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STRUCTURAL ORGANOTIN CHEMISTRY

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CONTENTS

I. INTRODUCTION

Organotin chemistry has been the subject of much research effort in recent years. The important place occupied by this branch of main group organometallic chemistry derives in part as a result of the stimulation provided by the success with which modern physical techniques can be applied to organotin compounds. Useful structural information has been derived from infrared and Raman frequencies[293], tin–proton and fluorine NMR coupling constants and tin NMR chemical shifts[207], mass spectral cracking patterns[156], and tin-119m Mössbauer isomer shifts and quadrupole splittings[283,318]. A large number of key organotin molecular structures are known from diffraction and microwave work for possible comparison. The point has now been reached where it is appropriate that the available structural data be gathered together in one place for fruitful scrutiny.

Organotin compounds assume a wide variety of structural types, which in the tin(IV) derivatives alone encompass four-, five-, six-, seven- and eight-coordination at tin in neutral cationic and anionic species, with intra- and intermolecular coordination to give dimers and other oligomers, and one-, two- and three-dimensional crystal lattices. Among the most interesting compounds are those for which the structural information is ambiguous. In these cases data from ancillary physical techniques can play an important role in establishing the true nature of the solid state structure.

This review will discuss examples for which the parameters of molecular structure, *i.e.*, internuclear distances and angles, have been measured by X-ray, neutron and electron diffraction and microwave studies. No structure of an organotin compound known to be associated in the vapor phase has yet been determined in that phase, although several examples are available for study*. Our reference will be exclusively the solid state, and we will use data from ancillary physical studies carried out in that phase, for example, from infrared, Raman, NQR and Mössbauer spectroscopies. Our primary focus will be on organotin compounds, *i.e.*, those containing at least one Sn–C linkage, but the structures of inorganic tin and organic derivatives of the other fourth group elements will be introduced for comparison. So, for that matter, will data from liquid and solution samples be cited as needed.

Our goal in preparing this review is (i) to provide a thorough bibliographic and tabular data source for organotin structures, (ii) to attempt some critical evaluation as a guide to the quality of the available data, and (iii) despite the wide diversity of structural types and the scattered nature of the examples of known structures available, to seek to establish a meaningful set of structural principles of organotin compounds. An additional goal is the stimulation of further structural investigations, badly needed in this fast-developing area. Past reviews[140,259] have not attempted to reach these goals. Literature has been covered to 1 June 1972.

A. *Classification*

It was common practice in the old textbooks to distinguish between solids of different physical properties on the basis of bonding. Hard, high melting solids such as aluminum fluoride were said to be ionic, while softer, more tractable materials were thought to be covalent. This view was revised in the light of structural information which revealed that solids can with greater generality be classified according to coordination number and connectivity as metallic, molecular, simple ionic, complex ionic and polymerized covalent, and that the bulk physical properties of solids can be understood qualitatively at least in a straightforward way on the basis of these structural types.

Tin and its compounds participate in each of the types enumerated above with the sole exception of the simple ionic form for which no example is known. The tin(II) and tin(IV) fluorides, the compounds most likely to adopt ionic structures, apparently do not. Tin(IV) fluoride crystallizes in a layer structure with bridging fluorine atoms in which tin takes part in octahedral coordination[217]. The structure of tin(II) fluoride is complex[135], and needs to be studied again to locate the fluorine atom positions, but the complexity of the

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* Mass spectral studies have revealed several examples of polytin ions from the vapors above associated organotin solids. See ref. 208 for a recent example.

structure is evidence against completely ionic character for this compound. Tin(II) oxide has the PbO structure in which each tin atom is at the apex of a square pyramid with four oxygen atoms in the base positions. There are adjacent layers of tin atoms at 3.70 Å[249]. Again, the structure is not typical of ionic MX salts. The metallic form is represented by β-tin (white tin)[305], the covalent by α-tin (grey tin)[305]*, the complex ionic by the recently studied terpyridyl complex of dimethyltin dichloride[47,48], or by the more recently examined chlorobis[bis(1,2-diphenylphosphino)ethane] cobalt(II) trichlorostannate(II) forms in which the $SnCl_3^-$ ions lie in an isolated position in the lattice[286]. Organotin nomenclature in part reflects these divisions. Higher coordinated complexes are named in accordance with the accepted inorganic rules, but tetracoordinated organotin(IV) compounds, on the other hand, are named by two different systems, the first being an extension of the principles of organosilicon and germanium nomenclature wherein compounds are named as derivatives of stannane, SnH_4. This nomenclature in organotin chemistry may not have been initially intended, but is now very frequently used to imply predominantly "organic-like" physical properties. The more "inorganic" names by which organotin and organolead compounds are generally referred mirror the more metallic character of these elements and conform to IUPAC rules for other organometallic compounds.

The modern view recognizes ambiguities in the sharp division into classes. The problem is particularly vexing with regard to the distinction between molecular solids into which individual molecules are held by Van der Waals forces, and associated solids, where the individual molecules preserve their integrity, but with additional components to the energy of the lattice. Where these additional lattice forces dominate the choice of crystalline arrangement and affect molecular geometry greatly, the existence of association in the solid is easily demonstrated. Where the forces produced by association in the solid are more feeble, the question often cannot be settled on the basis of structural information alone since the distortions wrought on the gas phase molecular structure by packing into the solid along with the various intermolecular juxtapositions of potentially bridging atoms may be only suggestive of association. Here information from physical techniques more sensitive to the energies involved may be brought fruitfully to bear on the problem. In these cases the perturbations of electric field gradients at tin or at halogen nuclei which are thought to be bridging are of interest and can be obtained from ^{119m}Sn Mössbauer quadrupole splitting values or from chlorine, bromine, or iodine nuclear quadrupole resonance frequencies. Departures from idealized molecular symmetries in the solid state can be detected in splittings in the vibrational spectral lines which arise from the removal of degeneracies or the alteration of selection rules in going to other, lower symmetries in the solid. Thermodynamic data such as heats of vaporization, entropies of the solid or specific heats can be interpreted in terms of intermolecular binding in the solid. The observation of fluorescence phenomena is also suggestive of association. Even more difficult is the question of potential intramolecular association leading to higher coordination number at tin, but no additional lattice binding forces. Unfortunately, at this time few examples have been studied sufficiently thoroughly to allow definitive answers concerning the presence of either type of association when it is feeble. Auxiliary techniques also assume major

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[*] The material formerly known as γ-tin has been shown to be a mixture of β-tin and tin(II) oxide.

importance in cases where structural data are ambiguous in other ways, for example, where crystal disorder prevents completely satisfactory structural analysis as in trimethyltin fluoride[40,41,108], or when only one of a pair of polymorphous crystals has been subjected to structural determination as might have been the case for trimethyltin *N,N*-dimethyldithiocarbamate which crystallizes in monoclinic as well as orthorhombic forms[94,95], or for bis(1,2-diethoxycarbonylethyl)tin dibromide where two distinct isomers, one with both rings in either the *d*- or *l*-form, and the other with one ring in the *d*- and one ring in the *l*-form, crystallize separately[78,109]. Phase changes intervening between room temperature and 77°K make comparisons of crystal structures carried out under ambient conditions and Mössbauer data usually recorded at liquid nitrogen temperatures ambiguous. In addition to these examples are situations in which the solution to the structural problem may be inaccessible. Extreme difficulties may be encountered in growing a single crystal because of a proclivity for twinning[41], or the crystal may decompose rapidly in the X-ray beam. The presence of the heavy tin atom may prevent accurate location of lighter atoms in the structure[135]. Gaseous tin hydride samples may decompose on contact with copper microwave guides as does methyltin hydride[34,80], while other compounds may become easily charged and then subsequently deflected on exit from the nozzle of an electron diffraction apparatus[6]. Problems of moisture and air-sensitivity may help turn the experimenter to compounds more likely to yield easier solutions.

While we are able to separate most of the known structures into the categories of molecular and associated crystals with relative ease, we are forced to relegate those whose exact status is in doubt to a separate category.

B. The quality of the data

Modern X-ray diffraction has been developed to a very highly refined stage of technology[289]. There is no reason to doubt that so far as the structural features, lengths and angles are concerned, the data which have been produced by three-dimensional studies will stand for all time. The earliest crystallographic work on organotin compounds dates from 1878 when the diphenyltin dichloride crystal was indexed[7]. The first organotin X-ray diffraction study, performed upon the fourth group tetraphenyls, was communicated by Sir William Bragg in 1926 from the Davy Faraday Laboratory of the Royal Institution from the group which included Bernal[62]. The compounds were found to be isomorphous, and the $^4D_{2d}$ space group assigned has since been confirmed in several subsequent reinvestigations down to the present day[1,2,35,63,72-75,82,98,110-111]. By the time other types of organotin compounds began to be subjected to X-ray study, the diffraction technique had been intensively developed, and the organometallic results we will discuss, with the few exceptions of structures solved on the basis of two-dimensional data pointed out in the text, all conform to modern standards.

Electron diffraction results are subject to limitations inherent in that method[228]. The first gas phase electron diffraction data on tetramethyltin was published by Brockway in 1936[25], and on methyltin chlorides, bromides and iodides by Sutton in 1944[96]. The results were in all cases unexceptional, and repeat of much of this early work with improved techniques[59,185,244] has substantiated the major conclusions, especially the shrinkage of the tin–chlorine internuclear distance with increased chlorine substitution in the methyltin compounds. Little microwave data have been published to date, excepting on the methyltin hydrides[34,80].

II. MOLECULAR SOLIDS

A. *Group IV derivatives and hydrides*

Tetraphenyltin and its tetrakis derivatives with CH_3, CH_3O and C_2H_5O groups at various positions on the phenyl rings have been investigated[62] and reinvestigated[1,2,35,63,72-75,82,98,110,111] beginning in 1926[62] at an increasingly fine level of detail in order most recently to provide a comparison with conformational analysis and lattice energy calculations which lead to predicted structures having the minimum potential energy[1,2,35]. The $^4D_{2d}$ space group initially proposed by George in the first organotin X-ray diffraction study[62] has been reverified in these recent studies. The crystalline form of tetraphenyltin is strictly molecular with the closest intermolecular contact distances corresponding to Van der Waals interaction radii (the closest carbon–carbon approach is 3.54 Å)[73]. The molecules themselves have $\bar{4}(S_4)$ symmetry, with each phenyl ring oriented so that it approximately eclipses one of the adjacent tin–carbon bonds related by an operation of the tetragonal $\bar{4}$ axis[35]. Given the restriction of T_d symmetry of the tin atom with respect to its four nearest carbon atom neighbors which is exactly obeyed within experimental error, the structures of all the members of this class can be characterized by two parameters: the angle of rotation of the phenyl group about the tin-carbon bond, ϕ, and the angle of rotation, ψ, of the molecule about the $\bar{4}$ axis, *i.e.*, the z-axis of the crystal. Detailed structural information is available for all the fourth group derivatives[149,157,194,292]. The angles ϕ decrease and the angles ψ increase after carbon in descending the fourth group to lead. The reduction of the high melting point of the tetraphenyl derivatives [m.p. of $(C_6H_5)_4Sn$ = 229°] on conversion to the tetratolyl derivatives [m.p. of *p*-, 230–233°, *o*-, 158–159°, *m*-, 128.5°] reflects the decrease in crystal symmetry with increase in size of the aryl group[110,111].

Gas phase structural data for the methyltin compounds would serve as useful comparisons for solid derivatives, but the data for tetramethyltin derives from Brockway's 1936 electron diffraction study[25], and the details of this structure for which T_d symmetry at tin and free rotation about the tin–carbon bond were assumed must be considered unreliable. The microwave spectrum of methyltin trihydride was recorded in 1951 on an impure sample which decomposed rapidly upon admission to a copper waveguide. Insufficient information was obtained, even by working quickly, for a complete structural determination which for CH_3SnH_3 involves three distances and two angles, but tin-carbon and tin-hydrogen distances were derived by assuming T_d symmetry at both carbon and tin (which is certainly incorrect for the latter) and a carbon–hydrogen distance of 1.090 Å[80]. The spectrum of a pure sample was recorded in 1961 with greater spectrographic sensitivity, but quantitative intensity measurements could not be made, and no molecular structure parameters were derived[34]. Fortunately, electron diffraction studies of the methyltin chlorides are underway[59,185,244], and preliminary results for tetramethyltin are available[244]. Tetrabenzyltin has a perfectly regular structure in contrast to the titanium, zirconium and hafnium analogues[44].

The symmetric top halostannanes, H_3SnX where X = Cl[234], Br[309] and I[310] have been studied by microwave techniques. The compounds are unstable, with half-lives in the waveguide of 60–90 seconds, giving rise to pressure broadening of the spectral lines as a result of the decomposition. The relatively small contribution of the hydrogen atoms to the moments of inertia and the presence of ground state vibrations make the determination of the Sn–H distances considerably less accurate. The lack of naturally occurring iodine isotopes other than ^{127}I increases the uncertainty of the Sn–I distance[310]. The Sn–H distance in the chlorostannane was derived on the assumption of T_d symmetry at tin[234] which is certainly incorrect, since the H–Sn–Br angle in the bromostannane was found to be 105.9°[309].

The true nature of the stable form of diphenyltin is the cyclic hexamer as revealed by X-ray studies which show a chair configuration of the ring of tin atoms. The tin–tin distances are all approximately equal, and are only slightly shorter than those in gray tin. There are two $[(C_6H_5)_2Sn]_6$ and four xylene molecules (the recrystallization solvent) per unit cell. The angles Sn–Sn–Sn are 114° while the diphenyltin angles are approximately tetrahedral. The above is based upon a fragmentary communication[86] for which the full report was never made. Di-t-butyltin in the solid state forms a unit cell with eight monomer units. Systematic absences indicate a C-centered cell and allow C_2, Cm and C^2m as possible space groups. It follows from this that di-t-butyltin may be mono-, di- or tetrameric, but it is not possible to have molecules larger than tetramers. The compound itself is insoluble, precluding molecular weight determination, but evidence for the tetrameric structure has come from the iodination product which is soluble[53]. Detailed X-ray analysis was not carried out.

B. *Some four-coordinated organotin sulfides*

The structure of monoalkyltin sesquisulfides is dimeric as suggested by mass spectrometric evidence. The methyl molecule, $[(CH_3Sn)_2S_3]_2$, lies on a crystallographic two-fold axis with space group C_{2c} and is in the adamantane form as shown in Fig. 1. Only the space group ($P1$) was determined for the n-butyl derivative[45]. The structure of the related cyclic trimeric diphenyltin sulfide as quoted in another paper shows the molecule in the boat conformation (see Fig. 2) with the internal sulfur angles at tin slightly opened from the tetrahedral while the diphenyltin angles are purely tetrahedral[93]. Full reports of these organotin sulfide structures have not yet appeared.

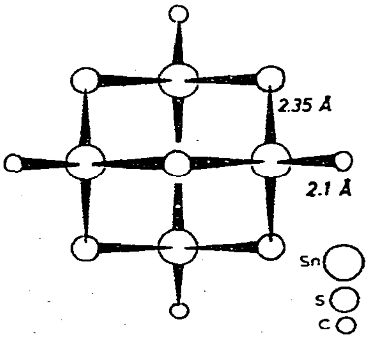

Fig. 1. Monomethyltin sesquisulfide along the b-axis.

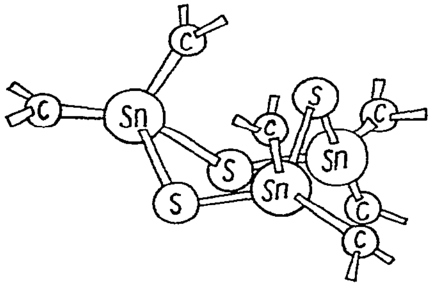

Fig. 2. The diphenyltin sulfide trimer.

C. Organotin transition metal compounds

The chemistry of Group IV–transition metal compounds is now very extensive and has been reviewed[290,313]. We can summarize the principle features of the tin compounds thus far studied as follows:

(i) the tin atom is attached directly to the transition metal by normal covalent bonds, and not, for example, as a donor–acceptor adduct;

(ii) the tin atom is generally four-coordinate;

(iii) tin appears as Sn^{IV} no matter what the oxidation state of the starting material used to prepare the transition metal derivative;

(iv) $(d \to d)\pi$ interactions along the tin–transition metal bond do not predominate in determining chemical, spectroscopic or structural properties;

(v) the transition metal–tin–transition metal angles are always larger than tetrahedral, while the angles involving carbon, oxygen or a halogen atom at tin are always smaller than tetrahedral*;

(vi) the tin–transition metal internuclear distances are found to be short with respect to estimates based upon covalent radius sums, while the distances involving organic groups, oxygen or the halogens are found to be long for their class**;

(vii) the coordination at the attached transition metal is generally found to be usual in number and geometry as for carbonyls and other organometallic derivatives;

(viii) crystal packing distorts the structures from ideal molecular geometry giving rise, for example, to slight departures from the linearity of transition metal carbonyl bonds, or from perfect octahedral or trigonal bipyramidal shapes about the transition metal, or giving rise to molecular configurations containing eclipsed groups;

(ix) in transition metal carbonyl derivatives, the metal carbonyl angles open out and the M–C≡O axes are often found to deviate from linearity so as to bring the carbonyl groups toward the tin atom in an "umbrella effect";

(x) in all the examples studied thus far the transition metal compounds crystallize as discrete molecules with no unusually short intermolecular contact distances;

(xi) all the compounds in which the tin atom is directly bound to the transition metal are diamagnetic; all paramagnetic species contain remotely positioned trihalostannate(II) ions;

(xii) the tin compounds are no different in general structural features than derivatives containing other Group IV elements.

We can now discuss each of the above summarizing statement in turn, with especial reference both to the extent of the data which supports it as well as to known examples to the contrary.

The initial formulation of the inorganic tin–transition metal compounds as adducts of the trihalostannate ion is faulty. The chemical and spectroscopic properties of the genuine

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* Angles at tin involving organic groups, halogens or oxygen become more acute in that order, while in derivatives containing these moieties the angles involving transition metals open more widely in the same order.

** The tin–transition metal internuclear distances decrease on replacement of organic groups at tin by halogen or oxygen.

trihalostannate species differ in important ways from those of the transition metal derivatives which fortuitously correspond.

The structural evidence which at one time might have been taken as conclusive, seems now, with the availability of more recent data for the trichlorostannate ion, more ambiguous. For example, Rundle and Olson assigned the covalent radii $r(\mathrm{Sn^{II}}) = 1.63$ Å and $r(\mathrm{Sn^{IV}}) = 1.40$ Å, giving the tin-chlorine internuclear distances as $d(\mathrm{Sn^{II}{-}Cl}) = 2.62$ Å and $d(\mathrm{Sn^{IV}{-}Cl}) = 2.39$ Å[277], on the basis of the three structures $SnCl_2$[277,297], $SnCl_2 \cdot 2H_2O$[225] and $K_2SnCl_4 \cdot H_2O$[226], each of which is derived from a minimum of data with relatively large errors for d(Sn–Cl). The full, three-dimensional structure of $SnCl_2$ from Rundle's laboratory has never been published, but is reported to have given the non-bridging d(Sn–Cl) as 2.67 Å[277], while in the three structures mentioned above the values range from 2.54 to 2.78 Å. More recent determinations give shorter distances. Study of a twinned crystal of cesium trichlorostannate gives 2.52 Å as the average Sn–Cl distance in the pyramidal ion[269], while the isolated $SnCl_3^-$ ions in $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]CoCl^+ \cdot SnCl_3^-$ have Sn–Cl distances which average 2.44 Å[286]. In the transition metal derivatives containing tin-chlorine bonds, on the other hand, d(Sn–Cl) ranges from 2.35 to 2.54 with the average of the internuclear distances measured as 2.42 Å, only a little longer than the calculated tin(IV) value, but yet shorter by more than an average of even just the more reliable tin(II) values measured so far. An elongation of the tin(IV)-chlorine bonds would be understandable in a general view based upon σ-electron redistributions[133] or electron pair repulsions[193] (*vide infra*).

The interpretation of the evidence offered by the bond angle data is even more difficult. The angles Cl-Sn-Cl in $SnCl_2 \cdot 2H_2O$[225] and $K_2SnCl_4 \cdot H_2O$[226], the latter of which contains discrete $SnCl_3^-$ units, are reported to be very acute, ranging from 83 to 91°. The recently investigated forms of $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2CoCl^+\ SnCl_3^-$ in which $SnCl_3^-$ units occupy remote positions in the lattice possess angles Cl-Sn-Cl in the range 91.3-96.2°[286], and the analogous angles in $CsSnCl_3$ are in the range 86.9-92.3°[269]. It might be expected that on coordination these angles would relax toward tetrahedral values as the lone pair of electrons available in this oxidation state, and presumably residing in predominantly s-orbitals in the above examples, takes on more directional, p-character. However, no authentic example exists in which the lone pair of electrons of a trichlorostannane ion has been used in coordination. The reported isolation of $Cl_3Sn{\rightarrow}BF_3^-$[223] has been retracted[306], and the only truly tin(II) adducts of transition metals are based upon dicyclopentadienyltin(II)[206,209] and on dialkyltin(II) species[242] for which no structural data are yet available. It is expected that the angles X–Sn–X in a trihalotin(IV) transition metal derivative would relax from the tetrahedral in such a way as to widen at the metal and become more acute at the halogens for both steric and electronic reasons as will be discussed below. The measured dichlorotin angles in transition metal derivatives of known structure range from 92.8 to 103.7° with an average value of 97.8° counting each measured angle separately. This information, which shows the angles in the $SnCl_3$ unit to have become larger than those in known trichlorostannate ions but smaller than tetrahedral values, is ambiguous in terms of deciding oxidation state or mode of attachment. Unfortunately, the completed gas phase structure of methyltin trichloride is not yet available[244], and the older results from electron diffraction[96] must be considered unreliable.

The interpretation of the data from ^{119m}Sn Mössbauer isomer shift (*IS*) measurements is much more straightforward. It is the practice of inorganic chemists to write electronic configurations such as Sn[Kr]$4d^{10}5s^2 5p^0$ for the formal oxidation state tin(II), $5sp^3$ for covalent tin(IV) and $5s^0p^0$ for ionized Sn^{4+}. The electron population in the 5*s* subshell decreases from 2 to zero as the list is descended, and the ^{119m}Sn Mössbauer *IS* values seem to follow the same change, as they would be predicted to do from first principles. Gray tin (α-tin) which adopts the tetrahedral diamond structure with an *IS* commonly quoted as ca. 2.10 mm/s with respect to tin(IV) oxide and its tetrahedral molecular tin cluster analogue, tetrakis(triphenylstannyl)tin (*IS* = 1.33 mm/s)[191] can be regarded as derivatives of the tin(IV) oxidation state. The metallic form of tin (white tin, β-tin) reacts with hydrogen chloride to produce tin(II) compounds[189], and its *IS*, commonly quoted as ca. 2.56 mm/s[288] may be taken as the dividing line between the two tin oxidation states: all tin(IV) compounds falling below and all tin(II) compounds above. This hypothesis has been used to show that compounds of the formula R_2Sn, believed to be organic derivatives of tin(II), are in fact tin(IV) species[196] as corroborated by the structure of $[(C_6H_5)_2Sn]_6$[86] discussed above in Section II. A.

In this view the *IS* values of all the tin–transition metal compounds which fall into the range 1.31 to 2.20 mm/s with the trihalotin derivatives occupying the smaller range 1.50 to 1.93 mm/s[318] must be considered as containing tin in the Sn^{IV} oxidation state. Comparison may be made with $SnCl_2$[317], $SnCl_2{\cdot}2H_2O$[317] and $K_2SnCl_4{\cdot}H_2O$[179] (*IS* = 3.51–3.63 mm/s) and with the organotin(IV) trihalides such as n-butyl- or phenyltin trichloride where the *IS* is 1.70 and 1.27, respectively[179]. The $(C_5H_5)_2Sn$ adducts of BF_3[209] or $FeCl_3$[206,209] exhibit *IS*'s of 3.79 and 3.73 mm/s, respectively, and the *IS* of the green and red forms of $\{[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2CoCl\}^+ SnCl_3^-$ in which the isolated nature of the trichlorostannate unit has been shown by X-ray studies are 3.08 and 3.10 mm/s, respectively[286].

Finally, chemical facts stubbornly refuse to be reconciled to the assignment of a tin(II) oxidation state. For example, the preparation of the same transition metal derivative may proceed from tin(II) or tin(IV) starting materials[179,313].

$$\left.\begin{array}{l} [\pi\text{-}C_5H_5Fe(CO)_2]_2 + SnCl_2 \\ \\ [\pi\text{-}C_5H_5Fe(CO)_2]_2Sn(C_6H_5)_2 + 2HCl \end{array}\right] \longrightarrow [\pi\text{-}C_5H_5Fe(CO)_2]_2SnCl_2$$

Likewise, π-$C_5H_5Fe(CO)_2I$ produces π-$C_5H_5Fe(CO)_2SnCl_2I$ on treatment with $SnCl_2$, a reaction which may proceed through an intermediate tin(II) chloride coordination with the metal followed by iodine migration or possibly via insertion of a tin(II) carbenoid species into the iron–iodine bond to give a tin(IV) product. Perhaps the most compelling evidence comes from the alkylation or arylation of trihalotin–transition metal compounds by organolithium or Grignard reagents to give products completely analogous to the triorganosilyl- and germyl–transition metal derivatives always assigned the usual group oxidation state of four[313]. It would be difficult to argue that these organolithium and organomagnesium agents could oxidize the tin.

The effect of $(d{\rightarrow}d)\pi$ interactions along the tin–transition metal bond has been inferred on the basis of various chemical[155], infrared[117,181,200,222,263,290], and NMR[237,262] evidence and from theoretical calculations[224]. According to a view once accepted, resolvable quadrupole splitting in asymmetrically-substituted organotin(IV) compounds arises only when the population of the empty $5d$-orbitals by electron pairs from adjacent atoms can take place[191,198]. Indeed, quadrupole splittings have been resolved in the Mössbauer spectra of several organotin derivatives of the type $R_{4-n}SnM_n$, although most such complexes give reasonably sharp, singlet resonances. These resolved splittings appear to be evidence for $(d \rightarrow d)\pi$ bonding.

