HETEROMETALLIC TIN COMPOUNDS: CLASSIFICATION AND ANALYSIS OF CRYSTALLOGRAPHIC AND STRUCTURAL DATA: PART II. TRIMERIC TO POLYMERIC DERIVATIVES

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ABSTRACT

Over 380 heterometallic tin compounds include 130 trimers, 100 tetramers, 30 pentamers, 45 hexamers, 15 heptamers, 12 octamers, 20 oligomers and 30 polymers. In these the Sn atom is found in oxidation states of 0, +2 and +4, with geometries including trigonal planar, tetrahedral, trigonal bipyramidal, octahedral and seven coordinate, with varying degrees of distortion. Of these, the first only exhibits Sn(0) and Sn(II) and the last only Sn(II) oxidation states, with tetrahedral geometry the most common overall. Examples of distortion isomers are reported, with many being exhibited within the same crystal. The heterometal atoms include the transition and lanthanide metals along with the non-transition metals. Outside the dimers, the shortest Sn-M(non-transition) bond distances are found in the tetramers and hexamers. Both Sn(IV) and Sn(II) are found bonded to a variety of "hard" and "soft" heterometal atoms. Comparisons are made with the much less rich chemistry of Pb.

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0. ABBREVIATIONS

ac	acetate
acac	acetylacetonate
ahb	o-(amino-_-hydroxybenzylidenehydrazonomethyl)phenyl
ampy	2-amino-6-methylpyridine
bpy	2,2'-bipyridine
Bu	tert-butyl
Bu ₂ bpy	4,4'-di-tert-butyl-2,2'-bipyridine
CH ₃ C ₅ H ₄	methylcyclopentadienyl
C ₄ H ₇	methylallyl
C ₅ H ₇ O ₂	2,4-pentanedionate
C ₆ H ₆	benzene
C ₆ H ₁₀	2,3-dimethylbuta-1,3-diene
C ₇ H ₈	bicyclo[2.2.1]heptadiene
C ₈ H ₉ NC	xylylisocyanide
C ₈ H ₁₀	naphthalene
C ₂₀ H ₁₄	tritycene
cit	citrate
cod	1,5-cyclooctadiene
cp*	pentamethylcyclopentadienyl

cpy	2- $\{(\text{Me}_3\text{Si})_2\text{C}\}\text{C}_5\text{H}_4\text{N}$
cy	cyclohexyl
db	1,3-diborolenyl
dedtc	N,N-diethyldithiocarbamate
1,4-dio	1,4-dioxane
dm	dioximate
dmso	dimethylsulphoxide
dmdtc	N,N-dimethyldithiocarbamate
dpma	bis(diphenylphosphinomethyl)phenylarsine
dppb	1,4-bis(diphenylphosphine)butane
dppm	bis(diphenylphosphine)methylene
dto	dithioxalate
en	ethylenediamine
fu	furyl
hfb	hexafluorobut-2-yne
imn	1-imidonaphthyl
m	monoclinic
ma	2-MeOC ₆ H ₄
Me	methyl
(Me ₃ Si) ₂ P	bis(trimethylsilyl)phosphanide
mes	mesityl
mit	N-methyl-imidazole-2-thio
nep	2,2-dimethylpropyl
nx	nioximate
or	orthorhombic
8-OHqu	8-hydroxyquinolate
Ph	phenyl
(Ph ₂ P) ₂ py	2,6-bis(diphenylphosphino)pyridine
phpr	2-phenyl-2-propanolate
phen	1,10-phenanthroline
PMe ₃	trimethylphosphine
PPh ₃	triphenylphosphine
ppn	(Ph ₃ P) ⁺ N ⁻
Pr ⁱ ₂ dab	N,N'-diisopropyl-1,4-diaza-1,3-butadiene
Ptol ₃	tritolyphosphine
pz	pyrazolyl
pzS ₈	porphyrazine-2,3,7,8,12,13,17,18-octathiolate
tb	2,4,6- $\{(\text{Me}_3\text{Si})_2\text{CH}\}_3\text{C}_6\text{H}_2$
tedip	(EtO) ₂ POP(OEt) ₂
tepid	tri-isopropylphosphoniodithioformate
tfmp	1,3,5-tris(trifluoromethyl)phenyl
thf	tetrahydrofuran
tip	2,4,6-(Me ₂ C) ₃ C ₆ H ₂
tol	toluene
tpsp	tri-iso-propylsilylphosphanide
tpspi	tri-iso-propylsilylphosphandiide
tpp	5,10,15,20-tetraphenylporphyrinate
tr	triclinic

1. INTRODUCTION

The last thirty years have seen many studies on the reaction of various metal salts with tin salts. In many cases compounds have been obtained for which crystallographic and structural data could be obtained. This review covers some 370 heterotin cluster complexes from trimers to polymers and complements a previous review of about 240 dimeric heterotin compounds [1]. Previous reviews have also covered some 600 tin coordination compounds [2], over 1,000 monomeric organotin compounds [3], over 260 dimeric organotin compounds [4] and almost 400 higher oligomers of organotin compounds [5]. The structures in this review are classified according to nuclearity, and within each subgroup by the increasing number of heterometal atoms. The factors relevant to the stereochemical interactions around these metals are discussed, and where appropriate

comparisons are made with other cluster systems.

2. TRIMERIC COMPOUNDS

There are almost 130 heterometallic tin compounds shown in Table 1, mostly with quite complex structures. Fifty five of these have two tin atoms and one heterometal atom, another sixty have one tin atom and two heterometal atoms, and eight contain one tin and two different heterometal atoms. These are listed in the Table by increasing number of heterometal atom and further subdivided into non-transition, transition and lanthanide compounds, and finally by increasing Sn-M distance.

2.1. Two Sn plus M

2.1.1 Non-Transition Metal M

A colourless Sn_2Li cluster [6] contains a $[\text{Li}(1,4\text{-dioxane})_4]^+$ cation and a $[\text{Sn}(\mu\text{-furyl})_3\text{Li}(\mu\text{-furyl})_3\text{Sn}]^-$ anion. In the latter the central Li atom has six furyl O atoms in an octahedral arrangement (LiO_6). Each satellite Sn(II) atom is bonded by three furyl carbon atoms in a typical pyramidal arrangement with C-Sn-C angles of $96(2)^\circ$.

There are four isostructural derivatives in which the heterometal atom is divalent Ca, Pb or Cd [7], or Sr [9], which have the composition $[\text{Sn}(\mu\text{-OBu})_3\text{M}(\mu\text{-OBu})_3\text{Sn}]$. In all cases the central M(II) atom is six coordinate (MO_6) while the outer Sn(II) atoms are three coordinate (SnO_3). The $\text{SnO}_3\text{MO}_3\text{Sn}$ framework is surrounded by six bulky tertiary butyl groups. The Sn-M and M-O distances increase as the ionic radius of M(II) increases, for example: 312.1(3) and 234(1) pm ($\text{M} = \text{Cd}$, 95 pm) < 313.3(3) and 237(1) pm (Ca , 100 pm) < 331.9(1) and 252.3(3) pm (Sr , 118 pm) < 336.1(1) and 256.0(9) pm (Pb , 119 pm). By contrast, the Sn-O values remain almost constant at 208 pm. Another colourless Sn_2Ca derivative [8] has the calcium atom on the crystallographic centre of inversion. It has a distorted octahedral coordination by two tin atoms (Sn-Ca, 327.2(3) pm) and four oxygen atoms from the (thf) ligands in a trans configuration. The Sn(II) atoms are also coordinated to three methyl groups. Barium is the "central" atom in another derivative [10] and is linked to four P atoms of $\text{P}(\text{SiMe}_3)_2$ groups which also bridge to the two outer Sn(II) atoms. These are also coordinated by terminal $\text{P}(\text{SiMe}_3)_2$ groups to give a pyramidal SnP_3 geometry. Finally, Pb is found in an "approximate" mirror plane of a Sn_2Pb derivative along with a $\mu_3\text{-oxo}$ bridge. The plane also bisects the Sn- $\mu_3\text{O}$ -Sn' link. The complex contains four syn-syn acetate ligands and four tert-butoxy ligands, two bridging and two terminal.

