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# SULPHUR-CONTAINING METAL COMPLEXES

# XXIII *. SYNTHESIS OF NEW COMPLEXES CONTAINING THE $Fe_2(CO)_6S_2$ BUTTERFLY UNIT. CRYSTAL AND MOLECULAR STRUCTURE OF $[Fe_2(CO)_6\{\mu\text{-}S_2P(C_6H_4OMe\text{-}p)Fe(CO)_4\}]$, DETERMINED FROM TWO DIFFERENT CRYSTAL MODIFICATIONS

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## Summary

Diiron nonacarbonyl, $[Fe_2(CO)_9]$, reacts with Lawesson's reagent, $\overline{(p\text{-}MeOC_6H_4)P(=S)SP(=S)(C_6H_4OMe\text{-}p)S}$, in tetrahydrofuran to give a number of products including $[Fe_2(CO)_6\{\mu\text{-}S_2P(C_6H_4OMe\text{-}p)Fe(CO)_4\}]$ (III). Single crystal X-ray analyses of this compound, show a dithionophosphine unit, S–P(R)–S (R = $C_6H_4OMe\text{-}p$), to bridge the iron–iron bond of $Fe_2(CO)_6$ via the two sulphur atoms and to link a $Fe(CO)_4$ moiety through coordination of the phosphorus atom. Reaction of $Me_2P(=S)P(=S)Me_2$ with $[Fe(CO)_5]$ under irradiation with ultraviolet light, affords the *anti* form of $[Fe_2(CO)_6\{\mu\text{-}SPMe_2\}_2]$ (V), as major product.

Two separate crystal structure determinations on compound III were carried out as it crystallizes under similar condition in two different crystal modifications. Two packing modes are possible because the near-mirror symmetry of the molecule allows two equivalent orientations in the crystal.

The addition of Lawesson's reagent, $\{(p\text{-}MeO)C_6H_4P(=S)S\}_2$, to organic ketones, is a well developed method for the preparation of thiocarbonyl compounds [2]. Our efforts to utilize such a reaction for the conversion of metal carbonyl complexes into thiocarbonyl complexes, were unsuccessful. During these attempts, however, other interesting compounds were formed. We describe, here the products produced by reaction of Lawesson's reagent with $Fe_2(CO)_9$. The major product and title compound, is a new member of the well established $[(CO)_3Fe(\mu\text{-}S\text{–}A\text{–}S)Fe(CO)_3]$

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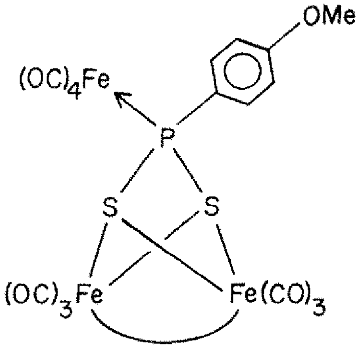
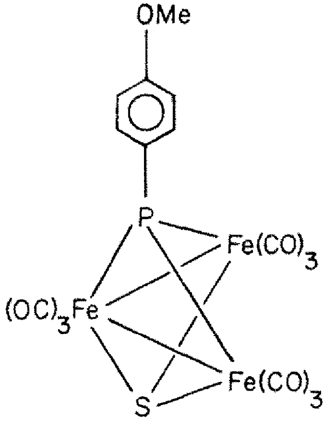
(A = bridging atom or group) class of compounds [3]. A successful first preparation of a diiron complex which contains two bridging thiophosphine groups, is also described.

## Results and discussion

Reaction of a 3-fold excess $[Fe_2(CO)_9]$ in tetrahydrofuran (THF) with $\{(p\text{-}MeO)C_6H_4PS_2\}_2$ at room temperature, produced, with evolution of CO, a number of compounds. Four were separated by column chromatography, recrystallized and isolated in pure form in yields which varied from 2–10%. The compounds $[Fe_3(CO)_9S_2]$ (I) and $[Fe_3(CO)_{12}]$ (II) have often been described in the literature [4]. The chemical composition of the air-stable compound III was determined by elemental analysis and spectroscopic methods. The cluster IV has very recently independently been described by Winter et al. [5] and Lindner et al. [6], and it was characterised by comparison of its IR, $^1H$ NMR and mass spectra with reported data.



(III)



(IV)

Whereas the infrared spectrum of III exhibited the complex pattern in the terminal CO region, associated with cluster compounds, the successive loss of ten CO ligands from the molecular ion and the conspicuous absence of a $Fe_3^+$ fragment ion in the mass spectrum, ruled out the well-known triangular tris(tricarbonyliron)(*2Fe–Fe*) structural type (also displayed by I, II and IV) for the three iron atoms present. The structure could not be assigned with confidence on the basis of spectroscopic data and a single crystal X-ray study was undertaken.

The two independent molecular structure determinations of compound III gave molecular parameters that differ by no more than experimental precision. As the determination of the orthorhombic structure was more successful (in terms of *R* factors, standard deviations and bond parameter equivalences) the discussion of the molecular structure is based on the orthorhombic results only.