However, in systems of the type $R_{4-n}SnX_n$ where X = halogen or a ligand containing nitrogen, oxygen or sulfur, $|\psi_{ns}(0)|^2$ and *IS* decrease generally with increasing n. The consequence of populating the empty tin $5d$-orbitals by $(p \rightarrow d)\pi$ bonding in these systems would be further reduction of $|\psi_{ns}(0)|^2$ by shielding. Thus both effects would change *IS* in the same direction, and the *IS* values cannot be used qualitatively to test for π-interactions. In the tin-transition metal systems, on the other hand, the *IS* would be expected to increase with the substitution of metal atoms in $R_{4-n}SnM_n$ or $X_{4-n}SnM_n$, but decrease as a result of the shielding introduced by π-interactions with the transition metal. It is clear from the representative data for both series plotted in Fig. 3 that if $(d \rightarrow d)\pi$ interactions are present at all in these systems, they are subordinate to other factors responsible for the distribution of electrons about the tin atom[178].

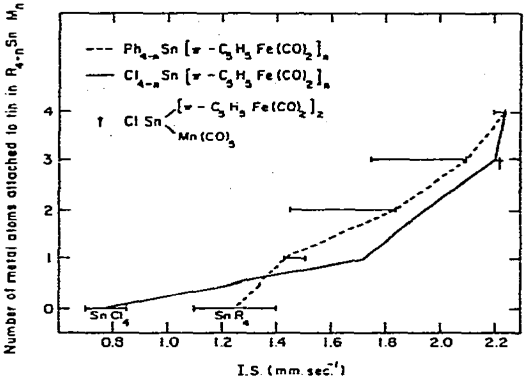

Fig. 3. ^{119m}Sn Mössbauer isomer shift *vs.* transition metal substitution at tin in $R_{4-n}SnM_n$ and $X_{4-n}SnM_n$. Horizontal bars represent the range of values reported.

It is apparent from Fig. 3 that the Mössbauer *IS* increases monotonically with the substitution by transition metal atoms. This corresponds in the theory of the ^{119m}Sn Mössbauer *IS* to an increase in $|\psi_{ns}(0)|^2$ viewed presumably isotropically from the tin nucleus. The NMR $J(^{119}Sn-C-^{1}H)$ in the methyltin derivatives is also related in the Fermi contact mechanism to the s-distribution at the tin atom, in this case viewed along the bonding axes to carbon. The NMR data indicate that the increase in $|\psi_{ns}(0)|^2$ at the tin nucleus on transition metal substitution is accompanied by a balancing decrease in the s-character of the tin–carbon bond in $(H_3C)_{4-n}SnM_n$. Given a fixed amount of $5s$-character to distribute, these observations dictate a parallel concentration of s-character in the orbitals, tin directs toward the transition metal. The enhanced s-character in the tin–transition metal bond is then reflected in the larger than tetrahedral angles M–Sn–M and also in the tendency for short d(Sn–M) and high bond stretching force constants.

Likewise, the larger residue of *p*-character in the orbitals tin directs toward the remaining ligands leads to smaller than tetrahedral angles C-Sn-C or X-Sn-X and to the tendency for long *d*(Sn-C) and *d*(Sn-X) with lower bond stretching force constants. Angle and length distortions are particularly evident when tin is bound to the highly electronegative oxygen. This explanation of the structural and spectroscopic observations can be derived directly from isovalent hybridization arguments[133]. Of course an equivalent explanation can be based upon the valence shell electron pair repulsion theory[193]. The exact role of steric effects, which in most of the cases studied must operate in the same direction, is not known.

The various departures from ideal molecular geometry which characterize most of the compounds studied can be discussed with reference to triphenyltin tetracarbonyltriphenylphosphinemanganese, $(C_6H_5)_3PMn(CO)_4Sn(C_6H_5)_3$[27,28], an example which illustrates at once several general categories of distortion. This compound adopts a configuration in the crystal in which the phenyl groups on phosphorus and tin are almost perfectly eclipsed along the *trans*-P-Mn-Sn axis as shown in Fig. 4. The P-Mn-Sn angle itself is 176.2°, a non-linearity which may find its cause in a Jahn-Teller distortion serving to produce an orbitally non-degenerate lowest energy level. The Mn-C≡O angle is likewise non-linear, averaging only 173.8°. This distortion combines with a bending of the Sn-Mn-C system (average angle = 86°) to produce a situation in which the carbonyl groups lean away from the phosphorus atom and toward tin. This "umbrella effect" can be seen in Fig. 4. The solid under discussion melts at 229°, and so the molecules are firmly held in the crystal. However, the intermolecular contact distances are long for their class, suggesting that the structure may be locally loose, but generally tight. This in turn leads to a view that the particular conformation found for the molecule in the crystal structure, with its many distortions, is dictated by packing considerations, and that in the isolated molecule there will be a large number of degrees of freedom, including only slightly hindered rotation

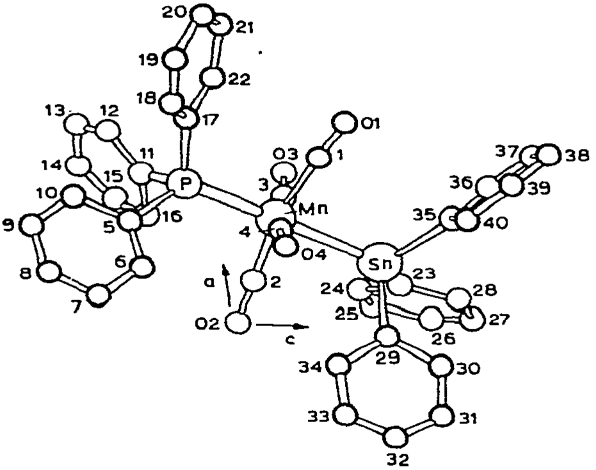

Fig. 4. Triphenyltin tetracarbonyltriphenylphosphinemanganese viewed down the b-axis.

about the P–Mn–Sn axis. Thus it is unlikely that the deformed P–Mn–Sn angle persists in the isolated molecule where the stresses which induce it in the crystal structure are absent. Very little energy is probably required to achieve deformations of linear systems of this kind. The widespread occurrence of non-linear carbonyl-metal systems in crystal structures should be noted in this connection, and care should be exercised in interpreting solid state spectra of such compounds. Comparison in the present case can be made to the structure of $(C_6H_5)_3SnMn(CO)_5$[83,104,105] in which the arrangement in the crystal is much more regular, and none of the steric constraint observed here occurs. An additional comparison, with $(C_6H_5)_3SnCo(CO)_3P(C_6H_5)_3$, will be possible if present work[112] is carried to completion. In this structure, as well as in others where the same effect is observed, the tendency of the carbonyl systems to lean toward the second metal atom is, we believe, only a consequence of the need to fill space more efficiently, and not due to any novel electronic effect which would be observable in the isolated molecule. The obvious inference from the presence of the many observed distortions is that it requires very little energy to deform the orbital directions in the d^2sp^3 and sp configurations. For large molecules of this kind there is little doubt that the lattice energy terms, which are dependent on coulombic interactions between molecules, far outweigh the terms involving intramolecular interactions, and that considerable deformation of the molecules can be tolerated in order to achieve the most satisfactory overall packing arrangement.

The "umbrella effect" is also seen in the following structures where the average M–C≡O and Sn–M–C angles are listed in parentheses: $Cl_2Sn[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$[256] (176.8°; 89.0°); $ClSn[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2\ [Mo(CO)_3\text{-}\pi\text{-}C_5H_5]$[255] (Mo, 173°; Fe_1, 176°; Fe_2, 174°; Fe_1, 91°; Fe_2, 87°; no Sn–Mo–C angle listed); $(ONO)_2Sn[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$[11,15] (170.9°; 87.3°); $Cl_3SnRu_2Cl_3(CO)_5$[174,267] (173°; 90°); $Cl_3SnFe(CO)_2\text{-}\pi\text{-}C_5H_5$[147,197] (176.5°; 90.6°); $Br_3SnFe(CO)_2\text{-}\pi\text{-}C_5H_5$[147,246] (178°; 90.3°); and $ClSn[Co(CO)_4]_3$[137] [167° (not average; only one angle given); 84.2°] for the derivatives in which tin holds inorganic ligands, and in $(C_6H_5)_3SnMn(CO)_5$[83,104-105] [173.6°; 86.7° (equatorial)]; $(C_6H_5)_3SnFe(CO)_2\text{-}\pi\text{-}C_5H_5$[29] (185.1°; 86.5° [averages over two conformationally different molecules present]; $(CH_3)_3SnMn(CO)_5$[31-32] [178.8°; 84.4° (equatorial)]; $(C_6H_5)_2Sn\ [Mn(CO)_5]\ [Co(CO)_4]$[10,12,14] [Mn, 170° (equatorial); Co, 172°; Sn–Mn–C, 86.0° (equatorial); Sn–Co–C, 82.7°]; $(CH_3)_2Sn[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$[11,13,15] (174°; 84.8°); $(C_5H_5)_2Sn[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$[11,17] (172.4°; 88.8°); and $C_6H_5Cl_2Sn\ Fe(CO)_2\text{-}\pi\text{-}C_5H_5$[65] (177.5°; 91.9°) where the tin atom is substituted by organic groups. It has been noted[105] that in the phenyltin derivatives the degree of non-linearity of the transition metal–carbonyl axis is controlled by the shortest intramolecular contact distance with the phenyl groups, and that the greatest bending takes place where the steric resistance is least. Moving, for example, from triphenyltin pentacarbonylmanganese[105] to the trimethyltin analogue[32] results in larger displacements of the carbonyl groups toward tin, presumably to take up the empty space between these moieties in the crystal structure. Perhaps similar packing forces are operating in bending the terminal nitrito-oxygen toward the tin atom in $(ONO)_2Sn[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$ where O–N–O = 122°, and 2.80 Å separates the tin and terminal oxygen atoms[11,15].

The eclipsing of groups discussed for tetracarbonyltriphenylphosphinemanganese triphenyltin[27-28] is also a feature of the crystal structure of $Cl_3SnFe(CO)_2\text{-}\pi\text{-}C_5H_5$[147,197] as shown projected down the Sn–Fe axis in Fig. 5. It is interesting to note that the corresponding groups in the bromine analogue are staggered[147,246], and the orientation about this axis is also different in the two crystallographically independent and conformationally different isomers in the unit cell of the triphenyltin derivative[29]. There are no limiting intramolecular contacts dictating this particular configuration adopted by the trichloro compound. A staggered configuration is also adopted by the phenyldichlorotin derivative[65] as shown in Fig. 6, as well as by $(h^5\text{-}C_5H_5)Fe(CO)(f_6fos)Sn(CH_3)_3$ in which $f_6$fos is $(C_6H_5)_2P\overline{C{=}C[P(C_6H_5)_2](CF_2)_2C}F_2$[49]. It may be concluded from this evidence that free rotation is possible about the Sn–Fe bond, and that the particular configuration imposed upon the molecule maximizes the utilization of space in the crystal.

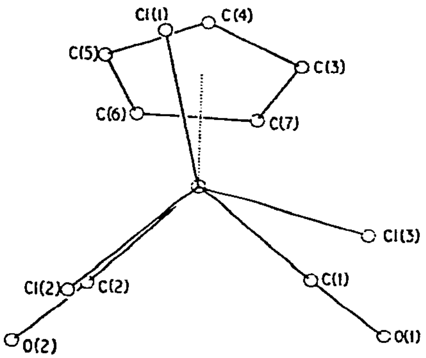

Fig. 5. Trichlorotin dicarbonylcyclopentadienyliron viewed down the Sn–Fe bond axis.

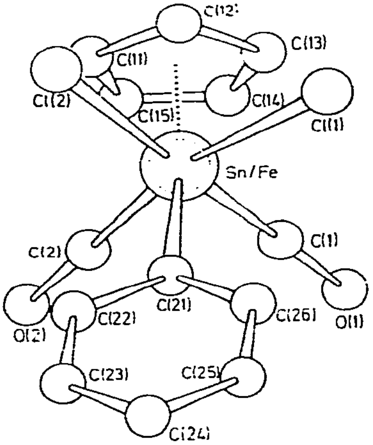

Fig. 6. Phenyldichlorotin dicarbonylcyclopentadienyliron viewed down the Sn–Fe bond axis.

In triphenyltin pentacarbonylmanganese the mean torsion angles around the Sn–Mn axis as shown in Fig. 7 combine the trigonal SnC_3 and tetragonal MnC_4 parts so that the whole has almost a mirror plane of symmetry, *i.e.*, rotation by ca. 3° would produce exact *m* symmetry[104-105]. This particular orientation is similar to that seen in the *trans*-

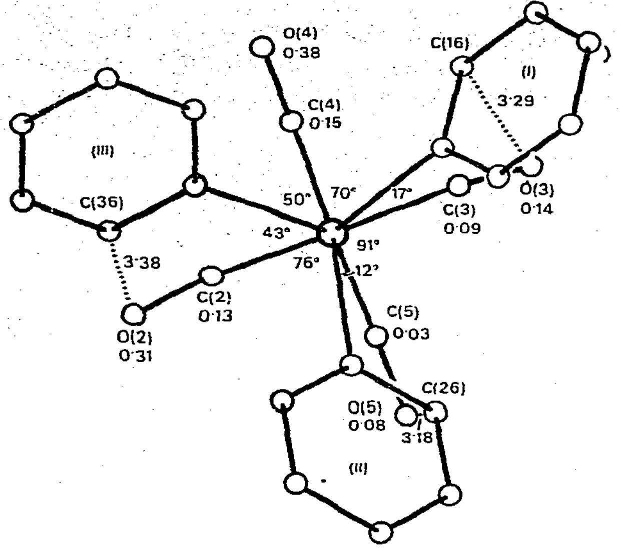

Fig. 7. Triphenyltin pentacarbonylmanganese viewed down the Sn–Fe bond axis. The heights of the atoms of the equatorial carbonyl groups above the plane of projection through the Mn atom (toward the tin atom) are given in Å, as are the closest contacts between the carbonyl and phenyl groups.

triphenylphosphine analogue[27-28] discussed above. In trimethyltin pentacarbonylmanganese the deviation from a conformation having mirror symmetry is only 1° of rotation. A view of this molecule in projection down the Sn–Mn axis is shown in Fig. 8.

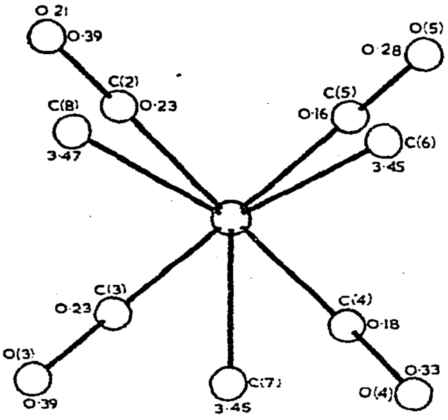

Fig. 8. Trimethyltin pentacarbonylmanganese viewed down the Sn–Mn axis. The heights of the atoms of the equatorial carbonyl groups above the plane of projection through the Mn atom (toward the tin atom) are given in Å.

A particularly interesting case is presented by the structures of dichloro- and diphenylbis-(2,3,5,6-*tetrahapto*-norbornadienedicarbonylcobalt)tin(IV)[22-23]. Schrauzer *et al.* showed that norbornadiene can be dimerized stereospecifically to a bis-nortricyclene (Binor-S) via intermediate π-complexes derived from heterometallic cobalt carbonyl compounds of the type $M[Co(CO)_4]_n$ where $n = 2$ or 3 and M = Zn, Cd, Hg or Ir[280]. Studies of the tin derivatives $X_2Sn[Co(CO)_4]_2$ show that these also actively catalyze the dimerization of norbornadiene, but in a manner remarkably sensitive to the substituent, X[139]. For X = Cl, Br, or I, the reaction is stereospecific for Binor-S, but for $X = CH_3$ or C_6H_5 a mixture of dimers other than Binor-S is obtained[279]. The dichloro and diphenyl derivatives named above were isolated from the residues of the respective reaction mixtures. These compounds are believed to be intermediates in the π-complex multicenter reaction, and they are themselves catalytically active. Their structures are characterized by the opening of the metal angles at tin by 10° (from 118 to 128°) on substituting chlorine for phenyl groups. Free rotation about the Sn–Co bonds would make all *axial* and all *equatorial* positions equivalent, but the NMR spectra of these compounds under ambient conditions show only a single resonance for the olefinic protons of the norbornadiene ligands, suggesting that exchange of positions can take place, presumably via a pseudorotation mechanism in which the norbornadiene slides over the apex opposite to tin while the equatorial carbonyls flip to the other side, which is equivalent to a two-fold application of a pseudorotation using the olefinic bonds, in turn, as pivots. The NMR coalescence temperature of the dichloro derivative is 65° lower than the diphenyl, consistent with the idea that the more opened angle at tin is associated with greater lability of the ligands at cobalt. Model studies show that the alignment of the dienes in the conformation adopted in the crystalline state is not favorable for forming Binor-S, even allowing free rotation about the Sn–Co bonds. However, if both the diene double bonds are *equatorial* in the transition state, then a suitable geometry for obtaining Binor-S by a concerted mechanism is readily constructed. Apparently, chlorine substitution and its concomitant angle changes serves to reduce the energy required to attain the Binor-S transition state by labilizing these ligands[22-23].

Certain of the tin–transition metal structures demand attention because they stand as exceptions to the general statements made at the opening of this Section. These will be discussed individually.

The generalization that the tin–transition metal angles are larger than the angles at tin involving other ligands breaks down when the metals are incorporated into a small ring. Three such examples have been studied, one involving a spirocyclic system of idealized D_{2d} ($\bar{4}2m$) symmetry centering on tin as shown in Fig. 9. In this compound, $(CH_3)_2Sn\{[Fe(CO)_4]_2\}Sn(CH_3)_2$[97], the three tin atoms fall almost in a line and are bridged by the four iron groups in such a manner that the central tin atom is surrounded by a somewhat elongated tetrahedron of iron atoms. The Sn_2Fe_2 rings are exactly planar and the two planes are virtually perpendicular. The "umbrella effect" is in evidence in that each equatorial group is seen to lean toward the terminal tin atom. The interior and terminal tin–iron–equatorial carbon atom angles are 106° and 84°, respectively. The molecular configuration can be regarded as a balance between maintaining regular O_h and T_d angles and normal equilibrium distances and the tendency for non-bonded atoms to achieve normal Van der Waals contacts. In the resulting compromise the O_h angle at iron is reduced by 12.1° while the T_d angle at tin is reduced by only 7.5° in the four-membered ring. The structure adopted brings the axial-carbonyl groups on one side of the central tin atom into close contact ($O \cdots O = 2.98$ Å) with equatorial groups on the other.

The cluster complex di-μ-dimethylstannylenebis[tricarbonyl(trimethylstannyl)-ruthenium][103] again contains a planar $Sn_2Ru_2^{III}$ four-membered ring (see Fig. 10),

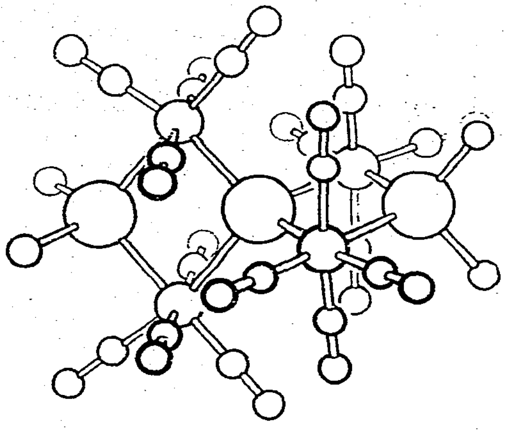

Fig. 9. The $(CH_3)_4Sn_3Fe_4(CO)_{16}$ molecule. In order of increasing size, the atoms are carbon, oxygen, iron and tin.

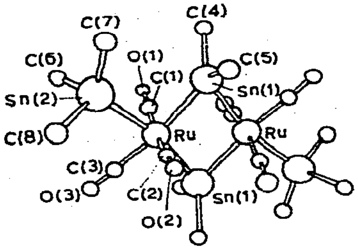

Fig. 10. The di-μ-dimethylstannylenebis-[tricarbonyl(trimethylstannyl)ruthenium] molecule, $[CH_3)_3Sn(CO)_3RuSn(CH_3)_2]_2$.

however, with an extremely acute angle (71.5°) at tin. The ring plane contains a crystallographic center of symmetry, and the molecule deviates only slightly from C_{2h} point group symmetry. The low spin magnetic moment of 2.0 B.M. expected of O_h Ru^{III} [180] is absent, and the ring structure shows that the angle at tin has sharply decreased to make spin-pairing possible across the Ru–Ru distance of 3.12 Å (*cf.* the corresponding non-bonded distance of 3.75 Å in $[(CO)_3RuBr_2]_2$[247] and the bonded distance of 2.85 Å in $Ru_3(CO)_{12}$)[163] although the dimethyltin angle in the bridging group remains at 109°. One methyl group on each terminal tin atom is locked between this dimethyltin moiety and repelled so that the Ru–Sn–C angle for this group opens to 120°. Even so, the hydrogen contact distances are 2.1 Å for both bridging methyl groups, comparable to the internuclear distance between hydrogen atoms on the same methyl group. It is obvious that for these three methyl groups free rotation is difficult, and the isotropic temperature factor for the terminal methyl group where the rotation function is double-valued is unexpectedly large[103]. This discussion is of particular interest with regard to the presumed instability of a proposed second isomer with the terminal trimethyltin groups in the axial position[163]. Model studies indicate that after the deformation brought about by the strong Ru–Ru interaction, the axial position would be extremely unfavorable for the trimethyltin group[103]. Apparently such a molecule would be paramagnetic.

The third of the three ring structures, tetrakis[tetracarbonyl iron]tin, is related to the spirocyclic compound discussed first (*vide supra*) in being isolated from the same reaction of tri-n-butyltin chloride with iron pentacarbonyl[162], and in being spirocyclic with a central tin atom[236]. In this instance, however, the D_{2d} ($\bar{4}2m$) molecule contains three-membered, $SnFe_2$ rings. There are no examples of three-membered rings authenticated by structural analysis in the chemistry of the fourth group elements below carbon except where the ring contains transition metal atoms[312]. The iron–iron bonding is necessary in $Sn[Fe(CO)_4]_4$ to account for the diamagnetism of the compound, and the molecule undergoes a tetragonal distortion which lowers the symmetry from T_d to D_{2d} and brings the iron atoms closer in pairs. Purely steric factors cannot account for this lowering of symmetry since it is possible to construct an entirely satisfactory model employing T_d tin and regular trigonal bipyramidal iron in which no oxygen–oxygen intracarbonyl contact distance is less than 3 Å. The acute-angled Fe–Sn–Fe triangles lie approximately perpendicular to each other (86.8°), and include a 68.9° angle at tin. The intra-ring iron atoms are 2.87 Å from one another, with the longer iron–iron distance at 4.65 Å[236].

The next two structures to be discussed involve five-coordinated tin atoms in a chlorine bridge arrangement which creates a three-membered ring by a donor–acceptor interaction. A methyldichlorostannyl group is present in each molecule, with the dichloro substitution enhancing the Lewis acid character of tin. The structure of μ-chloro(dichloromethyltin)-2,2′-bipyridyltricarbonylmolybdenum[50–51] in which the molybdenum is seven-coordinated in a capped octahedron and the tin five-coordinated in a distorted trigonal bipyramid is shown in Fig. 11. The related μ-chloro(dichloromethyltin)dithiahexanetricarbonyltungsten[52] is similar in geometry. The bridging tin–chlorine distances are 2.81 and 2.96 Å respectively for the molybdenum and tungsten compounds, and should be compared to the sum of the Van der Waals radii, 4.0 Å, to the sum of the covalent radii, 2.39 Å, and to the singly coordinated chlorine ligands in the two molecules which lie in the range 2.36 to 2.43 Å. The increase in the tin to bridging chlorine distance in the tungsten compound is accompanied by a shortening of the transition metal–chlorine distance from 2.56 Å in the molybdenum compound to 2.52 Å. Thus tin forms a stronger bond with chlorine in the molybdenum compound at the expense of the bond to the transition metal. The other internuclear distances are similar, for example, to tin (Mo, 2.75; W, 2.76 Å) or somewhat smaller for tungsten, for example, to the carbonyl groups [Mo, 1.98; W, 1.96 Å (mean)]. The weaker bridging chlorine interaction in the tungsten compound virtually removes the distinction between the axial and equatorial chlorine ligands with respect to the trigonal bipyramid at tin where a difference of only 0.01 Å is observed in the tungsten case *vs.* 0.08 Å in the molybdenum. It is interesting to note that the molybdenum–tin internuclear distance in the bridged compound is shorter than that found in $ClSn[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2[Mo(CO)_3\text{-}\pi\text{-}C_5H_5]$[256] (2.75 *vs.* 2.89 Å) in which the tin is four-coordinated. The angles within the three-membered rings subtended at tin are 54.8 and 68.0°, respectively, for the

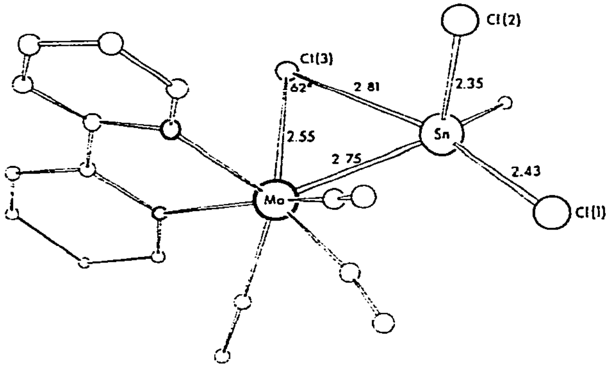

Fig. 11. The molecule $bipy(CO)_3ClMoSnCH_3Cl_2$ as viewed down the a-axis.

molybdenum and tungsten compounds, while the metal-bridging chlorine-tin angle closes from 62 to 59.9°.

Hydroxy bridging to form a four-membered Sn_2O_2 ring occurs in bis[(benzenesulfonato)-μ-hydroxophenylstanno]tetracarbonyldi-π-cyclopentadienyldiiron, $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}Sn(C_6H_5)(O_2SC_6H_5)OH$, which crystallizes as a centrosymmetric dimer with two five-coordinated tin atoms in a badly distorted trigonal bipyramidal geometry with axial oxygen bonds (angle O–Sn–O = 155.3°)[87].

The structure of the highly unusual cluster compound $(C_8H_{12})_3Pt_3(SnCl_3)_2$ [199] in Fig. 12 consists of a triangle of platinum atoms, each coordinated to a cyclooctadiene ring, and capped above and below by trichlorostannate groups 2.37 Å from the Pt_3 plane in a molecule of C_3 symmetry which would become C_{3v} if the staggered $SnCl_3$ groups were rotated by 15°. The angles related by the idealized C_3 axes are all close to 60°. The full report on this structure has not yet appeared.

