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The Structures of Di-μ-methylmercurithio-bis(dinitrosyliron) and Di-μ-methylmercurithio-bis(tricarbonyliron): A Comparison of (μ-$CH_3HgS)_2Fe_2(NO)_4$ and (μ-$CH_3HgS)_2Fe_2(CO)_6$

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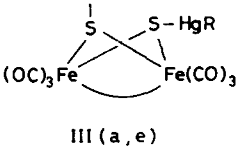
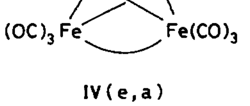
The structures of (μ-$CH_3HgS)_2Fe_2(CO)_6$, 1, *and* (μ-$CH_3HgS)_2Fe_2(NO)_4$, 2, *have been determined by X-ray diffraction. Compound* 2 *belongs to space group* $P\bar{1}$ *with* a = 6.626(2), b = 6.673(2), c = 8.116(3) Å, α = 104.13(3), β = 88.16(3) *and* γ = 100.64(3)°, Z = 1 *and* D_x = 3.530 Mg m^{-3}, *while compound* 1 *belongs to space group* C2/c *with* a = 21.52(2), b = 7.800(5), c = 20.64(2), β = 98.52(7)°, Z = 8 *and* D_x = 3.006 Mg m^{-3}. *The molecular structure of* 2 *has a center of symmetry and important bond lengths are: Hg–S, 2.362(8); Fe–Fe, 2.771(7); mean Fe–S, 2.27(1); mean Fe–N, 1.67(1) Å. The two* -$SHgCH_3$ *groups in* 1 *bend toward the same direction and the following mean distances were determined: Hg–S, 2.42(4); Fe–Fe, 2.49(2); Fe–S, 2.28(3) and Fe–C, 1.73(5) Å. The Fe–Fe bond length in the nitrosyl complex is significantly longer than that in the carbonyl complex.*

Introduction

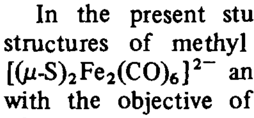
The preparation and the chemistry of the $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ anion have been developed in recent studies [1]. Among the derivatives prepared was (μ-$CH_3HgS)_2Fe_2(CO)_6$, *1* [2]. In parallel investigations [3] of the chemistry of Roussin's red salt, $[(\mu\text{-}S)_2Fe_2(NO)_4]^{2-}$, a reaction with methylmercuric chloride gave the complex (μ-$CH_3HgS)_2Fe_2(NO)_4$, *2*. A comparison of the structures of these two methylmercury derivatives was of interest. In the case of the simple ethyl derivatives of these anions a significant structural difference had been observed: The complex (μ-$C_2H_5S)_2Fe_2(CO)_6$ was found to have a 'butterfly' structure, with a puckered Fe_2S_2 ring [4]. Notable were Fe····Fe and S····S distances of 2.537 Å and 2.932 Å, respectively. The analogous (μ-$C_2H_5S)_2Fe_2(NO)_4$ has a planar Fe_2S_2 ring with large Fe····Fe and S····S distances of 2.720 Å and 3.633 Å, respectively [5]. In an X-ray crystallographic study of (μ-CH_3S)(μ-$CH_3HgS)Fe_2(CO)_6$ and (μ-C_2H_5S)(μ-$C_2H_5HgS)Fe_2(CO)_6$ it was found that of the four possible isomeric structures, I, II, III, IV, it was the e, a isomer IV which was present [6]. A weak Hg····S interaction was suggested to account for the preference for IV over II or III.



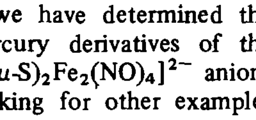
I (a,a)



II (e,e)



III (a,e)



IV (e,a)

In the present study we have determined the structures of methyl mercury derivatives of the $[(\mu\text{-}S)_2Fe_2(CO)_6]^{2-}$ and $[(\mu\text{-}S)_2Fe_2(NO)_4]^{2-}$ anions with the objective of looking for other examples of intra- and intermolecular Hg····S interactions.