The molecular conformation is illustrated in Fig. 1 and 2. The molecule can be viewed as consisting of two iron-containing moieties: a binuclear $Fe_2(CO)_6S_2$ unit and a mononuclear $Fe(CO)_4$ unit. These are joined by a $(p\text{-MeO})C_6H_4P$ group, bridging symmetrically via both sulphur atoms to the first and directly to the iron atom of the second unit.

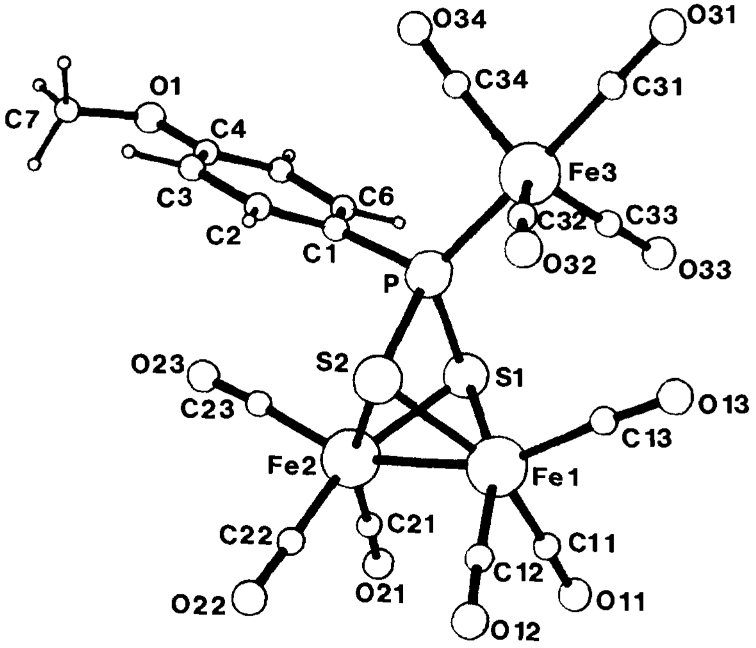


Fig. 1. Perspective drawing of a molecule of compound III with atom labels.

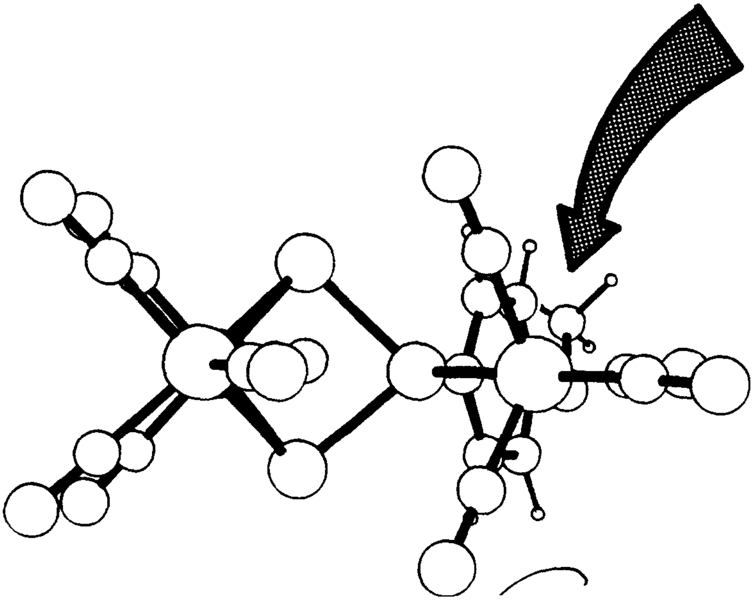


Fig. 2. Perspective drawing of a molecule of compound III, looking down the non-crystallographic "mirror plane". The arrow points out the single methyl group (C(7)) that prevents total mirror symmetry.

The crystal packing is explained in Fig. 3 and 4. Molecules of compound III exhibit mirror symmetry across a plane through the Fe and P atoms, with the exception of the methyl group (C(7)), as pointed out in Fig. 2. This small deviation from molecular symmetry results in two energetically equivalent packing modes as