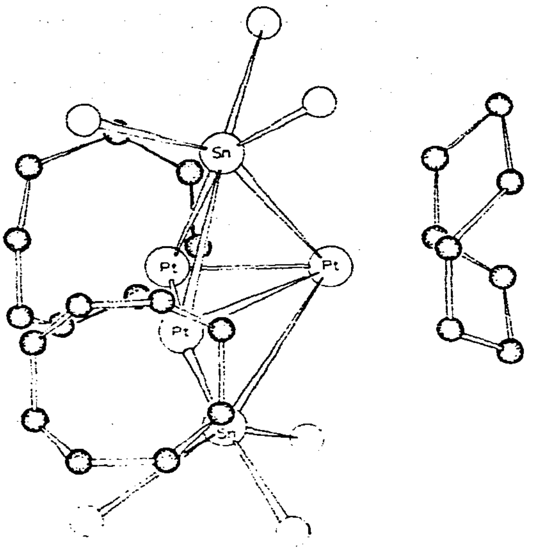

Fig. 12. The $(C_8H_{12})_3Pt_3(SnCl_3)_2$ molecule. The inset shows the configuration of the cycloocta-1,5-diene rings.

The structures of transition metal organometallic complexes with substituents on the organic ligands are of great interest because of the possibility for participation of the metal in direct, across-space interactions[152]. The crystals of $(CH_3)_2Sn(C_6H_5)_2 \cdot 2\ Cr(CO)_3$ which contain a linear dimethyltin group according to infrared and Raman spectra[266] are unfortunately twinned[308]. Another system, where tin is attached through an oxygen atom to a π-cyclopentadienyl group, is triphenylstannoxytetraphenylcyclopentadienyltricarbonylmanganese[30], shown in Fig. 13. It can be seen that not only do the manganese and tin atoms not draw near for interaction, but all the substituent groups on the cyclopentadienyl ring incline away from the manganese atom. There is no evidence to suggest that this arises from packing considerations, but the distances to the manganese from the α-atoms of the cyclopentadienyl ring would close from 3.34 to 3.23 Å if these atoms were in the ring plane. Some steric repulsion may be the cause, and similar, although smaller, distortions are seen in hexamethylbenzene chromiumtricarbonyl[118]. In the triphenylstannoxy unit the angles at tin are, in accordance with the isovalent hybridization arguments made above, greater than tetrahedral for the phenyl groups and less for oxygen.

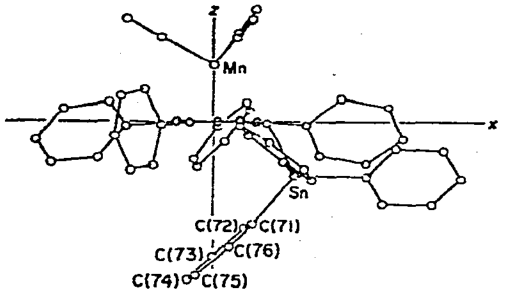

Fig. 13. Triphenylstannoxytetraphenylcyclopentadiene tricarbonylmanganese viewed parallel to the mean plane of the cyclopentadienyl ring.

Although a complete literature search has not been carried out for directly-bonded transition metal derivatives of the other fourth group elements below carbon, sixteen silicon structures are known to us: $X_3SiCo(CO)_4$ where X = H[274], F[175] and Cl[275], $(CH_3)_3SiMn(CO)_5$[201], $Cl_3SiFe(CO)_2\text{-}h^5\text{-}C_5H_5$[241], $Cl_3SiRhHCl[P(C_6H_5)_3]_2$[253], *trans*-$(C_6H_5)_2CH_3SiPtCl[P(CH_3)_2C_6H_5]_2$[227], $(C_6H_5)_2SiH_2Re_2(CO)_8$[173], $[(C_6H_5)_2Si]_2Re_2(CO)_8$[127], $[(C_6H_5)_2Si]_2Re_2H_4(CO)_6$[126], $(h^3\text{-}C_5H_5)Re(CO)_2HSi(C_6H_5)_3$[132], $(h^5\text{-}C_5H_5)MnH(CO)_2Si(C_6H_5)_3$[128], $(h^5\text{-}C_5H_5)MnH(CO)_2Si(C_6H_5)Cl_2$[130], $(C_6H_5)_3SiHFe(CO)_4$[131], $h^5\text{-}C_5H_5(CO)FeH(SiCl_3)_2$[241], and $W_2(CO)_8H_2[Si(C_2H_5)_2]_2$[129]; twelve germanium: $h^5\text{-}C_5H_5Ni[P(C_6H_5)_3]GeCl_3$[195], $Cl_2Ge[Fe(CO)_2\text{-}\pi\text{-}C_5H_5]_2$[150,151]; $[(C_2H_5)_2GeFe(CO)_4]_2$[315], $(C_6H_5)_3GeMn(CO)_5$[230], $[h^5\text{-}C_5H_5Co(CO)_2]_2(GeCl_2)_2Fe(CO)_4$[125], $Br_3GeMn(CO)_5$(electron diffraction)[187], $Br_3GeWBr(CO)_3$dipy[164], $[(C_6H_5)_2Ge]_2Fe_2(CO)_7$[172], $h^5\text{-}C_5H_5Fe(h^3\text{-}C_4H_6)\text{-}Ge(CH_3)Cl_2$, $[(CH_3)_2GeRu(CO)_3]_3$[164], $(C_6H_5)_3GeCo(CO)_3P(C_6H_5)_3$[285] and $C_6H_5GeCo_3(CO)_{11}$[119]; and one lead: $(CH_3)_2Pb[Fe(CO)_2\text{-}h^5\text{-}C_5H_5]_2$[138]. Several of these are homologues of the tin compounds we have discussed and the expected correlations may be drawn, but in one case, the germanium–tungsten bond is not bridged by halogen as in the five-coordinated tin–molybdenum and tungsten structures discussed above. Unfortunately, structures are not available for any complete series, carbon to lead, although several homologous sets are now known. However, one class of silicon–transition metal compounds demands special mention because it introduces a new feature, hydrogen bridging between the transition metal and the fourth group element. Di-μ-hydrido-diphenylsiliconbis(tetracarbonylrhenium), $(C_6H_5)_2SiH_2Re_2(CO)_8$, possesses C_{2v} symmetry as shown in Fig. 14 where one mirror plane passes through the Re_2Si three-membered ring, while the second passes through the silicon atom and the midpoint of the Re–Re bond. The internal angles subtended at silicon and rhenium are 75.7° and 52.2°, respectively, and the silicon–rhenium distance is 2.54 Å. The diphenylsilyl angles are tetrahedral. Evidence for the hydrogen atoms comes from the mass spectrum which shows twelve hydrogen atoms in the molecule, and from the proton NMR and infrared spectra which are consistent with the presence of two special hydrogen atoms[219]. The evidence from the X-ray study is indirect, since these hydrogen atoms were not located in the structure. However, inclusion of two hydrogen atoms in the Re_2Si ring plane at a distance from each rhenium of 1.68 Å and at 90° to the Re-Re bond leads to an Si-H distance of 1.59 Å and an H-Si-H angle of 156.1° with no intra- or intermolecular nonbonded contacts that are abnormally short. Thus an sp^3 hybridized silicon atom would have two orbitals directed toward the α-carbons of the phenyl groups and two towards the centroids of the Re-H-Si triangles[173]. Study of the analogous compounds $[(C_6H_5)_2Si]_2Re_2(CO)_8$[127] and $[(C_6H_5)_2Si]_2H_4Re_2(CO)_6$[126] confirm that the formation of the postulated silicon-hydrogen bond produces no obvious change in the geometry of the Re_2Si_2 unit, however, in the ditungsten derivatives the planar W_2Si_2 ring includes a W-W bond (3.18 Å) with an angle at silicon of 74°. The two distinct silicon-tungsten distances (2.59 and 2.70 Å) have been interpreted as a result of the longer bond being a bent, three-center, two-electron W-H-Si linkage, and this view is supported by the angular distribution of the ligands as emphasized in Fig. 15 and by

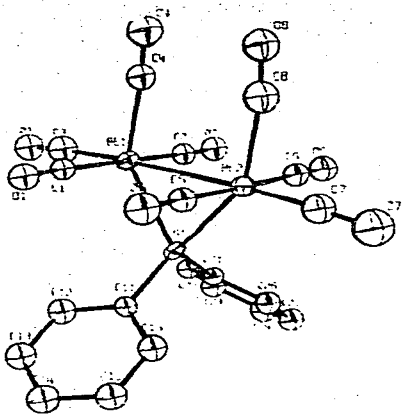

Fig. 14. Di-μ-hydridodiethylsiliconbis(tetracarbonylrhenium), $(C_6H_5)_2SiH_2Re(CO)_8$. The two hydrogens are presumed to bridge the Si-Re bonds, lying in the plane of the ReReSi triangle.

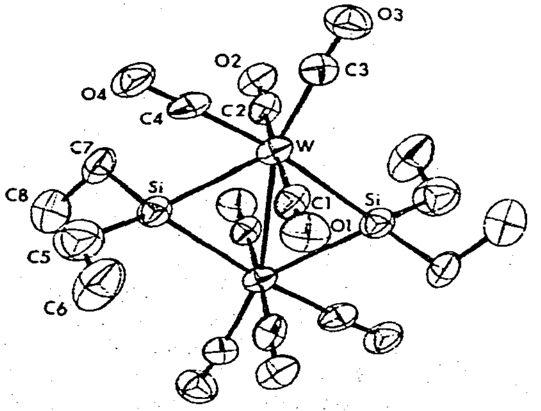

Fig. 15. Di-μ-hydridodiphenylsiliconbis(tetracarbonyltungsten), $(C_2H_5)_2SiH_2W_2(CO)_8$. The two hydrogens are presumed to bridge the Si-W bonds.

electron counting[129]. The compounds $(h^5\text{-}C_5H_5)Mn(CO)_2HSi(C_6H_5)_3$ [128] and $(h^5\text{-}C_5H_5)\text{-}Mn(CO)_2HSiCl_2C_6H_5$ [130] appear to include weak silicon–hydrogen bridge systems as well. Such arrangements should also be possible for tin, and suitable structures should be examined.

Internuclear distances in organotin transition metal compounds are listed in Table 1.

D. Organotin complexes and other higher coordinated molecular solids

1. Some organotin oxygen and sulfur structures

Before proceeding to the discussion of organotin complexes it is of interest to examine the structures of some of the organotin derivatives of oxygen and sulfur for evidence of intramolecular association. Certain of these compounds which are known to form associated lattices are treated later in Section III. The discussion of the structure of tribenzyltin acetate which might be included here is discussed instead with the other acetates in Section III as well. The structure of 1,4-bis(iododiphenyltin)butane is likewise included with the other halides.

The simple organotin ether, hexamethyl distannoxane is monomeric in the vapor phase, and molecular parameters have been derived from electron diffraction studies which give the angle at oxygen as 140°50′[102] as compared with 141° for the germanium analogue[102] and 144° for disiloxane, $(H_3Si)_2O$[115] (the angle was reported as 130±10°[311] in hexamethyldisiloxane). Apologia for the angle opening compared with the 111° in dimethyl ether may be offered *ad libitum*[170], and the same may be said for the angle of 117.5° at nitrogen in tetrakis(dimethylamino)tin, $[(CH_3)_2N]_4Sn$, which has also been studied by electron diffraction[302]. The solid state structure of tetrachloro-1,4-bis(triethylstannoxy)benzene investigated using two-dimensional X-ray data shows monomeric units in the *trans*-form with an angle of 127° at oxygen[107]. Intermolecular contact tin–oxygen distances, crucial to the question of possible association, were not derived, and the angles at tin were assumed to be tetrahedral.

Certain distannoxanes are dimeric in solution[205,259], and X-ray data reveals the nature of the association. For example, tetramethyl-1,3-bis(trimethylsiloxy)distannoxane exists in the crystal as a dimer with coordination from the distannoxane oxygen atom of one chain to a tin atom of the second chain. The resulting Sn_2O_2 ring is nearly square[85]. The terminal siloxy-units bend away from the ladder[258-259] as shown in Fig. 16. Unfortunately, the full report of this structure has not yet appeared.

Hexa-n-butyl-1,5-diazidotristannoxane is said to have a similar ladder structure on the basis of incomplete X-ray data[84].

Tetramethyl-1,3-diisothiocyanatodistannoxane, $\{[(CH_3)_2SnNCS]_2O\}_2$, also forms a dimeric ladder structure with a planar, central, four-membered, Sn_2O_2 ring with tin-oxygen distances of 2.15 and 1.99 Å for the in-chain and across-chain bonds, respectively[37] In this case, however, the nitrogen atoms of the linear isothiocyanate groups in each chain engage in additional coordination with tin atoms of the other chain to form two additional planar, four-membered, Sn_2NO rings as shown in Fig. 17. In addition, there is also coordination between the terminal sulfur atoms of one dimeric unit and tin atoms in adjacent units. This aspect of the structure will be discussed in Section III.B.2.

Coordination of sulfur to tin is also a feature of the structure of *N,N*-dimethyldithiocarbamatotrimethylstannane, which exists in two crystalline modifications, monoclinic[95] and orthorhombic[94]. Two crystallographically independent monomers exist in the unit cell of the latter form[94]. Thus, three monomeric structures shown in Fig. 18 are available for discussion and the structures of *N,N*-dimethyldithiocarbamatodimethylchlorostannane[60] and tetrakis(*N,N*-diethyldithiocarbamato)tin(IV)[204] are known in addition. The tin–sulfur distances in the trimethyltin compounds fall into two classes: 2.47 Å, (same for all three) and 3.16 and 3.33 Å (the latter for one of the molecules in orthorhombic modification), both classes being shorter than expected for a non-bonded distance. The accompanying distortion of the angles at tin, particularly the opening of one of the angles C–Sn–C in each molecule to 117–119° is consistent with the occurrence of intramolecular coordination. By chlorine-substitution and concomitant increase in Lewis acid strength at tin in $Cl(CH_3)_2SnS_2CN(CH_3)_2$, the two tin–sulfur distances become more nearly equal (at 2.48 and 2.79 Å), and the structure assumes a more nearly trigonal bipyramidal shape as shown in Fig. 19 in which the tin, sulfur and two carbon atoms lie in a plane, with the angle Cl–Sn–S (2) = 154.5°[60]. The equatorial placing of the methyl groups in such five-coordinate structure will be seen to be a general feature of organotin complexes in which the more electronegative atoms usually occupy axial positions. Moving to $Sn[S_2CN(C_2H_5)_2]_4$, the

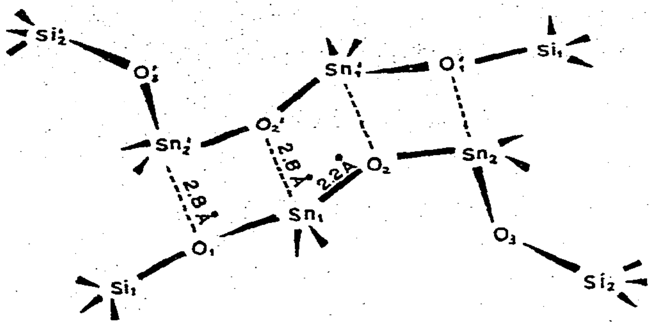

Fig. 16. The dimeric $[(CH_3)_3SiO(CH_3)_2SnOSn(CH_3)_2OSi(CH_3)_3]_2$ structure.

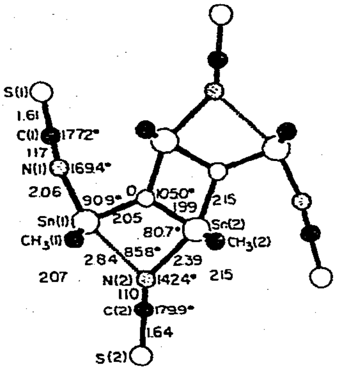

Fig. 17. The dimeric tetramethyl-1,3-diisothiocyanatodistannoxane, $\{[(CH_3)_2SnNCS]_2O\}$ structure.

structure changes to a distorted octahedral about tin where two of the dithiocarbamate ligands are bidentate and two are monodentate. The tin–sulfur distances in the chelating ligands are now virtually equal (2.53 and 2.56 Å) with the distance in the monodentate ligand only slightly smaller (2.50 Å)^{204}. There are no unusually short intermolecular contacts. This structure should be compared with the tetrakis-titanium, -vanadium and -zirconium analogues, which like tin(IV) nitrate discussed in Section II.D.6, below, are eight coordinated with dodecahedral geometry^{159}.

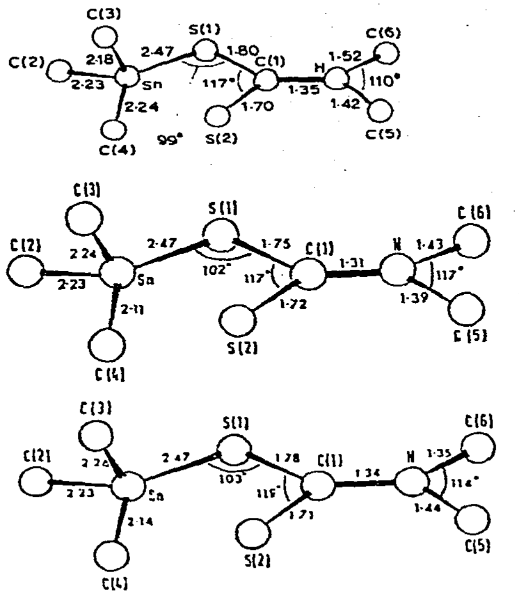

Fig. 18. *N,N*-Dimethyldithiocarbamatotrimethylstannane in two orthorhombic and one monoclinic forms.

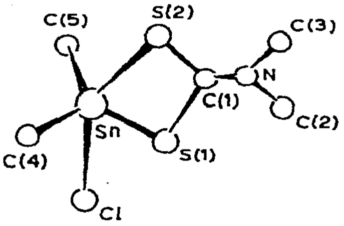

Fig. 19. *N,N*-Dimethyldithiocarbamatodimethyltin chloride.

Oxygen bridges appear in the dimeric, centrosymmetric structure of $[Cl_3SnOH{\cdot}H_2O]_2{\cdot}3C_4H_8O_2$ as shown in Fig. 20 in which the tin atoms are at the center of a distorted octahedral arrangement formed by the three chlorine atoms at neighboring vertices, two hydroxyl oxygen bridges and one water molecule. The three dioxane molecules are not coordinated to tin, but are hydrogen bonded to the oxygen atoms in the coordination sphere of tin. The angles subtended at tin in the Sn_2O_2 four-membered ring are very acute (69.2°) with more open angles of 110.8° at oxygen[141]. A similar dimeric complex containing six-coordinated tin has been found in the structure of $[Cl_3SnOCH_3 \cdot CH_3OH]_2$

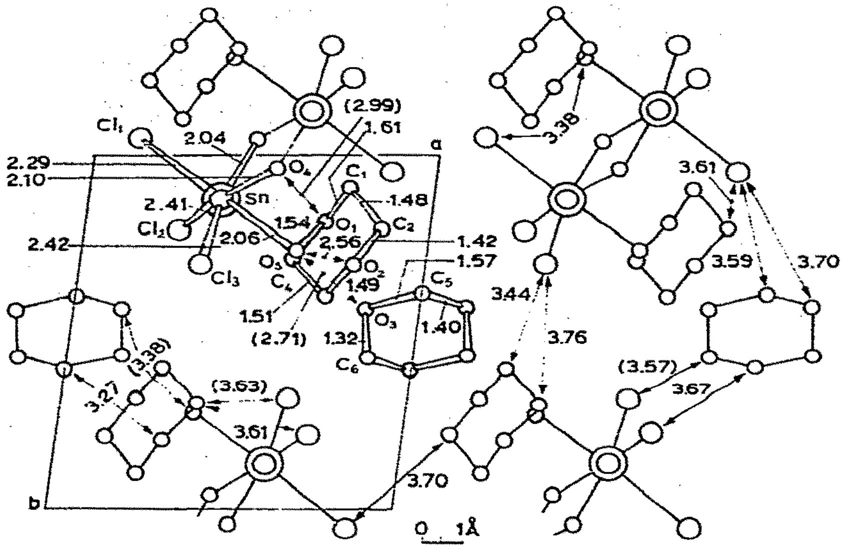

Fig. 20. The dimeric$[Cl_3SnOH \cdot H_2O]_2 \cdot 3C_4H_8O_2$ structure projected onto the ab face.

shown in Fig. 21 which was solved from a single projection only, and bond angles were not tabulated[287].

Another kind of tin–oxygen bridge appears in the structure of the dimeric bis(phosphoryl trichloride) hexachloroditin(IV)-di-μ-dichlorophosphate, $[SnCl_3(POCl_3)^+(PO_2Cl_2)^-]_2$, as

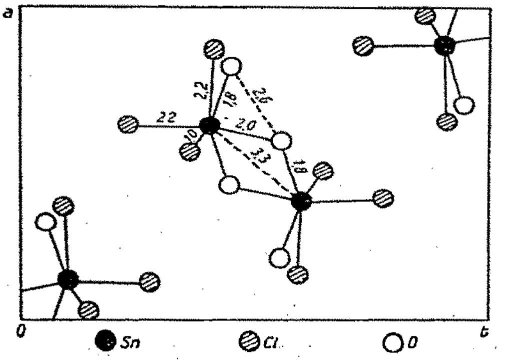

Fig. 21. The dimeric $[Cl_3SnOCH_3 \cdot CH_3OH]_2$ structure solved from projection data.

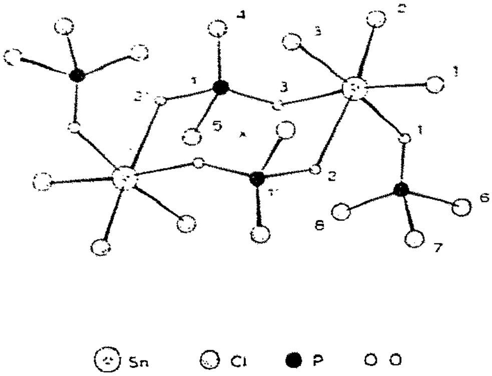

Fig. 22. The dimeric bis(phosphoryl trichloride) hexachloroditin(IV) di-μ-dichlorophosphate, $[SnCl_3(POCl_3)^+(PO_2Cl_2)^-]_2$ structure.

shown in Fig. 22, which contains tin at the center of an octahedral arrangement bridged by dichlorophosphate groups. The bridging oxygen angles subtended at tin (79.1°) are not as acute as in the four-membered ring distannoxanes, while those at phosphorus are much more nearly tetrahedral (106.9°). The eight-membered central ring is centrosymmetric, and the dimeric molecular units have no unusually short intermolecular contact distances[250-252].

In the sulfur series the hexathiodistannate(IV), $Na_4Sn_2S_6 \cdot 14H_2O$, which is isomorphous with its germanium analogue has been shown to contain a dimeric ion with tetrahedral tin bridged by sulfur atoms[233].

It is clear from the examples discussed above that the order of preference for atoms entering bridging to tin is $O > S$. While the preference $O > Cl$ is shown in several examples, the order $S > Cl$ is established on the basis of the structure of $(CH_3)_2SnCl[S_2CN(CH_3)_2]_2$[60] alone, a case in which steric factors probably play an important role in preventing intermolecular coordination involving chlorine.

2. *Five-coordinated molecular structures*

We will divide the structures to be discussed in these remaining sections into those containing five-, six-, seven- and eight-coordinated tin, but no distinction will be made based on formal charge.

The simplest five-coordinated tin structure is found in the pentachlorostannate anion whose regular, trigonal bipyramidal form was established in the study of the 3-chloro-1,2,3,4-tetraphenylcyclobutenium ion. The equatorial tin–chlorine distances are 2.30, 2.30 and 2.40 Å; the axial distances are 2.37 and 2.39 Å[146]. A full report of this structure has not yet been made.

The dimethyltrichlorostannate anion is found in the double salt $[(CH_3)_2SnCl \cdot terpy]^+$-$[(CH_3)_2SnCl_3]^-$ which contains a six-coordinated cation and a five-coordinated anion[47-48]. The only angular distortions from regular trigonal bipyramidal symmetry in the anion are within the equatorial plane where the dimethyl group subtends an angle of 140°, while the two methyl–tin–chlorine angles are 102 and 113° (the axial Cl–Sn–Cl angle seems nowhere listed). The mean length of the axial tin–chlorine bonds (2.54 Å) is greater than 2.32 Å, the corresponding length of the equatorial bonds, in contrast to the situation in $SnCl_5^-$ discussed above.

The structure of the trimethyldichlorostannate anion is known from a study of $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+[Sn(CH_3)_3Cl_2]^-$ in which the tin atom is found in an axially-distorted, trigonal-bipyramidal arrangement of C_{3v} symmetry with the methyl groups equatorial and the chlorine atoms axial. The two tin–chlorine internuclear distances are distinctly dissimilar at 2.57 and 2.70 Å, the latter being the longest such bond reported for a direct Sn–Cl interaction. Only a preliminary communication of these data is available as yet[101].

Trimethyltin nitrate monohydrate has a trigonal bipyramidal structure with planar, equatorial methyl groups and a unidentate nitrate group and a water molecule occupying apical positions. The tin–oxygen bonds are 2.22 (nitrate) and 2.47 Å (water). However, intermolecular hydrogen bonding (O···O contact = 2.72 Å) between the water of one molecule and the nitrate of an adjacent molecule holds the units into a one-dimensional polymer[46].

An additional variation on this theme is presented by the pyridine complex of trimethyltin chloride whose structure was the first conclusive evidence for five-coordination at tin when it was published in 1962[9]. The trigonal-bipyramidal structure with equatorial methyl groups is depicted in Fig. 23 where the axial chlorine distance is 2.43 Å. Projections were used to determine the geometry of the molecule, and the tin–chlorine distance was the only one accurately determined.

The structure of di-μ-acetatobis(diphenyltin), $(C_6H_5)_4Sn_2(O_2CCH_3)_2$, shown in Fig. 24 consists of a binuclear, five-coordinated tin complex with a tin–tin bond containing a center of symmetry at its midpoint. The attached diphenyl group is equatorial with an angle of 112°, while the mean phenyl–tin–tin angle is more open at 124°[8]. Only a preliminary communication is available at this writing.

