

Bis(1,2-diphenyl-1,2-ethylenedithiolato)trimethoxyphosphineiron(IV)

BY H. MIYAMAE, S. SATO AND Y. SAITO

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

AND K. SAKAI AND M. FUKUYAMA

Sagami Chemical Research Centre, Sagami-hara, Kanagawa 229, Japan

(Received 15 June 1977; accepted 1 August 1977)

Abstract. $[\text{Fe}(\text{S}_2\text{C}_2\text{Ph}_2)_2\text{P}(\text{OCH}_3)_3]$, $M_r = 302.23$, triclinic, $P\bar{1}$; $a = 12.393$ (1), $b = 12.747$ (1), $c = 11.798$ (2) Å, $\alpha = 110.71$ (1), $\beta = 98.43$ (1), $\gamma = 63.82$ (1)°, $U = 1564$ Å³; $Z = 2$, $D_x = 1.284$ g cm⁻³, $\mu(\text{Mo } K\alpha) = 8.46$ cm⁻¹. Block-diagonal least-squares calculations based on 5853 independent counter intensities reduced the R factor to 0.030. The Fe atom exhibits tetragonal-pyramidal coordination. Two dithiolate ions coordinate to the central Fe atom with four

S atoms approximately in a plane, and the trimethoxyphosphine molecule coordinates to the Fe atom through the P atom at an apical position. The four phenyl groups are inclined to the coordination plane with angles ranging from 40 to 60°.

Introduction. Dark-green crystals of the title compound were prepared by a procedure similar to that described by Weiher, Melby & Benson (1964). The products are

Table 1. Fractional atomic coordinates for the non-hydrogen atoms ($\times 10^4$) and for the hydrogen atoms ($\times 10^3$), with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>		<i>x</i>	<i>y</i>	<i>z</i>
Fe	2770 (0)	-78 (0)	2669 (0)	C(15)	2597 (4)	-5656 (3)	-29 (3)
S(1)	1122 (1)	-197 (1)	2861 (1)	C(16)	2233 (3)	-4387 (3)	512 (3)
S(2)	3632 (1)	-2069 (1)	1951 (1)	C(17)	5288 (2)	1803 (2)	4141 (2)
S(3)	4509 (1)	-11 (1)	3016 (1)	C(18)	5139 (3)	2913 (3)	4032 (3)
S(4)	1985 (1)	1764 (1)	3924 (1)	C(19)	6118 (3)	3194 (3)	4138 (3)
P	2690 (1)	199 (1)	964 (1)	C(20)	7235 (3)	2388 (4)	4355 (3)
C(1)	1428 (2)	-1733 (2)	2390 (2)	C(21)	7403 (3)	1296 (4)	4482 (3)
C(2)	2573 (2)	-2591 (2)	1941 (2)	C(22)	6423 (2)	1003 (3)	4379 (2)
C(3)	4261 (2)	1457 (2)	3937 (2)	C(23)	2757 (2)	3505 (2)	5310 (2)
C(4)	3099 (2)	2267 (2)	4382 (2)	C(24)	1721 (2)	4502 (2)	5180 (3)
C(5)	467 (2)	-2075 (2)	2528 (2)	C(25)	1350 (3)	5634 (3)	6090 (3)
C(6)	716 (3)	-2979 (3)	3055 (2)	C(26)	1987 (3)	5782 (3)	7133 (3)
C(7)	-185 (3)	-3292 (3)	3183 (3)	C(27)	3016 (3)	4806 (3)	7271 (3)
C(8)	-1317 (3)	-2730 (3)	2794 (3)	C(28)	3412 (2)	3673 (3)	6368 (2)
C(9)	-1582 (3)	-1844 (3)	2278 (3)	C(29)	1400 (3)	2592 (3)	1288 (3)
C(10)	-693 (2)	-1507 (3)	2144 (3)	C(30)	1559 (3)	-1118 (3)	-462 (3)
C(11)	2932 (2)	-3940 (2)	1392 (2)	C(31)	4017 (3)	-609 (3)	-993 (3)
C(12)	3990 (3)	-4772 (3)	1726 (4)	O(1)	2521 (2)	1510 (2)	977 (2)
C(13)	4341 (3)	-6030 (3)	1162 (4)	O(2)	1629 (2)	53 (2)	65 (2)
C(14)	3659 (4)	-6467 (3)	301 (4)	O(3)	3883 (2)	-677 (2)	181 (2)
H(1)	153 (3)	-341 (3)	331 (3)	H(16)	134 (2)	437 (2)	445 (2)
H(2)	2 (3)	-396 (3)	352 (3)	H(17)	67 (3)	625 (3)	601 (3)
H(3)	-194 (3)	-294 (3)	292 (3)	H(18)	171 (3)	685 (3)	775 (3)
H(4)	-237 (3)	-143 (3)	200 (3)	H(19)	344 (2)	486 (2)	795 (2)
H(5)	-90 (2)	-87 (3)	179 (2)	H(20)	407 (2)	304 (2)	645 (2)
H(6)	442 (3)	-441 (3)	244 (3)	H(21)	100 (4)	274 (4)	66 (4)
H(7)	501 (4)	-647 (4)	153 (4)	H(22)	101 (3)	276 (3)	204 (3)
H(8)	-388 (3)	-270 (3)	12 (3)	H(23)	159 (4)	336 (4)	163 (4)
H(9)	206 (3)	-586 (3)	-58 (3)	H(24)	760 (4)	187 (4)	59 (4)
H(10)	146 (2)	-383 (3)	26 (3)	H(25)	877 (4)	129 (4)	129 (4)
H(11)	438 (2)	344 (2)	387 (2)	H(26)	872 (4)	130 (4)	-7 (4)
H(12)	594 (3)	398 (3)	408 (3)	H(27)	529 (3)	119 (3)	128 (3)
H(13)	793 (3)	253 (3)	442 (3)	H(28)	664 (3)	81 (3)	161 (3)
H(13)	814 (3)	76 (3)	467 (3)	H(29)	608 (3)	-20 (3)	94 (3)
H(15)	653 (2)	27 (2)	445 (2)				