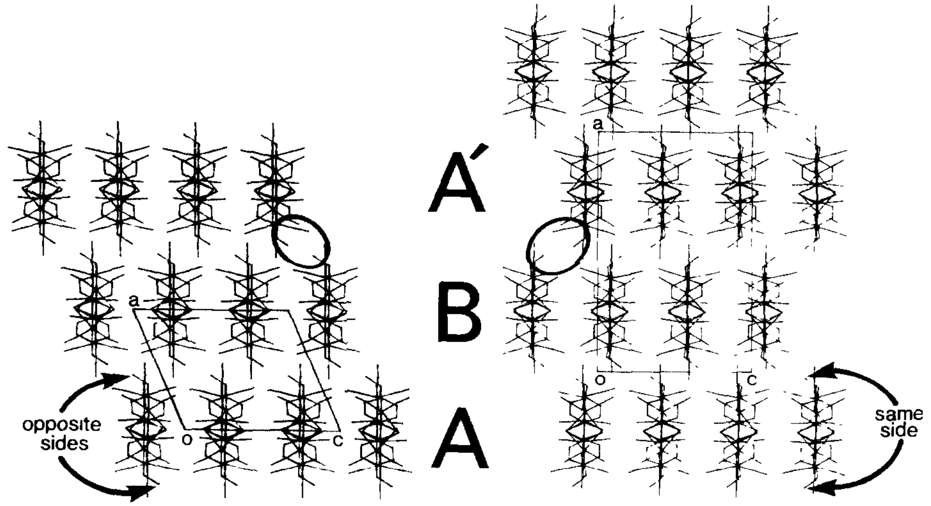


Fig. 3. Parallel projections down the *b*-axis of the crystal structures (bonds only) of the monoclinic and orthorhombic forms. The contents of only one cell down *b* is included, resulting in motifs consisting of two superimposed molecules. The different stacking modes, caused by the methyl group positions, are pointed out by the arrows. Molecular sheets A and B are exactly the same in both cases but sheet A′ is shifted in opposite directions. The intermolecular interactions causing the shifts are outlined in the circles.

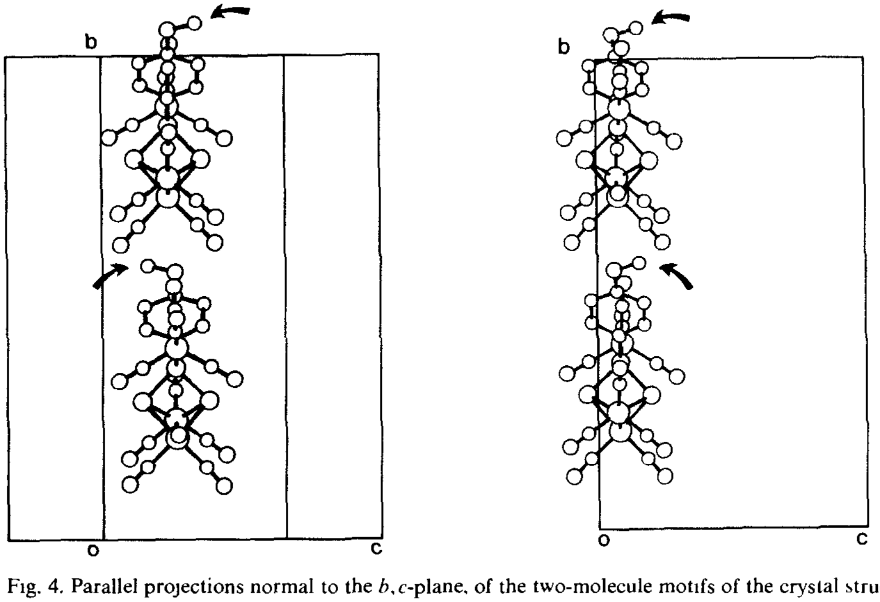


Fig. 4. Parallel projections normal to the *b*,*c*-plane, of the two-molecule motifs of the crystal structures as in Fig. 3. The arrows point out the configurations of the symmetry-breaking methyl groups, and thus the actions of the two-fold screw axis and the *b* glide plane in space groups $P2_1/c$ and *Pbca* respectively.

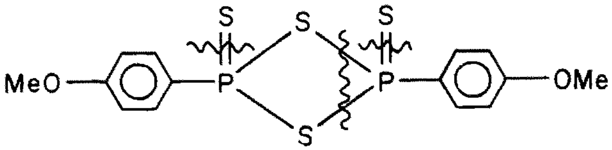
shown in Fig. 3. The relative positioning (on the same or opposite sides) of the methyl groups in molecular stacks along the direction of the *b* axis, is demonstrated by the crystallographic symmetry along the stacks (a screw-axis in the monoclinic case versus a glide plane in the orthorhombic case, Fig. 4), and results in a slight but opposite shift of sheets of molecules, along the *c* axis, in order to accomodate the repulsive intermolecular contacts between them. These shifts are illustrated in Fig. 3, where the relative positions of molecules in sheets labelled A′, are different. The two distinct crystal systems that result are evident.

The $Fe_2S_2$ skeleton of the $Fe_2(CO)_6S_2$ unit has a butterfly structure typical of the bridged diiron complexes of the type $[(CO)_3Fe(\mu\text{-}S{-}A{-}S)Fe(CO)_3]$, with A, in this unique case, being a substituted phosphorus atom. Complexes have been reported where A equals one or more carbon atoms, e.g. $[(CO)_3Fe(\mu\text{-}SCH_2S)Fe(CO)_3]$ [7] and $[(CO)_3Fe\{\mu\text{-}SC(Ph)C(Ph)S\}Fe(CO)_3]$ [8], or even substituted boron, e.g. $[(CO)_3FeS_2BNMe_2]$ [9]. Recently, the crystal structure of a dimeric molecule $[Fe_4(CO)_{12}(C_2S_4)]$, was reported, where two $Fe_2(CO)_6S_2$ units are linked and capped by a C=C fragment [10].

