deg	
	M–M	M–X	X···X	X–M–X	M–X–M
$[Fe(S_2CSR)_2(SR)]_2$[a] R = C_2H_5; X = S	2.62	2.22	3.99	108	72.4
$[Co(S_2CSR)_2(SR)]_2$[b] R = C_2H_5; X = S	3.32	2.25	3.02	84.5	95.3
$[Ni(S_2CSR)(SR)]_2$[c] R = C_2H_5; X = S	2.76	2.19	2.85	81	78.4
$[Co_2(NH_3)_8(NH_2)Cl]^{4+}$ [d] X = N, Cl	3.15	1.88 (N) 2.33 (Cl)	2.76	81.2	114 (N) 85 (Cl)
$[Fe(NO)_2I]_2$[e] X = I	3.05	2.58	4.15	107	73
$[Co(NO)_2I]_n$[e,f] X = I	3.86	2.59	3.86	96	96
$[Co(NO)_2Cl]_2$[e] X = Cl	3.20	2.13 2.33	3.12	88	92

[a] Reference 3. [b] This work. [c] Reference 9; dihedral angle between NiS_2 planes within the Ni_2S_2 ring, 110.2°. [d] R. Barro, R. E. Marsh, and W. P. Schaeffer, *Inorg. Chem.*, **9**, 2131 (1970). [e] Data taken from Table VI, ref 5. [f] Polymeric structure.

at the bridging sulfur atom, the M–S–M angle opening up from a value of 72.4° for M = Fe to one of 95.3° for M = Co, and (3) rearrangement of the ligand wrapping pattern from structural isomer I for M = Fe to isomer II for M = Co. Stereochemical consequences (1) and (2) are in good agreement with expectations based upon the analysis by Dahl, de Gil, and Feltham[5] of metal–metal interactions in ligand bridged complexes,[35] and reinforce the previous interpretation[3] of the geometry of the iron(III) dimer in terms of the bonding scheme shown in Figure 1. In the cobalt(III) compound, only the bridging mercaptide groups serve to hold the two halves of the dimer together. The cobalt–cobalt distance is clearly nonbonding, being 0.17 Å larger than in $[Co_2(NH_3)_8(NH_2)Cl]^{4+}$ (Table IX), which also contains six-coordinate cobalt(III), but which has a smaller bridging atom in the amido group (*cf.* the last two entries in Table IX and ref 5).

The occurrence of isomer II for the $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ complex is directly related to the absence of metal–metal bond formation. As pointed out previously,[3] the function of the thioxanthate and other $YCS_2{}^{m-}$ groups as bridging ligands appears to be facilitated by short metal–metal distances, which are a result of probable metal–metal bonding.[36] For the thioxanthate ligand to bridge the nonbonded cobalt–cobalt distance of 3.32 Å, the Co–S–C angle would have to be at least 120°, assuming the S–C–S angle does not become greater than 130° (it is 126.9° in the iron dimer).[3] Although M–O–C angles in carboxylate bridged dimers are quite often as large as or larger than 120°, and the carboxylate group often serves to bridge nonbonded metal–metal pairs,[38,39] a thorough survey of the literature reveals that in all but a few cases, M–S–C angles are not greater than 112° and frequently are less than 100°, irrespective of the nature of the sulfur–donor ligand. Thus in the absence of metal–metal bonding, a M–S–C bond angle of 120° or more would be expected to result in very poor metal–ligand overlap for isomer I, and it is not surprising that the cobalt dimer adopts structure II.

