Crystal and Molecular Structure of Di-μ-dimethylstannylene-bis(tetra-carbonyliron): A Metal Ring Compound

By C. J. Gilmore and P. Woodward,* Department of Inorganic Chemistry, The University, Bristol BS8 1TS

Crystals of $[(Me_2Sn)Fe(CO)_4]_2$ are orthorhombic, space group *Pbam*, with $Z = 4$ in a unit cell of dimensions $a = 12\cdot08$, $b = 12\cdot32$, $c = 13\cdot61$ Å. The structure was refined to R $0\cdot12$ for 544 independent reflexions: one of the two crystallographically distinct molecules shows short-range disorder. The tin and iron atoms alternate around a planar four-membered ring, with distorted octahedral co-ordination for the iron atoms and only slightly distorted tetrahedral co-ordination for the tin atoms. The idealised molecular symmetry is $D_{2h}(mmm)$. The two molecules are both astride centres of symmetry at the intersection of two-fold axes with mirror planes: in the first the tin atoms lie on the two-fold axis, in the second the iron atoms are so disposed. The Fe–Sn bond length of $2\cdot647(8)$ Å corresponds closely to the covalent radius sum for Fe^{II} and Sn^{IV}, and the Fe–C and C–O mean distances are 'normal' [$1\cdot68(8)$ and $1\cdot27(8)$ Å]. The Sn–Fe–Sn angle, however, is 77°; the metal atoms and the 'equatorial' carbonyl groups are coplanar, while the 'axial' carbonyl groups bend slightly inwards. The mean Sn–C distance is $2\cdot22(7)$ Å with a C–Sn–C angle not significantly different from tetrahedral.

OF the three known iron–tin ring cluster compounds [(I)—(III)] the structures of (II) and (III) have already been established.[1,2] Compound (I; R = Bu^n) was first reported;[3] and the analogue (I; R = Me, the subject

(I)

(II)

(III)
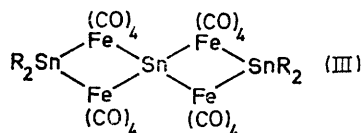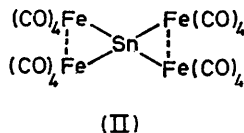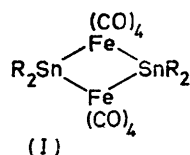
of this study) was later prepared from the reaction of dimethyl(diphenyl)tin with pentacarbonyliron.[4] The

crystals used for the present investigation were prepared by reaction of $MeSnCl_3$ with $Na_2Fe(CO)_4$. The chemistry of iron–tin compounds has recently been reviewed.[5] The gross structure of the compounds $[(R_2Sn)Fe(CO)_4]_2$ has been indicated by chemical[3] and spectroscopic[6,7] considerations.

EXPERIMENTAL

The crystals were yellow truncated octahedra showing development of {111} and {001} faces. Two crystals were used for collection of intensities because unavoidable delays resulted in deterioration of the first crystal by oxidation. Crystal (1), truncated at one end only, was of axial dimensions $0\cdot45 \times 0\cdot49 \times 0\cdot30$ mm and was used for reciprocal layers $hk0$—1, while crystal (2), truncated at both ends, was $0\cdot73 \times 0\cdot73 \times 0\cdot05$ mm and was used for $hk2$—9. Appropriate absorption corrections were computed.[8]

Approximately 1740 intensities were measured on a Buerger–Supper-Pace $0\cdot01°$-incrementing two-circle auto-diffractometer which utilises equi-inclination geometry

[1] P. F. Lindley and P. Woodward, *J. Chem. Soc. (A)*, 1967, 382.
[2] R. M. Sweet, C. J. Fritchie, and R. A. Schunn, *Inorg. Chem.*, 1967, **6**, 227.
[3] W. Hieber and R. Breu, *Ber.*, 1957, **90**, 1270.
[4] R. B. King and F. G. A. Stone, *J. Amer. Chem. Soc.*, 1960, **82**, 3833.

[5] E. H. Brooks and R. J. Cross, *Organomet. Reviews (A)*, 1970, **6**, 227.
[6] M. T. Jones, *Inorg. Chem.*, 1967, **6**, 1249.
[7] D. E. Fenton and J. J. Zuckerman, *J. Amer. Chem. Soc.*, 1968, **90**, 6226.
[8] N. W. Alcock, in 'Crystallographic Computing,' ed. F. R. Ahmed, Munksgaard, Copenhagen, 1970, 271—278.

