a function and error program by Busing and Levy; Johnson's ORTEP, a thermal ellipsoid plot program; FAME, a structure factor normalization program by Dewar; MULTAN, a direct-methods program by Main, Woolfson, and Germain.

(17) The data crystal was a red-brown regular parallelepiped with dimensions 0.02 × 0.02 × 0.03 cm. The crystal was mounted in a thin-walled glass capillary with the *b* axis nearly parallel to the $\phi$ axis of the diffractometer. The unit cell constants and crystal orientation were determined by a least-squares refinement using the setting angles for nine carefully centered reflections. The crystal gave $\omega$ scan widths at half-height of 0.10° for several low-angle reflections. The data were collected in the $\theta$–$2\theta$ scan mode with a scan rate of 2°/min from 0.70° below the $K\alpha_1$ peak to 0.70° above the $K\alpha_1$ peak. Stationary-crystal, stationary-counter background counts of 4 sec each were taken at the start and end of each scan. Intensity data for the unique form $\pm h,+k,+l$ were collected to a $2\theta$ angle of 52°, above which there were no significant intensity data. A symmetry-equivalent form $\pm h,k,-l$ was collected to 40°. The mirror-related form, $\pm h,-k,l$ was also collected out to $2\theta$ = 45°. During the data collection the intensities of the 201, 060, and 01$\bar{6}$ reflections were measured as standards after every 60 reflections. The standards showed a variation of about 10% throughout the experiment. The $F^2$ values from the intensity data were corrected for this fluctuation in the standards as described in ref 18. Copper foil attenuators were automatically inserted if the counting rate approached $10^4$ counts/sec. The takeoff angle for X-ray tube was 2° and the Bragg $2\theta$ angle for the graphite monochromator was 12.16°. The detector was located 32 cm from the source and had a 7 × 7 mm receiving aperture. The pulse height analyzer was set to a 95% window centered on the Mo $K\alpha$ peak.

(18) K. O. Hodgson and K. N. Raymond, *Inorg. Chem.*, **11**, 171 (1972).

(19) E. N. Duesler and K. N. Raymond, *Inorg. Chem.*, **10**, 1486 (1971).

(20) In all refinements the function minimized was $\sum w(|F_o| - |F_c|)^2$, where $F_o$ and $F_c$ are the observed and calculated structure factors. The weighting factor, *w*, is $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for the nonhydrogen atoms were taken from the tabulations of Cromer and Mann.[21] Hydrogen scattering factor values were those calculated by Stewart, Davidson, and Simpson.[22] Corrections for anomalous dispersion effects for Co were made using the $\Delta f'$ and $\Delta f''$ values of Cromer.[23]

(21) D. T. Cromer and B. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(22) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

(23) D. T. Cromer, *Acta Crystallogr.*, **18**, 17 (1965).

(24) $R_1 = \sum\lVert F_o| - |F_c\rVert/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The error in an observation of unit weight is defined as $[\sum w((|F_o| - |F_c|)^2)/(N_o - N_v)]^{1/2}$.

(25) M. R. Churchill, *Inorg. Chem.*, **12**, 1213 (1973).

(26) Supplementary material.

(27) Similar results for the cell constants have been obtained by Dr. J. J. Daly, Monsanto Research, Zurich, Switzerland; D. A. White, private communication.

(28) L. D. Brown, Ph.D. Thesis, University of California, Berkeley, Calif., 1974.

(29) The correlation coefficients between occupancy and thermal motion of a particular atom were quite acceptable, averaging about 0.60 and in no case greater than 0.75.

(30) J. A. Ibers, *Acta Crystallogr., Sec. B*, **27**, 250 (1971).

(31) C. S. Pratt, B. A. Coyle, and J. A. Ibers, *J. Chem. Soc. A*, 2146 (1971).

(32) K. N. Raymond, *Acta Crystallogr., Sect. A*, **28**, 163 (1972).

(33) L. D. Brown and K. N. Raymond, *Inorg. Chem.*, preceding paper in this issue.

(34) "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1969.

(35) The structure of the ordered adduct Co(*t*-Bsalten)(bzImid)($O_2$) has recently been completed.[36] We thank Dr. Schaefer for allowing us to quote the structural results prior to publication.

(36) R. S. Gall, J. F. Rogers, W. P. Schaefer, and G. G. Christoph, submitted for publication.

(37) M. Calligaris et al., *Inorg. Nucl. Chem. Lett.*, **9**, 419 (1973).

(38) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970).

(39) J. H. Bayston, N. K. King, D. F. Looney, and M. E. Winfield, *J. Am. Chem. Soc.*, **91**, 2775 (1969).

(40) J. W. Lauher and J. E. Lester, *Inorg. Chem.*, **12**, 244 (1973).

(41) J. C. W. Chien and L. C. Dickinson, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2783 (1972).

(42) B. S. Tovrog and R. S. Drago, *J. Am. Chem. Soc.*, **96**, 6765 (1974).

(43) Repetition of the preparation reported in ref 42 has shown that what was reported as a carbonyl complex is in fact the $O_2$ complex: B. M. Hoffman, T. Szymanski, and F. Basolo, *J. Am. Chem. Soc.*, **97**, 673 (1975).

(44) J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973).

---

Contribution from the Department of Chemistry,
Columbia University, New York, New York 10027

# Reaction of Diethylamine with Mercaptide-Bridged Binuclear Cobalt(III) and Iron(III) Thioxanthate Complexes. Crystal Structure of $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$[1]

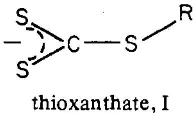
ROBERT A. WINOGRAD, DAVID L. LEWIS, and STEPHEN J. LIPPARD*

*Received March 10, 1975* AIC50178O

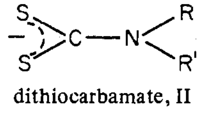
The ethyl mercaptide bridged dimers $Co_2(SC_2H_5)_2(S_2CSC_2H_5)_n[S_2CN(C_2H_5)_2]_{4-n}$, $n = 1$–3, and the mononuclear complex $Co(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_2$ have been synthesized by allowing diethylamine to react with $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$. Proton NMR, electronic, and infrared spectral data are reported for these compounds, and an interesting proton NMR solvent effect is examined. The chromatographic procedure for product separations also yielded $Co[S_2CN(C_2H_5)_2]_3$ and other unstable materials. The same reaction performed with $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ led only to the formation of $Fe[S_2CN(C_2H_5)_2]_3$ in tetrahydrofuran and $FeCl[S_2CN(C_2H_5)_2]_2$ in chloroform. The molecular structure of the complex $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$, determined in a single crystal X-ray diffraction study, contains the mercaptide-bridged binuclear $Co_2(SC_2H_5)_2$ core. Its geometry closely resembles that reported earlier for $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$. The nonbonded Co···Co distance is 3.350 (4) Å, and the average Co–S bond lengths are 2.251 (3) Å to the bridging ethyl mercaptide ligands, 2.268 (3) Å to the equatorial 1,1-dithiolate sulfur atoms in the plane of the $Co_2S_2$ rhombus, and 2.290 (3) Å to the out-of-plane, axial sulfur atoms. The thioxanthate ligand is equally disordered among the four terminal 1,1-dithiolate coordination sites. The molecule crystallizes in the triclinic space group $P\bar{1}$ with lattice constants $a = 8.150$ (7) Å, $b = 10.352$ (7) Å, $c = 13.613$ (11) Å, $\alpha = 68.60$ (2)°, $\beta = 79.11$ (2)°, and $\gamma = 109.90$ (3)°, with $Z = 1$. Full-matrix refinement converged at $R_1 = 0.050$.

## Introduction

Previous reports from this laboratory[2–6] have described the synthesis and characterization of iron(III) and cobalt(III) complexes of the thioxanthate ligand, I. Among the compounds investigated were the tris(alkyl thioxanthates) of cobalt(III). These complexes undergo carbon disulfide elimination reactions[4] to form the mercaptide-bridged dimers $[Co(SR)(S_2CSR)_2]_2$, eq 1. In the iron(III) system, only mononuclear tris(*tert*-butyl thioxanthato)iron(III) was isolated, the other alkyl thioxanthates forming $[Fe(SR)(S_2CSR)_2]_2$ under the conditions of the reaction.[2,3,7] The physical properties of these complexes have been extensively investigated and the crystal structures of $(t\text{-}C_4H_9SCS_2)_3Fe$,[5] $(C_2H_5SCS_2)_3Co$,[6] $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$,[3] and



thioxanthate, I



dithiocarbamate, II

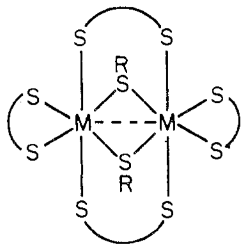
$$2Co(S_2CSR)_3 \rightarrow [Co(SR)(S_2CSR)_2]_2 + 2CS_2 \qquad (1)$$

**Table I.** Analytical Results for the Products Isolated from the Reactions of $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$ and $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ with Diethylamine

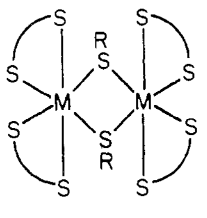
| | % calcd | | | | % found | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Compd[a] | C | H | N | S | C | H | N | S | Yield,[b] % | Color |
| $Co_2(SEt)_2(S_2CSEt)_3(S_2CNEt_2)$ | 27.0 | 4.41 | 1.75 | 52.1 | 27.0 | 4.31 | 1.68 | 52.9 | 10–15 | Brown |
| $Co_2(SEt)_2(S_2CSEt)_2(S_2CNEt_2)_2$ | 29.6 | 4.97 | 3.45 | 47.4 | 29.5 | 4.97 | 3.51 | 46.6 | 10–20 | Brown |
| $Co_2(SEt)_2(S_2CSEt)(S_2CNEt_2)_3$ | 32.1 | 5.52 | 5.11 | 42.9 | 32.1 | 5.35 | 5.27 | 43.0 | 10–15 | Brown |
| $Co(S_2CSEt)(S_2CNEt_2)_2$ | 31.7 | 5.11 | 5.69 | 45.6 | 31.9 | 4.88 | 5.53 | 44.8 | ~5 | Green |
| $Co(S_2CNEt_2)_3$ | 35.8 | 6.00 | 8.34 | 38.2 | 35.6 | 5.80 | 8.23 | 38.0 | >15 | Green |
| $FeCl(S_2CNEt_2)_2$[c] | 31.0 | 5.20 | 7.22 | 33.1 | 31.3 | 5.40 | 7.32 | 33.2 | 85[d] | Green |

[a] Et = Ethyl. [b] Based on the initial quantity of $[Co(SEt)(S_2CSEt)_2]_2$ starting material except as noted differently. [c] Chlorine: calcd, 9.14%; found, 9.23%. [d] Based on the initial quantity of dithiocarbamate ligand available from the starting reagent $Fe(S_2CNEt_2)_3$ using procedure (a). A high yield was also obtained from the alternative procedure (b).