2.1.2 Transition or Lanthanide Metal M

Four coloured Sn_2Ti derivatives have titanium as the "central" metal atom [12-15]. The red derivative [12] consists of NEt_4^+ cations and $[\text{Ph}_3\text{SnTiSnPh}_3(\text{CO})_5]^-$ anions, the latter having Ti(0) coordinated by five carbonyl groups and two Sn(II) atoms making it seven coordinate (Sn-Ti-Sn angle, $141.07(6)^\circ$). The Sn(II) atoms have tetrahedral arrangements composed of a titanium atom (Sn-Ti, 281.1(2) and 284.1(2) pm) and three phenyl groups (SnC_2Ti). A black derivative [13] has Ti(0) coordinated by two $\eta\text{-C}_{10}\text{H}_8$ groups and two Sn(II) atoms. The Sn-Ti distances are 286.5(3) and 286.9(3) pm, which are longer than those in the red example [12]. The Sn(II) atoms have a tetrahedral geometry with a Ti atom and three methyl groups (Sn-Ti-Sn', $76.44(6)^\circ$). A yellow derivative [14] has two Sn^+Me_3 and one $\text{Ti}^{2+}(\text{2,6-Ph}_2\text{C}_6\text{H}_3\text{O})_2\text{Cl}$ moieties connected by $\mu_3\text{-N}$ links. Another red derivative [15] has crystallographic C_2 symmetry. One cp^*Ti and two SnMe_3 units are perpendicularly bridged by an acetylene group. Each Sn(IV) atom has tetrahedral geometry (SnC_4), and the Ti(II) atom sits in a sandwich (cp) which incorporates both carbon atoms of the acetylene group.

A dark red Sn_2Zr derivative [16] shows a Zr(II) central atom with pseudo-tetrahedral geometry from two stannylene donors, with a 2-fold axis bisecting the cp-Zr-cp and Sn-Zr-Sn' angles. The $\text{CH}(\text{SiMe}_3)_2$ groups on tin are positioned above and below the plane defined by zirconium and the two tin atoms. The Sn-Zr distance is 287.15(11) pm and the Sn-Sn distance of 423.64 pm excludes a direct bond. Another dark red Sn_2Zr derivative [17] contains an approximately capped trigonal prismatic arrangement about zirconium, with one tin atom in a capping position. The mean Sn-Zr distance of 301.2(3) pm is approximately 14.1 pm longer than that in the previous example [16]. Each tin atom has pseudo-tetrahedral geometry (SnC_2Zr_2). A black Sn_2Hf derivative [18] is similar to that of the Sn-Zr derivative [16] with a Sn-Hf bond distance of 295.3(1) pm and Sn-Hf-Sn angle of $81.14(3)^\circ$. Each of the metal atoms has a pseudo-tetrahedral geometry.

The structure of an orange Sn_2V cluster [19] consists of discrete tetraethylammonium cations and bis(triphenyltin)pentacarbonylvanadate anions. The vanadium atom is heptacoordinated to the five carbonyl and two triphenyltin ligands as a monocapped trigonal prism. The Sn-V distances are 275.7(3) and 278.5(3) pm, with the Sn-V-Sn angle at $137.9(1)^\circ$. A red Sn_2Nb derivative is similar to the Sn_2Hf derivative [18] with Sn-Nb bond distances of 281.7(1) and 283.0(1) pm and Sn-Nb-Sn angle of $87.18(3)^\circ$.

There are four coloured Sn_2Cr derivatives [21-23]. The first has a $\text{Cr}(\text{CO})_4$ moiety connected to two cis-stannylene ligands with the Sn-Cr-Sn angle of $101.37(3)^\circ$ and mean Sn-Cr bond distance of 255.7(1) pm. This

distance is about 8.4 pm shorter than that found in a gold yellow derivative [22a] at 264.1(1) pm with a Sn-Cr-Sn angle of $127.49(4)^\circ$ which is about 26° more open than in the former case. Another yellow cluster has a central Sn atom bound by two $\text{Cr}(\text{CO})_5$ moieties with Sn-Cr bond distances of 271.6(2) and 275.5(2) pm. A quasi-tetrahedral environment about tin is completed by two terminal chlorine atoms (SnCl_2Cr_2). A fourth derivative [23] has two Me_3Sn moieties and a $\text{Cr}(\text{CO})_5$ unit held together by a $\mu_3\text{-S}$ atom. This completes a tetrahedral geometry about each Sn(IV) atom and an octahedral geometry about the chromium atom (CrC_5S). A yellow Sn-Mo derivative [24] consists of two crystallographically independent molecules differing mostly by degree of distortion. The Mo atom is π -bonded to two cyclopentadienyl rings and through σ -bonds to the two Sn atoms (mean Sn-Mo bond distances of 272.3(1) and 272.5(1) pm). The Sn-Sn distances of 361.6(1) and 362.6(1) pm indicate the absence of any direct bonding. The structure of a Sn-W derivative [23] is found to be very similar to the Sn-Cr counterpart discussed above [25].

There is one derivative [25] with Sn and Mn for which the structure is shown Figure 1. The complex contains both tri- and tetracoordinated tin atoms, *trans* across the manganese atom, with the stannyl group tin atom incorporated into a stannaindan ring system. The Sn-Mn-Sn bond angle is $168.2(2)^\circ$, and the Sn-Mn bond distances differ markedly at 251.3(2) and 270.0(2) pm indicating a double and a single bond, respectively. In a Sn-Re derivative [26] three units, $\text{cp}(\text{CO})_2\text{Re}$ and two SnPh_3 , are connected by direct Sn-Re bonds with a mean Sn-Re distance of 273.2(1) pm and Sn-Re-Sn angle of $135.74(3)^\circ$.

Fig. 1. Structure of $[2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_3]\{3,5\text{-Bu}^i_2\text{C}_6\text{H}_3\text{C}(\text{Me})_2\text{CH}_2\}\text{Sn}_2\text{Mn}(\text{CO})_4$ [25]

There are nine coloured Sn_2Fe derivatives. The unit cell of $\text{cp}(\text{CO})(\text{H})\text{Fe}(\text{SnPh}_3)_2$ [27] contains two crystallographically independent molecules with essentially the same geometry. The structure can be described as a four legged piano stool, with the SnPh_3 groups occupying the mutually *trans* basal positions. The mean Sn-Fe bond distances of 256.39(1) and 256.69(1) pm are the shortest found in this set of derivatives and the Sn-Fe-Sn angle is the largest at 117.1° . Another three derivatives [28-30] have structures similar to that shown in Figure 1 [27]. An orange derivative has one Ph_3Sn unit bound to one carbon atom of a η^5 -indenyl group (Sn-C = 214.8(11) pm) which also serves as a bridge between the tin and a $\text{Fe}(\text{CO})_2$ unit. The second Ph_3Sn unit is directly bonded to the Fe atom (Sn-Fe = 258.5(2) pm). Both Sn atoms have tetrahedral geometry SnC_4 and SnC_3Fe , respectively. Another orange derivative, $(\text{Me}_3\text{Sn})_2(\mu\text{-cp})_2\text{Fe}$ [32] has almost parallel cyclopentadienyl rings (tilted 0.7° towards the Sn-Sn pair) in a nearly eclipsed conformation (twist angle of 2.9°). The two Me_3Sn units are displaced from the eclipsed arrangement by a torsion angle of about 5.3° . The Sn-Sn distance of 276.2(1) pm is the shortest in the Sn_2M series of trimers, and each tin atom has a distorted tetrahedral geometry (SnC_3Sn). A nearly linear array of nine atoms (Cl-Sn-N-C-Fe-C-N-Sn-Cl) with a total length of about 1,500 pm is found in a yellow derivative [33]. A crystallographic inversion centre at the iron results from this linearity (180°) with the phenyl groups on the tin atoms arranged in a staggered geometry. The iron atom has essentially octahedral geometry (four CN carbon atoms and two dimethylsulphoxide sulphur atoms). The tin atoms have slightly distorted trigonal bipyramidal environments, with equatorial phenyl groups and a chlorine and a nitrogen atom occupying axial sites. A dark red derivative [34] has the Fe(II) atom encapsulated by the clatrocyclate nioximate ligand and surrounded by a distorted trigonal antiprismatic coordination sphere of six nitrogen atoms from three dioxime units. The Sn(IV) atoms have slightly distorted octahedral geometry (SnO_3Cl_3). The Fe(II) atom does not deviate much from the Sn..Sn axis (Sn-Fe-Sn = 178.8°). The Sn-Fe distances at 361.2(1) pm preclude a metal-metal bond. In a dark orange derivative $(\text{Ph}_3\text{Sn})_2(\mu\text{-C}_5\text{H}_4)_2\text{Fe}$ [35] the

cyclopentadienyl rings of the ferrocene moiety are planar, with a dihedral angle of $1.4(3)^\circ$ between them. However, the presence of two bulky triphenyltin groups attached in a *trans* configuration causes the rings to be slightly staggered, the largest torsion angle being $19.4(4)^\circ$. The tin atoms with their bonded cyclopentadienyl rings are coplanar. The non-bonded Sn-Fe distances are 374.2 and 374.6 pm.

