TABLE VII

MULLIKEN ATOMIC CHARGES AND DIPOLE MOMENT

H_1	0.063	H_3	0.036	Be	0.584
H_2	0.093	B_1	−0.52	D	4.17

TABLE VIII

OVERLAP POPULATIONS

B–Be	0.256	B–H_2	0.860	Be–H_3	0.310
B–H_1	0.874	B–H_3	0.522		

tions, given in Tables VII and VIII, indicate that the Be–B bonding involves a certain amount of ionic character. However, to the extent that covalent interactions are important, bonding seems to occur about equally through Be–H and Be–B, somewhat to our surprise. The bridge hydrogens are less positive than terminal hydrogens, opposite to the order found in the boron hydrides.[20–22] However, the significance of this observation is somewhat questionable due to the lack of optimized exponents for systems containing beryllium[23] and due to the use of a minimum-basis set of Slater orbitals.

The increase of the Be–B_2 bond length to 2.00 Å in the solid probably indicates an increase in the ionic character of the Be–B_2 interaction relative to Be–B_1. A degree of ionic character for one of the Be$\cdots$$BH_4$ interactions in the solid, as found in the crystal structure, is consistent with the infrared spectra of the solid,[24] but the helical polymeric chains in the solid suggest some compromise between extremes of covalency (the finite molecule) and of ionicity (an infinite three-dimensional ionic solid). Concerning the probable gas-phase structure, we wish to suggest a close relationship to the appropriate fragment of this solid-state structure, but we dare not do so!

Acknowledgment.—We wish to thank the Office of Naval Research and the Advanced Research Projects Agency for support of this study. Also support of D. S. M. by a National Science Foundation predoctoral fellowship is especially gratefully acknowledged.

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The Crystal and Molecular Structure of Tris(*tert*-butyl thioxanthato)iron(III)

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The structure of tris(*tert*-butyl thioxanthato)iron(III) has been determined in a single-crystal X-ray diffraction study. The coordination geometry of the iron atom is a distorted octahedron of sulfur atoms contributed by the three chelating thioxanthate ligands. The distortion may be expressed in terms of a twist angle $\alpha = 42°$, compared to the value of $\alpha = 60°$ required for a regular octahedron. The mean iron–sulfur bond distance is 2.297 (7) Å, and S–Fe–S intrachelate angle, 75.2 (2).° The geometries of coordinated 1,1-dithiolate ligands in the present and several related tris-chelate metal complexes are summarized. There is a significant amount (10–30%) of double-bond character in the C–X bond for coordinated $^{-}S_2CX$ (X = OR, SR) ligands, although appreciably less than for analogous dithiocarbamate (X = NR_2) compounds (40–50%). The complex $Fe(S_2CSC_4H_9)_3$ crystallizes in the triclinic system, space group $P\bar{1}$, with $a = 19.44$ (1) Å, $b = 5.917$ (4) Å, $c = 11.016$ (6) Å, $\alpha = 100.36$ (1)°, $\beta = 86.30$ (1)°, $\gamma = 90.84$ (2)°. The measured density of 1.48 ± 0.01 g/cm³ requires two molecules per unit cell ($\rho_{\text{calcd}} = 1.474 \pm 0.001$ g/cm³). From 2330 independent, statistically significant reflections collected by diffractometer, the structure was solved by the usual Patterson and Fourier synthesis methods. Least-squares refinement of all atoms including hydrogen converged at values for $R_1 = 0.060$ and $R_2 = 0.085$.

Introduction

The preparation and properties of tris(*tert*-butyl thioxanthato)iron(III) have been described previously.[2,3] Since detailed structural information about tris-1,1-dithiolate complexes is still relatively scarce,[4,5] an X-ray diffraction study of $(tert\text{-}C_4H_9SCS_2)_3Fe$ was carried out. Recently the independent synthesis of $Fe(S_2CSR)_3$ complexes was described, and the ethyl derivative was found to be diamagnetic.[6] This result is in apparent contradiction to the earlier magnetic work of Ewald and Sinn[2] and was ascribed to "spin pairing through a Fe–Fe interaction . . . or through a Fe–S–S–Fe interaction between molecules or a change in symmetry due to packing."[6] The information obtained from the structural investigation of $(tert\text{-}C_4H_9SCS_2)_3Fe$ may have some bearing on these suggestions, as will be discussed.

Experimental Procedure and Results

Collection and Reduction of X-Ray Data.—The complex, prepared as described previously,[3] crystallizes at 0° from CS_2–pentane as long black needles. Several of these were me-

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TABLE I[a,b]

