Derivatives of Divalent Germanium, Tin, and Lead. Part XII.[1] Crystal and Molecular Structure of Di-μ-bis(cyclopentadienyl)stannyl-bis(tetracarbonyliron)

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The product of the reaction between dicyclopentadienyltin and enneacarbonyldi-iron has been shown to be the dimeric species [$\{(C_5H_5)_2SnFe(CO)_4\}_2$] by an *X*-ray diffraction study. The structure was determined from diffractometer data by Patterson and Fourier techniques and refined to a final *R* of 0.049 using 2 767 independent non-zero reflections. Crystals are monoclinic, space group $C2/c$, a = 19.803(4), b = 8.938(1), c = 16.722(1) Å, β = 103.91(1)°, Z = 4. The overall symmetry of the molecule is C_i, and the molecule is characterised by a central lozenge-shaped four-membered Fe_2Sn_2 ring r(Sn–Fe) 2.651(1), 2.670(1) Å; Fe–Sn–Fe 102.04(3)°, Sn–Fe–Sn 77.96(2)°. The geometry at the iron and tin atoms is distorted from regular octahedral and tetrahedral, respectively. The two cyclopentadienyl rings, which are not equivalent, are attached to each tin atom in a monohapto-fashion, illustrating the change in tin–ring bonding on reaction of (η^5-$C_5H_5)_2Sn$ with $Fe_2(CO)_9$. Unusually, the cyclopentadienyl rings are planar, rather than puckered as has been deduced previously for [$\{(\eta$-$C_5H_5)Fe(CO)_2\}_2$-$Sn(C_5H_5)_2$] but still retain considerable diene character as inferred from the endocyclic C–C bond distances.

THE nature of the products resulting from the direct interaction of divalent tin species with various transition-metal carbonyls is a topic of much current interest and endeavour. Several modes of reaction occur depending upon the particular metal carbonyl and tin(II) compound used. With mononuclear carbonyls of Group VI, complexes of the type [$X_2SnM(CO)_5$] (M = Cr, Mo, or W) are produced seemingly regardless of the nature of the substituent X.[2] Different behaviour is possible with binuclear carbonyl derivatives. With dicobalt octacarbonyl, tin(II) halides undergo ready insertion into the cobalt-cobalt bond forming [$X_2Sn\{Co(CO)_4\}_2$] compounds,[3] but from the reaction with dicyclopentadienyltin only tetrakis(tetracarbonylcobaltio)tin, [$Sn\{Co(CO)_4\}_4$], was isolated.[4] Reaction of tin(II) compounds, SnX_2, with enneacarbonyl di-iron produces complexes of composition [$X_2SnFe(CO)_4$] in high yield.[1] Osmometric and spectroscopic data, however, show that, when X = Cl, Br, C_5H_5, MeC_5H_4, or acac, these products are dimeric, but with perfluoromethyl- and phenyl-substituted β-ketoenolato-groups attached to tin a monomer–dimer equilibrium is established which is displaced towards monomer as the bulkiness of the β-ketoenolate residue increases. Interaction of the products with strong bases such as pyridine promotes the formation of monomeric species. We now report the results of an *X*-ray diffraction study of the product of the reaction between dicyclopentadienyltin and enneacarbonyl di-iron.

EXPERIMENTAL

Deep red crystals of [$\{(C_5H_5)_2SnFe(CO)_4\}_2$] suitable for single-crystal *X*-ray studies were obtained by very slow evaporation *in vacuo* of a benzene solution. The compound was initially prepared by the heterogeneous reaction of enneacarbonyldi-iron and dicyclopentadienyltin in benzene in an inert atmosphere.[4] The dried crystals were mounted in Lindemann capillaries (0.3 mm) in a glove box.