The Fe–Fe bond length of 2.486(3) Å and the average directly bonded $Fe_2S$ distance of 2.288 Å in III, compares well with the lengths of similar bonds observed in comparable compounds containing the $(CO)_6Fe_2S_2$ butterfly fragment, and in which no formal direct bond exists between the two sulphur atoms. The nature of the substituent(s) bonded to the two sulphur atoms has a surprisingly small effect on the bonding characteristics of this system. The chelating bridges referred to above [7,8] as well as complexes containing individually alkylated or arylated sulphurs [11,12], exhibit Fe–Fe distances between 2.49 and 2.54 Å, and Fe–S distances over the range 2.22 to 2.29 Å. The distance between the two sulphur atoms in III is 2.878 Å.

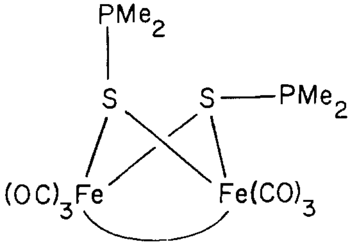
The coordination of iron in the $Fe(CO)_4$ unit of III is trigonal bipyramidal and closely resembles the structure of $[Fe(CO)_5]$ with substitution of one of the axial carbonyl ligands by a phosphorus donor atom [13]. Bond angles have near ideal values for this kind of structure. The Fe–P bond lengths of 2.203(3) Å is shorter than the value of 2.237(2) Å for $[Fe(CO)_4PHPh_2]$ [14] and comparable to the distances of 2.16(2) Å in the phosphite complex $[Fe(CO)_3\{P(OMe)_3\}_2]$ [15].

The precise interaction between the metal carbonyl and the donor system during the synthesis, can not be ascertained in terms of the structure of the complex. It is plausible that desulphurization of the thionophosphinesulphide dimer afforded compound II as well as the capping sulphur atom for IV. An unsymmetrical cleavage of the remaining dimeric fraction could then furnish the phosphorus-containing bridging groups for III and IV:



We found no evidence for the formation of compounds containing a phosphinothioylidene moiety, which has recently been characterized as a bridging ligand [16]. Compound II as well as compounds similar to IV form when phosphinothioylidenes RP=S (R = $p$-$MeC_6H_4$, $Bu^t$, Ph) react with $[Fe_3(CO)_{12}]$ in refluxing tetrahydrofuran [17]. A further study was undertaken by us to establish whether the sulphur atom in a phosphinesulphide can function as a donor atom towards iron carbonyl upon homolytic cleavage of one of the other phosphorus bonds.

The reaction of $[Fe(CO)_5]$ (in 4-fold excess) with $Me_2P(=S)P(=S)Me_2$ proceeded slowly under ultraviolet irradiation. After 5 h the brown reaction mixture was concentrated and chromatographed on $SiO_2$ to afford, after recrystallization, the new compound $[Fe_2(CO)_6(\mu\text{-}SPMe_2)_2]$ (V) (yield 18%) in analytically pure form.



(V)

From its $^1H$ NMR spectrum which contained two sharp doublets at respectively $\delta$ 2.09 and 1.75 ppm ($J$(P–CH) 9.2 Hz), we deduced that only the *syn* form of the compound was formed in isolable quantities [3]. The lines between the sharp signals of each $PMe_2$ unit, were insufficiently resolved for analysis and are due to virtual coupling between the methyl groups and the P atoms to which they are not directly bonded [18]. We conclude that a symmetrical bond cleavage of Lawesson's reagent during the formation of III, can also not be ruled out.

## Experimental

The Schlenk techniques used and instrumentation employed in this work, have been described previously [19]. Diiron nonacarbonyl was prepared according to a published procedure [20]. Lawesson's reagent the *p*-methoxyphenylthionophosphine sulphide dimer and tetramethylbiphosphine disulphide, purchased from Fluka and Strem respectively, were used without further purification. Thin layer chromatography (TLC) was used to monitor the progress of the reaction being studied.

### *Reaction of diiron nonacarbonyl with p-methoxyphenylthionophosphine sulphide*

$[Fe_2(CO)_9]$ (3.64 g, 10 mmol) and $(p\text{-}MeOC_6H_4PS_2)_2$ (1.63 g, 4 mmol) dissolved in THF (50 $cm^3$) were stirred at room temperature. The solution turned dark-red while CO came free. After 2 h, the solvent was removed at reduced pressure and the residue transferred to a cooled (−10°C) $SiO_2$ column. Elution with hexane/dichloromethane (2/1) produced consecutive dark-red, green and two orange zones which respectively afforded solid residues of compounds I–IV on stripping of solvent. The products were once again chromatographed (hexane/ether; 5/1) and finally recrystallized from ether/pentane mixtures (−30°C) to give the pure compounds. A second batch of crystals of III was prepared and recrystallized similarly.

