The Crystal Structure of Triphenyltin–Manganese Pentacarbonyl

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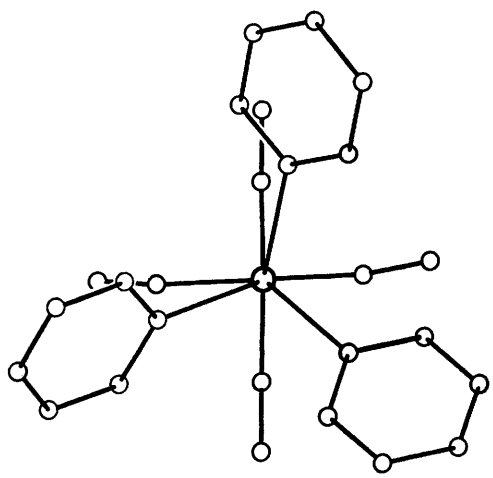
WE report the results of a three-dimensional *X*-ray-diffraction study of single crystals of triphenyltin–manganese pentacarbonyl,[1] which show that the metal–metal separation in this structure is intermediate in length between those found for triphenyltin–tetracarbonyltriphenylphosphinemanganese[2] and bis(pentacarbonylmanganese)–diphenyltin,[3] showing that the bond distance between the metals is acutely sensitive to the character of the attached ligands.

$Ph_3SnMn(CO)_5$ crystallises with space group $P2_1$, $a = 12{\cdot}17$, b = 32·22, $c = 11{\cdot}39$ Å, $\beta = 90°$ 33′. There are 8 molecules in the unit cell and the structure analysis therefore required the determination of the parameters for *four* individual, independent, molecules; a total of 120 atoms, other than hydrogen. The crystal structure was solved, using the heavy-atom method, from 2200 diffraction spectra and the positional and isotropic thermal parameters of the atoms were refined by least-squares methods to a final R of 5·9%.

The four molecules in the asymmetric unit have identical conformations, save for slight differences in the orientations of their phenyl groups with respect to the Sn–Mn axes. A general view of the molecular structure, looking down the metal–metal bond, is shown by the Figure. To a first approximation, the tin is tetrahedrally co-ordinated while the manganese is octahedrally surrounded by ligands. At least in the crystal, there are significant deformations from this ideal. From the Figure it may also be seen that the relative orientation of the Sn–C and Mn–C bonds is about 4° from the configuration possessing mirror symmetry.

The four Sn–Mn distances are: 2·670, 2·672, 2·676, and 2·678 Å, each with an e.s.d. of 0·008 Å, yielding a mean value of 2·674 ± 0·004 Å. This value lies between those found for the only other two compounds of this type, containing Sn–Mn bonds, so far examined, where the bond distances are 2·63 ± 0·01 Å[2] and 2·70 ± 0·01 Å.[3]

The mean value for the twenty Mn—C bond distances is 1·758 ± 0·009 Å; for the twenty C–O distances it is 1·184 ± 0·011 Å. Contrary to what is claimed in the case of dimanganese decacarbonyl,[4] there are no significant differences between equatorial and axial metal–carbon distances. The mean deviation from linearity in the Mn–C–O systems is 6·4°. Without exception, the atoms of the equatorial carbonyl groups are displaced toward the tin atom with respect to a plane perpendicular to the Sn–Mn axis, the mean Sn–Mn–C angle being 86·7°. This feature, observed in several related molecules,[5] is not thought to be an intrinsic property of the isolated molecule since, in the present case, it is clearly brought about so as to achieve an optimal packing of molecules within the crystal.



FIGURE

A generalised view of the molecule of $Ph_3SnMn(CO)_5$ *looking down the* Sn–Mn *axis. The axial carbonyl group is coincident in direction with this axis and is not shown. Individual molecules differ somewhat in the orientation of their phenyl rings with respect to the metal–metal axis.*

The mean of the twelve Sn–C bond lengths is 2·154 ± 0·014 Å. All of the C–Sn–C angles are reduced below the regular tetrahedral value, the mean being 106·0 ± 0·6°. Correspondingly, the mean Mn–Sn–C angle is 112·7 ± 0·4°.

For the seventy-two C–C distances in the phenyl rings a mean value of 1·395 ± 0·008 Å is obtained, in excellent agreement with the accepted value of 1·395 Å for bonds of this type.[6]

The intermolecular forces are all of the van der Waals type, the crystal structure being fairly loosely packed.

The crystals are subject to some reaction, the

nature of which is unknown to us, on irradiation with X-rays of the wavelength used ($\lambda = 0{\cdot}711$ Å) turning an intense brown colour from their normal colourless state.

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