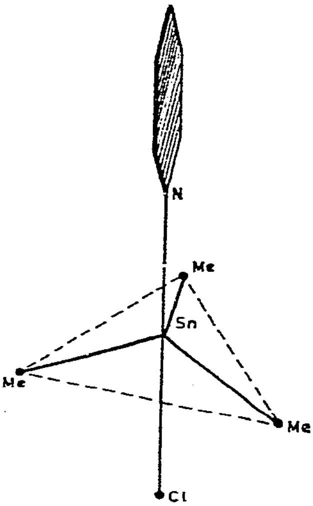

Fig. 23. The pyridine adduct of trimethyltin chloride.

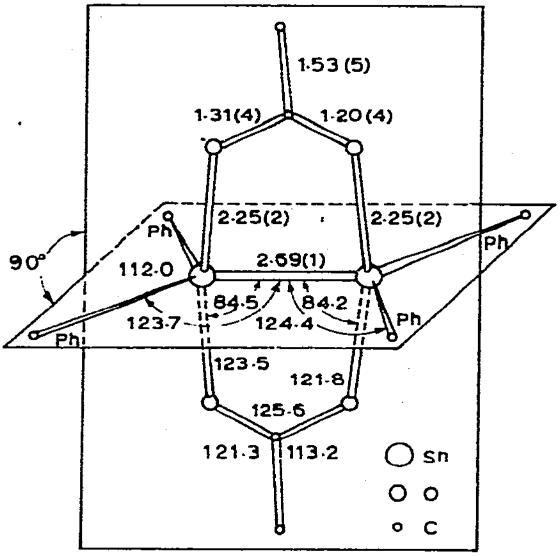

Fig. 24. Di-μ-acetatobis(diphenyltin $(C_6H_5)_4Sn_2(O_2CCH_3)_2$.

The five-coordinated tin(IV) structures available to us for discussion are all distorted trigonal bipyramidal in form. The details of lengths and angles establish two general principles, *viz.*, that the more electronegative ligands tend to occupy axial positions, and that for a given type the axial bonds tend to be longer than the equatorial bonds. This latter distinction tends to be accentuated in mixed ligand substitution, and the mean axial chlorine bond is seen to lengthen for the anion series $[SnCl_5]^-$ (2.38)[146], $[(CH_3)_2SnCl_3]^-$ (2.54)[47-48], $[(CH_3)_3SnCl_2]^-$[101] (2.64 Å) but the corresponding distance in $(CH_3)_3SnCl$ pyridine is 2.42 Å[69]. The adjustment of bond angles according to the electronegativity of the attached groups is also seen in the dimethyltrichlorotin anion where the angles involving chlorine are more acute than those involving only carbon [110 (mean) *vs.* 140°][47-48]. The same effect is seen to operate in $[(C_6H_5)_4Sn_2(O_2CCH_3)_2]$ to close the carbon–tin–carbon angles and open those angles involving the tin–tin bond [112° *vs.* 124.1°(mean)][8]. A large amount of data is available from the infrared spectra of trimethyltin complexes in which the absence of the SnC_3 symmetric stretching frequency in the KBr region is taken as evidence of planarity of the trimethyltin unit in an equatorial geometry[259,293].

3. *Six-coordinated molecular structures*

The ability of tin to form six-coordinated complexes was recognized early on, and the structures of the hexachlorostannate anions in the ammonium, potassium, rubidium, cesium and thallous salts were determined by X-ray studies in 1933, the tin–chlorine distances reported as 2.41, 2.45, 2.42, 2.43 and 2.39 Å, respectively, in the octahedral complexes[176]. The more recent structure of benzaldeminium hexachlorostannate shows three tin–chlorine distances at 2.42, 2.50 and 2.54 Å in the somewhat distorted tin octahedron[235]. The hexafluorostannate dianion is also somewhat distorted in Na_2SnF_6[210]. Recent vibrational and Mössbauer studies of the dichloryl hexachloro- and hexafluorostannates indicate significant departures from octahedral symmetry at tin[154], however, and suggest these compounds as prominent candidates for structural study. X-ray powder data has been recorded for the hexahydroxystannate(IV) anion with various cations[291]. The structures of 2,2′-bipyridyltetrafluorosilicon, -germanium and -tin are distorted *cis*-octahedral, as expected[114].

Various Lewis base adducts of tin(IV) chloride have likewise been known since the nineteenth century, although the mole ratios of the components have in some cases been in doubt until relatively recently[121]. The question of *cis–trans* isomerism in these structures is of immediate interest, but the choice of configuration seems to depend upon subtle influences, and little in the way of simplifying principle is available to guide our discussion. We will proceed from six-coordinated complexes of tin(IV) chloride to those containing organic substituents.

The structures of tin(IV) chloride adducts with three oxygen-containing ligand molecules are known, $OSeCl_2$[211], $OPCl_3$[144] and $OS(CH_3)_2$[203], with the ligands occupying *cis*-positions in each case. Full accounts have appeared for only the first two, and the structure of the phosphorus oxychloride adduct was solved on the basis of limited data. The first two structures show strikingly similar arrangements of bond angles about tin, with the tin–chlorine distance in the oxyselenium complex somewhat longer than in the corresponding phosphorus case. In both examples, there is an increase in distance in going from tin(IV) chloride (2.28 Å from a recent gas phase electron diffraction study[184] which supercedes previous reports [145,240,265]), but the distances reported for the phosphorus case are shorter (2.31–2.36 Å)[144] than for the selenium (2.36 and 2.41 Å)[211] which corresponds much more closely to those in the hexachlorostannate anion. In both the adducts the acute angles at tin involving oxygen are less than 90° while those involving only chlorine are greater than 90°.

In contrast with the *cis*-structures discussed above, tetrachlorobis(tetrahydrothiophen)-tin(IV) is *trans* in the solid state as estimated from preliminary X-ray data and supported by vibrational analysis, but not by the high solution dipole moment (4 Debye)[122]. Tetrachlorodipyridinetin(IV) is *trans* as well (the tetrabromo analogue is isomorphous) on the basis of two-dimensional analysis[123].

Tetrachlorotin(IV) bis-acetonitrile is, on the other hand, *cis*[304] as is the tin(IV) chloride adduct of glutaronitrile in which the bifunctional $N{\equiv}C{-}(CH_2)_3{-}C{\equiv}N$ ligand binds two different tin atoms[120]. Here again the acute angles at tin involving only chlorine are larger than 90° while those involving nitrogen are smaller than 90°. The tin–chlorine distances (2.34–2.36 Å) are greater than in tin(IV) chloride.

A new dimension is introduced in the structures of the dichlorophthalocyanato- and -porphinatotin(IV) complexes in which the chlorine groups are necessarily *trans*. Here the structural features are determined by the size of the tin atom with relation to the size of the central hole created by the nitrogen atoms of the macrocycle. It is well known that if the metal–pyrrole nitrogen internuclear distance is larger than the hole would allow, the metal atom will be forced out of the plane of the macrocycle, and the ring may show considerable ruffling[202,215]. The molecular dimensions of such systems may be varied by substituting macrocycles such as octaethylporphyrin in which the central hole formed by the four pyrrole groups is somewhat larger (nitrogen–nitrogen internuclear distances 4.21 and 4.16 Å across the center)[166] for the phthalocyanine ligand (4.10 Å across the center)[276], or by substituting the smaller Sn^{IV} for Sn^{II}. In the examples which have recently become available in the form of preliminary communications, the tin atom lies in the plane of the tetraphenylporphine[160] and octaethylporphyrin macrocycles in which the maximum deviation from the plane is only 0.02 Å[166], but causes severe crumpling of the phthalocyanine ligand. In the last complex the macrocycle suffers a stepped deformation as shown in Fig. 25 where the most severe offset, Δ, is 0.76 Å, and the atoms in each unit are coplanar to ± 0.04 Å (the perpendicular offset, Δ′, is 0.36 Å with coplanarity ± 0.01 Å). The regular SnN_4Cl_2 square bipyramid is substantially tilted with respect to the general plane, as shown in the Figure, with the isoindole groups hinged about the bonds joining the bridging atoms in the ring structure. The molecule is thus curled like two half-saucers, centrosymmetrically related[276]. Internuclear distances and angles for these two tin(IV) structures are shown in Figs. 26 and 27.

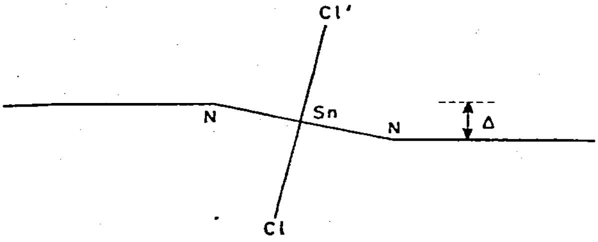

Fig. 25. The stepped deformation of the isoindole units in dichlorophthalocyaninatotin(IV).

The situation is very different in tin(II) phthalocyanine where the tin atom lies 1.11 Å above the plane formed by the four isoindole nitrogen atoms, with tin–nitrogen internuclear distances in the range 2.24–2.27 Å. The phthalocyanine is significantly non-planar, being deformed into a saucer-shape. There are no other atoms bonded to tin, whose environment is not square planar, but more like that found in the tetragonal form of tin(II) oxide[249]. The tin atom would have to be smaller in diameter by half an ångstrom unit to lie in the ring plane. About 3.4 Å above each tin phthalocyanine molecule lie the phthalocyanine moieties of two neighboring molecules which are approximately coplanar and nearly parallel to the reference molecule. They provide the four nearest non-bonded neighbors to the tin atom, comprising three symmetrically disposed hydrogen atoms at about 3.3 Å and one azamethine nitrogen atom at 3.79 Å. The resulting cavity above the tin(II) atom is ideally suited to the accommodation of a lone pair of electrons if these were directed along the four-fold axis of the SnN_4-core. Thus the tin(II) structure can be considered as square pyramidal with four bonding pairs and one non-bonding electron pair[183].

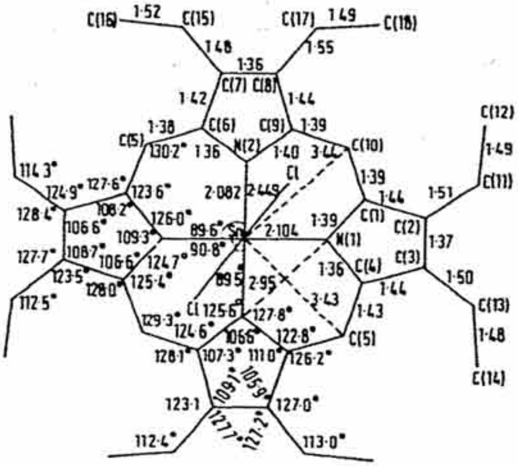

Fig. 26. The dichlorooctaethylporphinatotin(IV) molecule.

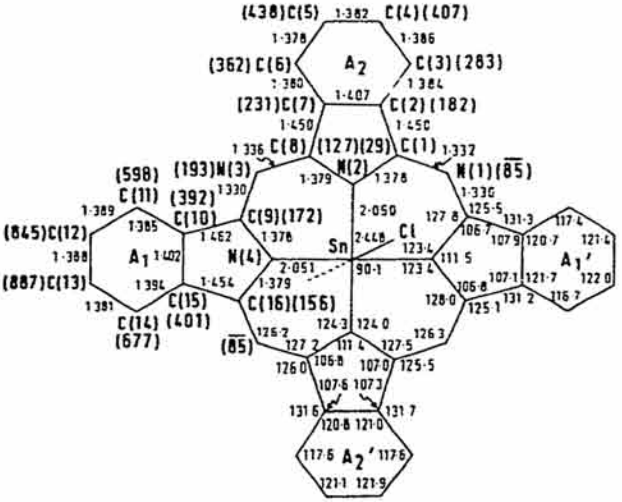

Fig. 27. The dichlorophthalocyaninatotin(IV) molecule.

Proceeding to dialkyltin complexes, the question of the arrangement of the C_2Sn skeleton assumes primary importance. While beyond the scope of this review, a large amount of information concerning the presence of linear (*trans-*) dimethyltin systems is known from infrared spectra in the KBr region, where the symmetric and asymmetric dimethyltin stretching frequencies make their appearence. The absence of the symmetric stretching absorbance is usually taken as evidence of linearity[259,293]. Our discussion will be confined to X-ray crystal data.

Two structures have been determined in which dimethyltin dichloride forms complexes with the oxygen ligands dimethylsulfoxide (DMSO)[70-71] and pyridine *N*-oxide[18]. In both structures the dimethyltin group is *trans*-, with a C–Sn–C angle of 170° in the former[70-71] which is rather imprecise in the methyltin result (no corresponding angle is listed for the pyridine *N*-oxide adduct[18]). The $SnCl_2$ and SnO_2 units are *cis* in the first, but *trans* in the second molecule, with the tin–chlorine distances in all cases longer (2.48–2.58 Å) than in the tin(IV) chloride adducts discussed above. The tin–oxygen distances in the DMSO complex are also longer (2.35 *vs.* 2.10–2.17 Å) than in the tin(IV) chloride analogue[203]. The structures of the complexes are shown in Figs. 28 and 29.

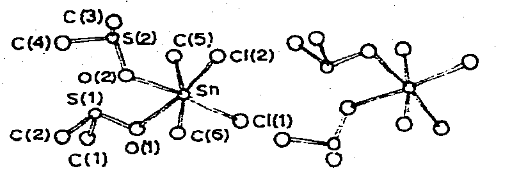

Fig. 28. The packing of *cis*-dichloro-*cis*-bis(dimethylsulfoxide)-*trans*-dimethyltin(IV) viewed along the c-axis.

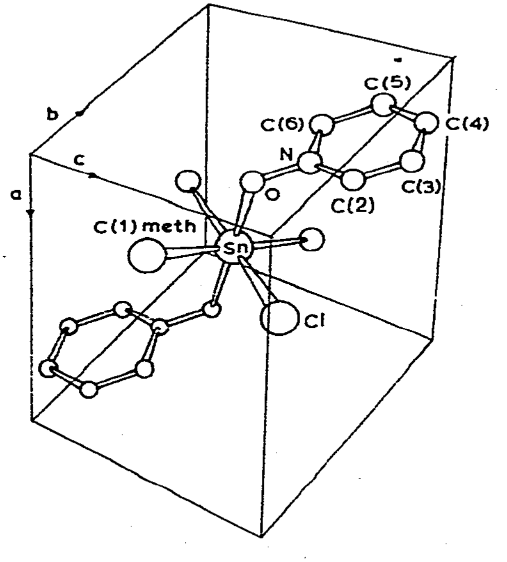

Fig. 29. Perspective view of *trans*-dichlorodimethylbis(pyridine *N*-oxide)tin(IV) with the triclinic unit cell outlined. The view is almost normal to the plane of the atoms Cl, C(1)(methyl) and O.

The related dimethyl bis(8-hydroxyquinolinate) assumes a structure with a *cis*-dimethyltin group (110.7°) as shown in Fig. 30 in which the oxygen atoms are *trans* (the O–Sn–O angle is not listed) and the nitrogen atoms are *cis* (the N–Sn–N angle = 75.8°)[92]. The nearly tetrahedral dimethyltin grouping has tin–carbon internuclear distances which are the same as those observed for the tetrahedral tin compounds, $(CH_3)_nSnX_{4-n}$ and CH_3SnH_3. The bonding of the oxinate ligand to tin resembles that for the corresponding uranium complex in that the tin–oxygen distances are shorter (by 0.25 Å) than the tin–nitrogen. For copper, zinc and palladium they are equal. The bond angles in the distorted $(CH_3)_2Sn(C_9H_6NO)_2$ range from 73.4 to 110.7°[92].

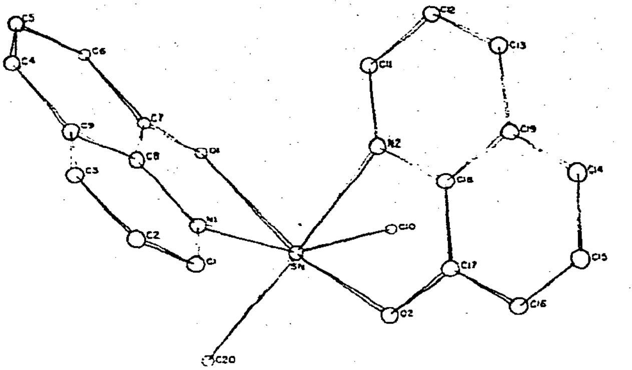

Fig. 30. Perspective view of *cis*-dimethyltin bis(8-hydroxyquinolinate), $(CH_3)_2Sn(C_9H_6NO)_2$.

Another chelated structure, this time containing an asymmetric carbon atom (the one attached to tin) in each ring, is provided by bis(1,2-diethoxycarbonylethyl)tin dibromide. The synthesis from diethyl bromosuccinate and tin metal produces two distinct isomers which crystallize separately, the high-melting (122–123°) isomer containing molecules of C_2 symmetry in which both puckered chelate rings are in either the *d*- or *l*- form at each tin atom, and the low-melting (114–115°) isomer which contains one *d*- and one *l*- form chelate ring at each tin atom. A representation of the molecular structure of the low m.p. isomer is presented in Fig. 31. In both isomers the carbon atoms are *trans* (the C–Sn–C angle = 148°[78,109]), while the bromine [the Br–Sn–Br angle = 99° (low m.p.)[109] and 101° (high m.p.)[78]] and oxygen atoms [the O–Sn–O angle = 78° (low m.p.)[109] and 79° (high

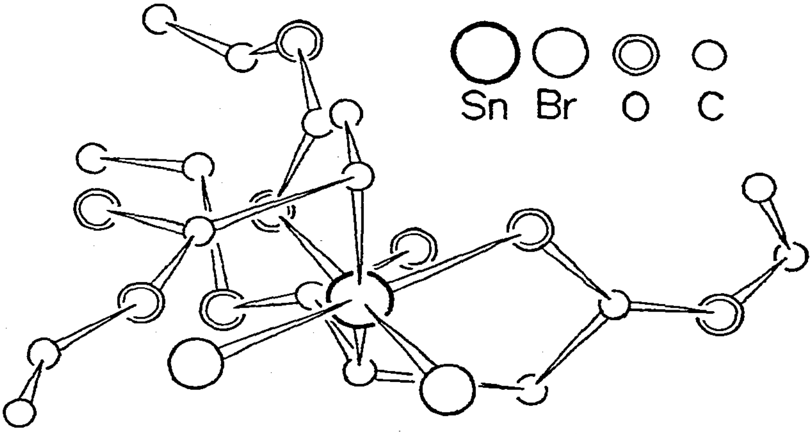

Fig. 31. The low melting point isomer of bis(1,2-diethoxycarbonylethyl)tin dibromide.

m.p.)[78]] are *cis*. In neither case are the crystals optically active, since there are equal numbers of *d*- and *l*- form antipodes in each unit cell which holds four molecules. The molecules are, as expected, found to be more densely packed in the high m.p. isomer.

As mentioned above in Section II.D.2, the terpyridyl adduct of dimethyltin dichloride crystallizes as a double salt, $[(CH_3)_2SnCl\cdot terpy]^+ [(CH_3)_2SnCl_3]^-$, containing a five-coordinated, trigonal bipyramidal anion with equatorial methyl groups, already discussed, and a six-coordinated, octahedral cation. The dimethyltin group in the cation is *trans* (the C–Sn–C angle = 159°), 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 system methyl, methyl, chlorine and nitrogen constitutes a flattened tetrahedron surrounding the tin atom. Two other types of distortion are worth noting, the bending of the methyl groups away from the terpyridyl ligand increases the N–Sn–C angles to a mean value of 98°, and the combination of a relatively large tin radius and the rigidity of the terpyridyl group requires that the N–Sn–N angles become decreased to an average value of 71°[47-48].

Reviewing the six-coordinated tin(IV) structures available at this time shows each to be octahedral, and distorted in ways which are understandable on the basis of isovalent hybridization[133] or valence shell electron repulsion[193] arguments. In addition there seems to be a tendency for *cis*-coordination of organic ligands when this arrangement is stereochemically possible. This is the case when the ligand in question is "pointed," *i.e.,* when the donor atom attached to tin holds only a single group. This feature distinguishes the pointed acetonitrile, dimethylsulfoxide, and phosphorus and selenium oxychloride ligands, all of which form *cis*-complexes with tin(IV) chloride, from tetrahydrothiophene or the methyl group in which the atom attached to tin itself holds more than one other atom. Such groups as these occupy *trans* positions. In the dimethyl bis(8-hydroxyquinolinate) complex the oxygen and nitrogen atoms are constrained by the chelate ring structure, and this allows the methyl groups to assume the apparently preferred *cis*-configuration. Similar conclusions have been reached from the application of a semi-quantitative stereochemical model to octahedral tin complexes[314]

4. *Seven-coordinated molecular structures*

Anhydrous methyltin trinitrate crystallizes with three chelating nitrate groups forming a pentagonal bipyramid about tin as shown in Fig. 32. In each nitrate group one oxygen distance to tin is longer by an average of 0.16 Å. The C–Sn–O axis of the pentagonal bipyramid is far from linear at 159°, but two of the nitrate groups are virtually coplanar (7° twist), with the third approximately normal to them[26]. Chelating nitrate groups are also found in the structures of dimethyltin dinitrate where the bidentate ligands are unsymmetrical by 0.4 Å (on the basis of an unrefined X-ray analysis)[213] and in tin(IV) tetranitrate[188] which will be discussed in Section II.D.5 where the ligands are symmetrical.

The tropolonate ion, $C_7H_5O_2^-$, by reason of its relatively small "bite" as a bidentate ligand (the corresponding bite of the nitrate ion, 2.14 Å, is also very small) is especially well adapted to the formation of stable complexes that utilize coordination numbers greater than six[248], and the structures of the crystalline solvates of tris(tropolonato)monochloro- and -monohydroxotin(IV) have been reported[261]. The two molecules are isodimensional

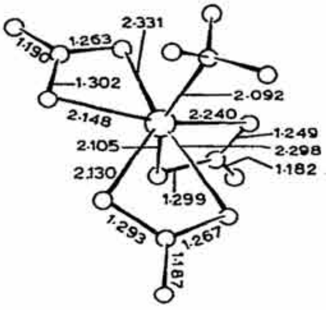

Fig. 32. The anhydrous methyltin trinitrate molecule.

and isostructural in being derived from pentagonal bipyramids as shown in Figs. 33 and 34 in which the six tropolonato oxygen atoms and the monodentate substituent X(= Cl or OH) coordinate to tin to give C_s symmetry. The axial bond to oxygen (2.05–2.06 Å) is ca. 0.10 Å shorter than the average for the five equatorial bonds, and the Sn–X and Sn–O axial bonds

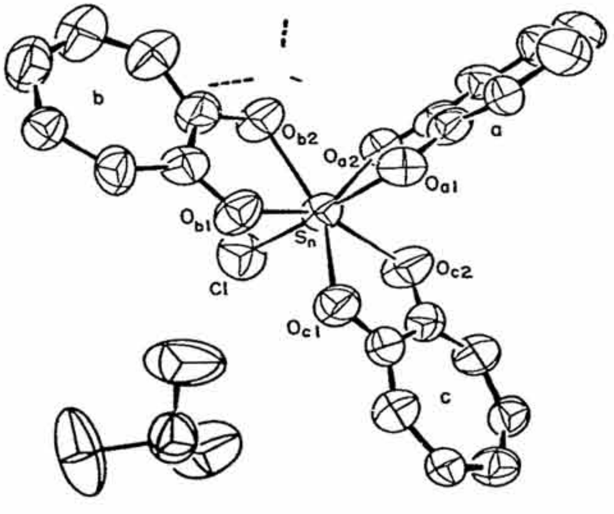

Fig. 33. Perspective views of the tris(tropolonato)monochlorotin(IV) and chloroform molecules. The dotted lines indicate the relative positioning in the crystal of the cloroform molecule that lies nearest to a molecule of complex.

are rotated off the quasi five-fold axis through small angles (7.3° and 9.0° for X = Cl and OH and 3.0° for both, respectively). This distortion, and the observed positioning of the tropolonato groups away from the ideal pentagonal bipyramidal geometry, takes the molecules halfway to that demanded by the dodecahedral geometry of the theoretically expected[216], but as yet unknown, eight-coordinated tetrakis(tropolonato)tin(IV) system. Each of the crystals discussed above is a solvate: $(C_7H_5O_2)_3SnCl{\cdot}CH_3Cl$ and $(C_7H_5O_2)_3$-$SnOH{\cdot}(3-2x)H_2O{\cdot}xCH_3OH$ (x = ca. 1/2)[261].

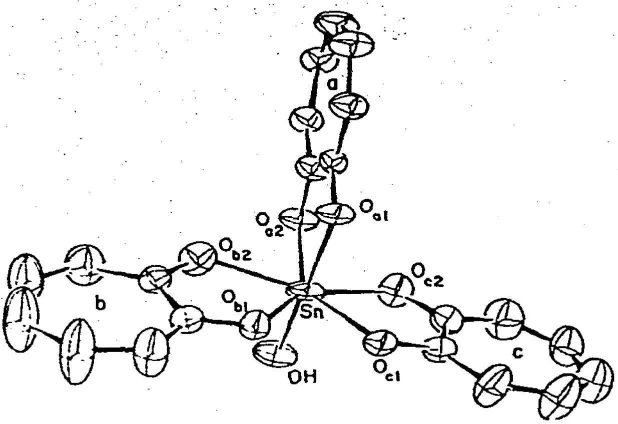

Fig. 34. Perspective view of the tris(tropolonato)monohydroxytin(IV) molecule (reduced in scale by *ca.* 15% from previous Figure).

Ethylenediaminetetraacetic acid forms a 1/1 complex with tin of the formula $Sn(OH_2)$-EDTA* whose seven-coordinated structure is shown in Fig. 35[272]. An approximate C_2 axis passes through the OH_2 ligand, the tin atom, and the C–C bond of the ethylenediamine moiety at its midpoint. Chelation of tin by EDTA results in the formation of five five-membered rings, four of the glycinate type and one based on the ethylenediamine fragment.

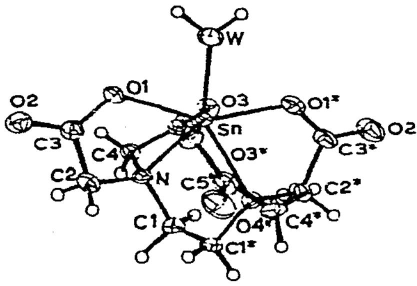

Fig. 35. The tin(IV) ethylenediaminetetraacetate monohydrate molecule.

