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SULFUR-BRIDGED DIMERS OBTAINED FROM μ-DITHIOBIS(TRICARBONYLIRON) *

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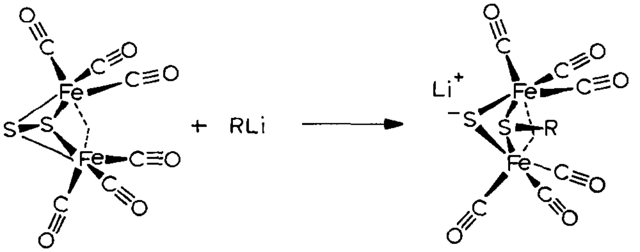
Summary

The reaction of SO_2Cl_2 with $(\mu\text{-MS})(\mu\text{-ArS})Fe_2(CO)_6$ (M = Li; Ar = Ph and M = MgBr; Ar = *p*-tolyl) results in oxidation of the latter and formation of S–S bonded "dimers". The "dimer" where Ar = Ph crystallizes in the space group $P\bar{1}$ with *a* 10.584(4), *b* 11.247(1), *c* 14.275(3) Å, α 104.20(2), β 90.80(4), γ 98.12(2)°, *V* 1629 Å^3 and *Z* = 2. Full matrix least-squares refinement yields a final *R* value of 4.4% based on 3986 independent reflections. The central S–S bond is longer than that in elemental sulfur or in $(\mu\text{-}S_2)Fe_2(CO)_6$.

Introduction

During the course of our studies of the anionic species derived from μ-dithiobis(tricarbonyliron) (**1**) [1] we found that organolithium reagents cleave the S–S bond of this compound to give products with a single bridging sulfido ligand (**2**) eq.1 [1a].



(1)

(**1**) (**2**)

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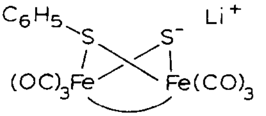
Grignard reagents, RMgX, react similarly to give **2**, but with a MgX^+ counterion [2]. Such monoanions may be alkylated, acylated, mercurated and protonated [1a]. We have continued our studies of the reactions of anions of type **2**, and we report here some examples in which two such anionic species have been linked together to give a neutral product with an S–S bond.

Results and discussion

There are many ways of forming an S–S bond, the most common of which is the oxidation of thiols or metal thiolates [3]. A very simple S–S bond synthesis uses sulfuryl chloride as the oxidizing agent [4]. The dianion derived from μ-dithiobis(tricarbonyliron), reacts with SO_2Cl_2 to regenerate the neutral S–S bonded complex, **1** [1b]. We have found that SO_2Cl_2 oxidation of **3** and **4**, obtained by reaction of



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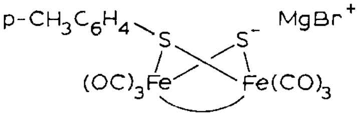
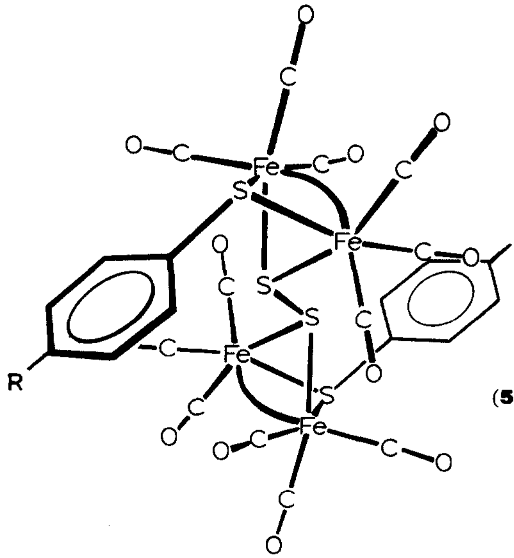


(4)

$(\mu\text{-}S_2)Fe_2(CO)_6$ with phenyllithium and *p*-tolylmagnesium bromide, respectively, occurs very readily to give the desired "dimers" (**5**) in good yield in the form of red-bronze crystals.