In $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ there are two chemically different types of cobalt–sulfur bonds, which may be recognized from their respective average bond lengths, 2.246 Å for Co–S(mercaptide) and 2.274 Å for Co–S(thioxanthate). A closer inspection of the metal–thioxanthate bond distances (Table IV), however, reveals the "equatorial" cobalt–sulfur bonds (trans to one bridging mercaptide group, that is, in the plane of the Co_2S_2 rhombus) to be significantly longer than the "axial" bonds (cis to both bridging groups). A similar situation occurs in the structure of the iron dimer and was attributed chiefly to the effects of ring size (structure I).[3] The present results suggest an additional source of the nonequivalence of axial and equatorial metal–sulfur bonds in $[M(S_2CSR)_2(SR)]_2$ complexes. In particular, if the trans influence of the bridging mercaptide groups is greater than that of the thioxanthate ligands, the equatorial Co–S bonds would be preferentially weakened and therefore longer. A similar argument was used to explain the nonequivalent bonds between the iron atom and sulfur atoms of the $RCS_2{}^-$ ligands in the structure of thio-*p*-toluoyldisulfidobis(dithio-*p*-toluato)iron(III), $Fe(TTD)(DTT)_2$.[40]

The average metal–terminal thioxanthate bond lengths in the complexes $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$,[3] $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$, and $[Ni(S_2CSC_2H_5)(SC_2H_5)]_2$[9] are 2.334, 2.274, and 2.211 Å, respectively, and show a trend that follows the expected contraction in metal ionic radii for the series Fe > Co > Ni.[41] The average metal–sulfur distances for the bridging ethyl mercaptide ligands in the same series of compounds, Co–S (2.246 Å) > Fe–S (2.218 Å) > Ni–S (2.186 Å), do not follow this trend. The cobalt and nickel values are each 0.03 Å less than the corresponding metal thioxanthate bond

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(35) For example, the metal–metal distance in $[Co(NO)_2I]_n$ is 27% greater than in $[Fe(NO)_2I]_2$, the latter having an iron–iron bond. Other comparisons are evident from Table IX.

(36) Implicit in this statement is the assumed planarity or near planarity of the $YCS_2{}^{m-}$ ligand and the metals to which it bonds. Clearly, ligands of $YCS_2{}^{m-}$ type are able to bridge nonbonded metal atoms when the M–SCS–M group is nonplanar.[37] In addition, the planar M–SCS–M group must be in the syn–syn configuration for the arguments to apply. This second condition is achieved in the $[M(S_2CSR)_2(SR)]_2$ complexes because of the presence of the bridging mercaptide ligands.

(37) For examples, see R. Eisenberg, *Progr. Inorg. Chem.*, 12, 295 (1970).

(38) C. Oldham, *ibid.*, 10, 223 (1968), and references cited therein.

(39) F. A. Cotton, *Rev. Pure Appl. Chem.*, 17, 25 (1967).

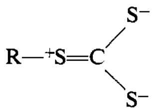
(40) D. Coucouvanis and S. J. Lippard, *J. Amer. Chem. Soc.*, **91**, 307 (1969).

(41) Since the d_{xy} orbitals on the iron atoms in $[Fe(S_2CSR)_2(SR)]_2$ participate in metal–metal bond formation, they are less available for π bonding to the terminal thioxanthate ligands than are the corresponding orbitals in the cobalt dimer. The four-coordinate nickel atoms in $[Ni(S_2CSR)(SR)]_2$ would have even greater π-bonding ability. Thus one can also rationalize the trend in metal–sulfur bond lengths for the series Fe > Co > Ni on the basis of π-bonding considerations.

lengths, but the value for iron is 0.11 Å less than the bond distance to the thioxanthate ligand. The inability of the cobalt and nickel complexes to form bonds to the bridging ethyl mercaptide ligands which are proportionally shorter than in the iron dimer may be related to the fact that, for cobalt and nickel, the nonbonded S···S contact distances in the M_2S_2 moiety are small compared to the corresponding distance for iron (Table IX). To shorten the M–S distances for M = Co, Ni would further increase the nonbonded S···S repulsions and is presumably unfavorable. It is interesting in this respect that for the analogous pair of compounds $[M(NO)_2I]_n$, M = Fe ($n = 2$), Co ($n = \infty$), the M–I distances do not reflect the relative ionic radii (or π bonding abilities)[41] Fe > Co (Table IX), possibly for similar reasons, whereas the M–N distances do (Fe–N = 1.67 Å (av), Co–N = 1.61 Å (av)).[5] The S···S distances in the cobalt and nickel thioxanthate dimers may be compared to the value of 2.89 Å found in bis(dithiobiureto)nickel(II), "the shortest nonbonded S–S distance observed to date."[42]