Final Positional and Thermal Parameters of the Atoms

Atom	x	y	z	β_{11}[c]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Fe	0.2457 (1)	−0.2152 (2)	0.0344 (1)	1.46 (4)	20.4 (5)	7.2 (1)	0.17 (9)	−0.14 (5)	4.2 (2)
S1	0.1783 (1)	0.0809 (4)	0.0027 (2)	1.98 (6)	18.0 (7)	10.1 (2)	0.4 (2)	−0.59 (9)	2.7 (3)
S2	0.1711 (1)	−0.3817 (4)	−0.1092 (2)	2.24 (6)	17.8 (7)	10.1 (2)	1.6 (2)	−1.4 (1)	1.5 (3)
S3	0.3150 (1)	−0.5321 (4)	0.0161 (2)	1.80 (6)	23.3 (8)	10.2 (2)	0.5 (2)	0.08 (9)	8.6 (3)
S4	0.3355 (1)	−0.1552 (4)	−0.1041 (2)	2.10 (6)	22.4 (8)	9.6 (2)	1.9 (2)	1.0 (1)	8.1 (4)
S5	0.1804 (1)	−0.3053 (4)	0.1998 (2)	1.92 (6)	27.5 (8)	9.1 (2)	−2.3 (2)	−0.01 (1)	4.6 (3)
S6	0.2924 (1)	−0.0008 (4)	0.2041 (2)	1.97 (6)	29.8 (8)	6.7 (2)	−2.3 (2)	0.05 (9)	4.8 (3)
S7	0.0693 (1)	−0.0268 (4)	−0.1686 (2)	2.79 (7)	23.0 (8)	13.3 (3)	1.4 (2)	−2.4 (1)	5.5 (4)
S8	0.4359 (1)	−0.5681 (3)	−0.1572 (2)	2.32 (6)	22.1 (8)	11.7 (3)	2.5 (2)	1.3 (1)	6.9 (4)
S9	0.2094 (1)	−0.0628 (4)	0.4458 (2)	2.67 (7)	31.8 (9)	7.3 (2)	−1.4 (2)	0.41 (9)	6.3 (4)
C1	0.1364 (4)	−0.120 (1)	−0.0984 (8)	1.6 (2)	22 (3)	9.3 (9)	1.1 (7)	0.8 (4)	6 (1)
C2	0.3667 (4)	−0.412 (1)	−0.0872 (7)	1.8 (2)	14 (3)	6.9 (8)	1.7 (6)	−0.6 (3)	3 (1)
C3	0.2303 (4)	−0.115 (1)	0.2886 (7)	1.5 (2)	22 (3)	7.1 (8)	0.1 (7)	0.2 (3)	5 (1)
C4	0.0236 (4)	−0.273 (2)	−0.2532 (9)	2.2 (3)	31 (4)	12 (1)	2.0 (8)	−1.1 (4)	3 (2)
C5	0.4938 (4)	−0.385 (1)	−0.2383 (7)	2.0 (2)	31 (3)	6.0 (8)	0.2 (7)	0.8 (3)	5 (1)
C6	0.2723 (4)	0.131 (1)	0.5283 (7)	2.3 (3)	18 (3)	7.4 (9)	1.1 (7)	0.3 (4)	2 (1)
C7	−0.0363 (6)	−0.159 (3)	−0.303 (1)	2.3 (3)	62 (6)	15 (2)	3 (1)	−3.4 (6)	6 (2)
C8	0.0698 (6)	−0.408 (3)	−0.360 (1)	3.3 (4)	64 (6)	10 (1)	5 (1)	−0.9 (6)	−5 (2)
C9	−0.0057 (6)	−0.421 (2)	−0.162 (1)	2.7 (4)	33 (5)	17 (2)	−1.7 (9)	−1.6 (6)	7 (2)
C10	0.4586 (6)	−0.311 (2)	−0.345 (1)	2.9 (4)	55 (5)	8 (1)	2 (1)	0.4 (5)	11 (2)
C11	0.5521 (5)	−0.552 (2)	−0.289 (1)	2.6 (3)	42 (4)	10 (1)	4.7 (9)	1.7 (5)	7 (2)
C12	0.5186 (5)	−0.184 (2)	−0.151 (1)	2.1 (3)	32 (4)	11 (1)	0.2 (9)	0.1 (4)	2 (2)
C13	0.3441 (6)	0.037 (2)	0.499 (1)	3.1 (4)	33 (4)	12 (1)	2 (1)	−0.9 (5)	6 (2)
C14	0.2497 (6)	0.131 (2)	0.663 (1)	4.0 (4)	43 (5)	8 (1)	1 (1)	0.1 (5)	4 (2)
C15	0.2659 (7)	0.373 (2)	0.498 (1)	4.0 (4)	22 (4)	13 (1)	1 (1)	−0.1 (6)	6 (2)

Final Positional Parameters of the Hydrogen Atoms[d]

Atom	x	y	z	Atom	x	y	z
H7A	−0.013 (6)	−0.08 (2)	−0.36 (1)	H11C	0.544 (6)	−0.61 (2)	−0.40 (1)
H7B	−0.069 (6)	−0.04 (2)	−0.22 (1)	H12A	0.543 (6)	−0.21 (2)	−0.07 (1)
H7C	−0.064 (6)	−0.29 (2)	−0.34 (1)	H12B	0.544 (6)	−0.11 (2)	−0.17 (1)
H8A	0.073 (6)	−0.34 (2)	−0.46 (1)	H12C	0.480 (6)	−0.07 (2)	−0.10 (1)
H8B	0.034 (6)	−0.58 (2)	−0.41 (1)	H13A	0.363 (7)	0.04 (2)	0.44 (1)
H8C	0.104 (6)	−0.44 (2)	−0.33 (1)	H13B	0.379 (7)	0.13 (2)	0.55 (1)
H9A	−0.038 (6)	−0.29 (2)	−0.05 (1)	H13C	0.347 (7)	−0.07 (2)	0.53 (1)
H9B	0.031 (6)	−0.50 (2)	−0.16 (1)	H14A	0.281 (6)	0.25 (2)	0.73 (1)
H9C	−0.023 (6)	−0.55 (2)	−0.22 (1)	H14B	0.246 (6)	−0.01 (2)	0.69 (1)
H10A	0.492 (6)	−0.26 (2)	−0.40 (1)	H14C	0.194 (6)	0.18 (2)	0.68 (1)
H10B	0.420 (6)	−0.21 (2)	−0.32 (1)	H15A	0.290 (6)	0.37 (2)	0.42 (1)
H10C	0.438 (6)	−0.43 (2)	−0.39 (1)	H15B	0.215 (6)	0.39 (2)	0.52 (1)
H11A	0.590 (6)	−0.47 (2)	−0.32 (1)	H15C	0.306 (6)	0.45 (2)	0.53 (1)
H11B	0.573 (6)	−0.62 (2)	−0.23 (1)				