$[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$[4] have been determined. The iron(III) dimers were found to have structure III whereas the binuclear cobalt(III) compounds exhibit structural form IV.



III



IV

A short metal–metal distance of 2.618 (2) Å demonstrated that metal–metal bonding occurs in the iron system; the corresponding nonbonded distance in the cobalt compounds is 3.321 (2) Å. The increased metal–metal length in the latter compounds is responsible for their having structural isomer IV, since the S···S bite distance of the thioxanthate ligand is unable to span a 3.32-Å distance.[4] The magnetic properties of these iron and cobalt complexes are consistent with low-spin ground-state configurations although the temperature dependence of the magnetic susceptibility of the iron thioxanthate monomers suggests a small contribution from a high-spin state.[3,7a] Extensive investigations in recent years of related tris(*N*,*N*-dialkyldithiocarbamato)iron(III) complexes, $Fe(S_2CNRR')_3$, have shown them to be equilibrium mixtures of low- and high-spin states. The temperature dependence of the spin equilibria of these complexes as well as their structural and other physical properties varies significantly with the identity of the groups R and R' in II.[8,9]

The reaction of coordinated thioxanthates (I) with diethylamine to form coordinated dithiocarbamates (II), eq 2,

$$[Ni(SR)(S_2CSR)]_2 + 2NH(C_2H_5)_2 \rightarrow Ni_2(SR)_2[S_2CN(C_2H_5)_2]_2 + 2RSH \qquad (2)$$

has been described.[10] Extension of this chemistry to the iron(III) and cobalt(III) thioxanthate dimers described above was attempted in order (1) to determine whether sulfur-bridged binuclear complexes of these metals would in fact undergo such a reaction and remain intact, (2) to provide further examples of tractable iron(III) thiolate complexes, a very limited class of compounds,[11] and (3) to examine the influence (if any) of the *N*,*N*-dialkyldithiocarbamate ligands on the structural and magnetic properties of III and IV. As described in this report, dithiocarbamate analogs of IV were prepared with cobalt, but no binuclear iron derivatives could be obtained. Reaction 3 produces a complex mixture of

$$Co_2(SC_2H_5)_2(S_2CSC_2H_5)_4 + NH(C_2H_5)_2 \rightarrow Co_2(SC_2H_5)_2(S_2CSC_2H_5)_n[S_2CN(C_2H_5)_2]_{4-n} + \text{other products} \qquad (3)$$

products that have been separated and partially characterized. The crystal and molecular structure of the dimer having $n = 1$ shows it to be isostructural with IV. Experiments with the iron system are also reported.

## Experimental Section[12]

**Materials and Physical Measurements.** $[Fe(SEt)(tx)_2]_2$, $[Co(SEt)(tx)_2]_2$, and $Co(dtc)_3$ were prepared with commercially available starting materials according to the procedures described previously.[2,4,13] $Fe(dtc)_3$ was prepared by the method used for the iron thioxanthate dimer replacing ethyl mercaptan by diethylamine; the infrared and electronic spectra of the product matched those reported by White et al.[14]

Microchemical analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Infrared spectra were recorded with a Perkin-Elmer Model 621 grating instrument using KBr pellets (1.5% sample by weight) in the region from 4000 to 350 $cm^{-1}$. Polystyrene peaks at 907.6 and 1601.4 $cm^{-1}$ were used to calibrate the spectra. Proton magnetic resonance studies were performed on a Varian Associates T-60 or HA-100 instrument; the latter was equipped with a variable-temperature probe. Samples were dissolved in $CS_2$ or $CDCl_3$, and tetramethylsilane was used as an internal standard. Electronic spectra of chloroform solutions were recorded on a Cary 17 spectrophotometer at concentrations of $10^{-4}$–$10^{-6}$ *M* using 1-cm matched quartz cells.

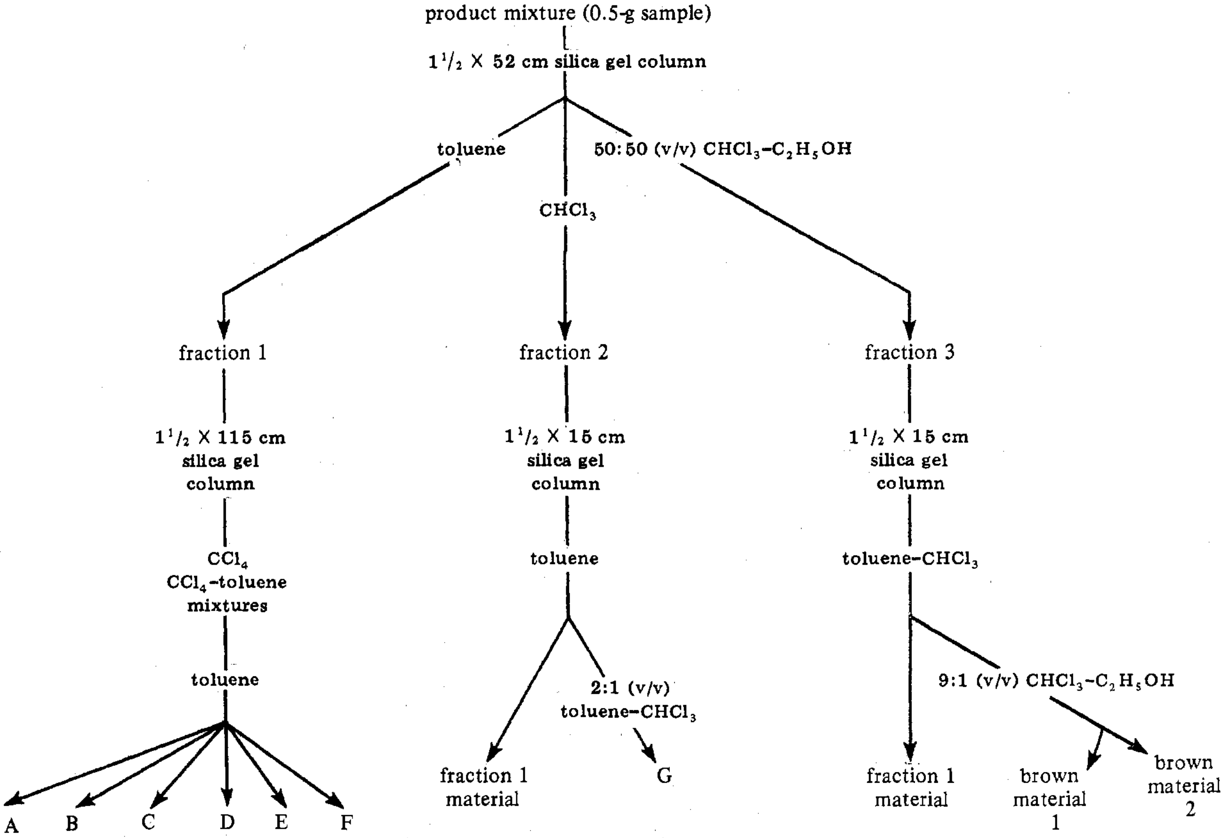
**Preparations. Mixed Dithiocarbamate–Thioxanthate Cobalt Monomers and Dimers.** Tetrakis(ethyl thioxanthato)-$\mu$-bis(ethanethiolato)-dicobalt(III) (1 g, 1.3 mmol) was dissolved in 100 ml of chloroform, and 2 ml (20 mmol) of diethylamine (Matheson Coleman and Bell) was added to this solution dropwise. After 3 hr of refluxing, a small amount of insoluble material was removed by filtration and the filtrate was evaporated to dryness. A chromatographic procedure, performed on Silica gel (Baker Analyzed) in a well-ventilated hood, was employed to separate nine components in the product mixture. This procedure is outlined in Figure 1.

A 1.5 × 52 cm silica column was prepared with $CCl_4$, and a 0.5-g portion of product material, dissolved in $CS_2$, was used to charge the column. Elution with toluene followed by chloroform and finally by a 50:50 (v/v) chloroform–ethanol mixture separated the product materials into three crude fractions.[15] These will be referred to as fractions 1, 2, and 3, respectively.

Fraction 1, after evaporation to dryness, was redissolved in $CS_2$ and rechromatographed on a 1.5 × 115 cm silica column. Slow elution with $CCl_4$ that was progressively enriched with toluene was carried out for a period of 75 hr or longer. Six materials, four brown and two green, were isolated and individually crystallized by a double-layering procedure. Each product was dissolved in a minimal quantity of $CS_2$ or $CHCl_3$ and a layer of ethanol, ether, or hexanes was slowly and carefully added on top. After 24–48 hr the crystalline precipitates were filtered, washed with ether, and dried in air. All six isolated materials have been identified and are listed together with their analytical data in Table I.

Fraction 2 was rechromatographed on a 10–20 cm silica column. Toluene was initially used as the solvent to elute rapidly small amounts of material composed of fraction 1. A 2:1 toluene–$CHCl_3$ solution then carried down a very small amount of brown material that was unstable, particularly in solution, over a period of a few days. Maximum yields of this material ranged from 1 to 3%. A $^1H$ NMR spectrum of the brown complex identified it as $[Co(SEt)(dtc)_2]_2$ (Figure 2e). The instability of this material and the small quantity available made its further investigation impractical.