and a stationary background–ω-scan–stationary background mode of measurement. The diffractometer settings Υ and ϕ were input from punched paper tape prepared on an Atlas computer.[9] For each recorded intensity the counter was automatically positioned to $\Upsilon(hkl)$ and the crystal rotated to $\phi_1 = [\phi_0(hkl) - \omega(hkl)/2]$, where ω is the scan interval. A background count N_1 was taken at ϕ_1 for 30 s. The crystal was then rotated at $1\cdot0°$ min^{-1} to $\phi_2 = [\phi_0(hkl) + \omega(hkl/2]$, during which time t_s the total count N_3 was recorded. The scan interval was $(2\cdot0 + 0\cdot2/L)°$, where L is the Lorentz correction for the reflection hkl. Finally, a second background count, N_2, was taken at ϕ_2, again for 30 s. The intensity of the reflection $I(hkl)$ is proportional to $[N_3 - (t_s/60)(N_1 + N_2)]$. Structure factors and their standard deviations were computed, by use of the punched paper tape output of the diffractometer, by means of a specially written data-reduction programme on an Atlas computer.[10] $F(hkl) = I(hkl)^{\frac{1}{2}}(S/Lp)^{\frac{1}{2}}$, where S is a scale factor arbitrarily assessed at 10; the standard deviation is given by: $\sigma(hkl) = (S/Lp)[N_3 + (t_s/60)^2(N_1 + N_2)]^{\frac{1}{2}}/2F(hkl)$. Reflections for which $F(hkl)/\sigma_F(hkl) < 2\cdot0$ (layers $hk0$—1) or $<3\cdot0$ (layers $hk2$—9) were regarded as 'unobserved' and were not included in the final refinement. This led to exclusion of an undesirably high proportion of the measured intensities, but ensured that those used were of relatively high quality. The stability of the apparatus and of the crystal were monitored by remeasuring the intensity of one particular reflexion on each layer between every 20 measured intensities. No significant deviation was observed. Peak profiles were checked on a chart recorder which also served to confirm the accuracy of centring of ϕ. Lattice parameters were measured from precession photographs using a very small crystal with zirconium-filtered Mo-K_α radiation.

Crystal Data.—$C_{12}H_{12}Fe_2Sn_2O_8$, $M = 634\cdot0$, Orthorhombic, $a = 12\cdot079(9)$, $b = 12\cdot329(9)$, $c = 13\cdot613(10)$, $U = 2026\cdot6$ Å^3, D_m (by flotation) $= 2\cdot02(5)$, $Z = 4$, $D_c = 2\cdot08$, $F(000) = 1200$. Mo-K_α radiation, $\lambda = 0\cdot7107$ Å; μ(Mo-K_α) $= 39\cdot5$ cm^{-1}. Space group $Pbam$. (Systematic absences of reflections occur for $0kl$ when k is odd and for $h0l$ when h is odd. The choice of space group $Pbam$ rather than $Pba2$ is justified later.[11])

Structure Solution and Refinement.—The co-ordinates of the metal atoms were extracted with difficulty from an unsharpened Patterson syntheses. Assuming the centrosymmetric space group $Pbam$, which is plausible in the light of the inherently high probable symmetry of the molecule, only half a molecule has to be located if $Z = 4$ (*i.e.*, one tin and one iron atom). It soon appeared, however, that all the metal atoms were in special positions either on two-fold axes or on mirror planes. What was needed, therefore, was the location of two half-atoms each of tin and iron, giving rise to two crystallographically different molecules. In the first of these, which lies astride a centre of symmetry at $(0,\frac{1}{2},\frac{1}{2})$, a two-fold axis passes through the tin atoms, while the iron atoms lie on the mirror plane at $z = \frac{1}{2}$. The molecular metal skeleton therefore lies in a plane parallel to z but oriented in an off-diagonal position with respect to x and y. In the second molecule, however, which lies astride a centre of symmetry at $(0,0,0)$, it is the iron atoms which lie on the two-fold axis and the tin atoms which are on the mirror plane at $z = 0$.

[9] J. Coppola, TAPSET, a Fortran program for computation of setting angles and Lorentz polarization corrections, adapted for use on an Atlas computer by S. F. Watkins.

