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THE STRUCTURAL CHEMISTRY OF BIVALENT GERMANIUM, TIN AND LEAD

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CONTENTS

A. INTRODUCTION

Germanium, tin and lead possess a valence shell electronic configuration of $ns^2np_xnp_y$, only two electrons of which are used in bond formation in the +2 oxidation state. However, examples of derivatives with a coordination number of two are quite rare *, and almost unknown in the solid phase **, since the availability of energetically-accessible vacant np_z and nd orbitals allows coordination numbers of up to twelve to be achieved. A second major factor which may be expected to influence the stereochemistries adopted by bivalent derivatives is the remaining lone pair of electrons. A priori, this may reside in the spherically-symmetric ns orbital or may exhibit stereochemical activity in a hybrid sp_n or sp_nd_m orbital. Both types of behaviour are quite clearly apparent from the available structural data, which is collected together in this article. Although transition metal—MX_3 (M = Ge, Sn, Pb; X = halogen) derivatives have been excluded because of the controversy surrounding the

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* The metal(II) dihalides and dicylopentadienyls possess monomeric angular structures in the vapour.

** $^5\eta$-C_5H_5SnCl appears to be the only characterised example of two-coordination in the solid if the $^5\eta$-C_5H_5 group is considered to occupy one coordination site.

nature of the Group IV metal in such compounds, an attempt has been made to keep the content otherwise comprehensive.

B. HALIDES, HALIDE COMPLEXES AND COMPLEX IONS

Qualitative information regarding the geometry of isolated MX_2 (M = Ge, Sn, Pb; X = Cl, Br) molecules has been obtained from Raman studies of the matrix-isolated species in solid argon or nitrogen [1]. The spectra obtained are fully consistent with the 'bent' structure deduced by Lister and Sutton [2] for the tin and lead dihalides in the vapour phase using electron diffraction techniques. A value of 95° for the valence angle was found to satisfactorily rationalise the data in all cases.

In the condensed phase, the structures of the dihalides and their hydrates are generally very complex. Germanium(II) fluoride is a strongly fluorine-bridged polymer (Fig. 1), in which the structural unit is a trigonal pyramid consisting of three fluorine atoms at distances of 1.79, 1.91 and 2.09 Å from an apical germanium atom. The F—Ge—F bond angles fall between 85.0 and 91.6°. The further fluorine atom bridges adjacent germanium atoms to form infinite —F—Ge—F—Ge— chains. Neighbouring chains are themselves linked by the interaction of the fluorine atom at 1.79 Å with the nearest germanium atom of an adjacent chain 2.57 Å distant. Each metal atom has therefore four fluorine atoms in its coordination sphere [3]. Tin(II) fluoride crystallises

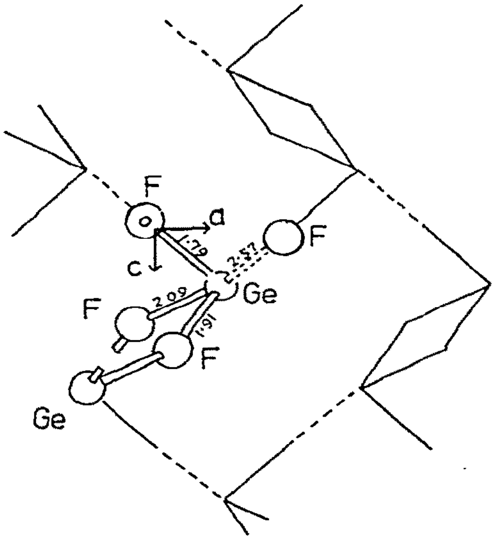


Fig. 1. Projection of the structure of GeF_2 along the *b* axis. (Reproduced by permission of the Chem. Soc.)

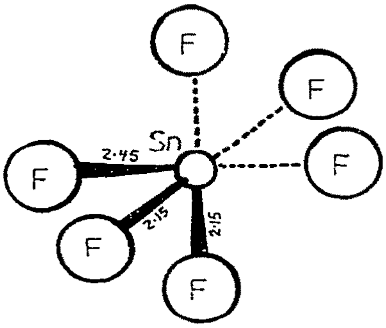
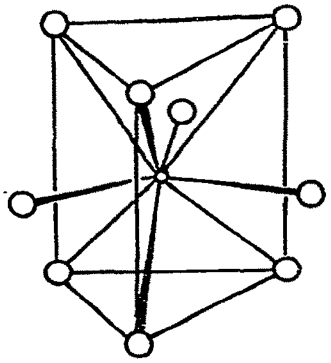


Fig. 2. The environment of the tin atoms in orthorhombic SnF_2. (Reproduced by permission of Pergamon Press.)

in both monoclinic and orthorhombic modifications [4]. The lattice of the former modification has been partly elucidated by Bergerhoff [5]. The unit cell contains sixteen formula units of SnF_2 and the tin atoms occupy three crystallographically different sites. The structure of the orthorhombic modification is simpler. The tin atoms have a trigonal pyramidal coordination with two short (2.15 Å) and one longer (2.45 Å) Sn—F bond distances and bond angles in the range 83.3—93.3°, similar to that in germanium(II) fluoride. However, in tin(II) fluoride, three longer (>2.80 Å) tin—fluorine interactions complete a distorted octahedral arrangement of fluorine atoms around the tin (Fig. 2) [6]. At normal temperatures lead(II) fluoride crystallises with the cubic fluorite lattice [7], but also forms a higher temperature orthorhombic modification with the $PbCl_2$ lattice, as do $SnCl_2$, $SnBr_2$ and $PbBr_2$ [8]. In this lattice, the metal atom is surrounded by nine halogen atoms for three different layers (Fig. 3). Six of the halogen atoms occupy apical positions of a trigonal prism about the metal, whilst a further three are disposed beyond the centres of the three prism faces. Examination of the available bond parameter data for $SnCl_2$ [9] and $PbCl_2$ [8] reveals that again the principal unit in the structure is the MX_3 trigonal pyramid. Figure 4 shows a projection of the structure of $SnCl_2$ along [001]. The tin atom at $z = 1/4$ has three chlorine neighbours in the same plane at distances of 3.22, 2.66 and 3.30 Å. The chlorine atoms at the apices of the trigonal prism are located in the planes $z = 3/4$ (shaded atoms) and $z = -1/4$ at distances of 2.78, 3.06 and 3.86 Å. The metal therefore forms three fairly strong, four medium, and two weak interactions [9]. The mixed halides SnICl, SnBrCl [10], PbClBr, PbClI and



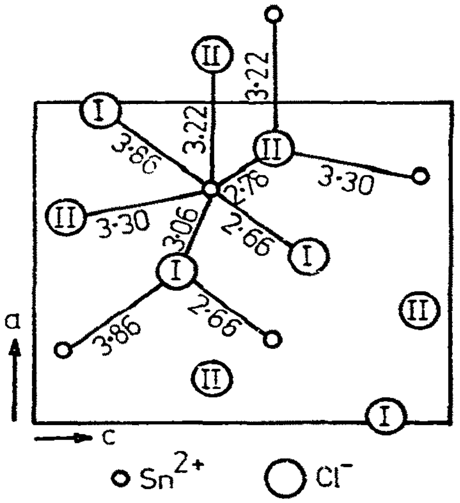
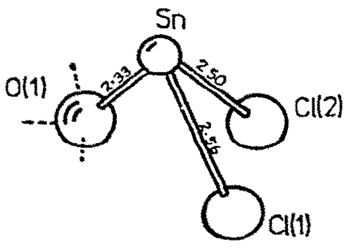


Fig. 3. Coordination of the metal in the $PbCl_2$-type lattice.

Fig. 4. Projection of the structure of $SnCl_2$ along [001]. (Reproduced by permission from ref. 9).

PbBrI [11] are isomorphous with $SnCl_2$ and $PbCl_2$, but no information is available concerning the distribution of the halogen atoms in the lattice. PbFCl, in contrast, forms a tetragonal layer lattice in which lead atoms are located between the layers of the two halogen atoms of different size in the sequence —Cl—Pb—F—Pb—Cl. Again the lead atoms form contacts with nine halogen atoms [8]. In the mixed tin(II) chloride fluoride, Sn_2F_3Cl, pyramidal $[SnF_3]$ groups are linked through common fluorine atoms, with chlorine atoms occupying large holes to form a three-dimensional network [12].

The structures of the tin and lead dibromide hydrates, $2\,SnBr_2 \cdot H_2O$ [13], $3\,SnBr_2 \cdot H_2O$ [14], $6\,SnBr_2 \cdot 5\,H_2O$ [15] and $3\,PbBr_2 \cdot 2\,H_2O$ [16], are also based on the trigonal prismatic structure. In all four hydrates, the metal atoms are surrounded by a trigonal prism of bromine atoms, with bromine atoms, water molecules or vacancies in the facially capping sites. Different coordination types may occur in the crystal. Thus in $2\,SnBr_2 \cdot H_2O$ [13], the tin atoms may experience one of three different lattice sites with coordination by eight bromines, seven bromines and a water molecule, or seven bromines. Tin(II) chloride dihydrate has a markedly different structure [17,18]. One of the water molecules is strongly coordinated to the tin atom forming the usual trigonal pyramidal geometry (Fig. 5), whilst the second water molecule is essentially a molecule of crystallisation. In the crystal, $[SnCl_2(OH_2)]$ units form double layers alternating with layers of water of crystallisation which serve to hold the layers of $[SnCl_2(OH_2)]$ units together via strong hydrogen bond formation (Fig. 6). Both kinds of water molecules are linked together by hydrogen bonds of 2.74, 2.79 and 2.80 Å into two-dimensional networks.



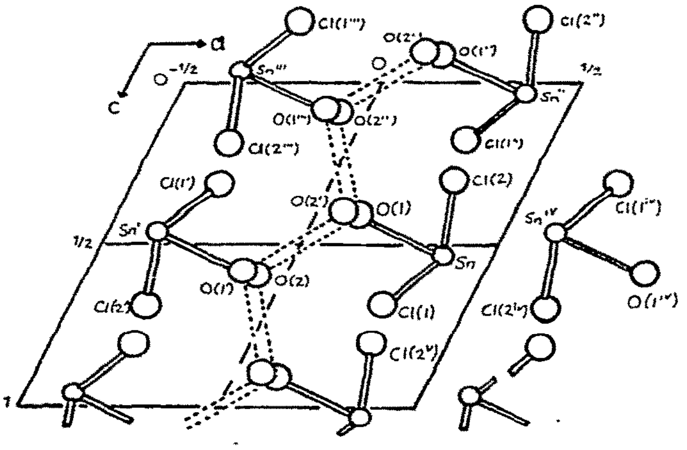


Fig. 5. The geometry of the trigonal pyramid, $[SnCl_2(OH_2)]$, in $SnCl_2 \cdot 2\,H_2O$. (Reproduced by permission of the Chem. Soc. Jpn.)

Fig. 6. The crystal structure of $SnCl_2 \cdot 2\,H_2O$ viewed along the *b* axis. Broken lines indicate hydrogen bonds. (Reproduced by permission of the Chem. Soc. Jpn.)

The structure of laurionite, the basic lead(II) chloride is known and contains lead atoms surrounded by five chlorine atoms at distances of 3.112—3.344 Å and four hydroxyl groups at 2.355—2.441 Å. The coordination polyhedron may be considered as a strongly distorted square antiprism, and is not isotypic with $PbCl_2$ as previously thought [19,20].

Germanium(II) and lead(II) iodides possess the hexagonal anti-CdI_2 lattice, in which the metal atom is surrounded octahedrally by six iodine neighbours [21]. However, both compounds exhibit a large number of modifications of this basic structure which differ in the layer sequence [22]. Crystals of tin(II) iodide are monoclinic and possess a unique layer lattice with the metal atoms occupying two distinct sites. Two-thirds of the tin atoms occupy sites based on the trigonal prismatic structure of $PbCl_2$. These tin atoms occur as symmetry-related pairs (Fig. 7), each metal atom being coordinated by six iodine atoms at the apices of the prism, and also by a seventh from the symmetry-related prism in a facial position. The remaining tin atoms are in $PdCl_2$-type chains which interlock with the $PbCl_2$-type part of the structure to give almost perfectly octahedral coordination (Fig. 8) [23,24].

Germanium(II), tin(II) and lead(II) halides are good Lewis acids and readily form complexes with donor molecules and accept further halide ion to form complex halogenometal(II) anions. Although a large number of complexes of the type $MX_2 \cdot L$ (M = Ge, Sn; X = halogen; L = oxygen or nitrogen donor ligand) are known, the structure of only one, the *N*-methylbenzimidazole complex of germanium(II) chloride has been determined. The complex is monomeric, and the germanium atom enjoys pyramidal coordination (bond angles at germanium = 91.6, 91.8 and 96.4°) forming bonds to both chlorine atoms (Ge—Cl = 2.258 Å) and the ring nitrogen atom (Ge—N =

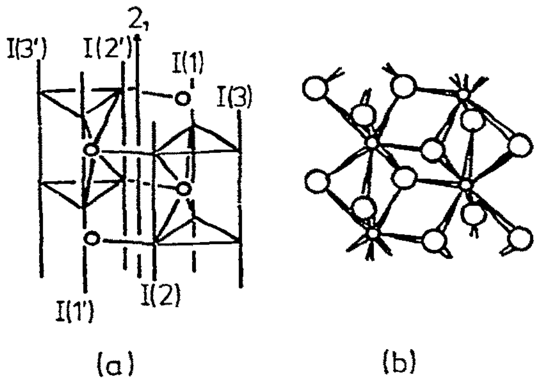


Fig. 7. The coordination of Sn(II) in SnI_2 (trigonal prismatic sites). (Reproduced by permission from ref. 24.)

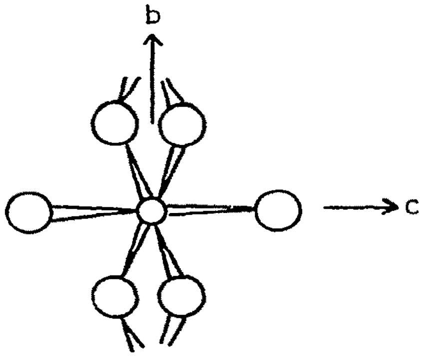


Fig. 8. Coordination of Sn(I) in SnI_2 (octahedral sites). (Reproduced by permission from ref. 24.)

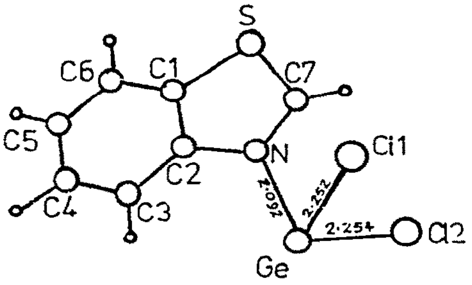


Fig. 9. The structure of the *N*-methylbenzimidazole complex of $GeCl_2$. (Reproduced by permission from ref. 25.)

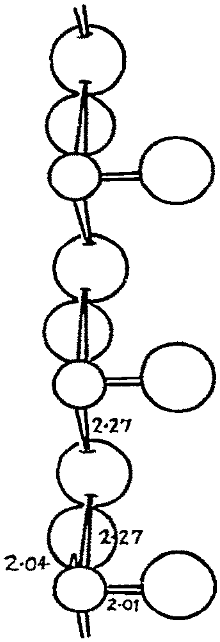


Fig. 10. $[SnF_3]_\infty^{\infty-}$ chains in $KSnF_3 \cdot \frac{1}{2}H_2O$. (Reproduced by permission from ref. 38.)

