reaction mixture was then poured into water (200 mL) and extracted with ethyl ether. Drying ($CaCl_2$) and evaporation yielded an oil that solidified upon standing. Recrystallization from hexane gave 3.37 g (82%) of 2-methyltellurobenzo[*b*]thiophene (**11**): mp 39 °C; MS, *m/e* (relative intensity) 278 (84), 263 (100), 133 (72); NMR δ 2.26 (s, 3 H), 7.24–7.32 (several peaks, 2 H), 7.56 (s, 1 H), 7.71–7.83 (several peaks, 2 H). Anal. Calcd for C_9H_8STe: C, 39.19; H, 2.92. Found: C, 39.30; H, 3.02.

Bis(benzo[*b*]thien-2-yltelluro)methane (13a). A solution of lithium 2-benzo[*b*]thiophenetellurolate was prepared in THF as described above for the preparation of 2-methyltellurobenzo[*b*]thiophene (**11**). Dry dichloromethane (40 mL) was added to this solution and stirring continued overnight at room temperature. The reaction mixture was then poured into water (200 mL) and extracted with more dichloromethane. Drying ($CaCl_2$) and evaporation afforded a solid that was recrystallized from CH_3CN to give 2.70 g (68%) of bis(benzo[*b*]thien-2-yltelluro)methane (**13a**): mp 125–127 °C; MS, *m/e* (relative intensity) 540 (2), 266 (18), 263 (8), 148 (18), 147 (100), 133 (24); NMR δ 3.93 (s, 1 H), 7.28–7.36 (several peaks, 2 H), 7.59 (s, 1 H), 7.72–7.83 (several peaks, 2 H). Anal. Calcd for $C_{17}H_{12}S_2Te_2$: C, 38.12; H, 2.26. Found: C, 38.12; H, 2.44.

Bis((*N*-tosyl-2-indolyl)telluro)methane (13b). A solution of lithium *N*-tosyl-2-indoletellurolate was prepared in THF as described above for the synthesis of bis(*N*-tosyl-2-indolyl) ditelluride (**8**). Dry dichloromethane (20 mL) was added to this solution and stirring continued overnight at room temperature. The reaction mixture was then poured into water (200 mL) and the solution extracted with more dichloromethane. Drying ($CaCl_2$) and evaporation afforded a semisolid that was submitted to chromatographic purification (SiO_2, CH_2Cl_2/hexane (2:3)). The yield of bis((*N*-tosyl-2-indolyl)telluro)methane (**13b**) was 2.43 g (67%): mp 182–183 °C (ether/hexane); NMR δ 2.33 (s, 3 H), 3.91 (s, 1 H), 6.68 (s, 1 H), 7.16–7.23 (several peaks, 4 H), 7.34–7.38 (m, 1 H), 7.84 (d, 2 H), 8.02–8.06 (m, 1 H). Anal. Calcd for $C_{31}H_{26}N_2O_4S_2Te_2$: C, 45.97; H, 3.24. Found: C, 45.85; H, 3.28.

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Registry No. **5**, 66697-24-3; **6**, 79045-78-8; **7**, 79991-46-1; **8**, 79991-47-2; **9**, 78301-14-1; **10**, 79991-48-3; **11**, 79991-49-4; **13a**, 79991-50-7; **13b**, 79991-51-8; thiopene, 110-02-1; furan, 110-00-9; *N*-tosylpyrrole, 17639-64-4; *N*-tosylindole, 31271-90-6; 2-bromopyridine, 109-04-6; dibenzothiophene, 132-65-0; benzo[*b*]thiophene, 95-15-8; lithium 2-benzo[*b*]thiophenetellurolate, 79991-52-9; lithium *N*-tosyl-2-indoletellurolate, 79991-53-0; tellurium, 13494-80-9.