[a] Atoms are labeled as indicated in Figure 2. [b] Standard deviations, in parentheses, occur in the last significant figure for each parameter. [c] The form of the anisotropic ellipsoid is given in the text. Values reported are $\times 10^3$. [d] Hydrogen atoms are labeled to correspond to the carbon atom to which they are attached. Each hydrogen atom was assigned a fixed isotropic thermal parameter $B = 6$ Å^2.

chanically cleaved to produce prismatic fragments which were mounted for study on the ends of glass fibers. Although the compound was found to decompose upon standing in air as judged by the evolution of a highly unpleasant odor and by anomalous magnetic behavior, special precautions were not found to be necessary for the single-crystal X-ray studies. Thus the standard reflections measured on the diffractometer during data collection (*vide infra*) gave no apparent indication of crystal decomposition.

Precession photographs using Ni-filtered Cu Kα radiation (λ 1.5418 Å) revealed no zones with Laue symmetry greater than $\bar{1}$ and no systematic absences. Triclinic unit cell parameters from the film data were refined by a least-squares method to give the best fit between observed and calculated settings for χ, ϕ, and 2θ for 20 independent reflections which were centered in the counter window of a Picker full-circle automated diffractometer.[7] The resultant parameters are $a = 19.44 \pm 0.01$ Å, $b = 5.917 \pm 0.004$ Å, $c = 11.016 \pm 0.006$ Å, $\alpha = 100.36 \pm 0.01°$, $\beta = 86.30 \pm 0.01°$, and $\gamma = 90.84 \pm 0.02°$. These parameters may be transformed into the equivalent unit cell defined by $a = 5.917$ Å, $b = 11.016$ Å, $c = 19.44$ A, $\alpha = 86.30°$, $\beta = 89.16°$, and $\gamma = 79.64°$, which satisfies the conditions for a positive type I reduced cell with no hidden symmetry.[8] The original parameters were used in all subsequent calculations. The density computed from the unit cell volume ($V = 1244$ Å^3) on the basis of two formula units of $C_{15}H_{27}S_9Fe$ per unit cell was 1.474 ± 0.001 g/cm^3, in substantial agreement with the value 1.48 ± 0.01 g/cm^3 experimentally observed by flotation in aqueous KI solution. The choice of space group $P\bar{1}$ was confirmed by the subsequent solution and successful refinement of the structure. The analogous cobalt derivative $Co(S_2CSR)_3$ (R = *tert*-C_4H_9), the chemistry of which is fully described elsewhere,[9] was found to be isomorphous.

Using a fragment of approximate dimensions 0.11 mm along a^*, 0.15 mm along b^*, and 0.32 mm along c^*, with b^* as the mounting axis, intensity measurements were taken with Ni-filtered Cu Kα radiation at *ca.* 22° on the Picker four-angle programmed diffractometer. The data were measured by the θ–2θ scan technique at a takeoff angle of 3°. A symmetric scan range of 1.25° was used for $2\theta \leqslant 90°$, and 1.5° was used for $2\theta > 90$. The scan rate was 1°/min, with stationary-counter, stationary-crystal background counts of 10 sec being measured at both ends of the scan. The (300), (002), ($\bar{2}$13), and (020)

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(7) Programs for an 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, 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.

(8) "International Tables for X-Ray Crystallography," Vol. I, 3rd ed, Kynoch Press, Birmingham, England, 1969, p 530 ff.

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

reflections were used to monitor the crystal and instrument stability after every 100 reflections. The integrated intensities of these standards varied randomly by less than ±3% of the mean values for the entire run. The data were collected with the indices of the shortest reciprocal cell edges varying fastest ($h > l > k$). A total of 2726 independent reflections within the sphere defined by $\theta \leqslant 49°$ were obtained.

The observed intensities were corrected for background, use of attenuators, Lorentz, polarization, and absorption effects (μ = 117 cm^{-1}) using ACAC-3 as described previously.[10] The resultant transmission factors ranged from 0.18 to 0.32. The value of ϵ used in determining $\sigma(I)$[10] was set at 0.04. Approximately 400 reflections for which $I \leqslant 3\sigma(I)$ were excluded from the refinement. The observed data were not corrected for secondary extinction.