2.092 Å) (Fig. 9) [25]. The caesium salts of the trishalogenometal(II) anions exhibit interesting electrical properties, and much crystal data are available. All the materials so far investigated exhibit high temperature structures with the perovskite lattice, although low temperature phases of lower symmetry have also been characterised for several materials. Both high and low temperature modifications (transition temperature = 155°) of caesium trichlorogermanate(II) have been subjected to a single-crystal study [26]. The high temperature form has an ideal perovskite lattice with the germanium atom octahedrally coordinated by six chlorine atoms at a Ge—Cl distance of 2.74 Å. Below 155° the lattice becomes rhombohedral, and the germanium now forms three short (2.318 Å) and three long (3.127 Å) interactions with the chlorine atoms. X-ray powder data show that $CsSnX_3$ (X = Cl, Br) [27], $CsPbX_3$ (X = Cl, Pb) [28] and the mixed phases $CsSnBr_nCl_{3-n}$ (n = 2.7, 2.3, 2.1, 1.5, 1) [27] also have (high temperature) cubic perovskite lattices. The corresponding iodides $CsMI_3$ (M = Sn, Pb) [29] exhibit high temperature black forms (tetragonal for M = Pb) [30] and yellow, low temperature orthorhombic modifications with very similar unit cell dimension indicating probable isostructurallity. The complete structure of orthorhombic $RbSnI_3$, which is isomorphous with the caesium salt, is known, and contains nearly octahedrally coordinated lead, indicating that the lead(II) lone pair of electrons is stereochemically inactive. The [PbI_6] octahedra are arranged in the form of double chains along the crystal *c*-axis, which are held together by rubidium atoms [31]. The mixed salts CsSnClBrI, CsSnClIF and CsSnIBrF possess distorted perovskite lattices [29]. Both ideal perovskite and non-cubic phases in which there is a random distribution of Group IV metal and halide ions have been obtained from the molten systems $CsPbCl_3$—$CsPbBr_3$ and $CsPbCl_nBr_{3-n}$—$CsSnCl_nBr_{3-n}$ [28]. Mössbauer spectra for those phases containing tin exhibit single narrow resonances indicating octahedral coordination of the tin atoms in the lattice. The Group IV metal is obviously stereochemically inactive in the $CsMX_3$ phases possessing the perovskite lattice, and it would seem likely that these electrons populate conduction bands giving rise to the electrical properties and colour (sometimes intense) observed.

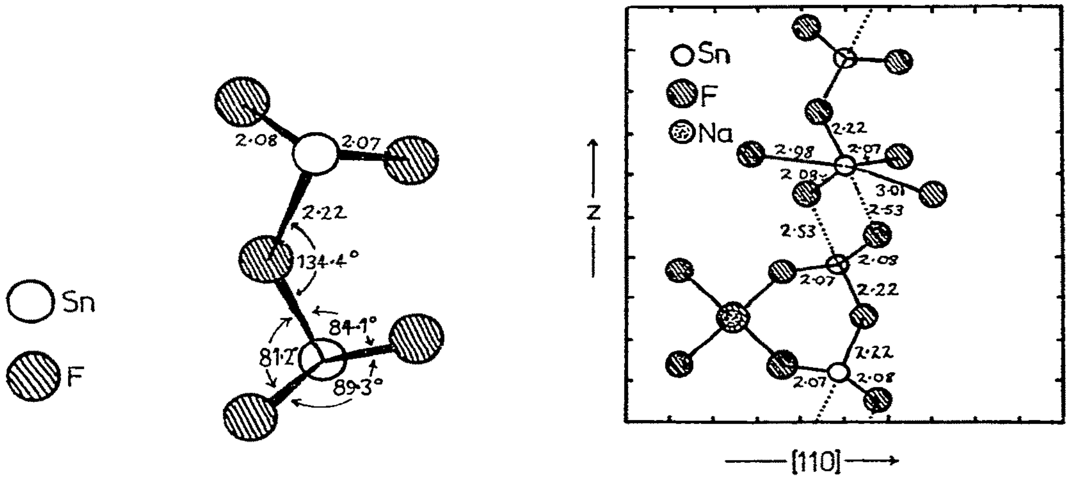
The low temperature modification of $CsSnCl_3$ is monoclinic and contains discrete pyramidal [$SnCl_3$] units packed with caesium atoms to form a layer structure. The material undergoes an irreversible phase transition at ca. 117° to cubic phases [32]. Isolated MX_3^- anions have also been characterised in [$C_{11}H_{17}N_2O_2^+$] [$GeCl_3^-$] · H_2O [33], KCl · $KSnCl_3$ · H_2O [34], the red and green isomeric forms of [$Co(dpe)_2Cl^+$] [$SnCl_3^-$] [35,36], and NH_4SnF_3 [37], and bonding data for these are collected in Table 1. The XMX valence bond angles all fall round about 90°, indicative of essentially p^3 hybridisation for the metal, in which case the lone pair of electrons is located in the *ns* orbital. The M—Cl bond distances of the isolated [MCl_3^-] units in [$C_{11}H_{17}N_2O_2^+$] [$GeCl_3^-$] · H_2O [33] and both forms of [$Co(dpe)_2Cl^+$][$SnCl_3^-$] [36] are identical within experimental error. A similar situation also pertains for

TABLE 1

Bond parameters for complexes containing discrete MX_3^- anions

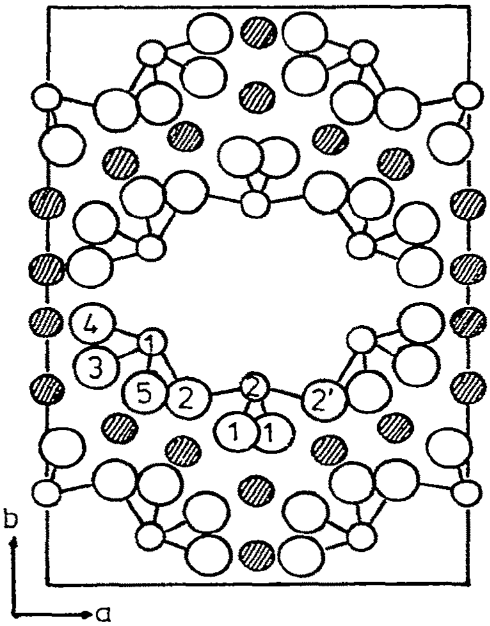
Compound	$\widehat{XMX}$ valence angles (°)	M—X bond distances (Å)	Other non-bonding M—X interactions (Å)
[$C_{11}H_{17}N_2O_2^+$]-[$GeCl_3^-$]H_2O [29]			
Molecule 1	95.6; 96.2; 95.0	2.268; 2.275; 2.277	
Molecule 2	96.1; 97.0; 96.4	2.285; 2.261; 2.289	
$CsSnCl_3$ [28]	86.9; 92.3; 90.2	2.50; 2.52; 2.55	3.21; 3.45; 3.77
KCl · $KSnCl_3$ H_2O [30]	87.7; 87.7; 90.8	2.54; 2.54; 2.63	
[$Co(dpe)_2Cl$]-$SnCl_3$ [32]			
Red isomer	94.8; 93.9; 94.6	2.440; 2.445; 2.447	
Green isomer	91.4; 96.2; 93.5	2.437; 2.429; 2.425	
NH_4SnF_3 [33]	83.1; 85.3; 85.9	2.10; 2.21; 2.05	2.89; 2.71; 2.83

$CsSnCl_3$ [32], although in this case, three additional (non-bonding) Sn—Cl contacts are found at distances of 3.21, 3.45 and 3.77 Å. However, in the $SnCl_3^-$ anion in $KCl \cdot KSnCl_3 \cdot H_2O$ [30] (the least accurate determination, and no estimated standard deviations are quoted), one chlorine occurs at a significantly longer distance (2.63 Å) than the other two (2.54 Å). The structure of NH_4SnF_3 consists of NH_4^+ and pyramidal SnF_3^- ions (Sn—F = 2.10(14), 2.21(14) and 2.05(14) Å) connected by one quadrifurcated and three normal hydrogen bonds to give a three-dimensional framework. As in $CsSnCl_3$ [32], distorted octahedral coordination at tin is completed by three additional long Sn—F contacts at 2.89, 2.71 and 2.83 Å [37]. In the potassium salt, $KSnF_3 \cdot 1/2\,H_2O$ [38], the fluorine bridging is much stronger, and the structure consists of infinite $[SnF_3]_\infty^{\infty-}$ chains parallel to the *c*-axis (Fig. 10). Each tin atom forms two long bonds (2.27 Å) to two bridging fluorine atoms within the —Sn—F—Sn—F— chain, and two short (2.01, 2.04 Å) to non-bridging fluorines in a distorted pseudo-trigonal pipyramidal arrangement [F_{eq}—Sn—F_{eq} = 89.7°; F_{ax}—Sn—F_{ax} = 156°], the lone pair occupying the remaining equatorial site. The geometry of the homologous $Sn_2F_5^-$ complex anion is shown in Fig. 11(a), and the bonding parameters indicate that it is best considered as two [SnF_3] units sharing one fluorine atom, although a fourth fluorine is found at a distance of only 2.53 Å from the tin resulting in infinite chains of $[Sn_2F_5]_\infty^{\infty-}$ parallel to the *c*-axis (Fig. 11(b)) [39]. The structure of the [$Sn_3F_{10}^{4-}$] anion in $Na_4Sn_3F_{10}$ [40] (Fig. 12) consists of three connected distorted [SnF_4] tetragonal pyramids similar to those found in $KSnF_3 \cdot 1/2\,H_2O$ [38]. A rather old paper refers to X-ray diffraction



(a) (b)

Fig. 11. (a) The geometry of the [$Sn_2F_5^-$] complex ion. (b) A portion of the unit cell of $NaSn_2F_5$ as viewed along [110]. (Reproduced by permission from ref. 39.)



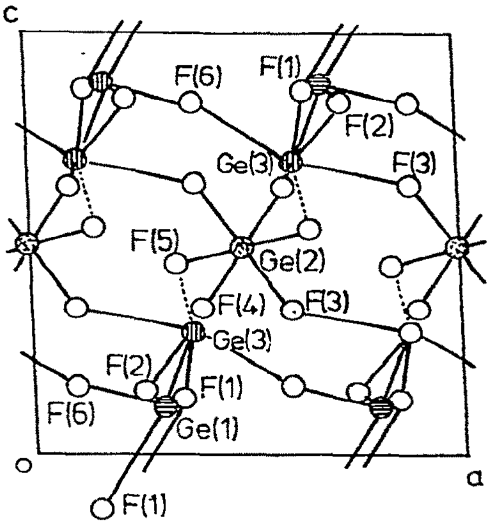
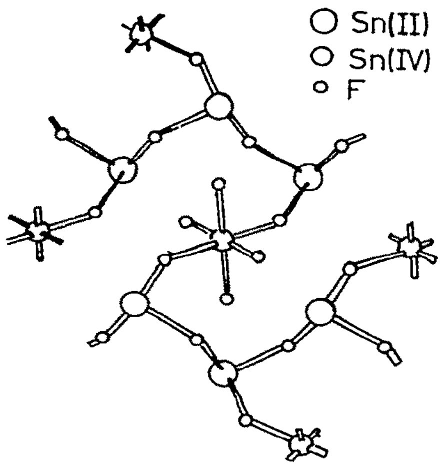


Fig. 12. Projection of $Na_4Sn_3F_{10}$ along the *c* axis. (Reproduced by permission from ref. 40.)

Fig. 13. Crystal structure of Ge_5F_{12} as viewed down the *b* axis. (Reproduced by permission of the Am. Chem. Soc.)

studies of the $M^IPb_2Br_5$ ($M^I = NH_4$, Rb, K) salts [41]. Whilst the data are most probably unreliable, the three complexes are isomorphous, and each lead has two nearest neighbours at 2.89(5) Å, two at 3.16(5) Å and four at 3.35(5) Å.

Cationic halogenotin(II) species are much rarer. Indeed, no discrete mononuclear cations have as yet been characterised in the solid phase, although cations of the type SnX^+ (X = F, Cl, Br) have been discerned in solution [42]. The mixed valence germanium(II,IV) fluoride, Ge_2F_{12} [43], contains two crystallographically distinct bivalent germanium atoms each having very similar geometry. The whole structure is built up by means of fluorine bridging between germanium atoms in the two valence states (Fig. 13). The stereochemistry at the two bivalent germanium atoms is that of a distorted square pyramid, and is very similar to that in germanium(II) fluoride itself [3], $KSnF_3 \cdot 1/2\,H_2O$ [38], and $Na_4Sn_3F_{10}$ [36]. Polymeric cationic fluorotin(II) networks have been characterised in the mixed-valence tin fluoride, Sn_3F_8 [44], and tritin(II) bromide pentafluoride [45], the structures of which are illustrated in Figs. 14 and 15, respectively. In both compounds, the tin(II) atoms enjoy pyramidal coordination with FSnF bond angles in the range 74.9—88.4°. In Sn_3F_8, all three fluorine atoms bound to bivalent tin form



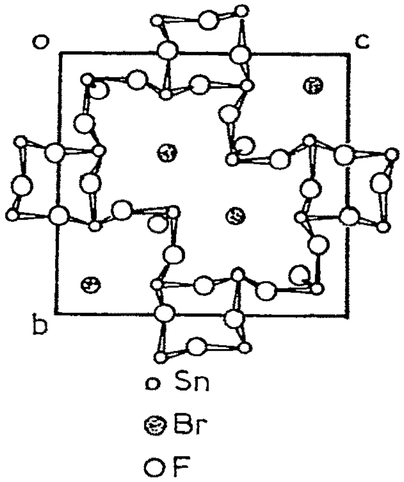


Fig. 14. The structure of Sn_3F_8. (Reproduced by permission of the Chem. Soc.)

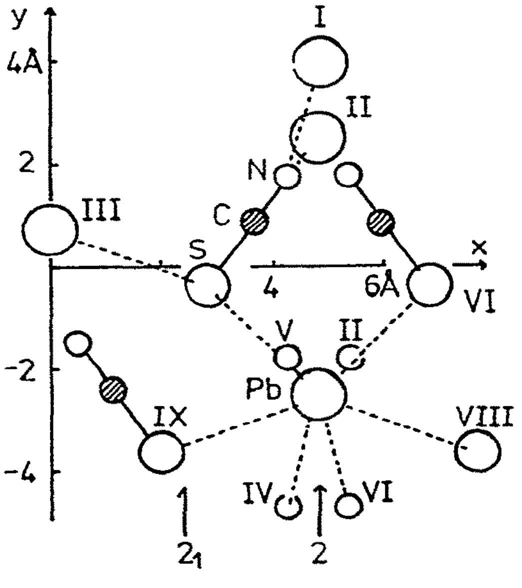
Fig. 15. Projection of the structure of Sn_3BrF_5 along [100]. (Reproduced by permission of the Chem. Soc.)

bridges to other tin atoms; two to other tin(II) atoms at Sn(II)—F bond distances of 2.10 and 2.17 Å, and one to the tin(IV) atom at the longer Sn(II)—F distance of 2.25 Å. The tin(IV) atom is octahedrally coordinated with the Sn(IV)—F distances falling in the range 1.95—1.98 Å, and the compound is essentially $[Sn_2^{II}F_2^+][Sn^{IV}F_6^-]$ [44]. The three tin(II) atoms of Sn_3BrF_5 are inequivalent. Two are bonded to three bridging fluorine atoms at Sn(II)—F distances in the range 2.11(5)—2.21(5) Å, whilst the third is bonded to two bridging fluorine atoms at distances of 2.12(5) and 2.15(5) Å and a terminal fluorine atom at a distance of 1.99 Å. All tin—bromine distances are considerably in excess of the sum of the ionic radii, and are therefore 'isolated' [45].