Structures of Two μ-(Alkylthio)-μ-(alkylmercurithio)-bis(tricarbonyliron) Complexes, $(\mu\text{-RS})(\mu\text{-RHgS})Fe_2(CO)_6$ (R = CH_3 and C_2H_5)

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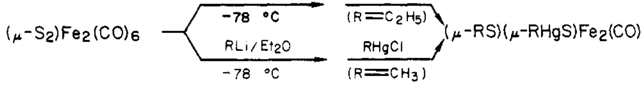
Received August 18, 1981

The structures of $(\mu\text{-RS})(\mu\text{-RHgS})Fe_2(CO)_6$ with R = CH_3 and C_2H_5 have been determined by X-ray diffraction. Crystals of both compounds are triclinic, belonging to space group $P\bar{1}$, and the cell constants are as follows: for R = CH_3, a = 7.841 (4) Å, b = 7.819 (3) Å, c = 13.197 (4) Å, α = 100.70 (3)°, β = 74.59 (3)°, γ = 107.13 (3)°; R = C_2H_5, a = 8.041 (5) Å, b = 8.463 (4) Å, c = 13.346 (6) Å, α = 101.35 (3)°, β = 79.94 (4)°, γ = 107.51 (4)°. The molecular structures consist of a dimeric unit, $[Fe(CO)_3]_2$, with short Fe–Fe distances of 2.512 (5) and 2.508 (4) Å, respectively, for R = CH_3 and C_2H_5. In addition, the Fe atoms are bridged by the two sulfur atoms of the alkylthio and alkylmercurithio groups. The angles between the three bonds, two Fe–S and one S–C or S–Hg, around the S atoms have the following average values for the complex with R = CH_3: FeSFe = 67.4 (2)°; FeSC = 115 (1)°; FeSHg = 110 (1)°. For the complex with R = C_2H_5 these angles are 66.9 (8), 116 (1), and 110 (1)°, respectively. Thus the four atoms Fe_2SC or Fe_2SHg are not coplanar, and in both compounds the S–C and S–Hg bonds of a molecule bend toward the same direction with respect to the Fe–S–Fe skeleton. This configuration is in agreement with that of $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$.

Introduction

The complexes $(\mu\text{-RS})(\mu\text{-RHgS})Fe_2(CO)_6$ were obtained by the reactions shown in Scheme I.[2] The formation of the complex with R = CH_3 was straightforward, but the isolation of the compound with R = C_2H_5 was unexpected and involved an unusual ethyl group transfer from boron to sulfur. Although the structures could with confidence be assigned on the basis of their IR, NMR, and mass spectra, their stereoconfigurations also were of interest, in particular, the relative positions of the RS and RHgS groups in the molecules. This paper reports the crystal-

Scheme I



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[1] (a) University of Waterloo. (b) Massachusetts Institute of Technology. (c) Visiting scholar at M.I.T., on leave from the Department of Chemistry, Nankai University, Tian-Jin, P.R.C.

[2] D. Seyferth, L.-C. Song, and R. S. Henderson, *J. Am. Chem. Soc.*, **103**, 5103 (1981).

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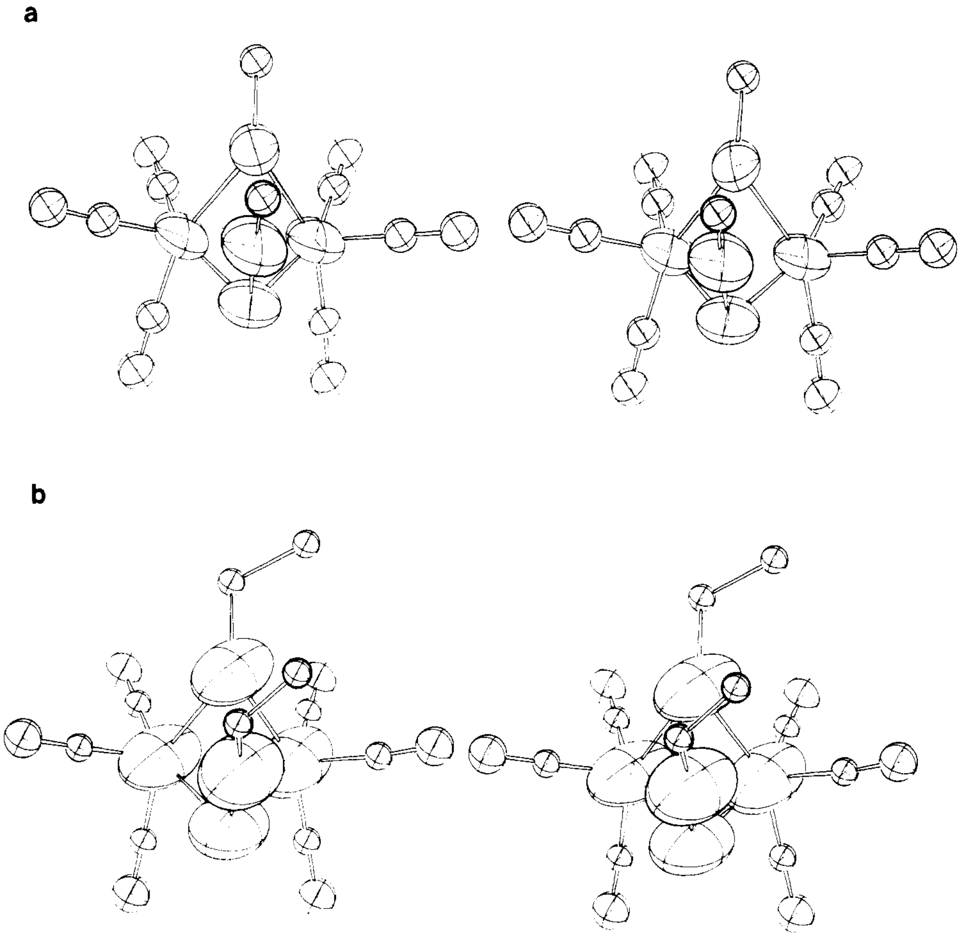