Determination and Refinement of the Structure.—A sharpened Patterson map was computed[7] using the corrected data. The map was contoured and solved for the coordinates (x, y, z) in the space group $P\bar{1}$ of the iron and six surrounding sulfur atoms. These positional coordinates were refined by least-squares methods for two cycles, and the resulting parameters were used in the calculation to produce a set of phased structure factors for a difference Fourier synthesis. This revealed the remaining three sulfur atoms and nine carbon atoms. Phasing on these atoms resulted in the location of the remaining six carbon atoms in the asymmetric unit. Five cycles of refinement on the positional parameters and anisotropic temperature factors of the 25 atoms led to convergence at values of 0.071 and 0.103 for the discrepancy factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = (\Sigma w \cdot (|F_o| - |F_c|)^2/\Sigma w F_o^2)^{1/2}$, respectively. In the refinement the weights, w, were taken as $4F_o^2/\sigma^2(F_o^2)$. Scattering factors for the zerovalent Fe, S, C, and H atoms were taken from ref 11, with the effects of anomalous dispersion[12] being included in the contributions of Fe and S to the calculated structure factors. The form of the anisotropic temperature factor is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. A difference Fourier calculated at this stage revealed several peaks of electron density ~0.6 e/Å^3 on a scale where the values for the carbon atoms ranged from 3 to 5 e/Å^3. Twenty-seven of these were at positions reasonable for hydrogen atoms. Subsequent introduction and refinement of their positional parameters, with their isotropic thermal parameters fixed at 6.0, reduced R_1 to 0.060 and R_2 to 0.085. During these calculations the parameters were included in two or three matrices, the positional and thermal parameters of a given atom and of atoms bonded to each other being refined simultaneously every second or third cycle (this blocking of parameters probably resulted in standard deviations that are underestimated somewhat). The final difference Fourier map showed no regions of significant electron density, and the structure was thus considered to be complete.[13]

The atomic positional and thermal parameters, along with their standard deviations as derived from the inverse matrix of the last least-squares cycle of refinement for that atom, are given in Table I. The root-mean-square amplitudes of vibration derived from the unit cell constants and the atomic anisotropic thermal parameters are summarized in Table II. Figure 1 shows a stereoscopic view of the packing of molecules in the unit cell. The atom-labeling scheme and relative orientations of the thermal ellipsoids are shown in Figure 2. A description of the molecular geometry in terms of bond distances and angles may be found in Tables III and IV.

Discussion

The Coordination Geometry.—The structure (Figure 1) consists of monomeric tris(*tert*-butyl thioxanthato)-iron(III) molecules of approximate octahedral sym-

TABLE II

ROOT-MEAN-SQUARE AMPLITUDES OF VIBRATION (IN Å)[a,b]

Atom	Min	Intermed	Max
Fe	0.167 (3)	0.174 (2)	0.213 (2)
S1	0.172 (4)	0.195 (3)	0.246 (3)
S2	0.156 (3)	0.201 (3)	0.261 (4)
S3	0.158 (4)	0.185 (3)	0.263 (3)
S4	0.155 (4)	0.183 (3)	0.271 (3)
S5	0.161 (3)	0.231 (3)	0.239 (4)
S6	0.158 (3)	0.205 (3)	0.245 (3)
S7	0.159 (4)	0.226 (3)	0.301 (3)
S8	0.162 (4)	0.199 (3)	0.288 (3)
S9	0.170 (3)	0.236 (3)	0.248 (3)
C1	0.16 (1)	0.17 (1)	0.25 (1)
C2	0.13 (2)	0.19 (1)	0.21 (1)
C3	0.16 (1)	0.18 (1)	0.22 (1)
C4	0.18 (1)	0.24 (1)	0.27 (1)
C5	0.15 (1)	0.21 (1)	0.24 (1)
C6	0.17 (1)	0.20 (1)	0.23 (1)
C7	0.14 (2)	0.32 (2)	0.34 (2)
C8	0.22 (2)	0.24 (2)	0.38 (2)
C9	0.21 (2)	0.24 (1)	0.34 (2)
C10	0.19 (1)	0.23 (1)	0.32 (1)
C11	0.18 (2)	0.23 (1)	0.31 (1)
C12	0.20 (2)	0.24 (1)	0.26 (1)
C13	0.21 (2)	0.26 (1)	0.28 (1)
C14	0.21 (1)	0.26 (1)	0.29 (1)
C15	0.19 (2)	0.27 (1)	0.29 (1)

[a] Taken along the principal axes of the thermal ellipsoids, the orientations of which may be seen from Figure 2. [b] See footnotes *a* and *b*, Table I.

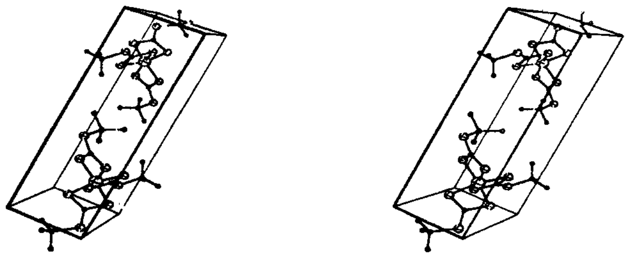

Figure 1.—A stereoscopic view of the structure showing the packing of molecules in the unit cell.