The complexes $[Fe_3(CO)_9(\mu_3\text{-}S)_2]$ (I) (5%) [21], $[Fe_3(CO)_{12}]$ (II) (3%) and

$[Fe_3(CO)_9(\mu_3\text{-}PC_6H_4OMe\text{-}p)(\mu_3\text{-}S)]$ (IV) (2%) [5,6], were identified by comparison of their melting points and infrared as well as mass spectra with published data.

Compound III was obtained as orange-brown crystals. Yield 10%. Decomposition at 110°C (both batches of crystals). MS (*m/z*, 70 eV): 650 ($M^+$); fragment ions at values corresponding to consecutive losses of ten carbonyl groups; 176 ($Fe_2S_2^+$), 144 ($Fe_2S^+$), 112 ($Fe_2^+$). IR Spectrum (CO-region, KBr): 2086w, 2952s, 2004s, 1976s, 1960s, 1948s $cm^{-1}$. $^1H$ NMR spectrum ($CDCl_3$, $\delta$-values in ppm rel. to int. $SiMe_4$): 3.70 (s, Me), 7.0 (m, $C_6H_4$). Analysis. Found: Fe, 25.9; C, 31.48; H, 0.99; S, 9.64. $Fe_3C_{17}H_7O_{11}PS_2$ calcd.: Fe, 25.78; C, 31.42; H, 1.09; S, 9.87%.

*Reaction of iron pentacarbonyl with tetramethylbisphosphine disulphide*

Irradiation of $\{Me_2P(=S)\}_2$ (0.186 g, 1 mmol) with $Fe(CO)_5$ (0.78 g, 4 mmol) in THF at room temperature for 5 h, produced a dark brown mixture from which the major product was obtained as a yellow solid by column chromatography ($SiO_2$, $-20$°C, $CH_2Cl_2$/hexane, 1/3). Two recrystallizations from $CH_2Cl_2$/pentane ($-30$°C) afforded 84 mg (18%) of V as orange plates. Decomposition at 150°C. MS (*m/z*, 70 eV): 466 ($M^+$); consecutive loss of 6 CO ligands; 144 ($Fe_2S^+$), 112 ($Fe_2^+$). IR spectrum (CO-region, hexane): 2068m, 2047w, 2030s, 1997vs, 1990sh, 1967m, 1960w $cm^{-1}$. $^1H$ NMR spectrum ($CDCl_3$, $\delta$-values in ppm rel. to int. $SiMe_4$): 2.09 d, 1.75 d ($J$(P–CH) 9.2 Hz) ($PMe_2$). Analysis. Found: Fe, 23.9; C, 25.68; H, 2.62; S, 13.72. $Fe_2C_{10}H_{12}O_6P_2S_2$ calcd.: Fe, 23.97; C, 25.77; H, 2.60; S, 13.76%.

## Structure determination

Crystals of compound III belonging to two different crystal systems (monoclinic and orthorhombic) were obtained by crystallization under similar conditions. No difference in colour, melting point and crystal habit could be observed and only by

TABLE 1

CRYSTAL DATA AND EXPERIMENTAL DETAILS FOR THE TWO INDEPENDENT STRUCTURE DETERMINATIONS OF COMPOUND III

| | | |
|---|---|---|
| Molecular formula | $Fe_3C_{17}H_7O_{11}PS_2$ | |
| Molecular mass | 649.88 | |
| Crystal system | monoclinic | orthorhombic |
| Space group | $P2_1/c$ | $Pbca$ |
| $a$ (Å) | 10.297(5) | 18.824(8) |
| $b$ (Å) | 21.237(9) | 21.206(10) |
| $c$ (Å) | 12.096(5) | 12.123(6) |
| $\beta$ (°) | 113.7(4) | – |
| $V$ (Å$^3$) | 2422.0 | 4839.3 |
| $Z$ | 4 | 8 |
| Calculated density (g $cm^{-3}$) | 1.78 | 1.78 |
| $\mu$(Mo-$K_\alpha$) ($cm^{-1}$) | 19.63 | 19.65 |
| Maximum $2\theta$ (°) | 44 | 46 |
| Scan rate (°$\theta$ $s^{-1}$) | 0.033 | 0.038 |
| Total reflections | 2786 | 3833 |
| Unobserved ($I < 2\sigma(I)$) reflections | 1347 | 1789 |
| $R$ | 0.087 | 0.057 |
| $R_w$ ($1/\sigma_F^2$ weights) | 0.061 | 0.043 |

TABLE 2

ATOMIC AND THERMAL PARAMETERS FOR COMPOUND III

A. ORTHORHOMBIC FORM

(Fractional coordinates ($\times 10^4$, $\times 10^5$ for Fe, S, P) and equivalent isotropic temperature factors (Å$^2$, $\times 10^3$, $\times 10^4$ for Fe, S, P) for the non-H atoms)

