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Crystal Structure of the Sulfur Dioxide Adduct of Bis[μ-(methylthio)]-bis[(trimethylphosphine)dicarbonyliron(I)]: A Product of Insertion of Sulfur Dioxide into the Metal–Metal Bond

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The crystal and molecular structure of $Fe_2(CO)_4(\mu\text{-}SO_2)(\mu\text{-}SMe)_2(PMe_3)_2 \cdot {}^1/_2(C_2H_5)_2O$ is described. The structure has been determined by using three-dimensional X-ray diffraction data collected by counter methods. Crystal symmetry is consistent with the tetragonal space group *I*4$_1$*md*. Unit cell parameters are $a = 13.164$ (1) Å, $c = 28.840$ (2) Å, $Z = 8$, $d_{calcd} = 1.518$ g cm^{-3}, $d_{measd} = 1.52$ g cm^{-3}, and μ(Mo Kα) = 15.84 cm^{-1}. The structure was solved by Patterson and subsequent Fourier techniques. Full-matrix least-squares refinement converged at $R = 0.037$ and $R_w = 0.043$ for 1286 reflections. The structure consists of two independent, similar molecules both possessing *mm* symmetry. Each molecule contains two iron atoms bridged by three sulfur ligands with average Fe–S(Me) = 2.356 Å and Fe–S(O$_2$) = 2.226 Å. Two terminal carbonyl groups (average Fe–C = 1.747 Å) and a trimethylphosphine (average Fe–P = 2.331 Å) complete the iron coordination sphere. The average nonbonding Fe–Fe contact is 3.117 Å with S(Me)–S(Me) contacts averaging 2.856 Å.

During the course of the study of the basicity of $[(\mu\text{-}SCH_3)Fe(CO)_2L]_2$ complexes we have shown that the metal–metal bond is a nucleophilic center toward a proton,[1] mercuric chloride,[2] and sulfur dioxide.[3] These results have been established by infrared and NMR spectroscopies and confirmed by an X-ray crystal structure in the case of the protonated complex.[4] Even though from the infrared and NMR results the SO$_2$ insertion into the metal–metal bond seems firmly established, a crystallographic characterization of $[(\mu\text{-}SCH_3)Fe(CO)_2P(CH_3)_3]_2SO_2$ has been undertaken in order to assess the influence of SO$_2$ on the known molecular structure of $[(\mu\text{-}SCH_3)Fe(CO)_2P(CH_3)_3]_2$.[5]

Experimental Section

$[(\mu\text{-}SCH_3)Fe(CO)_2P(CH_3)_3]_2SO_2$ has been prepared by a published procedure[3] and crystallized in a 90/10 CH$_2$Cl$_2$/diethyl ether mixture.

Crystal data for $C_{12}H_{24}Fe_2O_6P_2S_3 \cdot {}^1/_2C_4H_{10}O$: formula weight 571.22; tetragonal, space group *I*4$_1$*md* (C_{4v}^{11}, No. 109); $Z = 8$; $a = 13.164$ (1), $c = 28.840$ (2) Å; d(calcd) = 1.518, d(measd) = 1.52 g cm^{-3}; μ(Mo Kα) = 15.84 cm^{-1}; $F(000) = 2360$; $V = 4997.7$ Å^3.

Preliminary cell constants, the Laue symmetry (4/*mmm*) and systematic absences were determined from Weissenberg and precession photographs. The systematic absences *hkl*, $h + k + l \neq 2n$, and *hhl*, $2h + l \neq 4n$ are compatible with the space groups *I*4$_1$*md* and *I*$\bar{4}$2*d*. Accurate unit cell parameters were determined at ambient temperature from the least-squares refinement of the angular settings of 15 general reflections with 2θ values in the range 22–28°, carefully centered on a Syntex P2$_1$ diffractometer using Mo Kα radiation (0.71069 Å).

