Crystal Structure of Bis(dicarbonyl-π-cyclopentadienyliron)-dicyclopentadienyltin, $[\pi\text{-}C_5H_5Fe(Co)_2]_2Sn(C_5H_5)_2$

By B. P. BIR'YUKOV,* YU. T. STRUCHKOV, K. N. ANISIMOV, N. E. KOLOBOVA, and V. V. SKRIPKIN

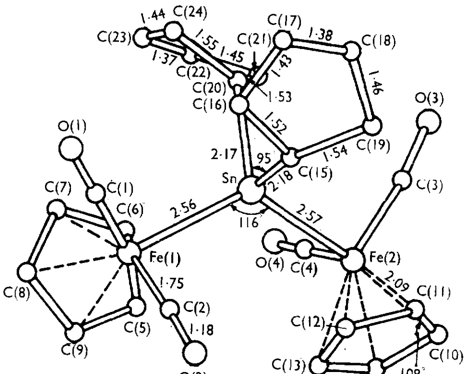
(*Institute of Organo-Element Compounds, Academy of Sciences of the U.S.S.R., Vavilova* 28, *Moscow*)

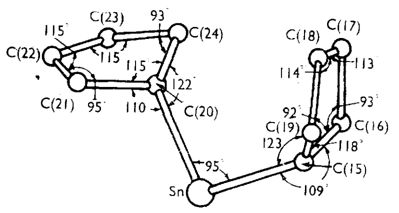
WE have reported[1] the X-ray investigation of two members of the series of polymetallic π-complexes containing an Fe–Sn bond and having general formula $[\pi\text{-}C_5H_5Fe(CO)_2]_2SnX_2$ (I; X = ONO, II; X = Me). These results together with those for the analogous structure[2] (III; X = Cl) allow us to estimate the influence of a substituent X on the metal–metal bond character and on the molecular stereochemistry.

We now report the crystal structure of compound (IV; $X = C_5H_5$) which is of interest because of the type of bonding and geometry of the cyclopentadienyl ligands. At room temperature the ^1H n.m.r. spectrum in tetrahydrofuran has a singlet signal (δ 5·00 p.p.m.)[3] showing the equivalence of C_5H_5 protons. Therefore we may consider this molecule as stereochemically non-rigid, *e.g.* undergoing valence tautomerism.

Orange needles of (IV), elongated along the c-axis, are orthorhombic, space group $P2_12_12_1$, $a = 19{\cdot}06 \pm 0{\cdot}02$, $b = 13{\cdot}58 \pm 0{\cdot}02$, $c = 8{\cdot}70 \pm 0{\cdot}01$ Å, $U = 2252$ Å^3, $D_m = 1{\cdot}64$, $D_c = 1{\cdot}69$ g. cm.$^{-3}$, $Z = 4$, $M = 603{\cdot}4$.

The intensities of *ca.* 700 independent non-zero reflections were estimated visually from Weissenberg photographs taken with unfiltered Cu-radiation; no absorption correction was made. The structure was determined by the standard heavy-atom method and refined by a full-matrix least-squares method with individual isotropic temperature factors to $R = 0{\cdot}11$ with an overall temperature factor $B = 4{\cdot}6$ Å^2. The standard deviations for the bond lengths are: Fe–Sn $\pm$ 0·004, Sn–C $\pm$ 0·015, Fe–C $\pm$ 0·020, C–O $\pm$ 0·025, and C–C $\pm$ 0·030 Å.





The tin atom has severely distorted tetrahedral co-ordination with the Fe(1)-Sn-Fe(2) angle 115·9 ± 0·2° and the C(15)-Sn-C(20) angle 95 ± 1° (Figure). These deformations are analogous to those found in molecules (I), (II), and (III). The piano-stool co-ordination of the iron atoms is usual for open-sandwich π-complexes. The average Fe–Sn bond length 2·570 Å falls within the previously found range.[1,2] With the increasing electronegativity of X in the series Me $<$ ONO $\leqslant$ C_5H_5 $<$ Cl this bond length is decreased from 2·60—2·492 Å.

Cyclopentadienyl rings are connected to the tin atom by σ-bonds of length 2·17 and 2·18 Å which do not differ significantly from the sum of the covalent radii, 2·14 Å.[4] As usual in metal–cyclopentadienyl compounds, the carbon atoms bonded to tin are displaced out of the planes of the other four ring-carbon atoms. Therefore the atoms C(16), C(15), C(19), and C(21), C(20), C(24) are displaced *ca.* 27° out of the plane of the ring. Analogous out-of-plane displacements at substituted carbon atoms have been reported.[5] The dihedral angles are 21·3, 36·5, 27, and 20·1° respectively.

The angles between the Sn–C bond and the bent-up triangular part of the C_5H_5 rings are *ca.* 37°. The bond angles at C(15) and C(20) indicate sp^3-hybridization [the increase of Sn–C(15)–C(19) and Sn–C(20)–C(24) angles up to 123 and 122° is caused by steric overcrowding between two C_5H_5 rings]. The C–C bond distances in the cyclopentadienyl rings vary from 1·37 to 1·54 Å, revealing rather complicated double bond delocalisation in the planar four-atom fragments.

The geometry of the π-$C_5H_5Fe(CO)_2$ fragments is normal. The proper molecular symmetry in crystal approximates C_2 as was found for (I), (II), and (III).

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