All show the significant deviations from planarity, typical of hexadentate, seven-coordinated complexes of EDTA. The coordination polyhedron about tin is drawn in Fig. 36. A description of this figure in terms of the more symmetrical geometries for seven-coordination (pentagonal bipyramidal or capped trigonal prism) seems unprofitable[272].

The analogous tin(II) $Sn_2EDTA \cdot 2H_2O$ structure[273] shown in Fig. 37 is generated by replacing the coordinated water molecule in $Sn^{IV}(OH_2)EDTA$ by the lone pair of electrons in the Sn^{II} oxidation state, and by expanding the bond distances to accommodate the larger radius of this tin atom. The resulting structure of the distannous ethylenediaminetetraacetate dihydrate has different environments about each tin and water molecule, and may be formulated as $Sn^{II}[Sn^{II}EDTA \cdot H_2O] \cdot H_2O$. The geometry of the inner coordination sphere about tin in the hexadentate ψ seven-coordinated SnEDTA

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* EDTA = ethylenediamine-*N*,*N*,*N'*,*N'*-tetraacetate.

moiety, which exhibits approximate C_2 symmetry, is a distorted pentagonal bipyramid where the ethylenediamine nitrogen atoms and the tin(II) lone pair electrons occupy equatorial positions. The remaining sites are taken by an oxygen atom from each of the four carboxylate substituents as shown in Fig. 38. Each SnEDTA unit is bonded to four Sn^{II} atoms of the second type via carboxylate oxygen atoms. ψ-Octacoordination about this tin atom is completed through longer bonds with three additional oxygen atoms. In this case the lone pair of electrons occupies the eighth coordination site with the overall configuration viewed as built up from two interlocking tetrahedra, one elongated and one flattened. The two water molecules which are hydrogen bonded to each other but not to tin are held in the lattice in different ways: the first is linked to two adjacent SnEDTA moieties through hydrogen bonds with two carboxylate oxygen atoms, but the second is

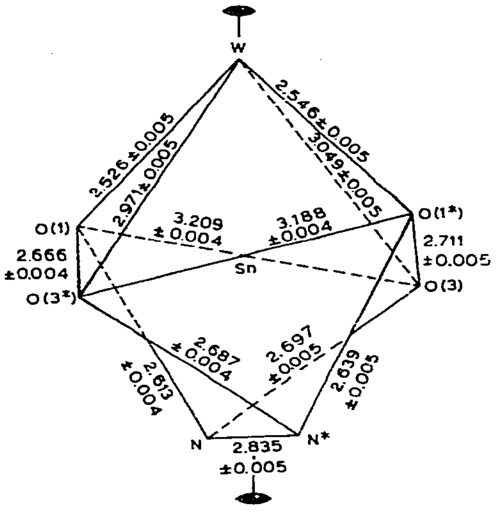


Fig. 36. The coordination polyhedron about tin in the tin(IV)ethylenediaminetetraacetate monohydrate molecule.

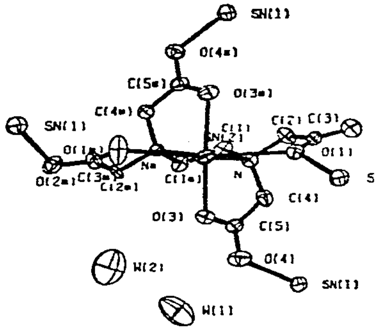


Fig. 37. Ditin(II) ethylenediaminetetraacetate dihydrate viewed along the approximate C_2 axis.

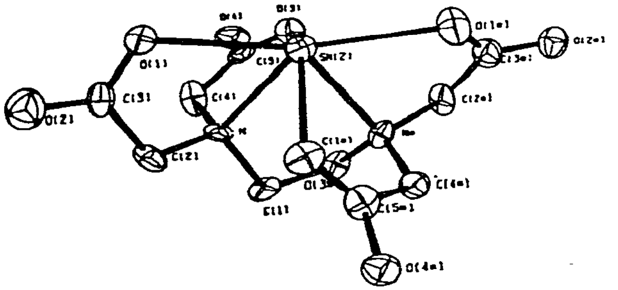


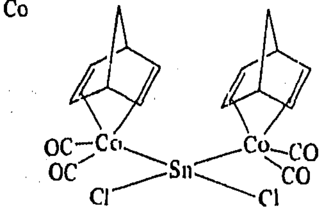
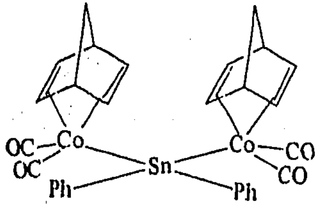
Fig. 38. The tin(II) ethylenediaminetetraacetate moiety in ditin(II) ethylenediaminetetraacetate dihydrate.

(text continued on p. 43)

TABLE I

Bond Lengths in Organotin Transition Metal Compounds[a]

Compound	$d(Sn\text{-}M)^b$(Å)	$d(Sn\text{-}C)^c$(Å)	$d(Sn\text{-}X)^d$(Å)	*Reference*
Tetra-coordinated tin				
M = Mn				
$Ph_3SnMn(CO)_4PPh_3$	2.627(10)	C = Ph, mean 2.17(4)		28
$Me_3SnMn(CO)_5$	2.674(2)	C = CH_3, 2.058(15) 2.162(15) 2.170(16)		32
$Ph_3SnMn(CO)_5$	mean 2.674(4)	C = Ph, mean 2.154(14)		105
$Ph_2Sn[Mn(CO)_5]_2$	mean 2.70(1)	*e*		77
$Ph_2Sn[Mn(CO)_5][Co(CO)_4]$	2.73(1)	C = Ph, mean 2.18(4)		14
$ClSn[Mn(CO)_5]_3$	mean 2.737		X = Cl, 2.429(8) 2.434(8)	294
M = Fe				
$Br_3SnFe(CO)_2(\pi\text{-}C_5H_5)$	2.462(2)		X = Br, mean 2.501(2)	246
$Cl_3SnFe(CO)_2(\pi\text{-}C_5H_5)$	2.467(2)		X = Cl, 2.350(2) 2.358(2) 2.373(2)	197
$PhCl_2SnFe(CO)_2(\pi\text{-}C_5H_5)$	2.467(2)	C = Ph, 2.126(13)	X = Cl, 2.383(3) 2.386(4)	65
$Ph_2ClSnFe(CO)_2(\pi\text{-}C_5H_5)$	2.504(3)	*e*		65
$Ph_3SnFe(CO)_2(\pi\text{-}C_5H_5)$	mean 2.536(3)	C = Ph, mean 2.134(15)		29
$Me_3SnFe(CO)(\pi\text{-}C_5H_5)(f_6\,fos)^f$	2.562(4) corrected 2.568(4)	C = Me, 2.11(3) 2.15(3) 2.15(3)		49

M = Fe				
$Cl_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2.492(8)		X = Cl, 2.43(1)	256
$(PhOSO)_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2.490(10) 2.507(10)		X = O, e	148
$(ONO)_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2.563(5)		X = O, 2.14(2)	15
$(\sigma\text{-}C_5H_5)_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2.568(3) 2.573(3)	C = C_5H_5, 2.17(2) 2.18(2)		17
$[(\pi\text{-}C_5H_5)(CO)_3Mo]ClSn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	2.583(7) 2.598(7)		X = Cl, 2.50(1)	255
$Me_2Sn[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	mean 2.605(4)	C = Me, mean 2.18(2)		15
M = Fe				
$Sn[Fe(CO)_4]_4$	mean 2.54			236
$Me_2Sn[Fe(CO)_4]_2Sn[Fe(CO)_4]_2SnMe_2$	terminal, mean 2.625(8) central, mean 2.747(8)	C = Me, 2.18(5) 2.19(5) 2.20(5) 2.31(5)		97
M = Co				
	2.498(1) 2.499(1)		X = Cl, 2.410(2) 2.412(2)	23
	2.566(3) 2.575(3)	C = Ph, 2.139(20) 2.190(17)		23
$ClSn[Co(CO)_4]_3$	2.58(1) 2.59(1) 2.62(1)		X = Cl, 2.54(1)	137
$[Mn(CO)_5]Ph_2Sn[Co(CO)_4]$	2.66(1)	C = Ph, mean 2.18(4)		14

(*to be continued*)

TABLE 1—*continued*

Compound	*d(Sn-M)*[b]*(A)*	*d(Sn-C)*[c]*(A)*	*d(Sn-X)*[d]*(A)*	*Reference*
M = Mo				
$[(\pi\text{-}C_5H_5)(CO)_2Fe]_2ClSn[Mo(CO)_3(\pi\text{-}C_5H_5)]$	2.891(5)		X = Cl, 2.50(1)	255
M = Ru				
$Cl_3SnRu_2Cl_3(CO)_5$	2.565(4)		X = Cl, mean 2.35	174
$[Me_3Sn(CO)_3RuSnMe_2]_2$	terminal *trans* to Me_2Sn, 2.686(2) $(RuSn)_2$ ring, *trans* to CO, 2.638(2) *trans* to Me_3Sn, 2.694(2)	C = Me, mean 2.16(1)		103
M = Pd				
$[(\pi\text{-}C_3H_5)(PPh_3)PdSnCl_3]\cdot 0.40Me_2CO$	2.563(1)		X = Cl, 2.370(4) 2.376(4) 2.399(3)	243
M = Ir				
$(C_8H_{12})_2IrSnCl_3$	2.642(2)		X = Cl, 2.384(10) 2.395(8) 2.406(12)	268
M = Pt				
$[Ph_3PMe]_3[Pt(SnCl_3)_5]$	mean 2.54		X = Cl,[e]	165
Penta-coordinated tin				
M = Fe				
$[(Ph)(OH)(OSOPh)SnFe(CO)_2(\pi\text{-}C_5H_5)]_2$	2.499(1)	C = Ph, 2.146(3)	X = OSOPh, 2.206(2) X = OH, in $[Sn\text{-}O(H)]_2$, 2.054(2) 2.231(2)	87
M = Mo				
$(C_{10}H_8N_2)(CO)_3MoClSnMeCl_2$	2.753(3)	C = Me, 2.12(2)	X = Cl, 2.358(6) 2.433(5) bridged Cl, 2.805(4)	51
M = W				
$(C_4H_{10}S_2)(CO)_3WClSnMeCl_2$	2.759(3)	C = Me, 2.12(5)	X = Cl, 2.379(12) 2.387(9) bridged Cl, 2.958(10)	52

Hexa-coordinated tin			
M = Pt			
$(C_8H_{12})_3Pt_3(SnCl_3)_2$	mean 2.80(1)	X = Cl, mean 2.39(2)	199
The $SnCl_3^-$ ion			
M = Co			
Red$[Co(PPh_2CH_2CH_2PPh_2)_2Cl][SnCl_3]$	non-bonded	X = Cl, 2.440(4) 2.445(3) 2.447(2)	286
Green$[Co(PPh_2CH_2CH_2PPh_2)_2Cl][SnCl_3]\cdot C_6H_5Cl$	non-bonded	X = Cl, 2.425(8) 2.429(8) 2.438(11)	286

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[a] Inorganic tin transition metal compounds are included where applicable.

[b] M is a transition metal and is defined individually.

[c] C represents an organic group and is defined individually.

[d] X is defined individually.

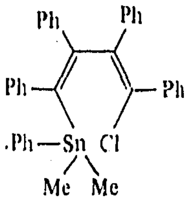
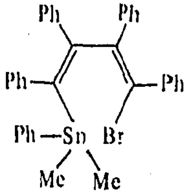
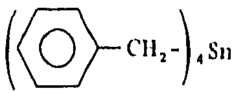
[e] Not given.

[f] $(f_6fos) \equiv (PPh_2)\overline{C{=}C(PPh_2)(CF_2)_2C}F_2$

TABLE 2

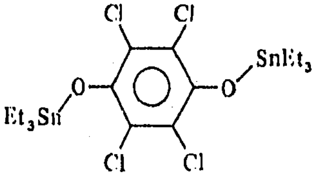
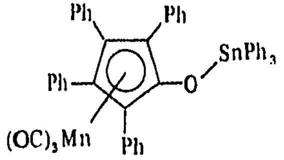
Bond Lengths of Tetra-coordinated Organotin Compounds[a]

Compound	*d(Sn–C)*[b]*(A)*	*d(Sn–X)*[c]*(A)*	*Reference*
Gas phase			
MeSnH$_3$[d]	2.143(2)	X = H, 1.700(15)	80
H$_3$SnCl		X = H, 1.70[e]	234
		X = Cl, 2.327(1)	
H$_3$SnBr		X = H, 1.76(7)[f]	309
		X = Br, 2.4691(3)	
H$_3$SnI		X = H, [g]	310
		X = I, 2.674(2)	
Me$_4$Sn	2.18(3)		25
	2.134(7)		59
Me$_3$SnCl	2.19(3)	X = Cl, 2.37(3)	96
	2.106(6)	X = Cl, 2.351(7)	244
Me$_2$SnCl$_2$	[g]	X = Cl, 2.34(3)	96
	2.108(7)	X = Cl, 2.327(3)	59
MeSnCl$_3$	2.19(5)	X = Cl, 2.32(3)	96
	2.104(16)	X = Cl, 2.304(3)	244
SnCl$_4$		X = Cl, 2.281(4)	184
		X = Cl, 2.29(2)	145
		X = Cl, 2.30(2)	265
		X = Cl, 2.31(1)	240
		X = Cl, 2.33(5)	307
Me$_3$SnBr	2.17(5)	X = Br, 2.49(3)	96
Me$_2$SnBr$_2$	~2.17	X = Br, 2.48(2)	96
MeSnBr$_3$	~2.17	X = Br, 2.45(2)	96
SnBr$_4$		X = Br, 2.44(2)	238
Me$_3$SnI	~2.17	X = I, 2.72(3)	96
Me$_2$SnI$_2$	[g]	X = I, 2.69(3)	96
MeSnI$_3$	[g]	X = I, 2.68(2)	96

SnI_4		X = I, 2.64(4)	238
$(Me_3Sn)_2O$	2.170(5)	X = O, 1.940(1)	102
$Sn(NMe_2)_4$		X = N, 2.045	302
Solid state			
	C = Ph, 2.116(9) C = Vinyl, 2.148(8) C = Me, 2.154(10) 2.180(11)	X = Cl, non-bonded 4.284(3)	21
	C = Ph, 2.141(13) C = Vinyl, 2.156(12) C = Me, 2.165(13) 2.188(15)	X = Br, non-bonded 4.346(2)	21
	C = benzyl, mean 2.18(1)		44
Ph_4Sn	C = Ph, 2.07, 2.08		63
	C = Ph, mean 2.14		35
	C = Ph, 2.14		2
Ph_3SnCl	C = Ph, 2.122(22)	X = Cl, 2.318(15)	24
Ph_2SnCl_2 molecule one	C = Ph, 2.105(5) 2.119(5)	X = Cl, 2.336(2) 2.353(2)	66
molecule two	C = Ph, 2.112(6) 2.118(5)	X = Cl, 2.336(2) 2.357(2) non-bonded Cl, 3.77	

(*to be continued*)

TABLE 2–*continued*

Compound	*d(Sn–C)*[b]*(Å)*	*d(Sn–X)*[c]*(Å)*	*Reference*
$Ph_2ISn(CH_2)_4SnIPh_2$	$C = -\overset{\vert}{C}H_2$, 2.14(2) C = Ph, 2.14(2) 2.16(2)	X = I, 2.729(2)	42
	C = Et, 2.15(6) 2.17(6) 2.21(6)	X = O, 2.08(6)	107
	C = Ph, 2.087(14) 2.134(14) 2.170(15)	X = O, 2.010(9)	30
$(MeSn)_4S_6$	C = Me, 2.1	X = S, 2.35	45
$(Ph_2SnS)_3$	C = Ph, mean 2.24(6)	X = S, mean 2.42(2)	93
$Na_4Sn_2S_6 \cdot 14H_2O$		X = S, 2.380	233
$(Ph_2Sn)_6 \cdot 2m$-xylene		X–Sn, 2.77 2.78 2.78	86

[a] Inorganic tin compounds are included where applicable.
[b] C = Me for gas phase structures; C is specified individually for solid state structures.
[c] X is defined individually.
[d] $MeSnH_3$ decomposes in the copper wave guide.
[e] Sn–H bond length is calculated assuming all angles to be tetrahedral.
[f] Sn–H bond length is found to be 1.46 Å, assuming all angles to be tetrahedral.
[g] Not given.

only hydrogen bonded to one SnEDTA unit via one oxygen atom. The SnEDTA moiety in this structure does not correspond to a sensibly discrete, doubly charged anion in view of its strong linking to the second tin. The configuration at this second tin atom as shown in Fig. 39 is highly irregular and appears to stem from the constraints imposed by its role as a bridging agent between four different SnEDTA units, while not identified with any particular one[273]. This structure was included in this Section because of its relation to that of Sn(OH$_2$)EDTA, although it is properly classed as an associated lattice.

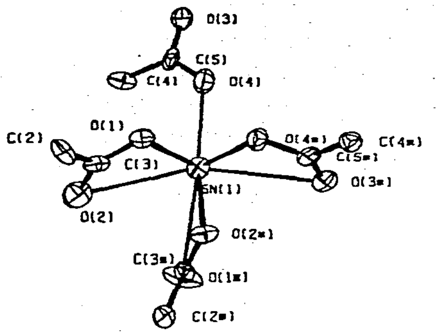


Fig. 39. The coordination about Sn(1) in ditin(II) ethylenediaminetetraacetate dihydrate.

5. *Eight-coordinated molecular structures*

Discounting the structure of distannous ethylenediamine dihydrate in which one of the tin(II) atoms can be viewed as eight coordinate by including the lone pair of electrons available in this oxidation state as occupying one vertex of the coordination polyhedron, there are two true members of this class, one in which the tin(IV) atom is surrounded by nitrogen atoms, and the second is tin(IV) nitrate[188] whose structure is shown in Fig. 40 where the dodecahedral arrangement of oxygen atoms about the tin atom approximates to D_{2d} symmetry. There is some distortion of one of the nitrato groups, probably arising from repulsions from neighboring molecules in the crystal, but in general the nitrato groups are equivalent, each being symmetrically bidentate to the tin atom. All available

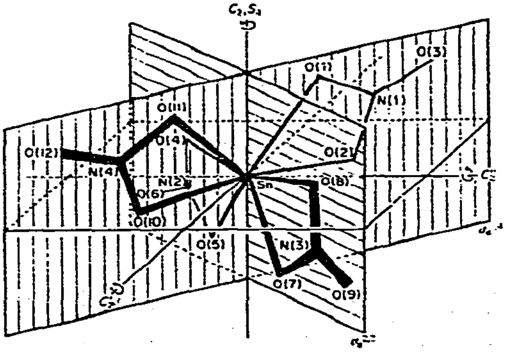


Fig. 40. The tin(IV) nitrate molecule, Sn(NO$_3$)$_4$, showing elements of symmetry.

space is occupied, and the pairs of oxygen atoms are held closer together (2.13 Å) than their Van der Waals radii would normally permit (ca. 2.8 Å). This gives rise to the suggestion that the structure be viewed as essentially a distorted tetrahedral coordination by four nitrato groups, two oxygen atoms of each occupying one coordination site[188].

The second eight-coordinated structure at tin is formed by bis(phthalocyaninato)tin(IV)[124], which like its uranium(IV) analogue[192] crystallizes in a bis-tetrapyrrole "sandwich" form in which the coordination at tin approximates a square antiprism (the deviation is ca.3°). The phthalocyanato ligand is saucer-shaped, with the four pyrrole nitrogens at the base of the saucer which curves away from the tin atom. The sp^2 orbitals of the nitrogen atoms are thus bent so as to be directed toward the tin atom. This leads to considerable deviation of the phthalocyanine system from its $4mm$ (C_{4v}) symmetry, especially since not all the pyrrole groups bend to the same degree.

6. *Miscellaneous structures*

We close this section with a description of a silyl-bridged boron–boron structure proposed to contain a localized three-center, two electron bridge[153]. The trimethylsilyl group in 1-bromo-μ-trimethylsilyl pentaborane-9 is linked in place of a bridging hydrogen atom to two basal boron atoms of the pentaborane-9 framework by means of a three-center, electron pair bond presumably involving a quasitetrahedral orbital on the silicon atom. Reaction of the lithium salt of the octahydropentaborate anion with fourth group compounds yields the unique pentaborane-9 derivatives μ-$(CH_3)_3MB_5H_8$ where M = Si, Ge, Sn or Pb, but not C[186]. The 1-bromo derivative was prepared by direct bromination of μ-$(CH_3)_3SiB_5H_8$ which is a liquid at room temperature. The structure as shown in Fig. 41 possesses C_s symmetry with the bromine, apical boron, silicon and one methyl group of the trimethylsilyl fragment lying on the mirror plane. The silicon atom is rendered five-coordinate by its connection (at 2.32 Å) to the two crystallographically equivalent basal boron atoms at a B–Si–B angle of only 42.6°. The three methyl groups at silicon are linked by two identical angles of 110. 8° and one of 106.1°[153]. We assume that the tin homologue possesses a similar structure.

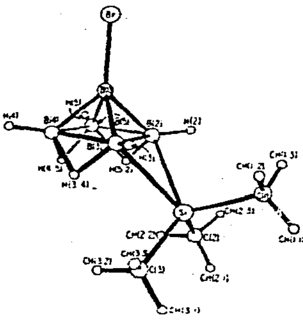


Fig. 41. The l-bromo-μ-trimethylsilylpentaborane-9 $(CH_3)_3SiB_5H_7Br$ molecule.

7. *Summary of section II.D*

Having considered the structures of a large number of higher coordinated inorganic and organotin complexes, we tabulate comparison data for various internuclear distances in Tables 1–3.

In attempting to summarize the data on higher coordinated complexes of tin we find in general little by way of overall principle or simple rule for predicting either which coordination number tin will take under any set of circumstances, or even which configuration a mixed set of ligands will adopt within any given coordination polyhedra. Each structure needs to be considered on its own merits, after reference to closely analogous systems.

Despite this we have in each instance attempted to delineate the generalizations which might apply to the systems discussed. A few summarizing statements of this kind now follow:

(i) The preferred equilibrium, solid-state structures for tin are trigonal bipyramidal for five-coordination, octahedral for six-coordination, pentagonal bipyramidal for seven-coordination, and dodecahedral for eight-coordination.

(ii) The observed angular distortions from perfect geometries are generally in the directions dictated by the isovalent hybridization[133] or valence shell electron repulsion[193] theories.

(iii) Electronegative atoms and groups tend to assume axial positions in the trigonal bipyramidal arrangements of the five-coordinated complexes.

(iv) Organic ligands tend to assume *cis*-configurations in the octahedral arrangements of the six-coordinated complexes if this is stereochemically feasible*.

(v) The tin(IV) compounds are no different in general structural features than derivatives of the other fourth group elements below carbon, except that the detailed geometry and isomeric form which depend on subtle steric interactions will change with the size of the central atom.

(vi) The success of semiquantitative models based upon intramolecular non-bonded interactions[314] suggests that the equilibrium geometry in the solid-state is predominantly controlled by the ligand repulsive energies, and that the energy necessary to distort the molecules from ideal geometries is very small.

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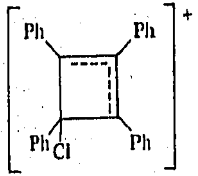
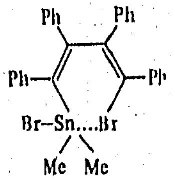
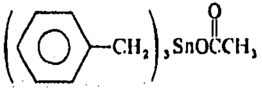
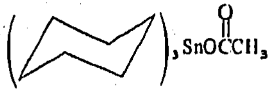
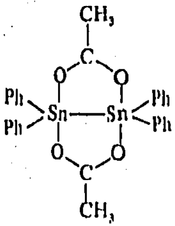
* Where the donor atoms themselves hold the organic substituents, the systems adopt *trans*-configurations to minimize the ligand–ligand repulsions; "pointed" ligands in which the donor atom is free of further substitution can take *cis*-positions. Methyl groups are usually forced *trans* except when the other ligands are part of chelate rings in which the bidentate portions have a small "bite".