Figure 1. Stereopairs of (μ-RS)(μ-RHgS)$Fe_2(CO)_6$: (a) R = CH_3; (b) R = C_2H_5. Spheres for O and C are drawn with arbitrary fixed isotropic temperature factors of 4.0 and 3.0, respectively.

Table I. Crystal Data for (μ-RS)(μ-RHgS)$(Fe(CO)_3)_2$

	R	
	CH_3	C_2H_5
formula	$C_8H_6Fe_2HgO_6S_2$	$C_{10}H_{10}Fe_2HgO_6S_2$
mol wt	574.3	602.8
crystal type	triclinic	
a, Å	7.841 (4)	8.041 (5)
b, Å	7.819 (3)	8.463 (4)
c, Å	13.197 (4)	13.346 (6)
α, deg	100.70 (3)	100.35 (3)
β, deg	74.59 (3)	79.94 (4)
γ, deg	107.12 (3)	107.51 (4)
υ, $Å^3$	740.4 (5)	842.7 (8)
space group	$P\bar{1}$	$P\bar{1}$
D(measd)	2.54	2.40
Z	2	2
D(calcd)	2.575	2.373
mp, °C	140 (sublimate)	112-113
μ-(Mo Kα), cm^{-1}	128	112
color	red	
2θ(max), deg	40	40
no. of ref lns	1397	1574
R	0.084	0.081

lographic results for the two compound with R = CH_3 and C_2H_5.

Results and Discussion

Crystals of the title compounds with R = CH_3 or C_2H_5 are triclinic; the pertinent crystal data are given in Table I. Although the cell constants for the two compounds are similar, they are not isostructural to the extent of having the same molecular orientations and locations in the unit cell.

Table II. Comparison of Bond Lengths (Å) and Angles (Deg)[a]

	(μ-S_2)-$(Fe(CO)_3)_2$	(μ-C_2H_5S)$_2$-$(Fe(CO)_3)_2$	(μ-RS)(μ-RHgS)-$(Fe(CO)_3)_2$	
			R = CH_3	R = C_2H_5
Fe-Fe	2.552 (2)	2.537 (10)	2.512 (5)	2.508 (4)
Fe-S	2.228 (2)	2.259 (7)	2.254 (4)	2.261 (5)
Fe-S(Hg)			2.276 (6)	2.293 (5)
Fe-CO	1.776 (5)	1.81 (2)	1.73 (3)	1.74 (2)
S-S	2.007 (5)			
S· · ·S		2.93 (1)	2.886 (8)	2.904 (8)
S-C		1.81 (3)	1.84 (3)	1.82 (3)
S-Hg			2.396 (6)	2.392 (5)
Hg· · ·S			3.244 (6)	3.207 (5)
Hg-C			2.13 (5)	1.98 (4)
(Fe)C-O	1.17 (3)	1.15 (2)	1.18 (2)	1.19 (3)
*Fe*SFe	69.9 (1)	68.3 (3)	67.4 (2)	66.9 (8)
SFeFe	55.1 (2)	55.8 (8)	56.3 (2)	56.6 (2)
SFeS	53.5 (1)	81.0 (3)	79.2 (3)	79.2 (3)
SFeC	101-104	84-103	86-105	85-104
	150-151	154-158	154-159	155-158
CFeC	93.9-98.8	86-104	93-101	92-102
FeSC		113.5 (7)	115 (1)	116.5 (5)
FeSHg			110 (1)	110 (1)
SHgC			177 (1)	177 (1)