C. PSEUDO-HALIDE DERIVATIVES

Remarkably little structural data are available for pseudo-halide derivatives of bivalent germanium, tin and lead. Unit cell data are known for tin(II) thiocyanate (triclinic) and $KSn(SO_4)NCS$ (orthorhombic) from single crystal work [46]. Infrared studies indicate Sn—NCS bonding for both, although extensive bridging was thought to occur in $Sn(NCS)_2$ analogous to that found in lead(II) thiocyanate, the full structure of which has been determined [47,48]. Crystals of the latter consist of an infinite array of Pb^{2+} and NCS^- ions. Both the Pb—S and Pb—N bond distances [Pb—N: 2.687(7), 2.781(7) Å; Pb—S: 2.996, 3.135(2) Å] exceed the Pauling covalent radii (Pb—N: 2.28 Å; Pb—S: 2.62 Å), and therefore have very little covalent character. The lead atom lies on a two-fold axis, and is surrounded in an irregular way by four nitrogen and four sulphur atoms from eight thiocyanate groups. The thiocyanate groups deviate little from linearity, and make contact with two lead atoms at each end (Fig. 16).

The structures of two complexes of lead(II) thiocyanate with multidentate macrocyclic ligands have also been determined. Both the thiocyanate groups in the 1,7,10-tetraoxa-4,3-diaza-cyclooctadecane complex of lead(II) thiocyanate are bonded via sulphur to lead, which lies in the plane of the four oxygen atoms of the ring. The interactions of the lead with the oxygen and nitrogen atoms are essentially electrostatic in character [Pb—N = 2.751(6) Å; Pb—O = 2.787(4), 2.879(5) Å], whereas the Pb—S bonds (2.894(3) Å), which are shorter than those in lead(II) thiocyanate itself, may be considered to have covalent character (Fig. 17) [49]. The structure of the lead cryptate, $(C_{18}H_{36}N_2O_6)Pb(SCN)_2$, also consists of discrete molecules (Fig. 18), in which the lead atom occupies a central position in the cavity of the macrocyclic ligand. One SCN group is attached via the sulphur at a distance of 3.121(3) Å, whilst the other is bonded via the nitrogen atom (2.642(10) Å). Ten-coordination at each lead atom is completed by additional interactions with the six oxygen and two nitrogen atoms of the cryptate [Pb—N 2.858(9), 2.909(9); Pb—O 2.729(7)—2.980(8) Å] [50].



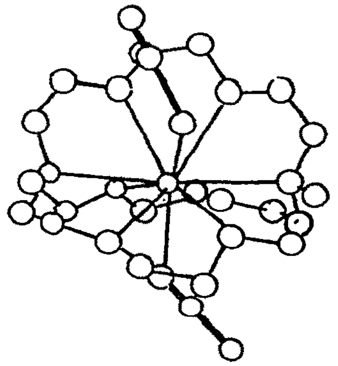


Fig. 16. The main features of the structure of $Pb(NCS)_2$. (Reproduced by permission from ref. 48.)

Fig. 17. The coordination of the lead atoms in $(C_{12}H_{26}N_2O_4)Pb(SCN)_2$. (Reproduced by permission from ref. 49.)

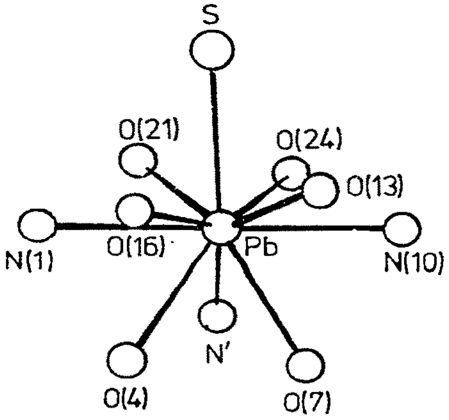


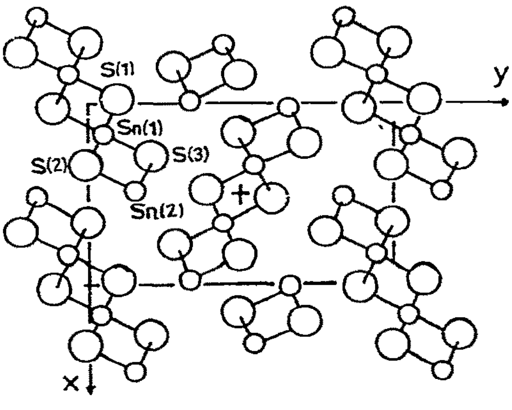
Fig. 18. Coordination of the lead atom in $(C_{18}H_{36}O_2N_6)Pb(SCN)_2$. (Reproduced by permission of the Am. Chem. Soc.)

D. CHALCOGENIDE LATTICES

Structural information for all the normal binary chalcogenide compounds of germanium, tin and lead is available with the exceptions of germanium(II) oxide and telluride. Tin(II) and lead(II) oxides both possess tetragonal lattices in which the metal sits at the apex of a distorted square pyramid of oxygen atoms (Sn—O 2.21(1) Å; Pb—O 2.30(1) Å; $\widehat{OMO}$ 75(4), 118(2)°) [51]. A second orthorhombic phase of PbO has been characterised by neutron diffraction [52,53]. Germanium(II) sulphide [54] and selenide [55,56] are also orthorhombic with distorted NaCl-type lattices. Ge—S bond distances vary from 2.47 to 3.00 Å (mean 2.78 Å). Tin(II) sulphide has a structure with parallel zig-zag —Sn—S—Sn—S— chains (Sn—S 2.68 Å), which are connected by short (2.62 Å) inter-chain tin—sulphur contacts. The next shortest Sn—S interactions are at 3.27 Å. The basic $[SnS_3]$ unit is pyramidal, with $\widehat{SSnS}$ bond angles of 88(2) and 96(2)° [57]. Tin(II) selenide possesses one phase which is isomorphous with the sulphide (Sn—Se 2.77, 2.82 Å; $\widehat{SeSnSe}$ 89(2), 96(2)°) [58], and a second cubic phase with the NaCl lattice (Sn—Se 3.00 Å) [59]. Tin(II) telluride [59], and lead(II) sulphide [59,60], selenide [59,61] and telluride [59,62] also have the NaCl structure [Sn—Te 3.14 Å; Pb—S 2.962 Å; Pb—Se 3.06 Å; Pb—Te 3.22 Å].

Although the mixed-valence oxides, Sn_2O_3 [63,64] and Pb_2O_3 [65], are definite compositions, their structures are unknown. However, those of the red modification of Pb_3O_4 [66] and of the mixed-valence tin sulphide, Sn_2S_3 [67], have been determined. In both materials the tetravalent metal atoms experience octahedral coordination forming chains of $[M^{IV}X_6]$ octahedra sharing a common edge. In Pb_3O_4 [66], such chains are connected by bivalent lead atoms which enjoy pyramidal coordination by three oxygen atoms at distances of 2.13 and 2.23 Å. Similar pyramidal coordination of the bivalent tin atoms also occurs in Sn_2S_3 [67] (Sn—S 2.644, 2.741 Å; $\widehat{SSnS}$ 83.5, 90.2°), but in this case the inter chain Sn—S interactions are very weak (3.152, 3.652 Å) (Fig. 19).

Tin and lead form a large number of double and multiple oxides and sulphides. The ternary lead oxides, $PbMO_3$ (M = Ti, Zr, Hf) all have the tetragonal perovskite lattice with one formula per unit cell [68,69]. β-$SnWO_4$ is cubic and the tin atoms have usual pyramidal $[SnO_3]$ geometry with three short Sn—O bonds (2.214(5) Å) and OSnO angles of 82.4°. Distorted octahedral coordination at tin is completed by three additional oxygen atoms 2.810(15) Å distant [70]. $PbWO_4$ (stultzite) and $PbMoO_4$ (wulfenite) possess the scheelite ($CaWO_4$) structure [71]. $PbCrO_4$ exists in monoclinic and orthorhombic modifications. In monoclinic $PbCrO_4$ (crocoite), lead is coordinated by ten oxygen atoms from seven $[CrO_4]$ tetrahedra at distances of 2.53—3.44 Å [72]. Orthorhombic $PbCrO_4$ is isomorphous with $PbSO_4$, and the lead atoms are surrounded by twelve oxygens at 2.64—3.57 Å [73]. $PbSeO_4$ is of the monacite ($CePO_4$) type [74]. $PbUO_4$ is not a true uranate, but rather its constitution is $Pb(UO_2)O_2$ and exhibits cubic and orthorhombic modifications. In the latter, the lead atoms are held in distorted eight-coordination between layers of composition $[(UO_2)O_2]^{2-}_{\infty}$ [75]. $SnPb_2O_4$ is tetragonal and isomorphous with Pb_3O_4 [76]. Orthorhombic Na_2PbO_2 has a layer lattice with the sequence $(Na_{1/2}Pb_{1/2})ONaO(Na_{1/2}Pb_{1/2})\cdots(Na_{1/2}Pb_{1/2})$-$ONaO(Na_{1/2}Pb_{1/2})$ [77]. The analogous silver salt, Ag_2PbO_2, is composed of infinite $[PbO_2^{2-}]_{\infty}$ chains linked together by silver atoms, thus forming a three-dimensional network [78]. $PbAs_2O_6$ has a trigonal lattice based on hexagonal



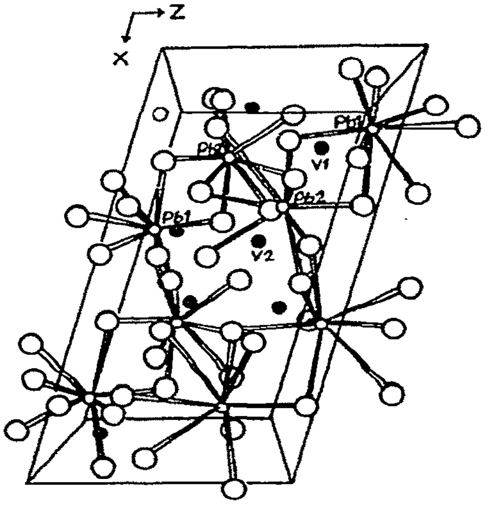


Fig. 19. The structure of Sn_2S_3. (Reproduced by permission from ref. 67.)

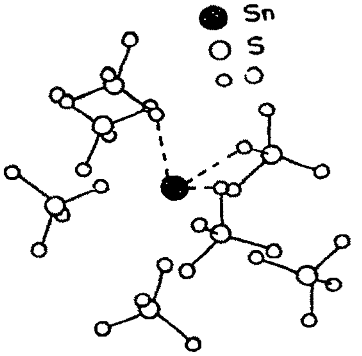
Fig. 20. Projection of $Pb_2V_2O_7$ along the *b* axis showing only Pb—O bonds. (Reproduced by permission from ref. 84.)

close packing of oxygen atoms with both cations in octahedral cavities [79]. Crystals of PbV_2O_6 [80] and $PbTi_3O_7$ [81] contain distorted corner and/or edge-sharing [MO_6] (M = V, Ti) octahedra. Oxygen atoms from these groups coordinate lead atoms in irregular seven- and nine-fold manners, respectively, at Pb—O distances ranging from 2.36 to 3.04 Å (Ti) and from 2.56 to 2.90 Å (V). Quenselite, $PbMnO_2(OH)$, has a structure based on hexagonal close packed oxygen layers stacked normal to [001], with lead ions nearly occupying anion sites. Layers of distorted [MnO_6] octahedra parallel to [001] sandwich infinite chains of [$PbO(OH)_3$] tetragonal pyramids (Pb—O 2.22(2) Å; Pb—OH 2.31(2), 2.37(2), 2.76(2) Å) resembling those in orthorhombic PbO [82]. The structures of both natural [83] and synthetic [84] chervetite, $Pb_2V_2O_7$, have been determined. Two types of lead(II) ion are irregularly coordinated by eight or nine oxygen atoms from [$V_2O_7^{4-}$] ions at distances of 2.40—3.20 Å (Fig. 20). Dilead pentaoxochromate(VI), Pb_2CrO_5 is isomorphous with the sulphur and selenium analogues, but the positions of only the lead and chromium atoms in the monoclinic lattice are known [85]. Natural barysilite is not $Pb_3Si_2O_7$ as first thought, but rather $MnPb_8(Si_2O_7)_3$. In this lattice, lead atoms are pyramidally coordinated by three oxygen atoms and thus connect three [Si_2O_7] double tetrahedra. Other lead atoms are irregularly coordinated [86]. The structure of synthetic barysilite, $Pb_3Si_2O_7$, is built up of isolated [Si_2O_7] double tetrahedra linked by some of the lead atoms which have pyramidal coordination, the remainder being located in channels parallel to the *c* axis [87]. Potassium lead pyrosilicate, $K_2Pb_2Si_2O_7$, has a similar structure, with layers of lead-bridged [$Si_2O_7^{6-}$] ions connected by potassium ions [88]. The europium lead silicate, $Er_4PbSi_5O_7$, contains both [$Si_3O_{10}^{8-}$] and [$Si_2O_7^{6-}$] anions. Lead enjoys distorted five-fold pyramidal coordination with Pb—O bond distances in the range 2.40(4)—2.51(4) Å [89]. $Pb_5(VO_4)_3Cl$ (vanadinite) [90]. $Pb_5(AsO_4)_3Cl$ (mimitesite) [90], and $Pb_5(GeO_4)(MO_4)_2$ (M = P, V) [91] all have the hexagonal apatite [$Ca_5(PO_4)_3F$] lattice. $Pb_5(AsO_3)_3Cl$ has a similar structure consisting of [AsO_3] pyramids packed with Pb^{2+} and Cl^- ions [92].

The structures of several mineral lead sulphosalts have been determined In these the coordination of lead by sulphur is highly variable and irregular. Both $BaSnS_2$ [93] and $PbSnS_2$ (teallite) [57] have distorted NaCl-type lattices. The tin atoms in the former compound occupy octahedral sites, but displaced to one of the triangular faces of the [S_6] octahedra so forming three short [2.577(6), 2.580(6) and 2.612(6) Å] and three much longer [3.586—3.786 Å] contacts [93]. $PbGeS_3$ consists of [GeS_4] tetrahedra linked to form infinite $[GeS_3]_n^{2n-}$ chains. The coordination sphere of the lead atoms is occupied by five sulphur atoms at distances of between 2.736 and 3.016 Å in a distorted square pyramidal arrangement, with the lone pair occupying the sixth octahedral site [94]. Baumhauerite, $Pb_5As_8S_{18}$, has an extremely complex structure containing pyramidal [AsS_3] units, in which one kind of lead is pyramidally coordinated whilst the others are located in octahedral sites [95]. The lead atoms in marrite, $AgPbAsS_3$ [96], a monoclinic sister structure of galenite, PbS, freieslebenite, $PbAgSbS_3$ [97], a superstructure of the PbS-type, and diaphonite, $Ag_3Pb_2Sb_3S_8$ [98], which has a lattice based on cubic closest packing of sulphur atoms, are also arranged in octahedral cavities. $PbCuAsS_3$ and $PbCuSnS_3$ (bourbonite) possess complicated rhombohedral lattices [99,100], but in aikinite, $PbCuBiS_3$, each lead atom is coordinated by five sulphur atoms at distances of 2.84—2.98 Å, with two additional sulphur atoms at 3.24 Å [101]. The lead atoms in galenobismuthite, $PbBi_2S_4$, are surrounded by seven sulphur atoms at distances of 2.85—3.21 Å, with one additional very long contact at 3.76 Å [102]. The lead atoms in galenobismuthite, $PbBi_2S_4$, are surrounded by seven sulphur atoms at distances of 2.85—3.21 Å, with one additional very long contact at 3.76 Å [102]. Cosalite, $Pb_2Bi_2S_5$, has two lead atoms in the unit cell with distorted octahedral coordination and two which are eight-coordinated with sulphur atoms at the apices of a trigonal prism with two additional sulphur atoms located in facial sites. The Pb—S distances fall in the range 2.72—3.47 Å [103]. Fülöppite, $Pb_3Sb_8S_{15}$, the first member of the plagionite, $Pb_{3+2n}Sb_8S_{15+2n}$, group, consists of two kinds of interleaving and interlocking Pb—Sb—S complex of composition $[Pb_2Sb_4S_6]$ and $[PbSb_4S_9]$, both parallel to [110]. In these, the lead atoms are irregularly coordinated by six and seven sulphur atoms at distances of 2.76—3.32 Å [104]. In plagionite itself, $Pb_5Sb_8S_{17}$, two lead atoms have six- and seven-fold coordination, respectively, in octahedral-like configurations. A third lead atom is surrounded by eight sulphur atoms in an arrangement which may be described as either a square antiprism or as a trigonal prism with neighbours along two face normals [105]. The first four members of the plagionite group [$n = 1$, plagionite, $Pb_5Sb_8S_{17}$ [106]; $n = 2$, $Pb_7Sb_8S_{19}$, heteromorphite [107]; $n = 3$, $Pb_9Sb_8S_{21}$, serseyite [108]] are all monoclinic, with a and b remaining constant, but c increases with n and β alternates between values of ca. 94° and 107° in successive members. These observations have enabled Kohatsu and Wuensch [109] to predict as yet undetermined structures for other known phases and higher hypothetical members of the series. In zickenite, $Pb_6Sb_{14}S_{27}$, there are three pure [Pb] and one mixed [Sb,Pb] positions. One of the lead sites and the mixed [Sb,Pb] site are eight-coodinated (mean Pb—S 3.14 Å), whilst the other two have nine nearest sulphur neighbours (mean Pb—S 3.23 Å) but are only 20% occupied [110]. Rathite, $(Pb,Tl)_3As_3(As,Ag)S_{10}$, has a layer lattice in which one [Pb,Tl] atom is surrounded by seven sulphur atoms [11]. The structure of jordanite is a deformed PbS-type lattice, and is made up of alternate layers of metal sites [Pb+As] and sulphur atoms. Some metal layers have statistical occupation (i.e. 0.5 Pb + 0.5 As), whilst others are occupied by 0.88 Pb, giving a unit cell content of $Pb_{27.8}As_{12.0}S_{45.8}$ [112].