Fraction 3 was also rechromatographed on a 10–20 cm silica column (Figure 1) to yield small amounts of fraction 1 and two unidentified brown products, neither of which could be obtained crystalline.



A = $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$
B = $Co_2(SC_2H_5)_2(S_2CSC_2H_5)_3[S_2CN(C_2H_5)_2]$
C = $Co(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_2$
D = $Co_2(SC_2H_5)_2(S_2CSC_2H_5)_2[S_2CN(C_2H_5)_2]_2$
E = $Co[S_2CN(C_2H_5)_2]_3$
F = $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$
G = $[Co(SC_2H_5)[S_2CN(C_2H_5)_2]_2]_2$

**Figure 1.** Chromatographic procedure used to separate product materials following the reaction of tetrakis(ethyl thioxanthato)-μ-bis(ethanethiolato)-dicobalt(III) with diethylamine. Solid samples from fractions B, C, D, E, and F were isolated and analyzed.

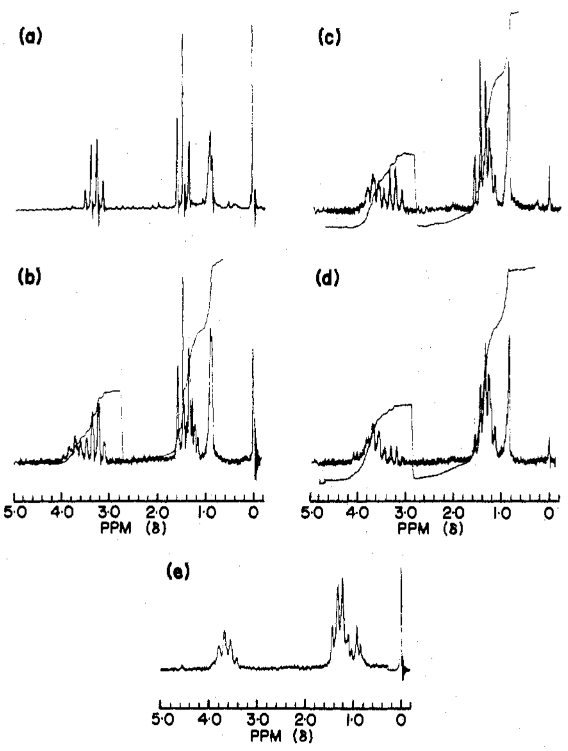


**Figure 2.** The 60-MHz proton NMR spectra of carbon disulfide solutions of $Co_2(SC_2H_5)_2(S_2CSC_2H_5)_n[S_2CN(C_2H_5)_2]_{4-n}$ for (a) $n = 4$, (b) $n = 3$, (c) $n = 2$, (d) $n = 1$, and (e) $n = 0$.

**Chlorobis(*N*,*N*-diethyldithiocarbamato)iron(III), FeCl(dtc)$_2$.** (a) A 0.49-g (0.6-mmol) amount of $[Fe(SEt)(tx)_2]_2$ and 1.19 g (2.5 mmol) of $Fe(dtc)_3$ were dissolved in 100 ml of chloroform. The resulting solution was refluxed over steam for 3 hr, rotoevaporated to one-third of its volume, and layered with approximately 50 ml of ethanol or hexanes. Green crystals, washed with ether and dried in air, were isolated from two crops.

(b) $[Fe(SEt)(tx)_2]_2$ (0.49 g, 0.6 mmol) was dissolved in 70 ml of chloroform and 1 ml (9.7 mmol) of diethylamine was added to this solution dropwise. After 3 hr of refluxing over steam, the green product was isolated by the procedure described above.

**X-Ray Diffraction Measurements. Collection and Reduction of the Data.** Crystals of the complex $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$ were isolated as thin plates from a chloroform solution layered with ethanol, and several of them were mounted for study on glass fibers. Zero-level precession photographs, taken with Ni-filtered Cu Kα radiation (λ 1.5418 Å), exhibited Laue symmetry $\bar{1}$, requiring the space group to be $P1$ or $P\bar{1}$. Unit cell dimensions were determined by least-squares refinement of the setting angles of 12 carefully centered high-angle reflections using a FACS-I-DOS diffractometer with Mo Kα radiation (λ 0.7093 Å). The results show that $a = 8.150$ (7) Å, $b = 10.352$ (7) Å, $c = 13.613$ (11) Å, $\alpha = 68.60$ (2)°, $\beta = 79.11$ (2)°, and $\gamma = 109.90$ (3)°. The calculated density of 1.455 g cm$^{-3}$ for one $Co_2C_{22}H_{45}N_3S_{11}$ formula unit per unit cell of 939 Å$^3$ volume is in excellent agreement with the 1.45 (±0.05) g cm$^{-3}$ value obtained by neutral buoyancy in an aqueous solution of potassium iodide. With $Z = 1$ and with a center of inversion within the dimer unlikely, the space group $P1$ was initially selected. A search for higher symmetry relations using the program TRACER[16] revealed none; the following triclinic to conventional reduced cell transformation matrix was generated: $(0\bar{1}0; 001; \bar{1}00)$. The original cell was used in all computations reported here.

The crystal chosen for data collection was mounted in an arbitrary orientation; it had the approximate dimensions 0.33 × 0.18 × 0.033 mm. Its mosacity was measured by means of narrow-source, open-counter ω scans. For 12 strong low-order reflections, the width at half-height ranged from 0.06 to 0.15°; the average value of 0.11° was the best from among many crystals examined. The crystals all had a small satellite that appeared in the $\omega$ scans for a few reflections, ~0.25° away from the peak maximum. The scan range was therefore chosen to be sufficiently wide to collect the entire reflection. Intensities were measured using Mo $K\alpha$ radiation by the $\theta-2\theta$ scan technique with a graphite monochromator in place. A 2.05° takeoff angle afforded 85% of the maximum intensity to be transmitted and the aperture, positioned in front of the counter 31 cm from the crystal, was set to 6.35 × 6.35 mm. A scan range of 2.0° in $2\theta$ plus the angular separation of $K\alpha_1$ and $K\alpha_2$ was used with a scan speed of 1°/min. Stationary-counter, stationary-crystal background counts of 20 sec were taken at each end of the scan.

A total of 2685 data having $+h,\pm k,\pm l$ were collected for $3° < 2\theta < 45°$. The intensities of three standards were monitored after every 97 reflections and at no time did they vary significantly ($\Delta(F^2)/\sigma(F^2) \approx \pm 0.6$). The data were reduced in the usual manner using a value of 0.04 for $\epsilon$.[17] An absorption correction was made with the program ORABS. Transmission factors ranged from 0.952 to 0.757 using a calculated linear absorption coefficient of 15.2 cm$^{-1}$. The reflections having the lowest transmission factors were observed visually on the diffractometer to correspond to the longest path lengths through the crystal.

The 1725 reflections which satisfied the condition $F^2 > 3\sigma(F^2)$ were included in the initial refinement of the structure. Scattering factors used were for neutral atoms.[18] Corrections for anomalous dispersion effects for the cobalt and sulfur atoms were taken from the compilation of Cromer and Liberman[19] and applied to the calculated structure factor amplitudes. The data were placed on an approximate absolute scale through a modification of Wilson's method which produced an estimated mean $B$ of 3.38 Å$^2$ and a scale factor of 1.32.

**Determination and Refinement of the Structure.** The coordinates of the two cobalt atoms, the two bridging sulfur atoms, and three of the eight terminally coordinated sulfur atoms (structure IV) were determined from an origin-removed, sharpened Patterson map. Positional parameters and isotropic temperature factors for these atoms and the scale factor were refined by successive cycles of least squares using unit weights. Subsequent difference Fourier maps revealed the carbon atoms of the bridging mercaptide ligands, the remaining cobalt-bound sulfur atoms, and the carbon atoms to which these sulfur atoms are attached. The atoms defined to this point are referred to as "core" atoms; their positions obviously indicate that all four 1,1-dithiolate ligands are coordinated in a terminal fashion to the metal centers (i.e., isomer IV, not III). The discrepancy factors at this point were 0.209 and 0.272 for $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$, respectively.

Phased on the "core" atoms, a new difference Fourier map did not reveal a strong peak that could be associated with the noncoordinated sulfur atom of the thioxanthate ligand. Evidence from further refinements strongly suggested the presence of a center of symmetry in the unit cell and therefore molecular disorder of the thioxanthate ligand among two or all four of the terminal coordination sites.

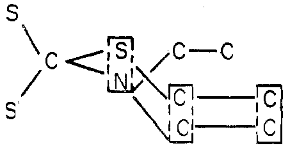
For the centric space group $P\bar{1}$, 224 equivalent $(0kl)$ and $(0\bar{k}\bar{l})$ reflections were averaged with an agreement factor $R$ of 0.028 where

$$R = \sum_{i=1}^{224} \sum_{j=1}^{2} |\overline{F}_i^2 - F_{ij}^2| / \sum_{i=1}^{224} \overline{F}_i^2$$

A total of 1578 independent reflections now satisfied the condition $F^2 > 3\sigma(F^2)$. Refining the core atoms with anisotropic thermal parameters and all of the other atoms isotropically, structure factor calculations were used to compute difference Fourier maps from which both thioxanthate and dithiocarbamate functions, excluding hydrogen atoms, were defined in the two crystallographically independent coordination sites. The structure factors at this time were assigned weights according to $w = 4F_o^2/\sigma^2(F_o^2)$, and the disordered thioxanthate and dithiocarbamate atoms were given occupancy factors of 0.25 and 0.75, respectively. It is important to note at this juncture that the $CS_2$ moieties common to both thioxanthate and dithiocarbamate functions in the two crystallographically independent coordination sites are exactly superimposed on one another. The Fourier map in these regions is clean and the values of the refined isotropic or anisotropic thermal parameters for these atoms are unexceptional. The $CS_2$ moieties were subsequently considered to be part of the "core" and therefore not part of the disorder.