TABLE III[a,b]

Intramolecular Bond Distances, Å

Fe–S1	2.292 (3)	C3–S9	1.727 (8)
Fe–S2	2.296 (3)	S7–C4	1.834 (9)
Fe–S3	2.297 (3)	S8–C5	1.851 (8)
Fe–S4	2.310 (2)	S9–C6	1.833 (8)
Fe–S5	2.291 (3)	C4–C7	1.532 (8)
Fe–S6	2.294 (2)	C4–C8	1.536 (9)
S1–C1	1.713 (9)	C4–C9	1.530 (10)
S2–C1	1.681 (8)	C5–C10	1.525 (8)
S3–C2	1.711 (8)	C5–C11	1.525 (8)
S4–C2	1.687 (8)	C5–C12	1.479 (8)
S5–C3	1.690 (8)	C6–C13	1.504 (8)
S6–C3	1.684 (7)	C6–C14	1.519 (8)
C1–S7	1.703 (8)	C6–C15	1.538 (8)
C2–S8	1.708 (8)	C–H(av)[c]	1.0 (2)

Nonbonded Intramolecular Contacts, Å

S1···S2	2.798 (3)	S2···S5	3.369 (4)
S1···S4	3.427 (3)	S3···S4	2.802 (3)
S1···S5	3.426 (3)	S3···S5	3.344 (4)
S1···S6	3.336 (3)	S3···S6	3.456 (4)
S2···S3	3.397 (4)	S4···S6	3.407 (4)
S2···S4	3.447 (4)	S5···S6	2.803 (3)

[a] See footnotes *a* and *b*, Table I. [b] Reported values have not been corrected for thermal motion. Note also that the value for the C9–H9A bond distance, 1.4 Å, is abnormally long. Apparently H9A refined to an unrealistic position, and bond distances and (especially) angles involving C9 may be slightly affected. [c] Range is 0.8–1.2 Å (see footnote *b*).

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

(11) "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1969, pp 202, 204.

(12) Reference 11, p 213 ff.

(13) 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 or $2.00 for microfiche.

TABLE IV

SELECTED INTRAMOLECULAR BOND ANGLES (DEG)[a]

S1–Fe–S2	75.15 (8)	Fe–S5–C3	86.1 (3)
S3–Fe–S4	74.93 (8)	Fe–S6–C3	86.1 (3)
S5–Fe–S6	75.37 (9)	S5–C3–S6	112.4 (5)
S1–Fe–S3	166.4 (1)	S5–C3–S9	117.0 (4)
S1–Fe–S4	96.26 (9)	S6–C3–S9	130.6 (5)
S1–Fe–S5	96.76 (9)	C3–S9–C6	111.1 (4)
S1–Fe–S6	93.35 (10)	S7–C4–C7	102.7 (5)
S2–Fe–S3	95.42 (9)	S7–C4–C8	111.6 (5)
S2–Fe–S4	96.96 (10)	S7–C4–C9	108.8 (5)
S2–Fe–S5	94.51 (9)	S8–C5–C10	111.0 (4)
S2–Fe–S6	163.9 (1)	S8–C5–C11	101.3 (4)
S3–Fe–S5	93.64 (9)	S8–C5–C12	111.0 (4)
S3–Fe–S6	97.68 (10)	S9–C6–C13	110.8 (4)
S4–Fe–S5	164.50 (9)	S9–C6–C14	102.6 (4)
S4–Fe–S6	95.47 (9)	S9–C6–C15	110.0 (5)
Fe–S1–C1	86.6 (3)	C7–C4–C8	111.0 (6)
Fe–S2–C1	87.2 (3)	C7–C4–C9	108.5 (5)
S1–C1–S2	111.0 (5)	C8–C4–C9	113.6 (6)
S1–C1–S7	117.2 (5)	C10–C5–C12	111.4 (5)
S2–C1–S7	131.7 (5)	C10–C5–C11	109.8 (5)
C1–S7–C4	110.0 (4)	C11–C5–C12	111.9 (5)
Fe–S3–C2	86.9 (2)	C13–C6–C15	112.0 (5)
Fe–S4–C2	87.1 (3)	C13–C6–C14	110.7 (5)
S3–C2–S4	111.1 (4)	C14–C6–C15	110.4 (5)
S3–C2–S8	117.1 (4)	H–C–H (av)	109 (5)
S4–C2–S8	131.8 (5)		
C2–S8–C5	109.7 (4)		

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

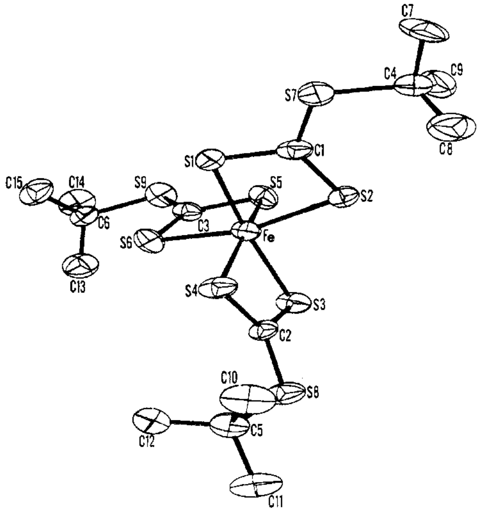
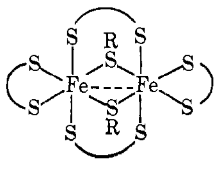


Figure 2.—The molecular structure showing the atom-labeling scheme and the 50% probability ellipsoids. Hydrogen atoms are omitted for clarity.

