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Crystal Structure of Beryllium Borohydride

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The crystal structure of $Be(BH_4)_2$ consists of a helical polymer of BH_4Be and BH_4 units. Within the BH_4Be unit the Be···B distance is 1.918 ± 0.004 Å, while each Be is linked to two remaining BH_4 units (and each BH_4 to two Be) at a Be···B distance of 2.001 ± 0.004 Å. Within the BH_4Be units there are two hydrogen bridges between B and Be, and in the helical polymer each B···Be contact has two hydrogen bridges. The hydrogen arrangement about Be is approximately a trigonal prism, but the H atoms are much closer to B (about 1.1 Å) than to Be (1.5–1.6 Å). The crystal structure is tetragonal, the space group is $I4_1cd$, with $a = 13.62 \pm 0.01$ Å and $b = 9.10 \pm 0.01$ Å. The disagreement factor is $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.04$ for the 276 distinct diffraction maxima. A self-consistent field wave function based upon a minimum Slater set of orbitals yields charges of about 0.6 on Be, −0.5 on B, and 0.04–0.09 on H atoms of the three types. Bonding from Be to BH_4 occurs about equally directly from Be to B as compared with bonding through bridge hydrogen atoms.

Beryllium borohydride, first synthesized in 1940 by Burg and Schlesinger,[1] has been the subject of many experimental[2-7] and some theoretical[8,9] studies. Both linear and triangular arrangements for B–Be–B have been proposed, with a variety of arrangements for bonds toward hydrogen atoms. An earlier X-ray diffraction study[10] established the correct space group and gave indirect evidence that the solid consisted of discrete molecules. However, prior to our preliminary report[11] the structure of beryllium borohydride in the solid phase was completely unknown. We present here the results of our single-crystal X-ray diffraction study, which has established that the solid consists of helical polymers, with a crystallographic polymeric unit, shown in Figure 1, a chemical repeat, shown in Figure 2, and a c-axis projection, shown in Figure 3.

Experimental Section

Beryllium borohydride was prepared by the reaction of beryllium chloride and lithium borohydride.[12] Commercial beryllium chloride (Alfa Inorganics) was dried *in vacuo* for 24 hr before use. Lithium borohydride (K & K) was purified by dissolving it in dry diethyl ether, followed by filtration under a nitrogen atmosphere and *in vacuo* evaporation and drying. The reaction was allowed to proceed at 155° for 6 hr. Yields which were obtained are comparable to those reported.

Beryllium borohydride has a vapor pressure of about 6 mm at room temperature and sublimes readily to form colorless crystals which are often irregularly shaped. Crystals suitable for X-ray analysis were grown as follows. About 1–5 mg of the compound was transferred from a vacuum line into a bulb made from 6-mm glass tubing, one end of which had previously been drawn into a capillary and sealed. The bulb was then sealed off from the vacuum line. Crystals were grown by immersing the bulb (but not the end drawn into a capillary) into a water bath at about 45°. This process was repeated until a single irregularly shaped crystal of approximate dimensions 0.5 × 0.5 × 0.5 mm was found near the top of the capillary. The capillary was then *carefully* sealed off from the bulb. This unusual care was necessary because of the unusually reactive, pyrophoric, and toxic properties of this compound.

The crystals are tetragonal, as indicated by Laue symmetry D_{4h}. The unit cell parameters, $a = 13.62 \pm 0.01$ and $c = 9.10 \pm 0.01$ Å, were determined by a least-squares fit of six reflections from measurements made with the use of a Picker automated diffractometer. Assumption of 16 formula weights in the unit cell leads to a reasonable calculated density of 0.609 g cm^{-3}. However, no experimental value is available for comparison. Weissenberg photographs of levels 1–7 about b taken with Cu Kα radiation established systematic absences of hkl when $h + k + l$ is odd, $h0l$ when l is odd, and hhl when $2h + l = 4n + 1$, 2, or 3. Thus, the space group is $I4_1cd$, in agreement with the result of the earlier study.[10]