The validity of the 0.25 and 0.75 occupancy factors assigned for the two different types of dithiolate ligands was next examined by varying the multiplier of one nitrogen atom and constraining the other occupancy factors appropriately. After a few cycles of least squares, the varied multiplier value converged at a value of 0.75, indicating random disorder among the four 1,1-dithiolate ligand coordination sites. At this stage the discrepancy indices were 0.054 and 0.066 for $R_1$ and $R_2$, respectively, and refinement was close to convergence.

Examination of the bond lengths and angles in the disordered portion of the ligands at this stage revealed several chemically unreasonable features. Moreover, the isotropic thermal parameters for a few of these atoms were abnormally high, with values between 10 and 18. Further attempts to improve on this refinement were unsuccessful, presumably because of the close proximity of pairs of atoms from the two dithiolate ligands (also observed on a difference Fourier map phased on core atoms only) and the diffuse electron density contributed from the hydrogen atoms in the disordered regions for which we did not account. It was therefore decided to complete the structure by refining atom pairs as single atoms in the manner (dashed boxes inscribe the atom pairs)



The multiplier values assigned were 1 for the carbon atom pairs and 1.32 for the nitrogen–sulfur pair; the nitrogen scattering factor table was employed for the latter. All atoms were then refined with anisotropic thermal parameters, allowing the thermal ellipsoids to adjust for any deficiencies in the atom pair assignments.

This approach proved to be very reasonable and the final structural tabulations are based on it. Prior to the last stages of refinement, two hydrogen atoms attached to the methylene carbon atom of the bridging mercaptide group were identified on a difference Fourier map. Attempts to locate and refine additional hydrogen atoms were unsuccessful. In the final refinement cycles the 189 parameters varied by no more than 0.01 of their estimated standard deviations and the discrepancy indices converged at $R_1 = 0.050$ and $R_2 = 0.063$. The value of the function $[(\sum w\Delta^2)/(m-n)]^{1/2}$ was 1.959 and the function $w\Delta^2$ did not show unusual dependence on $(\sin\theta)/\lambda$ or $|F_o|$. A final difference map showed only a slight residual electron density of ~0.6 e/Å$^3$, and nine of the ten top peaks on the Fourier list were located in the regions of the disordered dithiocarbamate–thioxanthate carbon atoms. The structure at this point was considered to be complete.

## Results

**Syntheses.** The displacement of the ethyl mercaptide moiety of the thioxanthate ligands (I) in $[Co(SEt)(tx)_2]_2$ by diethylamine was the only reaction that led to the isolation of binuclear complexes containing dithiocarbamate ligands (II). In this light it is interesting to examine the results of other synthetic approaches.

Brinkhoff[20] reported a few years ago that a ligand-exchange reaction occurred between $Co(dtc)_3$ and $Co(S_2COEt)_3$ when the two were refluxed in chloroform solution for 10 min. A similar exchange reaction was attempted with $Co(dtc)_3$ and $[Co(SEt)(tx)_2]_2$. A solution containing 0.5 g (1 mmol) of $Co(dtc)_3$ and 0.2 g (0.25 mmol) of $[Co(SEt)(tx)_2]_2$ dissolved in 100 ml of chloroform was refluxed over a steam bath for 24 hr. A silica gel chromatographic separation of the product mixture revealed the presence of both starting materials and a miniscule amount of an unidentified brown material. More drastic refluxing conditions in toluene resulted in the total decomposition of the cobalt thioxanthate dimer. $Co(dtc)_3$ remained unaffected and no other product materials were isolated.

The elimination of $CS_2$ from the mononuclear complex $Co(tx)(dtc)_2$ to form $[Co(SEt)(dtc)_2]_2$, analogous to the elimination reaction reported earlier for $Co(tx)_3$,[4] was attempted by refluxing the monomer in toluene solvent for 3 hr. Although a few products were observed chromatographically from this reaction, only $Co(dtc)_3$ was identified by proton NMR.

The unstable $[Co(SEt)(dtc)_2]_2$ compound and the two unstable, unidentified brown materials (Figure 1) were re-

**Table II.** Selected Mid-Infrared Spectral Frequencies (cm$^{-1}$) of Cobalt(III)–Thioxanthate–Dithiocarbamate Complexes in KBr Pellets[a]

| $\mathrm{Co(S_2CSC_2H_5)}_m\mathrm{[S_2CN(C_2H_5)_2]}_n$ | | $\mathrm{Co_2(SC_2H_5)_2(S_2CSC_2H_5)}_m\mathrm{[S_2CN(C_2H_5)_2]}_n$ | | | | Brown material no. 2[b] | Assignment[c] |
|---|---|---|---|---|---|---|---|
| $m = 0, n = 3$ | $m = 1, n = 2$ | $m = 4, n = 0$ | $m = 3, n = 1$ | $m = 2, n = 2$ | $m = 1, n = 3$ | | |
| 363 s | 366 m | | | | | | $\nu$(M–S) |
| | 465 w | 462 w | 460 w | 458 w | 458 w | | $\nu$(M–S), tx |
| | 513 w | 515 m | 515 w | 516 w | 514 w | | tx |
| | 582 w | | | | | | |
| | | 750 br, m | 760 br, m | 765 br, m | 765 m | | |
| 787 m | 786 m | | | | 780 m | 778 w | dtc |
| 855 m | 855 m | | 853 m | 853 m | 855 w | 855 w | dtc |
| 917 m | 920 sh, m | 927 sh, m | | 917 sh, w | 917 w | 912 w | |
| | 955 s | 953 s | 955 s | 956 s | 959 s | | $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$, tx |
| | 978 s | 979 s | 978 s | 980 s | 976 s | | $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$, tx |
| 1005 m | 1003 w | | | | | | |
| | | 1050 br, w | 1060 br, w | | | | |
| 1081 m | 1080 m | | | 1080 br, m | 1079 br, m | 1078 | dtc |
| 1140 s | | | | | | | |
| 1151 s | 1150 s | | 1149 m | 1151 s | 1149 s | 1148 | dtc |
| 1218 s | 1214 m | | 1211 m | 1213 m | 1215 m | 1200 | dtc |
| | | 1250 sh | 1248 sh | 1247 sh | 1252 sh, m | 1245 | |
| | | 1265 m | | | | | |
| 1270 s | 1271 s | 1275 sh | 1278 s | 1278 s | 1278 s | 1278 | |
| 1300 sh | 1300 m | | 1300 w, sh | 1301 w, sh | 1302 m, sh | | dtc |
| 1481 s | 1495 s | | 1497 s | 1497 s | 1495 s | 1505 br, s | $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$, dtc |
| | | | | | | 1554 | |
| | | | | | | 1610 | |

[a] Abbreviations: s, strong; m, medium; w, weak; br, broad; sh, shoulder. [b] Strong, broad background absorbance was observed in the 1000–1300-cm$^{-1}$ region. [c] Abbreviations: tx, ethyl thioxanthate ligand; dtc, diethyldithiocarbamate ligand.

chromatographed on a few occasions after having been initially "isolated". One decomposition product from all three compounds was again found by proton NMR to be Co(dtc)$_3$. In addition, [Co(SEt)(dtc)$_2$]$_2$ was observed by chromatography to decompose into the two unidentified brown materials.

The reaction of [Fe(SEt)(tx)$_2$]$_2$ with diethylamine in refluxing chloroform solution led to the reported synthesis of FeCl(dtc)$_2$. By using THF in place of chloroform and refluxing for 4 hr, black Fe(dtc)$_3$ was the only product isolated. This material was identified by its infrared and electronic spectra.[14] Silica gel thin-layer (TLC) studies using CCl$_4$, CHCl$_3$, and a chloroform–ethanol solvent mixture suggested that no other products are formed in this reaction. In an effort to determine the existence of intermediates that have lifetimes long enough for observation on TLC, the reaction was followed at 40° with a 2:1 ratio of diethylamine to [Fe(SEt)(tx)$_2$]$_2$. The very slow formation of a single product was observed.

The reaction of Fe(dtc)$_3$ with [Fe(SEt)(tx)$_2$]$_2$ in a 4:1 ratio in chloroform solution once again led to the production of green FeCl(dtc)$_2$. This same reaction carried out in toluene resulted only in the decomposition of the iron dimer. When Fe(dtc)$_3$ was refluxed in chloroform alone for 3 hr, FeCl(dtc)$_2$ did not readily form. The black color and infrared spectrum of the isolated material showed it to be the starting material.

The inadvertently synthesized FeCl(dtc)$_2$ complex was used in another synthetic scheme. A solution containing 0.41 g (1.3 mmol) of this complex, dissolved in 40 ml of THF, was added dropwise to a second THF solution containing phenyl mercaptan (0.16 g, 1.3 mmol) and NaH (0.06 g, 1.3 mmol). From the resulting brown solution was isolated a black product, the infrared spectrum of which matched that of Fe(dtc)$_3$; no phenyl ring absorptions were observed.

**Spectral Studies. Infrared Spectra.** A summary of selected mid-infrared spectral frequencies may be found in Table II. Certain bands may be identified as either dithiocarbamate or thioxanthate ligand vibrations. All of the complexes containing the dithiocarbamate ligand display a common $\mathrm{C}\overset{\cdots}{-}\mathrm{N}$ stretching mode at about 1495 cm$^{-1}$. The other spectral assignments made in Table II are derived from previously published studies. Absorbances in the 350–465-cm$^{-1}$ region are presumed to have considerable M–S character while the two strong absorbances observed around 957 and 978 cm$^{-1}$ are assigned to the S$_2$CS fragment of the thioxanthate ligand.[4]

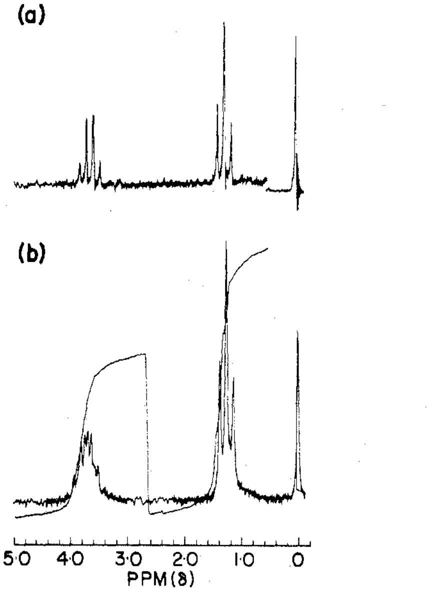


**Figure 3.** The 60-MHz proton NMR spectra of Co[S$_2$CN(C$_2$H$_5$)$_2$]$_3$ dissolved in (a) carbon disulfide and (b) chloroform.

