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The Crystal and Molecular Structure of $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$, A Monomeric, Five-Coordinate Dithiolene Complex of Iron

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The crystal and molecular structure of the title compound shows it to be monomeric in the solid state. The central iron atom has a square-pyramidal coordination geometry defined by the two perfluoromethyldithiolene ligands and the As atom of the axial $(C_6H_5)_3As$ group. The crystals are triclinic with a = *12.537(7),* b = *12.803(4),* c = *10.436(7) Å, α = 96.67(4), β = 92.30(2), γ = 117.21(6)°, ρ_o = 1.79(2), ρ_c = 1.82 gm cm^{-3} and z = 2. Least squares refinement of the positional and anisotropic thermal parameters yield final discrepancy factors of $R_1(F)$ = 0.047 and $R_2(F)$ = 0.059 for the 3703 structure factors with $F_o^2 \geqslant 3\sigma(F_o^2)$. The bonding parameters of the S–C–C–S fragment of the perfluoromethyldithiolene are closer to a dithioketone than a dithiol. The iron atom is not in the plane of the four sulfurs; instead, it is displaced 0.23 Å from the basal plane. The Fe–S bonds are short and range in length from 2.145(2) to 2.154(2) Å. The C–S bond lengths have an average value of 1.702 Å which is significantly shorter than those found for maleonitriledithiol complexes. The Fe–As distance of 2.325(2) Å is a little longer than the ones found for iron–arsine complexes of olefins. Short As–S* intramolecular *contacts were found in this molecule.*

Introduction

The initial preparation by Schrauzer [3] and by Gray and co-workers [4] of first-row transition metal complexes of *cis*-dithiols has been followed by extensive work directed towards understanding these substances. Our interest in bis-dithiolene complexes of iron began with the report [5] that at room temperature an acetone solution of the triphenylmethylphosphonium salt of the bis(maleonitriledithiolato)iron(III) ion, $Fe(MNT)_2^-$, has a magnetic susceptibility which corresponds to three unpaired electrons per metal atom; however, the $Fe(MNT)_2^-$ anion has been shown [6] to exist as discrete, compact dianion dimers $[Fe(MNT)_2]_2^{2-}$ in the solid state and measurements of the magnetic susceptibility [7] of the tetraethyl ammonium salt of this dimer clearly showed antiferromagnetic interactions between ions *via* a superexchange mechanism which involves the sulfur atoms. The structure of the isoelectronic $[Co(S_2C_2\{CF_3\}_2)_2]_2$ reveals [8] that this neutral molecule also exists as a compact dimer with the metals linked *via* a sulfur bridge. The stability of these dimeric species has been demonstrated [9] by their ability to undergo oxidation–reduction reactions without rupture of the dimer linkage. The stability of monomeric, four-coordinate, bis-dithiolene complexes has been discussed in connection with the structural determinations of several of these compounds [10–13].

Later, it was discovered that the dimeric species may be cleaved [14, 15] by certain *mono* and bidentate ligands to yield five and six-coordinated products, respectively. Of these, the compounds prepared by Balch [14] were of particular interest to us since he showed that the reaction of dimeric $[Fe(S_2C_2\{CF_3\}_2)_2]_2$ with ϕ_3P(As, Sb) yields a pentacoordinated, monomeric, neutral product formulated as $\phi_3XFe(S_2C_2\{CF_3\}_2)_2$. For X = P, it was found [14] that the neutral molecules can be reduced to monomeric anions whose magnetic susceptibility, at room temperature, corresponds to that of an s = 3/2 species, later shown [14b] to be $\phi_3POFe(S_2C_2\{CF_3\})_2$.

We, therefore, decided to ascertain the following: (a) the precise molecular geometry of the species in question (b) the intermolecular contacts in case any were either suspiciously short or outright indications of molecular association (c) the relationship between these substances and others with unusual spin states such as $Fe(MNT)_3^{2-}$, known to be an s = 1 species [17]. Here, we report the structure of the neutral, parent arsine.

Experimental

Unit Cell and Space Group

Crystals of $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$, mol. wt. = 914.4, are triclinic P1 with cell parameters *a* = 12.537(7), *b* = 12.803(4), *c* = 10.436(7), α = 96.67 (4)°, β = 92.30(2)°, γ = 117.21(6)°. The volume of the unit cell is 1473 Å^3; ρ_o = 1.79 g cm^{-3} by flotation in an aqueous $ZnBr_2$ solution, $\rho_c = 1.82$ g cm^{-3} for two molecules per unit cell. The total number of electrons in the unit cell, F(000) = 944. The choice of the centrosymmetric space group was verified by the satisfactory refinement of the structure.

X-Ray Data Collection

Crystals of $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$ were generously supplied by Professor A. L. Balch. These air stable, well shaped crystals are prismatic in form and deep red in color. One crystal was ground to a sphere of radius 0.35 mm and mounted on a programmed General Electric diffractometer equipped with a scintillation counter, a pulse height analyzer and controlled by a Datex system. Twenty reflections were carefully centered and used to define the orientation of the crystal on the diffractometer and to determine the cell parameters.

The data were collected by the θ–2θ scan technique at a scan rate of 1°/minute with Mo $K\bar{\alpha}$ radiation at a take-off angle of 2°. Stationary-counter background counts were taken for twenty seconds at each end of the 2θ scan range. The diffracted beams were filtered through niobium foil. The scan width and background points were varied with the Bragg angle to account for changes in the width of the peak and for the white radiation which remains on the low 2θ side of the peak when a niobium filter is used with Mo $K\alpha$ radiation.