(*text continued on p. 52*)

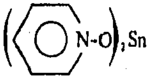
TABLE 3
Bond Lengths in Organotin Compounds with Coordination Higher Than four[a]

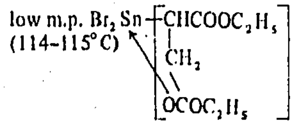
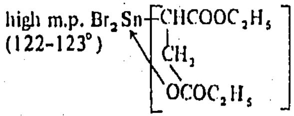
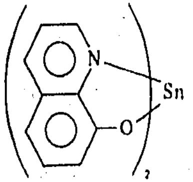
Compounds	*d(Sn-C)*[b](*Å*)	*d(Sn-X)*[c](*Å*)	*d(Sn-Y)*[d](*Å*)	*d(Sn-N)*[e](*Å*)	*Reference*
Five-coordinated tin					
Me_3SnF	C = Me, 2.1	X = F, 2.1 bridged 2.2-2.6			41
	f	X = F, 2.15 bridged 2.45			108
$Me_3SnCl \cdot py$	*f*	X = Cl, 2.42(4)		*f*	69
anion of $[Mo_3(\pi\text{-}C_5H_5)_3S_4]^+$ $[Me_3SnCl_2]^-$	C = Me, mean 2.12(1)	X = Cl, 2.572(4) 2.696(3)			101
anion of $[Me_2SnCl \cdot terpy]^+[Me_2SnCl_3]^-$	C = Me, 2.11(5) 2.12(4)	X = Cl, equatorial 2.32(1) axial 2.53(2) 2.55(2)			48
anion of  $[SnCl_5]^-$		X = Cl, equatorial 2.30 2.38 2.40 axial 2.37 2.39			146
	C = butadienyl, 2.206(21) C = Me, 2.150(22) 2.195(24)	X = Br, 2.504(5) coordinated, 3.774(5)			20
$Me_3SnNO_3 \cdot H_2O$	C = Me, mean 2.11(2)		Y = NO_3, 2.22(3) Y = OH_2, 2.47(2)		46

	C = benzyl, 2.15(3) 2.18(3) 2.18(3)		Y = O, 2.14(2) bridged 2.65(2)		3
	C = cyclohexyl, mean 2.19(3)		Y = O, 2.12(3) intra 2.95(4) inter 3.84		4
$[Me_3SiO(CH_3)_2SnOSn(CH_3)_2OSiMe_3]_2$			Y = O, $(SnO)_2$ ring in chain 2.2 cross chain 2.8		258
	C = Ph, mean 2.15(2) C = Sn, 2.69(1)		Y = O, 2.25(2) 2.25(2)		8
orthorhombic  $Me_3SnS\overset{S}{\overset{\Vert}{C}}NMe_2$ molecule one	C = Me, 2.18(4) 2.23(3) 2.24(3)		Y = S, 2.47(1) intra 3.16(1)		94
molecule two	C = Me, 2.14(3) 2.23(3) 2.26(4)		Y = S, 2.47(1) intra 3.33(1)		
monoclinic  $Me_3SnS\overset{S}{\overset{\Vert}{C}}NMe_2$	C = Me, 2.11(2) 2.23(2) 2.24(2)		Y = S, 2.47(1) intra 3.16(1)		95
 $Me_2ClSnS\overset{S}{\overset{\Vert}{C}}NMe_2$	C = Me, 2.17(5) 2.20(5)	X = Cl, 2.46(1)	Y = S, 2.48(1) 2.79(1)		60
Me_3SnNCS	C = Me, 2.10(5) 2.15(5) 2.15(6)		Y = S, inter 3.13(2)	2.15(6)	55
$(Me_3Sn)_2N_2C$	C = Me, mean 2.14(2)			2.47(1)	58

(to be continued)

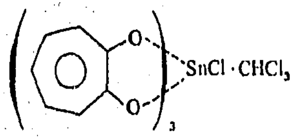
TABLE 3–*continued*

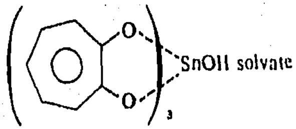
Compounds	*d(Sn-C)*^{b}*(Å)*	*d(Sn-X)*^{c}*(Å)*	d(Sn-Y)^d (Å)	*d(Sn-N)*^{e} *(Å)*	*Reference*
[(Me$_2$SnNCS)$_2$O]$_2$	C = Me, endocyclic (CN = 5) 2.15(3) exocyclic (CN = 6) 2.07(3)		Y = O (SnO)$_2$ ring 1.99(3) 2.15(4) (SnOSnN) ring 1.99(3) 2.05(5) Y = S inter 3.33(3)	2.06(4) (SnOSnN) ring 2.39(8) 2.84(4)	37
Me$_3$SnN(CN)$_2$	C = Me, 2.129(11) 2.130(8)			2.333(9) 2.338(9)	39
Me$_3$SnCN	C = Me, mean 2.16(3) C = CN, 2.49(2)			2.49(2)	90
Et$_3$SnCN	C = CN, 2.40				38
Six-coordinated tin					
Me$_2$SnF$_2$	C = Me, 2.08(1)	X = F bridged 2.12(1)			91
SnF$_4$		X = F, 1.88 bridged 2.02			217
Na$_2$SnF$_6$		X = F, 1.83 1.92 1.96			210
Me$_2$SnCl$_2$	C = Me, 2.16(18)	X = Cl, 2.41(4)			64
	C = Me, 2.21(8)	X = Cl, 2.40(4) bridged 3.54(5)			43
trans-Me$_2$-*cis*-Cl$_2$-*cis*-(DMSO)$_2$Sn	C = Me, 2.07(6) 2.08(5)	X = Cl, 2.48(1) 2.53(1)	Y = O, 2.32(3) 2.38(3)		71
trans-Me$_2$·*trans*-Cl$_2$·*trans*-$_2$Sn	C = Me, 2.225(25)	X = Cl, 2.584(10)	Y = O, 2.251(16)		18
cis-SnCl$_4$·2OSeCl$_2$		X = Cl, 2.360(7) 2.409(6)	Y = O, 2.121(16)		211
cis-SnCl$_4$·2OPCl$_3$		X = Cl, 2.31(2) 2.33(2) 2.36(2)	Y = O, 2.25(5) 2.30(4)		144

cis-$SnCl_4 \cdot 2NCCH_3$		X = Cl, 2.339(8) 2.341(7) 2.355(7) 2.356(7)		2.326(25) 2.336(23)	304
cis-$SnCl_4 \cdot NC(CH_2)_3CN$		X = Cl, 2.35(1)		2.29(2)	120
K_2SnCl_6		X = Cl, 2.45			177
$(NH_4)_2SnCl_6$		X = Cl, 2.41			177
Rb_2SnCl_6		X = Cl, 2.42			177
Cs_2SnCl_6		X = Cl, 2.43			177
Tl_2SnCl_6		X = Cl, 2.39			177
cation of $[Me_2SnCl \cdot terpy]^+ [Me_2SnCl_3]^-$	C = Me, 2.05(6) 2.09(5)	X = Cl, 2.65(2)		2.29(3) 2.33(4) 2.41(3)	48
 low m.p. Br_2Sn (114–115°C)	C = sub. ethyl, 2.26(5) 2.26(5)	X = Br, 2.516(6) 2.588(6)	Y = O, 2.44(3) 2.46(3)		109
 high m.p. Br_2Sn (122–123°)	C = sub. ethyl, 2.24(3)	X = Br, 2.504(5)	Y = O, 2.49(2)		78
$Me_2Sn(NO_3)_2$	*f*		Y = O, 2.11, 2.38 2.12, 2.65		213
$Me_2Sn(SO_3F)_2$	C = Me, 2.081		Y = O, 2.240 2.248		5
cis-Me_2-*cis*- 	C = Me, 2.15(2) 2.17(2)		Y = O, 2.10(1) 2.11(1)	2.31(1) 2.38(1)	92
 $Sn(\overset{S}{\overset{\|}{C}}NEt_2)_4$			Y = S, 2.504(7) 2.502(7) chelated 2.534(7), 2.557(7) 2.529(7), 2.554(7)		204

(*to be continued*)

TABLE 3–*continued*

Compounds	*d(Sn-C)*^{b} *(Å)*	*d(Sn-X)*^{c} *(Å)*	*d(Sn-Y)*^{d} *(Å)*	d(Sn-N)^e (Å)	*Reference*
$(SnCl_3OH{\cdot}H_2O)_2{\cdot}3C_4H_8O_2$		X = Cl, 2.29(2) 2.41(2) 2.42(2)	Y = O, 2.06(3) $(SnO)_2$ 2.05(3) 2.10(3)		141
$[(SnCl_3POCl_3)^+(PO_2Cl_2)^-]_2$		X = Cl, 2.317(9) 2.339(8) 2.346(8)	Y = O(PCl_3), 2.147(16) $(SnO_2PCl_2)_2$ ring 2.119(10) 2.120(12)		251
$Me_2Sn(NCS)_2$	C = Me, 2.14(3)		Y = S, bridged 3.21(1)	2.10(2)	36
	C = Me, 2.089(14)		Y = S, bridged 3.202(7)	2.139(13)	56
$Me_2Sn[N(CN)_2]_2$	C = Me, 2.091(8)			2.289(5) 2.289(6)	39
Dichlorophthalocyaninatotin(IV)		X = Cl, 2.448(1)		2.050(3) 2.051(3)	276
Dichlorooctaethylporphinatotin(IV)		X = Cl, 2.449(2)		2.082(6) 2.104(6)	166
$Me_2Sn(CN)_2$	C = Me, 2.11(5) C = CN, 2.27(7)			intermolecular 2.68(11)	79
Seven-coordinated tin					
$MeSn(NO_3)_3$	C = Me, 2.092		Y = O, chelated 2.105, 2.240 2.130, 2.298 2.148, 2.331		26
		X = Cl, 2.362(4)	Y = O axial, 2.050(6) equatorial 2.128(6) 2.130(6) 2.138(6) 2.162(7) 2.168(7)		261

	Y = OH, 1.974(6) axial 2.057(5) equatorial 2.133(5) 2.139(5) 2.148(5) 2.180(6) 2.220(7)		261
Sn(OH$_2$)EDTA	Y = EDTA, 2.074(3) 2.075(3) 2.088(3) 2.093(3) Y = OH$_2$, 2.124(3)	2.296(3) 2.329(3)	272
Eight-coordinated tin			
Sn(NO$_3$)$_4$	Y = O, chelated 2.139(7), 2.195(7) 2.145(6), 2.172(8) 2.151(7), 2.174(7) 2.154(7), 2.158(11)		188

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[a] Inorganic tin compounds are included where applicable.

[b] C = the fourth group, and will be specified individually if other than carbon.

[c] X = halogens, and will be specified individually.

[d] Y = chalcogens, and will be specified individually.

[e] N = nitrogen.

[f] Not given.

III. ASSOCIATED LATTICES

A. Tin(II)

We will confine our attention in the present Section to organic derivatives of tin(II) which possess at least the possibility of existing in molecular form. In so doing, we excluded the large class of minerals containing tin(II) and other inorganic solids which are beyond the scope of this review. The subject of tin(II) chemistry has been admirably covered by Donaldson in a recent review[167].

The so-called diorgano derivatives of tin(II) have been shown to contain tin(IV), and the cyclic structure of $[(C_6H_5)_2Sn]_6$ was discussed in Section II.A. Likewise, the tin-transition metal compounds in which the tin atoms are bonded directly to the metal are derivatives of tin(IV), and not of tin(II) as was once thought. These compounds were discussed in Section II.C.

We will consider only three types of tin(II) structures for discussion, but each of these is unique to itself, and completely outside the range available in the higher members of the fourth group.

The first of these is the paramagnetic salt $[Co(dpe)_2Cl]^+SnCl_3^-$ [dpe = $(C_6H_5)_2P(CH_2)_2P(C_6H_5)_2$] which can be crystallized in two forms, red and green, with the latter occluding a molecule of chlorobenzene, the recrystallization solvent. In each case the structure contains isolated trichlorostannate ions which are pyramidal, the only example of such an arrangement in the Group IV-transition metal derivatives. The structure of the green isomer is curious since the trichlorostannate ions lie close to a crystallographic center of symmetry of the unit cell, resulting in relatively short tin-tin distance of 3.60 Å (the three chlorine atoms bonded to each tin are all away from the tin-tin vector). However, this distance is much larger than the sum of the covalent radii for two tin atoms, and, furthermore, the tin atom is clearly pyramidal rather than tetrahedral so that the lone pair of electrons in this oxidation state can be assumed to occupy an orbital of predominantly *s*-character. The ^{119m}Sn Mössbauer results indicating the similarity between the tin atoms in the two isomers lend support to the hypothesis that there is no chemical interaction between the two adjacent trichlorostannate groups[286]. All other known tin-transition metal compounds are diamagnetic and tin(IV)[179], with the possible exception of the recently characterized $(C_5H_5)_2Sn^{II}$ adduct of iron(III) chloride[206], and a dialkylstannylene-pentacarbonylchromium complex[242].

The molecular structure of dicyclopentadienyltin(II) is known from the results of an electron diffraction study of its lead analogue which shows plumbocene and stannocene to be angular, *pentahapto* compounds in the gas phase[6]. These remarkable compounds are the only examples of main group elements so bonded, and as such are the analogues of indocene and thallocene which are also *pentahapto*, but have half-sandwich structures in the gas phase as shown by an electron diffraction study[281] and a preliminary microwave account[295]. The angular nature of the arrangement (135 ± 15° for Pb; 125° for Sn) is a result of the stereochemical activity of the tin(II) and lead(II) lone pairs of electrons. These data are compared in Table 4.

Drastic changes accompany crystallization of these compounds, however. The solid state structures of plumbocene[260] and indocene[182] are shown in Fig. 42 and Fig. 43, where crystallization is shown to have involved change in the mode of attachment of at least one cyclopentadienyl ring per molecule to form a "reverse sandwich" structure in which each ring is held between two metal atoms, at the bisector of, and normal to, the metal–metal axis. A triclinic modification of plumbocene has been identified[142], but was not investigated further. The data in Table 4 show that the terminal cyclopentadienyl rings lie closer to the lead atoms than do the bridging rings. The zig-zag chain of lead atoms is planar with the angles at lead close to trigonal. The polymerization can be considered to arise as a result of the interaction between the lone pair of electrons on one lead atom and a cyclopentadienyl ring of a neighboring monomer. The resulting *pentahapto* connection is longer than in the free molecule. These one-dimensional polymeric structures of dicyclopentadienyltin(II) and -lead(II) in the solid state are typical of the three-coordinated inorganic structures of tin(II) which include SnS, orthorhombic SnSe, $SnCl_2 \cdot 2H_2O$, $K_2SnCl_4 \cdot H_2O$ and $SnSO_4$[277], and especially of tin(II) chloride which is known to be angular in the gas phase from the results of an early electron diffraction study[239], and forms zig-zag tin–chlorine chains with shorter bonds to terminal chlorine atoms at each tin[297].

TABLE 4
Cyclopentadienyl and Related Compounds

Compound	*d(M–Y)*[a]*(A)*	*Method for study*	*Ref.*
$H_3SiC_5H_5$	Si–σ-C_5H_5, 1.881(10)	electron diffraction	134
$(CH_3)_3SiC_5H_5$	Si–σ-C_5H_5, 1.90(1) Si–CH_3, 1.90	electron diffraction	300
$(CH_3)_3GeC_5H_5$	Ge–σ-C_5H_5, 1.97(1)	electron diffraction	301
$(CH_3)_3SnC_5H_5$	Sn–σ-C_5H_5, 2.16(1)	electron diffraction	99
1,1-[$(CH_3)_3Sn]_2C_5H_4$	Sn–σ-C_5H_5, 2.16(1) Sn–CH_3, 2.16(1) Sn–CH_3, 2.16(1)	electron diffraction	100
InC_5H_5	In–π-C_5H_5, center of ring, 3.19(10)	two-dimensional X-ray	182
TlC_5H_5	Tl–π-C_5H_5, center of ring, 2.41(1)	microwave	295
$Sn(C_5H_5)_2$	Sn–π-C_5H_5, 2.706(24)	electron diffraction	6
$Pb(C_5H_5)_2$	Pb–π-C_5H_5, 2.778(16)	electron diffraction	6
$Pb(C_5H_5)_2$	Pb–π-C_5H_5, bridging, mean 3.06(10) non-bridging, mean 2.76(10) Pb–Pb, 5.636(1)	X-ray	260
$(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$	Sn–C_6H_6, mean 3.08 Sn–C_6H_6, center 2.74(3) equatorial Sn–Cl, 2.884(7)–3.291(7) axial Sn–Cl, 2.766(7)	X-ray	81
$C_6H_6SnCl(AlCl_4)$	Sn–C_6H_6, center 2.90 Sn–Cl, 2.61, 2.66, 2.84, 3.17, 3.33	X-ray	106
p-$C_8H_{10} \cdot SnCl(AlCl_4)$	Sn–C_8H_{10}, center 2.77 Sn–Cl, 2.62, 2.68 2.92, 3.21, 3.21	X-ray	106

[a] M–Y is defined individually.

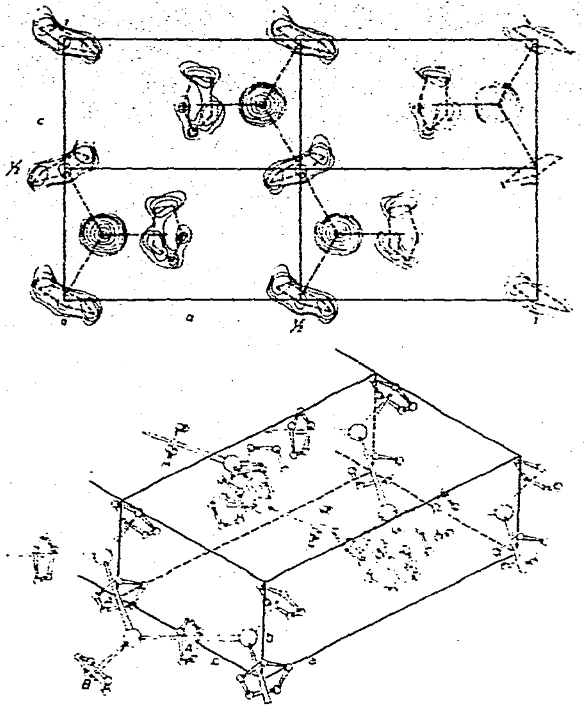

Fig. 42. Electron density projection on (010) with contours at intervals of $2e \cdot Å^{-3}$ (the levels for lead are arbitrary) and perspective view of the chains in dicyclopentadienyllead(II).

The dimensions and geometries of the tin(II) cyclopentadienyls in the gas phase and the solid state which are *pentahapto* should be compared with those derivatives of the fourth group in which the bonding of the rings is *monohapto*. Examples include $(h^1\text{-}C_5H_5)_2Sn[Fe(CO)_2h^5\text{-}C_5H_5]_2$[16-17] (X-ray), and $(CH_3)_3GeC_5H_5$[301], $H_3SiC_5H_5$[134] and $(CH_3)_3SiC_5H_5$[300], electron diffraction data, which are found in Table 4. The question of whether the cyclopentadienyl ring is flexed in these compounds is at present in dispute.

The third of the types of tin(II) associated lattices to be discussed, $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$, may be the most remarkable. The unit $(C_6H_6)Sn(AlCl_4)_2$ is highly symmetrical with a tin(II) moiety bonded to two chlorine atoms from each of three tetrachloroaluminate groups (*i.e.*, tris-chelated by, and sharing tetrahedral edges with, $AlCl_4$) to form a linear chain structure which is propagated left to right across Fig. 44. The tin(II) polyhedron is completed by a symmetrically axial, *hexahapto* coordination to one of the benzene rings that may be considered to lie on the surface of the chain with its center 2.74 Å from the tin atom. The benzene rings of adjacent chains are back to back. The dimensions of the benzene rings are indistinguishable from those in free benzene. A second molecule of benzene lies in a cleft between the chains and is regarded as a molecule of solvation. Assuming that the bonded benzene occupies one coordination site, the arrangement of tetrachloroaluminate groups gives tin a seven-coordinated, pentagonal, bipyramidal geometry. The structure of the tin(II) $Sn_2EDTA \cdot 2H_2O$ discussed in Section II.D.4, by contrast, lacks an attachment for the tin lone pair of electrons which are

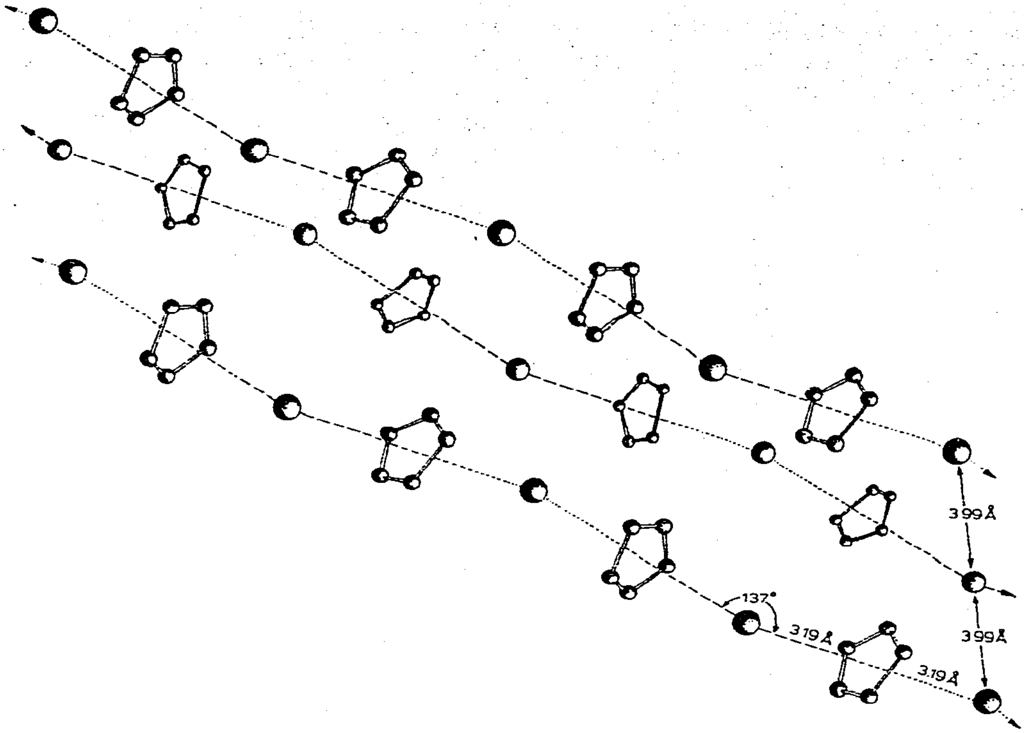

Fig. 43. Electron density projection on (001) with contours at intervals of 2e · Å^{-3} (the upper levels for indium are omitted) and perspective view of the chains in cyclopentadienylindium(I).

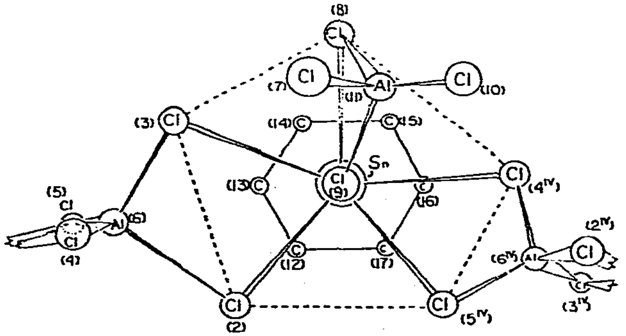

Fig. 44. An idealized view of the $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$ complex down the axial chlorine which is superimposed on the tin atom. The chain is built up by Cl(4) and Cl(5) bonded to an adjacent tin(II) to the left and Cl^{IV}(3) and Cl^{IV}(2) bonded to an adjacent tin(II) to the right. The dotted lines define the pentagonal plane.

assumed to occupy an axial position in the pentagonal bipyramid[273]. The tin atom in $(C_6H_6)Sn(AlCl_4)_2 \cdot C_6H_6$, on the other hand, is displaced by 0.6 Å from the plane of the five equatorial halogens toward the benzene ring along the axial axis which is linear. The angles at tin in the equatorial plane range from 73 to 81° *vs.* the 72° angles in a regular pentagon, while the axial chlorine distance is shorter (2.77 Å) than the equatorial (2.88 to 3.29 Å)[81].

Two other *hexahapto*-Sn^{II} chain structures have recently appeared[106], $C_6H_6SnCl(AlCl_4)$ and its *para*-xylene analogue, the former of which is shown in Fig. 45. These two, unlike the pentagonal bipyramidal tin(II) polyhedral structure of the first compound, contain lozenge-shaped, chlorine-bridged, Sn_2Cl_2 dimer units which bind together the $AlCl_4$ tetrahedra into $(SnAlCl_4)$ chains. The tin atom is at the center of a distorted octahedron.

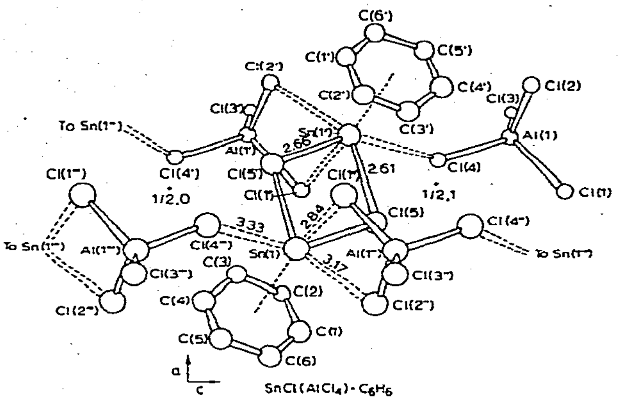

Fig. 45. Perspective view of the $C_6H_6 \cdot SnCl(AlCl_4)$ structure down the b-axis. The $Sn_2Cl_2^{2+}$ dimer is composed of atoms Sn(1), Cl(5), Cl(5') and Sn(1'). The $Sn(AlCl_4)^+$ chain goes from Sn(1''') at the lower far left through Sn(1) to Sn(1''') at the far right.

B. Tin(IV)

1. Oxygen bridges

The well-known property of the association of organotin units by oxygen bridges is based upon a wealth of spectroscopic data, but only few detailed studies of crystal structure. Only four oxide-bridged polymeric structures have been determined thus far, although several dimeric tin-oxygen molecular structures were discussed in Section II.D.1.

One of the simplest oxygen-containing organotin compounds is trimethyltin hydroxide whose one-dimensional structure in the solid state consists of chains of oxygen atoms, almost equidistant between planar trimethyltin groups which are inclined by 15° with respect to a plane perpendicular to the chain axis. This inclination gives rise to an 8_3 helical arrangement of tin atoms along the chain. There is no hydrogen bonding, and the chains are held in the crystal by Van der Waals forces[76,259]. The full report of this structure has not yet appeared.

The organotin acetates have been subjected to very extensive study by spectroscopic techniques, but little in the way of the details of molecular parameters are known. The simplest compound studied, trimethyltin formate, forms a structure of formoxy and planar trimethyltin groups arranged alternatively along a helical chain. The plane of the trimethyltin group is inclined from the crystal axis as shown in Fig. 46. The full report of this structure has never appeared, but the lattice parameters and space groups of the fourth group tetra-acetates have been reported, and the identity periods of the needle crystals of several trialkyltin carboxylates have been published[229,257,259]. It is expected that these carboxylates have analogous polymeric structures along the needle axis.

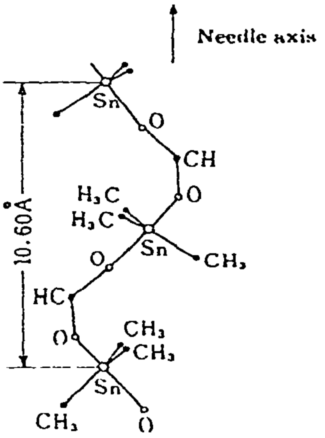

Fig. 46. The chain axis of trimethyltin formate.

Complete structural analysis has been carried out on two triorganotin acetates, the tribenzyl-[3] and tricyclohexyltin[4] derivatives which exemplify the two extrema observed in this class of compounds since the first (m.p. 112–113°) is unequivocally polymeric and crystallizes as elongated plates with a distinct needle axis, while the tricyclohexyl derivative (m.p. 61–63°C) crystallizes in a rod-like form with an almost square cross-section which contains discrete, monomeric molecules. In the tribenzyltin acetate each tin atom is rendered five-coordinate by attachment of the second oxygen of the acetate group of an adjacent molecule which gives a trigonal bipyramidal environment to tin with equatorial methylene groups. The acetate groups are symmetrical and coplanar with the tin atom with the direction of polymerization along a screw axis which swings through 60° with every acetate bridge as shown in Fig. 47. The benzyl groups are folded back at the methylene carbon in the shape of a paddle-wheel, thus providing easy access to the tin atom. The tin atoms themselves are slightly out of the plane formed by the three methylene groups (by 0.2 Å). The intramolecular tin–oxygen distance (2.14 Å) is shorter by half an ångstrom than the bridging oxygen distance (2.65 Å), with the axial oxygen–tin–oxygen angle at 169°[3].