[a] Average values from those within experimental errors are given.

The X-ray analysis confirmed the structures of (μ-RS)(μ-RHgS)$Fe_2(CO)_6$ with R = CH_3 and C_2H_5 as predicted.[2] In addition, it revealed the relative positions of the R and RHg groups in the molecules. The stereopairs of the molecules are shown in Figure 1; these diagrams were made in such a way that their orientations are the

Table III. Individual Bond Distances (Å) and Angles (Deg) for $(\mu\text{-}RS)(\mu\text{-}RHgS)(Fe(CO)_3)_2$

	R	
	CH_3	C_2H_5
	Distances	
Fe(1)-Fe(2)	2.512 (5)	2.508 (4)
Fe(1)-S(1)	2.257 (7)	2.256 (6)
Fe(2)-S(1)	2.251 (7)	2.266 (6)
Fe(1)-S(2)	2.271 (7)	2.296 (6)
Fe(2)-S(2)	2.280 (7)	2.290 (6)
Fe(1)-C(1)	1.78 (3)	1.75 (3)
Fe(1)-C(2)	1.74 (3)	1.72 (2)
Fe(1)-C(3)	1.69 (3)	1.74 (3)
Fe(2)-C(4)	1.75 (3)	1.74 (3)
Fe(2)-C(5)	1.71 (3)	1.70 (3)
Fe(2)-C(6)	1.72 (3)	1.76 (3)
S(1)-C(S)	1.84 (3)	1.82 (3)
S(2)-Hg	2.396 (6)	2.392 (5)
Hg-C(Hg)	2.13 (5)	1.98 (4)
C(Hg1)-C(Hg2)		1.51 (6)
C(1)-O(1)	1.14 (3)	1.17 (3)
C(2)-O(2)	1.19 (3)	1.20 (3)
C(3)-O(3)	1.18 (3)	1.16 (3)
C(4)-O(4)	1.19 (4)	1.17 (3)
C(5)-O(5)	1.20 (3)	1.23 (3)
C(6)-O(6)	1.19 (3)	1.18 (3)
	Angles	
Fe(1)S(1)Fe(2)	67.7 (2)	67.4 (2)
Fe(1)S(2)Fe(2)	67.0 (2)	66.3 (2)
Fe(1)S(1)C(S)	114.4 (9)	117.0 (8)
Fe(2)S(1)C(S)	115.9 (9)	115.9 (7)
Fe(1)S(2)Hg	108.8 (3)	111.4 (2)
Fe(2)S(2)Hg	110.6 (3)	109.1 (2)
S(1)Fe(1)Fe(2)	56.0 (2)	56.5 (2)
S(2)Fe(1)Fe(2)	56.7 (2)	56.7 (2)
S(1)Fe(1)S(2)	79.2 (3)	79.3 (3)
S(1)Fe(2)S(2)	79.1 (3)	79.2 (3)
S(1)Fe(1)C(1)	159 (1)	104 (1)
S(1)Fe(1)C(2)	103 (1)	155 (1)
S(1)Fe(1)C(3)	155 (1)	94 (1)
S(2)Fe(1)C(1)	87 (1)	104 (1)
S(2)Fe(1)C(2)	105 (1)	85 (1)
S(2)Fe(1)C(3)	155 (1)	158 (1)
S(1)Fe(2)C(4)	103 (1)	94 (1)
S(1)Fe(2)C(5)	94 (1)	156 (1)
S(1)Fe(2)C(6)	155 (1)	102 (1)
S(2)Fe(2)C(4)	105 (1)	156 (1)
S(2)Fe(2)C(5)	158 (1)	86 (1)
S(2)Fe(2)C(6)	86 (1)	102 (1)
C(1)Fe(1)C(2)	95 (1)	99 (1)
C(1)Fe(1)C(3)	93 (1)	98 (1)
C(2)Fe(1)C(3)	100 (1)	93 (1)
C(4)Fe(2)C(5)	98 (1)	92 (1)
C(4)Fe(2)C(6)	101 (1)	102 (1)
C(5)Fe(2)C(6)	92 (1)	101 (1)
S(2)HgC(Hg)	177 (1)	177 (1)
HgC(Hg1)C(Hg2)		121 (3)