The scan for a particular reflection hkl began at $2\theta_{\mathrm{low}} = 2\{\sin^{-1}(\lambda_{\mathrm{Mo\,K}\alpha_1}/2d_{\mathrm{hkl}})\} - \mathrm{CSCAN}$ if $\Delta_{\mathrm{hkl}} > \mathrm{CSCAN}$ or at $2\theta_{\mathrm{low}} = 2\{\sin^{-1}(\lambda_{\mathrm{Mo\,K}\alpha_1}/2d_{\mathrm{hkl}})\} - k\Delta$ if $\Delta_{\mathrm{hkl}} \leqslant \mathrm{CSCAN}$ where Δ_{hkl} is given by $2\{\sin^{-1}(\lambda_{\mathrm{Mo\,K}\alpha_1}/2d_{\mathrm{hkl}}) - \sin^{-1}(\lambda_{\mathrm{Nb}}/2d_{\mathrm{hkl}})\}$. For this crystal, CSCAN was 1.00° and k was 0.50. The scan was completed when $2\theta_{\mathrm{high}} = 2\{\sin^{-1}(\lambda_{\mathrm{Mo\,K}\alpha_2}/2d_{\mathrm{hkl}})\} + \mathrm{CSCAN}$. The pulse height analyzer was adjusted to receive approximately 90% of the diffracted radiation. The intensities of two standard reflections were measured periodically; no decay was discernible, and no individual measurement differed from the average by more than 3%. The intensities of nearly 7000 reflections in one asymmetric unit with $2\theta \leqslant 60°$ were measured.

The data were corrected for Lorentz and polarization effects. No absorption corrections were made. For $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$ the linear absorption coefficient for Mo $K\bar{\alpha}$ radiation is estimated from atomic absorption coefficients [18] to be 20.2 cm^{-1} and the transmission factors vary by less than 1% for a sphere of radius 0.35 mm. The estimated standard deviation was obtained from the expression $\sigma(F_o^2) = 1/L_p[(I + B)^2 + (0.05\,I)^2)^{1/2}$ where L_p is the Lorentz-polarization factor, I is the total integrated peak and B is the time scaled-background [19]. Those structure amplitudes for which $F_o^2 \leqslant 3\sigma(F_o^2)$ were considered to be unobserved. The remainder were averaged (where necessary) and the result of this procedure was 3703 independent data.

Determination of the Structure

An unsharpened, three-dimensional Patterson function was calculated using the complete set of data and interpreted to yield the approximate coordinates of the arsenic, iron, and four sulfur atoms. The remaining non-hydrogen atoms were located by a succession of difference Fourier syntheses which included the largest 1200 structure amplitudes. This trial structure was refined by a least squares procedure in which the C_6H_5 rings were treated as rigid groups (C–C = 1.395 Å, C–H = 1.00 Å) with individual, isotropic thermal parameters. The function minimized was $\Sigma w\Delta^2$, where $\Delta = |F_o| - |F_c|$ with $|F_o|$ and $|F_c|$ the observed and calculated structure amplitudes and $w = 4F_o^2/\sigma^2(F_o^2)$. Throughout the refinement the atomic scattering factors of Cromer [20] were used, and anomalous dispersion corrections for As, Fe and S [21] were applied to the calculated structure factors. The initial refinement, based on the largest 1200 structure amplitudes and carried out with all atoms constrained to *isotropic* vibration, converged to values of $R_1(F)$ and $R_2(F)$ of 0.145 and 0.162. Refinement of the structure using the 3703 independent reflections and anisotropic thermal parameters for all the atoms converged to $R_1(F) = 0.047$ and $R_2(F) = 0.059$. The error of fit $[(\Sigma\, w^2\Delta^2/(NO - NV)]^{1/2}$; NO = number of observations and NV = number of variables) was 1.67.

The positional and thermal parameters from the last cycle of refinement are given in Table I. The observed structure amplitudes, their estimated standard deviations and the calculated values of the structure amplitudes are listed in Table II. Intramolecular distances and angles with estimated standard deviations (which include the effect of the estimated errors in lattice parameters) are given in Table III. Equations of planes determined by a weighted least-squares method and the distances of atoms from these planes are given in Table IV. Significant intermolecular contacts are given in Table V. The following programs were used BEER (initial processing of punched cards for the GE diffractometer); DATAPH (Lorentz-polarization corrections); ESORTH (sorting and averaging); JIMDAP (local version of the Zalkin Fourier summation program); LINUS (modification of the Busing, Martin, and Levy ORFLS least-squares program) [22]; ORFFE (Function and error) [23]; RBANG (rigid group parameters) [24]; PLANET (least-squares planes) [25]; ORTEP (molecular plotting) [26].

Discussion

The molecular structure of $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$, which is shown in Figure 1, consists of an

TABLE I. Final Atomic Parameters with Their Standard Deviations[a].