The average value of the S–Co–S angle in the two crystallographically independent four-membered thioxanthate rings is 75.9 (2)°. This value is similar to that in the iron isomer (73.4°)[3] and to those observed previously for similar systems.[6,43–47]

The average bond distances and interbond angles in the ethyl thioxanthate ligands are in agreement with values found in earlier studies[3,9,40,43–47] of related compounds. A detailed analysis of the bonding within coordinated thioxanthate ligands and a comparison of the geometries of metal tris-xanthate, -thioxanthate, and -dithiocarbamate complexes will be the subject of a separate paper reporting the structural results for tris(*tert*-butyl thioxanthato)iron(III).[48] For the present, the following two conclusions are of importance: (1) the contribution of the resonance form



to the overall electronic structure of the coordinated thioxanthate ligands[3,47] is 27%; (2) the S$\overset{...}{-}$C$\overset{...}{-}$S angles within the $RSCS_2^-$ groups are decidedly nonequivalent (Table V), reflecting the intramolecular stereochemical requirements of the ethyl groups.[3,47,48]

Solution Structure and Discussion of Pmr Results. Molecular weight studies of the $[Co(S_2CSR)_2(SR)]_2$ complexes show them to be dimeric in chloroform. Comparison of the pmr spectra of the iron and cobalt ethyl dimers (Figure 3) proves them to be structural isomers, and the spectrum of the cobalt complex has been assigned on the basis of structure II (Figure 4).

As indicated in Figure 3 and by comparing the data of Table I with that of Table II, ref 2, the proton resonances in the cobalt dimer all occur at higher fields (0.2–1.6 ppm) than in the iron dimer. This effect is attenuated as the distance from a given type of proton to the metal atom increases. In order to evaluate the possibility that the upfield pmr shifts in the cobalt dimers may result in part from paramagnetic anisotropy effects,[49] $\Delta\sigma_i$ values, defined as $\tau(\mathrm{Co})-\tau(\mathrm{Fe})$ for the H_i different protons, were calculated using eq 9. In this

$$\Delta\sigma_i = {}^1/_3 R_i^{-3}\Delta\chi_{\mathrm{atomic}}(1 - 3\cos^2\gamma_i) \qquad (9)$$

calculation, the distances R_i were computed using the data of Table II, and the magnetic anisotropy was assumed to be largest along the Co···Co axis in the dimer so that $\Delta\chi_{\mathrm{atomic}} = \chi_M^{\mathrm{corr}}/N$ (N = Avogadro's number) and γ_i could be calculated as the angle between the Co···Co and Co···H_i vectors. The resultant values for $\Delta\sigma_i$ were positive and ranged from 0.2 to 2.2 ppm,[50] indicating that paramagnetic anisotropy is of the correct order of magnitude to contribute substantially to the observed shifts and may be the dominant factor for the methylene protons of the bridging ethyl mercaptide ligands.