**Proton Nuclear Magnetic Resonance Spectra.** The 60-MHz proton NMR spectra of the complexes dissolved in carbon disulfide or CDCl$_3$ are shown in Figures 2 and 3. The unusual chemical shift and splitting pattern observed for the bridging ethanethiolate ligands in dimers containing the Co$_2$(SC$_2$H$_5$)$_2$ moiety have been discussed previously.[4] The methylene resonances associated with the dithiocarbamate ligands always appear about 0.4 ppm downfield from those associated with the thioxanthate ligands as would be expected from the greater electronegativity of the nitrogen atom. This separation is convenient for the purpose of analysis. Normally the dithiocarbamate ligand methylene protons appear as multiply split quartets. In CS$_2$ and CDCl$_3$, however, the splitting patterns for these protons differ, implying a solvent effect that is particularly apparent in the spectrum of Co(dtc)$_3$ (Figure 3).

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

| | Absorption maxima × $10^{-3}$, $cm^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| Compd | Band 1 | Band 2 | Band 3 | Band 4 | Band 5 | Band 6 |
| $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$[b] | 16.7 sh | 22.3 sh | 26.4 sh | 29.7 sh | 31.9 (4.84) | |
| $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$ | 17.1 sh | 22.7 sh | 26.7 sh | 30.2 (4.67) | 34.7 (4.61) | |
| $Co(S_2CSC_2H_5)_3$[c] | 15.9 (2.97) | 20.0 sh | 25.8 (4.56) | 31.3 (5.02) | 33.3 sh | 38.5 (4.53) |
| $Co[S_2CN(C_2H_5)_2]_3$ | 15.6 (2.69) | 21.1 sh | 25.8 sh | 28.0 sh | 31.0 (4.33) | 36.6 (4.54) |

[a] Values in parentheses are molar extinction coefficients (log $\epsilon_{max}$); sh = shoulder. [b] Reported values amend those tabulated in ref 4. [c] Reference 4.

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

| Atom | $x$ | $y$ | $z$ | $\beta_{11}$[c] or $B$ | $\beta_{22}$ | $\beta_{33}$ | $\beta_{12}$ | $\beta_{13}$ | $\beta_{23}$ | Multiplier[d] |
|---|---|---|---|---|---|---|---|---|---|---|
| Co | 0.0927 (2) | 0.1656 (1) | −0.1208 (1) | 22.0 (3) | 11.6 (2) | 6.2 (1) | 9.0 (2) | −1.8 (1) | −2.7 (1) | 1.0 |
| S1 | −0.0793 (3) | −0.0894 (3) | −0.0593 (2) | 24.8 (6) | 12.5 (4) | 6.8 (2) | 9.6 (4) | −3.7 (3) | −3.9 (2) | 1.0 |
| S2 | −0.1433 (4) | 0.2315 (3) | −0.0914 (2) | 25.7 (7) | 16.4 (4) | 9.5 (2) | 12.6 (5) | −3.3 (3) | −4.3 (3) | 1.0 |
| S3 | 0.2402 (4) | 0.4211 (3) | −0.1629 (2) | 28.5 (7) | 12.4 (4) | 9.4 (3) | 8.2 (4) | −2.1 (3) | −2.9 (3) | 1.0 |
| S4 | 0.3601 (4) | 0.1544 (3) | −0.1919 (2) | 25.1 (7) | 18.9 (5) | 8.0 (2) | 12.5 (5) | −2.0 (3) | −4.2 (3) | 1.0 |
| S5 | 0.1280 (4) | 0.2302 (3) | −0.3059 (2) | 32.5 (8) | 18.9 (5) | 6.6 (2) | 13.9 (5) | −3.4 (3) | −3.0 (3) | 1.0 |
| NS1 | −0.0111 (17) | 0.5437 (10) | −0.1385 (7) | 96.6 (48) | 30.8 (20) | 11.7 (8) | 42.8 (29) | −14.6 (17) | −9.1 (11) | 1.32 |
| NS2 | 0.4696 (12) | 0.2501 (8) | −0.4237 (6) | 64.3 (31) | 23.0 (14) | 9.3 (7) | 20.3 (18) | −0.9 (12) | −5.4 (8) | 1.32 |
| C1 | −0.3175 (15) | −0.1299 (15) | −0.0568 (11) | 26.9 (29) | 17.7 (22) | 12.5 (13) | 9.4 (21) | −6.6 (15) | −7.7 (15) | 1.0 |
| C2 | −0.3347 (16) | −0.1020 (15) | −0.1703 (10) | 37.1 (36) | 38.7 (32) | 13.3 (13) | 17.8 (28) | −15.1 (18) | −10.2 (17) | 1.0 |
| C3 | 0.0243 (14) | 0.4120 (11) | −0.1327 (7) | 33.5 (29) | 15.3 (16) | 6.7 (8) | 13.4 (19) | −3.6 (12) | −3.0 (10) | 1.0 |
| C4 | 0.1470 (17) | 0.6877 (14) | −0.1691 (11) | 20.2 (31) | 7.4 (18) | 11.3 (14) | 2.1 (20) | −3.7 (16) | −4.8 (13) | 0.75 |
| C5 | 0.1953 (18) | 0.8034 (15) | −0.2879 (12) | 30.4 (40) | 14.3 (23) | 9.5 (14) | 0.6 (24) | −0.7 (18) | −2.5 (15) | 0.75 |
| CC6 | −0.1939 (20) | 0.5220 (14) | −0.1124 (13) | 36.4 (39) | 19.3 (23) | 22.1 (20) | 13.1 (26) | −10.2 (23) | −6.7 (17) | 1.0 |
| CC7 | −0.2487 (23) | 0.5489 (19) | −0.2160 (16) | 57.9 (57) | 38.6 (41) | 28.9 (27) | 24.8 (39) | −23.9 (33) | −9.5 (25) | 1.0 |
| C8 | 0.3276 (13) | 0.2134 (10) | −0.3167 (8) | 28.4 (26) | 13.2 (15) | 7.2 (8) | 9.9 (17) | −0.7 (12) | −2.4 (9) | 1.0 |
| CC9 | 0.4157 (20) | 0.3009 (16) | −0.5252 (9) | 54.2 (46) | 32.2 (31) | 6.3 (10) | 24.0 (32) | −1.4 (17) | −2.6 (15) | 1.0 |
| CC10 | 0.2986 (27) | 0.1548 (21) | −0.5410 (13) | 87.4 (74) | 45.7 (45) | 16.1 (18) | 30.3 (48) | −17.1 (29) | −14.9 (24) | 1.0 |
| C11 | 0.6188 (23) | 0.2111 (20) | −0.4160 (12) | 37.3 (48) | 32.7 (38) | 9.3 (14) | 27.0 (39) | −3.6 (21) | −4.9 (19) | 0.75 |
| C12 | 0.7856 (23) | 0.3562 (20) | −0.4527 (16) | 28.1 (46) | 23.6 (36) | 22.3 (26) | 8.8 (34) | −6.9 (27) | −1.4 (23) | 0.75 |
| H1 | −0.365 (15) | −0.234 (13) | −0.003 (9) | 6.3 (36) | | | | | | 1.0 |
| H2 | −0.348 (12) | −0.076 (10) | −0.023 (7) | 2.2 (23) | | | | | | 1.0 |

[a] Atoms are labeled as indicated in Figure 4. The hydrogen atoms are attached to carbon atom C1. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. Values reported are $\times 10^3$. For hydrogen atoms only, $\beta_{11} = B$, the isotropic thermal parameter in Å². [d] See text.

The methylene resonances of the thioxanthate ligands in $CS_2$ and $CDCl_3$ solvents have also been examined for the mixed dimer complexes at 100 MHz. $Co_2(SEt)_2(tx)_3(dtc)$ exhibits three thioxanthate methylene quartets with slightly different chemical shift ($\delta$) values of 3.31, 3.29, and 3.28 ppm, while the same resonances in $Co_2(SEt)_2(tx)_2(dtc)_2$ and $Co(SEt)_2(tx)(dtc)_3$ appear as a broadened quartet and as a simple unsplit quartet, respectively. Using $CDCl_3$ as solvent, the spectrum of $Co_2(SEt)_2(tx)_3(dtc)$ was found to display only two quartets with $\tau$ values of 3.35 and 3.36 ppm.

Recent proton NMR studies examining coalescence patterns in iron, cobalt, and ruthenium complexes[21,22] have provided mechanistic information regarding intramolecular rearrangement processes. The temperature dependence of the proton NMR spectrum of $Co(tx)(dtc)_2$ was examined at 100 MHz in both $CS_2$ and $CDCl_3$. The former solution was examined in the temperature range −90 to +20° while the latter solution was examined in the temperature range −40 to +20°. In $CDCl_3$ the averaging of a split quartet representing the two thioxanthate methylene protons was clearly seen. In $CS_2$ solvent, however, the quartet representing these same protons never appeared to be split, even at −90°. The dithiocarbamate methylene resonances in both solvents appeared as complex and dissimilar multiplets. In $CDCl_3$ a temperature effect was observed. No attempt was made to simulate the temperature dependence of the line shapes of these multiplets.