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|---|---|---|---|---|
| Fe(1) | 20617(6) | 29027(5) | 7850(11) | 456(7) |
| Fe(2) | 33072(6) | 25142(6) | 7458(11) | 485(7) |
| Fe(3) | 10785(7) | 10518(6) | 8880(13) | 560(8) |
| S(1) | 24455(13) | 21292(11) | −3938(17) | 444(13) |
| S(2) | 24848(13) | 21556(11) | 19786(17) | 439(13) |
| P | 21589(12) | 14495(10) | 8233(22) | 417(13) |
| C(11) | 2138(6) | 3502(5) | −269(8) | 60(7) |
| O(11) | 2193(5) | 3877(3) | −917(6) | 91(5) |
| C(12) | 2113(5) | 3506(5) | 1822(8) | 53(6) |
| O(12) | 2135(4) | 3895(3) | 2447(6) | 75(5) |
| C(13) | 1096(5) | 2830(4) | 800(10) | 64(6) |
| O(13) | 501(4) | 2826(3) | 792(9) | 98(5) |
| C(21) | 3697(6) | 2960(5) | −388(10) | 70(7) |
| O(21) | 3936(4) | 3236(4) | −1065(8) | 114(6) |
| C(22) | 3680(5) | 3010(5) | 1760(10) | 81(7) |
| O(22) | 3921(4) | 3334(4) | 2416(8) | 111(6) |
| C(23) | 3996(5) | 1910(5) | 792(10) | 64(6) |
| O(23) | 4446(3) | 1568(3) | 805(9) | 88(5) |
| C(31) | 858(6) | 1430(6) | −356(11) | 73(8) |
| O(31) | 700(5) | 1674(5) | −1164(7) | 110(6) |
| C(32) | 1451(5) | 255(5) | 917(13) | 84(8) |
| O(32) | 1643(4) | −242(4) | 980(12) | 118(7) |
| C(33) | 916(5) | 1475(6) | 2156(10) | 76(8) |
| O(33) | 789(5) | 1768(5) | 2916(8) | 125(7) |
| C(34) | 224(6) | 693(5) | 930(11) | 78(8) |
| O(34) | −324(4) | 461(4) | 923(9) | 103(6) |
| C(1) | 2866(4) | 878(4) | 792(9) | 41(5) |
| C(2) | 3174(5) | 657(4) | 1747(8) | 55(6) |
| C(3) | 3689(5) | 194(5) | 1729(9) | 61(6) |
| C(4) | 3882(5) | −58(4) | 725(11) | 57(6) |
| C(5) | 3561(6) | 136(5) | −229(9) | 60(7) |
| C(6) | 3060(5) | 609(4) | −200(8) | 49(5) |
| C(7) | 4802(6) | −665(5) | 1537(10) | 87(9) |
| O(1) | 4378(4) | −524(3) | 611(7) | 86(5) |

the determination of cell parameters could be discriminated between the two types of crystals. The cell parameters are very similar, as shown in Table 1, and differ only in the length and direction of one axis.

The crystal structure of the monoclinic form was determined first. A problematical refinement prompted a data recollection from another crystal (the original decomposed after irradiation) at which time the orthorhombic modification was discovered, and the second structure determination performed.

Both structures were determined by direct methods from data collected on a Philips PW1100 diffractometer using monochromated Mo-$K_\alpha$ radiation ($\lambda$ 0.7107 Å). They were refined by full-matrix least squares using the computer program SHELX-76 [22]. Hydrogen atoms were included in calculated positions. Crystal data

B. MONOCLINIC FORM

(Fractional coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å$^2$, $\times 10^3$) for the non-H atoms)