Figure 1, a projection down the c axis of the unit cell, shows this arrangement. It will be seen that the second molecule lies in a plane parallel to z very close to the diagonal of the ab plane and, because of the near-coincidence
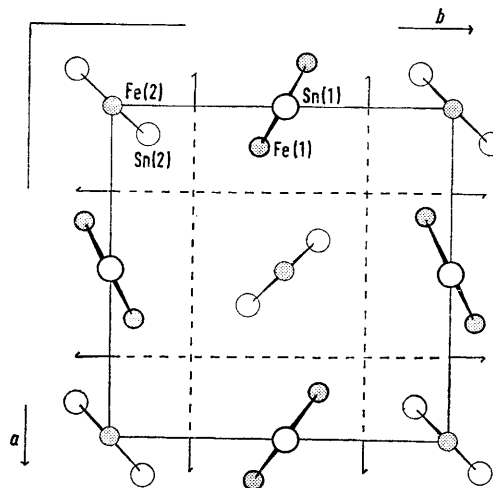

FIGURE 1 The contents of one unit cell in projection down c; molecule (1) lies astride a centre of inversion at $0,\frac{1}{2},\frac{1}{2}$, while molecule (2) lies astride the centre of inversion at the origin

of the lengths of a and b, a pseudo-tetragonal character is conferred on the whole structure by all the atoms except Fe(1). The essential correctness of this arrangement was supported by the results of attempts to refine the metal atom positions (unit weights) which gave R $0\cdot228$ (R' $0\cdot288$). Alternate cycles were used for refinement of scale factors and of z-co-ordinates for Sn(1) and Fe(2), as the data were collected around c.

Electron density difference syntheses were now computed to reveal the carbon and oxygen atoms, and although the results confirmed that the two molecules were indeed in
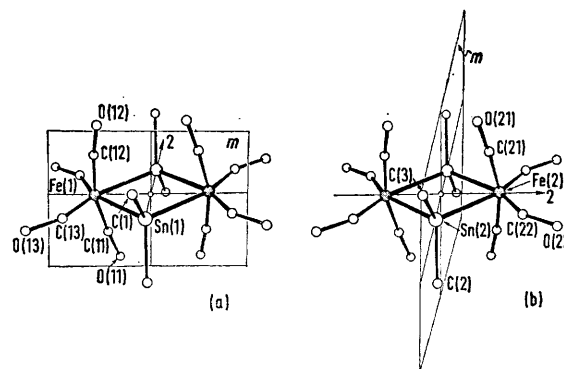

FIGURE 2 The relation between each of the two crystallographically distinct molecules and the symmetry elements of the space group; (a), molecule (1) and (b), molecule (2)

different orientations, the atoms for molecule (1) were much less clearly defined than those for molecule (2). Figure 2 shows the relation of the molecule to the crystallographic elements of symmetry, and the numbering system. Four further cycles of (alternating) least-squares refinement

[10] S. F. Watkins, SPADD, a Fortran data reduction program for use on an Atlas computer, modified by C. J. Gilmore.
[11] 'International Tables for X-Ray Crystallography,' vol. 1, Kynoch Press, Birmingham, 1952.

gave R 0·163 (R' 0·196), but with high thermal parameters for the atoms of molecule 1 ($B = 7·0$ Å² for Fe and 6·2 for Sn). Introduction of anisotropic thermal parameters for the metal atoms, with the necessary constraints [12] ($\beta_{13} = \beta_{23} = 0$ for both Fe and Sn), improved R to only a marginally significant extent: [13] four cycles gave R 0·145 (R' 0·172). An attempt was also made to improve the quality of the intensity data by eliminating random fluctuations in the background intensities and substituting a calculated average value for each small region of sin θ/λ. Refinement with unit weights, and anisotropic thermal parameters for metal atoms only, converged at R 0·122 (R' 0·132). A revised weighting scheme of the form $1/w = \sigma^2{}_F + 0·006|F_0|,²$ in which σ_F is the standard deviation derived from counting statistics, and the constant 0·006 is chosen to keep the variation of ΔF with F and with sin θ/λ to a minimum, was next applied, and refinement continued to convergence; this gave R 0·120 (R' 0·157) for 544 structure amplitudes. Although this refinement was satisfactory according to the usual criteria, the high residual indicates that the model used does not adequately describe the thermal motion and the X-ray scattering of the atoms in the unit cell.

Structure Solution by Direct Methods.—In order to remove any possible doubts about the correctness of the structure, a solution by direct methods was attempted both in *Pbam* and in *Pba2*. For the centric group,[14] Σ-2 relationships were computed for all E-values $>1·3$, and this resulted in the determination of 89 phases in terms of two symbols (p and q), as shown in Table 1. Solution (4) is seen to be

TABLE 1

Solution No.	p	q	No. of cycles of analysis	No. of Σ-2 relation-ships used	No. of discrep-ant re-lation ships	No. of phases $= +1$	No. of phases $= -1$
(1)	+1	−1	3	929	31	47	42
(2)	+1	+1	1	929	1	87	2
(3)	−1	+1	4	929	31	44	45
(4)	−1	−1	1	929	1	55	34

the one with fewest discrepant Σ-2 relationships and a balanced set of phases,[15] but for safety all four E-maps were computed. Only solution (4) gave a chemically reasonable result, and this solution was identical to our Patterson solution except for a change of origin. Finally, a direct solution for the non-centrosymmetric space group *Pba2* was sought.[16,17] With three origin-fixing phases, eight determined phases from Σ-1 relationships, and one symbol, the phases of 123 reflections were determined from 402 Σ-2 relationships. There were thus two solutions, both of which converged to situations where all phases were 0 or 180°, *i.e.*, to centrosymmetric solutions. One solution had *all* phases 0° and was therefore ignored; the other gave the same solution as was obtained from *Pbam*. Indeed, if the structure first proposed is correct, then it is unreasonable on purely chemical grounds (because of the symmetry of the molecule) for the space group to be anything other than centrosymmetric.