Collection and Reduction of the Intensity Data. The crystal used for data collection was an almost spherical complex polyhedron of diameter 0.27 ± 0.03 mm. The intensities of all 4036 *hkl* reflections ($3.0 \leq 2\theta \leq 60.0°$) were collected on the Syntex P2$_1$ diffractometer, equipped with a scintillation counter and a graphite monochromator, in the θ–2θ scan mode. The scan range was from 2θ(Mo Kα_1) − 0.8 to 2θ(Mo Kα_2) + 0.8° with background, stationary counter, and crystal measurements made at the beginning and end of each scan for one-fourth of the scan time. Variable 2θ scan speeds between 2.0 and 29.3° min^{-1} were used, the rate being dependent on the reflection intensity monitored in an initial fast scan. Two standard reflections (235 and 080) were checked every 100 reflections and exhibited ±2% variation during the data collection. These were used to scale the data to a common level. The intensities of 4036 reflections were averaged to give 2028 independent reflections of which 1286 with intensities $I > 3\sigma(I)$ were considered observed and used in the structure solution and refinement. Lorentz and polarization corrections were applied to the determination of structure amplitudes. In view of the crystal shape and small absorption coefficient, no absorption correction was applied.

Determination and Refinement of the Structure. Attempts to solve the structure by Patterson techniques in both *I*4$_1$*md* and *I*$\bar{4}$2*d* proved to be difficult. With $Z = 8$, the former space group requires that the expected molecule sit across a mirror plane while the latter requires twofold symmetry. Patterson solution for *I*4$_1$*md* with 16 iron atoms in general positions proved impossible, and this space group was rejected in favor of *I*$\bar{4}$2*d*. In this latter case, a solution was obtained utilizing all the major vectors except the strongest nonorigin peak at 0, 0, 0.42. Although the intensity of this vector was 47% of the origin and almost three times the next most intense peak in magnitude, it could only be interpreted as an iron–sulfur vector. A least-squares refinement based on the iron atom only gave a high R value of 0.55 [$R = \sum||F_o| - |F_c||/\sum|F_o|$], but from a Fourier synthesis phased with this atom, the phosphoruses were located despite considerable false symmetry. Subsequent least-squares refinements including these atoms reduced R to 0.252, but anomalously high electron density was found to be associated with the methyl sulfido group sulfur atom suggesting either a disorder of the iron site or an incorrect choice of space group. Attempts to resolve the disorder proved futile, so the search for a solution in *I*4$_1$*md* was resumed.

At this stage, the peak at 0, 0, 0.42 was recognized as possibly representing a translation within the asymmetric unit. The Patterson was then solved for two independent, one-fourth molecules per asymmetric unit separated by 0.42*c*, each possessing *mm* symmetry. Inclusion of both independent iron atoms in a least-squares refinement gave an R of 0.383, and a Fourier phased with these atoms yielded the positions of all the remaining atoms of the structure. The only noticeable difference between the two independent molecules was found to be the orientation of the trimethylphosphine methyl groups. The structure was refined with isotropic temperature factors to an R of 0.090 and with anisotropic thermal parameters to 0.068. At this stage, a difference Fourier map revealed the presence of an ether solvate molecule also sitting outside an *mm* symmetry position. Inclusion of the solvent atoms into the refinement gave convergence at $R = 0.037$ with the weighted residual R_w [$R_w = \{\sum w(|F_o| - |F_c|)^2/\sum sF_o^2\}^{1/2}$, $w^{-1} = 1.48 - 0.0114|F| + 0.00027|F|^2$] of 0.043. A final difference Fourier exhibited one peak of 0.65 e Å^{-3} in the vicinity of the iron atom of molecule A and a general maximum background noise of 0.35 e Å^{-3}. No methyl group hydrogen atoms were sufficiently resolved to warrant inclusion in the refinement. Atom scattering factors used were taken from ref 6 with corrections included for both the real and

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Table I. Atomic Coordinates (Fractional, × 10^4)

	x	y	z
		Molecule A	
Fe	0	1183 (1)	0
S(1)	0	0	−547 (1)
S(2)	1083 (2)	0	365.4 (9)
P	0	2282 (2)	639 (1)
O(1)	1618 (5)	2295 (5)	−449 (2)
O(2)	929 (9)	0	−833 (2)
C(1)	977 (6)	1876 (6)	−263 (2)
C(2)	2347 (9)	0	108 (4)
C(3)	0	1679 (11)	1208 (3)
C(4)	1079 (6)	3143 (7)	675 (3)
		Molecule B	
Fe	0	1184.7 (9)	4203.4 (5)
S(1)	0	0	3648 (1)
S(2)	1087 (2)	0	4559.1 (8)
P	0	2248 (2)	4844.9 (8)
O(1)	1625 (5)	2288 (5)	3765 (2)
O(2)	937 (6)	0	3362 (2)
C(1)	980 (6)	1868 (5)	3942 (2)
C(2)	2314 (8)	0	4275 (5)
C(3)	0	3598 (8)	4702 (4)
C(4)	1060 (8)	2100 (9)	5243 (4)
		Solvent	
O(3)	0	0	6165 (6)
C(5)	916 (17)	0	6363 (6)
C(6)	1840 (17)	0	6112 (7)