Intensities were recorded on the Picker automated diffractometer with the use of Ni-filtered Cu Kα radiation. A 2θ scan of 1°/min was used, and stationary background counts of 10 sec were taken 1° before and after the scan. The crystal was about 10 cm from the source and 10 cm from the detector. A 1-mm collimator was employed for the incident beam, which was at a takeoff angle of 4°, and the diffracted beam passed through a 2-mm collimator. After every 50 reflections, three zero-level check reflections were measured, but no significant variations in the intensities of these check reflections were found. All intensity data were taken on one crystal at 5°, in order to prevent sublimation of the crystal in the capillary. The crystal was mounted with the b axis nearly coincident to ϕ, and all accessible reflections having 2θ less than 110° were recorded. Included in this set were four to eight symmetry-equivalent reflections for each unique diffraction maximum. The absorption coefficient, $\mu = 1.08$, is so small that no absorption corrections were necessary for a crystal of the size noted above. After application of Lorentz and polarization corrections, the data yielded a correlation value of $R = \Sigma_{hkl}|I_{hkl} - \bar{I}_{hkl}|/\Sigma\bar{I}_{hkl} = 0.057$, where I_{hkl} is the intensity of reflection hkl and $\bar{I}_{hkl}$ the average value of reflection hkl. An initial estimate of the scale factor was obtained by Wilson's method, but this scale factor was subsequently refined. Two hundred and eighty-one unique diffraction maxima were recorded, of which 276 were used in the refinement.

Solution and Refinement of Structure.[13]—The three nonhydrogen atoms were located by analysis of the three-dimensional Patterson function and two-dimensional symmetry minimum function.[14,15] From the Patterson function a B–Be–B bond angle of about 120° was determined, assuming Be between two B atoms, and the relative z coordinates were obtained. One atom was assigned arbitrarily a coordinate $z = 0$, inasmuch as the origin along z is arbitrary in the spcae group $I4_1cd$.

The symmetry minimum function $S(x, y, z)$ summarizes all of

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(10) A. J. Stosick, *Acta Crystallogr.*, **5**, 151 (1952).

(11) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **93**, 2322 (1971).

(12) H. I. Schlesinger, H. C. Brown, and E. K. Hyde, *ibid.*, **75**, 209 (1953).

(13) A listing of 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.

(14) P. G. Simpson, K. Folting, R. D. Dobrott, and W. N. Lipscomb, *J. Chem. Phys.*, **39**, 2339 (1963).

(15) P. G. Simpson, R. D. Dobrott, and W. N. Lipscomb, *Acta Crystallogr.*, **18**, 169 (1965).

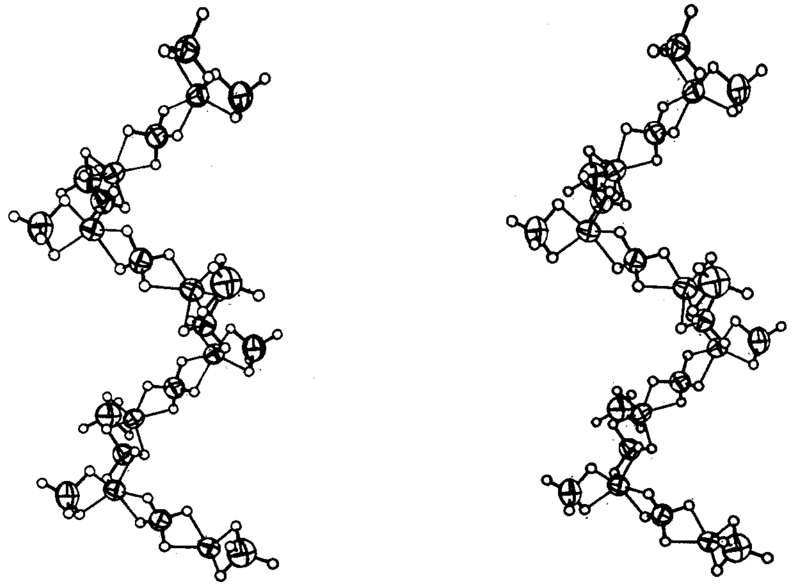

Figure 1.—Stereoview of the beryllium borohydride polymer.

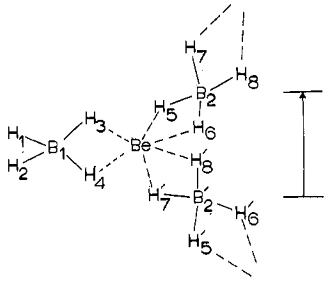

Figure 2.—The chemical repeat of the beryllium borohydride polymer.

the atomic positional information contained in the symmetry regions of the Patterson function. Essentially, $S(x, y, z)$ consists of all of the one-atom solutions to the Patterson function. Only two distinct sets of coordinates were consistent with both the 120° bond angle and the symmetry minimum function, and these sets were related by simply interchanging x and y. The correct choice of coordinates was then easily found by structure factor and Fourier analysis.