E. OXYACID DERIVATIVES

The structure of tin(II) sulphate consists of a framework of sulphate groups linked by O—Sn—O bridges. The tin(II) atoms have typical pyramidal coordi-



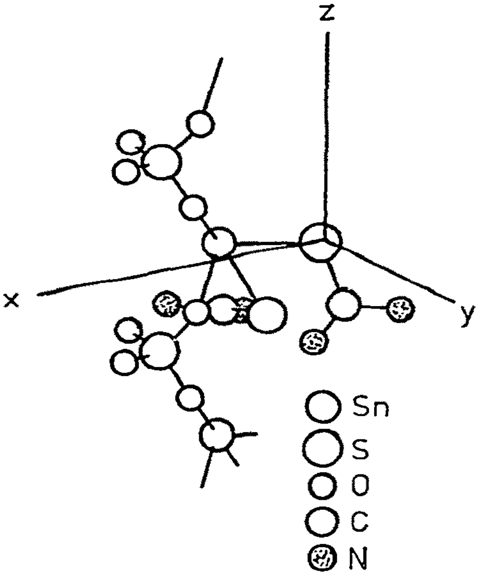


Fig. 21. Structure of $SnSO_4$. (Reproduced by permission from ref. 113.)

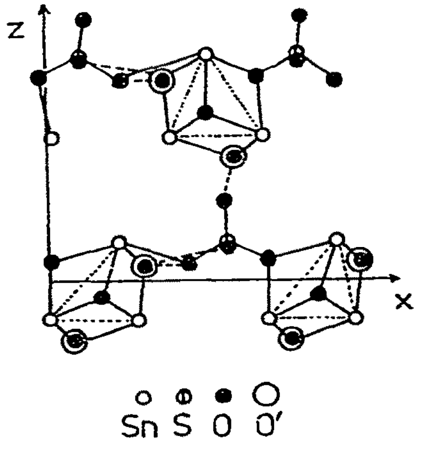
Fig. 22. Structure of $SnSO_4 \cdot 2\,SC(NH_2)_2$. (Reproduced by permission of the Chem. Soc.)

nation with Sn—O bond distances of 2.25—2.27 Å and $O\widehat{Sn}O$ bond angles of 77.1—79.0° (Fig. 21) [113]. In the thiourea complex, $SnSO_4 \cdot 2\,SC(NH_2)_2$, the tin atoms are in distorted pyramidal sites surrounded by two sulphate oxygen atoms at 2.41 and 2.24 Å, and by two thiourea sulphur atoms at 2.62 and 2.56 Å. The planar, but inequivalent, thiourea groups are linked to the sulphate ions by hydrogen bonds (Fig. 22) [114]. The structures of two basic tin(II) sulphates have been investigated. Crystals of Sn_2OSO_4 are tetragonal with eight formula units per unit cell. However, only positions of the tin atoms have been determined [115]. The structure of $Sn_3O(OH)_2SO_4$ is shown in Fig. 23. The three tin atoms form a triangle with one oxygen atom coordinated to all three tin atoms. The two hydroxide ions are each coordinated to two tin atoms. On the third side of the $[Sn_3]$ triangle, a sulphate oxygen atom bridges two tin atoms. Thus, two of the tin atoms are three-coordinated and the third four-coordinated by oxygen atoms. The $[Sn_3]$ triangles form a zig-zag chain running along the *b* axis [116].

Lead(II) sulphate (anglesite) is isomorphous with orthorhombic $BaSO_4$ which has twelve oxygen neighbours [117]. The structures of the mixed lead sulphates, $M^{I}_{2}Pb(SO_4)_2$ (M^I = K [118], NH_4 [119]) consist of layers of lead atoms separated by double layers of sulphate ions held together by M^I ions. The lead atoms enjoy pyramidal coordination in the basic mixed sulphate, $PbCuSO_4(OH)_2$ [120], whilst in lanarkite, $PbO \cdot PbSO_4$, the lead atom is at the apex of an approximate square of oxygen atoms, two of which are from sulphate groups [121]. The two independent lead atoms in 4 PbO · $PbSO_4$ both have distorted tetragonal oxygen coordination similar to that in PbO [122].

Tin(II) nitrate is unknown, but crystals of lead(II) nitrate are cubic with Pb—O distances of 2.805 Å (neutron diffraction study) [123]. The structure of two nitrato-tin(II) compounds have, however, been determined, Ph_3Sn^{IV}-$Sn^{II}(NO_3)$ [124] and (2-aminobenzothiazolato)nitratotin(II) [125]. In the former compound, the tin(II) atom is five-coordinated in an irregular way by four oxygen atoms from two nitrate groups (Sn—O 2.38—2.84 Å) and the tetravalent tin atom (Fig. 24) [124]. Coordination about the tin in (2-aminobenzothiazolato)nitratotin(II) is unusual (Fig. 25). Two nitrate groups chelate the tin, each forming one short (2.50, 2.69 Å) and one long (2.92, 2.82 Å) Sn—O bond. The 2-aminobenzothiazole group is attached via the ring nitrogen atom (Sn—N 2.23 Å), but there is also a short (2.50 Å) interaction between the tin and the phenyl ring of an adjacent 2-aminobenzothiazole molecule [125].

$SnHPO_4$ [126] and $SnHAsO_4$ [127] are isomorphous. The structure of the former compound contains pairs of hydrogen-bonded [HPO_4^{2-}] ions, which lie in sheets parallel to the [100] plane with the tin(II) ions lying midway between the phosphate sheets. Each tin has a total of eight oxygen neighbours, three at an average distances of 2.26 Å, two at an average distance of 2.66 Å, and three at an average distance of 3.27 Å, from six different phosphate ions. The coordination of the tin is shown in Fig. 26 [126]. Tin(II) monofluorophosphate, SnO_3PF, has a very similar structure, in which tin ions also lie midway between sheets of [PO_3F^-] anions. However, tin now has six oxygen and two fluorine neighbours. Three of the oxygens are at short distances



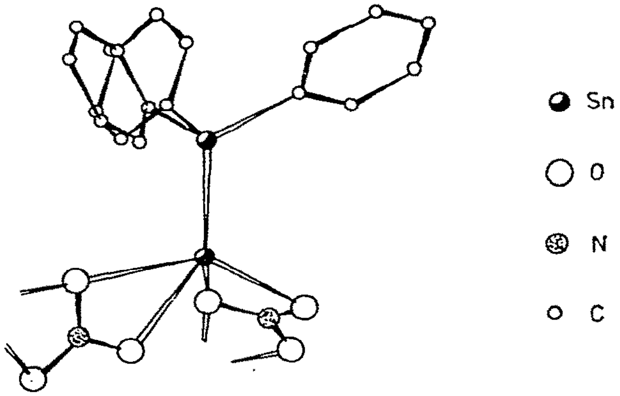
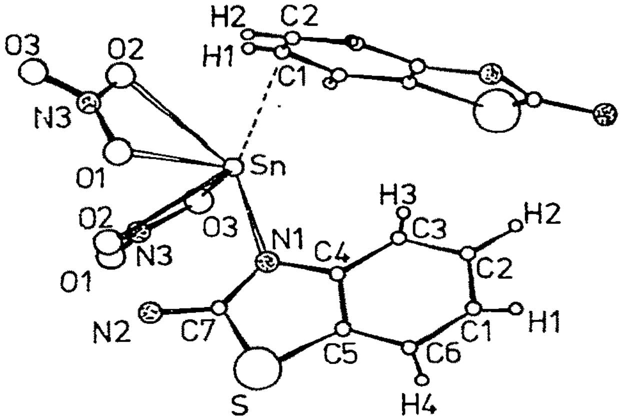


Fig. 23. Structure of $Sn_2O(OH)_2SO_4$. (Reproduced by permission from ref. 116.)

Fig. 24. Structure of $Ph_3Sn^{IV}Sn^{II}NO_3$.



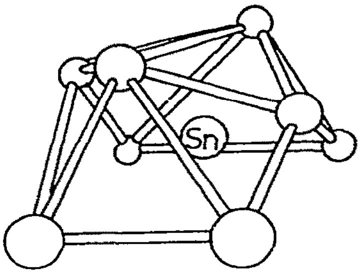
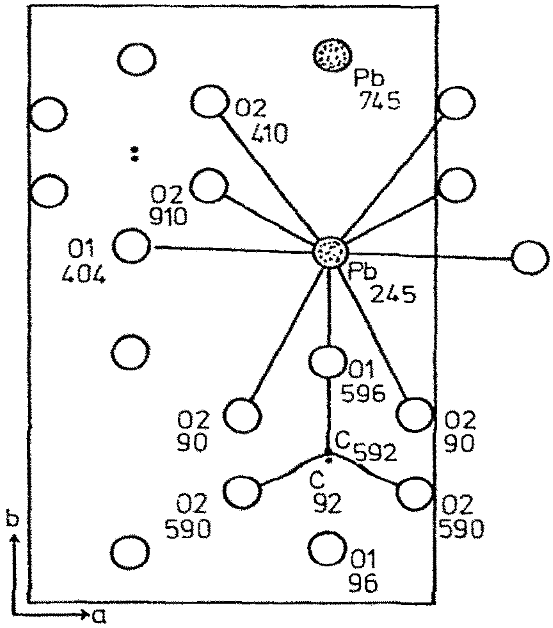


Fig. 25. Projection of the structure of (2-aminobenzothiazolato)nitratotin(II). (Reproduced by permission of the Chem. Soc.)

Fig. 26. The configuration of the oxygen atoms about tin in $SnHPO_4$. (Reproduced by permission from ref. 126.)

(mean 2.15 Å), whilst the other three are at an average distance of 3.49 Å. The two fluorine atoms are at an average distance of 3.49 Å from the tin [128]. Thus, in both materials tin experiences basic typical pyramidal coordination. $Pb_5(PO_4)_3Cl$ (pyromorphite) [90] and $Pb_5(PO_4)_3OH$ [129] both possess the apatite structure. $Pb_3(PO_4)_2$ has a low-temperature monoclinic (α) phase which transforms reversibly at 185° to a rhombohedral (β) phase [130,131]. Both modifications contain two inequivalent lead cations coordinated by tetrahedral $[PO_4^{3-}]$ anions. In α-$Pb_3(PO_4)_2$, one of the lead ions lies on a two-fold axis with distorted octahedral coordination (Pb—O 2.54, 2.59, 2.73 Å). The second lead atom has irregular ten-fold coordination with Pb—O bond distances in the range 2.46—3.37 Å. β-$Pb_3(PO_4)_2$ is isostructural with $Ba_3V_2O_8$ [132], and one lead has six oxygen neighbours at 2.62 Å and six others at 3.21 Å. The second lead ion has six oxygens at 2.83 Å, three at 2.95 Å, and one at 2.37 Å.

The structures of lead(II) carbonate (cerussite) and basic lead(II) carbonate (hydrocerussite) have both been determined. In cerussite [133] the lead atoms are in nine-fold coordination, with one oxygen at 2.62 Å, and two each at 2.66, 2.68, 2.71 and 2.77 Å (Fig. 27). Hydrocerussite [134] is hexagonal, and [PbOH] layers are bounded by CO_3^{2-} and Pb^{2+} ions. Crystals of $[Pb_4(OH)_4]_3(CO_3)(ClO_4)_{10} \cdot 6\,H_2O$ [135] and $[Pb_4(OH)_4](ClO_4)_4 \cdot 2\,H_2O$ [136] both contain discrete $[Pb_4(OH)_4]^{4+}$ ions in which the lead atoms occupy the corners of a slightly distorted tetrahedron with the hydroxide groups located outside the faces of the tetrahedron. The homologous $[Pb_6O(OH)_6^{4+}]$ cation is present in the α- and β-modifications of



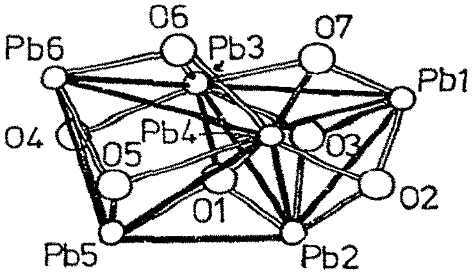


Fig. 27. The coordination of the lead atoms in cerussite, $PbCO_3$. (Reproduced by permission from ref. 133.)

Fig. 28. The structure of the $[Pb_6O(OH)_6^{4+}]$ cation. (Reproduced by permission from ref. 138.)

$[Pb_6O(OH.$ $O_4) \cdot H_2O$ [137,138]. The six lead atoms of this cation occupy the corners of three distorted tetrahedra connected by common faces (Fig. 28). The central tetrahedron contains an oxygen atom at its centre, whilst the outer tetrahedra have one hydroxide oxygen atom outside each of their six unshared faces. Thus tin complex oxo-cation may be considered as arising from two $[Pb_4(OH)_4^{4+}]$ tetrahedra which share a common edge, and in which the two adjacent hydroxyl groups have condensed to a central shared oxide.

F. CARBOXYLATES AND RELATED OXYGEN DERIVATIVES

No structural information is available for simple germanium, tin or lead carboxylates, although potassium tris(formato)stannate(II) contains isolated $[Sn(O_2CH)_3^-]$ anions in typical pyramidal coordination (Sn—O 2.139—2.182 Å) [139]. The structures of three rather sophisticated tin carboxylates, in which the coordination number at tin is six, have been determined. In crystals of dihydrogen ethylenediaminetetra-acetatostannate(II), the tin atom is centred in the rectangular face of a distorted triangular prism, and is coordinated by two nitrogen atoms at 2.338 and 2.442 Å and by four oxygen

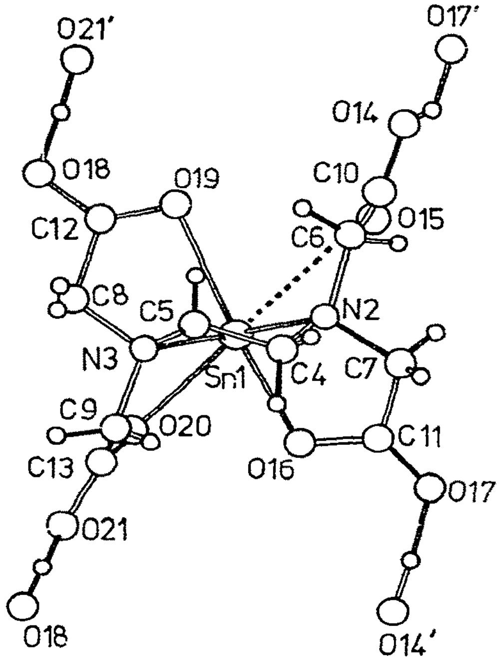


Fig. 29. Structure of dihydrogen ethylenediaminetetraacetatostannate(II). (Reproduced by permission of the Chem. Soc.)