Three other possibilities were considered in trying to explain the inadequate refinement.

(i) *Disorder*. In all the electron density maps based on metal atom positions, satellite peaks appeared at mirror-image locations relative to planes (100) and (010); these were interpreted as arising from the pseudo-tetragonal symmetry, and were not evident in the difference maps computed after refinement of the total structure. Nevertheless, the possibility of disorder in the distribution of the metal atoms, according to the model in Figure 3, was investigated by refinement of an occupation parameter for Fe(1), starting from two half-atoms on the mirror-related sites. For the metal atoms only, this gave R 0·27 and occupation numbers 0·96 for Fe(1) and 0·04 for Fe(1'), from which we conclude that the iron atoms are not disordered. It is probably not meaningful to attempt the same procedure for Sn(2), as the alternative orientation of the molecule is already present in the structure relative to the centre of symmetry at $\frac{1}{2},\frac{1}{2},0$.
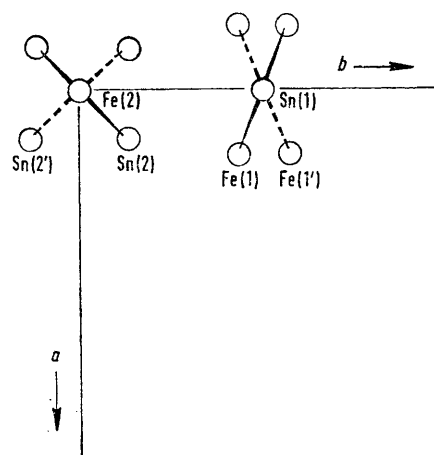

FIGURE 3   Disorder models used in attempting to explain the poor refinement of the structure

(ii) *Crystal twinning*. Some crystals that give X-ray diffraction patterns of Laue group *mmm* actually belong to the monoclinic system, but have $\beta = \beta^* = 90°$ and are microtwinned,[18-21] usually by a twinning mirror perpendicular to one of the crystal axes. Such crystals usually give diffraction patterns that exhibit systematic absences not characteristic of any orthorhombic space group. Although [(Me₂Sn)Fe(CO)₄]₂ does not fulfil this last condition, it seemed worth examining the possibility of twinning. Now, if crystals are twinned normal to one of the crystallographic axes, two of the three sets of projection data will give Patterson syntheses unaffected by the mirror plane. Twinning normal to a, for example, would give
$|F(hkl)_o|² = m|F(hkl)_{o'}|² + (1 - m)|F(\bar{h}kl)_{o'}|²$ and
$|F(hkl)_c|² = m|F(hkl)_{c'}|² + (1 - m)|F(\bar{h}kl)_{c'}|²,$ where
$|F(hkl)_o|$ and $|F(hkl)_c|$ are the observed and calculated

[12] H. A. Levy, *Acta Cryst.*, 1956, **9**, 679.
[13] W. C. Hamilton, *Acta Cryst.*, 1965, **18**, 502.
[14] J. M. Stewart, SIGMA-2 and PHASE, Fortran programs for the determination of crystal structures by direct methods, University of Maryland, 1969.
[15] I. L. Karle, T. B. Owen, and J. L. Hoard, *Acta Cryst.*, 1965, **18**, 345.

[16] P. Main, M. M. Woolfson, and G. Germain, MULTAN, a system of computer programs for the automatic solution of non-centrosymmetric structures, University of York, 1970.
[17] G. Germain, P. Main, and M. M. Woolfson, *Acta Cryst.*, 1970, B, **26**, 274.
[18] J. D. Dunitz, *Acta Cryst.*, 1964, **17**, 1299.
[19] C. H. Wei, *Inorg. Chem.*, 1969, **8**, 2384.
[20] S. C. Chang, D. Y. Park, and N. C. Li, *Inorg. Chem.*, 1968, **7**, 2144.
[21] V. Nawata, H. Iwasaki, and Y. Saito, *Bull. Chem. Soc. Japan*, 1967, **40**, 515.

structure factors for the orthorhombic twinned composite; the corresponding 'dashed' quantities are those for the two component parts and m is the fraction of one part. For any monoclinic crystal in general $|F(hk0)| = |F(\bar{h}k0)|$, and so the correct intensities will be obtained for $(hk0)$ reflections whether the crystal is twinned or not. Likewise, true intensities will be given by the $(0kl)$ reflections. But for the $(h0l)$ reflections false information would be obtained because $F(h0l) \neq F(\bar{h}0l)$.