The unrefined coordinates of Be and B yielded a value of $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.38$, assuming an isotropic thermal parameter of 4.6 Å^2 obtained from a Wilson plot. Subsequent refinement of coordinates, isotropic thermal parameters, and the scale factor lead to a value of $R = 0.23$. The function minimized in these refinements was $\Sigma w(k^2|F_o|^2 - |F_c|^2)^2$, where $\sqrt{w} = 1/|F_o|^2$ for $|F_o| > 5.0$, $\sqrt{w} = 1/5.0|F_o|$ for $|F_o| < 5.0$, and k is the scale factor.

A difference electron density map at this point revealed only four of the eight hydrogens, several other peaks in chemically unreasonable positions, and residual peaks at the boron and beryllium positions. The isotropic thermal parameter of one of these hydrogens diverged upon several cycles of least-squares refinement in which R reached only 0.21. For this reason the boron and beryllium coordinates with anisotropic thermal parameters were refined to $R = 0.168$. No hydrogen atoms were included in this refinement. A new difference map then clearly showed seven hydrogens, which were included in subsequent refinements with isotropic thermal parameters. Refinement then yielded $R = 0.10$. A third difference map located the last hydrogen atom, and successive further refinements in which isotropic thermal parameters were used for hydrogen atoms gave $R = 0.050$. Because of the probable anisotropic nature of this polymeric structure, anisotropic thermal parameters for all atoms were subjected to two cycles of least-squares refinement, yielding a final R value of 0.040. A final difference map showed no peak higher than 7 on a scale on which a hydrogen atom is 60.

Self-Consistent Field Calculation.—Since the polymeric nature of the solid precludes the calculation of an accurate SCF wave function, we have undertaken a study of one $Be(BH_4)_2$ unit of the polymer, idealized to C_{2v} geometry, in order to study the bonding. This calculation should provide some indication of the relative degrees of ionic and covalent character of the bonding. The LCAO-SCF calculation was carried out with the program described by Stevens.[16] A minimum basis set of Slater orbitals was used, and all molecular integrals were accurately evaluated. For the orbital exponents we chose 1.2 for hydrogen, and Slater values for the boron and beryllium 1s, 2s, and 2p orbitals. Bond lengths were assumed to be $B-H_t = 1.21$ Å, $B-H_b = 1.30$ Å, $Be-H_b = 1.58$ Å, and $B-Be = 1.94$ Å. Coordinates are listed in Table I.

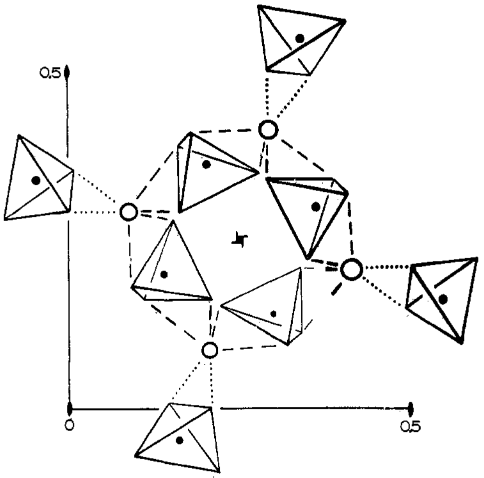

Figure 3.—Portion of the unit cell, showing one helical polymeric chain around a 4_1 axis and projected along the c axis.

TABLE I

COORDINATES FOR BERYLLIUM BOROHYDRIDE MO STUDY[a]

	x	y	z
H_1	−0.909	5.121	0.0
H_2	−4.252	2.997	0.0
H_3	−1.194	1.878	1.990
H_4	−1.194	1.878	−1.990
H_5	−1.194	−1.878	1.990
H_6	−1.194	−1.878	−1.990
H_7	−0.909	−5.121	0.0
H_8	−4.252	−2.997	0.0
B_1	−1.965	3.095	0.0
B_2	−1.965	−3.095	0.0
Be	0.0	0.0	0.0

[a] Coordinates in atomic units.