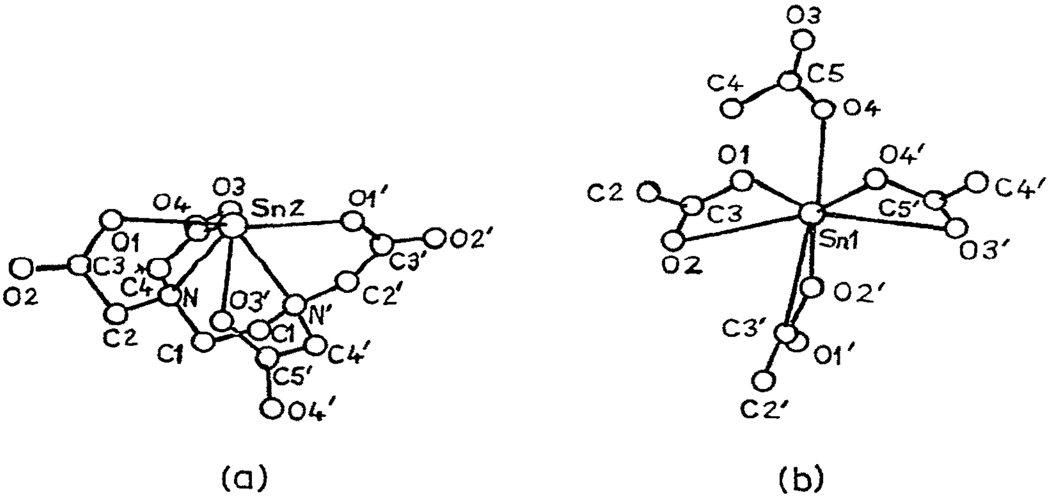


Fig. 30. (a) and (b) Geometry about the two different tin atoms in distannous ethylenediaminetetraacetate. (Reproduced by permission of the Am. Chem. Soc.)

atoms at 2.196, 2.343, 2.635 and 3.057 Å (Fig. 29). Intermolecular hydrogen bonding links carboxy groups from adjacent molecules forming a one-dimensional polymer [140]. Distannous ethylenediaminetetra-acetate dihydrate has a completely different structure in which the two tin atoms are located in different environments. One experiences pseudo-sever coordination in a pentagonal bipyramidal arrangement, with the tin lone pair and the two EDTA nitrogen atoms occupying equatorial positions. The remaining coordination sites are taken by oxygen atoms from the chelating EDTA molecule (Fig. 30(a)). This type of tin is connected to four of the second type by carboxylate bridges. The geometry about this type of tin is irregular and is illustrated in Fig. 30(b). Oxygen atoms from one unidentate and three anisobidentate carboxylate groups are bonded to the metal, and the valence bond angles at tin indicate that the lone pair of electrons is again stereochemically active [141].

Crystals of $[Sn_2(O_2C \cdot C_6H_4 \cdot NO_2\text{-}o)_4O \cdot C_4H_8O]_2$ consist of independent tetranuclear cluster molecules containing two tetravalent and two bivalent tin atoms. The central feature of the macromolecule is a lozenge-shaped four-membered $[Sn_2^{IV}O_2]$ ring. Octahedral coordination at each tin(IV) atom is completed by oxygen atoms from four *ortho*-nitrobenzoate groups, which

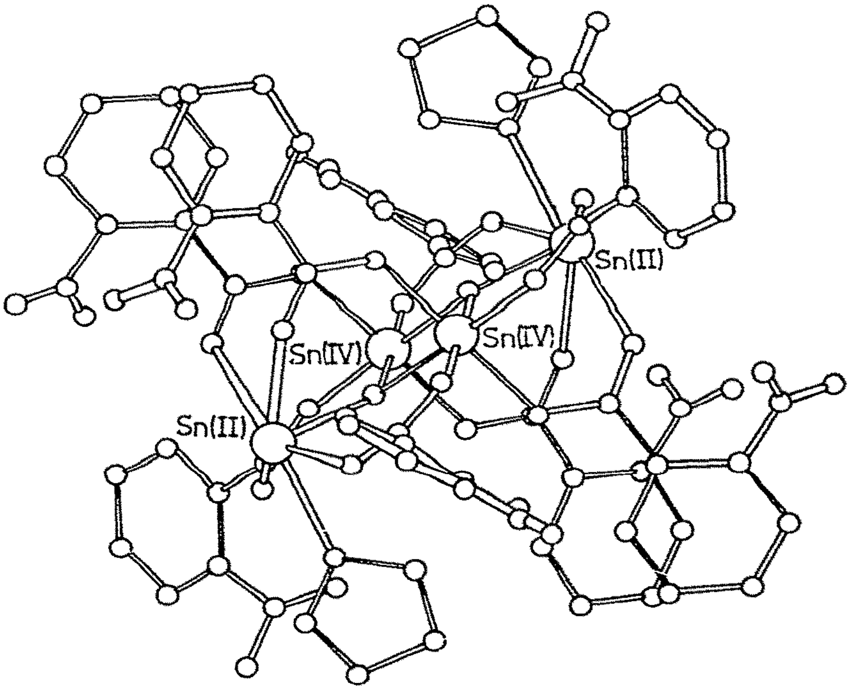


Fig. 31. Structure of $[Sn_2(O_2C.C_6H_4.NO_2\text{-}o)_4O.C_4H_8O]_2$. (Reproduced by permission of the Chem. Soc.)

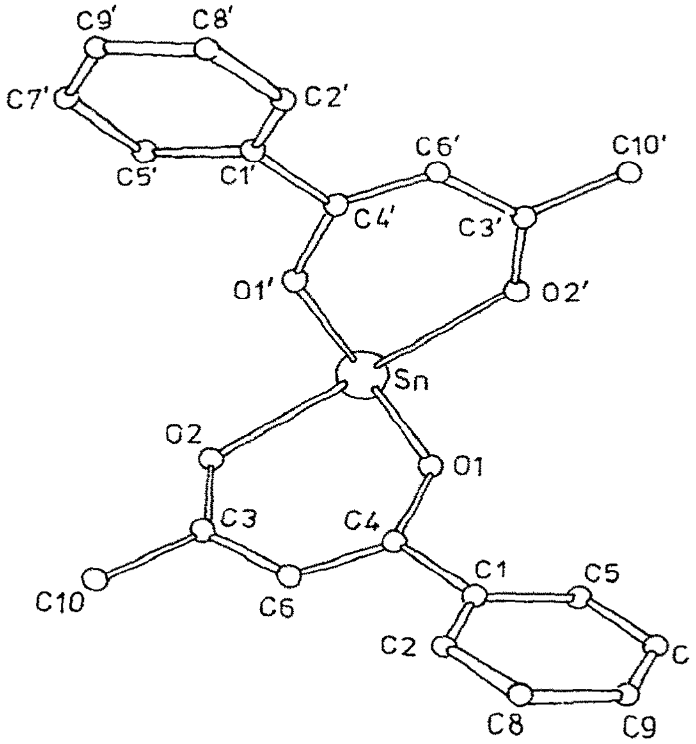


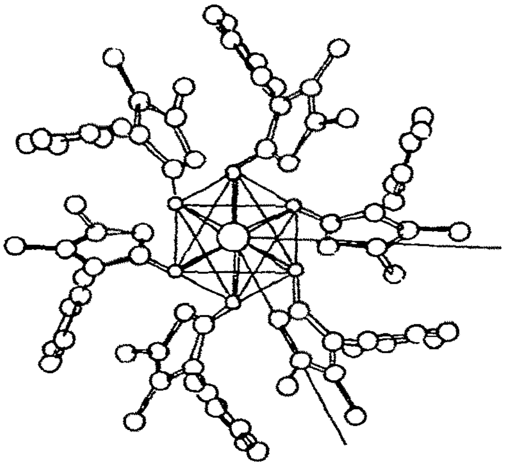
Fig. 32. Structure of bis(1-phenylbutane-1,3-dionato)tin(II). (Reproduced by permission of the Chem. Soc.)

form bridges between the tin atoms in each valence state. The geometry at the bivalent tin atoms is that of a distorted pentagonal pyramid with oxygen atoms from four bridging carboxylate groups and the solvating THF molecule occupying equatorial positions at bond distances in the range 2.409(8)–2.661(9) Å. The apical site of the pentagonal pyramid is occupied by the oxygen atom of the $[Sn_2^{IV}O_2]$ ring at the extremely short tin(II)—oxygen distance of 2.113(7) Å. The tin(II) lone pair occupies the remaining apical position of a pseudo-pentagonal bipyramid (Fig. 31) [142].

The structures of several thiourea complexes of lead(II) carboxylates and of *D*-penicillaminatolead(II) are discussed later (Sect. G).

No structures of simple alkoxy derivatives have been determined. That of bis(1-phenylbutane-1,3-dionato)tin(II) shows that the compound is molecular in the crystal, with both ligands chelating the tin, each spanning equatorial and axial sites of a distorted pseudo-trigonal bipyramid (Fig. 32) [$Sn—O_{ax}$ 2.290(6) Å; $Sn—O_{eq}$ 2.135(1) Å; $O_{ax}\widehat{—Sn—}O_{ax}$ 150.4(2)°; $O_{eq}\widehat{—Sn—}O_{eq}$ 94.7(1)°] [143].

The lead atom in lead hexa-antipyrine perchlorate is surrounded by six



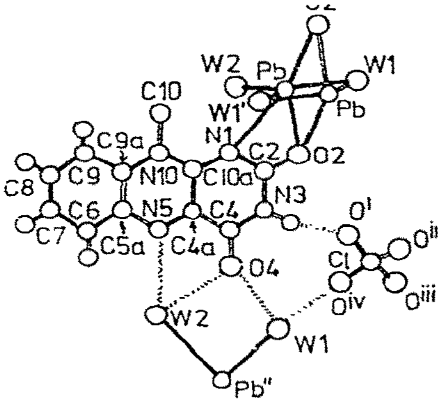


Fig. 33. Coordination of the lead cations in lead hexa-antipyrine perchlorate. (Reproduced by permission from ref. 144.)

Fig. 34. Flavin—lead coordination and hydrogen bonding in bis(10-methylisoalloxazine)-lead(II) perchlorate tetrahydrate. (Reproduced by permission of the Chem. Soc.)

antipyrine oxygen atoms in a slightly distorted octahedral form with Pb—O distance of 2.446(16) Å. The tetrahedral perchlorate ions do not interact with the lead ions, but occupy voids provided by adjacent antipyrine groups (Fig. 33) [144]. The lead atoms in bis(10-methylisoalloxazine)lead perchlorate tetrahydrate are disordered in two sites 0.75 Å above and below a plane of four oxygen atoms, two of which are from carbonyl groups and two from water molecules (Fig. 34) [145]. The coordination of the lead is therefore similar to that of the metal in SnO and PbO.

G. OTHER TIN- AND LEAD—SULPHUR BONDED COMPOUNDS

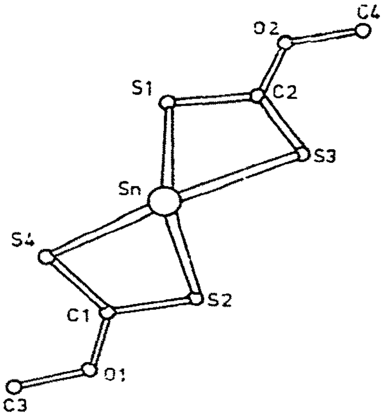
The structures of several *O*-alkyldithiocarbonato- (xanthato) [146—148] and *N,N*-dialkyldithiocarbamato- [149,150] derivatives of bivalent tin and lead have been determined. All contain discrete molecules in the crystal. The geometry at the metal is similar in every case, with both groups functioning as bidentate ligands towards the metal atoms, which enjoy a distorted square pyramidal configuration. Valence bond angles at the metal, and the molecular packing in the crystal, indicate that the lone pairs of electrons exhibit stereochemical activity, thus resembling closely the structure of $Sn(O \cdot CPh.CH{=}CO \cdot Me)_2$ [143]. Lead(II) diethyldithiophosphoridate [151] and lead(II) bis(8-mercaptoquinolate) [152,153] have very similar structures. The structure of $Sn(S_2COMe)_2$, a typical example, is illustrated in Fig. 35, whilst valence bond distance and angle data are collected in Table 2. The partial structure

TABLE 2

Bond parameters for compounds with the distorted pseudo-trigonal bipyramidal geometry

Compound	$\widehat{\mathrm{M{-}X}}_{ax}$ (Å)	$\mathrm{M{-}X}_{eq}$ (Å)	$\mathrm{X}_{ax}\widehat{\mathrm{MX}}_{eq}$ (°)	$\mathrm{X}_{ax}\widehat{\mathrm{MX}}_{ax}$ (°)	$\mathrm{X}_{eq}\widehat{\mathrm{MX}}_{eq}$ (°)
$Sn(OCPh \cdot CH \cdot COMe)_2$ [123]	2.290	2.135	81.2	150.4	94.7
$Sn(S_2COMe)_2$ [126]	2.802 2.813	2.603 2.644	66.18 65.56	140.81	99.28
$Sn(S_2CNEt_2)_2$ [129]	2.765 2.819	2.574 2.592	67.4 65.9	139.6	96.2
$Pb(S_2COEt)_2$ [127]	2.838 2.950	2.742 2.785		137.2	98.2
$Pb(S_2CO^nBu)_2$ [128]	2.77 3.03	2.83 2.76	65.8 58.6	141.2	91.7
$Pb(S_2CNEt_2)_2$ [130]	2.885 2.940	2.744 2.786	64.1 61.9	133.2	96.2
$Pb[S_2P(OEt)_2]_2$ [131]	2.996 3.022	2.754 2.790	71.1 70.6	138.2	94.1
$Pb(SC_9H_6N)_2$ [133]	2.485 [a]	2.714	71.5		

[a] Pb—N.



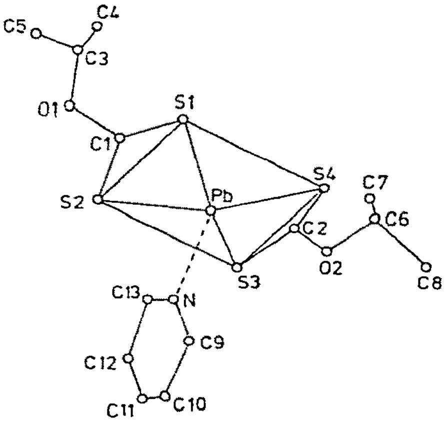


Fig. 35. Structure of $Sn(S_2COMe)_2$. (Reproduced by permission of the Chem. Soc.)