**Electronic Spectra.** The electronic spectral bands for four cobalt complexes are presented in Table III. The data are unexceptional apart from a 14-nm shift observed for band 1 in the two monomeric complexes $Co(tx)_3$ and $Co(dtc)_3$. This band is assigned to the $^1A_{1g} \rightarrow {}^1T_{1g}$ transition.[4]

**Table V.** Intramolecular Bond Distances (Å)[a]

| | | | |
|---|---|---|---|
| Co···Co | 3.350 (4) | NS1–CC6 | 1.382 (14) |
| Co–S1 | 2.249 (3) | C8–NS2 | 1.504 (11) |
| Co–S1′ | 2.253 (3) | NS2–CC9 | 1.494 (14) |
| Co–S2 | 2.264 (3) | NS2–C11 | 1.417 (14) |
| Co–S3 | 2.288 (3) | C1–C2 | 1.508 (15) |
| Co–S4 | 2.271 (3) | C4–C5 | 1.493 (17) |
| Co–S5 | 2.291 (4) | CC6–CC7 | 1.517 (20) |
| S1–C1 | 1.832 (11) | CC9–CC10 | 1.605 (19) |
| S2–C3 | 1.696 (10) | C11–C12 | 1.469 (21) |
| S3–C3 | 1.691 (10) | S1···S1′ | 3.008 (5) |
| S4–C8 | 1.690 (10) | S2···S3 (bite) | 2.801 (5) |
| S5–C8 | 1.679 (9) | S4···S5 (bite) | 2.800 (4) |
| C3–NS1 | 1.465 (11) | C1–H1 | 0.94 (10) |
| NS1–C4 | 1.446 (13) | C1–H2 | 0.91 (8) |

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

**Crystallographic Results for $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$.** Table IV contains the final positional, thermal, and occupancy parameters for all atoms with their standard deviations as determined from the inverse matrix of the final least-squares refinement cycles. Tables V and VI summarize intramolecular bond distances and angles, respectively. On deposit are Table VII listing root-mean-square amplitudes of thermal vibration and Table VIII which provides the final observed and calculated structure factor amplitudes (see paragraph at end of paper regarding supplementary material). Finally, Figure 4 shows the atom labeling scheme and the relative orientations of the thermal ellipsoids.

## Discussion

**Reactions and Products.** The reaction of diethylamine with $[Co(SEt)(tx)_2]_2$, eq 3, appears to proceed in the manner

**Table VI.** Intramolecular Bond Angles (deg)[a]

| | | | |
|---|---|---|---|
| S1-Co-S1′ | 83.84 (10) | Co-S4-C8 | 86.1 (3) |
| S1-Co-S2 | 98.59 (12) | Co-S5-C8 | 85.7 (4) |
| S1-Co-S3 | 172.44 (10) | S1-C1-C2 | 112.9 (8) |
| S1-Co-S4 | 91.76 (11) | S2-C3-S3 | 111.6 (5) |
| S1-Co-S5 | 93.94 (11) | S2-C3-NS1 | 125.0 (8) |
| S1′-Co-S2 | 92.73 (11) | S3-C3-NS1 | 123.4 (9) |
| S1′-Co-S3 | 91.13 (11) | S4-C8-S5 | 112.4 (5) |
| S1′-Co-S4 | 98.23 (11) | S4-C8-NS2 | 121.7 (7) |
| S1′-Co-S5 | 173.54 (12) | S5-C8-NS2 | 125.8 (8) |
| S2-Co-S3 | 75.96 (12) | C3-NS1-C4 | 118.0 (11) |
| S2-Co-S4 | 165.67 (10) | C3-NS1-CC6 | 118.0 (11) |
| S2-Co-S5 | 93.60 (11) | C4-NS1-CC6 | 124.0 (9) |
| S3-Co-S4 | 94.55 (12) | C8-NS2-CC9 | 113.6 (8) |
| S3-Co-S5 | 91.65 (11) | C8-NS2-C11 | 118.6 (9) |
| S4-Co-S5 | 75.73 (11) | CC9-NS2-C11 | 126.9 (9) |
| Co-S1-Co′ | 96.16 (10) | NS1-C4-C5 | 110.5 (11) |
| Co-S1-C1 | 110.4 (4) | NS1-CC6-CC7 | 110.3 (13) |
| *Co′-S1-C1* | *106.8 (4)* | NS2-CC9-CC10 | 110.9 (10) |
| Co-S2-C3 | 86.5 (3) | NS2-C11-C12 | 106.8 (13) |
| Co-S3-C3 | 85.9 (4) | H1-C1-H2 | 108.9 (91) |

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

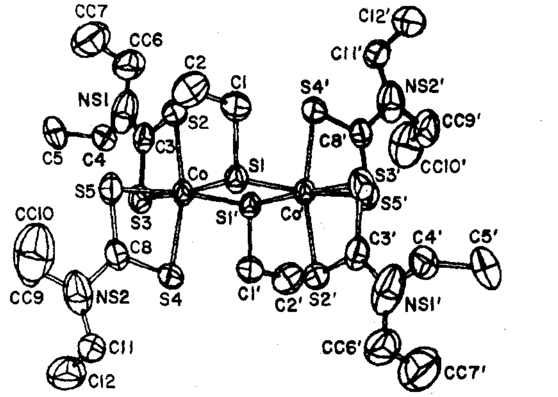


**Figure 4.** Molecular structure of $Co_2(SC_2H_5)_2(S_2CSC_2H_5$-$[S_2CSN(C_2H_5)_2]_3$ showing the atom labeling scheme and the 40% probability thermal ellipsoids. Primed and unprimed atoms are related by a crystallographically required inversion center. The disorder of this molecule is discussed in the text.

suggested by Fackler and Seidel for similar systems.[10] Nucleophilic attack of diethylamine on the carbon atom of the $CS_2$ moiety in each thioxanthate ligand converts the thioxanthate dimer into a dithiocarbamate dimer. Each intermediate in this process, $Co_2(SEt)_2(tx)_n(dtc)_{4-n}$ where $n = 1, 2$, or 3, is stable and has been isolated. At room temperature no intermolecular ligand exchange was found to occur in the mixed-ligand complexes; this result is in accord with the kinetically inert character of low-spin octahedral Co(III) complexes.

The unstable fully dithiocarbamate-substituted complex $[Co(SEt)(dtc)_2]_2$ (identified by proton NMR) decomposes into the two unidentified brown materials and into $Co(dtc)_3$. The reaction sequence involved here is uncertain. The two unidentified brown materials may be intermediates in the ultimate decomposition of $[Co(SEt)(dtc)_2]_2$ into $Co(dtc)_3$. An infrared spectrum of the second brown material (Table II) suggests the presence of dithiocarbamate ligands in the complex. Neither trithiocarbonate nor thioxanthate ligands are present since strong bands in the 900–1000-cm$^{-1}$ region characteristic of these two ligands are absent.[2,4,10] The proton NMR spectrum of this complex has three multiplets centered at approximate $\delta$ values of 3.6, 3.1, and 1.4 ppm. Two distinct methylene proton environments are suggested by this spectrum.

The compound may contain an ionic, uncoordinated dithiocarbamate ligand, which is not without precedence. Alison and Stephenson[23] have isolated the ionic, unstable, chloroform-soluble complex $[Pt(S_2CNEt_2)(PMePh_2)_2]S_2CNEt_2$ from the reaction of $Pt(S_2CNEt_2)_2$ with excess $PMePh_2$. If the brown cobalt complex obtained here is in fact ionic, then the lack of an observed N–H stretching frequency in the 3400-cm$^{-1}$ region indicates that diethylamine is not a coordinated ligand. The ionic species could, however, be related to the novel dimeric complex $[Co_2(S_2CNR_2)_5]^+$ recently reported by Hendrickson and Martin.[24] The $C\overset{\cdots}{=}N$ stretching frequencies in the $[Co_2(S_2CNR_2)_5]^+$ dimers are shifted by 15–19 cm$^{-1}$ to higher energy from the values in the $Co(S_2CNR_2)_3$ monomers. This shift is similar to the 10-cm$^{-1}$ shift observed for the present unidentified brown complex. The instability and red-brown color of this material may be contrasted with the stability and green-brown color of the $[Co_2(S_2CNR_2)_5]^+$ dimers, however.

Studies of the spin equilibria in iron(III) 1,1-dithiolate complexes have shown that thioxanthate ligands provide a slightly stronger crystal field for Fe(III) than do dithiocarbamate ligands.[7,8] By analogy one might expect the crystal field stabilization energies (CFSE) of the binuclear cobalt complexes to decrease as the conversion shown in eq 3 takes place. The electronic spectral data for $Co(tx)_3$ and $Co(dtc)_3$ support this view.

The fully dithiocarbamate-substituted cobalt(III) dimer core decomposes to form the thermodynamically more stable $Co(dtc)_3$ complex, a result not observed in the thioxanthate analog. The rapid decomposition of $[Fe(SEt)(tx)_2]_2$ into $Fe(dtc)_3$ in the presence of diethylamine follows directly from this observation and reflects the fact that iron complexes are usually kinetically more labile than their cobalt analogs. The relative thermodynamic stability of $Fe(dtc)_3$ is manifest in several ways: (1) $Fe(dtc)_3$ is produced in the reaction of $FeCl(dtc)_2$ with sodium phenyl mercaptide; (2) the ligand-exchange reaction of $[Fe(SEt)(tx)_2]_2$ with $Fe(dtc)_3$ led only to the decomposition of the dimer, $Fe(dtc)_3$ being unaffected; (3) Büttner and Feltham[25] have reported an attempt to synthesize a methyl mercaptide bridged dithiocarbamato iron(III) dimer by the oxidative addition of $[(CH_3)_2NCS_2]_2$ to $[Fe(SCH_3)(CO)_3]_2$. Only $Fe(dtc)_3$ was isolated from the reaction mixture.