Crystal Data.—$C_{28}H_{20}Fe_2O_8Sn_2$, M = 833.54, Monoclinic, a = 19.8031(41), b = 8.9385(11), c = 16.7219(14) Å, β = 103.91(1)°, U = 2873.1 Å^3, Z = 4, D_c = 1.94, $F(000)$ = 1 616. Mo-K_α *X*-radiation, λ = 0.71 069 Å, μ(Mo-K_α) = 27.90 cm^{-1}. Space group $C2/C$ or Cc from systematic absences: hkl for $h + k = 2n + 1$; $h0l$ for $l = 2n + 1$.

Oscillation, zero-, and first-layer Weissenberg photographs obtained on an equi-inclination Weissenberg camera identified the crystal system as monoclinic, and gave initial approximate cell parameters. A crystal of dimensions *ca.* 0.3 × 0.25 × 0.4 mm was used for cell dimension refinement and to collect intensity data up to θ 27.50° on a Hilger and Watts Y 290, using monochromatic Mo-K_α radiation. Each reflection was counted for 20 s and the two associated background counts for 10 s, and was brought to the same relative intensity by referencing after every 100 reflections. The diffractometer orientation was also referenced after every 200 reflections recorded. Background counts were of low intensity and were subtracted in the usual fashion from the relative intensities. Systematically absent reflections and those with a corrected count of $<3\sigma(I)$ were considered unobserved and discarded, thus reducing the number of counted reflections from 3 558 to 2 803. The reflections were further corrected for Lorentz and polarisation effects, but because of the low μ value absorption corrections were not considered necessary.

Structure Determination and Refinement.—During the initial steps a number of the less intense reflections were discarded to facilitate computer storage, reducing the number to 2 197; however these were reintroduced at the later stages of refinement. A three-dimensional Patterson synthesis provided a complex pattern of vectors, which could not be readily solved. Application of a direct methods approach using MULTAN[5] showed the space group to be $C2/c$, and gave the positions of the iron and tin atoms in the asymmetric unit, which was subsequently confirmed

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[1] Part XI, A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 2017.

[2] X = $(Me_3Si)_2CH$: P. J. Davison and M. F. Lappert, *J.C.S. Chem. Comm.*, 1973, 317; X = Cl, Br, or I: D. Uhlig, H. Behrens, and E. Lindner, *Z. anorg. Chem.*, 1973, **401**, 233; X = β-ketoenolate: A. B. Cornwell and P. G. Harrison, *J.C.S. Dalton*, 1975, 1486.

[3] D. J. Patmore and W. A. G. Graham, *Inorg. Chem.*, 1966, **5**, 1405.

[4] A. B. Cornwell, P. G. Harrison, and J. A. Richards, *J. Organometallic Chem.*, 1974, **76**, C26.

[5] G. Germain, P. Main, and M. W. Woolfson, *Acta Cryst.*, 1971, **A27**, 368.

by a reinterpretation of the Patterson synthesis. The asymmetric unit comprised half the molecule, which was symmetry-related to the other half by a centre of symmetry. Two cycles of least-squares isotropic refinement on the heavy atom positions reduced R from 0.792 to 0.209, and a subsequent Fourier synthesis gave the positions of all other atoms except hydrogen. Two cycles of isotropic full-matrix refinement followed by two further cycles of anisotropic two-block least-squares refinement resulted in convergence at R 0.048. The positions of the hydrogen atoms of the two rings were calculated assuming that the tin-bound carbon atoms exhibited tetrahedral geometry whilst the others had trigonal geometry. The previously discarded reflections were reintroduced at this stage and isotropic refinement of the hydrogen atom positions attempted. The positions of the hydrogen atoms during seven cycles of least squares gradually deteriorated into non-chemical positions although R improved marginally. Hydrogen atoms were therefore not included. Analysis in terms of intervals of F_o after a further cycle of least squares resulted in the application of the weighting scheme: $w = 1/[1 + (F_o - 20)/44.8]^2$. At this stage, 36 reflections which exhibited values $w\Delta F > 8.0$ were excluded from the final refinement. Many of these reflections exhibited integrated count values in the region where counter saturation had previously been observed. A further eight cycles of full-matrix anisotropic least-squares refinement brought R to 0.049 for 2 767 reflections. The maximum atomic shift-to-error ratio for the last cycle was 0.002, and was generally considerably less than this.