The structure of tricyclohexyltin acetate shown in Fig. 48 is more ambiguous. The compound crystallizes in a discrete, molecular structure with the shortest intermolecular tin–oxygen contact distance at 3.84 Å (*cf.* 2.65 Å for the intermolecular bridging distance above). However, the second atom of the carboxylate group lies only 2.95 Å from the tin atom, which raises the question of possible intramolecular association to form a chelated ring structure. Although such association would have to be very weak since it compares with tin–oxygen distances of 2.12 Å for the directly bonded acetate, of 2.25 Å in the five-coordinated di-μ-acetatobis(diphenyltin), and the range 2.11 to 2.49 Å for six-coordinated chelate complexes, the magnitude of the Mössbauer quadrupole splitting argues for this result. The basic structure is thus that of a flattened tetrahedron with wide

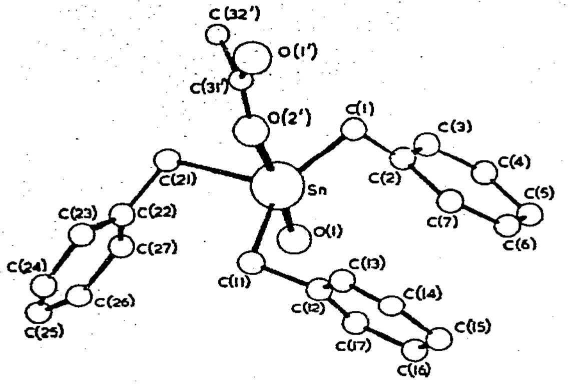

Fig. 47. A portion of the tribenzyltin acetate structure. The primed atoms of the acetate group are related to the atoms of the acetate group next down the chain by a screw axis.

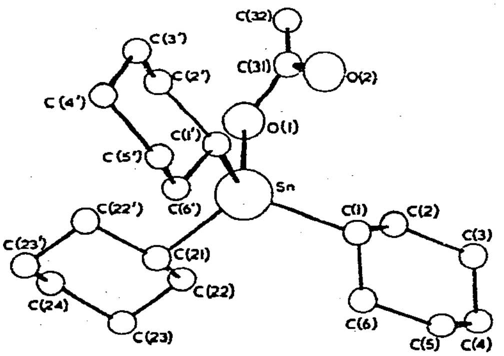

Fig. 48. The tricyclohexyltin acetate molecule. Primed atoms are related to unprimed ones by a mirror plane.

carbon angles at tin as expected from both electron redistributions in the σ-framework and steric repulsion of the bulky cyclohexane rings. Unlike the tribenzyl analogue, the rings in this case may prevent the close approach of a bridging acetate group[4].

By contrast with the usual triorganotin acetate arrangement the structure of potassium triformatostannate(II) consists of the close packing of discrete, pyramidal $Sn(OOCH)_3^-$ ions and potassium ions with no compelling evidence for the formation of chains, the shortest interionic tin–oxygen contact distance being 3.00 Å. However, the tin distance to the terminal formate oxygen atom is only 2.88 Å[220]. The tin(II) oxygen distances in distannous ethylenediaminetetraacetate dihydrate discussed above in Section II.D.4 range from 2.14 to 3.18 Å[273]. Given the observed range of tin–oxygen distances in bridging and molecular acetates, it cannot be said with certainty whether the terminal carboxylate oxygen atoms have a chemical interaction with tin.

The two-dimensional lattice of dimethyltin bis(fluorosulfate) shown in Fig. 49 is much more straightforward. The crystals contain polymeric sheets with fluorosulfate groups of C_{3v} symmetry acting as bridges between linear (*trans*) dimethyltin units so that the tin atoms are coordinated octahedrally. This arrangement with the sheets held together by Van der Waals forces is similar to that of dimethyltin difluoride discussed in Section IV.A, below. The two crystallographically independent tin-oxygen distances are equal at 2.27 Å, but the *trans*-dimethyltin angle is nowhere listed. In the symmetric fluorosulfate group, rather long tin-oxygen distances and short tin-carbon bonds (2.08 Å) can be interpreted alternatively in terms of an ionic structure consisting $[(CH_3)_2Sn]^+$ and $[SO_3F]^-$ units[5], but this is not a suggestion which we favor.

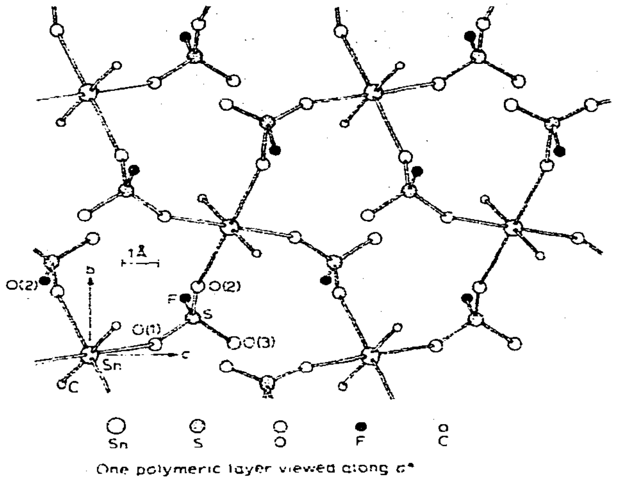

Fig. 49. The two-dimensional lattice of dimethyltin bis(fluorosulfate), $(CH_3)_2Sn(SO_3F)_2$, viewed along the a-axis.

2. *Pseudohalide bridges*

Several groups have undertaken the analysis of the gas phase structures of silyl[190,212,214,221,231] and germyl[270] isocyanates[190,212,214,231,270] and isothiocyanates[221,231], the effort being stimulated both by the question of possible linearity of the pseudohalogen group which has some bearing on the controversy over the influence of $(p\rightarrow d)\pi$ bonding and by the various tentative suggestions for the structures of these compounds put forward on the basis of infrared and Raman results. The data from microwave[298] and electron diffraction studies show that the groups at the fourth group atom are freely rotating, and that the pseudohalide is bent at nitrogen by 136-145° in the chlorosilanes[212], by 150-154° in the trimethylsilanes [231], by 146° in the tetraisocyanate[214], and by an indeterminant amount in the germyl derivative[270]. The silyl derivatives are linear, however[190,221]. All the reported angles are larger than for the corresponding methyl or hydrogen derivatives. Silylazide is, on the other hand, according to a preliminary microwave study, an asymmetric top molecule, contrary to expectations, with a non-linear Si-N-N-N chain[171].

The situation in the solid state is altogether changed from that in the gas phase since in each case thus far studied a polymeric structure involving pseudohalogen bridges is found. In each example discussed (no solid state structural studies of the centrosymmetric azide group have been carried out) there arises the question of identifying which terminal atom is bonded to tin, *i.e.*, whether the pseudohalide is iso or normal.

a. Cyanides. The structures of the dimethyldicyano compounds of silicon, germanium, tin and lead, the latter from powder data, show all to be true cyanides, and all to be associated in the solid state[79]. In the silicon and germanium compounds, approximately

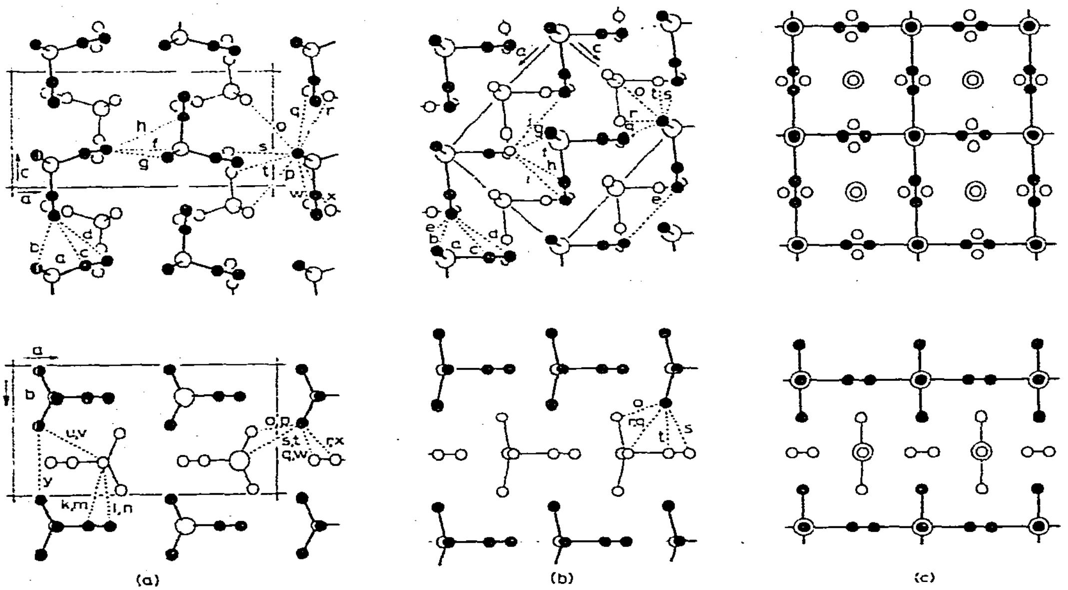

Fig. 50. The structures of (a) $(CH_3)_2Si(CN)_2$ and $(CH_3)_2Ge(CN)_2$; (b) $(CH_3)_2Sn(CN)_2$ and $(CH_3)_2Pb(CN)_2$; (c) unrealized tetragonal limiting case with disordered CN groups. Fourth group atoms are open, carbon atoms black, nitrogen shaded, and disordered carbon and nitrogen atoms cross-hatched; hydrogen atoms are not shown. Top view each case is perpendicular to the plane formed by the interacting molecules. Bottom view is at right angles to this, along c in the first case, along (101) in the second, and along a in the third. The different orientations are chosen to emphasize the similarities among the three structural types.

tetrahedral molecules form linear chains through weak cyanide bridges. In the tin, and presumably the lead, compounds stronger bridging gives rise to planar sheets in which the molecules are distorted to a nearly octahedral arrangement with *trans*-dimethyltin groups (angle C-Sn-C = 148.7°) perpendicular to the sheets (angle NC-Sn-CN = 85.3°). The layers pack with the methyl groups of one sheet nestled among the methyl groups of the next layer (*cf.* $(CH_3)_2SnF_2$ discussed in Section IV.A, below). The intermolecular interactions are not equivalent in the silicon and germanium compounds, with the second cyanide bridge (which points directly at the heavy atom of an adjacent molecule) much weaker than the first (3.48 and 3.97 Å for N···Si, and 3.28 and 3.84 Å for N···Ge), unlike the tin analogue for which both Sn···N distances are 2.68 Å. The argument for six-coordination is based upon the alignment of the CN group toward the adjacent heavy atom, the decrease in bridging distances from silicon to tin, and that the fourth group element–methyl distances are in all three cases shorter than the cyanide distances in the same molecule ($Sn–CH_3$ = 2.11; Sn–CN = 2.27 Å). The structures are compared in Fig. 50.

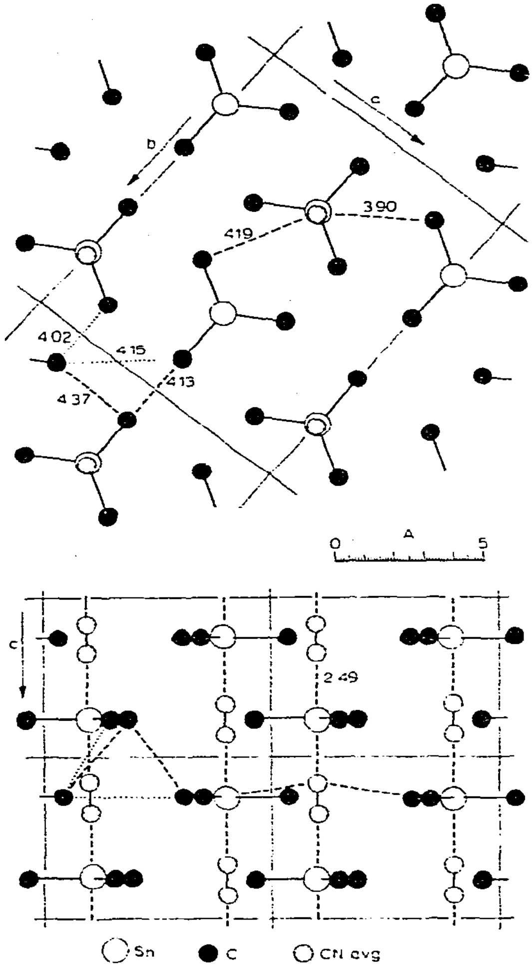

Fig. 51. The chain structure of trimethyltin cyanide.

Trimethyltin cyanide (m.p. 189°) forms needle crystals in which trigonal bipyramidal tin atoms with equatorial methyl groups of D_{3h} symmetry are bridged by equidistant axial cyanide groups, which form infinite chains as shown in Fig. 51. The trimethyltin groups appear to be eclipsed. The tin–carbon and tin–nitrogen distances to the cyanide are equal within a rather large experimental error at 2.49 Å, and the question of whether trimethyltin cyanide is a normal or isocyanide cannot be answered from the present solid state determination. One view of the structure is as an arrangement of $[(CH_3)_3Sn]^+$ and CN^- ions with the CN units ordered in the direction of the infinite axis but disordered in orientation along this axis[90]. This view is supported by the short C≡N distance (1.09 Å), more like that in the ionic sodium cyanide (1.05 Å) than the usual covalent cyanide distance (1.16 Å). We, however, prefer the alternative, more general view that places this structure in the same category as other covalently bridged examples. Unit cell data for triethyltin cyanide have been published, but the structure was not completed because of large thermal motions in the solid at ambient temperatures[38]. It is of interest to compare the data for trimethylgermanium cyanide (m.p. 38°) whose structure is shown in Fig. 52. It is clear that the structure of the germanium analogue lies somewhere intermediate between the completely symmetrically bridged tin form and a completely

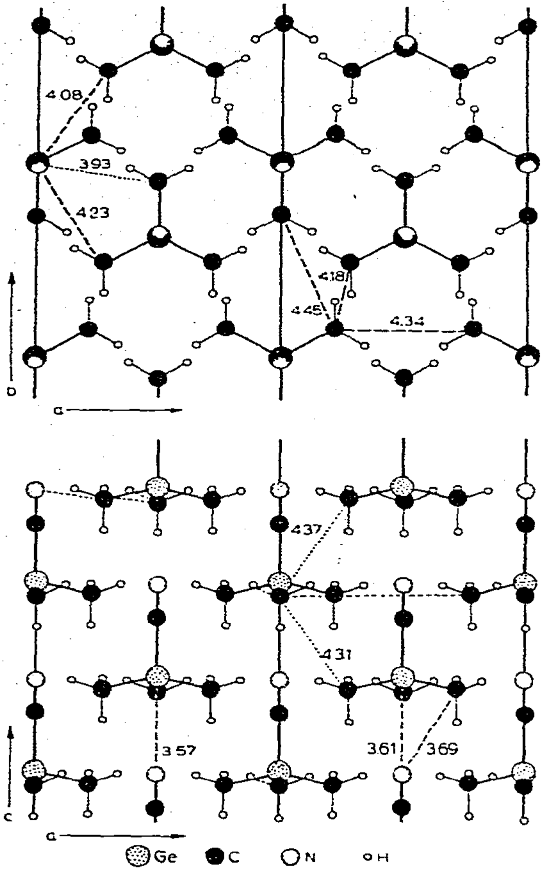

Fig. 52. The structure of trimethylgermanium cyanide. Top view is down the c-axis. Bottom view is along the b-axis. Interatomic distances are in Å. The hydrogen positions are assumed on the basis of normal C–H distances and a staggered configuration about the Ge–C bond.

discrete, molecular form. The solid has the normal cyanide structure with a covalent Ge–CN link, and no or little bridging to adjacent germanium atoms. The carbon angles at germanium are opened to 115°[278] in the direction expected for the onset of five-coordi-

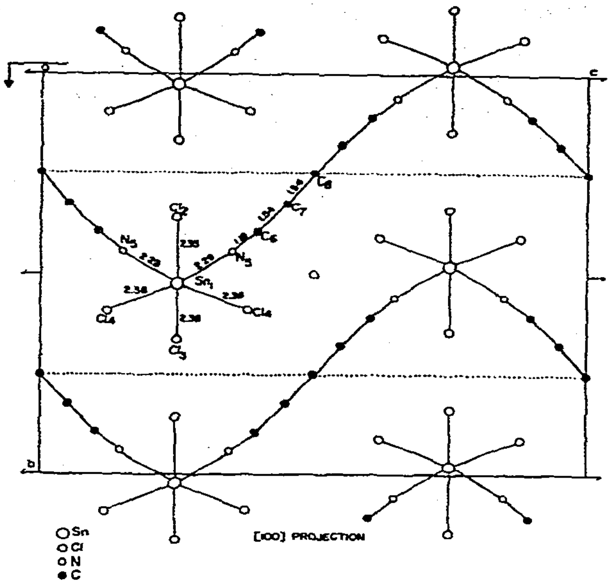

Fig. 53. Projection of the structure of tin(IV) chloride glutaronitrile, $SnCl_4 \cdot NC(CH_2)_3CN$, down the a-axis.

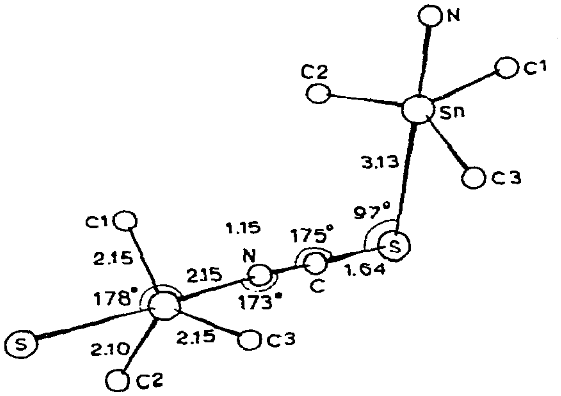

Fig. 54. The chain structure of trimethyltin isothiocyanate.

nation, but also in the direction expected on the basis of isovalent rehybridization[133] or valence shell electron repulsion[193] arguments.

An interesting variation on this theme is provided by the tin(IV) chloride complex of glutaronitrile shown in Fig. 53 which crystallizes as a one-dimensional polymer with the glutaronitrile groups acting to bridge the octahedrally coordinated tin units[120]. The nitrogens are attached *cis* (the angle N–Sn–N is nowhere listed) at a distance of 2.29 Å from the tin atom. The *cis* arrangement is in accord with the generalization that "pointed" ligands can take the preferred orientation, which is *cis*. The tin–nitrogen internuclear distance is 0.2 Å shorter than in trimethyltin cyanide. The C_8 carbon in Fig. 53 is on the two-fold axis so that half of the glutaronitrile ligand is related to the other half by two-fold symmetry.

Unlike their tin analogues, the structures of both the silyl[254] and germyl[299] cyanides have been studied in the gas phase by microwave techniques. Both are normal cyanides, rather than iso. The C≡N distance was assumed in the silyl case[254], but found to be 1.16 Å in H_3GeCN[299].

b. Isothiocyanates. The structure of trimethyltin isothiocyanate[54-55] consists of zig-zag, infinite chains, bent only at the sulfur atom with nearly planar trimethyltin groups as shown in Fig. 54. The S–Sn–N–C–S skeleton is linear within experimental error. The compound is definitely in the isothiocyanate form, since the tin–sulfur distance (3.13 Å) is appreciably longer than the value of 2.47 Å found for the tin–sulfur direct bond in $(CH_3)_3SnSC(S)N(CH_3)_2$ discussed in Section II.D.1, although it is close to the coordinated tin–sulfur distances in that compound (3.16 and 3.33 Å)[94-95].

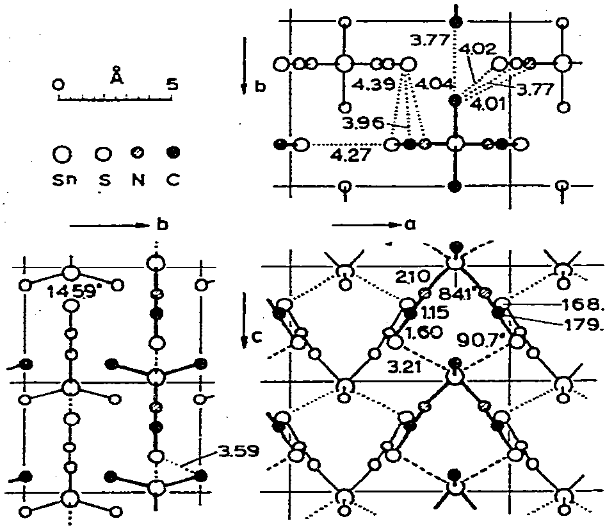

Fig. 55. The chain structure of dimethyltin diisothiocyanate. Top view is along the c-axis; bottom left view is along the a-axis; bottom right view is along the b-axis.

The infinite chain structure of dimethyltin diisothiocyanate has been determined by two groups[36,56]. The dimethyltin moieties are linked by sulfur–tin interactions into a polymer of planar $Sn(NCS)_2$ groups as shown in Fig. 55 with the dimethyltin axis perpendicular. The geometry at tin is that of a distorted tetrahedron, with the methyl-tin-methyl angle opened to 148.9°. However, compared with the data for trimethyltin isothiocyanate there is a general trend to more "normal" values of the N–C and C–S bond lengths and Sn–N–C and C–Sn–C angles. The tin–sulfur distance is slightly greater (3.20 Å) than in the dimethyl derivative.

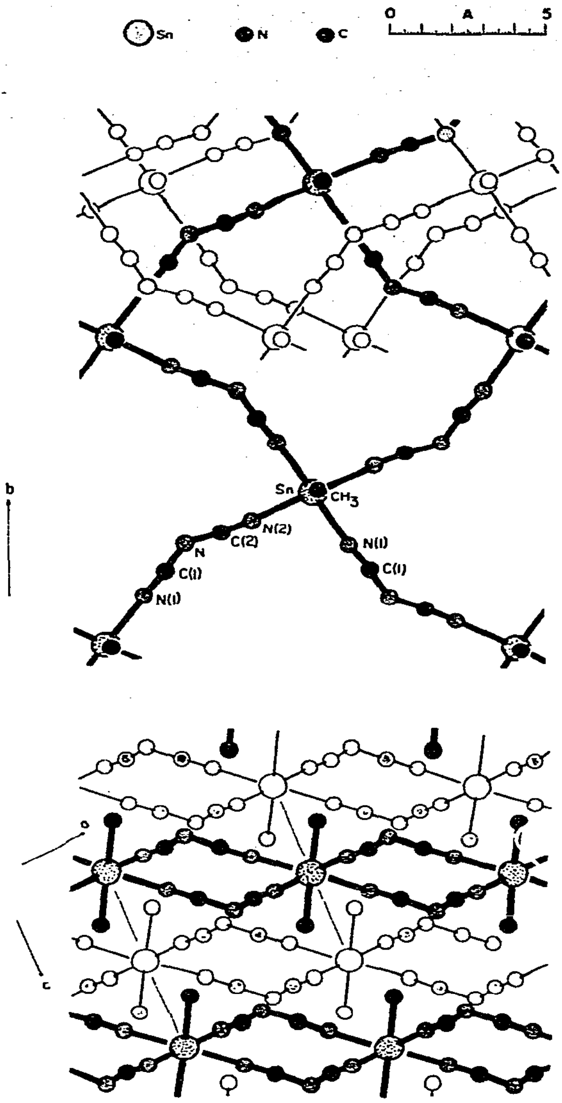

Fig. 56. The two-dimensional network structure of dimethyltin bis(dicyanamide), $(CH_3)_2Sn[N(CN)_2]_2$. Top view is on the $(\bar{1}02)$ plane; bottom view is on the (010) plane.

Further to this point is the structure of the dimeric tetramethyl-1,3-diisothiocyanato-distannoxane[37], some of the aspects of which were discussed in Section II.D.1. Apart from the coordination shown in Fig. 17, there is additional, weaker coordination by the terminal sulfur atoms of one dimeric unit to tin atoms in adjacent units. The tin–sulfur distance here is 3.33 Å, equal to the largest such distance known in $(CH_3)_3SnSC(S)N(CH_3)_2$. This interaction results in distorted octahedral hexacoordination for the exocyclic tin atoms and a polymeric crystal structure in which the internuclear distances and angles are similar to those in dimethyltin dicyanide[232] and diisothiocyanate[36,56].

c. Cyanamides. The nature of the pseudohalide in this case raises the question of whether the structures will be found in the cyanamide or carbodiimide form. In both dimethyltin bis(dicyanamide) and trimethyltin dicyanamide planar $N(CN)_2$ groups are symmetrically disposed on either side of the organotin moieties which are linear (angle not listed) and planar (C–Sn–C angles 118.2–120.9°), respectively[39]. The structure of the former compound consists of an infinite two-dimensional network of tin atoms and bridging dicyanamide groups with methyl groups above and below completing the slightly distorted octahedral coordination at tin as shown in Fig. 56. This structure is similar to that of dimethyltin difluoride, but here the bridging dicyanamide groups serve to form twelve-membered, $\overline{\text{Sn–N–C–N–C–N–Sn–N–C–N–C–N}}$ rings. The structure of trimethyltin dicyanamide, on the other hand, is similar to that of trimethyltin cyanide, consisting of infinite, one-dimensional chains. The tin atoms are in a trigonal bipyramidal environment with equatorial methyl groups and equidistant, axial dicyanamide groups, giving approximate D_{3h} symmetry at tin as shown in Fig. 57.

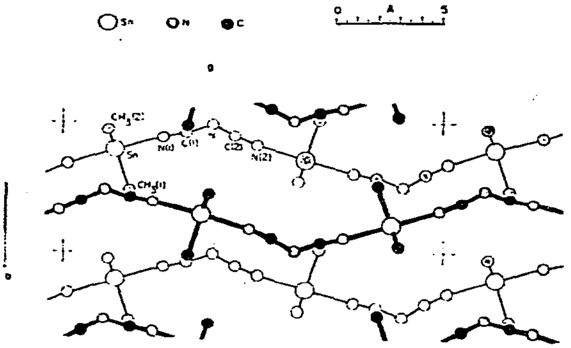

Fig. 57. The one-dimensional structure of trimethyltin dicyanamide, $(CH_3)_3Sn[N(CN)_2]_2$, viewed on the (001) plane.