There are three yellow and one brown Sn_2Co and derivatives [36-38]. In the latter [36] the central $\text{Co}(\text{CO})_3$ unit is bound to two SnCl_3 units with Co-Sn bond distances of 244.1(1) and 244.4(1) pm, respectively. Two crystallographically independent molecules are found in this system. The Sn-Co-Sn is almost linear, with an angle of $178.9(1)^\circ$ in one and $179.4(1)^\circ$ in the other. The tin atoms have distorted tetrahedral geometry (SnCl_3Co) with the central cobalt in a trigonal bipyramidal arrangement ($\text{Co}(\text{CO})_3\text{Sn}_2$). The three yellow derivatives [37,38] are isostructural with the Sn_2Fe derivative discussed above [34]. The Co atoms are encapsulated by the macrocyclic dioximate ligand and surrounded by a distorted trigonal antiprismatic coordination of six nitrogen donor atoms. Each Sn(IV) atom has a slightly distorted octahedral environment (SnO_3X_3 , X = Cl or Br). The mean Sn-Co distance is 360 pm which does not indicate a metal-metal bond. The Sn-Co-Sn angle is very similar in all three complexes with a mean value of 179.5° .

The structure of a brown-black Sn_2Ni derivative [39] is shown in Figure 2. Cyclopentadienyl ligands are coordinated sandwich fashion to the three metal atoms. One cp ligand is π -bonded to the Ni atom such that the centre of the cp ligand and the three metal atoms lie almost within a plane. The second cp ligand symmetrically bridges the two stannylene units via the Sn atoms in a π -bonded manner with Sn-C distances of 270.2(12) and 260.8(11) pm, respectively. In a blue derivative [40] two dithioxalate groups (tetradentate O_2S_2) serve as bridges between the three metal atoms. The central Ni(II) atom is sulphur bonded (square planar NiS_4) and the Sn(IV) are octahedrally coordinated (SnO_2Cl_4).

Fig.2. Structure of $[\text{cpNi}\{\text{Sn}(\text{NBu})_2\text{SiMe}_2\}_2(\mu\text{-cp})]$ [39]

A pink Sn-Ru derivative [41] has a slightly distorted octahedral geometry in which the SnPh_3 units occupy axial positions about ruthenium ($\text{Ru-Sn} = 268.6(2)$ and $269.1(2)$ pm). The Sn-Ru-Sn angle is nearly linear at $173.45(7)^\circ$ with a staggered conformation of phenyl groups. The Ru atom is six coordinate ($\text{RuCl}_2\text{N}_2\text{Sn}_2$).

A Sn-Rh complex [42] crystallises in a highly distorted square-planar *cis* geometry. The plane defined by Rh-P(1)-P(2) is twisted by 15.8° relative to the plane defined by the three metal atoms. The complex may be considered as an insertion of a stannylene unit into the Rh-Cl bond of the $\text{RhCl}(\text{PPh}_3)_3$ moiety. The most unusual feature of the structure is the chlorine bridged chelating bis(stannylene) ligand. This complex is somewhat reminiscent of the Sn_2Cl_5^- complex anion. Both Sn-Rh bond distances are almost equal (257.1(2) and 257.7(2) pm).

Yellow $(\text{PMe}_3)_2\text{Pd}(\text{SnMe}_3)_2$ [43] has a twisted square planar structure. The distortion can be seen as a 16.8° dihedral angle between the PdP_2 and PdSn_2 planes. The Sn-Pd bond distances are almost equal (260.4(1) and 260.7(1) pm) with the Sn-Pd-Sn angle at $80.71(3)^\circ$.

There are two Sn-Os derivatives in this series, in both cases with six coordinate osmium atoms [44,45]. The Sn atoms are located at the apical positions and are tetrahedrally coordinated (SnCl_3O [44] and SnCl_3O_3 [45]). The Sn-Pd distances are 264.8(1) and 271.7(1) pm, respectively, with an almost linear Sn-Os-Sn angle.

A red green derivative [46] contains complex anions with Sn_2Ir and complex cations with SnIr_2 frames. The complex anion has a trigonal bipyramidal iridium (IrP_2CSn_2) with Co and P as the axial ligands (C-Ir-P angle = $178.9(9)^\circ$). The Sn-Ir bond distances are 256.9(2) and 259.2(3) pm with Sn-Ir-Sn angle of $108.7(2)^\circ$. The complex cation consists of the intact 12 atom metallocyclic ring $(\text{-IrPCAsCP-})_2$ with the tin symmetrically

bound to the two iridium atoms and a chlorine atom (Ir-Sn distances 274.1(2) pm, 274.2(2) pm; Sn-Cl = 244.3(7) pm and Ir-Sn-Ir angle = 146.1(1)° in a planar arrangement.

There are seven Sn-Pt derivatives, one colourless and the rest yellow. Two of them, triclinic and monoclinic [47] contain *cis*-[Cl₂Pt(SnCl₃)₂]⁻ anions disordered in such a way as to be pseudo-centrosymmetric. This disordering involves half of the occupied PtCl₂ sites appearing on either side of the centre. Simultaneously, one chlorine from each SnCl₃ unit changes side while the other chlorine atoms appear in average positions with very small displacements between their positions. The Pt-Sn distance (235.56 pm ave.) is the shortest in the Sn₂Pt derivatives. The Sn-Pt-Sn angle is 111.48(3)°. Somewhat longer Sn-Pt bonds (248.9(1) pm) were found in another *cis*-[Cl₂Pt(SnCl₃)₂]⁻ anion with a smaller Sn-Pt-Sn angle of 97.8(2)° [48]. Yellow (PPh₃)₂Pt{Sn(acac)₂}₂ complex [49] has three metal moieties directly held by Sn-Pt bonds at an average distance of 255.8(1) pm. Square planar geometry is found in another complex, {P(OPh)₃}₂Pt(SnCl₃)₂ [50] with SnCl₃ ligands in *trans* positions. Each Sn(II) atom has a distorted tetrahedral geometry (SnCl₃Pt), and the Sn-Pt bond distances are 258.8(2) pm. Another yellow complex [51] has three metal atoms bridged by two sulphur atoms in a 5 membered metallocyclic ring (-Pt-Sn-S-Sn-S-) with a Pt-Sn distance of 255.2(1) pm and Sn-S-Pt and Sn-S-Sn angles of 108.2(1)° and 100.1(1)°. The Pt(IV) atom has pseudo-octahedral arrangement (PtN₂C₂SSn) and each tin atom is tetrahedrally coordinated (SnC₂S₂ and SnC₂SPt). The colourless complex [52] also has a 5 membered metallocyclic ring (Pt-Sn-O-Sn-O-) with a Sn-Pt distance of 262.8(1) pm. All metals are four coordinate but each is different. The Pt atom is square planar (PtP₂OSn), and the Sn atoms have tetrahedral geometry with different sets of donor atoms (SnC₂O₂ and SnC₂OPt, respectively).

There are two Sn-Yb complexes, dark orange [53] and yellow [54]. A noteworthy feature of the former is the pseudo-tetrahedral geometry about the Yb(II) atom (YbO₂Sn), and the apparently long Yb-Sn bond of 321.6(1) pm. Each tin is tetrahedrally coordinated (SnC₃Yb) with a Sn-Yb-Sn angle of 132.34(3)°. The other Yb complex [54] has a distorted octahedral structure. The Yb atom has four (thf)-O atoms in the equatorial plane and two Ph₃Sn tin atoms in axial positions. The Sn-Yb distance of 330.5(1) pm is about 8.9 pm longer than that of the orange derivative [53]. The Sn-Yb-Sn angle of 164.5(1)° is larger than that of the orange case. Both tin atoms are again tetrahedrally coordinated (SnC₃Yb).

2.2 Sn plus Two M

2.2.1 Non-Transition Metal M

A colourless lithium derivative [55] shows a complex structure in which six membered stannasiloxane rings are coplanar with each other and with four membered lithiostannoxane rings. The lithium atoms are tetrahedrally coordinated (LiO₄) and the tin atom is octahedrally configured (SnO₄Cl₂). As indicated in Table 1 the Sn-Li distance is 301.3(11) pm.