TABLE 1

Final fractional atomic co-ordinates, with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c
C(1)	0 4293(3)	0 3237(6)	0.4954(3)
C(2)	0.4711(3)	0.2156(7)	0.5499(4)
C(3)	0.4954(4)	0.2788(10)	0.6251(5)
C(4)	0.4715(4)	0.4283(10)	0.6208(5)
C(5)	0.4332(3)	0.4575(7)	0.5450(5)
C(6)	0.3152(3)	0.1443(6)	0.3352(3)
C(7)	0.3323(4)	0.2686(7)	0.2870(3)
C(8)	0.3969(5)	0.2432(8)	0.2768(4)
C(9)	0.4247(4)	0.1071(9)	0.3154(4)
C(10)	0.3750(4)	0.0432(7)	0.3489(4)
C(11)	0.1775(3)	0.3332(6)	0.3599(3)
C(12)	0.1469(3)	0.5762(7)	0.4369(4)
C(13)	0.2705(3)	0.5667(6)	0.3875(4)
C(14)	0.2682(3)	0.5237(6)	0.5421(3)
O(1)	0.1504(3)	0.2608(6)	0.3050(3)
O(2)	0.1018(3)	0.6541(6)	0.4325(4)
O(3)	0.3025(3)	0.6405(6)	0.3556(3)
O(4)	0.2967(3)	0.5731(6)	0.6035(3)
Fe(1)	0.221 35(4)	0.453 80(7)	0.443 47(4)
Sn(1)	0.319 88(2)	0.244 38(3)	0.460 29(2)

Refinement was carried out by use of the X-Ray program system, and the scattering factors for tin, carbon, oxygen, and hydrogen [6a] and for iron [6b] were those for the neutral atoms. Final atomic co-ordinates and anisotropic thermal parameters are listed in Tables 1 and 2, respectively, whilst intramolecular bond parameters are collected in Table 3. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21412 (11 pp., 1 microfiche).*

TABLE 2

Anisotropic thermal parameters (Å^2 × 10^2),* with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	4.0(2)	4.8(3)	4.1(3)	−0.5(2)	1.0(2)	−0.1(2)
C(2)	4.2(3)	5.5(3)	5.7(4)	0.6(2)	0.7(3)	−0.7(3)
C(3)	5.6(4)	9.6(5)	5.0(4)	0.1(4)	0.4(3)	−0.5(4)
C(4)	5.9(4)	9.8(6)	6.2(4)	−1.6(4)	1.5(3)	−3.9(3)
C(5)	4.4(3)	4.3(3)	8.0(4)	−1.2(2)	1.4(3)	−1.0(3)
C(6)	5.4(3)	4.8(3)	2.4(2)	0.0(2)	1.3(2)	−0.6(2)
C(7)	7.8(4)	6.2(4)	2.3(2)	−0.4(3)	1.5(3)	0.1(2)
C(8)	9.0(6)	8.3(5)	3.6(3)	−2.4(4)	3.0(3)	−0.5(3)
C(9)	6.5(4)	8.6(5)	5.1(3)	0.0(3)	2.5(3)	−1.1(3)
C(10)	7.0(4)	5.3(3)	4.0(3)	0.8(3)	2.2(3)	−0.7(2)
C(11)	4.5(3)	4.8(3)	3.2(2)	0.6(2)	0.9(2)	0.6(2)
C(12)	5.2(3)	4.4(3)	5.4(3)	0.8(2)	1.6(3)	1.1(2)
C(13)	5.1(3)	4.8(3)	4.8(3)	0.5(2)	1.4(2)	1.5(2)
C(14)	5.9(3)	3.3(2)	4.5(3)	−0.9(2)	2.1(2)	−0.0(2)
O(1)	6.2(3)	8.2(4)	3.9(2)	−0.6(2)	0.2(2)	−1.1(2)
O(2)	6.5(3)	5.3(3)	10.5(4)	2.1(2)	2.8(3)	1.3(3)
O(3)	7.5(3)	7.0(3)	6.9(3)	−0.8(3)	2.9(2)	2.9(2)
O(4)	8.4(3)	6.7(3)	4.9(2)	−2.4(3)	2.1(2)	−2.4(2)
Fe(1)	4.06(3)	2.93(3)	2.88(3)	0.27(3)	0.99(2)	0.58(2)
Sn(1)	3.66(2)	3.18(2)	2.37(2)	−0.04(1)	0.74(1)	0.07(1)