0020-1693/83/$3.00

TABLE I. Crystal Data and Experimental Parameters.

Formula	$C_2H_6Fe_2Hg_2N_4O_4S_2$ $[CH_3HgSFe(NO)_2]_2$	$C_8H_6Fe_2Hg_2O_6S_2$ $[CH_3HgSFe(CO)_3]_2$
Molecular weight	727.09	775.13
Cell constants		
a Å	6.626(2)	21.52(2)
b Å	6.673(2)	7.800(5)
c Å	8.116(3)	20.64(2)
α deg	104.13(3)	–
β deg	88.16(3)	98.52(7)
γ deg	100.64(3)	–
V Å^3	342.0(2)	3425(5)
Z	1	8
d (calcd) g cm^{-3}	3.530	3.006
Crystal size mm	0.12 × 0.26 × 0.30	0.07 × 0.24 × 0.32
Intensity decline	0%	20%
μ(Mo-Kα) cm^{-1}	247.58	197.80
Mean μR	3.0	2.2
Transmission factor	0.006–0.029	0.005–0.043
Scan type	$\theta-2\theta$	$\theta-2\theta$
Scan speed deg m^{-1}	2.55–9.77	1.50–4.19
Scan range (2θ)	1° below $K_{\alpha 1}$ and 1° above $K_{\alpha 2}$	
Collection range	$h, \pm k, \pm l$	$h, k, \pm l$
2θ deg	$0 < 2\theta < 50$	$0 < 2\theta < 40$
Radiation	graphite monochromated Mo-Kα (λ, 0.71069 Å)	
Temperature °C	22 ±1	22 ± 1
No. of unique data	1183	1210
No. of observed F	1125 ($>3\sigma_F$)	834 ($>2\sigma_F$)
No. of variables	74	111
R	0.076	0.136
R_w	0.113	0.158
Weighting scheme	$[\sigma^2\lvert F\rvert + 0.002\lvert F\rvert^2]^{-1}$	$[\sigma^2\lvert F\rvert + 0.005\lvert F\rvert^2]^{-1}$
Largest shift	0.01	0.1
Standard reflections	$0\bar{2}4, 11\bar{0}, 1\bar{1}0$	$\bar{1}\bar{1}1, \bar{1}11, 11\bar{1}$
No. of reflections between checks	125	125
Extinction parameter	1.06×10^{-6}	–

Experimental

Preparations

(1) (μ-$CH_3HgS)_2Fe_2(CO)_6$, *1*, was prepared as described previously [2]; deep red crystals, m.p. ~113 °C (dec).

(2) The preparation of (μ-$CH_3HgS)_2Fe_2(NO)_4$ was as follows. A 300 ml round-bottomed Schlenk flask equipped with a serum stopper and a magnetic stir-bar was charged with 1.002 g (2.06 mmol) of Roussin's red sodium salt, $Na_2[(\mu\text{-}S)_2Fe_2(NO)_4]\cdot 8H_2O$ [7], and then flushed with nitrogen. THF (75 ml) was added by syringe to give a deep red solution. To the latter was added, with stirring, 1.00 g (4.0 mmol) of CH_3HgCl against a counter-flow of nitrogen. The reaction mixture was stirred for 12 h and then the solvent was removed at reduced pressure. The solid residue was purified by column chromatography (Florisil, dichloromethane eluent). The component traveling as a red-brown band was isolated in the form of a red, crystalline solid. Recrystallization from dichloromethane gave 0.951 g (66%, based on CH_3HgCl) of dark red crystals of (μ-$CH_3HgS)_2Fe_2(NO)_4$, m.p. 201–204 °C (dec). IR (CH_2Cl_2): ν(NO) 1765(s), 1742(s) cm^{-1}. Mass spectrum (70 eV), m/z (rel. intensity, %): 727 (M^+, 0.3), 698 (M^+ – 1NO, 0.4), 667 (M^+ – 2NO, 0.3), 637 (M^+ – 3NO, 0.1), 464 ($HgSFe_2N_4O_4$, 0.9), 451 (CH_3-

TABLE II. Fractional Atomic Coordinates and Thermal Parameters* ($\times 10^2$) for (μ-$CH_3HgS)_2Fe_2(NO)_4$.