The structure of an orange SnCa₂ complex [56] has a three coordinated Sn(II) atom (SnP₃) with six coordinated Ca(II) atoms (CaO₃P₃ and CaP₄O₂). There are two crystallographically independent molecules present in the crystal. The average separation of 385 pm between Ca atoms excludes a real metal-metal bond.

There is one SnAl₂ derivative [57] which crystallizes in the centrosymmetric space group *Pi*. The molecular structure consists of a central Sn(IV) atom with an octahedral arrangement of two terminal iodine atoms in *cis* positions, with four isopropoxy oxygen atoms of two bidentate {Al(OPr)ⁱ}⁻ anions.

2.2.2. Transition or Lanthanide Metal M

One SnTi₂ derivative [57] crystallize in the acentric space group *P2₁*. In other respects the structure mirrors that of the SnAl₂ derivative mentioned above [57], except for the bidentate aluminium alkoxy anions which are now {Ti(OPr)₃}⁻ anions. Again, the Sn(IV) atom is in an octahedral arrangement of two iodine atoms and four oxygen atoms.

There is a red-orange and an orange SnNb₂ derivative [58] both of which contain the Nb-Sn-Nb metal chain, with mean Nb-Sn bond distances of 284.0(2) and 286.2(1) pm. The angle at the tin atom is 140.69° in one case and 129.44° in the other (Table 1).

Four yellow and two orange derivatives are found with chromium as the heterometal atoms [59-62]. The four yellow derivatives [59,60] contain the Cr-Sn-Cr metal chain with Sn-Cr distances from 261.4(1) to 270.1(2) pm (average 266 pm). As the Sn-Cr distance increases the Cr-Sn-Cr angle closes, for example: 261.9(1) pm and 138.80(3)° [59]; 264.2(4) pm and 131.6(1)° [59]; 268.4(1) pm and 130.72(5)° [59]; 269.7(2) pm and 130.2(1)° pm [60]. In each case the tin is in a tetrahedral environment. The remaining two orange complexes [61,62] contain a tin atom bonded to two methyl and two mesityl [61] or phenyl [62] groups. Each mesityl or phenyl group is also bonded to a Cr(CO)₃ moiety in a η⁵ fashion. The geometry around the tin atom is distorted tetrahedral (SnC₄).

A yellow [63] and an orange [57] SnMo₂ cluster are isostructural with an Mo-Sn-Mo metal chain with a mean Mo-Sn distance of 300 pm and Mo-Sn-Mo angle of 133.9(3)°. Each tin atom is tetrahedrally coordinated

(SnX_2Mo_2 , where $X = \text{Br}$ [63] or I [57]). The molybdenum atoms are also tetrahedrally coordinated (MocpC_3). There are four Sn-W derivatives [59,64-66]. The yellow-orange derivative has the W-Sn-W metal chain with Sn-W distances of 280.9(2) pm and interbond angle of $130.62(4)^\circ$. The tin atom has a tetrahedral arrangement (SnBr_2W_2) and the tungsten atoms are pseudo-octahedral (WC_5Sn). The other SnW_2 derivatives do not contain a metallic chain. Seven coordinate tungsten (4 + 3 geometry) is found in another derivative. One tungsten is bonded to three bridging chlorine atoms and four CO groups, the other is bonded to three bridging chlorine atoms, three CO groups and the Sn atom of a SnCl_3 moiety (a W-W-Sn arrangement). The W-Sn bond distance is 273.1(1) pm and the two neighbouring tungsten atoms are 352.5(1) pm apart. The tin atom has a distorted tetrahedral arrangement (SnCl_3W). The structure of a blue complex is shown Figure 3 [65] and shows a W_2Sn cluster with a (diethylamino)carbyne ligand bridging the tungsten atoms. The W-W axis is bridged by one $[\text{S}_2\text{CNEt}_2]^-$, one $[\text{S}]^{2-}$ and the unusual dithiostannate(IV) ligand $[\text{S}_2\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}_2]^{2-}$. A chelating dithiocarbamate ligand completes the roughly octahedral coordination environment around each tungsten (WS_5C). A W-W bond distance of 261.4(2) pm and acute W-S-W angle of $69.3(2)^\circ$ and W-C-W angle of $77.5(6)^\circ$ are observed. The Sn(IV) atom has a tetrahedral environment SnC_2S_2 . An emerald complex [66] is observed to have a SnW_2 cluster with a sulphide and an alkyne bridge between the tungsten atoms. One of the tungsten atoms is linked to the tin atom by two sulphide bridges. The W(III)-W(IV) distance is 281.9(3) pm, the former being surrounded by four S and one C atom (WS_4C), while the W(III) atom has three of each (WC_3S_3). The Sn(II) atom is tetrahedrally coordinated (SnC_2S_2).

Fig.3. Structure of $\text{W}_2(\text{dedtc})_3(\text{CNEt}_2)(\text{S})_2\text{Sn}(\text{CH}(\text{SiMe}_3)_2)_2$ [65]

There are ten derivatives with manganese as the heterometal atom [67-73]. Nine of these contain Mn-Sn-Mn chains with Sn-Mn distances from 243.7(2) to 271.3(1) pm (average 254 pm). There is a trend for the Sn-Mn bond distance to increase as the metal chain angle at tin closes: 245.8(2) pm and $142.6(1)^\circ$ [67], 251.3(3) pm and $134.4(1)^\circ$ [70], 264.2(3) pm and $125.88(9)^\circ$ [71], 271.2(1) pm and $121.9(1)^\circ$ [72]. Tin atoms in oxidation states of zero and +4 are observed. There are 3-coordinated $\text{Sn}(\text{O})$ examples (SnXMn_2) with $X = \text{Cl}$, Br or I [67], and 4-coordinated $\text{Sn}(\text{O})$ examples (Sn_2Mn_2) [68,69]. All of the Sn(IV) atoms have tetrahedral geometry (SnX_2Mn_2) where $X = \text{Cl}$ or Br [71] or phenyl [72]. For the 3-coordinate $\text{Sn}(\text{O})$ species the Sn-X bond distance increases with covalent radius of X: 250.1(3) pm (Cl , 99 pm) < 275.5(3) pm (Br , 114 pm) < 298.5(1) pm (I , 133 pm). At the same time the Sn-Mn bond distances also increase in the same order: 245.8(2) pm < 246.4(3) pm < 246.8(2) pm. The same trends can be seen for the 4-coordinate Sn(IV) atoms with mean Sn(IV)-X and Sn-Mn bond distances of: 238.5(2) and 263.5(1) pm ($X = \text{Cl}$) [71], and 254.8(2) and 264.2(3) pm ($X = \text{Br}$) [71]. Manganese atoms with Sn(O) atoms are all coordinated by cyclopentadienyl ring ligands plus two CO groups (MnC_7). Manganese atoms with Sn(IV) atoms are mostly bonded to five CO groups (MnC_5) except one study [72] where the manganese is bonded to four CO groups and one MeNC ligand (MnC_5). In the tenth SnMn_2 example [73] the central SnCl_2 moiety bridges two $\text{C}_5\text{H}_4\text{Mn}(\text{CO})_3$ units through one carbon atom of each C_5H_4 ligand. The Sn(IV) atom has a distorted tetrahedral geometry (SnC_2Cl_2) with a mean Sn-C bond distance of 210.6(6) pm. Three derivatives have two Re atoms [74,75]. In two examples, colourless and dark red, a SnX_2 moiety bridges two $\text{Re}(\text{CO})_4(\text{PPh}_3)$ units. The Sn-Re bond distances are 273.0(2) and 274.1(2) pm ($X = \text{Br}$) and

277.7(5) and 278.1(4) pm ($X = \text{Cl}$). The corresponding Re-Sn-Re angles are $124.8(1)^\circ$ and $131.1(2)^\circ$. The Sn(IV) atom has a distorted tetrahedral configuration (SnX_2Re_2). The third example is centrosymmetric $\text{Sn}(\text{tpp})\{\text{Re}(\text{CO})_3(\text{C})\}_2$ [75] which contains two $\text{Re}(\text{CO})_3$ groups, one above and one below the plane of the porphyrin ring around the Sn(IV) atom. The tin and rhenium atoms are linked by a carbido C atom. The Sn(IV) atom has a tetragonal bipyramidal arrangement with four tetraphenylporphyrinate N atoms in the plane and a carbon atom at the apical positions.