* In the form: $\exp[-2\pi^2U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl]$.

TABLE 3

Intramolecular bond parameters, with estimated standard deviations in parentheses

(*a*) Bond distances (Å)

Sn(1)–C(1)	2.220(5)	C(14)–O(4)	1.135(7)
Sn(1)–C(6)	2.257(5)	C(1)–C(2)	1.445(8)
Sn(1)–Fe(1)	2.670(1)	C(2)–C(3)	1.356(10)
Sn(1)–Fe(1′)	2.651(1)	C(3)–C(4)	1.413(13)
Fe(1)–C(11)	1.813(5)	C(4)–C(5)	1.338(10)
Fe(1)–C(12)	1.817(6)	C(5)–C(1)	1.447(9)
Fe(1)–C(13)	1.812(6)	C(6)–C(7)	1.459(9)
Fe(1)–C(14)	1.798(5)	C(7)–C(8)	1.351(13)
C(11)–O(1)	1.146(7)	C(8)–C(8)	1.424(9)
C(12)–O(2)	1.122(8)	C(9)–C(10)	1.368(10)
C(13)–O(4)	1.133(9)	C(10)–C(6)	1.463(9)

(*b*) Bond angles (°)

C(1)–Sn(1)–C(6)	101.0(2)	Sn(1)–Fe(1)–Sn(1′)	77.96(2)
C(1)–Sn(1)–Fe(1)	116.5(2)	O(1)–C(11)–Fe(1)	177.4(5)
C(1)–Sn(1)–Fe(1′)	118.5(1)	O(2)–C(12)–Fe(1)	178.6(6)
C(6)–Sn(1)–Fe(1)	108.3(1)	O(3)–C(13)–Fe(1)	177.0(5)
C(6)–Sn(1)–Fe(1′)	110.4(1)	O(4)–C(14)–Fe(1)	177.3(5)
Fe(1)–Sn(1)–Fe(1′)	102.04(3)	Sn(1)–C(1)–C(2)	109.1(4)
C(14)–Fe(1)–Sn(1)	86.8(2)	Sn(1)–C(1)–C(5)	109.3(3)
C(14)–Fe(1)–Sn(1′)	80.9(2)	C(1)–C(2)–C(3)	109.2(6)
C(14)–Fe(1)–C(11)	163.6(2)	C(2)–C(3)–C(4)	108.0(7)
C(14)–Fe(1)–C(12)	94.5(3)	C(3)–C(4)–C(5)	109.7(7)
C(14)–Fe(1)–C(13)	93.3(3)	C(4)–C(5)–C(1)	108.9(6)
C(13)–Fe(1)–Sn(1)	88.6(2)	C(5)–C(1)–C(2)	104.3(5)
C(13)–Fe(1)–Sn(1′)	165.5(2)	Sn(1)–C(6)–C(7)	104.3(4)
C(13)–Fe(1)–C(11)	98.6(3)	Sn(1)–C(6)–C(10)	104.4(3)
C(13)–Fe(1)–C(12)	99.4(3)	C(6)–C(7)–C(8)	107.1(6)
C(12)–Fe(1)–Sn(1)	171.9(2)	C(7)–C(8)–C(9)	111.1(7)
C(12)–Fe(1)–Sn(1′)	94.3(2)	C(8)–C(9)–C(10)	107.7(7)
C(12)–Fe(1)–C(11)	94.6(3)	C(9)–C(10)–C(6)	108.3(5)
C(11)–Fe(1)–Sn(1)	82.3(2)	C(10)–C(6)–C(7)	105.7(5)
C(11)–Fe(1)–Sn(1′)	84.9(2)		