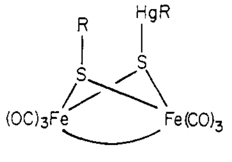
Table IV. Fractional Atomic Coordinates (×10^4) for $(\mu\text{-}CH_3S)(\mu\text{-}CH_3HgS)(Fe(CO)_3)_2$

atom	x	y	z
Hg	2149 (1)	3169 (1)	359 (1)
Fe(1)	3324 (5)	5102 (4)	3021 (3)
Fe(2)	4415 (5)	2289 (5)	2392 (3)
S(1)	1455 (9)	2331 (8)	2745 (6)
S(2)	4556 (9)	4292 (9)	1299 (5)
O(1)	6726 (38)	7930 (31)	3006 (17)
C(1)	5384 (36)	6834 (36)	3024 (20)
O(2)	997 (30)	7409 (28)	2981 (16)
C(2)	2003 (44)	6525 (41)	2988 (23)
O(3)	2594 (33)	5028 (36)	5262 (19)
C(3)	2872 (39)	5042 (36)	4341 (23)
O(4)	4537 (38)	−1069 (38)	980 (21)
C(4)	4439 (44)	268 (43)	1568 (24)
O(5)	4020 (33)	914 (33)	4371 (19)
C(5)	4194 (41)	1505 (40)	3561 (24)
O(6)	8319 (31)	3935 (29)	2195 (16)
C(6)	6721 (38)	3251 (35)	2293 (20)
C(S)	0 (38)	1395 (36)	3958 (21)
C(Hg)	105 (72)	2086 (70)	−541 (38)

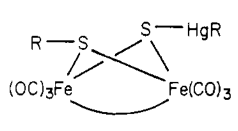
same with respect to the Fe–Fe and Fe–S(Hg) vectors so that a direct comparison can be made. It should be noted though that both compounds exist as a racemic mixture and that half of the molecules are the enantiomers of their respective molecules shown in the diagrams.

The average bond lengths and angles for the two compounds are compared with those of $(\mu\text{-}S_2)Fe_2(CO)_6$[3a] and $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$[3b] in Table II. The similarity between the latter and the two structures reported in this paper is evident from their molecular parameters. A detailed listing of the observed bond distances and angles is given in Table III. The labeling of the carbon and oxygen atoms does not have an exact correspondence in terms of molecular orientation, and, therefore, the values for the CFeC angles cannot be compared directly.

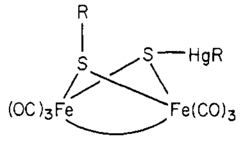
For the $(\mu\text{-}RS)(\mu\text{-}RHgS)Fe_2(CO)_6$ complexes four-conformations, I (a,a), II (e,e), III (a,e), and IV (e,a),[4] are



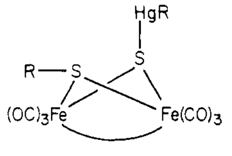
I (a,a)



II (e,e)



III (a,e)