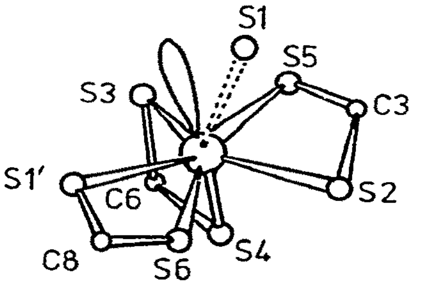
Fig. 36. Coordination of lead in $Pb(S_2COC_3H_7)_2 \cdot C_5H_5N$. (Reproduced with permission from ref. 155.)

of $Pb(S_2CNEt_2)_2$ determined by Zvonkova et al. [154] by two-dimensional methods bears no relationship to the full structure determination [150], and is most probably in error. In the pyridine adduct of lead(II) bis(isopropylxanthate), both xanthate residues again chelate the lead in a distorted square pyramidal fashion, but the proximity of the pyridine nitrogen atom to the lead (2.55 Å) is close enough to represent a bonding interaction (Fig. 36) [155].

A five-membered $\overline{Pb{-}S{-}N{-}N{-}S}$ heterocyclic ring is present in the adduct $PbN_2S_2 \cdot NH_3$ (Pb—N 2.29 Å; Pb—S 2.73 Å), and pyramidal coordination is completed by the ammonia molecule ($Pb{-}NH_3$ 2.24 Å; valence angles at lead 77.4, 87.8, 94.8°) [156].

Tetraethylammonium tris(ethylxanthato)lead(II) [157], *O,O'*-diisopropylphosphorodithioatolead(II) [158], and *D*-penicillaminatolead(II) [159] have structures based on pseudo-pentagonal bipyramidal geometry at lead. In the $[Pb(S_2COEt)_3^-]$ anion, the three xanthate groups chelate the lead giving a distorted pentagonal pyramid (Fig. 37). The lone pair again appears to be stereochemically active, occupying the other apical position of a bipyramid, although a sulphur atom of a neighbouring anion approaches to within 3.68 Å. $Pb[S_2P(O^{iso}C_3H_7)_2]_2$ forms polymeric chains in which nearly planar $[Pb(S_2P)_2]$ units are stacked one above the other giving six-coordinated lead in an almost ideal pseudo-pentagonal bipyramidal arrangement with the lead lone pair occupying an equatorial site (Fig. 38). Two of the Pb—S bonds in the equatorial plane are short (2.761, 2.772 Å), whilst the other two, and the bridge Pb—S distances, fall in the range 2.985—3.232 Å [158]. The same geometry is present in *D*-penicillaminatolead(II) (Fig. 39), in which the amino acid functions as a terdentate ligand forming three strong interactions (Pb—O 2.444 Å; Pb—N 2.444 Å; Pb—S 2.716 Å). Additional weak Pb—S (3.160 and 3.480 Å) and Pb—O (2.768 Å) interactions complete the coordination sphere [159].

The structures of a number of thiourea complexes of lead salts have been



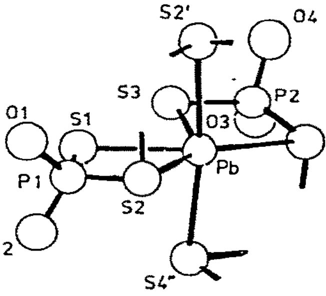
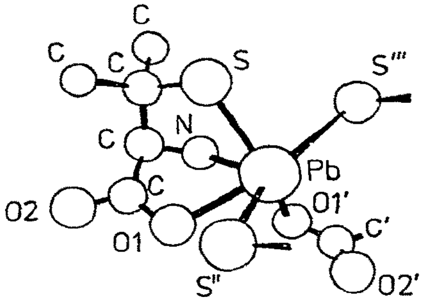


Fig. 37. Coordination around the lead atom in tetraethylammonium tris(ethylxanthato)-lead(II). (Reproduced by permission of Pergamon Press.)

Fig. 38. Coordination around the lead atom in $Pb[S_2P(OC_3H_7)_2]_2$. (Reproduced by permission of the Am. Chem. Soc.)



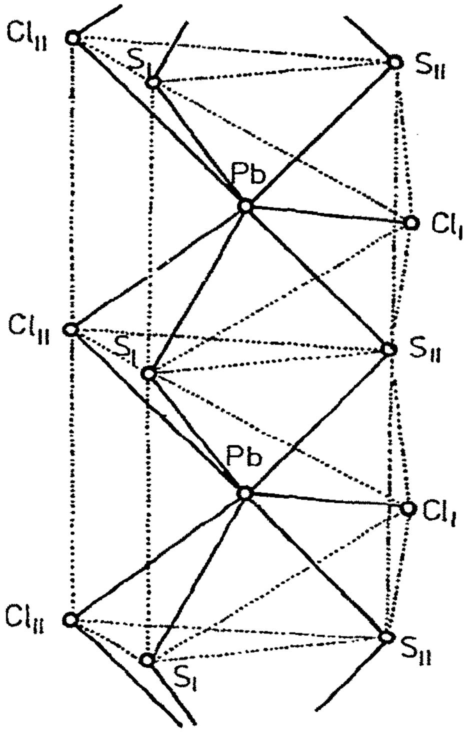
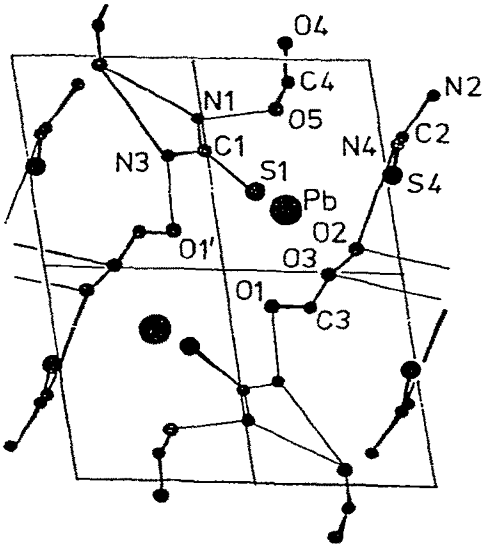


Fig. 39. Coordination of the lead atom in *D*-penicillaminatolead(II). (Reproduced by permission of the Chem. Soc.)

Fig. 40. Clinographic projection of the polymeric chain structure of dichlorobisthiourea)-lead(II). (Reproduced by permission from ref. 160.)

determined. Dichlorobis(thiourea)lead(II) has a chain structure in which the coordination polyhedron at lead is based on a distorted trigonal prism with four sulphur and two chlorine atoms at the apices. A third chlorine is located near the centre of a prism face giving a coordination number of seven (Fig. 40) [160]. The first coordination sphere of lead in $Pb(O_2CH)_2 \cdot 2\,SC(NH_2)_2 \cdot H_2O$ has three sulphur and five oxygen atoms in a distorted dodecahedral arrangement. Two parallel $\cdots S \cdots Pb \cdots S \cdots$ chains extend along [001], with each pair of centrosymmetrically related lead ions bridged by two similarly related formate ions. The sulphur atoms of the thiourea molecules are bicoordinated, whilst each bridging formate ion has one unicoordinate and one bicoordinate oxygen atom. The remaining thiourea molecule, water molecule, and formate ion are unicoordinatively bonded to the same lead ion (Fig. 41) [161]. Eight-coordination of lead is found in $3/4\,Pb(O_2CH)_2 \cdot 4\,SC(NH_2)_2$. The lead is surrounded by twisted tetragonal prisms of sulphur atoms of thiourea molecules (Fig. 42). Every fourth lead position is vacant, the vacan-



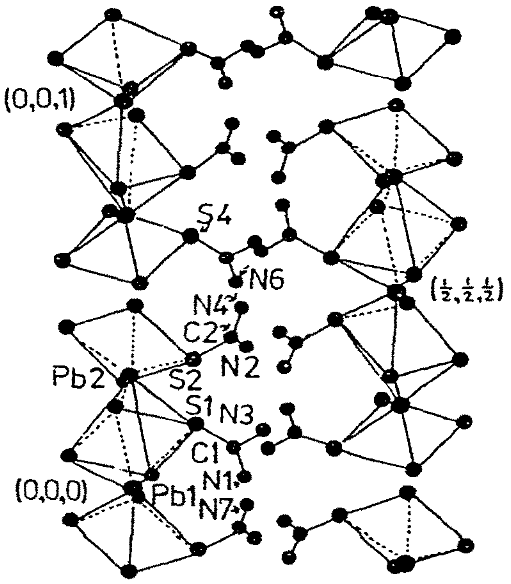


Fig. 41. Structure of $Pb(HCO_2)_2 \cdot 2\,SC(NH_2)_2.H_2O$. (Reproduced with permission from ref. 161.)

Fig. 42. Arrangement of two parallel lead—thiourea chains in 3/4 $Pb(HCO_2)_2 \cdot 4\,SC(NH_2)_2$. (Reproduced with permission from ref. 162.)

cies being fully ordered [162]. The structure of $Pb(O_2CCH_3)_2 \cdot SC(NH_2)_2$ consists of chains of distorted pentagonal bipyramidal polyhedra, made up of three sulphur and four oxygen atoms about lead, and linked by sulphur atoms (Fig. 43) [163,164]. $Pb(picrate)_2 \cdot 4\,SC(NH_2)_2$ contains polymeric chains of edge-sharing distorted $[Pb[SC(NH_2)_2]_6]$ octahedra (Fig. 44), and stacks of picrate ions. Crystals are made up of interleaving parallel cationic and anionic sheets, with interconnecting hydrogen bonding [165]. $[Pb[SC(NH_2)_2]_6](ClO_4)_2$ contains rather closely packed $[Pb[SC(NH_2)_2]_6]^{2+}$ cations and ClO_4^- anions. The cation has six-fold coordination of sulphur atoms about lead in a distorted octahedral arrangement (Fig. 45) [166].

H. NITROGEN DERIVATIVES

Few nitrogen derivatives of bivalent germanium, tin and lead have been synthesised [167—169], and the structures of only $PbN_2S_2 \cdot NH_3$ [156] discussed above and tin(II) phthalocyanine [170] have actually been determined. The tin atoms in the latter compound lie 1.11 Å above the plane of the four isoindole nitrogen atoms (mean Sn—N 2.25 Å), giving a geometry at tin closely resembling that in tetragonal SnO. The molecular packing in the crystal

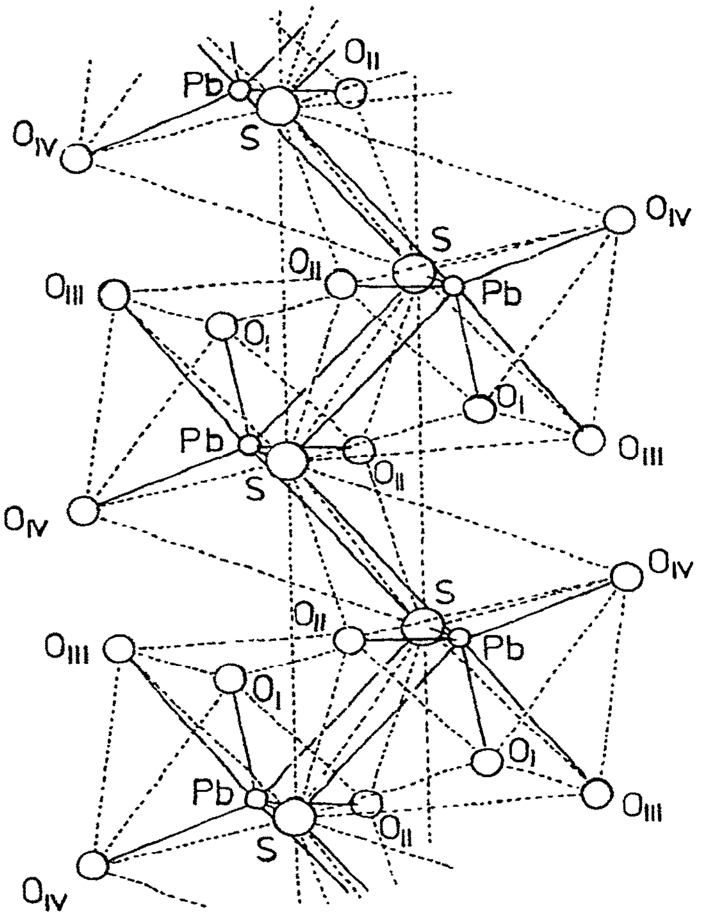
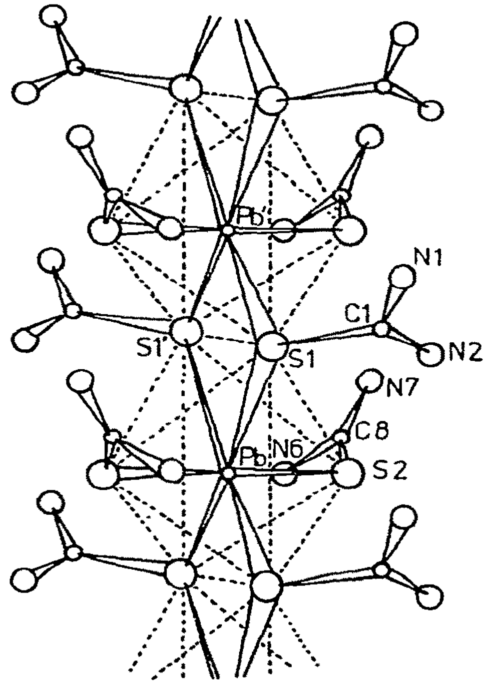


Fig. 43. Clinographic projection of a double chain of coordination polyhedra in monothiourea-lead acetate. (Reproduced with permission from Acta Cryst.)

suggests that the tin lone pair is stereochemically active, and is directed away from the organic residue along the four-fold axis of the [SnN_4] core.

I. ORGANOMETALLIC DERIVATIVES OF GERMANIUM(II), TIN(II) AND LEAD(II)

Simple σ-bonded diorganogermanium(II), —tin(II), and —lead(II) compounds are unstable with respect to the metal—metal bonded diorganometal(IV) oligomers, but have been stabilised as pyridine or dimethyl sulphoxide solvated pentacarbonylchromium and tetracarbonyliron complexes [171—174]. Metal-(II)—carbon σ-bonds are also present in the [$Me_2SnCl_2^{2-}$] anion [175] and [$(Me_3Si)_2CH]_2M$ (M = Sn, Pb) [176] and their complexes [176,177]. The structures of [$(Me_3Si)_2CH]_2Sn \cdot Cr(CO)_5$ [177] and $C_5H_4N \cdot t\text{-}Bu_2Sn \cdot$



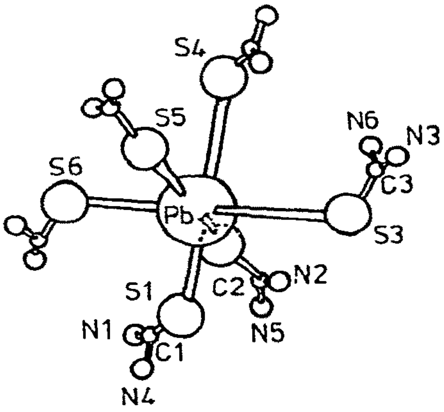
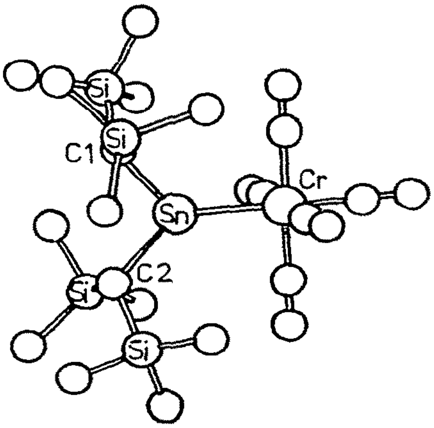


Fig. 44. The polymeric chain of edge-sharing octahedra in tetrakis(thiourea)lead(II) picrate. (Reproduced with permission from ref. 165.)

Fig. 45. Structure of the $[Pb[SC(NH_2)_2]_6]^{2+}$ cation in hexakis(thiourea)lead(II) perchlorate. (Reproduced with permission from ref. 166.)