(**5a**, R = H; **5b**, R = CH_3)

Their constitution was proven by combustion analysis, field desorption mass spectrometry, which showed the molecular ion for each **5**, and infrared spectroscopy. The conformation of the S_2Fe_2 clusters about the S–S bond was a point of interest, and in order to answer this question, a single crystal X-ray diffraction study of **5a** was undertaken.

Final positional parameters for the atoms are given in Table 1. Table 2 contains

TABLE 1

POSITIONAL PARAMETERS FOR $(C_6H_5S)Fe_2(CO)_6SS(CO)_6Fe_2(SC_6H_5)$

Atom	*x*	*y*	*z*
Fe(1)	0.39104(12)	0.25033(10)	0.46903(7)
Fe(2)	0.25523(12)	0.41041(11)	0.54849(8)
Fe(3)	0.81321(10)	0.03769(9)	0.13609(7)
Fe(4)	0.75523(9)	−0.13378(8)	−0.01538(7)
S(1)	0.3083(2)	0.2608(2)	0.6169(1)
S(2)	0.4700(2)	0.4461(2)	0.5488(1)
S(3)	0.7501(2)	−0.1646(2)	0.1363(1)
S(4)	0.9559(1)	−0.0574(1)	0.0420(1)
O(11)	0.2012(9)	0.0283(7)	0.3972(6)
O(12)	0.4095(7)	0.2941(5)	0.2755(4)
O(13)	0.6180(8)	0.1289(7)	0.4710(6)
O(21)	0.2016(8)	0.6195(7)	0.7045(5)
O(22)	−0.0045(8)	0.2749(11)	0.5150(5)
O(23)	0.2111(8)	0.5200(8)	0.3873(5)
O(31)	0.8220(6)	0.2502(5)	0.0491(4)
O(32)	0.5676(6)	0.0817(7)	0.2199(5)
O(33)	0.9920(8)	0.1656(8)	0.3020(5)
O(41)	0.7501(6)	0.0038(5)	−0.1646(4)
O(42)	0.4763(5)	−0.1766(7)	−0.0240(5)
O(43)	0.8145(7)	−0.3619(5)	−0.1454(5)
C(11)	0.2732(11)	0.1148(9)	0.4251(6)
C(12)	0.4033(9)	0.2774(7)	0.3509(5)
C(13)	0.5297(9)	0.1760(8)	0.4699(6)
C(21)	0.2234(9)	0.5391(9)	0.6469(7)
C(22)	0.0995(10)	0.3246(12)	0.5289(6)
C(23)	0.2322(10)	0.4784(10)	0.4494(6)
C(A1)	0.4306(7)	0.3125(6)	0.7122(5)
C(A2)	0.4299(9)	0.4230(7)	0.7824(5)
C(A3)	0.5189(11)	0.4504(9)	0.8618(6)
C(A4)	0.6004(10)	0.3743(9)	0.8702(6)
C(A5)	0.6018(9)	0.2643(9)	0.8008(7)
C(A6)	0.5154(9)	0.2350(8)	0.7224(6)
C(31)	0.8201(7)	0.1675(6)	0.0828(5)
C(32)	0.6630(8)	0.0667(8)	0.1870(6)
C(33)	0.9225(9)	0.1138(8)	0.2409(6)
C(41)	0.7534(7)	−0.0478(6)	−0.1058(5)
C(42)	0.5849(7)	−0.1604(8)	−0.0203(6)
C(43)	0.7876(7)	−0.2760(7)	−0.0954(6)
C(B1)	0.8761(6)	−0.2426(6)	0.1619(5)
C(B2)	0.9664(8)	−0.1906(7)	0.2366(5)
C(B3)	1.0560(8)	−0.2589(7)	0.2597(6)
C(B4)	1.0578(8)	−0.3786(7)	0.2095(6)
C(B5)	0.9677(9)	−0.4317(7)	0.1349(6)
C(B6)	0.8779(8)	−0.3654(7)	0.1112(6)
H(A2)	0.364(6)	0.476(5)	0.780(4)
H(A3)	0.511(7)	0.521(6)	0.904(5)
H(A4)	0.662(7)	0.382(7)	0.923(5)
H(A5)	0.666(6)	0.215(6)	0.807(5)
H(A6)	0.511(6)	0.159(6)	0.679(5)
H(B2)	0.965(6)	−0.110(6)	0.271(5)
H(B3)	1.118(6)	−0.223(6)	0.307(5)
H(B4)	1.122(6)	−0.423(6)	0.228(4)
H(B5)	0.966(6)	−0.514(6)	0.108(5)
H(B6)	0.811(7)	−0.402(6)	0.070(5)