considered to be a model of Fe-S proteins and have been examined for their catalytic activities in the reduction of organic compounds; the results will be published elsewhere.

Intensities were measured on a Rigaku automated four-circle diffractometer with a crystal of dimensions $0.28 \times 0.36 \times 0.47$ mm. Reflexions with $2\theta \leq 55^\circ$ were collected by the ω - 2θ scan technique with Mo $K\alpha$ radiation monochromated by a graphite plate. 7138 reflexions were measured and significant counts were recorded for 5853 of these [$|F| \geq 3\sigma(|F|)$]. The intensities were corrected for Lorentz and polarization effects but no correction was made for absorption. The positions of all the non-hydrogen atoms were located by the routine application of the heavy-atom method followed by Fourier syntheses, space group $P\bar{1}$ being assumed. The structure was refined by the block-diagonal least-squares method. Positional parameters of the non-hydrogen atoms were refined with anisotropic thermal factors for the Fe, S and P atoms and with isotropic thermal factors for C, H and O. The structure converged at $R = 0.089$. A difference synthesis gave the positions of all the H atoms. During further refinement the atomic parameters of the H atoms were allowed to vary by assuming isotropic thermal motion. Anisotropic thermal parameters were introduced for all the non-hydrogen atoms. The final R value was 0.030 for 5853 independent reflexions. A final difference synthesis showed no peaks greater than $0.26 \text{ e } \text{\AA}^{-3}$. The atomic scattering factors for the non-hydrogen atoms were those listed in *International Tables for X-ray Crystallography* (1962) and

for H atoms the values given by Stewart, Davidson & Simpson (1965) were used. Atomic coordinates are listed in Table 1.*

Discussion. A projection of the structure along c is shown in Fig. 1, together with the labelling of the atoms. Molecules are packed *via* van der Waals forces. Fig. 2

* Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32916 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

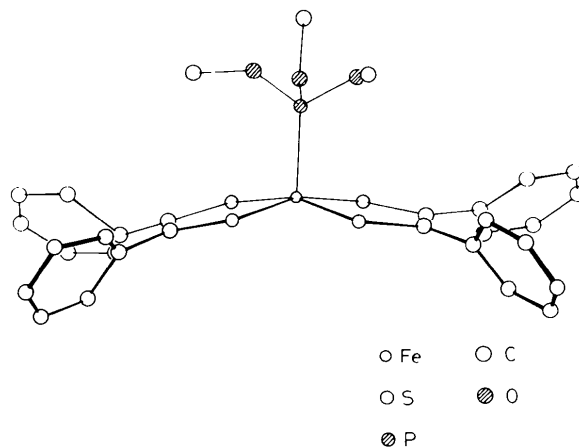


Fig. 2. The molecular structure.