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Hg	0.1846(2)	–0.2850(1)	0.2112(1)	6.88(8)	6.01(8)	5.36(8)	1.86(4)	–0.29(5)	–1.62(5)	5.93(5)
Fe	0.0850(5)	–0.1056(6)	–0.1463(4)	5.2(2)	6.4(2)	4.7(2)	1.1(2)	–0.2(1)	1.9(2)	5.4(1)
S	–0.095(1)	–0.245(1)	0.0563(9)	7.1(4)	5.8(3)	5.8(4)	1.7(3)	–0.1(3)	1.6(3)	6.1(2)
O(1)	–0.1031(5)	–0.264(4)	–0.467(3)	12(2)	12(2)	4(1)	1(1)	–2(1)	–1(2)	9(1)
O(2)	0.495(3)	–0.177(4)	–0.187(3)	6(1)	14(2)	9(2)	1(1)	1(1)	4(1)	10(1)
N(1)	–0.054(4)	–0.198(4)	–0.325(3)	10(1)	7(1)	4(1)	1.9(9)	–2(1)	3(1)	6.8(9)
N(2)	0.330(2)	–0.142(4)	–0.155(3)	5(1)	7(1)	7(1)	1(1)	–1(10)	2(1)	6.4(8)
C	0.413(8)	–0.305(6)	0.350(4)	16(4)	8(2)	6(2)	3(1)	2(2)	5(2)	9(2)

*Thermal parameter defined as $T = \exp[-2\pi^2 \Sigma_i \Sigma_j a_i^* a_j^* h_i h_j U_{ij}]$; U_{eq} is the equivalent isotropic temperature factor calculated as one-third of the trace of the orthogonalized U_{ij} matrix.

$HgS_2Fe_2N_2O_2$, 0.9), 423 ($CH_3HgS_2Fe_2NO$, 0.7), 391 ($CH_3HgS_2Fe_2$, 0.4), 202 (Hg, 100.0), 200 (Hg, 75.1), 176 (S_2Fe_2, 15.2) 56 (Fe, 16.8). *Anal.* Calcd. for $C_2H_6O_4N_4S_2Fe_2Hg_2$: C, 3.30; H, 0.83. Found: C, 3.36; H, 0.92.

Crystallographic Study

Both compounds were obtained in the form of black or dark-red prismatic crystals. Both are slightly sensitive to moisture, and we had no solvent readily available to attempt density measurements by flotation.

Crystal data and information pertinent to data collection and structural determination are given in Table I. Intensities of reflections were measured on a Nicolet R3m automated four-circle diffractometer with graphite-monochromatized Mo K_α radiation. For both crystals, absorption corrections were applied using an empirical method based on a pseudo-ellipsoidal treatment of the crystal from the scans of a few reflections at different azimuthal angles.

For *2* direct phase determination assuming space group *P*1 revealed the position of the two Hg atoms; two Fe and two S atoms were assigned to a group of the next four highest peaks. Values of the refined thermal parameters after two cycles of least-square refinement were used as a guide to differentiate between the Fe and S positions. A three-dimensional difference Fourier map at this point revealed the positions of the remaining non-hydrogen atoms. Several cycles of least-square refinement were carried out for the structure, and the molecular shape seemed to possess a center of symmetry. Thus the refinement was converted to space group $P\bar{1}$, but with half of the number of parameters. Further block-cascade refinement converged to an *R* value of 0.076, with the weighting scheme and extinction coefficients given in Table I.