Table II. Anisotropic Thermal Parameters (Fractional, × 10^4)

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
			Molecule A			
Fe	50 (1)	57 (1)	8.9 (3)	0	0	1.9 (3)
S(1)	61 (3)	67 (3)	7.9 (5)	0	0	0
S(2)	42 (2)	57 (2)	9.8 (4)	0	0.1 (5)	0
P	47 (2)	52 (2)	10.0 (4)	0	0	0.5 (6)
O(1)	105 (6)	104 (6)	22 (1)	−26 (5)	19 (2)	10 (2)
O(2)	80 (6)	92 (6)	11 (1)	0	11 (2)	0
C(1)	79 (6)	77 (6)	10.1 (9)	−10 (5)	2 (2)	−0 (2)
C(2)	61 (9)	110 (12)	17 (2)	0	9 (3)	0
C(3)	81 (9)	94 (9)	9 (1)	0	0	2 (3)
C(4)	73 (6)	78 (6)	16 (1)	−27 (5)	1 (2)	−3 (2)
			Molecule B			
Fe	46 (1)	34.9 (8)	7.5 (2)	0	0	0.6 (3)
S(1)	59 (2)	44 (2)	5.9 (4)	0	0	0
S(2)	49 (2)	39 (1)	10.5 (3)	0	−6.6 (6)	0
P	50 (2)	38 (1)	8.4 (3)	0	0	−2.9 (5)
O(1)	92 (5)	82 (5)	21 (1)	−31 (4)	14 (2)	7 (2)
O(2)	92 (7)	74 (6)	9.1 (9)	0	12 (2)	0
C(1)	65 (5)	44 (4)	10.2 (7)	−1 (4)	3 (2)	2 (1)
C(2)	38 (6)	71 (8)	28 (2)	0	8 (3)	0
C(3)	273 (23)	32 (6)	14 (2)	0	0	4 (3)
C(4)	102 (8)	128 (10)	24 (2)	27 (7)	−30 (3)	−31 (4)
			Solvent			
O(3)	160 (22)	182 (20)	19 (3)	0	0	0
C(5)	155 (23)	155 (24)	19 (3)	0	−8 (7)	0
C(6)	139 (20)	236 (39)	24 (3)	0	7 (8)	0

Table III. Bond Lengths (A) and Angles (Deg)

	molecule A	molecule B	av
	Lengths		
Fe–Fe′	3.115 (2)	3.119 (2)	3.117
Fe–S(1)	2.217 (3)	2.235 (2)	2.226
Fe–S(2)	2.360 (2)	2.352 (2)	2.356
Fe–P	2.342 (3)	2.320 (3)	2.331
Fe–C(1)	1.749 (8)	1.745 (7)	1.747
S(1)–O(2)	1.474 (8)	1.484 (8)	1.479
S(2)–S(2)′	2.851 (3)	2.861 (3)	2.856
S(2)–C(2)	1.823 (13)	1.812 (12)	1.817
P–C(3)	1.823 (11)	1.825 (11)	1.824
P–C(4)	1.821 (9)	1.816 (10)	1.819
C(1)–O(1)	1.143 (11)	1.133 (9)	1.138
	Angles		
S(1)–Fe–S(2)	81.6 (0)	81.4 (0)	
S(1)–Fe–P	173.5 (0)	172.9 (0)	
S(1)–Fe–C(1)	93.3 (2)	92.8 (2)	
S(2)–Fe–S(2)′	74.3 (0)	74.9 (0)	
S(2)–Fe–P	93.2 (0)	93.0 (0)	
S(2)–Fe–C(1)	95.4 (2)	94.6 (2)	
S(2)–Fe–C(1)′	169.0 (2)	168.6 (2)	
P–Fe–C(1)	91.1 (2)	92.0 (2)	
C(1)–Fe–C(1)′	94.6 (3)	95.4 (3)	
Fe–S(1)–Fe′	89.3 (0)	88.5 (0)	
Fe–S(1)–O(2)	113.4 (2)	113.5 (2)	
O(2)–S(1)–O(2)′	112.1 (3)	112.5 (3)	
Fe–S(2)–Fe′	82.6 (0)	83.1 (0)	
Fe–S(2)–C(2)	111.7 (3)	110.2 (3)	
Fe–P–C(3)	116.1 (3)	114.0 (3)	
Fe–P–C(4)	115.4 (2)	116.0 (3)	
C(3)–P–C(4)	102.7 (4)	104.3 (4)	
C(4)–P–C(4)′	102.5 (3)	100.3 (4)	