TABLE 2

INTERATOMIC DISTANCES (Å) AND BOND ANGLES (°) FOR $(C_6H_5S)Fe_2(CO)_6$-$SS(CO)_6Fe_2(SC_6H_5)$

Fe(1)-Fe(2)	2.525(1)	Fe(3)-C(32)	1.796(7)
Fe(1)-S(1)	2.280(2)	Fe(3)-C(33)	1.831(7)
Fe(1)-S(2)	2.250(2)	Fe(4)-S(3)	2.275(1)
Fe(1)-C(11)	1.800(8)	Fe(4)-S(4)	2.238(1)
Fe(1)-C(12)	1.789(6)	Fe(4)-C(41)	1.795(6)
Fe(1)-C(13)	1.790(8)	Fe(4)-C(42)	1.783(6)
Fe(2)-S(1)	2.272(2)	Fe(4)-C(43)	1.804(6)
Fe(2)-S(2)	2.251(2)	S(1)-C(A1)	1.793(6)
Fe(2)-C(21)	1.826(8)	S(2)-S(2')	2.108(3)
Fe(2)-C(22)	1.769(10)	S(4)-S(4')	2.104(3)
Fe(3)-C(23)	1.794(8)	S(3)-C(B1)	1.778(5)
Fe(3)-Fe(4)	2.520(1)	⟨C-H⟩	0.93
Fe(3)-S(3)	2.279(2)	C(12)-O(32)	3.245(8)
Fe(3)-S(4)	2.245(1)	O(12)-O(32)	3.063(7)
Fe(3)-C(31)	1.798(6)	O(12)-C(43)	3.237(7)

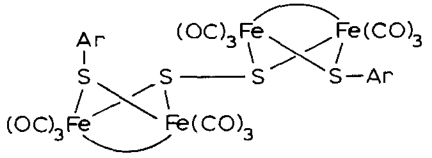
Symmetry transformations: (a) x, y, z (b) $1-x$, $-y$, $-z$