DISCUSSION

The X-ray diffraction study confirms that the dimeric nature deduced by osmometry in benzene solution is preserved in the crystal. Figure 1 illustrates the molecular structure which is characterised by a lozenge-shaped

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue.

[6] (*a*) ' International Tables for X-ray Crystallography, vol. III, p. 202; (*b*) *Acta Cryst.*, 1965, **18**, 104.

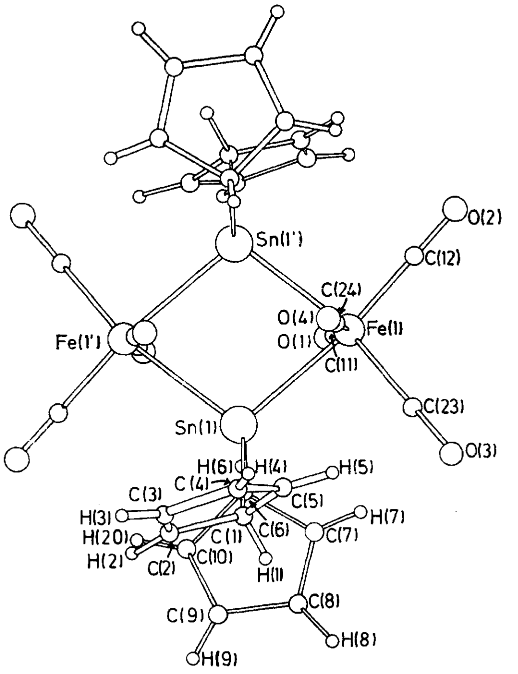

FIGURE 1 The structure showing atomic numbering. Symmetry-related atoms are primed

four-membered Fe_2Sn_2 ring, the overall symmetry of the molecule being C_i. The intra-ring bond angles of the ring are essentially identical with those of the methyl homologue $[\{Me_2SnFe(CO)_4\}_2]$,[7] but contain slightly longer Sn–Fe bond distances [(2.651(1) and 2.670(1) Å)]. The disparity of these distances is small, but is much larger than the estimated standard deviations of the two measurements. The geometries at iron and tin deviate somewhat from regular octahedral and tetrahedral co-ordination, respectively. The distortion at iron involves reduction of the Sn–Fe–Sn and C_{ax}–Fe–C_{ax} bond angles from the ideal values of 90 and 180° to 77.96(2) and 163.6(2)°, respectively, with concomitant opening of the C_{eq}–Fe–C_{eq} bond angle to 99.4(3)°. Similarly at tin, the Fe–Sn–Fe angle is widened to 102.04(3)° and the C–Sn–C angle closed to 101.0(2)° from the tetrahedral value.

TABLE 4

Weighted least-squares equations ($w = Z$) in their normal form of the mean planes through groups of atoms, and in square brackets deviations (Å) of relevant atoms from these planes (Å)*

Equations in the form: $PX + QY + RZ = S$, where X, Y, and Z are orthogonal co-ordinates in Å, related to the monoclinic co-ordinates by: $X = x + z\cos\beta$; $Y = y$; $Z = z\sin\beta$.