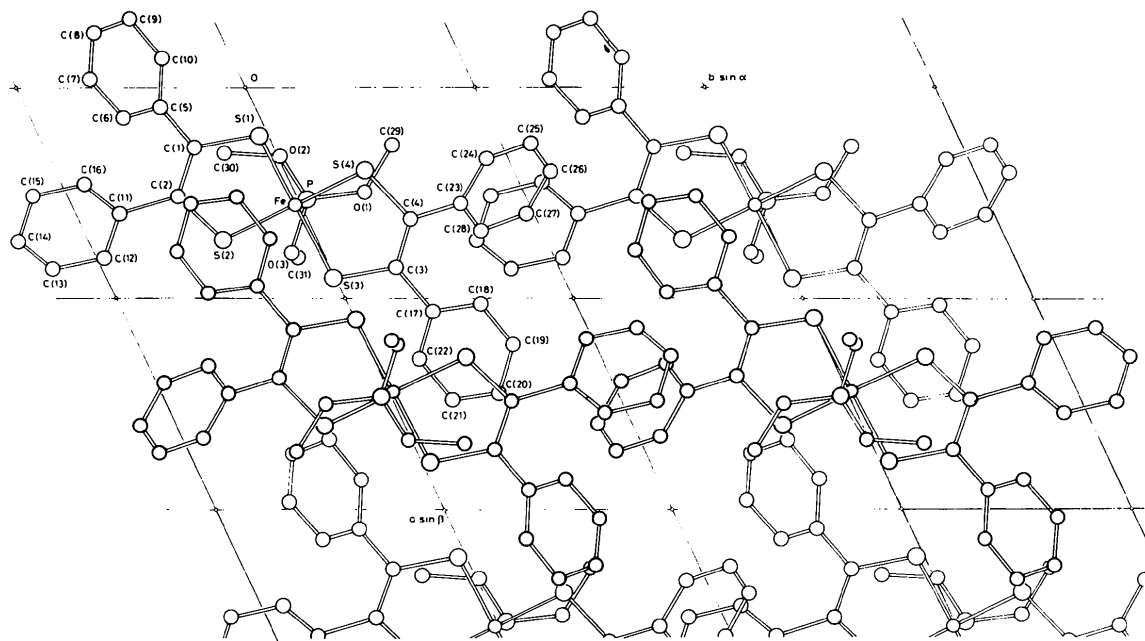


Fig. 1. A partial projection of the crystal structure along c .

Table 2. *Interatomic distances (Å) and bond angles (°) with their estimated standard deviations in parentheses*