S(1)-Fe(1)-S(2)	78.7(1)	S(4)-Fe(3)-C(33)	97.3(2)
S(1)-Fe(1)-C(11)	86.4(1)	C(31)-Fe(3)-C(32)	91.4(3)
S(1)-Fe(1)-C(12)	156.3(2)	C(31)-Fe(3)-C(33)	97.3(3)
S(1)-Fe(1)-C(13)	105.6(2)	C(32)-Fe(3)-C(33)	100.2(3)
S(2)-Fe(1)-C(11)	157.7(3)	S(3)-Fe(4)-S(4)	78.4(1)
S(2)-Fe(1)-C(12)	95.3(2)	S(3)-Fe(4)-C(41)	156.6(2)
S(2)-Fe(1)-C(13)	100.8(3)	S(3)-Fe(4)-C(42)	87.7(2)
C(11)-Fe(1)-C(12)	91.7(3)	S(3)-Fe(4)-C(43)	106.9(2)
C(11)-Fe(1)-C(13)	99.0(4)	S(4)-Fe(4)-C(41)	96.3(2)
C(12)-Fe(1)-C(13)	98.0(3)	S(4)-Fe(4)-C(42)	159.5(2)
S(1)-Fe(2)-S(2)	78.8(1)	S(4)-Fe(4)-C(43)	97.8(2)
S(1)-Fe(2)-C(21)	107.1(2)	C(41)-Fe(4)-C(42)	90.5(3)
S(1)-Fe(2)-C(22)	86.4(3)	C(41)-Fe(4)-C(43)	96.4(3)
S(1)-Fe(2)-C(23)	154.4(3)	C(42)-Fe(4)-C(43)	100.7(3)
S(2)-Fe(2)-C(21)	101.4(3)	Fe(1)-S(1)-Fe(2)	67.4(1)
S(2)-Fe(2)-C(22)	158.0(3)	Fe(1)-S(1)-C(A1)	111.5(2)
S(2)-Fe(2)-C(23)	94.3(3)	Fe(2)-S(1)-C(A1)	115.2(2)
C(21)-Fe(2)-C(22)	98.5(4)	Fe(1)-S(2)-Fe(2)	68.2(1)
C(21)-Fe(2)-C(23)	98.3(3)	Fe(1)-S(2)-S(2)	110.9(1)
C(22)-Fe(2)-C(23)	92.0(4)	Fe(2)-S(2)-S(2)	110.7(1)
S(3)-Fe(3)-S(4)	78.2(1)	Fe(3)-S(3)-Fe(4)	67.2(1)
S(3)-Fe(3)-C(31)	152.8(2)	Fe(3)-S(3)-C(B1)	114.2(2)
S(3)-Fe(3)-C(32)	86.5(2)	Fe(4)-S(3)-C(B1)	112.4(2)
S(3)-Fe(3)-C(33)	109.8(2)	Fe(3)-S(4)-Fe(4)	68.4(1)
S(4)-Fe(3)-C(31)	96.2(2)	Fe(3)-S(4)-S(4')	110.5(1)
S(4)-Fe(3)-C(32)	159.9(2)	Fe(4)-S(4)-S(4')	110.1(1)

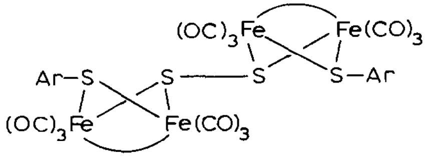
the most important interatomic distances and bond angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted, and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 shows a stereoview of one of the two molecules in the asymmetric unit. The other molecule differs little except in the orientation of the phenyl ring. Each has a crystallographically imposed center of inversion in the middle of the S-S bond.

The Fe–Fe bridging is only slightly unsymmetrical as expected from the unequal sulfur substituents, C_6H_5 and $SFe_2(CO)_6SC_6H_5$. The phenyl substituents are axial to the Fe_2S_2 centers, while the $SFe_2(CO)_6SC_6H_5$ substituents are equatorial, an *a*, *e* isomer [1] (**5**).

In principle, isomers of the "dimers" other than **5** are possible, viz., **6** and **7**, if the intercluster S–S bond is maintained in the *e*, *e* manner as shown. The 270 MHz proton NMR spectrum of the solid product obained when Ar = *p*-tolyl showed the presence of three isomers in 12/2/1 ratio. The major isomer, represented in the NMR spectrum by the methyl proton resonance at δ 2.17 ppm, most probably has structure **5**, the *a*, *e* isomer in practically all cases of $(\mu\text{-RS})(\mu\text{-R'S})Fe_2(CO)_6$ complexes being by far the most abundant. Another weak resonance at δ 2.10 ppm would then be due to the axial *p*-tolyl group of isomer **6**, while two weak resonances at δ 2.29 and 2.24 ppm would be due to the equatorial *p*-tolyl groups in **6** and **7**. NMR spectroscopy provided no information concerning the presence of isomers in the product where Ar = phenyl. However, one might hope that in sampling the solid product for crystals suitable for a single crystal X-ray diffraction study a crystal of the major isomer was selected. Table 3 compares the features of the Fe_2S_2 clusters with literature values [5–7]. The bond lengths and angles are reasonably similar to the literature values listed in Table 3, with the biggest difference being from those of $(\mu\text{-}S_2)Fe_2(CO)_6$ [6], which contains a somewhat different Fe_2S_2 linkage. The central S–S bond (2.108(3) Å) is lengthened from the single S–S bond (2.037(5) Å) in