The iron containing SnM_2 derivatives are the most abundant with sixteen examples [76-87]. Eleven of them [76-85] contain three metallic chains with Sn-Fe distances ranging from 249.0 to 265.0(4) pm (average 254 pm) and Fe-Sn-Fe angles from $115.9(1)^\circ$ to $135.7(1)^\circ$ (average 126.3°). There are another four derivatives [86] which are isostructural and contain a metal triangle with Sn-Fe bond distances from 260.3(2) to 261.6(21) pm (average 261 pm) and Fe-Fe bond distances from 278.8(2) to 279.7(2) pm (average 279.4 pm). The Fe-Sn-Fe ring angles have a small range of 64.6° to $64.9(1)^\circ$ (64.7°), but the Fe-Fe-Sn angles are about 7° smaller (57.6° to $58.0(1)^\circ$, average 57.7°). The most recent SnFe_2 cluster [87] utilizes SnCl_2 as a bridge between two $(\text{C}_5\text{H}_4)\text{Fe}(\text{cp})$ moieties, with Sn-Cl bond distances of 208.1(15) pm. The Sn-Fe distance of 354 pm precludes a direct metal-metal bond. In the sixteen clusters each Sn(IV) atom is tetrahedrally coordinated, SnX_2Fe_2 [76-86] and SnCl_4 [87], but with differing degrees of distortion. The $\{\text{Fe}(\text{CO})_4\}_2\text{Sn}(2,4,6\text{-Pr}_3\text{C}_6\text{H}_2)$ structure [87] contains two crystallographically independent clusters representing distortion isomers.

Eight derivatives contain SnCo_2 clusters [88-94]. Five of them have a trimetallic Co-Sn-Co chain with Sn-Co bond distances from 249.8(91) to 257.5(8) pm (average 253 pm) and Co-Sn-Co bond angles from 118.3° to $129.3(1)^\circ$ (average 127°). A red derivative [92] contains a trimetallic ring with Sn-Co bond distances of 256.4(3) and 259.1(3) pm and Co-Co bond distance of 262.6(94) pm. The Co-Sn-Co angle of $61.24(9)^\circ$ is larger than the Sn-Co-Co angles of $58.88(8)^\circ$ and $59.88(9)^\circ$. The two cobalt atoms are bridged by carbonyl group. In five of the clusters [88-91] the Sn(IV) atoms are tetrahedrally coordinated SnX_2CO_2 ($X = \text{Cl}$ [88-91], $X = \text{Ph}$ [88]) and in one case octahedrally coordinated SnO_2Cl_2 [92]. A light yellow cluster [93] has a central Sn(II) atom and two Cocp units at an angle, linked by two tripod ligands through O atoms to Sn(II) and P atoms to Cocp . The Sn(II) atom has an octahedral environment SnO_6 and the Co atoms are in tetrahedral environments cpCoP_3 . The Sn-Co distance of 437.2(8) pm (mean) is too large to consider as a metal-metal bond. Dark orange $\{\text{cpCo}(\text{db})\}_2\text{Sn}$ [94] contains two crystallographically independent molecules differing mostly by degree of distortion. Two virtually identical $\text{cpCO}(\text{C}_2\text{B}_2\text{C})$ sandwich units are bound to the central tin atom in a η^2 fashion via the bridging 1,3-biborolenyl ligands. The tetra-decker complex exhibits a bent structure in which the Sn-Co vectors form a 130° angle.

A green SnNi_2 cluster [95] contains a trimetallic ring (Ni-Sn-Ni) with Sn-Ni bond distances of 246.5(91) and 246.9(1) pm, with Ni-Sn-Ni angle of $133.8(1)^\circ$.

Three derivatives [96-98] contain SnRu_2 clusters. A pale yellow one [96] has the three metals in a ring with Sn-Ru bond distances of 269.9(1) and 271.5(1) pm and a Ru-Ru bond distance of 295.4(2) pm. The Ru-Sn-Ru angle of $66.1(1)^\circ$ is about 9° more open than the Sn-Ru-Ru angles of $56.7(1)^\circ$ and $57.2(1)^\circ$. The Sn atom is tetrahedral, SnC_2Ru_2 . The structure of a derivative with a quadricyclic SnS_2Ru_2 ring is shown in Figure 4 [97]. The Ru(1)-Ru(2) bond distance is 263.7(2) pm and the Ru-S-Ru angle is 65.7° compared to the mean Ru-S-Sn bond angle of 90.8° . In another derivative [98] the ruthenium atoms are both six coordinate, each bonded to three chlorine atoms on the outer side and two carbonyl groups plus a SnCl_3 moiety on the inner side. The Sn-Ru bond distance of 256.4(4) pm is much shorter than that between the two ruthenium atoms (Ru-Ru distance = 315.7(4) pm).

There are three SnRh_2 clusters [99,100]. In one of them [99] all three metals form a chain (Rh-Sn-Rh) with Sn-Rh bond distances of 256.5(94) pm and two equal Rh-Sn-Rh bond angles of $143.52(3)^\circ$. The Sn(II) atom is pyramidally coordinated (SnCl_2Rh) while each Rh(I) atom has a trigonal bipyramidal arrangement. A pale yellow SnRh_2 cluster [100] has $(\text{cod})\text{Rh}^+$ cations coordinated to two ethoxide ligands to produce a molecule with approximate C_2 molecular symmetry. Of the six ethoxide ligands coordinated to tin, two *cis*-pairs are coordinated to Rh(1) and Rh(2), resulting in a distortion of the octahedral coordination environment for tin and distortion of the square-planar coordination environment of rhodium.

There is only one derivative with a SnPd_2 cluster [101]. The X-ray analysis shows three metal atoms forming a nearly linear Pd-Pd-Sn chain (angle $165.8(1)^\circ$). The Sn-Pd and Pd-Pd distances are 258.5(92) and 264.4(2) pm, respectively. Two dppm ligands bridge two Pd atoms. The outer Pd atom is also coordinated by a chlorine atom to complete a distorted square planar arrangement (PdP_2ClPd). The inner Pd atom also has a distorted square planar geometry (PdP_2SnPd). The Sn(II) atom has tetrahedral geometry (SnCl_3Pd).

A green SnIr_2 cluster [102] consists of the intact metallomacrocyclic $(\text{IrPC}_4\text{P})_2$ with the Sn(II) atom bonded to it through the two Ir atoms. It has a crystallographically imposed C_2 symmetry with C_2 axis running through the tin atom and bisecting the Cl-Sn-Cl angle. The Sn(II) atom has a distorted tetrahedral environment (SnCl_2Ir_2). The Sn-Ir bond distances are equal at 275.1(1) pm, and the Ir-Sn-Ir angle has the value $138.8(1)^\circ$.

Finally, a dark ruby red cluster [103] contains two ytterbium atoms connected by three bridging phenyl rings. One of the Yb atoms is bonded to a triphenyltin moiety ($\text{Sn-Yb} = 337.9(1) \text{ pm}$) and two tetrahydrofuran molecules. The second Yb atom is surrounded by three molecules of tetrahydrofuran, and the Yb-Yb distance is $322.6(1) \text{ pm}$.

Fig. 4. Structure of $(\text{CO})_4\text{Ru}_2(\mu\text{-S})_2\text{Sn}(\text{tb})(\text{tip})$ [97]

2.3 Sn plus M and M'

There are eight trimetallic derivatives that contain tin plus two different heterometal atoms, and their crystallographic and structural data are given in Table 1. The first, an orange-red $\text{cp}_2\text{W}(\text{SnPh}_3)\text{HgI}$ cluster [104], has a cp_2W unit directly bonded to HgI ($\text{W-Hg} = 263.4(1) \text{ pm}$) and SnPh_3 ($\text{W-Sn} = 276.8(2) \text{ pm}$). The Hg-W-Sn angle is $78.87(6)^\circ$.

The yellow derivative $[\text{MeGa}(\mu\text{-}\eta^5\text{-pz})_3\text{Mo}(\text{CO})_3\text{SnPh}_3]$ cluster [105] has MeGa and $\text{Mo}(\text{CO})_3$ moieties connected by three η^5 -pyrazolyl groups. The $\text{Mo}(\text{CO})_3$ unit is also connected to SnPh_3 with a Mo-Sn bond distance of $285.79(3) \text{ pm}$. Both gallium and tin are tetrahedrally coordinated (GaN_3C and SnC_3Mo), and the central molybdenum atom is seven-coordinate ($\text{MoN}_3\text{C}_3\text{Sn}$). Another Mo/Sn cluster includes thallium [106], this time with the tin atom in the centre. Three tert-butoxy groups bridge the Sn(II) and Tl(I) atoms, bringing them within $329.8(1) \text{ pm}$. In addition, a $\text{Mo}(\text{CO})_3$ moiety is bonded to Sn(II) to complete 4-coordination with a Sn-Mo bond distance of $277.0(2) \text{ pm}$. The Mo-Sn-Tl bond angle is almost linear at $178.8(1)^\circ$.