IV (e,a)

possibile. The a,a isomer is sterically hindered and has been found only for R = H and for bridged compounds (e.g., those in which a methylene or a vinylene unit bridges the sulfur atoms) in the case of $(\mu\text{-}RS_2)Fe_2(CO)_6$ complexes. Usually the a,e and the e,e isomers are formed in reactions leading to $(\mu\text{-}RS)_2Fe_2(CO)_6$ compounds, with the a,e isomer predominating. In the case of the $(\mu\text{-}RS)(\mu\text{-}RHgS)Fe_2(CO)_6$ complexes, only one isomer could be detected by ^1H and ^{13}C NMR,[2] and X-ray crystallography now has shown this to be the e,a isomer, IV.[5] This, we believe is significant. For both $(\mu\text{-}RS)(\mu\text{-}RHgS)Fe_2(CO)_6$ structures the S–Hg bonds are bent toward the other sulfur atom, with a Hg···S distance of 3.2 Å (Table II). Thus it is tempting to suggest that this is a result of a weak Hg···S interaction and that it is this interaction which is responsible for the formation of IV rather than II or III. In mercury compound structures it is a rather common phenomenon for the Hg atom in an RHg group to have a weak secondary interaction of this kind.[6] The configuration of the a,e isomer of $(\mu\text{-}C_2H_5S)_2Fe_2(CO)_6$ is similar to those found in the $(\mu\text{-}RS)(\mu\text{-}RHgS)Fe_2(CO)_6$ compounds in that one of the

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(3) (a) C.-H. Wei and L. F. Dahl, *Inorg. Chem.*, **4**, 1 (1965); (b) L. F. Dahl and C.-H. Wei, *ibid.*, **2**, 328 (1963).

(4) The abbreviations a = axial and e = equatorial follow the nomenclature of A. Shaver, P. J. Fitzpatrick, K. Steliou, and I. S. Butler, *J. Am. Chem. Soc.*, **101**, 1313 (1979).

(5) In our preparative paper,[2] we favored the e,e structure III, for the $(\mu\text{-}RS)(\mu\text{-}RHgS)Fe_2(CO)_6$ complexes. Proton NMR indicated that the R substituents on sulfur were in the equatorial position, and on steric grounds, we suggested that the RHg substituents also should be in equatorial positions.

(6) C. Chieh, *Can. J. Chem.*, **54**, 3077 (1976).

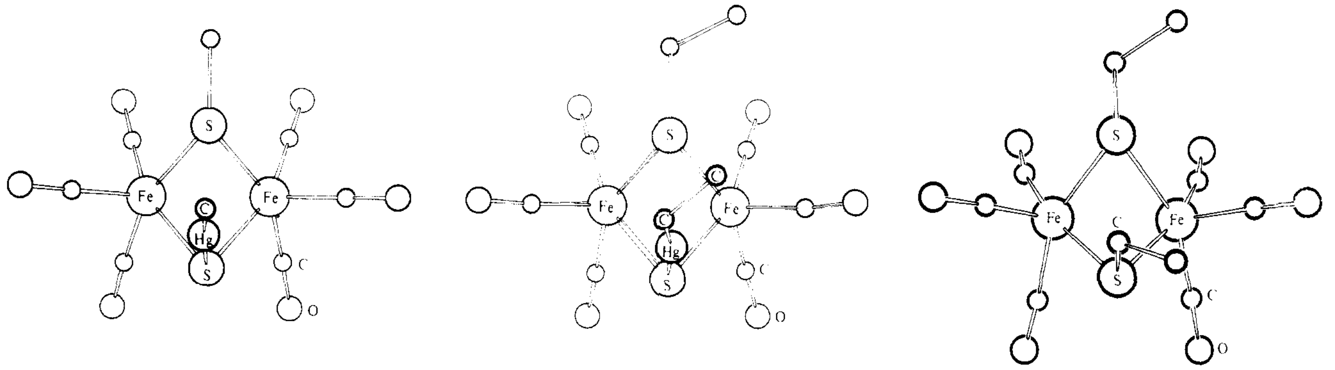

Figure 2. Comparison of the molecules (μ-CH_3S)(μ-CH_3HgS)$Fe_2(CO)_6$, (μ-C_2H_5S)(μ-C_2H_5HgS)$Fe_2(CO)_6$, and (μ-$C_2H_5S)_2Fe_2(CO)_6$. Sizes of circles are fixed for each atom type.