The bridging ethyl mercaptide groups in $[Ni(S_2CSC_2H_5)(SC_2H_5)]_2$[6] may also be experiencing the influence of anisotropic residual TIP, since the methylenic protons of this ligand are shifted upfield (Figure 3). It is interesting in this respect that the pmr spectrum of the nickel ethyl mercaptide hexamer[51] has also been observed to be a complex multiplet.[6] The collapse of the ethyl group pmr spectrum has been reported previously, for example, in the chloroethylgermanes.[51,52] Because of the complexity of the ethyl group's pmr spectrum in $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$, study of possible syn–anti isomerism was precluded.[28,53]

From the similarities between the electronic and pmr spectra of the n-propyl and ethyl dimers, the former is concluded to have structure II. The $Co(S_2CSR)_3$ monomers have distinct electronic spectra, which are consistent with pseudooctahedral symmetry. A pseudooctahedral structure has recently been proved by X-ray diffraction for the closely related tris(*tert*-butyl thioxanthato)iron(III) monomer.[48]

Electrochemical, Magnetic, and Spectroscopic Studies. (a) Electrochemistry. The monomeric tris(alkyl thioxanthato)cobalt(III) complexes all undergo reversible, or nearly reversible, one-electron reductions at potentials ranging from −0.80 to −1.00 V. Tris(*tert*-butyl thioxanthato)iron(III) also exhibits a reversible, one-electron reduction wave at −0.36 V.[2] The more negative potentials observed for the cobalt monomers are to be expected for reduction of low-spin Co(III) ($t_{2g}^6 \rightarrow t_{2g}^6e_g$) compared to low-spin iron(III) ($t_{2g}^5 \rightarrow t_{2g}^6$). As evident from Table VI, there is some variation of the reduction potentials of the cobalt complexes with the R group, although the correlation of $E_{1/2}$ values with the relative inductive effects[54] of the substituents, $\sigma_R{}^*$, is not

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perfect. The dependence of the half-wave potentials of the reversible one-electron transfer processes of metal thioxanthate complexes on the choice of metal atom and the ligand substituent R is not unexpected in view of previous results on the more extensively investigated metal–1,2-dithiolenes[55,56] and related compounds.[57] The present results, together with the recent findings of reversible electron-transfer behavior for tris(dithioacetylacetonato)metallate(III)[58] and dithiocarbamate[59] complexes, serve to illustrate further[2] that electron-transfer reactions involving metal complexes with chelating sulfur–donor ligands are not necessarily limited to the 1,2-dithiolenes.

The $[Co(S_2CSR)_2(SR)]_2$ dimers exhibit an irreversible oxidation wave which probably corresponds to the removal of an electron from the $\sigma^*(xy)$ orbital (Figure 1). The irreversibility would then result from the structural rearrangement required for the oxidation product to accommodate a formal cobalt–cobalt bond order of one-half. The irreversibility of the two-electron reduction and one-electron oxidation waves of the iron(III) dimers[2] may also be explained by the structural changes (*e.g.*, I → II) brought about by alteration of the metal–metal bond order. Because of the difficulties in defining precisely the causes of electrochemical irreversibility, arguments of this kind may very well be oversimplified. The fact remains, however, that electrons cannot be reversibly added to or removed from the orbitals involved in metal–metal bonding for the binuclear iron and cobalt complexes of general formula $[M(S_2CSR)_2(SR)]_2$. This result may be contrasted with the reversible electron transfer behavior exhibited by other sulfur-bridged iron and cobalt dimers,[56,60,61] in which gross structural rearrangements (such as I → II) of the products are less likely.

(b) Magnetic Behavior. The complexes are all essentially diamagnetic and therefore contain low-spin cobalt(III). The small temperature-independent paramagnetism is typical for compounds of this kind.[62–64]

(c) Electronic and Infrared Spectroscopy. The values derived from eq 6 and 7 of $\Delta \sim 16.6 \times 10^3$ cm^{-1} and $B \sim 297$ cm^{-1} may be compared to values for $Co(S_2COC_2H_5)_3$[31] of 16.9×10^3 cm^{-1} and 320 cm^{-1}, respectively. The thioxanthate ion is therefore seen to provide a slightly weaker crystal field than the corresponding xanthate ligands, as noted previously for related compounds.[65,66]

Examination of the infrared spectra of the iron[2] and cobalt (Table VII) thioxanthate complexes between 800 and 1000 cm^{-1} reveals their close similarity, except for an intense absorption between 874 and 884 cm^{1} that occurs only in the iron dimers. This band may be characteristic of the bridging thioxanthate group, and has been observed in other compounds thought to contain bridging trithiocarbonate groups.[67] Assignments for the other selected mid-infrared absorptions of the cobalt thioxanthate compounds are suggested in Table VIII. Based on the more detailed analysis of the xanthate analogs,[33] it is expected that most of the bands have contributions from several individual oscillators.