Accordingly, two new data sets were obtained for $[(\mathrm{Me_2Sn})\mathrm{Fe(CO)_4}]_2$, $(0kl)$ and $(h0l)$, and the appropriate Patterson projections computed, together with the projection from the existing $(0kl)$ data. In every case the solution obtained was compatible with that already deduced in space group $Pbam$, and refinement of the metalatom parameters, with unit weights and isotropic thermal parameters, gave R 0·24, 0·23, and 0·23 for $0kl$, $h0l$, and $hk0$ respectively. Thus, we could obtain no evidence for the presence of a twinned monoclinic lattice.

TABLE 2
Atomic positional and thermal parameters with estimated standard deviations * in parentheses

Atom	x/a	y/b	z/c	$B/\text{Å}^2$
Molecule (1)				
Fe(1)	0·1543(11)	0·4270(10)	0·5 †	
Sn(1)	0 †	0·5 †	0·3806(6)	
C(11)	0·056(9)	0·307(11)	0·5 †	9·4(31)
O(11)	0·010(5)	0·224(5)	0·5 †	5·6(12)
C(12)	0·195(5)	0·582(5)	0·5 †	4·3(15)
O(12)	0·224(4)	0·663(5)	0·5 †	6·5(13)
C(13)	0·237(5)	0·384(5)	0·403(5)	5·5(14)
O(13)	0·291(6)	0·359(6)	0·349(6)	14·9(21)
C(1)	0·056(5)	0·622(5)	0·288(6)	7·6(16)
Molecule (2)				
Fe(2)	0 †	0 †	0·1517(7)	
Sn(2)	0·0954(3)	0·0965(3)	0 †	
C(21)	0·097(4)	−0·097(4)	0·135(4)	4·2(9)
O(21)	0·167(3)	−0·162(3)	0·112(3)	5·7(8)
C(22)	0·085(5)	0·083(5)	0·215(6)	6·1(14)
O(22)	0·125(3)	0·127(3)	0·297(3)	7·1(10)
C(2)	0·063(6)	0·280(6)	0 †	4·8(16)
C(3)	0·271(5)	0·069(5)	0 †	3·9(14)

* Estimated standard deviations include cell parameter errors. † Special position, not refined.

Anisotropic thermal parameters ($\times 10^4$) for Fe and Sn ‡

Atom	β_{11}	β_{22}	β_{33}	β_{12}
Molecule (1)				
Fe(1)	114(11)	81(10)	117(12)	−2(8)
Sn(1)	99(5)	126(6)	75(5)	−15(5)
Molecule (2)				
Fe(2)	60(6)	44(5)	31(9)	−1(6)
Sn(2)	46(2)	40(2)	44(4)	−7(3)

‡ In the form: $[(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$. (The symmetry requires $\beta_{13} = \beta_{23} = 0$).

(iii) *Short range disorder in the atomic positions for molecule* 1. The third, and to us most probable, explanation of the poor agreement between observed and calculated structure factors is that the atoms of molecule (1) show short-range disorder which the least-squares refinement attempts to compensate by converging to high thermal parameters. A similar situation has been encountered in the structure determination of the tetragonal form of elementary boron.[22] The difficulties of formulating a

[22] J. L. Hoard, R. E. Hughes, and D. E. Sands, *J. Amer. Chem. Soc.*, 1958, **80**, 4507.