A. Positional Parameters

	X	Y	Z
AS	0.33121(5)	0.14576(5)	0.30070(5)
FE	0.14606(7)	0.09166(6)	0.18633(7)
S1	0.05921(13)	−0.09323(12)	0.20678(14)
S2	0.04757(13)	0.11721(12)	0.33969(13)
S3	0.20035(14)	0.27079(13)	0.15174(14)
S4	0.20098(14)	0.04764(13)	0.00443(14)
C1	0.1630(5)	−0.1000(5)	−0.0069(5)
C2	0.1005(5)	−0.1634(5)	0.08656(5)
C3	0.2098(7)	−0.1468(6)	−0.11937(7)
C4	0.0641(7)	−0.2923(6)	0.0915(7)
C5	0.1532(5)	0.3332(4)	0.2747(5)
C6	0.0818(5)	0.2633(4)	0.3534(5)
C7	0.1967(7)	0.4656(6)	0.2821(7)
C8	0.0315(6)	0.3022(6)	0.4698(6)
F3-1	0.2319(4)	−0.0815(4)	−0.2151(4)
F3-2	0.3103(4)	−0.1484(4)	−0.0825(4)
F3-3	0.1311(4)	−0.2567(4)	−0.1724(4)
F4-1	−0.0298(4)	−0.3652(4)	0.0086(5)
F4-2	0.0356(5)	−0.3228(4)	0.2049(4)
F4-3	0.1514(4)	−0.3199(4)	0.0650(5)
F7-1	0.2642(5)	0.5118(4)	0.1928(5)
F7-2	0.2600(5)	0.5243(4)	0.3933(5)
F7-3	0.1086(5)	0.4927(4)	0.2695(5)
F8-1	0.1080(5)	0.3573(6)	0.5678(5)
F8-2	−0.0104(8)	0.3719(7)	0.4461(6)
F8-3	−0.0548(5)	0.2192(4)	0.5116(5)
C1-1	0.3676(11)	0.0152(8)	0.3077(7)
C1-2	0.4394(2)	−0.0011(5)	0.2170(6)
C1-3	0.4626(7)	−0.0981(8)	0.2131(7)
C1-4	0.4139(12)	−0.1787(8)	0.3000(8)
C1-5	0.3421(9)	−0.1624(6)	0.3907(7)
C1-6	0.3190(7)	−0.0653(8)	0.3946(6)
C2-1	0.3376(6)	0.2136(5)	0.4789(4)
C2-2	0.4082(5)	0.3350(5)	0.5212(5)
C2-3	0.4076(6)	0.3831(4)	0.6481(6)
C2-4	0.3363(6)	0.3097(6)	0.7325(5)
C2-5	0.2656(5)	0.1883(6)	0.6902(5)
C2-6	0.2663(6)	0.1402(4)	0.5633(6)
C3-1	0.4769(4)	0.2608(8)	0.2389(5)
C3-2	0.5846(6)	0.2999(4)	0.3178(4)
C3-3	0.6938(4)	0.3773(7)	0.2764(6)
C3-4	0.6953(5)	0.4154(8)	0.1563(6)
C3-5	0.5877(6)	0.3762(5)	0.0774(4)
C3-6	0.4784(5)	0.2988(7)	0.1188(5)
H1-2	0.4743(13)	0.0567(7)	0.1546(9)
H1-3	0.5140(11)	−0.1098(12)	0.1480(9)
H1-4	0.4305(20)	−0.2482(13)	0.2972(12)
H1-5	0.3072(14)	−0.2202(8)	0.4530(10)
H1-6	0.2675(11)	−0.0536(13)	0.4597(9)
H2-2	0.4594(7)	0.3876(7)	0.4606(8)
H2-3	0.4582(9)	0.4701(4)	0.6704(9)
H2-4	0.3358(10)	0.3442(8)	0.8234(5)
H2-5	0.2145(8)	0.1358(8)	0.7507(7)
H2-6	0.2156(8)	0.0532(4)	0.5330(8)
H3-2	0.5835(8)	0.2726(6)	0.4039(5)
H3-3	0.7710(5)	0.4054(12)	0.3330(8)
H3-4	0.7735(6)	0.4708(13)	0.1267(9)
H3-5	0.5887(9)	0.4035(7)	−0.0087(5)
H3-6	0.4012(6)	0.2707(12)	0.0623(7)

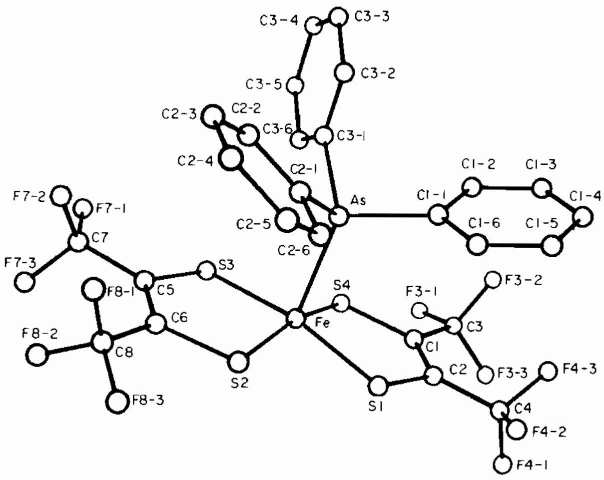

Figure 1. A perspective drawing of $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$. For the sake of clarity the thermal ellipsoids have been made isotropic and equal.

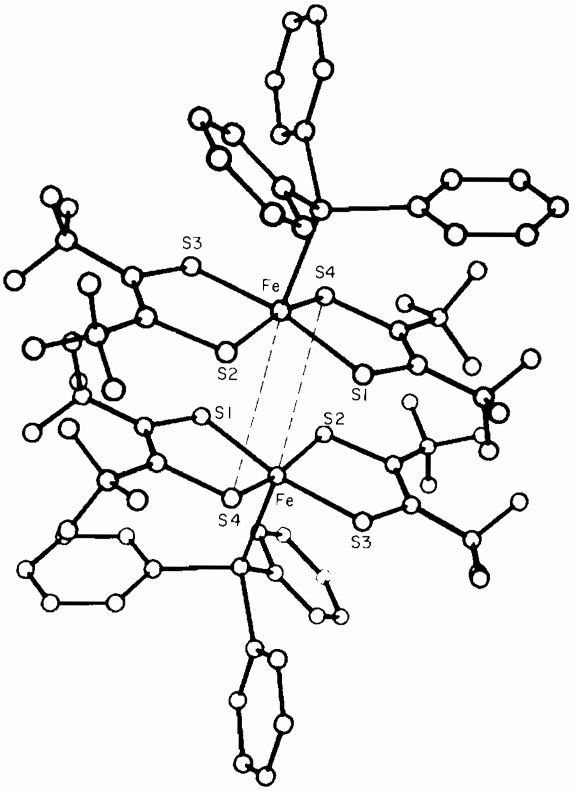

Figure 2. A perspective view of the pair of monomers which are related by a center of symmetry. The indicated Fe···S distances is 4.178(4) A.

iron atom surrounded by the four sulfur atoms of a pair of perfluoromethyldithiolene ligands and by the arsenic atom of the axial $(C_6H_5)_3As$ group in such a fashion as to give a square-pyramidal coordination geometry. This species is the product of cleaving the

TABLE I. (Continued)