solvent bonds		solvent angles	
O(3)–C(5)	1.33 (2)	C(5)–O(3)–C(5)′	129.3 (9)
C(5)–C(6)	1.42 (3)	O(3)–C(5)–C(6)	123.8 (8)

Table IV. Bond Lengths (A) and Bond Angles (Deg) in $[(FeSCH_3(CO)_2P(CH_3)_2C_6H_5)_2H]^+$ and $[FeSCH_3(CO)_2P(CH_3)_3]_2SO_2$

	$[(FeSCH_3(CO)_2$-$P(CH_3)_2C_6H_5)_2H]^+$	this work
Fe–Fe	2.594 (3)	3.117 (2)
Fe–S	2.274 (4)	2.356 (2)
Fe–S–Fe	69.5 (1)	82.9 (0)
dihedral angle Fe_1–S_1–S_2/ F_2–S_1–S_2	93.3	108
Fe–P	2.242 (5)	2.331 (3)
Fe–C (CO)	1.758 (2)	1.747 (8)

imaginary parts of the anomalous dispersion of iron.

Final positional parameters are listed in Table I with anisotropic thermal parameters in Table II. Bond lengths and angles are listed in Table III. The observed and calculated structure factor amplitudes are available as supplementary data. An ORTEP plot of both independent molecules and the solvent is shown in Figure 1. Thermal ellipsoids represent 30% probability.

Discussion

An ORTEP plot of both independent molecules and the solvent molecule is shown in Figure 1 with the atomic numbering scheme. As we can see the two independent molecules differ only by the orientation of the methyls of the trimethylphosphine group.

The structure found in the solid state is wholly consistent with the structure we proposed for the molecule in solution on the basis of spectroscopic data. The molecule is derived from the starting material *syn*-$[(\mu\text{-}SCH_3)Fe(CO)_2P(CH_3)_3]_2$ (I) by insertion of sulfur dioxide into the metal–metal bond with retention of C_{2v} symmetry. Each molecule contains two iron atoms bridged by the sulfurs of the two methylthio groups and the sulfur of the sulfur dioxide group. Two terminal carbonyl groups and one phosphine ligand complete a distorted octahedral environment of each iron atom.

The methyl groups on the sulfur bridges are in the syn position as in I.

The phosphorus ligands are nearly trans to the sulfur of the sulfur dioxide group, the S–Fe–P angle being 173.5° for molecule A and 172.9° for molecule B. The Fe–P distance of 2.330 (3) Å (average) appears very long compared with the Fe–P length of 2.221 (2) Å in I[5] and in other mononuclear iron phosphine complexes.[7] This lengthening should be at-

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(6) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, pp 202–11.

Table V. Bond Length (Å) and Bond Angles (Deg) around Sulfur in Some Dinuclear Complexes Bridged by SO_2

	$Pd_2(\mu\text{-}SO_2)$-$(Ph_2PCH_2PPh_2)_2Cl_2$[12]	$Fe_2(CO)_8SO_2$[13]	$[CpFe(CO)_2]_2SO_2$[14]	$Cp_2Fe_2(CO)_3SO_2$[15]	this work
M-S	2.237 (3)	2.216 (5)	2.2790 (06)	2.187 (1)	2.226 (3)
S-O	1.47 (1)	1.45 (1)	1.479 (2)	1.468 (3)	1.479 (8)
M-S-M	94.8 (2)	75.6	118.00 (02)	72.93 (04)	88.8 (0)
O-S-O	110.6 (6)	113.9 (7)	112.91 (08)	112.78 (17)	112.5 (3)
M-S-O	113.4 (4)	115.4 (5)	106.54 (06)	116.47 (12)	113.4 (2)