metry (Figure 2). Equal numbers of *d* and *l* enantiomers are accommodated by the centrosymmetric lattice. The distortion from regular octahedral symmetry around each iron atom is demonstrated by the angles S1–Fe–S3, S2–Fe–S6, and S4–Fe–S5 which are 166.4 (1), 163.9 (1), and 164.5 (1)°, respectively (Figure 2). Similar results have been obtained for related tris(1,1-dithiolate)iron(III) compounds (*cf.* the value of 164.1° in $Fe(S_2COC_2H_5)_3$).[5f] A major source of the distortion from perfect octahedral symmetry is the constraint imposed on the geometry of the molecule by the four-membered chelate rings, in which the S–Fe–S angles have been reduced from their normal values of 90° to ~75° (Table IV).[10]

The influence of small-ring constraints on the metal–ligand geometry is discussed in more detail elsewhere.[10] The present results confirm and extend the earlier analysis, as may be seen by comparing the S···S bite and S–C bond distances and Fe–S–C and C–S–C angles (Tables III and IV) with the values obtained previously.[5,9,10] The average Fe–S bond length of 2.297 ± 0.007 Å in $(\textit{tert}\text{-}C_4H_9SCS_2)_3Fe$ may be compared with the value of 2.338 ± 0.004 Å for the Fe–S distance in the terminal thioxanthate chelate rings of the ethyl thioxanthate dimer, $[Fe(S_2CSC_2H_5)_2(SC_2H_5)]_2$, structure I.[10] The shorter bond length in the *tert*-butyl



I

analog is consistent with the greater inductive effect of the branched-chain alkyl group and is comparable to the Fe–S bond length (2.287 ± 0.002 Å) in the bridging chelate rings of the dimer I.

A geometric parameter of interest in describing the structures of tris-1,1-dithiolate complexes is the twist angle, α, defined as the angle through which one triangular face perpendicular to the pseudo-threefold axis of the coordination polyhedron is rotated with respect to the parallel triangular face.[5a,f] In a regular octahedral complex, $\alpha = 60°$, whereas a trigonal-prismatic structure would have a completely eclipsed configuration, with $\alpha = 0°$. For $(\textit{tert}\text{-}C_4H_9SCS_2)_3Fe$, the dihedral angle between the two nearly equilateral (Table III) triangles defined by S_1–S_4–S_6 and S_2–S_3–S_5 is 1.0 ± 0.2°, and α is computed to be 42 ± 2°. The latter result is in good agreement with the value of $\alpha = 41°$ obtained for $Fe(S_2COC_2H_5)_3$.[5f] In both of these complexes the thermal equilibrium between the two possible ground states, $^2T_2 \rightleftharpoons {}^6A_1$, lies largely to the left at room temperature.[2,3,14] In the predominantly high-spin $[(n\text{-}C_4H_9)_2NCS_2]_3Fe$ complex, however, $\alpha = 32°$.[5a] It would therefore appear that the ground-state electronic configuration can combine with the geometric constraints imposed by the four-membered chelate rings to distort even further these tris-1,1-dithiolate complexes from pseudooctahedral toward trigonal-prismatic geometries.[15] The relationship between such observed solid-state distortions and the intramolecular rearrangement reactions of tris-chelate complexes in solution has been recently discussed.[16]

Geometry and Bonding within the Thioxanthate Ligands.—A least-squares best-plane calculation through each of the three (FeS_2CS) atom groupings reveals them to be nearly planar. The mean and maximum deviations of individual atoms from the planes are 0.024 and 0.043 Å, respectively.

Examination of the average C–S distances in the thioxanthate ligands (Table III) reveals an appreciable contribution of canonical form IV, as noted earlier in the determination of several related structures.[4,5,9,10]

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[14] A. H. Ewald, R. L. Martin, E. Sinn, and A. H. White, *Inorg. Chem.*, **8**, 1837 (1969), and references cited therein.

[15] It should be noted, however, that the structure of $[(n\text{-}C_4H_9)_2NCS_2]_3$-Fe[5a] has not yet been reported in sufficient detail to enable a completely satisfactory comparison with the geometries of other tris-1,1-dithiolate complexes.

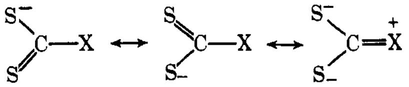
[16] L. H. Pignolet, R. A. Lewis, and R. H. Holm, *J. Amer. Chem. Soc.*, **93**, 360 (1971).