B. Thermal Parameters[b]

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
AS	0.00662(5)	0.00591(5)	0.00961(7)	0.00316(4)	0.00260(4)	0.00305(4)
FE	0.00721(8)	0.00595(7)	0.00834(9)	0.00391(6)	0.00225(6)	0.00230(6)
S1	0.00877(14)	0.00605(12)	0.01040(17)	0.00372(11)	0.00313(12)	0.00226(11)
S2	0.00756(13)	0.00603(11)	0.00960(16)	0.00337(10)	0.00296(11)	0.00226(10)
S3	0.01020(15)	0.00704(12)	0.01041(17)	0.00518(12)	0.00378(13)	0.00386(12)
S4	0.00997(15)	0.00761(13)	0.00858(15)	0.00489(12)	0.00272(12)	0.00247(11)
C1	0.0061(6)	0.0070(5)	0.0096(7)	0.0039(4)	0.0006(5)	0.0000(4)
C2	0.0082(6)	0.0065(5)	0.0090(6)	0.0041(4)	0.0008(5)	0.0010(4)
C3	0.0114(8)	0.0103(7)	0.0128(9)	0.0062(6)	0.0031(7)	0.0007(6)
C4	0.0135(8)	0.0076(6)	0.0115(8)	0.0054(6)	0.0019(7)	0.0014(6)
C5	0.0090(6)	0.0055(4)	0.0102(6)	0.0045(4)	0.0017(5)	0.0016(4)
C6	0.0080(5)	0.0064(5)	0.0090(6)	0.0043(4)	0.0013(5)	0.0008(4)
C7	0.0149(9)	0.0065(6)	0.0143(9)	0.0053(6)	0.0034(8)	0.0023(6)
C8	0.0113(7)	0.0078(6)	0.0115(8)	0.0043(6)	0.0031(6)	−0.0003(6)
F3-1	0.0201(6)	0.0155(5)	0.0114(5)	0.0103(5)	0.0065(4)	0.0032(4)
F3-2	0.0111(4)	0.0168(5)	0.0175(6)	0.0094(4)	0.0018(4)	−0.0012(4)
F3-3	0.0139(5)	0.0118(4)	0.0153(5)	0.0058(4)	0.0013(4)	−0.0039(4)
F4-1	0.0166(6)	0.0082(4)	0.0237(7)	0.0030(4)	−0.0039(5)	0.0006(4)
F4-2	0.0329(9)	0.0092(4)	0.0180(6)	0.0113(5)	0.0095(6)	0.0051(4)
F4-3	0.0194(6)	0.0117(4)	0.0250(7)	0.0117(4)	0.0056(5)	0.0034(4)
F7-1	0.0315(9)	0.0082(4)	0.0257(8)	0.0069(5)	0.0165(7)	0.0079(5)
F7-2	0.0252(8)	0.0074(4)	0.0201(7)	0.0029(4)	−0.0043(6)	−0.0010(4)
F7-3	0.0217(7)	0.0098(4)	0.0327(9)	0.0110(5)	0.0011(6)	0.0026(5)
F8-1	0.0167(7)	0.0390(12)	0.0168(7)	0.0072(7)	0.0017(6)	−0.0143(8)
F8-2	0.0562(17)	0.0389(12)	0.0258(9)	0.0424(13)	0.0229(11)	0.0138(9)
F8-3	0.0248(8)	0.0123(5)	0.0277(9)	0.0046(5)	0.0189(7)	−0.0011(5)
C1-1	0.0065(5)	0.0062(5)	0.0129(7)	0.0030(4)	−0.0005(5)	0.0028(5)
C1-2	0.0131(8)	0.0074(6)	0.0181(10)	0.0058(6)	0.0045(7)	0.0017(6)
C1-3	0.0160(10)	0.0101(8)	0.0247(13)	0.0083(7)	0.0051(9)	0.0022(8)
C1-4	0.0106(8)	0.0087(7)	0.0276(14)	0.0054(6)	−0.0027(8)	0.0020(8)
C1-5	0.0234(14)	0.0175(11)	0.0322(16)	0.0142(11)	0.0098(12)	0.0159(11)
C1-6	0.0223(12)	0.0172(9)	0.0319(15)	0.0156(9)	0.0151(11)	0.0173(10)
C2-1	0.0066(5)	0.0073(5)	0.0088(6)	0.0037(4)	0.0011(4)	0.0016(4)
C2-2	0.0168(9)	0.0076(6)	0.0151(9)	0.0058(6)	0.0079(7)	0.0032(6)
C2-3	0.0213(11)	0.0082(6)	0.0175(11)	0.0065(7)	0.0089(9)	0.0005(7)
C2-4	0.0130(8)	0.0129(8)	0.0111(8)	0.0069(7)	0.0018(7)	0.0010(6)
C2-5	0.0176(10)	0.0124(8)	0.0106(8)	0.0058(8)	0.0042(7)	0.0037(6)
C2-6	0.0143(8)	0.0096(7)	0.0097(7)	0.0032(6)	0.0029(6)	0.0035(6)
C3-1	0.0064(5)	0.0055(4)	0.0124(7)	0.0023(4)	0.0040(5)	0.0028(5)
C3-2	0.0076(6)	0.0078(6)	0.0126(8)	0.0024(5)	0.0022(6)	−0.0013(5)
C3-3	0.0084(7)	0.0092(6)	0.0188(11)	0.0027(5)	0.0030(7)	−0.0027(6)
C3-4	0.0108(8)	0.0079(6)	0.0216(11)	0.0022(6)	0.0079(8)	0.0001(7)
C3-5	0.0144(9)	0.0112(8)	0.0185(10)	0.0056(7)	0.0099(8)	0.0062(7)
C3-6	0.0102(7)	0.0097(6)	0.0125(8)	0.0042(5)	0.0055(6)	0.0047(6)

[a] The standard deviations for the positional coordinates of the rigid group atoms were estimated from standard deviations in the rigid group positional and orientation parameters. [b] The thermal parameters for the hydrogen atoms were isotropic and fixed throughout the refinement. The values were B = 7.50, 6.00, and 6.00 Å^2 for groups 1, 2, and 3, respectively.

