Crystal Structure of Bis-(π-cyclopentadienyldicarbonyliron)dinitritotin $[\pi\text{-}C_5H_5Fe(CO)_2]_2Sn(ONO)_2$

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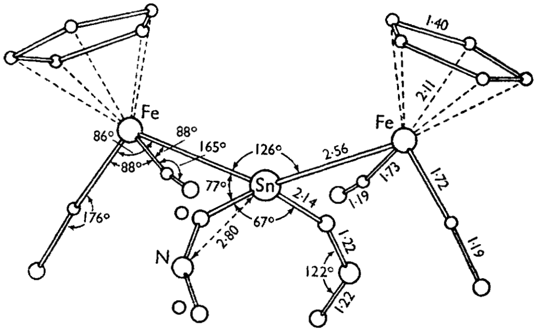
RECENTLY three of us have synthesized[1] a series of polymetallic compounds containing an Fe–Sn bond and having the general formula $[\pi\text{-}C_5H_5Fe(CO)_2]_n\text{-}SnX_{4-n}$ where $n = 2, 3, 4$, and X denotes an inorganic (Cl, Br, NO_2) or organic (Me, Ph, cyclopentadienyl, allyl) ligand. Our *X*-ray study of this series of compounds is intended to determine the metal-to-metal bond distances, to clarify the general stereochemistry of such complexes (*e.g.*, co-ordination type and bond angles at metal atoms), and to elucidate the general mode of Sn–X bonding.

We have now determined the basic *X*-ray data for a group of such compounds with $n = 3$ and X = Ph; $n = 2$ and X = Me, Ph, cyclo-C_5H_5, allyl, Cl. The present Communication records the crystal and molecular structure of bis-(π-cyclopentadienyldicarbonyliron)dinitritotin $[\pi\text{-}C_5H_5Fe(CO)_2]_2Sn(ONO)_2$.

Crystal data. The orange, plate-like crystals, elongated along *b*, are monoclinic: $a = 20{\cdot}26$, $b = 7{\cdot}30$, $c = 14{\cdot}65$ Å, $\beta = 123{\cdot}4°$, $V = 1809$ Å^3, $D_m = 2{\cdot}1$, $D_c = 2{\cdot}08$ g.cm.$^{-3}$ for $Z = 4$, $M = 565{\cdot}47$. Space group is $C2/c$ (by intensity distribution and structure determination) with the molecules in special positions on diad axes.

The intensities of *ca.* 700 nonzero independent reflexions were estimated visually from Weissenberg diagrams taken with unfiltered Cu–*K* radiation. Absorption correction was neglected. The structure was determined by the standard heavy-atom method and refined by a full-matrix least-squares method with individual isotropic temperature-factors, and also by a three-dimensional difference synthesis. At the present stage of refinement the discrepancy index is 0·156 with an average temperature-factor $B = 5{\cdot}5$ Å^2. Further refinement is now in progress.

The crystal is built up of discrete molecules (see Figure) with a severely distorted tetrahedral co-ordination of the Sn atom. The Sn–O intramolecular distances are 2·14 and 2·80 Å, and the Sn–N separation is about 2·80 Å. These values can be taken as unequivocal evidence for ligand co-ordination through only one of the oxygen atoms. Moreover the Sn–O bond distance is of a realistic value (by analogy with some Ni complexes[2]) and naturally longer than the formal sum of single-bond covalent radii, 2·06 Å.[3] So in this molecule an NO_2 group is a nitrite ligand, –O–N=O. To accommodate the bulky $C_5H_5(CO)_2Fe$ ligand, the bond angle Fe–Sn–Fe is considerably increased (126°) as in the analogous Ge compound[4] [π-$C_5H_5Fe(CO)_2]_2GeCl_2$ (the Fe–Ge–Fe angle is 128°). The geometry of the Sn–$Fe(CO)_2 \cdot C_5H_5$ fragment is similar to that found[5] in the structure of [π-$C_5H_5Fe(CO)_2]SnPh_3$. The Fe atom co-ordination is a "piano stool", a typical one for semi-sandwiches. The mean Fe–C(cyclopentadienyl) interatomic distance is 2·11 Å, distinctly longer than those found in ferrocene (2·045 Å) and very near to the corresponding value in [π-$C_5H_5Fe(CO)_2]SnPh_3$ (2·095 Å). The Fe–C(carbonyl) and C–O bond lengths (1·72 and 1·19 Å respectively) are very close to the values for the latter compound[5] (1·71 and 1·17 Å). However the most interesting distance is the Fe–Sn bond length, 2·56 Å, which is somewhat longer than 2·537 Å in [π-$C_5H_5Fe(CO)_2]SnPh_3$ and considerably shorter than the sum of Fe octahedral and of Sn tetrahedral radii (*ca.* 2·67 Å).[3] In the more complex structure of $Me_4Sn_3Fe_4(CO)_{16}$ the terminal Sn–Fe bonds are 2·64 Å in length but the bridging ones are much longer (2·75 Å).[6] A more detailed discussion of these varied metal-to-metal bond-distances will be possible only after completion *X*-ray studies of the series of compounds.



FIGURE

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