The Crystal Structure of Trimethyltin–Manganese Pentacarbonyl

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IN a recent Communication[1] the *X*-ray structural analysis of triphenyltin–manganese pentacarbonyl was reported. The Sn–Mn bond distance was found to be 2·674 ± 0·004 Å as the mean of four independent measurements of the distance in the four molecules in the asymmetric unit of the crystal. This bond length was intermediate between the 2·627 ± 0·01 Å found for triphenyltin tetracarbonyltriphenylphosphinemanganese[2] and the value of 2·70 ± 0·01 Å observed for each of the two Sn–Mn bonds in bis(pentacarbonylmanganese)diphenyltin,[3] and the suggestion was made that the bond distance between the two metal atoms was acutely sensitive to the nature of the attached ligands.

In order to separate the effects of substituents on the Group IV metal from those caused by ligands attached to the transition metal, an analysis has been carried out, by *X*-ray diffraction methods, of the crystal structure of trimethyltin–managnese pentacarbonyl. It has been found that the Sn–Mn distance is precisely the same as that found in the triphenyl analogue, 2·674 ± 0·003 Å, arguing that at least for these two compounds the bond energy is unaffected by simple changes in the ligands attached to the tin atom and that differences in reactivity of the metal–metal linkage in this case[4] are to be ascribed to steric effects of the ligands.

$Me_3SnMn(CO)_5$ crystallises with space group $P2_1/n$, $a = 7{\cdot}018$, $b = 13{\cdot}389$, $c = 14{\cdot}662$ Å, $\beta = 114°30'$; $Z = 4$. the melting point of the compound is 29·5° and it was expected that the structure analysis would have to be conducted with intensity data collected at low temperature. Surprisingly, it was found that at 18° the diffraction pattern of a reasonably-sized crystal of the material extended well beyond 1 $Å^{-1}$. Accordingly it was possible to measure close to 1400 significant reflections with Mo-*K* radiation at room temperature using a Hilger Watts linear diffractometer and balanced filters without any sign of decay in the diffraction pattern. Corrections for absorption and an allowance for the real part of the anomalous dispersion correction for the metal atoms were made. The heavy-atom method was used and the structure refined by Fourier, difference Fourier, and least-squares methods to a final *R* over all observed reflections of 4·4%. Anisotropic thermal parameters were employed for all atoms except hydrogen. The anisotropy of the metal atoms is barely significant but the oxygen atoms and the methyl-carbon atoms are making fair excursions in directions perpendicular to the respective metal–atom axes. The values of the thermal parameters are comparable to those observed in substances of much higher melting point and the accuracy of the determination seems not to have been prejudiced by the use of room-temperature measurements of the diffracted spectra.

The overall geometry of the molecule is similar to that found for the triphenyl analogue with the tin atom tetrahedrally co-ordinated, the manganese atom octahedrally. The Sn–C distances are 2·06, 2·16, and 2·17 Å each with an e.s.d. of 0·015 Å. Mn–C ranges from 1·75 to 1·84 Å with individual e.s.d. of 0·012, indicating significant differences between individual bond distances. The terminal Mn–C bond is no longer than two of the equatorial bonds. The C–O distances also show significant differences, ranging from 1·12 to 1·19 Å with e.s.d. of 0·016 Å. The carbonyl systems are closely linear, the maximum deviation from linearity being 2·6°, and are bowed towards the tin atom in an 'umbrella' fashion in the same way as in the triphenyl derivative. The mean Sn–Mn–C angle is 84·4°. Similarly, the mean Mn–Sn–C angle is increased over the tetrahedral value to 112·2° and the C–Sn–C angle reduced to a mean value of 107·4°.

The SnC_3 and MnC_5 fragments are related about the Sn–Mn axis in a manner very similar to that observed in the triphenyl compound except that here the deviation from a configuration having mirror symmetry is only 1° of rotation rather than 4°. This confirms that there is the possibility for at least a modicum of rotation around the metal–metal axis.

As in the case of the triphenyl analogue a discoloration of the crystals is noted after prolonged exposure to *X*-rays but it is not so pronounced as in the former case and is much slower in making its appearance.

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[1] H. P. Weber and R. F. Bryan, *Chem. Comm.*, 1966, 443.

[2] R. F. Bryan, *J. Chem. Soc.* (*A*), 1966, 172.

[3] B. T. Kilbourn and H. M. Powell, *Chem. and Ind.*, 1964, 1578.

[4] H. C. Clark (private communication). I am indebted to Professor Clark for a sample of trimethyltin–manganese pentacarbonyl.