Geometric Results

The solid state contains helical polymers situated about crystallographic 4_1 axes (Figure 1). Half of the BH_4 units link beryllium atoms in the polymeric chain, while the remaining BH_4 units are linked to one beryllium atom only. Of the eight different H atoms in the formula $Be(BH_4)_2$, only two (H_1 and H_2) are not involved in some degree of bonding to beryllium. The hydrogen coordination about beryllium is approxi-

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TABLE II

COORDINATES AND ANISOTROPIC THERMAL PARAMETERS[a,b]

Atom	x	y	z	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
B_1	0.1638 (3)	−0.0491 (2)	0.0090 (6)	115 (3)	71 (2)	238 (7)	−41 (4)	74 (4)	10 (8)
B_2	0.1386 (2)	0.1935 (2)	0.1204 (5)	65 (2)	66 (2)	158 (4)	4 (3)	−2 (6)	−15 (5)
Be	0.1998 (2)	0.0869 (2)	0.0	65 (2)	68 (2)	131 (5)	−4 (3)	−21 (53)	2 (6)
H_1	0.0955 (26)	−0.0687 (30)	0.0598 (58)	93 (23)	132 (30)	388 (96)	−72 (52)	15 (96)	109 (900)
H_2	0.2193 (28)	−0.1012 (26)	−0.0418 (39)	144 (30)	72 (23)	220 (75)	47 (46)	57 (84)	−48 (71)
H_3	0.2069 (17)	−0.0033 (20)	0.0982 (33)	72 (16)	35 (13)	150 (54)	−8 (31)	−7 (56)	21 (50)
H_4	0.1413 (20)	0.0083 (19)	−0.0841 (29)	92 (20)	43 (16)	102 (48)	−39 (32)	−44 (48)	−66 (46)
H_5	0.1054 (16)	0.1564 (16)	0.0252 (23)	54 (15)	46 (13)	15 (32)	1 (25)	−6 (35)	−7 (35)
H_6	0.2122 (15)	0.1626 (17)	0.1404 (27)	29 (14)	52 (16)	94 (41)	13 (25)	1 (49)	−80 (46)
H_7	0.1450 (14)	0.2714 (13)	0.1015 (25)	30 (13)	17 (11)	86 (36)	1 (19)	−37 (37)	−17 (38)
H_8	0.0899 (20)	0.1850 (15)	0.2261 (36)	71 (18)	36 (14)	173 (47)	1 (27)	107 (59)	−40 (45)

[a] Standard deviations in the last significant figure are in parentheses. [b] Anisotropic temperature factors are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$.

mately trigonal prismatic; however the average distance from Be to H_5, H_6, H_7', and H_8' is 1.62 Å, compared with 1.53 Å for the average from Be to H_3 and H_4. Both of these distances are longer than the only other known beryllium–hydrogen bridge of 1.48 Å in $NaOEt_2 \cdot Et_4Be_2H_2$.[17] The average B–H bond lengths are 1.14 Å to B_1 and 1.11 Å to B_2 in the $Be(BH_4)_2$ crystal structure, but all of these distances are expected to be short by about 0.1 Å because of the use of spherical atoms in the refinement[18] and neglect of torsional oscillation. The two BH_4 units are approximately tetrahedral with the exception of the H_1–B_1–H_2 angle of 127°. Distances for B_1–Be = 1.92 Å and Be–B_2 = Be–B_2' = 2.00 Å are comparable with 1.94 Å, the sum of covalent radii.[19] The shortest interhelical H–H and B–B contacts are 2.73 and 3.74 Å, respectively. Parameters in Table II yield the bond lengths and angles in Tables III and IV. Rms displacements are listed in Table V.

TABLE III

BOND LENGTHS (Å)

Be–B_1	1.918 (4)	B_1–H_4	1.19 (3)	Be–H_4	1.54 (3)
Be–B_2	2.001 (4)	B_2–H_5	1.10 (2)	Be–H_5	1.61 (2)
Be–B_2'	1.999 (5)	B_2–H_6	1.10 (2)	Be–H_6	1.65 (2)
B_1–H_1	1.07 (4)	B_2–H_7	1.08 (2)	Be–H_7'	1.61 (2)
B_1–H_2	1.14 (4)	B_2–H_8	1.17 (3)	Be–H_8'	1.59 (2)
B_1–H_3	1.18 (3)	Be–H_3	1.52 (3)		

TABLE IV

BOND ANGLES (DEG)