(**6**)



(**7**)

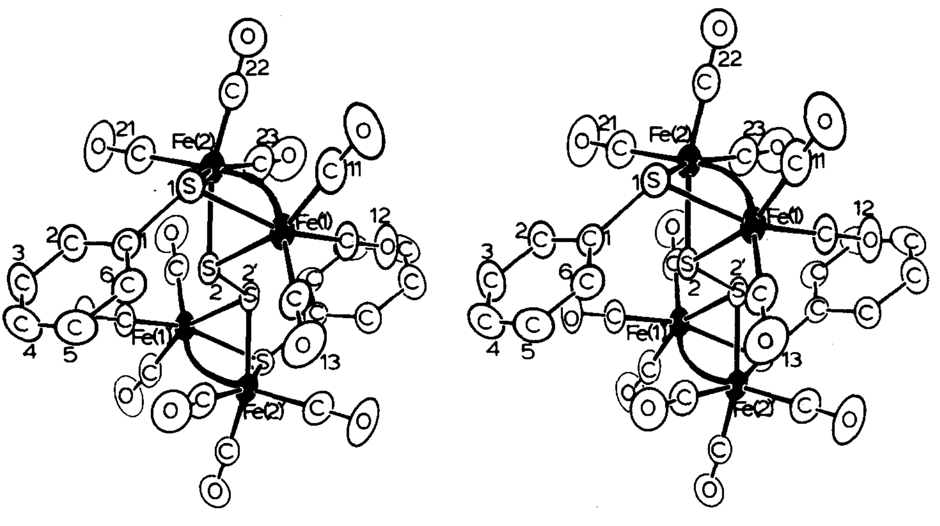


Fig. 1. A stereoview of $[(\mu\text{-}C_6H_5S)Fe_2(CO)_6(\mu\text{-}S)]_2$.

TABLE 3

COMPARISON OF AVERAGE BOND LENGTHS (Å) AND BOND ANGLES (°) FOR (A) PRESENT COMPLEX, (**B**) $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6$ [6], (**C**) $(\mu\text{-SC}_2\text{H}_5)_2\text{Fe}(\text{CO})_6$ [5], (**D**) $(\mu\text{-SCH}_3)(\mu\text{-SHgCH}_3)\text{Fe}_2(\text{CO})_6$ [7], (**E**) $(\mu\text{-SC}_2\text{H}_5)(\mu\text{-SHgC}_2\text{H}_5)\text{Fe}_2(\text{CO})_6$ [7]

	A	B	C	D	E
Fe–Fe	2.525(2)	2.552(2)	2.537(10)	2.512(5)	2.508(4)
Fe–S	2.261 [a]	2.228(2)	2.259(7)	2.254(4)	2.261(5)
5-S	2.862(6)		2.93(1)	2.886(8)	2.904(8)
S–C	1.786(8)		1.81(3)	1.84(3)	1.82(3)
Fe–S–Fe	67.8 [b]	69.9(1)	68.3(3)	67.4(2)	66.9(8)
S–Fe–S	78.5(2)	53.5(1)	81.0(3)	79.2(3)	79.2(3)
S–S	2.106(3)	2.007(5)			

[a] Average of two averages 2.246, 2.277 Å. [b] Average of two averages 67.3(1), 68.3(1)°.

elemental sulfur [8]. It is also lengthened compared to the S–S bond (2.007(5) Å) of $(\mu\text{-S})_2\text{Fe}_2(\text{CO})_6$. However, the latter bond may be foreshortened by having each of the sulfur atoms bonded to the same iron atoms. The overall cluster features are similar.