TABLE V

COMPARISON OF RELATIVE CONTRIBUTIONS OF RESONANCE FORMS II–IV FOR SEVERAL TRIS-1,1-DITHIOLATE COMPLEXES[a]

Compound	X	S–C, Å Calcd	S–C, Å Obsd	C–X, Å Calcd	C–X, Å Obsd	% contribution II	% contribution III	% contribution IV	Ref
$Fe(S_2COC_2H_5)_3$	O	1.677	1.685	1.322	1.328	39	39	22	5f
$Co(S_2COC_2H_5)_3$	O	1.669	1.673	1.359	1.359	43.5	43.5	13	5d
$Fe[S_2CS(\textit{tert}\text{-}C_4H_9)]_3$	S	1.683	1.694	1.702	1.713	36	36	28	*b*
$[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$[c]									
Terminal ligand	S	1.677	1.679	1.718	1.720	39	39	22	10
Bridging ligand	S	1.672	1.680	1.737	1.743	42	42	16	10
$[Co(SC_2H_5)(S_2CSC_2H_5)_2]_2$	S	1.682	1.688	1.704	1.708	36.5	36.5	27	9
$Co[S_2CN(C_2H_5)_2]_3$	N	1.699	1.704	1.314	1.319	29	29	42	5b
		1.709	1.718	1.297	1.308	24.5	24.5	51	5c
$Ni[S_2CN(n\text{-}C_4H_9)_2]_3{}^+$	N	1.699	1.707	1.314	1.322	29	29	42	5e

[a] See text and ref 5b and 5d for definition of terms and discussion. [b] This work. [c] Structure I.



II III IV

Using the Pauling bond order–bond length relation (1)

$$r_x = r_1 - (r_1 - r_2)\frac{3x}{2x + 1} \qquad (1)$$

as stated by Merlino,[5b,d] where x is the fractional double-bond character ($0 \leqslant x \leqslant 1$) in a bond of length r_x, with the single-bond length (r_1) taken as S—C = 1.812 Å, C—O = 1.437 Å, and C—N = 1.475 Å and the double-bond distances (r_2) as S═C = 1.607 Å, C═O = 1.185 Å, and C═N = 1.24 Å,[5b,d] the relative contributions of resonance forms II–IV to the overall electronic structures of coordinated 1,1-dithiolate ligands in several complexes were computed. The results are summarized in Table V. Omitted from the tabulation are data for the complex $Fe[S_2CN(n\text{-}C_4H_9)_2]_3$,[5a] since the observed bond lengths were not in good agreement with values calculated from eq 1 for any values of x.[15] Comparison of the per cent contributions for the two independent crystallographic determinations of tris(*N*,*N*-diethyldithiocarbamato)cobalt(III) places a lower limit of ±10% on the reliability of such calculations. Furthermore, no attempt has been made to correct for any shortening of the C–X bonds which, being adjacent to a sterically constrained ring, might be expected to be somewhat contracted.[17] Nevertheless, it is clear from Table V that, in the xanthate and thioxanthate complexes, exocyclic double-bond delocalization occurs to a significant extent (13–28%) but much less than in related dialkyldithiocarbamate complexes (42–51%). This conclusion has been reached previously on the basis of infrared, structural,[4,5] and other criteria.[19] The results for tris(*tert*-butyl thioxanthato)iron(III) are quite similar to those for the other thioxanthate structure determinations summarized in Table V.

A further point of interest with regard to the ligand geometry is the nonequivalence of the angles S–C–S [for example, S1–C1–S7 = 117.2 (5)° and S2–C1–S7 = 131.7 (5)°] and S–C–C [for example, S7–C4–C8 = 111.6 (5)°, S7–C4–C9 = 108.8 (5)°, and S7–C4–C7 = 102.7 (5)°] within each *tert*-butyl thioxanthate ligand. Reference to Table IV and Figure 2 clearly reveals for each ligand that the larger S–C–S angle occurs on the same side of the ligand as the *tert*-butyl group. Also, the small S–C–C angle always involves the carbon atom directed away from the coordinated sulfur atom. Both of these distortions serve to minimize nonbonded contacts between the methyl groups and the sulfur atoms of the ligand. For the thioxanthate ligand cited in the above example, the nonbonded contact distances less than 3 Å are as follows (Figure 2): S7···H7A, 2.7 Å; S7···H7B, 2.8 Å; S7···H8C, 2.8 Å; S7···H9A, 2.8 Å; S2···H8C, 2.8 Å; S2···H9B, 2.9 Å. These values may be compared to the sum of the van der Waals radii for sulfur and hydrogen atoms, 3.05 Å.[20] Clearly the observed distortions, noted in previous structural determinations of xanthate and thioxanthate complexes,[5d,f,9,10] serve to minimize intraligand nonbonded repulsions.

Finally, the effect of substituting the *tert*-butyl group in $RXCS_2^-$ ligands for smaller ethyl groups is quite evident. In $[Fe(SC_2H_5)(S_2CSC_2H_5)_2]_2$ and $Fe(S_2COC_2H_5)_3$, the larger of the two S–C–X angles is approximately 126°; for the $(\textit{tert}\text{-}C_4H_9SCS_2)_3Fe$ complex, the average value is 131.4°.

Crystal Packing and Intermolecular Interactions in $Fe(S_2CSR)_3$ Complexes.—Inspection of an extensive listing of interatomic distances revealed no iron–sulfur intermolecular contacts under 4 Å and no sulfur–sulfur intermolecular contact less than 3.48 Å, the packing of monomeric tris(*tert*-butyl thioxanthato)iron(III) molecules in the lattice being determined primarily by van der Waals interactions (Figure 1). This behavior is typical for tris-1,1-dithiolate complexes,[4,5] although recent work[21] revealed a binuclear structure for $(C_2H_5)_4N[Pb(S_2COC_2H_5)_3]$. Apparently, the long metal–sulfur bond lengths (2.84–3.13 Å) in the lead complex expand the coordination sphere of the metal atom to permit dimerization through an even longer intermolecular interaction (3.68 Å).