| | $x/a$ | $y/b$ | $z/c$ | $U_{eq}$ |
|---|---|---|---|---|
| Fe(1) | −863(4) | 2101(2) | 2337(3) | 44(2) |
| Fe(2) | 1618(4) | 2479(2) | 3177(3) | 48(2) |
| Fe(3) | −2826(4) | 3953(2) | 1658(4) | 56(2) |
| P | −667(7) | 3553(3) | 2379(6) | 46(4) |
| S(1) | −73(6) | 2864(3) | 3793(5) | 43(3) |
| S(2) | −85(6) | 2853(3) | 1395(5) | 45(3) |
| C(11) | −743(26) | 1471(12) | 3446(28) | 23(18) |
| O(11) | −687(21) | 1095(10) | 4086(16) | 75(13) |
| C(12) | −724(27) | 1502(10) | 1312(26) | 48(17) |
| O(12) | −655(24) | 1131(8) | 726(19) | 90(15) |
| C(13) | −2915(34) | 2193(12) | 1665(28) | 60(20) |
| O(13) | −4016(21) | 2161(13) | 1304(23) | 119(19) |
| C(21) | 2447(29) | 2066(16) | 4530(30) | 82(24) |
| O(21) | 2879(21) | 1748(10) | 5401(21) | 96(16) |
| C(22) | 2434(30) | 2014(14) | 2435(27) | 73(22) |
| O(22) | 2817(23) | 1665(10) | 1892(21) | 108(17) |
| C(23) | 2974(25) | 3083(13) | 3618(26) | 43(18) |
| O(23) | 3882(20) | 3411(9) | 3902(21) | 86(15) |
| C(31) | −4520(32) | 4286(13) | 1053(28) | 84(23) |
| O(31) | −5632(21) | 4552(9) | 734(22) | 106(16) |
| C(32) | −3262(28) | 3553(15) | 300(28) | 63(21) |
| O(32) | −3574(23) | 3278(11) | −646(20) | 94(16) |
| C(33) | −3198(28) | 3567(16) | 2790(30) | 91(29) |
| O(33) | −3389(21) | 3317(12) | 3570(20) | 127(18) |
| C(34) | −2080(29) | 4756(14) | 1869(33) | 65(23) |
| O(34) | −1707(26) | 5241(10) | 1976(29) | 101(20) |
| C(1) | 774(24) | 4126(9) | 2876(24) | 30(15) |
| C(2) | 1348(27) | 4350(12) | 2077(22) | 46(17) |
| C(3) | 2334(30) | 4805(12) | 2351(29) | 68(20) |
| C(4) | 2789(32) | 5033(12) | 3559(34) | 44(20) |
| C(5) | 2169(31) | 4855(14) | 4335(26) | 60(20) |
| C(6) | 1204(27) | 4400(12) | 3965(24) | 49(17) |
| C(7) | 4538(36) | 5657(14) | 3225(31) | 107(27) |
| O(1) | 3979(23) | 5536(9) | 3940(18) | 84(15) |

and details of the data collection and refinement procedures are given in Table 1. Atomic and thermal parameters are listed in Table 2.

The atom numbering scheme is shown on the perspective drawing of the molecule in Fig. 1. Relevant bond distances and angles for the orthorhombic structure are tabulated in Table 3. Tables of observed and calculated structure factors and anisotropic thermal parameters are available upon request from the authors (GJK).

## Acknowledgement

We thank the South African Council for Scientific and Industrial Research for permission to use their diffractometer, computing facilities, and for financial assistance.

TABLE 3

BOND LENGTHS (A) AND ANGLES (°) FOR THE ORTHORHOMBIC STRUCTURE OF III

*Bond lengths*

| | | | |
|---|---|---|---|
| Fe(1)–Fe(2) | 2.486(2) | C(1)–C(2) | 1.376(15) |
| Fe(1)–S(1) | 2.293(3) | C(2)–C(3) | 1.380(15) |
| Fe(1)–S(2) | 2.289(3) | C(3)–C(4) | 1.373(18) |
| Fe(1)–C(11) | 1.800(11) | C(4)–C(5) | 1.372(18) |
| Fe(1)–C(12) | 1.803(11) | C(5)–C(6) | 1.375(15) |
| Fe(1)–C(13) | 1.823(11) | C(6)–C(1) | 1.380(14) |
| Fe(2)–S(1) | 2.283(3) | C(4)–O(1) | 1.366(12) |
| Fe(2)–S(2) | 2.282(3) | O(1)–C(7) | 1.409(15) |
| Fe(2)–C(21) | 1.817(12) | C(11)–O(11) | 1.127(13) |
| Fe(2)–C(22) | 1.772(12) | C(12)–O(12) | 1.113(13) |
| Fe(2)–C(23) | 1.823(10) | C(13)–O(13) | 1.121(13) |
| Fe(3)–P | 2.203(3) | C(21)–O(21) | 1.105(15) |
| Fe(3)–C(31) | 1.759(14) | C(22)–O(22) | 1.139(15) |
| Fe(3)–C(32) | 1.825(12) | C(23)–O(23) | 1.115(12) |
| Fe(3)–C(33) | 1.807(13) | C(31)–O(31) | 1.146(17) |
| Fe(3)–C(34) | 1.781(11) | C(32)–O(32) | 1.123(14) |
| P–S(1) | 2.132(3) | C(33)–O(33) | 1.134(17) |
| P–S(2) | 2.140(3) | C(34)–O(34) | 1.143(14) |
| P–C(1) | 1.801(8) | | |

*Angles around Fe(1)*

| | Fe(2) | S(1) | S(2) | C(11) | C(12) |
|---|---|---|---|---|---|
| S(1) | 56.9(1) | | | | |
| S(2) | 56.9(1) | 77.8(1) | | | |
| C(11) | 93.3(4) | 92.1(4) | 154.9(4) | | |
| C(12) | 101.5(3) | 158.3(3) | 91.8(3) | 89.5(5) | |
| C(13) | 155.8(3) | 105.1(3) | 106.4(3) | 98.4(5) | 96.0(5) |