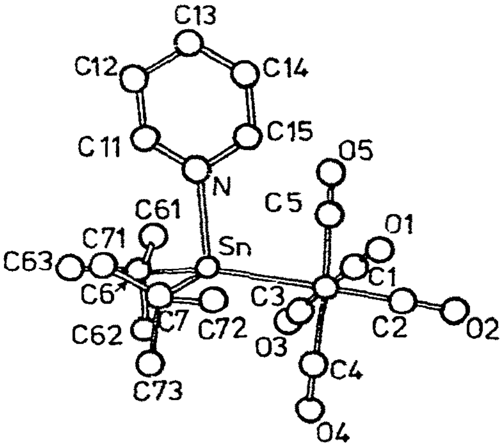
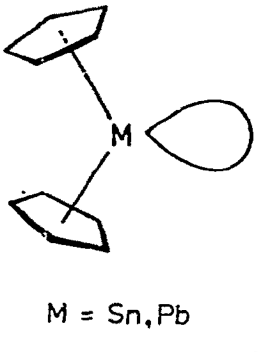


Fig. 46. Structure of $[(Me_3Si)_2CH]_2Sn—Cr(CO)_5$. (Reproduced by permission of the Chem. Soc.)

Fig. 47. Structure of t-$Bu_2SnCr(CO)_5 \cdot C_5H_5N$. (Reproduced by permission of the Am. Chem. Soc.)

$Cr(CO)_5$ [174] have both been determined and are depicted in Figs. 46 and 47, respectively. The central [C_2SnCr] unit of the former complex is planar, whilst the presence of coordinated pyridine in the latter distorts the geometry at tin towards tetrahedral, and is also the probable cause of the longer Sn—C and Sn—Cr bond distances [Sn—C 2.18, 2.19 Å vs. 2.24, 2.25 Å; Sn—Cr 2.562 Å vs. 2.653 Å].

The dicyclopentadienyl—metal derivatives are the only organo derivatives of the metals in the +2 oxidation state which contain only carbon and hydrogen in addition to the metal. The structure of $(C_5H_5)_2Ge$ is unknown, but IR data [178] strongly suggest that it is isostructural with the tin and lead analogues. The structures of these derivatives in the vapour phase have been determined by electron diffraction [179]. Both are angular sandwich molecules, with the metal associated equally with all five carbon atoms in each ring (Fig. 48). The angle subtended at the metal by the two C_5 axes (Sn ca. 125°; Pb 135 ± 15°) suggest sp^2 hybridisation, in which case the lone pair would be located in an sp^2 hybrid orbital and hence stereochemically active. Support for this hypothesis arises from the facile formation of the complexes $(C_5H_5)_2Sn \cdot M^{III}X_3$ ($M^{III}X_3 = BF_3, BBr_3, AlCl_3, AlCl_3$) [180,181], $(C_5H_5)_2Sn \cdot M(CO)_5$ (M = Cr, Mo, W) [182], and $(C_5H_5)_2Pb \cdot BF_3$ [183]. The structure of $(C_5H_5)_2Sn$ in the crystal is unknown, but that of $(C_5H_5)_2Pb$ [184] consists of infinite zig-zag —(C_5H_5)—Pb—(C_5H_5)—Pb— chains, similar to those present in crystals of $(C_5H_5)In$ and $(C_5H_5)Tl$, with each lead atom carrying a second, non-bridging, cyclopentadienyl group (Fig. 49). The lead



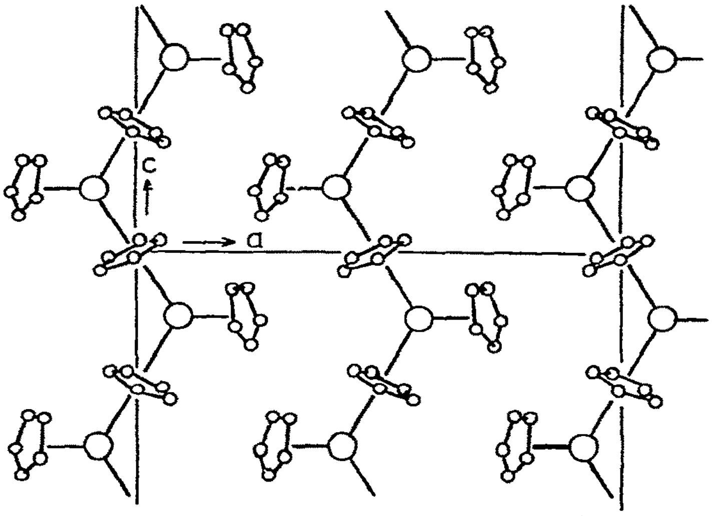


Fig. 48. Angular sandwich structure of $(C_5H_5)_2M$ (M = Sn, Pb) in the vapour phase.

Fig. 49. Perspective view of the chains in $Pb(C_5H_5)_2$. (Reproduced with permission from ref. 184.)

atoms are equidistant between the alternating cyclopentadienyl rings (mean Pb—C 3.06 Å); the second cyclopentadienyl ring is more tightly bound to the lead (mean Pb—C 2.76 Å; cf. 2.778 Å for $(C_5H_5)_2Pb$ in the vapour phase) Essentially monomeric, angular $[(C_5H_5)SnCl]$ units are present in crystals of cyclopentadienyltin chloride [185]. Only one close chlorine atom is found near tin (at 2.689 Å); the next two closest chlorine neighbours are located at 3.24 and 3.26 Å, which are rather long distances for bridging interactions originally proposed for this compound. The plane of the cyclopentadienyl ring is not quite perpendicular to the tin—centre-of-ring axis, and the Sn—C bond distances range from 2.45 to 2.74 Å (cf. 2.71 Å found for $(C_5H_5)_2Sn$ in the vapour [179]).

Several carborane derivatives of germanium, tin and lead have been synthesised and characterised spectroscopically, but no structural information is as yet available [186—191];

Both tin and lead form isomorphous benzene—metal complexes of composition $[(C_6H_6)M \cdot (AlCl_4)_2 \cdot (C_6H_6)]$ (M = Sn, Pb). One of the benzene molecules is weakly bound to the metal in a *hexahapto* fashion (mean Sn—C 3.08 Å; mean Pb—C 3.11 Å). The second molecule of benzene is far removed from the metal, occupying a cleft position in the lattice. Metal atoms are linked by $[AlCl_4]$ tetrahedra to form infinite chains, whilst the second $[AlCl_4]$

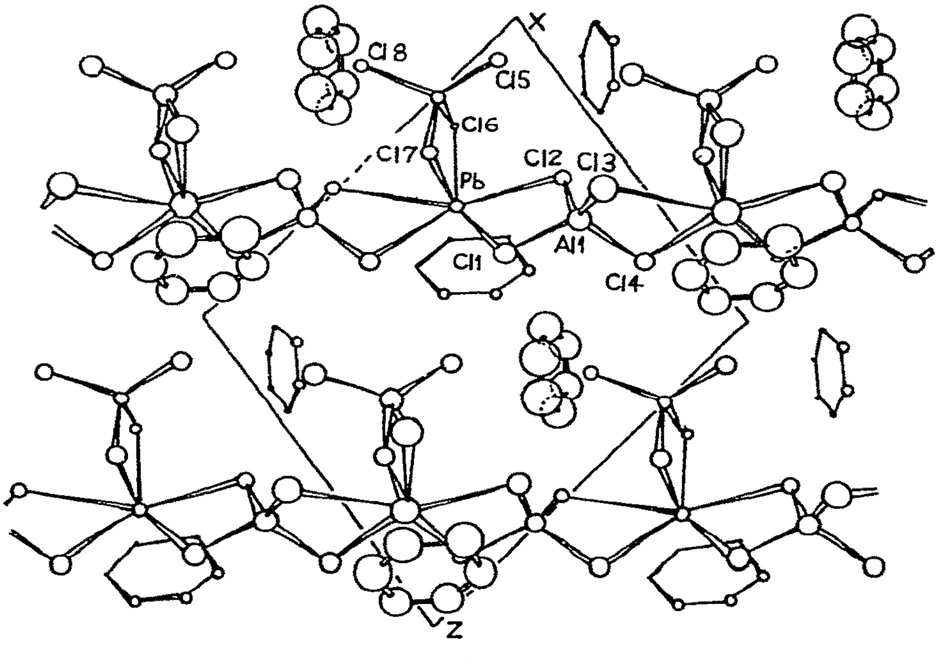


Fig. 50. Chain structure of $(C_6H_6)Pb(AlCl_4)_2 \cdot C_6H_6$. (Reproduced by permission of the Am. Chem. Soc.)

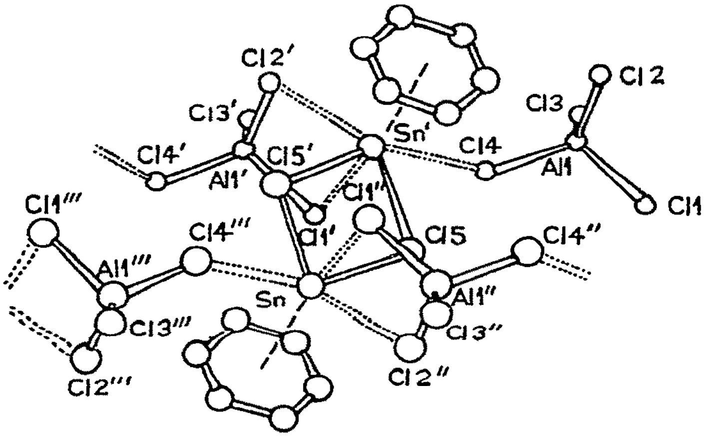


Fig. 51. Perspective view of the structure of $[(C_6H_6)SnCl(AlCl_4)]_2$. (Reproduced by permission of the Am. Chem. Soc.)

group chelates the metal via axial and equatorial positions of a distorted pentagonal bipyramid. The remaining equatorial sites of the bipyramid are occupied by chlorine atoms from bridging $[AlCl_4]$ groups, and the second axial site by the $^6\eta$-C_6H_6 molecule (Fig. 50) [192,193]. The related arene complexes $[Ar \cdot SnCl(AlCl_4)]_2$ ($Ar = C_6H_6$, *para*-xylene) also contain *hexahapto* arene molecules, which occupy one site of a distorted octahedron about tin. The overall structures are made up of $[Sn(AlCl_4)]$ chains connected by bridging chlorine atoms to form $[Sn_2Cl_2]$ rings (Fig. 51) [194].

REFERENCES

1 G.A. Ozin and A. Vander Voet, J. Chem. Phys., 1192, 56, 4768.
2 M.W. Lister and L.E. Sutton, Trans. Farad. Soc., 37 (1941) 406.
3 J. Trotter, M. Akhtar and N. Bartlett, J. Chem. Soc. A, (1966) 30.
4 J.D. Donaldson, R. Oteng and B.J. Senior, Chem. Commun., (1965) 618.
5 G. Bergerhoff, Acta Crystallogr., 15 (1962) 509.
6 J.D. Donaldson and R. Oteng, Inorg. Nucl. Chem. Lett., 3 (1967) 163.
7 A. Byström, Ark. Kemi, Mineral. Geol., 24A (1947) No. 33.
8 I. Naray-Szabo, Inorganic Crystal Chemistry, Akademiai Kiado, Budapest, 1969, p. 215.
9 J.M. van den Berg, Acta Crystallogr., 14 (1961) 1002.
10 S.S. Batsanov, V.F. Lyakhova and E.M. Moroz, Russ. J. Inorg. Chem., 16 (1971) 1233.
11 J. Goodyear, S.A.D. Ali and W.J. Dufin, Acta Crystallogr., Sect. B, 25 (1969) 796.
12 G. Bergerhoff and L. Goost, Acta Crystallogr., Sect. B, 30 (1974) 1362.
13 J. Andersson, Acta Chem. Scand., 26 (1972) 1730.
14 J. Andersson, Acta Chem. Scand., 26 (1972) 3813.
15 J. Andersson, Acta Chem. Scand., 26 (1972) 2543.
16 J. Andersson and G. Lundgren, Acta Chem. Scand., 24 (1970) 2670.
17 N. Kamenar and D. Grdenic, J. Chem. Soc., (1961) 3954.
18 H. Kiryama, K, Kitahama, O. Nakamura and R. Kiriyama, Bull. Chem. Soc. Jpn., 46 (1973) 1389.

19 I. Naray-Szabo, Inorganic Crystal Chemistry, Akademiai Kiado, Budapest, 1969, p. 269.
20 C.C. Venetropoulos and P.J. Rentzeperis, Z. Kristallogr., 141 (1975) 246.
21 H.M. Powell and F.M. Bruaer, J. Chem. Soc., 21 (1938) 197.
22 CdI_2 : R.S. Mitchell, Z. Kristallogr., 111 (1959) 372; PbI_2 : M. Chand and G.C. Trigunayat, Acta Crystallogr., Sect. B, 31 (1975) 1222, and refs. therein.
23 W. Moser and I.C. Trevena, Chem. Commun., (1969) 25.
24 R.A. Howie, W. Moser and I.C. Moser, Acta Crystallogr., Sect. B, 28 (1972) 2965.
25 P. Jutzi, H.J. Hoffman, D.J. Brauer and C. Kruger, Angew. Chem., Int. Ed. Engl., 12 (1973) 1002.
26 A.N. Christensen and S.E. Rasmussen, Acta Chem. Scand., 19 (1965) 421.
27 J. Barrett, S.R.A. Bird, J.D. Donaldson and J. Silver, J. Chem. Soc. A, (1971) 3105.
28 J.D. Donaldson, D. Laughlin, S.D. Ross and J. Silver, J. Chem. Soc., Dalton Trans., (1973) 1985.
29 J.D. Donaldson and J. Silver, J. Chem. Soc., Dalton Trans., (1973) 666.
30 K.N. Moller, Mat. Fys. Medd. Dan. Vid. Selsk, (1959) 32.
31 H.J. Haupt, F. Huber and H. Preut, Z. Anorg. Chem., 408 (1974) 209.
32 F.R. Poulsen and S.E. Rasmussen, Acta Chem. Scand., 24 (1970) 150.
33 S. Fregerslev and S.E. Rasmussen, Acta Chem. Scand., 22 (1968) 2541.
34 B. Kamenar and D. Grdenic, J. Inorg. Nucl. Chem., 24 (1962) 1039.
35 J.K. Stalick, D.W. Meek, B.Y.K. Ho and J.J. Zuckerman, J. Chem. Soc., Chem. Commun, 1972, 630.
36 J.K. Stalick, P.W.R. Corfield and D.W. Meek, Inorg. Chem., 12 (1973) 1668.
37 G. Bergerhoff and L. Goost, Acta Crystallogr., Sect. B, 29 (1973) 632.
38 G. Bergerhoff, L. Goost and E. Schultze-Rhonhof, Acta Crystallogr., Sect. B, 24 (1968) 803.
39 R.R. McDonald, A.C. Larson and D.T. Cromer, Acta Crystallogr., 17 (1964) 1104.
40 G. Bergerhoff and L. Goost, Acta Crystallogr., Sect. B, 26 (1970) 19.
41 H.M. Powell and H.S. Tasker, J. Chem. Soc., (1937) 119.
42 J.D. Donaldson, Prog. Inorg. Chem., 8 (1967) 287.
43 J.C. Taylor and P.W. Wilson, J. Am. Chem. Soc., 95 (1973) 1834.
44 M.F.A. Dove, R. King and T.J. King, J. Chem. Soc., Chem. Commun., (1973) 944.
45 J.D. Donaldson and D.C. Puxley, J. Chem. Soc. Chem. Commun., (1972) 289.
46 B.R. Chamberlain and W. Moser, J. Chem. Soc. A, (1969) 354.
47 J.A.A. Mokuolu and J.C. Speakman, Chem. Commun., (1966) 25.
48 J.A.A. Mokuolu and J.C. Speakman, Acta Crystallogr., Sect. B, 31 (1975) 172.
49 B. Metz and R. Weiss, Acta Crystallogr., Sect. B, 29 (1973) 1088.
50 B. Metz and R. Weiss, Inorg. Chem., 13 (1974) 2094.
51 W.J. Moore and L. Pauling, J. Am. Chem. Soc., 63 (1941) 1392.
52 J. Leciejewicz, Acta Crystallogr., 14 (1961) 66.
53 M.I. Kay, Acta Crystallogr., 14 (1961) 80.
54 W.H. Zachariasen, Phys. Rev., 40 (1932) 917.
55 A. Okazaki, J. Phys. Soc. Jpn, 13 (1958) 1151.
56 C.R. Kannewurf, A. Kelly and R.J. Cashman, Acta Crystallogr., 13 (1960) 449.
57 W. Hoffman, Z. Kristallogr., 92 (1935) 161.
58 A. Okazaki and I. Ueda, J. Phys. Soc. Jpn., 11 (1956) 470.
59 R.E. Rundle and D.H. Olsen, Inorg. Chem., 3 (1964) 596.
60 E. Zeipel, Ark. Mat. Astron. Fys., 25A (1935) 1.
61 J.W. Earley, Am. Mineral., 35 (1950) 338.
62 V.M. Goldschmidt, Geochem. Verteilungsgesetze, Skrifter Akad., Oslo, 1926.
63 G. Murken and M. Trömel, Z. Anorg. Allg. Chem., 397 (1973) 117.
64 K. Hasselbach, G. Murken and M. Trömel, Z. Anorg. Allg.Chem., 397 (1973) 127.
65 A. Byström, Ark. Kemi, Mineral. Geol., 20A (1943) No. 11.
66 A. Byström and A. Westgren, Ark. Kemi, Mineral. Geol., 16B (1943) No. 14.