Assuming that the present structure determination can serve as a prototype for $Fe(S_2CSR)_3$ complexes, the explanation suggested by Pelizzi and Pelizzi to account for their observation that "$Fe(S_2CSC_2H_5)_3$" is diamagnetic[6] seems implausible. Since tris(alkyl thioxanthate)metal(III) complexes of iron and cobalt are known[3,14] to eliminate carbon disulfide in solution according to eq 2, it seems more likely to us that the ob-

$$2M(S_2CSR)_3 \longrightarrow [M(SR)(S_2CSR)_2]_2 + 2CS_2 \qquad (2)$$

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[17] Note, however, that in bicyclopropyl, the internal and external C–C bond lengths are identical.[18]

[18] O. Bastiansen and A. de Meijera, *Angew. Chem.*, **78**, 142 (1966).

[19] For references, see D. Coucouvanis, *Progr. Inorg. Chem.*, **11**, 233 (1970).

[20] L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 260.

[21] W. G. Mumme and G. Winter, *Inorg. Nucl. Chem. Lett.*, **7**, 505 (1971).

served diamagnetism resulted from material that had dimerized, possibly upon recrystallization of an authentic sample of $Fe(S_2CSC_2H_5)_3$. This suggestion is further supported by the fact that solution electronic spectra (especially the visible and near-ir bands) reported in ref 6 for the iron thioxanthate complexes correspond more closely to the results for the dimers[3] than for the monomeric $Fe(S_2CSR)_3$ compounds.[2,3] The results of the crystal structure analysis of $(n\text{-}C_3H_7SCS_2)_3Fe$, reportedly in progress,[6] will be of interest.

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The Crystal and Molecular Structure of Diiodocarbonylferrocene-1,1′-bis(dimethylarsine)nickel(II). A Nickel(II) Carbonyl Complex

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The crystal and molecular structure of the five-coordinate complex diiodocarbonylferrocene-1,1′-bis(dimethylarsine)-nickel(II), $NiI_2(CO)(fdma)$, has been determined from three-dimensional X-ray data collected by the θ–2θ scan technique. The structure was solved by standard heavy-atom methods and has been refined by least-squares procedures to a conventional R factor of 0.038 for 1733 nonzero reflections. The complex crystallizes in space group $P2_12_12_1$ of the orthorhombic system in a cell of dimensions a = 15.16 (1), b = 11.51 (1), c = 12.01 (1) Å, and V = 2096 Å^3. There are four molecules per unit cell (ρ_{exptl} = 2.32 (2) g/cm^3; ρ_{calcd} = 2.326 g/cm^3). The coordination geometry about the Ni(II) ion is a nearly regular trigonal bipyramid with the fdma ligand occupying both an axial and an equatorial position. The $Ni\text{–}As_{ax}$ and $Ni\text{–}As_{eq}$ bond lengths are 2.310 (3) and 2.331 (3) Å, respectively. The carbonyl ligand is located in the other axial position with an Ni–C bond length of 1.82 (2) Å. The fdma ligand chelates with a stepped configuration in which the Ni, Fe, and two As atoms are not coplanar. The dihedral angle between the $NiAs_2$ and $FeAs_2$ planes is 46.6 (1)°. The cyclopentadienyl rings exhibit a twist angle (ω) of 8.8° from the completely eclipsed configuration.

Introduction

Many five-coordinate low-spin Ni(II) complexes have been reported within the past decade,[2] and a number of them have been structurally characterized by single-crystal X-ray methods.[3–10] In none of these systems, however, has carbonyl been found to exist within the coordination sphere. This apparent reluctance of Ni(II) to coordinate CO is well known and has been ascribed to the relatively stable and contracted 3d orbitals of the Ni(II) ion which render back-donation into the carbonyl π^* functions much less effective.[11,12] It was therefore of some structural interest when Bishop and Davison[13] reported the complexes $NiI_2(CO)(fdma)$ and $NiI_2(CO)(fdpa)$ (fdma = ferrocene-1,1′-bis(dimethylarsine) and fdpa = ferrocene-1,1′-bis(diphenylarsine)) as authentic five-coordinate carbonyl complexes of Ni(II). We report herein the structure determination of the $NiI_2(CO)$(fdma) complex which was undertaken in part to establish the coordination geometry about the Ni(II) ion in these systems.

A second important reason for examining the structure of $NiI_2(CO)$(fdma) lies in establishing the chelating properties of the fdma ligand, which at least generically is similar to the well-studied chelating agent *o*-phenylenebis(dimethylarsine) or diars.[14] The most significant difference between these two ligand systems is that whereas the C–C distance within the five-membered chelate ring in diars complexes is approximately 1.40 Å, the corresponding C···C separation in fdma complexes is at least the ferrocene inter-ring distance of *ca.* 3.30 Å. In order to take this increased separation and its consequent steric effects into account, Bishop and Davison[15] have proposed two different chelate conformations for the fdma (and fdpa) ligands. In the first case (structure I), the cyclopentadienyl rings are in a staggered configuration and the metal–fdma moiety possesses C_2 symmetry, whereas in the second case (structure II), the rings are in an eclipsed configuration and the metal, the two As donor atoms, and the ferrocene Fe are no longer coplanar. This latter conformation has been called "stepped"

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(1) National Institutes of Health Predoctoral Fellow, 1969–1971.

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