dimeric $[Fe(S_2C_2\{CF_3\}_2)_2]_2$ molecule by the two-electron donor $(C_6H_5)_3As$ group [14]. The product is diamagnetic and *monomeric*. However, a residual non-bonded interaction between monomers remains, as is shown in Figure 2. The monomers are related in pairs by a center of symmetry such that the planar base of one monomer is above the other but staggered in such a way that the iron atom of one molecule is opposite a sulfur atom of the second one. This non-bonded Fe···S distance is 4.178(4) Å. The two symmetry related iron atoms are separated by 4.788(4) Å. The four independent iron–sulfur bond lengths are approximately the same. The range of distances is 2.145 to 2.154 Å (average e.s.d. = 0.002 Å). The observed iron-sulfur distance in FeS_2 is 2.27 Å [27], a value which indicates some degree of multiple

TABLE II. Structure Amplitudes.

K	H	FOBS	FCALC
11	-4	26	27
11	-3	8	7
11	0	23	26
12	-8	23	23
12	-7	17	18
12	-5	18	17
12	-4	11	10
12	-1	30	28
12	0	27	26
13	-9	13	15
13	-8	9	8
13	-5	19	19
13	-2	12	12
14	-6	24	22
14	-4	12	12
14	-1	10	9
16	-7	10	8
16	-5	9	7

L= 4

K	H	FOBS	FCALC
-16	9	13	11
-16	10	9	8
-16	13	12	11
-14	4	8	7
-14	7	23	23
-14	11	14	12
-14	12	9	9
-14	13	14	14
-13	3	25	27
-13	4	11	10
-13	5	19	19
-13	6	26	26
-13	7	37	37
-13	8	10	11
-13	11	13	13
-12	4	11	12
-12	5	8	8
-12	6	41	41
-12	8	28	28
-12	9	10	9
-12	10	14	18
-12	12	23	22
-12	13	12	10
-11	2	38	39
-11	4	13	14
-11	5	22	21
-11	6	36	36
-11	7	21	22
-11	8	14	13
-11	9	19	20
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-2	2	16	17
-2	4	8	7
-1	-6	14	15
-1	-5	11	12
-1	-3	8	10
-1	-2	24	25
-1	0	9	9
-1	1	9	9
-1	4	15	14
0	-7	19	18
0	-5	9	10
0	-3	10	9
0	-2	13	13
0	-1	24	24
0	0	13	10
0	3	15	13
0	4	15	13
1	-6	8	9
1	-3	15	16
1	-1	20	21
1	3	13	15
2	-5	10	8
2	-4	12	11
2	-3	12	12
2	-2	25	24
2	-1	16	15
2	4	15	12
3	-7	9	9
3	-4	10	11
3	-3	15	15
3	-2	26	29
3	-1	8	7
4	-3	13	14
4	-2	10	9
6	1	10	9
8	-3	12	10

L= 12

K	H	FOBS	FCALC
-6	5	15	12
-5	1	9	13
-4	-2	23	21
-4	-1	15	14
-4	0	15	14
-4	5	11	12
-3	-3	13	12
-3	-2	25	27
-3	0	17	17
-2	-3	18	18
-2	-2	9	8
-2	-1	17	18
-2	5	13	15
-1	-3	14	13
-1	-1	14	15
0	-2	14	13
0	2	10	11
0	3	13	12
1	-2	14	13
2	-3	12	10
2	-2	10	7
2	1	13	10
2	2	13	11
6	-3	9	7

L= 13

K	H	FOBS	FCALC
-8	5	10	8
-6	4	11	11
-4	5	10	10

L= 14

K	H	FOBS	FCALC
-4	2	11	10
-4	3	11	9

TABLE III. Interatomic Distances and Angles[a].

A. Intramolecular Distances with their Standard Deviations

Fe–S1	2.149(2)	
Fe–S2	2.145(2)	
Fe–S3	2.154(2)	
Fe–S4	2.146(2)	
	2.148	
Fe–As	2.325(2)	
As–S1	3.383(4)	
As–S2	3.451(3)	
As–S3	3.232(2)	
As–S4	3.259(3)	
S1–S4	3.021(3)	
S2–S3	3.023(3)	
S1–S2	2.952(2)	
S3–S4	3.087(2)	
C1–S4	1.713(5)	
C2–S1	1.692(5)	
C5–S3	1.700(5)	
C6–S2	1.702(5)	
	1.702	
C1–C2	1.374(8)	
C5–C6	1.370(7)	
	1.372	
C1–C3	1.514(8)	
C2–C4	1.507(8)	
C5–C7	1.516(8)	
C6–C8	1.485(8)	
	1.506	
C3–F(3-1)	1.334(7)	1.362(8)[b]
F(3-2)	1.328(8)	1.340(8)
F(3-3)	1.313(7)	1.352(8)
	1.325	1.351
C4–F(4-1)	1.315(8)	1.361(8)
F(4-2)	1.301(7)	1.354(7)
F(4-3)	1.324(7)	1.366(7)
	1.313	1.360
C7–F(7-1)	1.329(8)	1.364(8)
F(7-2)	1.311(8)	1.370(8)
F(7-3)	1.307(8)	1.360(8)
	1.316	1.365
C8–F(8-1)	1.264(8)	1.392(8)
F(8-2)	1.267(8)	1.416(8)
F(8-3)	1.259(7)	1.344(7)
	1.263	1.384
As–C(1-1)	1.931(-)	
C(2-1)	1.941(-)	
C(3-1)	1.944	
	1.939	