TABLE 3
Molecular geometry

Molecule (1)		Molecule (2)	
(a) Metal ring (Å)			
Fe(1)–Sn(1)	2·631(11)	Fe(2)–Sn(2)	2·647(8)
Fe(1)–Fe(1$^\text{I}$)	4·139(15)	Fe(2)–Fe(2$^\text{II}$)	4·131(19)
Sn(1)–Sn(1$^\text{III}$)	3·250(15)	Sn(2)–Sn(2$^\text{IV}$)	3·312(8)
(b) Metal–axial carbonyl groups (Å)			
Fe(1)–C(11)	1·89(13)	Fe(2)–C(21)	1·69(5)
C(11)–O(11)	1·17(12)	C(21)–O(21)	1·21(8)
Fe(1)–C(12)	1·97(7)		
C(12)–O(12)	1·06(7)		
(c) Metal–equatorial carbonyl groups (Å)			
Fe(1)–C(13)	1·74(7)	Fe(2)–C(22)	1·68(7)
C(13)–O(13)	1·02(8)	C(22)–O(22)	1·33(8)
(d) Metal–methyl group (Å)			
Sn(1)–C(1)	2·08(7)	Sn(2)–C(2)	2·30(7)
		Sn(2)–C(3)	2·15(6)
(e) Bond angles (°)			
Fe(1)–Sn(1)–Fe(1$^\text{I}$)	103·7(4)	Fe(2)–Sn(2)–Fe(2$^\text{II}$)	102·6(3)
Sn(1)–Fe(1)–Sn(1$^\text{III}$)	76·3(4)	Sn(2)–Fe(2)–Sn(2$^\text{IV}$)	77·4(3)
C(11)–Fe(1)–C(12)	156(4)	C(21)–Fe(2)–C(21$^\text{IV}$)	165(4)
C(11)–Fe(1)–C(13)	97(3)	C(21)–Fe(2)–C(22)	94(2)
C(12)–Fe(1)–C(13)	99(2)		
C(13)–Fe(1)–C(13$^\text{III}$)	99(3)	C(22)–Fe(2)–C(22$^\text{IV}$)	119(5)
C(1)–Sn(1)–C(1$^\text{I}$)	105(4)	C(2)–Sn(2)–C(3)	109(2)
Sn(1)–Fe(1)–C(11)	80(3)	Sn(2)–Fe(2)–C(21)	85(2)
Sn(1)–Fe(1)–C(12)	81(2)		
Sn(1)–Fe(1)–C(13)	92(2)	Sn(2)–Fe(2)–C(22)	82(3)
Sn(1)–Fe(1)–C(13$^\text{III}$)	168(2)	Sn(2)–Fe(2)–C(22$^\text{IV}$)	159(3)
Fe(1$^\text{I}$)–Fe(1)–C(11)	72(2)	Fe(2$^\text{II}$)–Fe(2)–C(21)	82(2)
Fe(1$^\text{I}$)–Fe(1)–C(12)	79(2)		
Fe(1)–C(11)–O(11)	170(10)	Fe(2)–C(21)–O(21)	172(5)
Fe(1)–C(12)–O(12)	175(6)		
Fe(1)–C(13)–O(13)	175(7)	Fe(2)–C(22)–O(22)	153(5)

Roman numerals as superscripts refer to the following symmetry operations relative to the reference atom at x, y, z.

I $-x, 1-y, z$ III $x, y, 1-z$
II $x, y, -z$ IV $-x, -y, z$

TABLE 4
Analysis of thermal motion
(a) Metal atoms

Atom	R.m.s. displacement along principal axes of thermal ellipsoid (Å)	R.m.s. displacement along orthogonal crystal axes (Å)	Direction cosines, principal relative to crystal axes		
Fe(1)	0·244	0·283	−0·008	−0·997	0·000
	0·283	0·243	−0·998	0·068	0·000
	0·307	0·307	0·000	0·000	−1·000
Fe(2)	0·154	0·204	0·000	0·000	−1·000
	0·178	0·178	−0·028	−1·000	0·000
	0·206	0·159	−1·000	0·028	0·000
Sn(1)	0·256	0·257	0·000	0·000	0·000
	0·257	0·307	−0·928	−0·373	0·000
	0·314	0·257	0·373	−0·928	0·000
Sn(2)	0·158	0·179	−0·593	−0·805	0·000
	0·188	0·167	−0·805	0·593	0·000
	0·190	0·190	0·000	0·000	−1·000

(b) Carbon and oxygen atoms

Atom	R.m.s. displacement (Å)	Atom	R.m.s. displacement (Å)
C(11)	0·350	C(21)	0·227
C(12)	0·223	C(22)	0·279
C(13)	0·261	O(21)	0·262
C(1)	0·294	O(22)	0·294
O(11)	0·265	C(2)	0·236
O(12)	0·275	C(3)	0·209
O(13)	0·426		

suitable model for the investigation of short-range disorder problems, and the inadequacy of the original intensity data to deal with sophistications of this kind, have precluded further study of this problem. The complete final analysis is recorded here, but the discussion is based mainly on the results for molecule (2). Final atomic positional and thermal parameters with their standard deviations are in Table 2, bond lengths and angles in Table 3, and an analysis of the thermal motion of the atoms in the two molecules in Table 4. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20389 (3 pp., 1 microfiche).*