There are two derivatives with MnMoSn clusters [107,108]. The first is red and consists of $\text{Mn}(\text{CO})_2$ and $\text{Mo}(\text{CO})_2\text{SnPh}_3$ units bridged by S_2CPcy_3 and trisisopropylphosphoniodithioformate ligands [107]. The Mn-Mo bond distance of $293.7(8) \text{ pm}$ is about 13.8 pm longer than the Mo-Sn distance ($279.9(5) \text{ pm}$). The three metals have different stereochemistry. Tin is tetrahedrally coordinated (SnC_3Mo), molybdenum is six coordinate ($\text{MoC}_2\text{S}_2\text{PMn}$) and manganese is seven coordinate ($\text{MnC}_3\text{S}_2\text{PMo}$), and the Mn-Mo-Sn angle is bent at $139.9(2)^\circ$. The second is yellow-orange and has $\text{Mn}(\text{CO})_3$ and $\text{Mo}(\text{CO})_3(\text{SnPh}_3)$ units bridged by the S_2CPPr^t ligand [108]. The Mn-Mo bond distance of $287.7(1) \text{ pm}$ is somewhat shorter than in the previous example [107], while the Mo-Sn bond distance of $281.0(1) \text{ pm}$ is about 1.1 pm longer than previously. The stereochemistry about the atoms is similar to the other example [107], with the Mn-Mo-Sn angle about 5° smaller at $134.9(2)^\circ$.

The structure of a pale yellow MnSnCo cluster [108] consists of a trimetallic chain with a tin atom in the middle. All the metal atoms are covalently bonded with distances of $272.8(10) \text{ pm}$ (Sn-Mn) and $265.7(10) \text{ pm}$ (Sn-Co), and a Mn-Sn-Co bond angle of $114.4(2)^\circ$. The tin atom has a tetrahedral environment (SnC_2MnCo) and the other two metals are octahedrally coordinated (MC_5Sn).

A deep red cluster [110] contains an almost linear Fe-Pd-Sn chain with bond distances of $266.55(6) \text{ pm}$ (Fe-Pd), $259.50(5) \text{ pm}$ (Pd-Sn) and an Fe-Pd-Sn bond angle of $169.34(2)^\circ$. The Sn and Pd atoms are four coordinate, tetrahedral SnC_3Pd and square planar PdOPSnFe , while the Fe atom is six coordinate (FeC_2PSiPd). A bright yellow cluster [111] has a trimetallic chain of Fe-Sn-Pt atoms. The bond distances are $256.8(2) \text{ pm}$ (Sn-Fe) and $252.4(2) \text{ pm}$ (Sn-Pt), with an Fe-Sn-Pt bond angle of $115.8(1)^\circ$. The Pt and Fe atoms are bridged by a dppe ligand giving a six membered metallocyclic ring. The tin atom is tetrahedrally coordinated.

TABLE 1. Crystallographic and Structural Data for Trimeric Hetero Metallic Tin Compounds*

COMPOUND (colour)	Crys. cl. Sp. Grp	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo- phore.	M-L [pm]	M-M [nm] M-L-M [°]	L-M-L [°]	Ref
2Sn + M								
[Li(1,4-dio) ₄]	tr ₁	1089(1)	102.5(1)	Sn ^{IV} C ₃ (x2)	μ L ^b , C ^b 218.8(9)		C-C ^b 96(2)	6
[Sn(μ-fu) ₃]	P ₁	1372(1)	104.6(1)					
Li(μ-fu) ₃ Sn ^c	2	1974(3)	92.25(8)	Li ^I O ₃	μ O _L 209.6(9) 229(1)		O-O 90(-.3)	
(colourless)								
[Sn(μ-OBu) ₃ Ca]	or	2008.2(17)		Sn ^{IV} O ₃ (x2)	μ O _L 208.7(9)	Ca 313.3(3)	O-O 81.8(2)	7
(μ-OBu) ₃ Sn	Pnma	1713.6(14)						
(colourless)	4	998.5(9)		Ca ^{IV} O ₃	μ O _L 237(1)		O-O 70.4(1)	
[M ₃ SnCa ₂ Sn ^{IV} Me ₃	tr ₁	94.3(0)	62.75(1)	Sn ^{IV} C ₃ Ca (x2)	C _{Me} 219.8(5.3)	Ca 327.21(3)	C-C 96.5(3.1.4)	8a
(thf) ₄]	P ₁	991.3(1)	71.09(1)				C-Ca 120.4(2.4.3)	
(colourless)	1	1053.3(1)	63.58(1)	Ca ^{IV} O ₃	O _{Me} 235.3(3) 2394(3)		O-O no: given	
(thf) ₂ CaSn ₂	or	2247.7(2)		Sn ^{IV} P ₃	μ P 254.2(1.1)	Ca 355.6(1.11)	O-Ca 89.1(8.1.7)	8b
{μ-P (SiMe ₃) ₂ } ₂	Pnma	1868.9(1)			P 2(8.3(2.4)			
(μ-P (SiMe ₃) ₂	4	1168.0(1)		C ^{IV} O ₃ P ₄	O _{Me} 234.4(3.) μ P 291.2(2.9)		O-P 100.3(1.1.8)	
(colourless)							P-P 78.8(5.4.5)	
[Sn(μ-OBu) ₃]	$\bar{4}_2$	1017(1)		Sn ^{IV} O ₃ (x2)	μ O _L 207.8(3)	Sr 331.9(1)	157.53(6)	9
Sr (μ-OBu) ₃ Sn]	R ₃						O-O 65.6(1)	
(colourless)	3	2986(2)		Sr ^{IV} O ₃	μ O _L 252.3(3)		82.3(1)	
							O-O 90±24.4	
[{(Me ₃ Si) ₂ P ₂ Sn} ₂	or	1265.1(1)		Sn ^{IV} P ₃ (x2)	P 260.1(3.4)		P-P 92.3(1.3.9)	10
{μ-(Me ₃ Si) ₂ P ₂ Ba]	P2 ₁ 2 ₁ 2 ₁	2290.1(3)			μ P 268.4(3.24)		105.1(1.8)	
(colourless)	4	2731.9(3)		Ba ^{IV} P ₄	μ P 323.8(3.74)		72.2(1.3)	
at 173K							122.6(1.5.3)	
							150.30(8)	