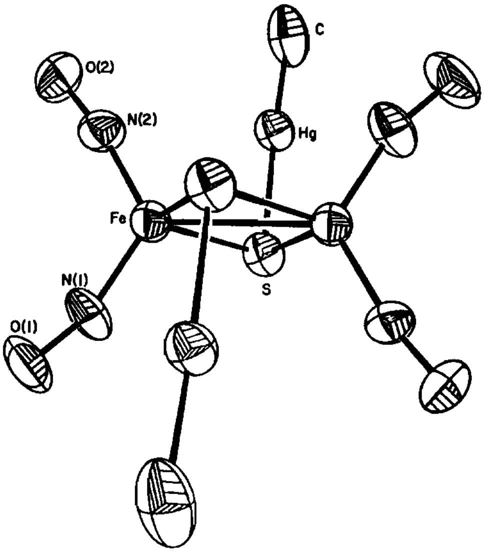


Fig. 1. Molecular structure of (μ-$CH_3HgS)_2Fe_2(NO)_4$.

The structural analysis for *1* was similar to that of *2*, but in its own space group *C*2/*c*. The intensities of the standard reflections declined by 20% at the end of data collection, and the structural refinement of *1* converged to an *R* value of only 0.136 due to the poor quality of the crystals. At least three crystals were used in attempts to improve the quality or accuracy of the results, but all three sets of data suffer the same degree of weakness. In one case, the crystal was ground to an ellipsoidal shape, but that set of data showed worse results than those reported here. There were not enough data to warrant a refinement using anisotropic thermal parameters; this is part of the reason for the high *R* value.

All computations were carried out on a Nova 3/12 minicomputer with the SHELXTL program package [8, 9]. Analytical expressions of neutral atomic scattering factors were employed [10] with anomal-

TABLE III. Fractional Atomic Coordinates and Thermal Parameters* ($Å^2 \times 10^2$) for $(\mu\text{-CH}_3\text{HgS})_2\text{Fe}_2(\text{CO})_6$.

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}/U_{iso}
Hg1	0.4136(2)	0.4129(6)	0.2665(3)	8.2(3)	7.2(3)	7.3(4)	−0.8(3)	2.0(3)	0.9(3)	7.5(2)
Hg2	0.5450(2)	0.0899(6)	0.0944(2)	7.6(3)	7.8(3)	6.1(4)	−2.0(3)	−1.5(2)	0.9(3)	7.4(2)
Fe1	0.3801(6)	0.057(2)	0.1247(8)	5.3(9)	7(1)	6(1)	−1(1)	−1.3(7)	−0.9(8)	6.4(6)
Fe2	0.3893(6)	0.346(2)	0.0754(7)	5.0(8)	6.2(9)	3.5(9)	−0.4(8)	1.3(7)	1.0(7)	4.8(5)
S1	0.444(1)	0.275(3)	0.169(1)	8(2)	3(1)	5(2)	−3(1)	−2(1)	1(1)	6(1)
S2	0.438(1)	0.106(3)	0.044(1)	10(2)	3(1)	5(2)	0(1)	2(1)	1(1)	6(1)
O11	0.298(4)	−0.12(1)	0.032(5)							16(4)
O12	0.286(3)	0.116(9)	0.204(4)							9(2)
O13	0.437(4)	−0.23(1)	0.202(5)							14(3)
O21	0.455(3)	0.628(9)	0.026(4)							10(3)
O22	0.308(5)	0.53(1)	0.133(6)							14(4)
O23	0.294(4)	0.30(1)	−0.040(4)							12(3)
C11	0.323(4)	−0.03(1)	0.072(4)							7(3)
C12	0.321(3)	0.09(1)	0.171(4)							5(3)
C13	0.406(7)	−0.13(2)	0.165(8)							16(7)
C21	0.425(3)	0.510(7)	0.044(4)							3(2)
C22	0.324(7)	0.43(3)	0.10(1)							27(14)
C23	0.329(4)	0.33(1)	0.010(4)							9(3)
C1	0.389(6)	0.55(1)	0.343(5)							10(4)
C2	0.623(4)	0.05(2)	0.159(6)							14(6)

*Anisotropic thermal parameter defined as $T = \exp[-2\pi^2 \Sigma_i \Sigma_j a_i^* a_j^* h_i h_j U_{ij}]$; U_{eq} is the equivalent isotropic temperature factor calculated as one-third of the trace of the orthogonalized U_{ij} matrix.