*Angles around Fe(2)*

| | Fe(1) | S(1) | S(2) | C(21) | C(22) |
|---|---|---|---|---|---|
| S(1) | 57.3(1) | | | | |
| S(2) | 57.2(1) | 78.2(1) | | | |
| C(21) | 102.9(4) | 90.9(4) | 160.1(4) | | |
| C(22) | 99.4(4) | 156.6(4) | 90.6(4) | 93.3(5) | |
| C(23) | 154.6(3) | 105.9(4) | 103.3(4) | 95.7(5) | 96.6(5) |

*Angles around Fe(3)*

| | P | C(31) | C(32) | C(33) |
|---|---|---|---|---|
| C(31) | 90.7(4) | | | |
| C(32) | 90.1(4) | 121.9(7) | | |
| C(33) | 89.9(4) | 117.6(6) | 120.4(7) | |
| C(34) | 177.2(4) | 90.5(6) | 87.1(5) | 91.9(6) |

*Other angles*

| | | | |
|---|---|---|---|
| Fe(1)–S(1)–Fe(2) | 65.8(1) | S(1)–P–S(2) | 84.7(1) |
| Fe(1)–S(2)–Fe(2) | 65.9(1) | S(1)–P–C(1) | 104.7(3) |
| Fe(1)–S(1)–P | 88.4(1) | S(2)–P–C(1) | 105.8(3) |
| Fe(2)–S(1)–P | 90.1(1) | C(1)–C(2)–C(3) | 121.5(10) |
| Fe(1)–S(2)–P | 88.3(1) | C(2)–C(3)–C(4) | 118.7(10) |
| Fe(2)–S(2)–P | 90.0(1) | C(3)–C(4)–C(5) | 120.8(10) |
| Fe(3)–P–S(1) | 121.1(1) | C(4)–C(5)–C(6) | 119.8(10) |
| Fe(3)–P–S(2) | 120.6(1) | C(5)–C(6)–C(1) | 120.5(9) |
| Fe(3)–P–C(1) | 115.2(3) | C(6)–C(1)–C(2) | 118.7(8) |
| | | C(4)–O(1)–C(7) | 116.9(10) |

## References

1 H.G. Raubenheimer, G.J. Kruger, A. van A. Lombard, L. Linford and J.C. Viljoen, Organometallics, in press.

2 See for example: B.S. Pederson, S. Scheibye, N.H. Nilson and S.O. Lawesson, Bull. Soc. Chim. Belg., 87 (1978) 223 and ref. therein.

3 U. Krüerke (Ed.) Gmelin Handbuch der Anorganischen Chemie, Teil C1, Springer-Verlag, Berlin, 1979, p. 115

4 P R Raithby, in B.F.G. Johnson (Ed.), Transition Metal Clusters, John Wiley, New York, 1980, p. 5.

5 A Winter, L. Zsolnai and G. Huttner, J. Organomet. Chem., 234 (1982) 337.

6 E. Lindner, G.A. Weiss, H. Hiller and R. Fawzi, J. Organomet. Chem., 255 (1983) 245.

7 A. Shaver, P.J. Fitzpatrick, K. Stelion and I.S. Butler, J. Am. Chem. Soc., 101 (1979) 1313

8 H.P Weber and R.F. Bryan, J. Chem. Soc., A, (1967) 182.

9 H. Nöth and U. Schuchardt, Z. Anorg. Allgem. Chem., 418 (1975) 97.

10 P.V. Broadhurst, B.F.G. Johnson, J. Lewis and P.R Raithby, J. Chem. Soc, Chem. Commun., (1982) 140.

11 L.F. Dahl and C.H. Wei, Inorg. Chem., 2 (1963) 328.

12 R E Davis and W. Henslee, Cryst. Struct Commun., 1 (1972) 403.

13 A.W. Hanson, Acta Cryst., 18 (1962) 502.

14 B T. Kilbourn, K.N. Raeburn and D.T. Thompson, J. Chem. Soc. A, (1969) 1906.

15 D. Ginderow, Acta Cryst., B, 30 (1974) 2798

16 H Alper, F.W.B. Einstein, J.F. Petrignani and A.C. Willis, Organometallics, 2 (1983) 1422.

17 D Seyferth and H.P. Withers, Organometallics, 1 (1982) 1294.

18 L.M. Jackman and S. Sternhell, Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry, 2nd edit., Pergamon Press, London 1969, p. 147.

19 G.J. Kruger, L. Linford, H.G. Raubenheimer and A.A. Chalmers, J. Organomet. Chem., 262 (1984) 69.

20 E.H. Braye and W. Hübel, Inorg. Synth., VIII (1966) 178.

21 R.B. King, Inorg. Chem., 2 (1963) 326.

22 G.M. Sheldrick in H. Schenck, R. Olthof-Hazekamp, H. van Koningsveld and G.C. Bassi (Eds.), Computing in Crystallography, Delft, University Press, 1978.