Plane (1): Sn(1), Fe(1), Sn(1′), Fe(1′)

$$0.3526X + 0.4726Y + 0.8076Z = 8.6477$$

[Sn(1) 0, Sn(1′) 0, Fe(1) 0, Fe(1′) 0, C(12) −0.079, C(13) −0.166, O(2) −0.117, O(3) 0.328]

Plane (2): C(1)—(5)

$$0.9121X + 0.2976Y - 0.2819Z = 4.5414$$

[C(1) −0.010, C(2) 0.008, C(3) −0.004, C(4) −0.003, C(5) 0.008]

Plane (3): C(6)—(10)

$$0.1931X + 0.4872Y + 0.8557Z = 6.1921$$

[C(6) 0.015, C(7) −0.007, C(8) −0.004, C(9) 0.014, C(10) −0.018]

Plane (4): Fe(1), C(11), O(1), C(14), O(4)

$$0.9563X - 0.1386Y - 0.2574Z = 0.0723$$

[C(11) −0.010, O(1) 0.006, C(14) 0.010, O(4) −0.006, Fe(1) 0]

Plane (5): Fe(1), C(12), O(2), C(13), O(3)

$$0.2671X + 0.4275Y + 0.8636Z = 8.6359$$

[C(12) −0.001, O(2) 0.001, O(3) 0.015, Fe(1) 0.010, Fe(1′) 0.219, Sn(1) −0.0518, Sn(1′) 0.280]

Angles (°) between planes:

(1)–(2) 76.43, (1)–(3) 9.53, (2)–(3) 83.35, (1)–(4) 86.34, (2)–(4) 25.36, (3)–(4) 84.14, (1)–(5) 6.41, (2)–(5) 82.68, (3)–(5) 5.49, (4)–(5) 99.51

TABLE 5

Comparison of the bond parameters in $[\{(C_5H_5)_2SnFe(CO)_4\}_2]$ with those in related compounds. Distances in Å, angles in °

Compound	r(Sn–Fe)	Fe–Sn–Fe	Sn–Fe–Sn	r(Sn–C)	C–Sn–C	C–Sn–Fe
$[\{(C_5H_5)_2SnFe(CO)_4\}_2]$ [a]	2.670(1) 2.651(1)	102.04(3)	77.96(2)	2.220(5) 2.257(5)	$101.0_5(2)$	117.5(1) 109.3(1)
$[\{Me_2SnFe(CO)_4\}_2]$ [b]	2.647(8)	102.6(3)	77.4(3)	2.30(7) 2.15(6)	109(2)	
$[\{MeSn[Fe(CO)_4]_2\}_2]Sn$ [c]	2.625(8) (terminal) 2.747(8) (central)			2.18(5), 2.19(5) 2.20(5), 2.31(5)		
$[(C_5H_5)_2Sn\{Fe(CO)_2(C_5H_5)\}_2]$ [d]	2.568(3)	115.9(1)		2.17(2)	95.2(8)	106.8(5), 111.8(5)
	2.573(3)			2.18(2)		107.1(5), 116.2(5)
$[Me_2Sn\{Fe(CO)_2(C_5H_5)\}_2]$ [e]	2.605(4)			2.18(2)		
$[Cl_2Sn\{Fe(CO)_2(C_5H_5)\}_2]$ [f]	2.492(8)					
$[Me_3Sn(C_5H_5)]$ [g]				2.16(1) (C_5H_5) 2.16(1) (Me)		

[a] This work. [b] Ref. 7. [c] R. M. Sweet, C. J. Fritchie, and R. A. Schunn, *Inorg. Chem.*, 1967, **6**, 749. [d] Ref. 9. [e] B. P. Biryukov and Yu. T. Struchkov, *J. Struct. Chem.*, 1968, **9**, 412. [f] J. E. O'Connor and E. R. Corey, *Inorg. Chem.*, 1967, **6**, 968. [g] By electron diffraction, N. N. Veniaminov, Yu. A. Ustynyuk, N. V. Alekseeve, I. A. Ronova, and Yu. T. Struchkov, *Doklady Chem.*, 1971, **199**, 577.