Sulfur-Bridged Dimers and the Fe_2S_2 Proteins. As stated previously, our studies of iron–sulfur and related coordination compounds have been inspired by the existence of the class of non-heme iron proteins that contain Fe_nS_n units and have low redox potentials.[4] The present results and those obtained earlier for the iron complexes[2,3,24] indicate that the metal–metal bond order has a profound influence on the geometry of M_2S_2 units and on the choice of geometric isomer for bridged, binuclear thioxanthate complexes. Based on studies of sulfur-bridged iron carbonyl and related molecules, Dahl and coworkers previously arrived at similar conclusions,[5] which have more recently been reinforced.[68] With respect to biological relevance, these latter authors have interpreted their results to imply that the geometries of the ferredoxins, or low-potential Fe_nS_n proteins,[4] may *differ markedly* with respect to the iron–iron distances in the oxidized and reduced forms. Assuming that metal–metal bonding is indeed an important feature of these proteins, we prefer an alternative, and equally speculative, interpretation, namely, that the geometries of the Fe_2S_2 proteins may be constrained by the polypeptide backbone to be the *same* in both oxidized and reduced forms.[69] If reduction of the protein involves the population of a metal–metal antibonding orbital, analogous to $\sigma^*(xy)$ in Figure 1, failure of the Fe_2S_2 unit to make a geometric adjustment to the change in electronic configuration would make the protein in its reduced form an extremely good electron donor. This would account for the most notable biological feature of these proteins, their low redox potentials.

A currently popular model used to explain many of the physical properties of the oxidized Fe_2S_2 proteins involves antiferromagnetically coupled, tetrahedrally coordinated, high-spin diiron(III) centers which upon reduction are converted to one iron(III) and one iron(II) center, also antiferromagnetically coupled.[4a,71,72] The rationale proposed above to account for the low redox potentials should also be valid for this model, the two major assumptions again being that (1) the electron enters a relatively high energy state[73] and (2) the protein

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does not make a geometric adjustment to accommodate the extra electron. Slight changes in geometry brought about by differences in amino acid composition could alter the relative energies of the reduced form of the proteins and thus also provide an explanation for the differences in redox potential of, for example, spinach ferredoxin ($E_0' = -0.430$) and putidaredoxin ($E_0' = -0.235$ V).[4a] Certain features of the proposed explanation which are subject to experimental testing are currently being investigated.

Summary

The main findings of this work may be summarized as follows. (1) There exists a series of binuclear complexes $[Co(S_2CSR)_2(SR)]_2$ analogous to those of iron(III). These can be prepared by the thermal elimination of carbon disulfide from $Co(S_2CSR)_3$. The reaction is first order in monomer, with the rate-determining step being cleavage of the $CoS_2C–SR$ bond. (2) The solid state structure of $[Co(S_2CSC_2H_5)_2(SC_2H_5)]_2$ contains bridging ethyl mercaptide groups in the anti configuration, four terminal thioxanthate ligands, and no metal–metal bond. The differences between this structure (II) and that of the iron complex of identical composition (I) are a consequence of their different electronic structures (Figure 1). (3) In solution, the cobalt dimers have structure II, as determined by pmr studies. Paramagnetic anisotropy effects are shown to be of the correct order of magnitude to account for the large upfield shifts of the methylenic protons attached to bridging sulfur atoms. (4) The monomeric complexes $Co(S_2CSR)_3$ exhibit reversible one-electron reduction waves, extending the number of known compounds containing only four-membered chelate rings that show reversible electrochemical behavior. (5) The electrochemical behavior of sulfur-bridged dimers may be influenced by the geometric constraints on, and metal–metal bonding within, the M_2S_2 moiety. Such an argument has been introduced to rationalize the low redox potentials of the Fe_2S_2 non-heme iron proteins.