B. Intramolecular Angles (Degrees) with their Standard Deviations

Angles Centered on Fe	
As–Fe–S1	98.2(1)
As–Fe–S2	101.0(1)
As–Fe–S3	92.3(1)
As–Fe–S4	93.5(1)
S1–Fe–S4	89.4(1)
S2–Fe–S3	89.4(1)
S1–Fe–S2	86.9(1)
S3–Fe–S4	91.8(1)
S2–Fe–S4	165.4(1)
S1–Fe–S3	169.4(1)
Angles Centered on the Sulfur Atoms	
Fe–S1–C2	106.4(2)
Fe–S2–C6	106.1(2)
Fe–S3–C5	105.6(2)
Fe–S4–C1	105.4(2)
	105.9
Angles Centered on the "Ethylenic" Carbon Atoms	
S4–C1–C2	119.4(4)
S1–C2–C1	118.5(4)
S3–C5–C6	119.3(4)
S2–C6–C5	118.8(4)
	119.0
S4–C1–C3	114.5(4)
S1–C2–C4	116.2(4)
S3–C5–C7	115.4(4)
S2–C6–C8	114.5(4)
	115.2
C3–C1–C2	125.8(5)
C4–C2–C1	125.4(5)
C7–C5–C6	125.3(5)
C8–C6–C5	126.6(5)
	125.8
Angles Centered on the Arsenic Atom	
Fe–As–C(1-1)	113.8(-)
Fe–As–C(2-1)	110.9(-)
Fe–As–C(3-1)	118.7(-)
Angles Within the Perfluoromethyl Groups	
F(3-1)–C3–F(3-2)	107.4(7)
F(3-1)–C3–F(3-3)	105.9(7)
F(3-2)–C3–F(3-3)	107.4(7)
F(4-1)–C4–F(4-2)	105.9(7)
F(4-1)–C4–F(4-3)	106.1(8)
F(4-2)–C4–F(4-3)	105.6(8)
F(7-1)–C7–F(7-2)	106.5(7)
F(7-1)–C7–F(7-3)	104.9(7)
F(7-2)–C7–F(7-3)	106.8(7)

TABLE III. (Continued)

F(8-1)–C8–F(8-2)	104.6(8)
F(8-1)–C8–F(8-3)	104.9(8)
F(8-2)–C8–F(8-3)	103.7(7)

[a] Standard deviations of last significant figures are given in parentheses. [b] These bond lengths were computed using a riding model (see ORFFE, reference 23) in which the fluorine atoms were assumed to ride on the carbon atoms.

TABLE IV. Planes and Dihedral Angles Between Planes.

A. Equations of Planes and Distances (Å) of Atoms from these Planes[a].

a) Plane containing S1, S2, S3, S4

0.8098X + 0.1416Y + 0.5693Z − 1.9527 = 0

S1	−0.037	As	−2.549
S2	+0.034	Fe	−0.232
S3	−0.039		
S4	+0.380		

b) Plane containing S2, S3, C5, C6

0.7959X + 0.1329Y + 0.5907Z − 1.989 = 0

S2	0.000	Fe	−0.213
S3	0.000	C7	−0.073
C5	−0.015	C8	+0.020
C6	+0.014	As	−2.524

c) Plane containing C5, C6, C7, C8

C5	+0.004	As	−2.582
C6	−0.004	Fe	−0.278
C7	−0.003	S2	−0.074
C8	+0.003	S3	+0.010

d) Plane containing S1, S4, Cl, C2

0.8162X + 0.1618Y + 0.5547Z − 1.9389 = 0

S1	+0.004	As	−2.562
S4	−0.004	Fe	−0.241
Cl	+0.013	C3	−0.027
C2	−0.012	C4	−0.044

e) Plane containing C1, C2, C3, C4

0.8052X + 0.1888Y + 0.5622Z − 1.8730 = 0

C1	+0.007	As	−2.648
C2	−0.006	Fe	−0.328
C3	−0.005	S1	−0.031
C4	+0.005	S4	−0.056

f) Plane containing C1-1, C2-1, C3-1

0.8085X + 0.1495Y + 0.5691Z − 5.3083 = 0

As	0.8017

g) Plane containing Fe, S2, S3

0.7205 X + 0.2329Y + 0.6532Z − 2.3055 = 0

h) Plane containing Fe, S1, S4

0.8792X + 0.0408Y + 0.4748Z − 2.0119 = 0

B. Angles (Degrees) Between Normals to Planes

a–b	1.6	c–d	4.5
a–c	3.0	c–e	5.6
a–d	1.5	c–f	3.4
a–e	2.8	c–g	9.4
a–f	0.5	c–h	9.1
a–g	8.8	d–e	1.7
a–h	8.9	d–f	1.2
b–c	2.0	d–g	8.9
b–d	2.9	d–h	9.1
b–e	3.6	e–f	2.3
b–f	1.7	e–g	7.6
b–g	8.0	e–h	10.7
b–h	9.8	f–g	8.5
		f–h	9.2
		g–h	17.6

[a] The equations of the planes and distances and angles were obtained from the Smith plane program [25]. Unit weights were used in the calculations. The equation of the plane is expressed in orthogonal coordinates which are related to the fractional coordinates x, y, z by the transformation:

$$X = ax + by \cos\gamma + cz \cos\beta$$
$$Y = by \sin\gamma + cz\,(\cos\gamma - \cos\beta\cos\gamma)/\sin\gamma$$
$$Z = cz(1 - \cos^2\alpha - \cos^2\beta - \cos^2\gamma + 2\cos\alpha\cos\beta\cos\gamma)^{1/2}/\sin\gamma$$

Individual weights in the calculation of the planes were assigned according to the relation:

[illegible]

the atomic fractional coordinates x_k, y_k, and z_k, respectively.

bonding between the metal and sulfur atoms in $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$.

In $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$ the average C–S bond length is 1.702(5) Å a distance which is close to the values 1.65 and 1.66 Å found for carbon–sulfur double bonds in tetraethylthiuram disulfide [28] and allylthiourea [29], respectively. The carbon–sulfur bonds in the MNT compounds range from 1.71 to 1.75 Å and are closer to the carbon–sulfur distances of 1.767(10) and 1.776(5) Å found [30, 31] in compounds where sulfur is attached to unsaturated carbon atoms.