DISCUSSION

The symmetry of the $[(Me_2Sn)Fe(CO)_4]_2$ molecule closely approximates to D_{2h} (mmm), although for each of the two crystallographically distinct molecules in the
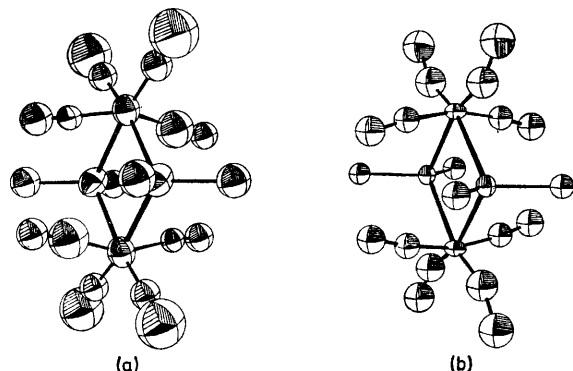

FIGURE 4 Illustration of apparently different thermal activity in the two crystallographically distinct molecules (a), molecule (1), (b), molecule (2); the 50% probability thermal ellipsoids are drawn to the same scale

crystal, the required symmetry is only C_{2h} ($2/m$). In molecule (1) the iron atoms and the 'equatorial' carbonyl groups lie in the mirror plane, in molecule (2)

thermal ellipsoids for the two molecules are drawn on the same scale.[23] For the rest of this discussion therefore, we shall confine our attention to molecule (2).

The planar Fe_2Sn_2 ring is most simply regarded as the fusion of two octahedral $Fe(CO)_4$ moieties through tetrahedral $SnMe_2$ bridges, with Fe–Sn 2·65 Å (Figure 5). With an angle of 77° at the iron atom in the ring, the valence distortion is much greater for the iron atom than for the tin atom. The two 'equatorial' carbonyl groups on the iron atom (*i.e.* those coplanar with the ring) enclose an angle of 119°, thus compensating for the reduction of the angle at the iron atom in the ring from 90 to 77°. The 'axial' carbonyl groups lie approximately perpendicular to the plane of the ring but with a significant lean inwards of some 8°. The reasons for this are discussed below. The angle between the two Sn–C(Me) bonds is not significantly different from tetrahedral, and the bond length of 2·23 Å [molecule (2)] is not only close to the sum of the covalent radii for $Sn^{IV}(sp^3)$ and $C(sp^3)$, but also close to the values found in other compounds.[2,24] This geometry of the whole system is closely similar to that found in $Me_4Sn_3Fe_4(CO)_{16}$,[2] in which two Fe_2Sn_2 rings share a central tetrahedral tin atom.

It is difficult to draw any firm conclusions about the nature of the Sn–Fe bond from its length (2·64 Å). In $Me_4Sn_3Fe_4(CO)_{16}$,[2] where the central tin atom is in a different environment from the other two tin atoms, bond lengths of 2·61—2·64 were found between the iron atoms and the 'outer' tin atoms, but of 2·73—2·76 Å between the iron atoms and the 'central' tin atom. The chemical environment of the bonds in $[(Me_2Sn)Fe(CO)_4]_2$ is obviously comparable with that of the 'outer' bonds between tin and iron in $Me_4Sn_3Fe_4(CO)_{16}$ and the agreement is close. Although these bonds are shorter than the 'central' Sn–Fe bonds in the
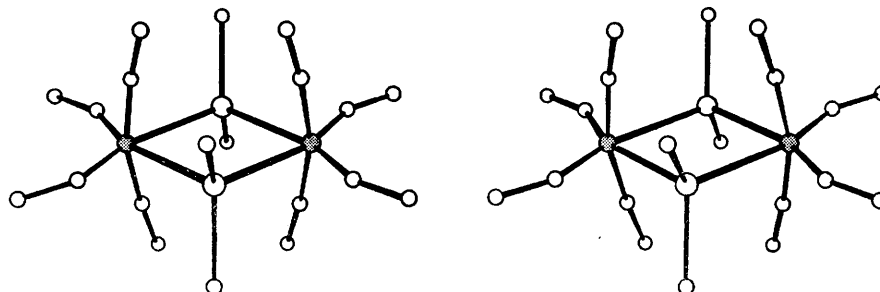

FIGURE 5 Stereoscopic drawing of the configuration of the molecule, based on the parameters derived for molecule (2)

the tin atoms and the methyl groups are so oriented. For reasons already discussed, the refined parameters for molecule (1) give a less well-defined result than is obtained for molecule (2); the difference is illustrated in Figure 4 where the 50% probability

same molecule, they are longer than those found in compounds $[(\pi\text{-}C_5H_5)(CO)_2Fe]_2SnX_2$, where the Sn–Fe distances range from 2·49—2·60 Å depending on the nature of X,[24–27] and again longer than those in compounds $[(\pi\text{-}C_5H_5)(CO)_2Fe]SnXYZ$ (X, Y, Z = halogen or