B_1–Be–B_2	124.8 (0.5)	H_5–B_2–H_8	112 (2)	H_4–Be–H_6	151 (2)
B_1–Be–B_2'	123.5 (0.5)	H_6–B_2–H_7	109 (2)	H_4–Be–H_7'	93 (2)
H_1–B_1–H_2	127 (3)	H_6–B_2–H_8	110 (2)	H_4–Be–H_8'	118 (2)
H_1–B_1–H_3	105 (3)	H_7–B_2–H_8	106 (2)	H_5–Be–H_6	67 (2)
H_1–B_1–H_4	104 (3)	H_3–Be–H_4	76 (2)	H_5–Be–H_7'	91 (2)
H_2–B_1–H_3	106 (3)	H_3–Be–H_5	116 (2)	H_5–Be–H_8'	143 (2)
H_2–B_1–H_4	107 (3)	H_3–Be–H_6	93 (2)	H_6–Be–H_7'	109 (2)
H_3–B_1–H_4	106 (2)	H_3–Be–H_7'	151 (2)	H_6–Be–H_8'	90 (2)
H_5–B_2–H_5	109 (2)	H_3–Be–H_8'	92 (2)	H_7'–Be–H_8'	69 (2)
H_5–B_2–H_7	111 (2)	H_4–Be–H_5	94 (2)		

TABLE V

RMS AMPLITUDES AND DIRECTION COSINES[a] OF THERMAL MOTION

Atom	Rms amplitude	Cos A	Cos B	Cos C
B_1	0.242	0.362	0.928	−0.091
	0.316	−0.028	0.109	0.994
	0.340	0.932	−0.357	0.065
B_2	0.241	0.928	−0.362	−0.091
	0.247	0.109	0.028	0.994
	0.263	0.357	0.932	−0.065
Be	0.225	−0.548	−0.033	−0.836
	0.250	0.483	0.803	−0.348
	0.258	0.683	−0.595	−0.425
H_1	0.249	0.799	0.558	−0.227
	0.357	0.583	−0.624	0.520
	0.430	−0.150	0.548	0.823
H_2	0.225	−0.326	0.287	0.458
	0.313	0.153	0.524	−0.838
	0.383	−0.933	−0.203	−0.297
H_3	0.178	−0.088	−0.976	0.199
	0.250	−0.464	−0.137	−0.875
	0.264	−0.881	0.169	0.441
H_4	0.116	−0.300	−0.705	−0.642
	0.250	0.064	0.657	−0.751
	0.306	−0.952	0.266	0.152
H_5	0.079	0.040	0.056	0.998
	0.207	−0.070	0.996	−0.053
	0.226	0.997	0.068	−0.044
H_6	0.130	−0.382	0.615	0.689
	0.169	−0.918	−0.105	−0.362
	0.265	−0.109	−0.771	0.628
H_7	0.119	0.297	0.876	0.380
	0.146	0.769	−0.455	0.448
	0.212	−0.566	−0.159	0.809
H_8	0.159	0.412	−0.762	−0.499
	0.208	0.631	0.634	−0.448
	0.323	−0.658	0.130	−0.742

[a] Direction cosines are relative to crystallographic axes.

TABLE VI

TOTAL ENERGIES AND EIGENVALUES[a]

Energies	
Nuclear attraction	−260.319
Nuclear repulsion	52.418
Two-electron	71.415
Kinetic	68.088
Total	68.398
$-E/T$	1.0046

Orbital Eigenvalues

−7.623	−0.759	−0.484
−7.623	−0.579	−0.464
−4.864	−0.528	−0.457
−0.822	−0.491	−0.019[b]

[a] Energies in atomic units. [b] Unoccupied.

Results of SCF Calculation

The total energies, orbital eigenvalues, and the virial ratio are given in Table VI. We note that the total energy for this structure is considerably lower than has been obtained from other *ab initio* calculations[9] on assumed structures for $Be(BH_4)_2$. The relatively low eigenvalue of the lowest unoccupied orbital suggests that the structure may form a stable negative ion in a nonreactive environment.

The Mulliken atomic charges and overlap popula-

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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···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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[23] Recent studies in this laboratory (D. S. Marynick, J. Hall, and W. N. Lipscomb, to be submitted for publication) have shown that optimum Be 2s and 2p exponents are generally closer to 1.2 than the Slater value of 0.975; however, this is not expected seriously to affect our results.

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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 ($\rho_{calcd} = 1.474 \pm 0.001$ 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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