A common feature of the interaction between the metal and sulfur atoms in $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$ and related maleonitrile and perfluoromethyl compounds is the similarity of their M–S–C bond angles. In $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$ these angles range from 105.4 to 106.4° (average e.s.d. = 0.2°) and are in close agreement with typical S–S–S angles found for sulfur atom chains [32] and with S–S–C bond in angles in organosulfur compounds [31, 33]. The similarity of metal–sulfur bond lengths

TABLE V. Non-bonded Contacts Less Than 3.0 Å[a,b].

F(3-1)–S4	2.81
F(3-1)–H(2-5)	2.95
F(3-1)–H(1-3)′	2.99
F(3-2)–H(1-2)′	2.59
F(3-2)–F(4-3)	2.86
F(3-3)–F(4-3)	2.73
F(3-3)–F(4-1)	2.82
F(3-3)–C4	2.94
F(3-3)–C2	2.94
F(4-1)–H(3-4)	2.85
F(4-2)–S1	2.81
F(4-2)–F(8-1)	2.99
F(4-3)–C1	2.94
F(4-3)–C3	2.96
F(7-1)–H(3-5)′	2.68
F(7-1)–S3	2.78
F(7-1)–H(1-4)	2.86
F(7-2)–H(3-2)′	2.97
F(7-2)–H(3-3)	2.99
F(7-2)–F(8-1)	3.00
F(7-3)–F(8-2)	2.60
F(8-1)–H(3-3)	2.74
F(8-2)–C5	2.94
F(8-3)–H(1-6)′	2.60
F(8-3)–S2	2.78

[a] Non-bonded contacts between fluorine atoms of a perfluoromethyl group not included. [b] Primes indicate an atom whose coordinates are related by a center of symmetry to those given in Table I.

and bond angles at the sulfur atoms in metal dithiolene complexes indicate a considerable degree of flexibility for the sulfur atoms in bond formation. Despite the variety of chemical environments, the sulfur atom appears capable of rehybridization in such a way that similar bond lengths and angles result.

The displacement of the metal atom from the plane of the four sulfur atoms in these bis-dithiolene compounds varies according to the degree of interaction between the metal atom and ligands in the axial direction. The bis-MNT complexes of Cu^{3+} [12], Ni^{2+} [11], Ni^{3+} [16], and Co^{2+} [12] exhibit square planar coordination for the metal atom, which is essentially in the plane of the attached ligands. Displacements of 0.23 Å and 0.37 Å exist for the Fe (reported here) and Co [8] complexes of the bis-perfluoromethyl ligands. Despite the variety of metal atoms and their formal electronic configurations the metal–sulfur bond lengths are all quite similar, as shown in Table VI. The 0.23 Å displacement of the iron atom from the plane of the four sulfur atoms in $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$ is such that the dihedral angle formed by planes defined by the atoms Fe, S1, S4 and by S1, S4, C1, C2 is 8° while the dihedral angle formed by similar planes on the opposite side of the metal is 10°. This folding about the S···S vector displaces the dithiolene ligand towards the $(C_6H_5)_3As$ group. A similar folding (8°) has been observed for *one* of the two dithiolene ligands in $[Co(S_2C_2\{CF_3\}_2)_2]_2$ [8]. For this cobalt compound the folding has been ascribed to repulsions exerted on the CF_3 groups of one dithiolene moiety by the sulfur atoms of a dithiolene ligand which belongs to the second portion of the dimer. In $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$ no such repulsions can occur because of the large separation of individual monomer molecules. Rather, the folding may be due to a reorientation of the ligands such that sulfur atom orbitals may overlap with those of the arsenic atom. The sum of van der Waals radii for sulfur and arsenic is 3.8 Å [34]. The short arsenic to sulfur distances of 3.232(2) and 3.259(3) Å (to S3 and S4) and 3.383(4) and 3.450(3) Å (to S1 and S2) reflect this weak interaction. The weak arsenic–sulfur interaction may account for an unusual feature of the geometry of the dithiolene ligands. Although the four sulfur atoms conform to a plane to within 0.04 Å, the sulfur polygon is a trapezoid rather than a rectangle. The non-bonding S···S distances between atoms within a dithiolene are 3.021(3) and 3.023(3) Å while the interligand distances are 2.952(2) and 3.087(2) Å.

The perfluoromethyl dithiolene ligands are planar moieties with the exception of the fluorine atoms.

TABLE VI. Selected Bond Lengths.

Metal Ion	Fe^{4+}	Ni^{2+}	Co^{2+}	Ni^{3+}	Ni^{2+}	Cu^{3+}
No. d Electrons	4	8	7	7	8	8
Ligand	PDT[a]	PDT[a]	MNT[b]	MNT[b]	MNT[b]	MNT[b]
M–S	2.148(2)	2.122(3)	2.161(3)	2.146(1)	2.16(1)	2.170(4)
M–L[d]	2.325(2)	–	–	3.59	–	4.43, 4.03
S–C	1.702(5)	1.71(1)	1.723(7)	1.714(4)	1.750(-)	1.72(1)
"C=C"	1.372(7)	1.38(2)	1.34(1)	1.356(7)	1.30(-)	1.32(2)
C–C	1.506(8)	1.48(2)	1.40(1)	1.430(5)	1.43(-)	1.43(2)
Δ[c]	0.23	Planar	Planar	Planar	Planar	Planar
Reference	This Work	10	12	16	11	12

[a] PDT = Perfluorodithietene. [b] MNT = Maleonitrile. [c] Displacement of the metal from the plane of the sulfurs. [d] The axial ligand is the As of ϕ_3As; all other axial ligands in this Table are sulfurs.

As discussed earlier, the C–S bond lengths are shorter and the "C=C" bond lengths are longer than the values found for MNT ligands. Bond angles wich are centered about the "ethylenic" carbon atoms have the systematic character that they are less than 120° if a sulfur atom is involved and greater than 120° if perfluoromethyl carbon atoms are involved.