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Carbonylation of Hydridopentacyanocobaltate(III)

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Abstract: Carbon monoxide was found to react with hydridopentacyanocobaltate(III) in aqueous solution according to the stoichiometry: $Co(CN)_5H^{3-} + 2CO + OH^- \rightarrow Co(CN)_3(CO)_2{}^{2-} + 2CN^- + H_2O$. Kinetic measurements yielded the rate law, $-d[Co(CN)_5H^{3-}]/dt = k[Co(CN)_5H^{3-}][OH^-]$ where $k = 6.3 \times 10^{-3}\ M^{-1}\ sec^{-1}$ at 23° and 1 M ionic strength. The results are interpreted in terms of the mechanistic sequence, $Co(CN)_5H^{3-} + OH^- \rightleftarrows Co(CN)_5{}^{4-} + H_2O$ (k_5, k_{-5}); $Co(CN)_5{}^{4-} \rightarrow Co(CN)_4{}^{3-} + CN^-$ (k_6); $Co(CN)_4{}^{3-} + 2CO \rightarrow Co(CN)_3(CO)_2{}^{2-} + CN^-$ (fast). In combination with previously determined values of k_5 and k_{-5}, the present kinetic measurements yield $k_6 = 4.5 \times 10^3\ sec^{-1}$.

Extending our earlier studies on the carbonylation of pentacyanocobaltate(II),[1] we have found that, in the presence of excess base, carbon monoxide reacts with hydridopentacyanocobaltate(III) in aqueous solution in accord with the stoichiometry described by eq 1. In this paper we describe a study of the kinetics of this reaction and discuss its mechanism. The results of these studies are also of some interest in relation to several other reactions of $Co(CN)_5H^{3-}$, studies of which have recently been reported.[2–4]

$$Co(CN)_5H^{3-} + 2CO + OH^- \longrightarrow Co(CN)_3(CO)_2{}^{2-} + 2CN^- + H_2O \quad (1)$$

Experimental Section

Materials. Solutions of $Co(CN)_5{}^{3-}$ of the desired composition were prepared by dissolving analytical reagent grade cobalt(II) chloride, sodium cyanide, sodium hydroxide, and sodium chloride (used to adjust the ionic strength) in distilled water with rigorous exclusion of oxygen (achieved by purging with nitrogen which had been passed twice through acidified chromium(II) chloride solution). Solutions of $Co(CN)_5H^{3-}$ (typically *ca.* 0.03 M) were prepared by hydrogenation of corresponding solutions of $Co(CN)_5{}^{3-}$ according to eq 2 in a glass-lined Parr Series 4500 stirred autoclave, pressurized with approximately 20 atm of H_2 as previously described.[5] Under these conditions the equilibrium of reaction 2 lies sufficiently far to the right (and the reverse reaction following release of the hydrogen pressure is sufficiently slow) that interference from reaction of residual $Co(CN)_5{}^{3-}$ was negligible. The $Co(CH)_5H^{3-}$ concentration was determined spectrophotometrically using the 305-nm absorption band (ϵ 610). Carbon monoxide and hydrogen gases were Matheson CP grade.

$$2Co(CN)_5{}^{3-} + H_2 \rightleftarrows 2Co(CN)_5H^{3-} \quad (2)$$

Stoichiometry Measurements. In addition to the spectrophotometric measurements to be described, the stoichiometry of the reaction was confirmed by direct determination of the uptake of CO and the release of CN^-. The volume of CO taken up at constant

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