The structures of the analogous tricyanomethanide derivatives are similarly constructed of chains in the trimethyltin case and layers in dimethyltin bis(tricyanomethamide)[158].

Bis(trimethyltin) cyanamide crystallizes in an infinite helical network of planar trimethyltin groups linked by linear NCN units as shown in Fig. 58. The Sn_2NCNSn_2 moieties have D_2 symmetry with a trigonal bipyramidal $N–SnC_3–N$ environment at tin and a dihedral angle of 68° between the two Sn_2NC planes. The helix is formed about screw triad axes parallel to the needle axis of the crystal. The NCN units are also parallel to the needle axis and are each part of two helices of the same hand. The absolute configuration was determined for the particular crystal studied, but even if discrete molecules exist in solution and are enantiomorphous, there is no reason to doubt that the crystal should not dissolve to give a racemic mixture[57-58].

Given the crystallographically equivalent tin-nitrogen internuclear distances in the three compounds examined, it is impossible to decide between the carbodiimide, cyanamide, or even ionic formulations for the pseudohalide.

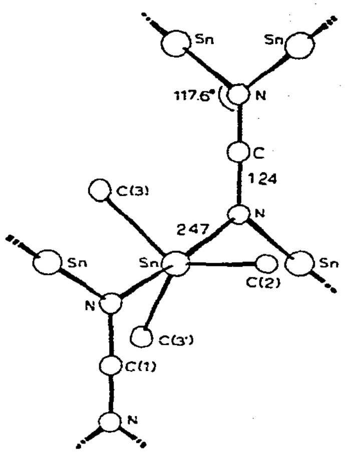

Fig. 58. The environment of the tin atoms and NCN-units in the helical network of bis(trimethyltin) cyanamide, $[(CH_3)_2Sn]_2NCN$.

IV. THE ORGANOTIN HALIDES

In some of the compounds we have discussed thus far there have been sufficient ambiguities to allow alternative views about the coordination number at tin to survive after knowledge of the details of structure was available. Only few such problems are found to be really vexing, since examination of the internuclear distances to potentially coordinating atoms in the immediate vicinity of the tin atom generally settles the question. However, in the organotin halide series there are questions of this type which stubbornly refuse to be clearly resolved, despite the availability of rather complete data on solid state structural parameters and from spectroscopic techniques. For this reason we have gathered information on these systems into a separate section. Within this section we can separate the organotin fluorides, all of which form higher coordinated, polymeric lattices.

A. Organotin fluorides

Only the inorganic hexafluorostannate dianion forms a discrete unit in the solid[210]. All other tin–fluorine structures, including that of the $Sn_2F_5^-$ anion, are part of a polymerized lattice in the solid state. In $NaSn_2F_5$, the complex ion shown in Fig. 59 is linked together by tin–fluorine bonds of 2.53 Å to form infinite chains of six-coordinated tin(II) atoms[245]. In tin(II) fluoride, which exists in two crystallographic forms[168], the structure is complex, and not made up of discrete units.

Tritin(II) bromide pentafluoride contains an infinite tin(II) fluoride cationic network and free bromide ions with each tin as part of a pyramidal, three-coordinated environment[169]. Potassium trifluorostannate(II)[136] hemihydrate, $KSnF_3\cdot\frac{1}{2}H_2O$, consists of distorted tetragonal SnF_4 pyramids with a tin atom at the top where connections at corners form parallel chains of $[SnF_3]_n$. The structure of tin(IV) fluoride, presumed to be tetrahedral in the gas phase by analogy with tin(IV) chloride[145,184,240,265], is six-coordinated and

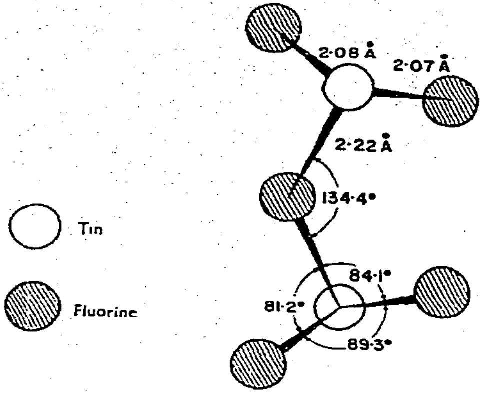

Fig. 59. A portion of the sodium pentafluoroditin(II), $NaSn_2F_5$, lattice.

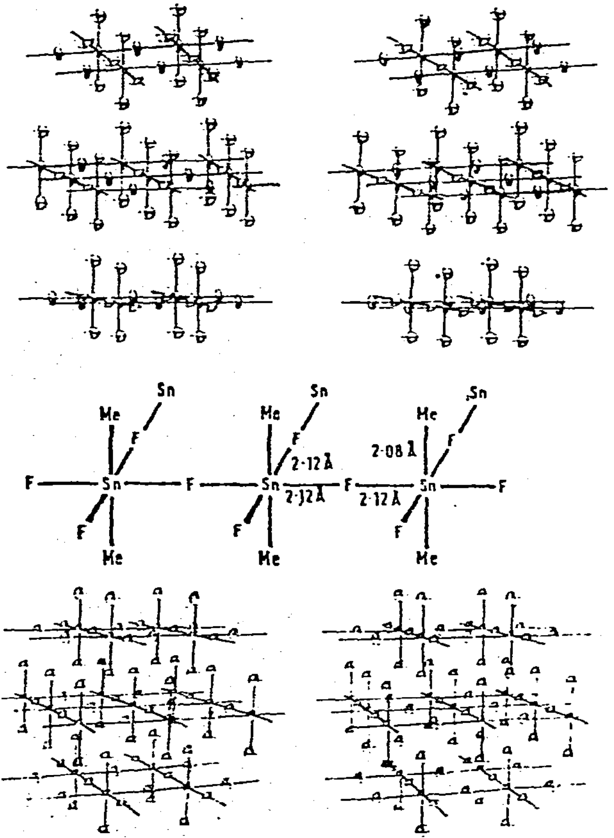

Fig. 60. The structures of dimethyltin difluoride, $(CH_3)_2SnF_2$, and tin(IV) fluoride, SnF_4. The square planar networks are composed of tin atoms at the square corners and fluorine atoms at the centers of the square edges to give an infinite sheet with the formula $[SnF_2]_n$. The vertical appendages are methyl groups in the top view and fluorine atoms in the bottom view. An idealized rendering of dimethyltin difluoride is also shown at center.

polymeric through tin–fluorine bridging in the solid state. Claims have been put forth for the monomeric nature of highly substituted triorganotin fluorides such as the trineophyl derivative (m.p. 98–100°)[271], but no structural data are yet available.

The two key organotin compounds, dimethyltin difluoride and trimethyltin fluoride, have now been very thoroughly investigated. The structure of the former is very closely analogous to that in tin(IV) fluoride itself, and is illustrated with it in Fig. 60. The tin atoms are in an octahedral environment in each with four equatorial bridging fluorine atoms. The unit cell dimensions, however, reflect the substitution of two methyl groups perpendicular to the infinite sheet, with larger cell constants (c = 14.16 *vs.* 7.93 Å) in the dimethyl derivative reflecting the much greater interlayer separation owing to the greater Van der Waals diameter of the methyl group. The layers are able to pack much more closely together in tin(IV) fluoride where the two planes of non-bridging fluorine atoms are coplanar between the layers of tin and bridging fluorine atoms. However, the two planes of carbon atoms between the layers of tin and fluorine atoms in the dimethyl derivative are far from coplanar, being separated by 2.95 Å along the perpendicular, c axis[91]. Neutron diffraction results indicate a low barrier to rotation of the methyl groups in the solid state, reflecting the small interaction with other methyl groups and atoms in the lattice[89]. This situation should be compared with that of $(CH_3)_2Sn(CN)_2$ in which the methyl groups of adjacent layers are intermingled.

The crystals of trimethyltin fluoride constitute a difficult problem because of disorder, and a completely satisfactory solution may not be possible[40-41]. It is clear, however, that trimethyltin groups and fluorine atoms are arranged alternatively along an infinite chain axis in which the tin atoms are five-coordinate in an approximately trigonal bipyramidal geometry as shown in Fig. 61. The two possibilities illustrated arise because of anomalies

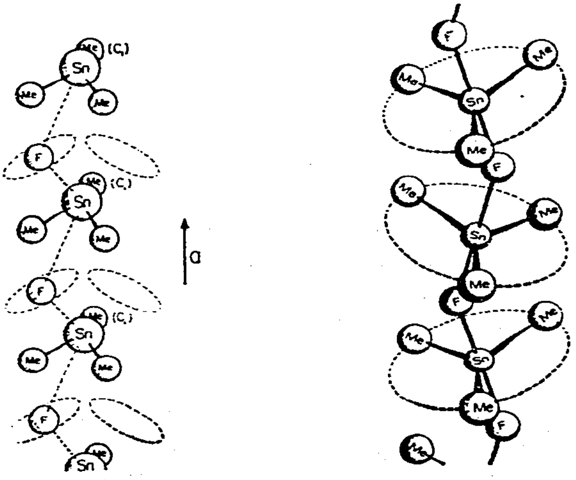

Fig. 61. Possible structures for trimethyltin fluoride, $(CH_3)_3SnF$.

in the electron density projections resulting from disorder of fluorine atoms within each chain and disorder of the chains with respect to one another. As a consequence it is impossible from the X-ray data alone to distinguish between the two structures shown. In the first, two atoms C_2 and C_3 are ordered and both displaced from the plane in the opposite direction to the tin–fluorine bond, while the fluorine atoms are disordered, occupying any position on parts of a spherical surface 2.1 Å from one tin atom so that Sn–F· · ·Sn is not linear. The chains can align themselves in either direction along the a axis. The trimethyltin group is non-planar.

In the second structure the trimethyltin groups are planar and tilted alternatively with respect to a. The fluorine atoms must be ordered with respect to their alternate placing on either side of the tin-tin axis[40-41]. The higher symmetry structure is preferred on the basis of vibrational data which argues for a planar trimethyltin group[108]. A reasonable arrangement is shown in Fig. 62.

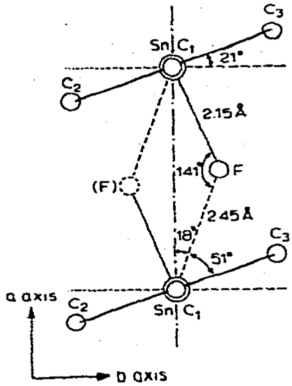

Fig. 62. A projection of the probable structure of trimethyltin fluoride on the (001) plane. The symbols F and (F) indicate the two possible fluorine atom positions.

B. *The methyl- and phenyltin chlorides*

In this section we come upon the most difficult problems of attempting to interpret molecular structure data in terms of intermolecular association and the coordination number at tin. The results of gas phase studies agree that the series of methyltin chlorides, $(CH_3)_nSnCl_{4-n}$ where $n = 0$[240], 1, 2, 3 and 4 are discrete, monomeric molecules and, excepting for the end members, containing tin atoms of slightly distorted tetrahedral symmetry[59,96,185,244]. The early electron diffraction work did not reveal the small angular distortions which might be discussed in terms of electron redistributions in the σ-frameworks of the methyltin chloro, bromo and iodo derivatives, and these results for the chlorides must be considered as superseded by more recent, for the most part unpublished, data[59,185,244]. However, no data are now available which would support a view that there are large deviations from tetrahedral symmetry in the free methyltin chloride molecules. It should be recalled that such deviations seen in the tin–transition metal derivatives are understandable on the large electronegativity differences between the metal and other ligands.

The crystal structures tell a different, if not altogether, clear story. Data are available for dimethyltin dichloride (m.p. 104°; *cf.* dimethyltin difluoride, dec. 360°) and two phenyltin chlorides. Preliminary X-ray data on dimethyltin dichloride were based upon an incorrect choice of space group[64]. Figure 63 shows an artist's rendering of the results of the complete structural analysis in which the similarities to the dimethyltin difluoride structure are emphasized. The individual units are severely distorted from tetrahedral symmetry with Cl-Sn-Cl angles of 93° and C-Sn-C angles of 123.5°. Furthermore, the molecular units are aligned so that unsymmetrical tin–chlorine bridges appear (containing tin–chlorine distances of 2.40 and 3.54 Å), and the individual molecules form a one-dimensional chain of tin atoms, each with an environment substantially distorted toward the octahedral. The tin and chlorine atoms in each chain are coplanar, with the methyl groups situated above and below the plane. The tin atoms in a chain are not colinear, but are slightly offset in a zig-zag fashion[43]. This arrangement differs, of course, in important ways from the two-dimensional polymeric structure of dimethyltin difluoride in which the tin atoms are held by bridges of a single fluorine atom as seen in Fig. 60. An important objection to the suggestion of bridging chlorines in the structure of dimethyltin dichloride arises from the tin–chlorine internuclear distances. The short distance is not very long compared to those measured in six-coordinated structures, but the long distance is very much longer than any we have discussed in genuinely bridged tin atoms, for example, the five coordinated tin–transition metal derivatives where the tin–chlorine distances are 2.81 and 2.96 Å for the molybdenum and tungsten compounds[50-52]. Both the long and short distances are less than the generally accepted Van der Waals radii of 4.1 Å[143] and greater than the tin–chlorine distance of 2.33 Å from the most recent electron diffraction study of $(CH_3)_2SnCl_2$[59]. Perhaps the most compelling evidence for the associated structure is that a more efficient packing arrangement for regular tetrahedral molecules is available in space group *Amma*, rather than the space group *Imma* actually adopted.

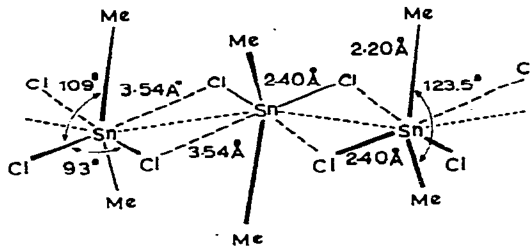

Fig. 63. An idealized rendering of the structure of dimethyltin dichloride, $(CH_3)_2SnCl_2$, which emphasizes the similarities with the structure of dimethyltin difluoride.

The phenyltin chloride structures become more ambiguous with regard to the question of association. The arrangement of diphenyltin dichloride molecules in the unit cell is shown in Fig. 64 where two crystallographically independent, but almost identical molecules are found[66]. The mean values for the Cl-Sn-Cl (100°) and C-Sn-C (125.5°) angles again show considerable distortion from tetrahedral geometry, as in the dimethyl derivative. The two shortest intermolecular tin–chlorine contacts of 3.77 Å and 3.78 Å compared with 3.54 Å for both in the dimethyl case are again smaller than the sum of the Van der Waals radii. The mean directly bonded tin–chlorine distance of 2.35 Å is somewhat shorter than in the dimethyl compound (2.40 Å). It is possible to perceive a zig-zag tin axis running through Fig. 64, but as the numerical data show, the association is weaker here. The interpretation is greatly hindered by the lack of gas phase angular data.

Lastly, we have the structure of triphenyltin chloride as shown in Fig. 65 where the mean C–Sn–C (112.3°) angle is closer to the tetrahedral value. Again two crystallographically independent molecules of almost identical geometry are contained in the unit cell. The mean tin–chlorine distance is 2.32 Å, down from 2.35 Å in the diphenyl compound, and the shortest tin–chlorine contact between molecules associated with the center of symmetry amounts to ca. 6 Å with the distances between molecules associated with a b translation exceeds 8 Å. Thus we have a structure containing truly discrete organotin molecules, and comparison is drawn to the (4-chloro-1,2,3,4-tetraphenyl-*cis*, *cis*-1,3-butadienyl)dimethylphenyltin discussed below in Section IV.C in which the non-bonded tin–chlorine contact is 4.28 Å. However, it is known from nuclear quadrupole resonance results that a phase transition takes place in triphenyltin chloride in cooling to 77 K, and that this change is accompanied by a strong lowering of the chlorine frequency, consistent

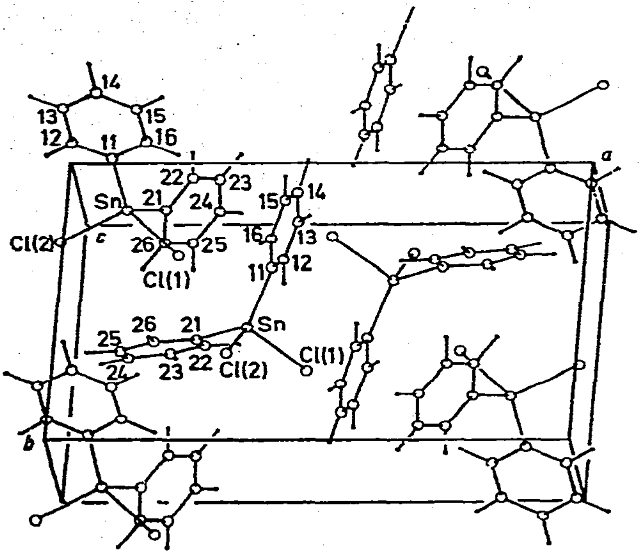

Fig. 64. The unit cell of diphenyltin dichloride, $(C_6H_5)_2SnCl_2$, with the origin at the top left-hand corner of the cell outlined. The ab plane of the figure is parallel to the plane of the paper.

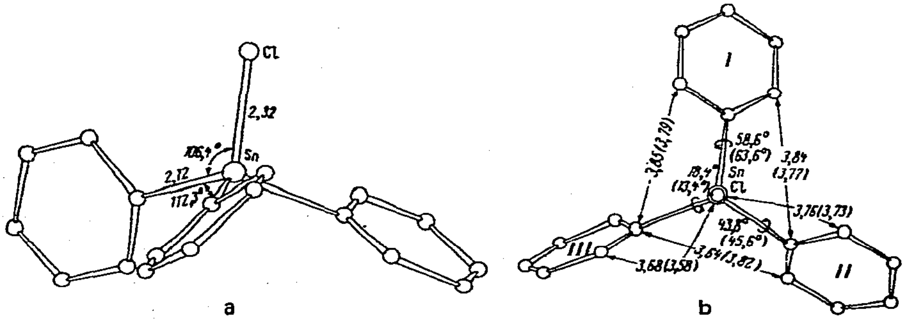

Fig. 65. The triphenyltin chloride molecule.

with the onset of coordination by chlorine[284]. This observation is particularly important since the ^{119m}Sn Mössbauer quadrupole splitting data which suggest higher coordination at tin are recorded at 77 K[318]. Examination of the intramolecular contact distances reveals that transformation of the ambient form of the molecule to one with trigonal bipyramidal symmetry with a Cl–Sn–Cl angle of 90° would be permissible[24].

C. Other organotin halides

A series of crystal structure determinations has recently become available which is of great importance to the question of the interaction of chlorine and bromine atoms with tin across space. The molecular conformation of (4-bromo-1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide as shown in Fig. 66 includes a weak tin–bromine interaction (at 3.77 Å), 0.4 Å less than the sum of the Van der Waals radii. Other evidence for five-coordination at tin comes from the butadienyl carbon–tin–methyl angle which has opened to 129.0° and the dimethyltin angle of 112.7°. These angles, with the Br–Sn· · ·Br value of 149.5°, argue for the expected axially-substituted trigonal bipyramid with equatorial organic groups[19,20].

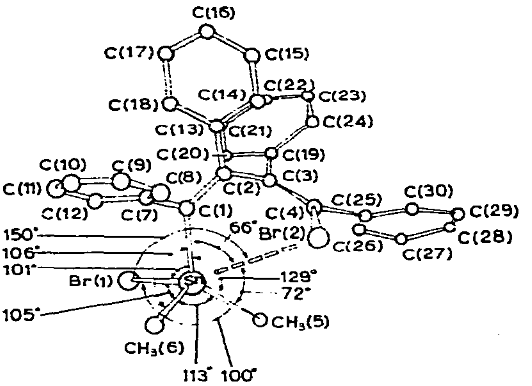

Fig. 66. The 4-bromo-(1,2,3,4-tetraphenyl-*cis,cis*-1,3-butadienyl)dimethyltin bromide molecule. The intramolecular tin–bromine interaction is shown by the dashed line.

Replacement of the bromine at tin by a phenyl group, on the other hand, has been investigated in the series of 4-chloro- and -bromo-compounds, and it is found that there is no intramolecular coordination to the tin atom which is now tetraalkyl-substituted. The tin–chlorine (4.28 Å) and tin–bromine (4.35 Å) distances exceed the respective sums of the Van der Waals radii (4.00 and 4.15 Å) and appear to be limited by contacts with the organic groups at tin. By contrast, the tin–bromine distance in the previous example was 0.38 Å less than the sum of the Van der Waals radii and 0.57 Å less than the similar distance here. Likewise the dimethyltin angle in the former is 129.0° against 117.1° here and 116.5° in the chlorine analogue[21]. Whether this angle opening arises to permit the vinyl halogen to pack between the butadienyl and methyl carbons leading to incipient five-coordination is conjectural. Any such interaction would have to be exceedingly weak.

The molecular configuration of 1,4-bis(iododiphenyltin)butane[42] as shown in Fig. 67 is more clearcut. The discrete, centrosymmetric arrangement includes approximately tetrahedral coordination about tin with the angles involving carbon larger (mean 113.6°) and the angles involving iodine smaller (mean 104.9°) than tetrahedral as expected. The dipole moment in benzene of 5.24 Debye[316] suggests that a solution conformation involving intramolecular coordination may be possible.

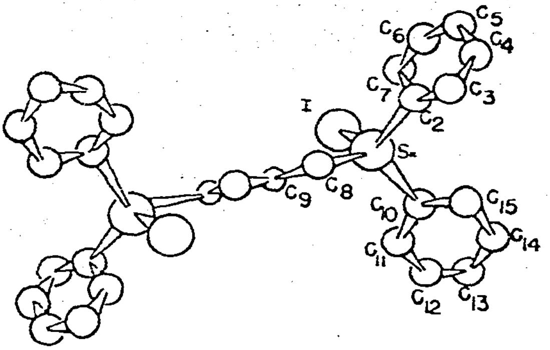

Fig. 67. The 1,4-bis(iododiphenyltin) butane, $I(C_6H_5)_2Sn(CH_2)_4Sn(C_6H_5)_2I$, molecule.

V. TIN RADII

The size of an atom in a molecule is a function of, *inter alia*, the temperature, the particular atoms and groups to which it is joined, its coordination number, its oxidation state, the phase in which the molecule is found, whether the molecule carries a formal charge or is a radical, the external pressure applied, whether the molecule is in the ground or an excited state, its hybridization, the ionicity of the bonds it exerts, whether it forms multiple bonds with neighboring atoms, etc. No real significance can be attached to a number purporting to represent the radius of an atom in a molecule unless at least some of the parameters enumerated above were to be specified. To do so would have the consequence of generating a family of numbers, each one applicable to only a limited number of examples.

When Pauling first assigned the covalent radius of tin as 1.40 Å[264] no structural data on a material containing stannous tin were available. Between the publication date of the third edition of *The Nature of the Chemical Bond* (1960) and 1963, three structures containing tin(II)-chlorine bonds became available, and Rundle and Olson assigned the tin(II) covalent radius as 1.63 Å in that year[277]. By 1967 data for nearly 20 compounds could be assembled, and Donaldson's review lists radii ranging from 1.35 to 1.86 Å found in inorganic stannous salts[167]. Of the structures discussed in this article, the greater size requirements of the tin(II) atom can be seen in the phthalocyanines in which the tin(II) atom is clearly out of the ring plane[183], whereas the tin(IV) atom can be accommodated in the molecular cavity[160,166,276], as well as in the tin(II) and tin(IV) EDTA complexes[272-273]. In addition, of course, the tin(II) structures invariably show evidence for the presence of the lone pair of electrons in this oxidation state.

The problem of assigning a covalent radius for tin(IV) is less acute because of the availability of the gray (α) form of elemental tin which possesses the diamond structure and a tin–tin internuclear distance of 2.80 Å[308]. The value 1.40 Å is still the generally accepted covalent radius of tin[161]. Again, however, precise calculations will demand adjustment of this value on the basis of the factors enumerated above.

More recently Slater has advocated returning to the simple scheme first proposed by Bragg in 1920 of having a single radius assigned to each type of atom applicable within broad limits (± 0.12 Å, generally). The Bragg–Slater atomic radius for tin is 1.45 Å[282]. A radius defined by the principal maxima in the radial distribution functions, $r^2\psi_i^2(r)$, of the outermost orbitals has been given for tin by Waber and Cromer[303] as 0.416 (4*p*), 0.460 (4*d*), 1.027 (5*s*) and 1.240 Å (5*p*). The Van der Waals radius of tin has been assigned a value of 2.17 Å on the basis of critical volume data[143].

VI. BIBLIOGRAPHY OF ORGANOTIN STRUCTURES

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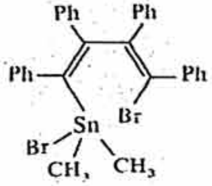

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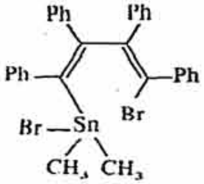

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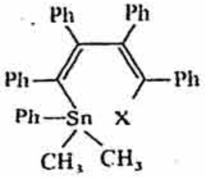

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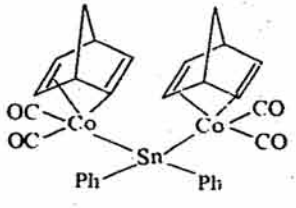

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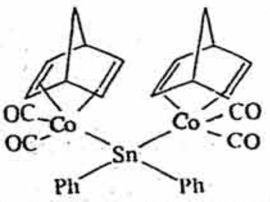

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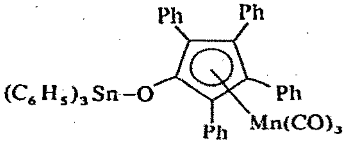

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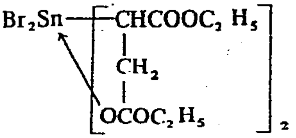
high m.p. isomer 

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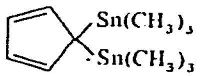
* 

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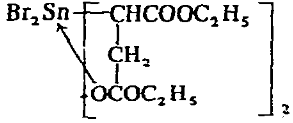
low m.p. isomer 
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