The iron–arsenic bond length of 2.325(2) Å compares favorably with the distances 2.311(7) and 2.336(7) Å [35] and 2.300(6) Å found in the compounds $[Fe(CO)_3]_2(AsCH_3)_4$ and $(CH_3)_2AsC{=}C(As(CH_3)_2)CF_2CF_2 \cdot Fe_3(CO)_{10}$ [36]. The Fe-As vector makes an angle of 4.8° with respect to the normal to the best plane through the four sulfur atoms and an angle of 4.6° with respect to the three-fold axis defined by the carbon atoms of the phenyl groups which are attached to the arsenic. The plane which contains the phenyl group 3 is disposed such that it is nearly orthogonal to the plane through the four sulfur atoms (dihedral angle = 95°).

The "ethylenic" carbon–perfluoromethyl carbon bond lengths average 1.505(7) Å for $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$, a value close to the distance which is expected for a C_{sp^2}–C_{sp^3} bond. This average value compares favorably with the average value 1.506(12) Å found for the equivalent bonds in $[Co(S_2C_2\{CF_3\}_2)_2]_2$ and 1.485(20) Å for the perylene complex of $Ni(S_2C_2\{CF_3\}_2)_2$. The average ethylenic carbon–cyanide carbon bond lengths are 1.43(1), 1.40(1), 1.44(2), and 1.430(5) Å for the MNT complexes $Ni(MNT)_2^{2-}$ [11], $Co(MNT)_2^{2-}$ [12], $Cu(MNT)_2^{1-}$ [12], and $Ni(MNT)_2^{1-}$ [16].

The bond lengths and angles based on the output of the final cycle of refinement within the perfluoromethyl groups in $(C_6H_5)_2AsFe(S_2C_2\{CF_3\}_2)_2$ are in good agreement with the previously reported values [8, 10] for metal complexes of the type described here. For the groups at carbon atoms C3, C4, and C7, the C–F bond lengths are all in the range 1.292 to 1.344 Å (average e.s.d. = 0.008 Å) while the F–C–F bond angles are in the range 104.9 to 107.9° (average e.s.d. = 0.6°). The bond lengths and angles for the group at C8 are slightly smaller than the averages for the other perfluoromethyl groups. However, the perfluoromethyl group at C8 is subject to greater thermal motion than the other three groups. The carbon–fluorine bond lengths and angles for the group at C8 range from 1.259 to 1.267 Å and from 103.7 to 104.9°, respectively. When the bond lengths are corrected for thermal vibration according to a "riding" model [23], then the range of carbon–fluorine bond lengths for the groups at C3, C4, and C7 range from 1.340 to 1.370 Å (average e.s.d. = 0.008 Å). At C8 the range of carbon–fluorine bond lengths is now 1.344 to 1.416 Å (see Table IV). The packing of molecules in the triclinic unit cell is given in Figure 3.

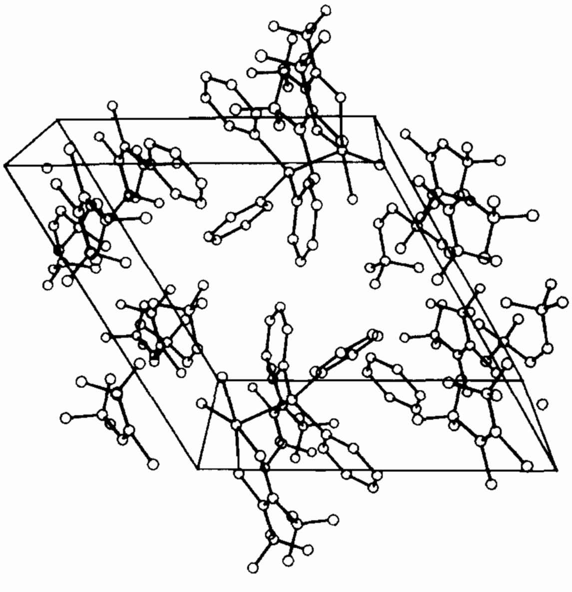

Figure 3. A perspective view of the unit cell of $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$.

The following conclusions can be derived by considering the structural details of $(C_6H_5)_3AsFe(S_2C_2\{CF_3\}_2)_2$ and the related bis-dithiolenes which appear in Table VI: a) the maleonitrile compounds have significantly shorter "C=C" bond lengths and longer S–C bond lengths than the perfluoromethyl derivatives. The electron localizing perfluoromethyl groups appear to stabilize a more "dithioketonic" form for the sulfur containing ligand rather than the "dithiolate" form of the MNT complexes. The perfluoromethyl ligands in the *dimeric* complex $[Co(S_2C_2\{CF_3\}_2)_2]_2$ also possess a more "dithioketonic" form [8]. As a limiting case the maleonitrile ligand is characterized by a π-delocalization over the *entire* ligand, a delocalization which extends to the metal atom. The perfluoromethyl ligand may be described in the limit as having π-density localized in the C–S bond and to some degree in the "ethylenic bond". b) The metal–sulfur bond lengths are essentially the same despite the variety of metal ions and their formal electronic configurations. The perylene complex of nickel dithiolene [10] may be an exception to this generalization. However, in this system an electron transfer process appears to occur which involves orbitals capable of π-bonding in the axial direction of the nickel dithiolene moiety [10] and it is this interaction which may account for the slightly shorter metal sulfur distances. c) The bis-MNT complexes are characterized by a square-planar coordination about the central metal ion with the metal in, or very nearly in, the plane of the four sulfur atoms and by weak interactions, if any, in the axial direction. The perfluoromethyl compounds thus far known are characterized by significantly stronger interactions in the axial direction. The formation by the MNT compounds of metal–dithiolene rings with more aromatic character than those for the more electronically localized perfluoromethyl ligands should lead to a more nearly planar metal dithiolene system. Thus, for the bis-MNT compounds metal d orbitals would be employed to a greater extent than in the perfluoromethyl complexes in the formation of metal–sulfur π-bonds. One result of such relatively strong metal–sulfur π-bond formation would be a reduction in the availability of these metal π orbitals for bonding to a fifth ligand in the axial direction.

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