TABLE IV. Comparison of Bond Lengths (Å) and Angles (deg).

Bond	$[\mu\text{-C}_2\text{H}_5\text{SFe(NO)}_2]_2$	$[\mu\text{-CH}_3\text{HgSFe(NO}_2]_2$	$[\mu\text{-CH}_3\text{HgS})(\mu\text{-CH}_3\text{S})(\text{Fe(CO)}_3]_2$	$[\mu\text{-CH}_3\text{HgSFe(CO)}_3]_2$
Fe–Fe	2.72(3)	2.771(7)	2.512(5)	2.49(2)
Fe–S	2.26(4)	2.266(7)	2.254(4)	2.24(3)
	2.28(4)	2.283(8)	2.276(6)	2.28(3)
Fe–N	1.67(4)	1.67(2)		
N–O	1.17(4)	1.17(2)		
Fe–CO			1.73(3)	1.73(6)
C–O			1.18(2)	1.1(1)
C–S	1.84(1)		1.84(3)	
Hg–S		2.362(8)	2.396(6)	2.42(5)
Angles				
FeFeS	52.9(1)	52.2(2)	56.0(2)	57.4(7), 56.4(8)
	53.4(1)	52.7(2)	56.7(2)	58.2(7), 54.0(7)
SFeS	106.3(1)	104.9(3)	79.1(3)	79(1)
			79.2(3)	81(1)
SFeN		107–112		
HgSFe		98.6(3)	110(1)	116(1)
		100.8(3)		116(1)
FeSFe	74(1)	75.1(3)	67.0(2)	66.2(9)
			67.7(2)	67.7(8)

ous dispersion corrections incorporated for the Hg, Fe and S atoms. The final positional and thermal parameters for *2* and *1* are given in Tables II and III, respectively, and Tables of observed and calculated structure factors for both compounds are available as supplementary material.

Results and Discussion

The molecular structure of $(\mu\text{-CH}_3\text{HgS})_2\text{Fe}_2(\text{NO})_4$ has a center of symmetry as seen in Fig. 1. Two Fe and two S atoms form a rhombus in a plane and the major features of the molecules are very

TABLE V. Bond Lengths (Å) and Bond Angles (deg) in (μ-$CH_3SHg)_2Fe_2(NO)_4$.

Hg–S	2.362(8)	S–Hg–C	177(1)
Hg–C	1.96(5)	Fe'–Fe–S	52.2(2)
Fe–Fe'	2.771(7)		
Fe–S	2.283(8)	Fe'–Fe–S'	52.7(2)
Fe–S'	2.266(7)	S–Fe–S'	104.9(3)
Fe–N(1)	1.66(2)	S–Fe–N(1)	106.5(9)
Fe–N(2)	1.68(2)	S–Fe–N(2)	112(1)
N(1)–O(1)	1.16(3)	S'–Fe–N(1)	109.3(9)
N(2)–O(2)	1.17(3)	S'–Fe–N(2)	106.6(8)
		N(1)–Fe–N(2)	117(1)
		Hg–S–Fe	98.6(3)
		Hg–S–Fe'	100.8(3)
		Fe–S–Fe'	75.1(3)
		Fe–N(1)–O(1)	163(3)
		Fe–N(2)–O(2)	170(2)

similar to those of (μ-$C_2H_5S)_2Fe_2(NO)_4$ [5], but the bent ethyl groups are replaced by the linear H_3CHg groups. The bond lengths and angles of these two compounds are in good agreement. Comparisons of important bond distances and angles in these two compounds and those of the carbonyl complexes are presented in Table IV. The two Fe–S bond lengths in each of the two nitrosyl compounds are not significantly different on consideration of their standard deviations, but both compounds have the same trend, indicating that the S-bridges are not symmetric with respect to the two Fe atoms. Furthermore, the FeNO groups deviate from linearity to 10° or more in both nitrosyl compounds.