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phenyl) where distances 2·46—2·54 Å have been recorded.[28-30] Variations in bond length have been attributed to variations in the s-character of the tin

TABLE 5
Short non-bonded contact distances (Å) between peripheral atoms of the molecules in the crystal

(a) Intramolecular contacts in molecule (1)

$O(11^I) \cdots O(13^I)$	>3·6	ax–eq
$O(12^I) \cdots O(13^I)$	>3·6	ax–eq
$O(13^I) \cdots O(13^{II})$	>3·6	eq–eq
$O(11^I) \cdots O(12^{III})$	3·15(8)	ax–ax
$C(1^I) \cdots O(12^I)$	3·57(8)	Me–ax
$C(1^I) \cdots O(11^{III})$	3·55(8)	Me–ax

(b) Intramolecular contacts in molecule (2)

$O(21^I) \cdots O(22^I)$	>3·6	ax–eq
$O(21^{IV}) \cdots O(22^I)$	>3·6	ax–eq
$O(22^I) \cdots O(22^{IV})$	>3·6	eq–eq
$O(21^I) \cdots O(21^V)$	3·06(5)	ax–ax
$C(3^I) \cdots O(21^I)$	3·47(7)	Me–ax
$C(2^I) \cdots O(21^{IV})$	3·49(7)	Me–ax

(c) Intermolecular contacts

$O(11^I) \cdots O(22^I)$	3·32(5)	ax–eq
$O(12^I) \cdots O(22^{VI})$	3·34(5)	ax–eq
$O(13^I) \cdots O(21^{VI})$	3·28(9)	eq–ax
$O(12^I) \cdots O(11^{VI})$	3·30(8)	ax–ax
$O(12^I) \cdots O(13^{VI})$	3·17(9)	ax–eq
$O(13^I) \cdots O(22^{VI})$	3·52(8)	eq–eq
$O(13^I) \cdots O(11^{VII})$	3·50(9)	eq–ax
$C(1^I) \cdots O(13^{VI})$	3·56(9)	Me–eq

Roman superscripts refer to the following symmetry operations:

I x, y, z II $x, y, 1 - z$ III $-x, 1 - y, 1 - z$
IV $-x, -y, z$ V $x, y, -z$ VI $\frac{1}{2} - x, \frac{1}{2} + y, z$
       VII $\frac{1}{2} + x, \frac{1}{2} - y, z$

ax = Axial carbonyl group, eq = equatorial carbonyl group; Me = methyl group; van der Waals radius of oxygen ca. 1·4 Å, of Me group ca. 2·0 Å.

orbitals depending on the electronegativity of the attached groups,[30] rather than to $d_\pi-d_\pi$ interations. Indeed, our bond length for Sn–Fe in $[(Me_2Sn)Fe(CO)_4]_2$ is close to the sum of the covalent radii for tetrahedral Sn^{IV} (1·40 Å) and octahedral Fe^{II} (1·23 Å), supporting the view that π interactions between d orbitals in this case are small. A preliminary note on the structure of the

closely related molecule $[(C_2H_5)_2GeFe(CO)_4]_2$ gives the Ge–Fe bond length as 2·49 Å.[31] This differs from our Sn–Fe bond length by 0·15 Å, which is close to the difference recorded between these two bond lengths in $[(\pi-C_5H_5)(CO)_2Fe]_2SnCl_2$ (2·49 Å)[24] and $[(\pi-C_5H_5)(CO)_2Fe]_2GeCl_2$ (2·36 Å).[32]

For the carbonyl ligands, the mean Fe–C and C–O distances are 1·79 and 1·14 Å, and as usual there is some evidence for deviation from linearity. Our measurements are not, however, sufficiently accurate to detect small differences between 'equatorial' and 'axial' Fe–C distances such as might be expected from the analysis of the i.r. spectrum.[33] The mean values are similar to those found in comparable compounds and call for no comment.

Non-bonded Interatomic Distances.—The shortest non-bonded contacts between oxygen atoms are slightly >3 Å; all such contacts <3·35 Å are listed in Table 5, together with some significant longer distances. It will be seen that the shortest distance occurs between the oxygen atoms of the axial carbonyl groups in any molecule [mean for molecules (1) and (2) 3·09 Å], but that all the other oxygen–oxygen intramolecular distances are >3·6 Å. It also appears, however, that short contact distances occurs between oxygen atoms of different molecules, and especially between axial groups of one molecule and equatorial groups of another (Table 5). In so far, therefore, as the 'inward lean' of the axial carbonyl groups can be ascribed to stereochemical effects, these are seen to be inter- and not intra-molecular in character. The approximate constancy of the intermolecular contact distances also helps acceptance of the strange nature of the overall crystal structure.

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