Fe-P	2.152 (1)	S(1)-C(1)	1.716 (3)	C(5)-C(6)	1.401 (5)	C(17)-C(18)	1.400 (5)
Fe-S(1)	2.171 (1)	S(2)-C(2)	1.717 (3)	C(6)-C(7)	1.389 (6)	C(18)-C(19)	1.393 (6)
Fe-S(2)	2.164 (1)	S(3)-C(3)	1.717 (2)	C(7)-C(8)	1.366 (4)	C(19)-C(20)	1.372 (4)
Fe-S(3)	2.177 (1)	S(4)-C(4)	1.719 (3)	C(8)-C(9)	1.367 (6)	C(20)-C(21)	1.379 (7)
Fe-S(4)	2.152 (1)	C(1)-C(2)	1.394 (3)	C(9)-C(10)	1.399 (6)	C(21)-C(22)	1.403 (6)
P-O(1)	1.591 (2)	C(3)-C(4)	1.399 (3)	C(5)-C(10)	1.390 (3)	C(17)-C(22)	1.391 (3)
P-O(2)	1.604 (2)	C(1)-C(5)	1.490 (4)	C(11)-C(12)	1.390 (4)	C(23)-C(24)	1.394 (3)
P-O(3)	1.587 (2)	C(2)-C(11)	1.488 (3)	C(12)-C(13)	1.391 (4)	C(24)-C(25)	1.388 (4)
O(1)-C(29)	1.444 (3)	C(3)-C(17)	1.490 (4)	C(13)-C(14)	1.355 (6)	C(25)-C(26)	1.368 (5)
O(2)-C(30)	1.442 (4)	C(4)-C(23)	1.486 (3)	C(14)-C(15)	1.379 (5)	C(26)-C(27)	1.378 (4)
O(3)-C(31)	1.462 (4)			C(15)-C(16)	1.398 (4)	C(27)-C(28)	1.385 (4)
				C(11)-C(16)	1.387 (4)	C(23)-C(28)	1.396 (3)
P-F-S(1)	106.95 (3)	S(2)-C(2)-C(1)	118.7 (2)	C(12)-C(11)-C(16)	119.2 (3)		
P-Fe-S(2)	95.16 (3)	S(3)-C(3)-C(4)	118.2 (2)	C(11)-C(12)-C(13)	119.8 (3)		
P-Fe-S(3)	90.28 (3)	S(4)-C(4)-C(3)	118.2 (3)	C(12)-C(13)-C(14)	121.1 (3)		
P-Fe-S(4)	103.69 (3)	S(1)-C(1)-C(5)	117.9 (2)	C(13)-C(14)-C(15)	119.9 (3)		
S(1)-Fe-S(2)	88.83 (3)	S(2)-C(2)-C(11)	117.0 (2)	C(14)-C(15)-C(16)	120.1 (4)		
S(2)-Fe-S(3)	90.47 (2)	S(3)-C(3)-C(17)	117.3 (2)	C(11)-C(16)-C(15)	120.0 (3)		
S(3)-Fe-S(4)	88.63 (3)	S(4)-C(4)-C(23)	116.3 (2)	C(3)-C(17)-C(18)	120.4 (2)		
S(1)-Fe-S(4)	86.51 (3)	C(2)-C(1)-C(5)	123.7 (2)	C(3)-C(17)-C(22)	120.8 (3)		
Fe-P-O(1)	118.1 (1)	C(1)-C(2)-C(11)	124.3 (3)	C(18)-C(17)-C(22)	118.8 (3)		
Fe-P-O(2)	117.8 (1)	C(4)-C(3)-C(17)	124.4 (2)	C(17)-C(18)-C(19)	120.3 (3)		
Fe-P-O(3)	113.3 (1)	C(3)-C(4)-C(23)	125.3 (2)	C(18)-C(19)-C(20)	120.3 (4)		
Fe-S(1)-C(1)	107.0 (1)	C(1)-C(5)-C(6)	120.3 (2)	C(19)-C(20)-C(21)	120.6 (4)		
Fe-S(2)-C(2)	107.0 (1)	C(1)-C(5)-C(10)	121.2 (3)	C(20)-C(21)-C(22)	119.7 (3)		
Fe-S(3)-C(3)	106.9 (1)	C(6)-C(5)-C(10)	118.5 (3)	C(17)-C(22)-C(21)	120.4 (3)		
Fe-S(4)-C(4)	107.6 (1)	C(5)-C(6)-C(7)	120.1 (3)	C(4)-C(23)-C(24)	120.4 (2)		
O(1)-P-O(2)	123.0 (2)	C(6)-C(7)-C(8)	120.6 (4)	C(4)-C(23)-C(28)	121.0 (2)		
O(1)-P-O(3)	121.2 (2)	C(7)-C(8)-C(9)	120.5 (4)	C(24)-C(23)-C(28)	118.8 (3)		
O(2)-P-O(3)	121.6 (2)	C(8)-C(9)-C(10)	120.1 (3)	C(23)-C(24)-C(25)	120.4 (3)		
P-O(1)-C(29)	98.9 (1)	C(5)-C(10)-C(9)	120.3 (3)	C(24)-C(25)-C(26)	120.5 (3)		
P-O(2)-C(30)	100.8 (1)	C(2)-C(11)-C(12)	120.6 (2)	C(25)-C(26)-C(27)	119.8 (3)		
P-O(3)-C(31)	104.7 (1)	C(2)-C(11)-C(16)	120.3 (3)	C(26)-C(27)-C(28)	120.8 (3)		
S(1)-C(1)-C(2)	118.4 (2)			C(23)-C(28)-C(27)	120.2 (3)		

shows the molecular structure. The complex comprises an Fe atom, two diphenylethylenedithiolate ions and a trimethoxyphosphine molecule, and has pseudo mirror symmetry. The Fe and four S atoms are nearly planar. The Fe atom deviates from the average plane of the four S atoms by 0.32 Å towards the P atom.

The bond lengths and angles are listed in Table 2 and may be compared with those observed for $[\text{Fe}^{\text{III}}(\text{MNT})_2]_2^{2-}$ * (Hamilton & Bernal, 1967). The average Fe-S distance of 2.167 (2) Å in the present complex is significantly shorter than the 2.23 Å in $[\text{Fe}^{\text{III}}(\text{MNT})_2]_2^{2-}$, indicating that the oxidation state is +4 in the present compound. The S-C and ethylenic C-C bond lengths as well as the bond angles in the chelate ring in the present compound agree with those of $[\text{Fe}^{\text{III}}(\text{MNT})_2]_2^{2-}$. The observed geometry of the present complex suggests extensive delocalization of the π electrons in the ethylenic C-C bond. On the other hand, the electron

depopulation of the four phenyl groups cannot be expected, since the average planes of the phenyl groups are inclined to that formed by the four S atoms with angles ranging from 40 to 60°.

Calculations were carried out on the FACOM 230/48 computer of this Institute and the HITAC 8800/8700 computer at the Computer Centre of the University of Tokyo.

References

- HAMILTON, W. C. & BERNAL, I. (1967). *Inorg. Chem.* **6**, 2003-2008.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175-3187.
 WEIHER, J. F., MELBY, L. R. & BENSON, R. E. (1964). *J. Am. Chem. Soc.* **86**, 4329-4333.

* MNT = 1,2-dicyano-1,2-ethylenedithiol.