The Fe–Fe distances of 2.72(3) and 2.771(3) Å in the nitrosyl complexes are significantly greater than those in the carbonyl compounds (Table IV). For the latter, the Fe–Fe distances range from 2.508(4) in (μ-C_2H_5S)(μ-$C_2H_5HgS)Fe_2(CO)_6$ [6] to 2.53(10) Å in (μ-$C_2H_5S)_2Fe_2(CO)_6$ [4]. This difference in the Fe····Fe distances has been rationalized as due to the coordination numbers of Fe in the two types of compounds and a possible bent Fe–Fe bond in the carbonyl complexes [4]. In addition, the Fe–Fe distances in Roussin's black salt, $CsFe_4S_3(NO)_7 \cdot H_2O$, fall in line with those of the nitrosyl complexes [11]. The bond lengths and angles of the nitrosyl compound are given in Table V.

Aside from the low accuracy of the bond lengths and angles, the structure of the carbonyl complex has been determined beyond any doubt. The major feature of interest in this compound is the relative arrangement of the two methylmercury groups; see Fig. 2. Of the two sterically possible isomers, (e, e) and (a, e), it is the (a, e) isomer which is present [12]*. In this isomer one S–Hg bond is bent toward the other sulfur atom in the molecule, and as pointed out [6], it is this orientation which allows supplementary, weak Hg····S interaction. It may be the operation of this interaction which causes preferred formation of the (a, e) rather than the (e, e) isomer. The structural parameters of (μ-$CH_3HgS)_2Fe_2(CO)_6$ and (μ-CH_3S)(μ-$CH_3HgS)Fe_2(CO)_6$ agree very well; see Table IV. Other features such as the coordination around the Fe atoms and the somewhat symmetrical bridging of the S atoms of these compounds are essentially the same. Due to the large values of the standard deviations, a table of bond lengths and angles for the carbonyl compound is relegated to the supplementary material section.

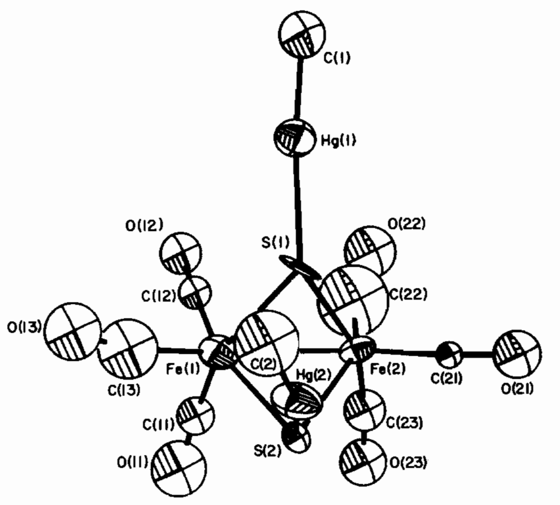
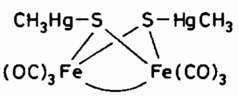
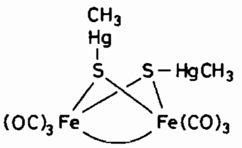


Fig. 2. Molecular structure of (μ-$CH_3HgS)_2Fe_2(CO)_6$.



(e,e)



(a,e)

Acknowledgement

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*In the proton NMR spectrum of (μ-$CH_3HgS)_2Fe_2(CO)_6$ a single resonance was observed at δ 0.834 ppm and, for this reason, we suggested in our preparative paper [2] that it was the (e, e) isomer which was present. However, after our structure determination of (μ-RHgS)(μ-RS)$Fe_2(CO)_6$, we predicted that the (μ-$RHgS)_2Fe_2(CO)_6$ (R = CH_3 and C_2H_5) complexes would be formed as the (a, e) isomers [6].

Supplementary Material

Table VI. Bond lengths and bond angles in (μ-$CH_3HgS)_2Fe_2(CO)_6$. Tables of observed and calculated structure factors may be obtained from C. Chieh.

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