The $(\mu\text{-S}_2)$ bridge, which opens on addition of S-ethyl substituents to the unsubstituted parent [5,6], results in shorter Fe–Fe distances. With the larger substituents in the present complex, the Fe–Fe distances are even shorter, even though not as short as in $(\mu\text{-RS})(\mu\text{-RHgS})\text{Fe}_2(\text{CO})_6$ ($\text{R} = \text{CH}_3$, C_2H_5) [7]. The overall cluster features are similar over the series of complexes so that a bent σ bond and a direct π interaction between the iron centers may be proposed for each [8].

Experimental section

General comments. All reactions were carried out under nitrogen. All solvents were rigorously dried.

IR spectra were obtained with a Perkin–Elmer Model 457A grating infrared spectrometer, NMR spectra on a Hitachi Perkin–Elmer R20B spectrometer.

μ-Dithiobis(tricarbonyliron) was prepared by the literature method [9] as described in ref. 3.

Reaction of μ-dithiobis(tricarbonyliron) with phenyllithium and sulfuryl chloride

A 200 ml three-necked flask equipped with a magnetic stir-bar, two no-air septa and a nitrogen inlet tube was charged with 1.0 g (2.91 mmol) of $\text{S}_2\text{Fe}_2(\text{CO})_6$ and 60 ml of dry THF. The resulting red solution was cooled to -78°C and 2.4 ml of 1.23 M $\text{C}_6\text{H}_5\text{Li}$ in diethyl ether was added by syringe. The green solution which was formed was stirred at -78°C for a few minutes and then 0.15 ml ($\sim$ 1.45 mmol) of SO_2Cl_2 was added. The reaction mixture became red in color again. TLC (silicic acid, 10% CH_2Cl_2/pentane) indicated the presence of a single product. The reaction mixture was concentrated at reduced pressure and the residue was chromatographed (silicic acid column, 20% CH_2Cl_2/pentane). The red solid which was obtained was recrystallized from CH_2Cl_2/pentane to give **5a** in 75% yield. The red-bronze crystals changed to black at 141–142°C but did not melt.

Anal. Found: C, 34,23; H, 1.34. $\text{C}_{24}\text{H}_{10}\text{O}_{12}\text{S}_4\text{Fe}_4$ calcd.: C, 34.24; H, 1.20%.

FD mass spectrometry showed the molecular ion, M^+, $= m/z$ 841.6. The IR spectrum (in CH_2Cl_2) showed bands at 2065, 2042 and 2002 cm^{-1} in the terminal carbonyl region. The NMR spectrum showed the expected phenyl proton signals as a multiplet at δ 7.07–7.26 ppm (in $CDCl_3$).

Reaction of of μ-dithiobis(tricarbonyliron) with p-tolylmagnesium bromide and sulfuryl chloride

The same procedure was used in the reaction of 4 ml of 1 *M* p-$CH_3C_6H_4MgBr$ in THF with 2.91 mmol of $S_2Fe_2(CO)_6$ in 60 ml of THF at −78°C, followed by addition of 1.7 mmol of SO_2Cl_2. The product, **5b**, was isolated in the form of red-orange crystals which decomposed at 135°C without melting.

Anal. Found: C, 35.64; H, 1.76. $C_{26}H_{14}O_{12}S_4Fe_4$ calcd.: C, 35.89; H, 1.62%.

IR (CH_2Cl_2): ν(C≡O): 2085s, 2065v,s, 2002v,s cm^{-1}. 270 MHz ^1H NMR (CD_2Cl_2): singlets at δ 2.17 (major isomer, **5**), 2.10 and 2.24 (assigned to isomer **6**) and 2.29 ppm (assigned to isomer **7**). The integrated intensities of these signals gave an isomer ration of **5**/**6**/**7** = 12/2/1.

Crystal data for $(C_6H_5S)Fe_2(CO)_6S_2(CO)_6Fe_2(SC_6H_5)$

$Fe_4S_4O_{12}C_{24}H_{10}$, mol. wt. 842, space group $P\bar{1}$, $Z = 2$, a 10.584(4), b 11.247(1), c 14.275(3) Å, α 104.20(2), β 90.80(3), γ 98.19(2)°, V 1629 Å^3, ρ_{calc} 1.72 g cm^{-3}, μ(Mo-K_α) 20.9 cm^{-1}.