67 D. Mootz and H. Puhl, Acta Crystallogr., 23 (1967) 471.
68 H.D. Megaw, Proc. Phys. Soc., 58 (1946) 133.
69 G. Shirane and R. Pepinsky, Phys. Rev., 91 (1953) 812.
70 W. Jeitschko and A.W. Sleight, Acta Crystallogr., Sect. B, 28 (1972) 3174.
71 L.G. Sillen and A. Nylander, Ark. Kemi Mineral. Geol., 17A (1943) No. 4.
72 I. Naray-Szabo and Gy. Argay, Acta Chim. Hung., 40 (1964) 283; S. Quareni and R. De Peri, Acta Crystallogr., 19 (1965) 287.
73 G. Colloti, L. Conti and M. Zocchi, Acta Crystallogr., 12 (1959) 416.
74 C.W. Pistorius and M.C. Pistorius, Z. Kristallogr., 117 (1962) 259.
75 C. Frondel and L. Barnes, Acta Crystallogr., 11 (1958) 562.
76 S. Stahl, Ark. Kemi Mineral. Geol., 17B (1943) No. 5.
77 P. Panek and R. Hoppe, Z. Anorg. Allg. Chem., 400 (1973) 219.
78 A. Byström and L. Evers, Acta Chem. Scand., 4 (1950) 613.
79 A. Magneli, Ark. Kemi Mineral. Geol., 15B (1941) No. 3.
80 K. Kato, I. Kawada and K. Muramatsu, Acta Crystallogr., Sect. B, 30 (1974) 1634.
81 B.D. Jordan and C. Calvo, Can. J. Chem., 52 (1974) 2701.
82 R.C. Rouse, Z. Kristallogr., 134 (1971) 321.
83 A. Kawahara, Bull. Soc. Fr. Mineral. Crystallogr., 90 (1967) 279.
84 R.D. Shannon and C. Calvo, Can. J. Chem., 51 (1973) 70.
85 J.C. Ruckmann, R.T.W. Morrison and R.H. Buck, J. Chem. Soc., Dalton Trans., 1972, 426.
86 J. Lajzerowicz, Acta Crystallogr., 20 (1965) 357.
87 W. Petter, A.B. Harnik and U. Keppler, Z. Kristallogr., 133 (1971) 445.
88 I. Naray-Szabo and A. Kalman, Silikattechnik, 12 (1961) 316.
89 G.B. Ansell and B. Wanklyn, J. Chem. Soc., Chem. Commun., (1975) 794.
90 S.B. Hendricks, M.E. Jefferson and V.M. Mosley, Z. Kristallogr., 81 (1931) 352.
91 J. Wondratschek and L. Merker, Naturwissenschaften, 43 (1956) 494.
92 A. Gabrielson, Ark. Kemi Mineral. Geol., 2 (1955) 1.
93 J.E. Inglesias and H. Steinfink, Acta Crystallogr., Sect. B, 29 (1973) 1480.
94 M. Ribes, J. Olivier-Fourcade, E. Phillipot and M. Maurin, Acta Crystallogr. Sect. B, 30 (1974) 1391.
95 M.T. Le Bihan, C. R., 249 (1959) 719; Acta Crystallogr., 14 (1961) 1210.
96 B.J. Wuensch and W. Nowacki, Am. Crystallogr. Ass., Winter Meeting, Atlanta, 1967.
97 T. Ito and W. Nowacki, Z. Kristallogr., 139 (1974) 85.
98 E. Hellner, Z. Kristallogr., 110 (1958) 169.
99 E. Hellner and G. Leineweber, Z. Kristallogr., 107 (1956) 150.
100 G. Leineweber, Z. Kristallogr., 108 (1956) 161.
101 I. Kohatsu and B.J. Wuensch, Acta Crystallogr., Sect. B, 27 (1971) 1245.
102 Y. Iitaka and W. Nowacki, Acta Crystallogr., 15 (1962) 691.
103 T. Srikrishnan and W. Nowacki, Z. Kristallogr., 140 (1974) 114.
104 E.W. Nuffield, Acta Crystallogr., Sect. B, 31 (1975) 151.
105 S.A. Cho and B.J. Wuensch, Z. Kristallogr., 139 (1974) 351.
106 S.A. Cho and B.J. Wuensch, Nature, (London), 225 (1970) 444.
107 J.L. Jambor, Mineral. Mag., 37 (1969) 442.
108 J.T. Kohatsu, Ph.D. Thesis, Massachussetts Institute of Technology, 1973.
109 J.T. Kohatsu and B.J. Wuensch, Acta Crystallogr., Sect. B, 30 (1974) 2935.
110 J.C. Portheine and W. Nowacki, Z. Kristallogr., 141 (1975) 75.
111 F. Marumo and W. Nowacki, Z. Kristallogr., 112 (1965) 433.
112 T. Ito and W. Nowacki, Z. Kristallogr., 139 (1974) 161.
113 J.D. Donaldson and D.C. Puxley, Acta Crystallogr., Sect. B, 28 (1972) 864.
114 J.D. Donaldson, D.G. Nicholson, D.C. Puxley and R.A. Howie, J. Chem. Soc., Dalton Trans., (1973) 1810.
115 G. Wernfors, Acta Chem. Scand., 15 (1961) 1007.
116 S. Grimvall, Acta Chem. Scand., 27 (1973) 1447.

117 H.E. Swanson and R.K. Fuyat, Nat. Bur. Stand. (U.S.), Circ., 1953, Vol. III.
118 A. Bellanca, Period. Mineral., 15 (1946) 1.
119 C. Moller, Acta Chem. Scand., 3 (1954) 81.
120 H.G. Bachmann and J. Zemann, Acta Crystallogr., 14 (1961) 747.
121 W.P. Binnie, Acta Crystallogr., 4 (1951) 471.
122 K. Sahl, Z. Kristallogr., 141 (1975) 79.
123 W.C. Hamilton, Acta Crystallogr., 10 (1957) 103.
124 M. Nardelli, C. Pelizzi and G. Pelizzi, J. Organometal. Chem., 85 (1975) C43.
125 M. Nardelli, C. Pelizzi and G. Pelizzi, J. Chem. Soc., Dalton Trans., (1975) 1595.
126 A.F. Berndt and R. Lamberg. Acta Crystallogr., Sect. B, 27 (1971) 1092.
127 A.F. Berndt, Acta Crystallogr., Sect. B, 27 (1971) 1837.
128 A.F. Berndt, Acta Crystallogr., Sect. B, 30 (1974) 529.
129 R. Kement, Z. Anorg. Chem., 237 (1938) 161.
130 H.N. Ng and C. Calvo, Can. J. Chem., 53 (1975) 42.
131 U. Keppler, Z. Kristallogr., 132 (1970) 228.
132 P. Süsse and M.J. Buerger, Z. Kristallogr., 131 (1970) 161.
133 K. Sahl, Z. Kristallogr., 139 (1974) 215.
134 J.M. Cowley, Acta Crystallogr., 10 (1957) 103.
135 S.H. Hong and A. Olin, Acta Chem. Scand., 27 (1973) 2304.
136 S.H. Hong and A. Olin, Acta Chem. Scand., 28 (1974) 233.
137 T.G. Spiro, D.H. Templeton and A. Zalkin, Inorg. Chem., 8 (1969) 856.
138 A. Olin and R. Sönderquist, Acta Chem. Scand., 26 (1972) 3505.
139 A. Jelen and O. Lindquist, Acta Chem. Scand., 23 (1969) 3071.
140 K.G. Shields, R.C. Seccombe and C.H.L. Kennard, J. Chem. Soc., Dalton Trans., (1973) 741.
141 F.P. van Remoortere, J.J. Flynn, F.P. Boer and P.P. North, Inorg. Chem., 10 (1971) 1511.
142 P.F.R. Ewings, P.G. Harrison, A. Morris and T.J. King, J. Chem. Soc., Chem. Commun., (1974) 53; J. Chem. Soc., Dalton Trans., (1975) in press.
143 P.F.R. Ewings, P.G. Harrison and T.J. King, J. Chem. Soc., Dalton Trans., (1975) 1455.
144 M. Vijayan and M.A. Viswamitra, Acta Crystallogr., 21 (1966) 522.
145 M.W. Yu and C.J. Fritchie, J. Chem. Soc., Dalton Trans., (1975) 377.
146 P.F.R. Ewings, P.G. Harrison and T.J. King, J. Chem. Soc., Dalton Trans., in press.
147 H. Hagihara and S. Yamashita, Acta Crystallogr., 21 (1966) 350.
148 H. Hagihara, Y. Watanabe and S. Yamashita, Acta Crystallogr., Sect. B, 24 (1968) 960.
149 J. Potenza and D. Mastropaolo, Acta Crystallogr., Sect. B, 29 (1973) 1830.
150 H. Iwasaki and H. Hagihara, Acta Crystallogr., Sect. B, 28 (1972) 507.
151 T. Ito, Acta Crystallogr., Sect. B, 28 (1972) 1034.
152 V.M. Agre and E.A. Shugam, J. Strukt. Khim., 12 (1971) 84.
153 E.A. Shugam, V.M. Agre, Yu.A. Bankovskii and E.A. Lukasha, J. Strukt. Khim., 8 (1967) 145.
154 Z.V. Zvonkova, A.N. Khvatkina and N.S. Ivanova, Sov. Phys. Crystallogr., 12 (1968) 926.
155 H. Hagihara, N. Yoshida and Y. Watanabe, Acta Crystallogr., Sect. B, 25 (1969) 1775.
156 H. Weiss, Z. Anorg. Allg. Chem., 343 (1966) 315.
157 W.G. Mumme and G. Winter, Inorg. Nucl. Chem. Lett., 7 (1971) 505.
158 S.L. Lawton and G. Kokotailo, Inorg. Chem., 11 (1972) 363.
159 H.C. Freeman, G.N. Stevens and I.F. Taylor, J. Chem. Soc., Chem. Commun., (1974) 366.
160 M. Nardelli and G. Fava, Acta Crystallogr., 12 (1959) 727.
161 I. Goldberg and F.H. Herbstein, Acta Crystallogr., Sect. B, 29 (1973) 246.
162 I. Goldberg and F.H. Herbstein, Acta Crystallogr., Sect. B, 28 (1972) 410.
163 M. Nardelli and G. Fava, Proc. Chem. Soc., (1959) 194.
164 M. Nardelli, G. Fava and G. Branchi, Acta Crystallogr., 13 (1960) 898.

165 F.H. Herbstein and M. Kaftony, Acta Crystallogr., Sect. B, 28 (1972) 405.
166 I. Goldberg and F.H. Herbstein, Acta Crystallogr., Sect. B, 28 (1972) 400.
167 C.D. Schaeffer and J.J. Zuckerman, J. Am. Chem. Soc., 96 (1974) 7160.
168 D.H. Harris and M.F. Lappert, J. Chem. Soc., Chem. Commun., (1974) 895.
169 P. Foley and M. Zeldin, Inorg. Chem., 14 (1975) 2264.
170 M.K. Friedel, B.F. Hoskins, R.L. Martin and S.A. Mason, Chem. Commun., (1970) 400.
171 T.J. Marks, J. Am. Chem. Soc., 93 (1971) 7090.
172 T.J. Marks and A.R. Newman, J. Am. Chem., 95 (1973) 769.
173 G.W. Grynkewich, B.Y.K. Ho, T.J. Marks, D.L. Tomaja and J.J. Zuckerman, Inorg. Chem., 12 (1973) 2522.
174 M.D. Brice and F.A. Cotton, J. Am. Chem. Soc., 95 (1973) 4529.
175 N.N. Greenwood and B. Youll, J. Chem. Soc., Dalton Trans., (1975) 158.
176 P.J. Davidson and M.F. Lappert, J. Chem. Soc., Chem. Commun., (1973) 317.
177 J.D. Cotton, P.J. Davidson, D.E. Goldberg, M.F. Lappert and K.M. Thomas, J. Chem. Soc., Chem. Commun., (1974) 893.
178 J.V. Scibelli and M.D. Curtis, J. Am. Chem. Soc., 95 (1973) 924.
179 A. Almenningen, A. Haaland and T. Motzfeldt, J. Organometal. Chem., 7 (1967) 97.
180 P.G. Harrison and J.J. Zuckerman, J. Am. Chem. Soc., 92 (1970) 2577.
181 P.G. Harrison and J.A. Richards, J. Organometal. Chem., 108 (1976) 35.
182 A.B. Cornwell, P.G. Harrison and J.A. Richards, J. Organometal. Chem., 108 (1976) 47
183 A.K. Holliday, P.H. Makin, R.J. Puddephatt and J.D. Wilkins, J. Organometal. Chem., 57 (1973) C45.
184 C. Pannatoni, G. Bombieri and U. Croatto, Acta Crystallogr., 21 (1966) 823.
185 K.D. Bos, E.J. Bulten, J.G. Noltes and A.L. Spek, J. Organometal. Chem., 99 (1975) 71.
186 A.Yu. Aleksandrov, V.I. Bregadze, V.I. Goldanskii, L.I. Zakharkin, O.Yu. Okhlobystin and V.V. Khrapov, Dokl. Akad. Nauk S.S.S.R., 165 (1965) 804.
187 R.L. Voorhees and R.W. Rudolph, J. Am. Chem. Soc., 91 (1969) 2173.
188 R.W. Rudolph, R.L. Voorhees and R.E. Cochoy, J. Am. Chem. Soc., 92 (1970) 3351.
189 V. Chowdhry, W.R. Pretzer, D.N. Rai and R.W. Rudolph, J. Am. Chem. Soc., 95 (1973) 4560.
190 D.C. Beer and L.J. Todd, J. Organometal. Chem., 50 (1973) 93.
191 R.W. Rudolph and V. Chowdhry, Inorg. Chem., 13 (1974) 248.
192 H. Lüth and E.L. Amma, J. Am. Chem. Soc., 91 (1969) 7515.
193 A.G. Gash, P.F. Rodesiler and E.L. Amma, Inorg. Chem., 13 (1974) 2429.
194 M.S. Weininger, P.F. Rodesiler, A.G. Gash and E.L. Amma, J. Am. Chem. Soc., 94 (1972) 2135.