Table V. Fractional Atomic Coordinates ($\times 10^4$) for (μ-C_2H_5S)(μ-C_2H_5HgS)$(Fe(CO)_3)_2$

atom	x	y	z
Hg	1844 (1)	2520 (1)	290 (1)
Fe(1)	2629 (4)	306 (4)	2370 (2)
Fe(2)	15 (4)	1432 (4)	2980 (2)
S(1)	2786 (7)	3059 (7)	2618 (4)
S(2)	676 (8)	306 (7)	1304 (4)
O(1)	5862 (24)	14 (25)	1048 (15)
C(1)	4536 (32)	158 (31)	1535 (19)
O(2)	847 (24)	−3267 (24)	2324 (15)
C(2)	1550 (31)	−1797 (30)	2321 (18)
C(3)	3442 (32)	421 (31)	3518 (18)
O(3)	3939 (24)	516 (24)	4297 (16)
C(4)	112 (33)	1828 (34)	4305 (22)
O(4)	192 (23)	2113 (24)	5192 (15)
C(5)	−1579 (34)	−401 (34)	3075 (20)
O(5)	−2858 (28)	−1632 (29)	3178 (17)
C(6)	−1241 (36)	2734 (37)	2838 (21)
O(6)	−2136 (28)	3622 (30)	2873 (17)
C(S1)	3834 (30)	4361 (31)	3717 (19)
C(S2)	3140 (35)	5877 (38)	4100 (23)
C(Hg1)	2814 (50)	4269 (54)	−615 (31)
C(Hg2)	2754 (56)	6051 (61)	−229 (33)

two S–C bonds bends toward the other sulfur atom. The configurations of these molecules are compared in Figure 2. Therefore, these steric requirements when compounded with the weak Hg···S interaction make it predictable that (μ-RS)(μ-RHgS)$Fe_2(CO)_6$ complexes should always have the configuration shown in Figure 1. In the case of (μ-$RHgS)_2Fe_2(CO)_6$ complexes,[2] we predict that it is the a,e isomer which is formed since there is only enough room to accommodate one RHg group in the space between the two sulfur atoms of the molecule.

The opening of the S_2 bridge of (μ-S_2)$Fe_2(CO)_6$ in the formation of the (μ-$RS)_2Fe_2(CO)_6$ complexes[7] results in shorter Fe–Fe distances, and still shorter Fe–Fe distances were observed when RHg groups are present (Table II). However, the gross features of the bonding in these molecules remain the same as in the parent compound. A recent theoretical approach to interpret the photoelectron spectrum of (μ-S_2)$Fe_2(CO)_6$ led to the conclusion that there is a slightly bent σ bond and a significant direct Fe–Fe π bond between the iron centers.[8]

Experimental Section

Irregular crystals of the two compounds with the maximum linear dimension of 0.15 mm were mounted on a Syntex $P2_1$ computer-controlled diffractometer in an arbitrary orientation. Rotation photographs were taken, and film coordinates for 15 reflections were measured for each crystal. From these coordinates, angles for each reflection were calculated and refined by repetitive measurements. From these refined angles, cell dimensions and orientation matrices were calculated by least-squares methods.

The structures were solved by the heavy-atom method and refined by full-matrix least-squares methods using the SHELX system.[9] The weighting function $(\sigma^2(F) + 0.0001F^2)^{-1}$ was used for both structures, and the final R $(=\sum(|F_o| - |F_c|)/\sum F_o)$ and R_w $(=\sum w^{1/2}(|F_o| - |F_c|)/\sum w^{1/2}|F_o|)$ were 0.084 and 0.091 for the compound where $R = CH_3$. For the ethyl derivative, these values wer 0.081 and 0.090, respectively. In both structural analyses, Hg, Fe, and S atoms were given anisotropic temperature factors, whereas O and C atoms assumed isotropic temperature factors in the refinement by full-matrix least squares. Final atomic coordinates are given in Tables IV and V. Tables of structure factors are available as supplementary material.

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Registry No. IV (R = Me), 79733-77-0; IV (R = Et), 79813-72-2.

Supplementary Material Available: Listings of structure amplitudes for (μ-CH_3S)(μ-CH_3HgS)$Fe_2(CO)_6$ (Table VI) and for (μ-C_2H_5S)(μ-C_2H_5HgS)$Fe_2(CO)_6$ (Table VII) (17 pages). Ordering information is given on any current masthead page.

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