**The Chloroform Reaction.** A reaction of chloroform and methylene chloride solvents with $Pt(dtc)_2$, when $PR_3$ is present in excess, has recently been reported.[23] The compound $CH_2(S_2CN(C_2H_5)_2)_2$ was isolated from the methylene chloride reaction filtrate, and the platinum-containing product obtained from both solvent media was suggested to be $[Pt(dtc)(PR_3)_2]Cl \cdot H_2O$. Interestingly, the sodium salt of the dithiocarbamate ligand itself has been found to react with $CHCl_3$ and $CH_2Cl_2$; $CH_2(S_2CN(C_2H_5)_2)_2$ can be isolated in high yield from the latter solvent.[26] With chloroform a proton abstraction was postulated, followed by partial decomposition of the *N,N*-dithiocarbamic acid intermediate to give diethylammonium *N,N*-diethyldithiocarbamate.

The chloroform reaction that takes place when $[Fe(SEt)(tx)_2]_2$ is refluxed in the presence of either $Fe(dtc)_3$ or $HN(C_2H_5)_2$ does not occur with the cobalt analogs.[27] Moreover, $Fe(dtc)_3$ and $Fe[S_2CSC(CH_3)_3]_3$ are both inert when refluxed alone in chloroform solution for a few hours. There appears to be a correlation between the breakup of the iron dimer core and the formation of $FeCl(dtc)_2$. In this connection it is interesting to note that one reported synthesis of $FeCl(dtc)_2$ involves the addition of a small quantity of concentrated hydrochloric acid to $Fe(dtc)_3$ in benzene solution.[28] Besides being a source of chloride ions, the acid may serve to labilize the dithiocarbamate functions allowing greater access to the metal center and to the unchelated ligand. With regard to the $FeCl(dtc)_2$ complex itself, its physical properties and crystal structure have already been reported, together with studies of the bromide and iodide analogs.[28-30]

**Proton Nuclear Magnetic Resonance Spectra.** The proton

**Table IX.** Structural Features[a] of Coordinated Thioxanthates and Dithiocarbamates.

| Complex | M–S[b,c] | S–C | S–M–S | M–S–C | S–C–S | Ref |
|---|---|---|---|---|---|---|
| $Co(S_2CNEt_2)_3$ | 2.258 (2) | 1.704 (5) | 76.4 (2) | 86.9 (3) | 109.8 (6) | 32a |
| | 2.267 (3) | 1.718 (5) | 76.3 (1) | 87.4 (3) | 109.5 (5) | 32b |
| $Co(S_2CSEt)_3$ | 2.266 (7) | 1.688 (5) | 76.2 (1) | 85.9 (3) | 111.8 (2) | 6 |
| $[Co(SEt)(S_2CSEt)_2]_2$ | 2.286 $(2)_a$ | 1.687 (7) | 76.4 (2) | 86.1 (3) | 111.9 (4) | 4 |
| | 2.263 $(2)_e$ | | | | | |
| $Co_2(SEt)_2(S_2CSEt)(S_2CNEt_2)_3$ | 2.290 $(3)_a$ | 1.689 (10) | 75.8 (2) | 86.0 (3) | 112.0 (5) | This work |
| | 2.268 $(3)_e$ | | | | | |
| $Fe(S_2CNEt_2)_3$ 298° | | 1.711 (10) | 74.3 (2) | 86.6 (4) | 112.7 (5) | 9c |
| 79° | | 1.721 (4) | 75.9 (1) | 86.5 (2) | 111.1 (2) | |
| $Fe[S_2CN(n\text{-}C_4H_9)_2]_3$ | | 1.71 (2) | 72.7 | | 105 | 9a |
| $Fe[S_2CN(CH_2)_4]_3$ | | 1.70 (3) | 74.5 (5) | 84 (1) | 117 (2) | 9b |
| $Fe(S_2CNMePh)_3$ | | 1.69 (3) | 75.1 (4) | 86 (1) | 114 (2) | 9b |
| $Fe[S_2CS(t\text{-}C_4H_9)]_3$ | | 1.694 (8) | 75.2 (2) | 86.6 (5) | 111.5 (6) | 5 |

[a] Bond distances are in angstroms, and bond angles, in degrees. Root-mean-square deviations or estimated standard deviations are in parentheses. [b] For M = Co only. [c] The subscripts a and e refer to axial and equatorial, respectively, the latter bonds being in the plane of the $M_2(SR)_2$ rhombus.

NMR spectra of all complexes containing the dithiocarbamate ligand show a solvent effect that is illustrated in the spectrum of $Co(dtc)_3$ (Figure 3). Using carbon disulfide as solvent, the methylene protons in this complex display a simple quartet, while in deuteriochloroform the same protons appear as a complex multiplet. If optical inversion occurs slowly on the NMR time scale, then two diastereotopic proton environments exist. When the magnetic nonequivalence at 60 or 100 MHz is sufficiently great, a complex AB splitting pattern for these protons can be expected. Siddall[13] has examined $Co(dtc)_3$ in $CDCl_3$ and has interpreted his data in this way. When $CS_2$ solvent is used, the complex AB splitting disappears. One or both of the following suggestions could apply: (1) optical inversion is much faster in $CS_2$ than in $CDCl_3$, averaging the two proton environments; (2) the chemical shift values for the two protons in $CS_2$ are accidentally degenerate. A third possibility, intermolecular exchange, is considered unlikely since it does not occur when $Co(S_2CSC_2H_5)_3$ and $Co[S_2CN(C_2H_5)_2]_3$ are allowed to interact in $CS_2$ solvent at room temperature over a period of 3 days. The solvent dependence of the *N*-methylene resonance of $Co(dtc)_3$ has been independently observed.[31]

The present temperature-dependent studies of $Co(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_2$ in $CDCl_3$ can be explained by optical inversion. The coalescence phenomena observed for the two diastereotopic thioxanthate proton resonances are unlikely to occur by intermolecular exchange. The compound is stable in $CS_2$ and $CHCl_3$ solvents at room temperature and no species that can be attributed to ligand exchange appear after 3 days.

**Molecular Structure of $Co_2(SC_2H_5)_2(S_2CSC_2H_5)[S_2CN(C_2H_5)_2]_3$.** The structure of the molecule is shown in Figure 4. The centrosymmetric $Co_2(SC_2H_5)_2$ rhombus is rigorously planar with the ethyl groups of the two bridging mercaptide ligands in the anti configuration. Coordination about the cobalt atoms is essentially octahedral with distortions arising, at least in part, from the geometric constraints of four-membered chelate rings. The coordination geometry is basically that of structure IV, with random substitution of thioxanthate for dithiocarbamate in one of every four terminal 1,1-dithiolate sites. The carbon atoms labeled C4, C5, C11, and C12 in Figure 4 are unique to the dithiocarbamate ligands.

The metal–ligand geometry in $Co_2(SEt)_2(tx)(dtc)_3$ is identical with that observed for $[Co(SEt)(tx)_2]_2$.[4] In both structures, the centrosymmetric isomer IV is found to the exclusion of other possible isomers such as III. This observed geometry minimizes nonbonding interactions between the bridging mercaptides and the 1,1-dithiolate ligands. The anti conformation of the bridging ligands, also observed in $[Co(SEt)(tx)_2]_2$[4] and $[Fe(SEt)(tx)_2]_2$,[3] further serves to minimize nonbonding interactions.

The cobalt–cobalt distance of 3.350 (3) Å is 0.03 Å longer than that observed in $[Co(SEt)(tx)_2]_2$. This small difference is statistically significant although unlikely to be of any chemical importance. All other bond distances associated with the core atoms tabulated in Table V are within three standard deviations of those reported for $[Co(SEt)(tx)_2]_2$, and bond angles (Table VI) are all within 1° of those found in the thioxanthate dimer.[4]

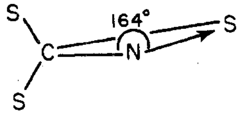
Each $S_2C$ moiety (core atoms) in the disordered dimer is a weighted average of contributions from a thioxanthate and a dithiocarbamate ligand. The structural features for both types of ligand are summarized in Table IX. From the table it is apparent that the present structural results are in excellent agreement with earlier studies of these ligands, as expected from the spectroscopic data discussed above.

In both of the crystallographically independent 1,1-dithiolate coordination sites a group of seven atoms are all within 0.15 Å of being planar. The seven include Co, S2, S3, C3, NS1, CC6, and C4 from one site (plane 1) and Co, S4, S5, C8, NS2, CC9, and C11 from the second site (plane 2) (Figure 4). The methyl carbon atoms C5 and CC7 are geometrically distinctive in that both are located on the same side of plane 1. This unusual feature is not observed for carbon atoms CC10 and C12 which are positioned on opposite sides of plane 2. The latter, or anti, configuration is observed in 11 of 13 diethyldithiocarbamate structural determinations referred to in Table VI of ref 33 and in ref 9c, 29a, 30, 32, and 34; $FeCl[S_2CN(C_2H_5)_2]_2$[29a] and $ReN[S_2CN(C_2H_5)_2]_2$[34c] are exceptions. The proximity of carbon atoms C5 and CC7, 3.36 Å, is substantially less than the sum of their van der Waals radii.[35] An explanation for the presence of this energetically unfavorable conformation is not readily apparent. A short nonbonded contact interaction is also observed for the methyl carbon atom C12, which is just 3.34 Å from a symmetry-related C12 atom in a neighboring unit cell. This interaction, however, occurs in only a fraction of the unit cells, since it depends upon a dithiocarbamate ligand being located in both of the interacting ligand sites. When a thioxanthate ligand is present in the site, its two carbon atoms could occupy positions labeled CC9 and CC10 in order that no interaction with a symmetry-related C12 takes place.