Cell dimensions and space group data were obtained by standard methods on an Enraf–Nonius four-circle CAD-4 diffractometer. The θ-2θ scan technique was used, as previouly described [10], to record the intensities for all non-equivalent reflections for which $1° < 2\theta < 58°$. Scan widths were calculated as $(A + B \tan \theta)$, where A is estimated from the mosaicity of the crystal and B allows for the increase in peak width due to K_{α_1}–K_{α_2} splitting. The values of A and B were 0.5 and 0.35, respectively.

The intensities of three standard reflections showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz-polarization effects and absorption. Of the 5845 independent intensities, there were 3986 with $F_0^2 > 3\sigma(F_0^2)$, where F_0^2 was estimated from counting statistics [11]. These data were used in the final refinement of the structural parameters.

Structure determination. A three-dimensional Patterson synthesis was used to determine the heavy atom positions, which phased the data sufficiently well to permit location of the remaining non-hydrogen atoms from Fourier syntheses. The unit cell (Fig. 2) was found to contain two molecules, each of which has a crystallographic center of inversion at the central S–S bond. Full-matrix least-squares refinement was carried out as previously described [10]. Anisotropic temperature factors were introduced for the non-hydrogen atoms. Further Fourier difference functions permitted location of the hydrogen atoms, which were included in the refinement for four cycles of least-squares refinement and then held fixed.

The model converged with $R = 4.4\%$ and $R_w = 5.2\%$. A final Fourier difference map was featureless. A listing of the observed and calculated structure factor is available, together with calculated thermal parameters and selected least-squares planes through groups of atoms [12]. The principal programs used are as described previously [10].

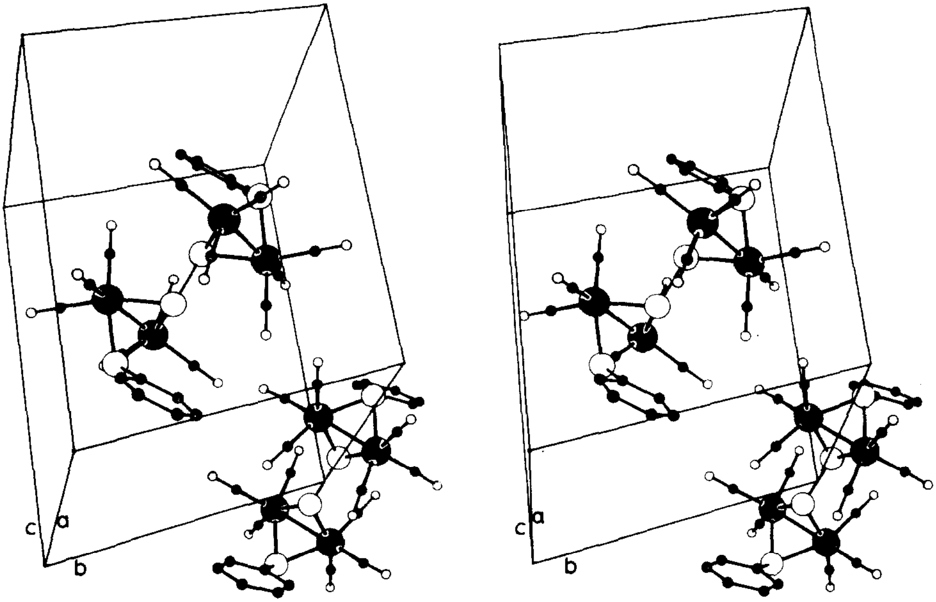


Fig. 2. A stereoview of the unit cell.

Acknowledgements

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Supplementary Material Available. Calculated thermal parameters and selected least squares planes and a listing of the observed and calculated structure factor amplitudes for **5a** may be obtained from E. Sinn.

References and notes

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