$[(\text{thf})_4\text{Ba}\{\text{Sn}(\mu\text{-P}(\text{SiMe}_3)_2)\}_2(\mu\text{-P}(\text{SiMe}_3)_2)]^{\text{e}}$ (colourless) at 173K	m P2 ₁ /c 8	1301.9(2) 2316.3(3) 3968.7(5)	99.29(1)	$\text{Sn}^{\text{IV}}\text{P}_3$ (x2) $\text{Ba}^{\text{II}}\text{O}_4\text{F}_4$	μP 262.6(2,11) $\mu_3\text{P}$ 268.5(2,3) O 272.5(4,49) μP 322.3(2,58) $\mu_3\text{P}$ 332.2(1)	Ba 400.2(-1)	P,P 80.5(1,3) 91.4(1,1,3) O,O 73.2(2,1) 106.9(1) P,P 64.47(4) 71.9(1,9); 136.86(4) P,P 81.2(1,1) 92.5(1,1,5) O,O 73.5(1,4,6) 136.6(1) P,P 62.6(3) 69.7(1,1,5); 132.26(3) O,O 82.5(4,1,2)	10
$\text{Sn}(\mu\text{-O}(\text{Bu})_3)_2\text{Pb}(\mu\text{-O}(\text{Bu})_3)_2$ (colourless)	m P2 ₁ /c 4	1003.6(5) 3361.6(16) 1159.3(7)	114.88(5)	$\text{Sn}^{\text{IV}}\text{O}_3$ (x2) $\text{Pb}^{\text{IV}}\text{O}_6$	μP 263.1(1,14) $\mu_3\text{O}$ 268.4(1,5) O 283.2(4,28) μP 332.4(1,56) $\mu_3\text{P}$ 345.2(1)	Ba 412.3(-35)	P,P 81.2(1,1) 92.5(1,1,5) O,O 73.5(1,4,6) 136.6(1) P,P 62.6(3) 69.7(1,1,5); 132.26(3) O,O 82.5(4,1,2)	7
$\text{Pb}_2\text{Sn}_2(\mu\text{-O})_2(\mu\text{-ac})_4(\mu\text{-OCu})_2$ (pale yellow)	tr P1 2	1187.1(8) 1306.9(8) 1368.9(8)	118.74(3) 92.32(3) 94.09(4)	$\text{Sn}^{\text{IV}}\text{O}_6$ (x2) $\text{Pb}^{\text{IV}}\text{O}_5$	$\mu_3\text{O}$ 199.7(5,4) μO not given μO_2 not given O_{Bu} 193.7(4) μO 222.8(6) μO not given μO_2 not given μO_L 208.0(9)	$\mu_3\text{O}$ 129.0(6) $\mu_3\text{O}$ 109.4(2,6) Cd 312.1(3)	O,O 64.5(3,1,0) 115.3(3,7,1) 174.1(3,2,0) O,O 178.7(2,8)	11
$\text{Sn}(\mu\text{-O}(\text{Bu})_3)_2\text{Cd}(\mu\text{-O}(\text{Bu})_3)_2$ (colourless)	or Pnma 4	1999.1(13) 1723.7(11) 997.6(9)		$\text{Sn}^{\text{IV}}\text{O}_3$ (x2) $\text{Cd}^{\text{IV}}\text{O}_5$ $\text{Sn}^{\text{IV}}\text{C}_3\text{Ti}$ (x2)	μO_L 234(1) C_{Ti} 220(1)		O,O 81.1(2)	7
$[\text{Ph}_3\text{SnTiSnPh}_3(\text{CO})_5](\text{NEt}_4)_2$ (red)	m P2 ₁ /a 4	3135.2(8) 1633.9(3) 1077.7(8)	95.62(5)	$\text{Ti}^{\text{IV}}\text{C}_3\text{Sn}$ $\text{Sn}^{\text{IV}}\text{C}_3\text{Ti}$ (x2)	OC 204(1,3) C_{Me} 219(2)	Ti 282.6(2,15)	O,O 70.5(2) not given	12
$[\eta^4\text{-C}_{10}\text{H}_8)_2\text{Ti}(\text{SnMe}_3)_2]$ [K(15-crown-5)] (black) at 162K	m P2 ₁ /n 4	1609.4(6) 1873.2(9) 2748(1)	103.71(3)	$\text{Ti}^{\text{IV}}\text{C}_3\text{Sn}$ $\text{Sn}^{\text{IV}}\text{C}_3\text{Ti}$ (x2)	OC 204(1,3) C_{Me} 219(2)	Ti 286.7(3,2) Sn 3.54	Sn,Sn 141.0(6) not given	13
$[(2,6\text{-Ph}_2\text{C}_6\text{H}_3\text{O})_2\text{ClTi}(\mu_3\text{-N})(\text{SnMe}_3)_2]$ (yellow)	tr P1 2	1124.1(2) 1857.5(8) 1103.6(2)	106.95(3) 113.65(1) 75.20(3)	$\text{Sn}^{\text{IV}}\text{C}_3\text{N}$ (x2) TiO_2NCl	C_{Me} no given μO 211.3(2,7) O 180.6(1,2) μN 180.0(1) Cl no given	N 149.96(4)	not given O,O 114.98(4)	14

15	cp*, T ₁ {μ-η ² -C ₂ (SnMe ₃) ₂ } (red)	m C2/c 4	1587.9(15) 1185.1(11) 1755.5(13)	109.60(5)	Sn ^{IV} C ₄ (x2)	C _{Me} μC C _{ep} μC C 225.6(7)	211.5(19.2) 213.1(19) 211.4(11) 242(2) 209.6(11) 223.3(6)	not given	15
16	(c ₉ Me)/Zr{[SnCH(SiMe ₃) ₂] ₂ (dark red)	m C2/c 4	2545.5(14) 1156.3(3) 1947.1(11)	93.46(5)	T ^{II} cp ₂ C ₂ Sn ^{IV} C ₂ Zr (x2)	μC C _{ep} μC C 225.6(7)	211.4(11) 242(2) 209.6(11) 223.3(6)	cp, ep 141.2(5) μC, μC 36.8(4) C/C 102.4(2) C/Zr 128.7(2.7.2)	16
17	[(CO) ₅ Zr(SnMe ₃) ₂] (K(15-crown-5)) ₂ (deep red)	or Pbca 8	1809(1) 2621.0(8) 2924.9(6)		Zr ^{II} cp ₂ Sn	cp	219.6(8)	cp, ep 131.5(3) cp, Sn 106.1(2.1.9) Sn, Sn 95.06(4)	17
18	(tol) ₂ Hf(SnMe ₃) ₂ (black)	m C2/c 4	1402.7(3) 971.4(3) 1794.6(8)	111.11(4)	Sn ^{IV} C ₃ Zr (x2)	C _{Me} not given		not given	18
19	(NEt ₄)[(CO) ₅ V(SnPh ₃) ₂] (orange)	m P2 ₁ /n 4	1042.8(2) 2096.2(5) 2114.6(3)	95.67(1)	Zr ^{IV} C ₃ Sn Sn ^{IV} C ₃ Hf(x2) HfC ₁₂ Sn SnC ₃ V (x2) V ₅ Sn	OC C _{Me} not given C _{Me} not given C _{Me} not given C _{Me} not given OC 194(2.5)	218.3(3) 218.8(10.15) 248(1.5) 218.8(10.15) 194(2.5)	Sn, Sn 81.14(3) C/C 102.6(3.3.6) C/V 115.7(3.3.7) C/C 105.8(3.11.3) C/Sn 77.0(5.10.1) 117.6(6.8.8)	19
20	[K(18-crown-6)] [cf. Nb(SnMe ₃) ₂] (red)	or Pnma 4	1684.4(7) 2000.5(4) 1055.6(3)		SnC ₃ Nb (x2) Nbcp ₂ Sn	C _{Me} cp no. given	219.3(3.6)	Sn, Sn 137.9(1) C, Nb 113.8(3) Sn, Sn 87.18(3)	20
21	(CO) ₄ Cr {Sn[N(SiMe ₃) ₂] ₂ } ₂ (red)	m P2 ₁ /c 4	2569.1(2) 1173.1(5) 1738.2(4)	97.83(1)	SnN ₂ Cr (x2) CrO ₄ Sn	N OC	205.1(5.18) 186.7(7.24)	NN 105.0(2.2) N/Cr 127.0(1.5.6) C/C 89.9(3.4.4) 177.1(3) C/Sn 88.2(2.3.6) 172.1(2.1.0) Sn, Sn 101.37(3)	21