Unlike the $CS_2$ fragments common to both 1,1-dithiolate ligands, the $SC_2H_5$ and $N(C_2H_5)_2$ moieties are not directly superimposed. In the refinement of this structure, however, the close proximity of specific atom pairs from the two moieties required that they be refined as single atoms. These "single atom pairs" are identified in Figure 4 as NS1, NS2, CC6, CC7, CC9, and CC10. The bond angle and bond distance distortions caused by refining the structure in this way are quite evident from Tables V and VI. The $C\overset{\cdots}{-}NS$ bond distances of 1.47 and 1.50 Å agree well with the value of 1.48 Å calculated for a 0.57/0.43 weighted average of ideal 1.31 Å $C\overset{\cdots}{-}N$

and 1.71 Å $\mathrm{C}\underset{\cdots}{-}\mathrm{S}$ bond length values[36] based on electron density and atomic occupancy factors. The NS1–C4 and NS2–C11 bond distances of 1.45 and 1.42 Å are compressed slightly from the ideal N—C bond values of 1.48 Å. The C3–NS1–C4 and C8–NS2–C11 bond angles of 118 and 119° are similarly compressed slightly from the expected C–N–C bond angle of 120°. Other distortions are more difficult to assess because more than one atom pair is involved, but the general trends are chemically reasonable.

In refining the atom pairs it was expected that abnormally asymmetric thermal ellipsoids might help to define the orientation of one atom in the pair relative to the other. Cursory inspection of the thermal ellipsoids reveals NS1 and NS2 to be the only two that are unusually distorted. The angles between the largest principal thermal axes of atoms NS1 and NS2 and the vectors defined by C3–NS1 and C8–NS2 respectively are 90 and 104°. These values may be contrasted with the angle of 164° calculated by assuming that each thermal ellipsoid would be elongated along a vector defined by the ideal positions of the nitrogen and sulfur atoms, V.



V

**Acknowledgment.** We are grateful to the National Institutes of Health for support of this research under Grant No. GM 16449 and to the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant applied to the purchase of the automated diffractometer. We also thank Drs. D. Coucouvanis and H. Rabinowitz for their help.

**Registry No.** $Co_2(SEt)_2(S_2CSEt)_3(S_2CNEt_2)$, 56335-31-0; $Co_2(SEt)_2(S_2CSEt)_2(S_2CNEt_2)_2$, 56363-21-4; $Co_2(SEt)_2(S_2CSEt)(S_2CNEt_2)_3$, 56335-32-1; $Co(S_2CSEt)(S_2CNEt_2)_2$, 56335-33-2; $Co(S_2CNEt_2)_3$, 13963-60-5; $FeCl(S_2CNEt_2)_2$, 36759-32-7; $[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$, 35785-04-7; $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$, 31213-51-1; diethylamine, 109-89-7; $[Co(SEt)(S_2CNEt_2)_2]_2$, 56335-34-3; $Fe(S_2CNEt_2)_3$, 13963-59-2.

**Supplementary Material Available.** Tables VII and VIII, showing amplitudes of vibration and structure factor amplitudes, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (150 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC50178O-11-75.

## References and Notes

(1) Abstracted in part from the Ph.D. dissertation of R. A. Winograd, Columbia University, 1974.

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

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

(4) D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *J. Am. Chem. Soc.*, **94**, 1563 (1972).

(5) D. F. Lewis, S. J. Lippard, and J. A. Zubieta, *Inorg. Chem.*, **11**, 823 (1972).

(6) T.-i Li and S. J. Lippard, *Inorg. Chem.*, **13**, 1791 (1974).

(7) The synthesis and properties of other mononuclear tris(alkyl thioxanthato)iron(III) complexes have been reported: (a) A. H. Ewald and E. Sinn, *Aust. J. Chem.*, **21**, 927 (1968); (b) G. C. Pelizzi and C. Pelizzi, *Inorg. Chim. Acta*, **4**, 618 (1970); (c) S. A. Cotton and J. F. Gibson, *J. Chem. Soc. A*, 803 (1971).

(8) (a) R. L. Martin and A. H. White, *Transition Met. Chem.*, **4**, 299 (1968), and references therein; (b) A. E. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969); (c) R. R. Eley, R. R. Myers, and H. V. Duffy, *ibid.*, **11**, 1128 (1972); (d) B. N. Figgis and T. E. Toogood, *J. Chem. Soc., Dalton Trans.*, 2177 (1972).

(9) (a) B. E. Hoskins and B. P. Kelly, *Chem. Commun.*, 1517 (1968); (b) P. C. Healy and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1163 (1972); (c) J. G. Leipoldt and P. Coppens, *Inorg. Chem.*, **12**, 2269 (1973).

(10) J. P. Fackler and W. C. Seidel, *Inorg. Chem.*, **8**, 1631 (1969).

(11) Other examples in this class are described: (a) J. J. Mayerle, R. B. Frankel, R. H. Holm, J. A. Ibers, W. D. Phillips, and J. F. Weiher, *Proc. Natl. Acad. Sci. U.S.*, **70**, 2429 (1973); (b) M. R. Snow and J. A. Ibers, *Inorg. Chem.*, **12**, 249 (1973); (c) T. Herskovitz, B. V. DePamphilis, W. O. Gillum, and R. H. Holm, *ibid.*, **14**, 1426 (1975).

(12) Abbreviations used in this section: Me, methyl; Et, ethyl; Ph, phenyl; tx, ethyl thioxanthate, $C_2H_5SCS_2^-$; dtc, diethyldithiocarbamate, $(C_2H_5)_2NCS_2^-$.

(13) T. H. Siddall, *Inorg. Nucl. Chem. Lett.*, **7**, 545 (1971).

(14) A. H. White, R. Roper, E. Kokot, H. Waterman, and R. L. Martin, *Aust. J. Chem.*, **17**, 294 (1964).

(15) Excellent separations may also be obtained using carbon disulfide–chloroform solvent mixtures in place of carbon tetrachloride, chloroform, and toluene. Because of the volatility and low flash point of carbon disulfide, however, the latter system is advised.

(16) Programs for the IBM 360-91 computer used in this work include, in addition to various local data reduction routines, TRACER-II, the Lawton lattice transformation and cell reduction program; ORABS, the Wehe–Busing–Levy absorption correction program; XDATA, the Brookhaven Wilson plot and scaling program; FOURIER, the Dellaca and Robinson Fourier program based on Zalkin's FORDAP; CUGLS, a local version of the Busing–Martin–Levy least-squares refinement and structure factor calculation program ORFLS, modified by Ibers and Doedens; ORFFE, the Busing–Martin–Levy molecular geometry and error function program; and ORTEP, the Johnson thermal ellipsoid plotting program.

(17) J. T. Gill and S. J. Lippard, *Inorg. Chem.*, **14**, 751 (1975), and references cited therein.

(18) H. P. Hanson, F. Herman, J. D. Lee, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(19) D. T. Cromer and D. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).

(20) (a) H. C. Brinkhoff, *Inorg. Nucl. Chem. Lett.*, **7**, 413 (1971). (b) Despite ref 20a, intermolecular exchange of dithiocarbamate ligands was not found upon refluxing nitrobenzene-$d_5$ solutions of $Co(S_2CNR_2)_3$ and $Co(S_2CNR'_2)_3$ for several hours at 195°.[21c]

(21) (a) L. H. Pignolet, D. J. Duffy, and L. Que, Jr., *J. Am. Chem. Soc.*, **95**, 295 (1973); (b) B. L. Edgar, D. J. Duffy, M. Palazzotto, and L. H. Pignolet, *ibid.*, **95**, 1125 (1973); (c) M. C. Palazzotto, D. J. Duffy, B. L. Edgar, L. Que, Jr., and L. H. Pignolet, *ibid.*, **95**, 4537 (1973), and references cited therein.

(22) For a review see N. Serpone and D. G. Bickley, *Prog. Inorg. Chem.*, **17**, 391 (1972).

(23) J. M. C. Alison and T. A. Stephenson, *J. Chem. Soc., Dalton Trans.*, 254 (1973).

(24) A. R. Hendrickson and R. L. Martin, *J. Chem. Soc., Chem. Commun.*, 873 (1974).

(25) H. Büttner and R. D. Feltham, *Inorg. Chem.*, **11**, 971 (1972).

(26) P. R. Heckley, D. G. Holah, A. N. Hughes, and F. Leh, *Can. J. Chem.*, **48**, 3827 (1970).

(27) The two unidentified brown materials (Figure 1) gave a negative silver nitrate test when dissolved in concentrated nitric acid.

(28) (a) R. L. Martin and A. H. White, *Inorg. Chem.*, **6**, 712 (1967); (b) H. H. Wickman and A. M. Trozzolo, *ibid.*, **7**, 63 (1968).

(29) (a) B. F. Hoskins and A. H. White, *J. Chem. Soc. A*, 1668 (1970); (b) J. L. K. F. deVries, C. P. Keijzers, and E. de Boer, *Inorg. Chem.*, **11**, 1343 (1972).

(30) P. C. Healy, A. H. White, and B. F. Hoskins, *J. Chem. Soc., Dalton Trans.*, 1369 (1972).

(31) (a) R. M. Golding, P. C. Healy, P. W. G. Newman, E. Sinn, and A. H. White, *Inorg. Chem.*, **11**, 2435 (1972); (b) footnote 12 in R. M. Golding, P. C. Healy, P. Colombera, and A. H. White, *Aust. J. Chem.*, **27**, 2089 (1974).

(32) (a) S. Merlino, *Acta Crystallogr., Sect. B*, **24**, 1441 (1968); (b) T. Brennan and I. Bernal, *J. Chem. Phys.*, **73**, 443 (1969).

(33) R. Eisenberg, *Prog. Inorg. Chem.*, **12**, 295 (1970).

(34) (a) D. Johnston, W. Rohrbaugh, and W. DeW. Horrocks, *Inorg. Chem.*, **10**, 1474 (1971); (b) S. R. Fletcher and A. C. Skapski, *J. Chem. Soc. Dalton Trans.*, 1073 (1972); (c) S. R. Fletcher and A. C. Skapski, *ibid.*, 1079 (1972).

(35) L. Pauling, "The Nature of the Chemical Bond", 3rd ed, Cornell University Press, Ithaca, N.Y., 1960, p 260.

(36) Ideal values quoted here are based upon information available in ref 3, 4, 6, and 32.