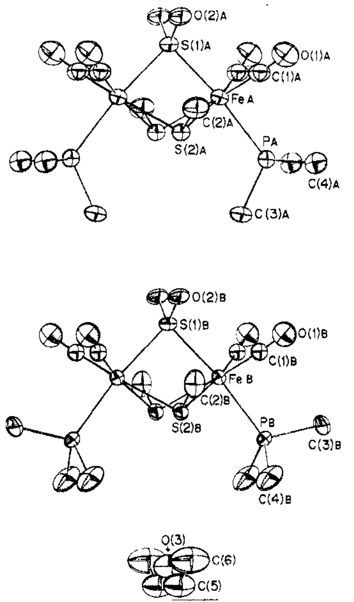

Figure 1. Perspective view of the both independent molecules of $[Fe(SCH_3)(CO)_2(P(CH_3))_3]_2SO_2{\cdot}{}^1/_2(C_2H_5)_2O$ showing the atomic numbering scheme used.

tributed to two effects. First, the metal–metal bond trans to the phosphine ligand in I is now engaged in a bond with the SO_2 molecule, and consequently the electron density around the iron atom is lowered, as the increase in frequencies of the ν(CO) stretching bands of 50 cm^{-1} compared to those of I gives evidence.[3] Second, the importance of this lengthening which is not so great in the protonated compound[4] $[((\mu\text{-}SCH_3)Fe(CO)_2P(CH_3)_2C_6H_5)_2H]^+$ (Fe–P = 2.242 Å) suggests a possible trans influence of the SO_2 group.

A similar lengthening has been observed with the $[NiSO_2(OC_2H_5)N(C_2H_4P(C_6H_5)_2)_3]^+$ molecule where the Ni–N bond trans to the $SO_2(OC_2H_5)$ group is longer than in $[NiClN(C_2H_4P(C_6H_5)_2)_3]^+$ molecule.[8]

We also observe a lengthening of the Fe–Fe distance which changes from 2.518 (1) Å in I to 3.117 (2) Å (average) in the SO_2 adduct. This bond length is in the range of values found for nonmetal–metal bonded sulfur-bridged dinuclear iron complexes as for $[Fe_2(SCF_3)_3(CO)_6]^{+}$[9] (3.062 (4) Å), $[FeSCF_3(CO)_3]_2C_4F_6$[10] (3.266 (1) Å), or $[FeSCH_3(CO)_3]_2CF(CF_3)$[11] (2.958 (1) Å).

This is the second case where it is shown that the SO_2 insertion into a metal–metal bond is accompanied by a metal–metal bond cleavage, the first case being a dinuclear palladium complex.[12]

It must be noted that, on the contrary, protonation only slightly affects the iron–iron distance (Table IV). It seems difficult to attribute this difference only to the bigger atomic radius of sulfur because the known structures where SO_2 is inserted between two metal atoms show that it can accommodate situations where the metal–metal bond does and does not occur as for instance in $Fe_2(CO)_8SO_2$[13] and $[C_5H_5Fe(CO)_2]SO_2$.[14,15] The combination of poor σ- and moderate π-acceptor character of SO_2 compared with the Lewis acid character of the proton is certainly the main reason for this difference. This is illustrated by the fact, that the ν(CO) stretching frequencies of the protonated complex[1a] are 18 cm^{-1} higher than that of the SO_2 adduct.

The lengthening of the metal–metal bond is accompanied by an increase in the Fe–S(CH_3) bond length, but this is not really characteristic of the SO_2 insertion: it seems to be a general trend for the nonmetal–metal bonded dinuclear complexes with a $Fe_2(SR)_2$ core: $[Fe_2(SCF_3)_3(CO)_6]^+$,[9] 2.305 (4) Å; $[FeSCH_3(CO)_3]_2C_2F_4$,[11] 2.310 (3) Å; $([FeSCH_3CO[P(CH_3)_3]_2]CH_3COOCCHCOOCH_3)^+$,[16] 2.339 (1) Å.

In Table V we have gathered X-ray crystallographic results for molecules where SO_2 bridges two metal atoms, and it appears that the distances and bond angles around sulfur atom are nearly the same compared with those of the SO_2 adduct of I.

Registry No. $[Fe(SCH_3)(CO)_2(P(CH_3)_3)]_2SO_2{\cdot}{}^1/_2(C_2H_5)_2O$, 73296-22-7.

Supplementary Material Available: A listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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