A Compound Containing Tin(IV) in both Five-fold and Six-fold Co-ordination

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THE adduct of 2,2′,2″-terpyridyl with dimethyltin dichloride has been described by Fergusson, Roper, and Wilkins[1] who gave evidence that the compound should be formulated as $[Me_2SnCl,\text{terpyridyl}]^+$ $[Me_2SnCl_3]^-$. We have confirmed this by a complete crystal-structure analysis which provides details of the different stereochemistries exhibited by tin in the cation and the anion.

The crystals are triclinic with space group $P\bar{1}$. There are two formula units in a unit cell with the following dimensions:

$$a = 15\cdot71,\quad b = 10\cdot04,\quad c = 10\cdot30\text{Å};$$
$$\alpha = 67\cdot7°,\quad \beta = 115\cdot9°,\quad \gamma = 119\cdot6°,$$

giving a calculated density of 1·80 $g.cm.^{-3}$

Co-ordinates of tin and chlorine atoms were obtained in a straightforward manner from the three-dimensional Patterson function. Subsequent electron-density difference functions revealed the positions of all carbon and nitrogen atoms, and refinement of positional and individual isotropic thermal parameters for all atoms has been carried out by block-diagonal least-squares procedures. The R-factor is 0·15 for all 1578 observed reflections.

In the anion $[Me_2SnCl_3]^-$, the co-ordination about tin is trigonal bipyramidal with both methyl groups occupying equatorial positions at a mean distance of 2·19 Å (σ = 0·07 Å) from the tin atom and subtending an angle of 139° (σ = 3°). The equatorial Sn–Cl distance is 2·35 Å while both axial Sn–Cl distances are 2·54 Å (σ = 0·03 Å). That the more electronegative chlorine atoms are preferentially bonded in the axial positions is in accord with the general observations of Muetterties, Mahler, Packer, and Schmultzer[2] on trigonal bipyramidal structures. The pronounced differentiation between axial and equatorial Sn–Cl lengths may be contrasted with the situation in the $SnCl_5^-$ anion[3] where there is no significant difference. Similarly, Bartell and Hansen[4] have observed that whereas in PF_5 the bonds are nearly equal, in $MePF_4$ and Me_2PF_3 the axial and equatorial P–F lengths are very different.

In the cation $[Me_2SnCl,\text{terpyridyl}]^+$, the tin atoms have a highly distorted octahedral environment with the methyl groups in *trans*-relation and approximately normal to the least-squares plane of the terpyridyl group. The chlorine atom, *trans* to the nitrogen atom of the central ring of the terpyridyl group, is displaced in the direction of one of the outer rings, while the two methyl groups are displaced in the opposite direction so that the group Me, Me, Cl, N constitutes a flattened tetrahedron surrounding the tin atom. Completing the six-fold co-ordination are the nitrogen atoms from each of the two outer rings of the terpyridyl group. The Sn–Cl length is 2·63 Å ($\sigma = 0{\cdot}024$), or 0·1 Å greater than any previously reported. The terpyridyl group shows distortions from planarity very similar to those which it exhibits in $ZnCl_2$,terpyridyl,[5] the pyridine rings being twisted about the bonds linking them by +8° and −8° respectively, compared with +6° and −4° in $ZnCl_2$,terpyridyl.

In seeking an explanation for the very long Sn–Cl bond in the cation, we note that of all the six co-ordinating atoms, the chlorine atom is the only one which is highly electronegative. Application of Bent's[6] proposals regarding second-order hybridisation would indicate almost complete absence of *s*-character in the Sn–Cl bond and would predict that it should be inherently long, aside from any purely steric factors.

(*Received, September 7th,* 1966; *Com.* 666.)

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