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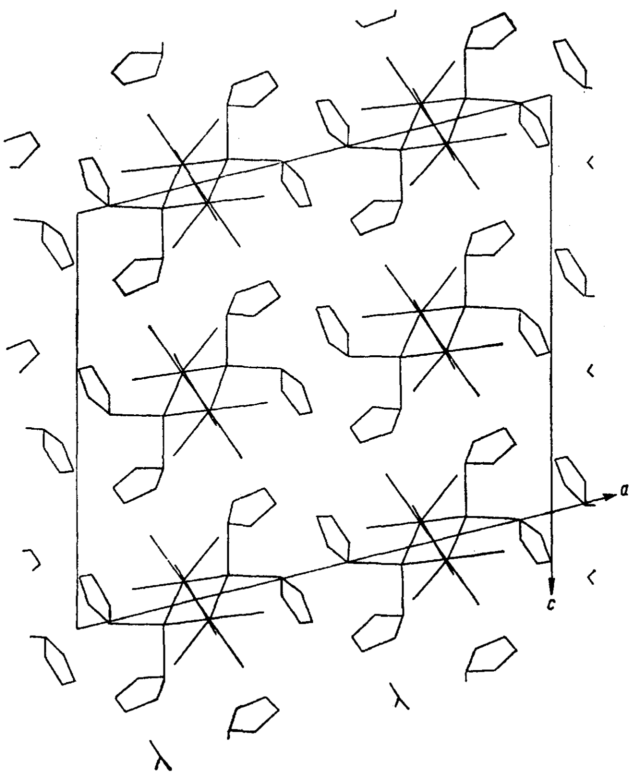

FIGURE 2 Projection of the unit cell on the *ac* plane

The nature of the cyclopentadienyl rings in this compound is extremely interesting. The structure of the starting material, $(C_5H_5)_2Sn$, is known from an electron-diffraction study [8] to consist of an angular sandwich in which the tin atom is associated equally with all five ring-carbon atoms. The present results illustrate the drastic change in the mode of attachment of the rings to tin from pentahapto in $(\eta^5\text{-}C_5H_5)_2Sn$ to monohapto in $[\{(\eta^1\text{-}C_5H_5)_2SnFe(CO)_4\}_2]$. In addition, both rings in $[\{(\eta^1\text{-}C_5H_5)_2SnFe(CO)_4\}_2]$ are planar (Table 4) rather than puckered as in the similar compound $[(\eta^1\text{-}C_5H_5)_2Sn\{Fe(CO)_2(\eta^5\text{-}C_5H_5)\}_2]$.[9] A similar change in mode of attachment of cyclopentadienyl rings to tin upon reaction has been observed in the reaction of $(\eta^1\text{-}C_5H_5)_2Sn$ with $SnCl_2$. In this case, an *X*-ray diffraction study of the product, $(C_5H_5)SnCl$, showed that the ring is tilted and the tin is preferentially associated with only two of the ring carbon atoms, *i.e.* a dihapto metal–ring compound.[10] The two cyclopentadienyl rings are not equivalent in $[\{(\eta^1\text{-}C_5H_5)_2SnFe(CO)_4\}_2]$, but (Figure 1) one ring is almost parallel whilst the second is perpendicular to the central Fe_2Sn_2 ring.

Nevertheless, the bond parameters within each ring are similar. Both contain two long, one intermediate, and two short carbon–carbon bond distances [ring (1): 1.446(9), 1.413(13), 1.347(10) Å; ring (2): 1.461(9), 1.424(9), 1.360(13) Å], indicating the essentially diene nature of the rings.

Figure 2 illustrates the packing of the molecules in the crystal, which is made up of layers of isolated dimeric $[\{(C_5H_5)_2SnFe(CO)_4\}_2]$ molecules stacked parallel to the *ab* plane.

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[5/427 *Received, 3rd March,* 1975]

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