$[(C_6H_6)(CO)_2$ $Cr(SrPh_2Cl)_2] CH_2Cl_2$ (gold-yellow)	m P2 ₁ /c 4	1009(2) 1556(1) 1985(3)	100.55(1)	$SnC_2Cl_2(Cr(x2))$	C_{2h} not given Cl 238.7(2,3)	Cr 254.1(1,6)	C ₂ Cl 102.1(5,6) C ₂ Cr 178.0(2,3,0) C ₂ Cr 107.9(1,3) C ₂ Cr 103.3(3) C ₂ Sn 74.1(2,4) Sn ₂ Sn 127.49(4) C ₂ Cl 94.7(1) C ₂ Cr 130.7(1) C ₂ Cr 106.4(1,2) C ₂ Cr 112.4(5,2,4) C ₂ S 106.3(4,4,6)	22a
$\{K(12-crown-4)_2\}_2$ $[{(CO)_5Cr_2} \{SnCl_2\}]$ (yellow-orange) $[{(Me_3Sn)_2} (\mu_3 S)]$ $Cr(CO)_5$	m Cc 4 m P2 ₁ /m 4	1462.6(7) 2478(2) 1608(2) 1408.7(3) 1418.2(3) 968.5(2)	96.06(4) 94.59(2)	$SnCl_2Cr_2$ CrC_2Sn $Sn^{IV}C_2S(x2)$	Cl 247.8(2,6) OC not given C ₂ 215.1(2) $\mu_3 S$ 245.6(2,1)	Cr 266.6(2,3)	C ₂ Cl 94.7(1) C ₂ Cr 130.7(1) C ₂ Cr 106.4(1,2) C ₂ Cr 112.4(5,2,4) C ₂ S 106.3(4,4,6)	22b
$Cp_2Mo(SnMe_2Cl)_2$ (yellow)	m P2 ₁ /m 8	3051.9(6) 1395.3(2) 908.2(2)	106.50(1)	$SnC_2Cl_2Mo(x2)$ $MoCp_2Sn$	OC 190(1,2) $\mu_3 S$ 252.2(13) C ₂ 215.7(13,16) Cl 247.2(4,4) C ₂ 229.0(11)	Mo 272.3(1,17) Sn 361.6(1)	C ₂ 89.1(5,2,8) 176.7(5,7) C ₂ S 91.5(4,5,3) 175.5(4) C ₂ 106.3(4,2,0) C ₂ Cl 95.3(3,2,0) C ₂ Mo 122.0(3,1,8) C ₂ Mo 108.6(2,6,2) Cp, Cp 140.8 Sn ₂ Sn 83.2(1) C ₂ 106.1(4,1,7) C ₂ Cl 96.0(3,1,6) C ₂ Mo 121.6(3,2,8) C ₂ Mo 109.0(1,5,7) Cp, Cp 140.9(2) Sn ₂ Sn 83.4(1) C ₂ Cl 95.6(1) Mo ₂ Mo 129.9(1) C ₂ Mo 106.6(1,3,5) C ₂ Cl 96.0(1) W, W 130.0(1) C ₂ W 106.4(1,4,2)	24
$\{Na(12-crown-4)_2\}_2$ $[{(CO)_5Mo}_2 \{SnCl_2\}]$ (yellow-orange) $\{Na(12-crown-4)_2\}_2$ $[{(CO)_5W}_2 \{SnCl_2\}]$ (yellow-orange)	m P2 ₁ /c 4 m P2 ₁ /c 4	1459.1(6) 2498(1) 1583.2(5) 1459.1(6) 2514(1) 1580.0(6)	98.87(3) 98.83(3)	$SnCl_2Mo_2$ MoC_2Sn $SnCl_2W_2$	Cl 249.3(3,1) OC not given Cl 248.8(1,4)	Mo 273.5(2,20) W 280.3(1,5)	C ₂ Cl 95.6(1) Mo ₂ Mo 129.9(1) C ₂ Mo 106.6(1,3,5) C ₂ Cl 96.0(1) W, W 130.0(1) C ₂ W 106.4(1,4,2)	22b

(Me ₂ Sn) ₂ (μ ₃ -S) W(CO) ₅ I	m P2 ₁ /n 4	1416.3(3) 1433.5(3) 980.6(3)	94.35(2)	SnC ₃ S (x2) WC ₅ S	C ₄ H ₆ 216.3(4) μ ₃ S 258.0(2,3) OC 201(2,7) μ ₃ S 273.6(3)	103.9(1) 108.7(1,7)	C,C 112.8(10,2,2) C,S 105.9(7,5,3) C,C 89.3(9,2,0) 177.3(9,7) C,S 91.2(7,5,8) 173.7(6)	23
[2,4,6-Bu ^t ₃ C ₆ H ₃] [C ⁺ ,5-Bu ^t ₃ C ₆ H ₃ - C ⁻ Me ₂ CH ₂ }] SnI ₂ Mn(CO) ₁₄ (pale yellow) Cp(CO) ₂ Ru(SnPh ₃) ₂	tr P1 1	989.0(1) 1421.4(2) 1470.3(1)	94.11(1) 98.02(1) 110.07(1)	SnC ₃ Mn SnC ₃ Mn MnC ₁₄ Sn SnC ₃ Re (x2) RecpC ₂ Sn	C 216.2(6) 225.5(3) C 219.4(3) 224.7(6,0) OC 182.0(7,9) C _{Ph} 216(1,2) OC 191(1,1) C _{ep} 230(4,9)	Mn 270.0(2) R: 273.2(1,2)	C,C 113.3(2) C,Mn 173.3(2,4,5) not given Sn,Sn 168.4(2) not given	25
cp(CO) ₂ (H)Fe (SnPh ₃) ₂ (yellow)	tr P1 4	1624.8(7) 1964.6(6) 1144.3(5)	93.32(3) 93.67(4) 97.09(3)	SnC ₃ Fe (x2) FeC ₃ H ₃ Sn SnC ₃ Fe (x2)	C _{Ph} 215.6(5,20) OC 172.8(3) H 140(3) C _{ep} 208.1(5,14) C _{Ph} 215.9(4,18)	Fe 256.3(1,6) Fe 256.6(1,3)	C,C 102.4(5) C,Sn 76.1(4,3,6) Sn,Sn 135.74(3) C,C 105.2(2,3,2) C,Fe 13.5(1,4,9) Fe,Fe 117.10(2) C,H 109(2) C,Sn 85.9(2,0) H,Sn 62(2,1) C,C 105.4(2,3,0) C,Fe 113.2(1,5,4) Fe,Fe 117.21(4) C,H 104(2) C,Sn 85.2(2,1) H,Sn 61(2,2)	27
(CO) ₄ (PPh ₃)Fe (SnMe ₂ Cl) ₂ (pale yellow)	m P2 ₁ /c 4	1195.5(3) 1259.5(5) 1985.5(5)	90.80(2)	FeC ₆ H ₃ Sn SnC ₃ ClFe (x2) FeC ₃ P ₃ Sn	OC 172.9(5) H 143(3) C _{ep} 209.5(5,14) C _{Me} 212.5(13,25) Cl 242.5(4,14) OC 175.5(14,21) P _{Ph} 225.1(3)	Fe 259.2(2,1)	C,C 98.1(5,4,9) 160.7(5) C,P 95.3(4,3,8) C,Sn 85.2(4,7,8) P,Sn 95.61(9) 172.39(1) Sn,Sn 88.83(5)	28

(CO) ₃ (dppm)Fe (³¹ PPh ₃ Cl) ₂ (yellow)	m	1746.7(5)	SnC ₂ ClFe (x2)	C _{Ph} 215.1(0) Cl 247.4(3,37)	Fe 260.5(1,3)	CC 112.8(3,4) CCl 95.3(3,3,4) C ₂ Fe 121.7(2,6,4) Cl ₂ Fe 98.3(1,2,7) CC 97.2(4,3,8) 159.4(4)	29
	P2 ₁ /c 4	1189.6(3) 2444.8(7)					
(CO) ₄ Fe(SnPh ₃) ₂ (yellow)	tr ₋ P1 2	1314.796 1098.8(4) 1287.5(6)	SnC ₃ Fe (x2) FeC ₄ Sn	C _{Ph} 215.4(8,13) OC 179.4(9,19)	Fe 266.0(1,6)	C ₂ P 94.0(3,7,5) C ₂ Sn 83.9(3,3,1) P ₂ Sn 98.0(1,6) 171.2(1) S ₁ Sn 90.7(1,4) CC 105.5(3,4,6) C ₂ Fe 112.9(2,5,5) C ₂ C 96.0(4,4,1) 159.6(4) C ₂ Sn 84.3(3,5,5) 174.2(3,1,4) Sn ₂ Sn 95.9(4) CC 103.1(4,2,1) C ₂ Fe 115.0(3,1,7) CC 111.4(5,8,2)	30
	or P _{bca} 8	1234.0(4) 1812.0(4) 4017.0(8)					
[Ph ₃ SnF ₂ (CO) ₂ {μ-C ₉ H ₇ (³¹ Me ₃)} SnPh ₃] (orange)	tr ₋ P1 4	1723.9(3) 1391.5(2) 1114.0(2)	SnC ₃ Sn (x2)	C _{Ph} 214.7(11) C _{Ph} not given μC _L 214.8(11) OC 176.2(14,3) μC not given C _{Me} 213.5(8,5) μC _p 214.0(6,8)	Fe 258.5(2) Sn 275.2(1)	C ₂ C 92.7(6) C ₂ Sn 88.2(4,1) CC 108.9(3,1,5) μC ₂ Sn 97.6(1,1) C ₂ Sn 115.9(2,1,2)	31
	m P2 ₁ /c 4	1309.0(2) 657.5(2) 1887.4(2)					
(ppm) ₂ [(Ph ₃ Cl ₂ Sn) ₂ (μ-NC) ₂ Fe(CN) ₂ (dmsol) ₂] (yellow)	tr ₋ P1 1	106.65(1) 87.10(2) 99.46(2)	Fe ₂ Sn SnC ₃ NCI (x2) FeC ₄ Sn ₂	cp not given C _{Ph} 214.4(6,5) μCN 214.0(7) Cl 253.5(3) OC 194.1(9) μNC 191.2(8) S _{dmsol} 22.1(2)	N ₂ Cl 175.5(2)	not given	33
	m P2 ₁ /c 4	100.76(2)					

$[(Cl_3Sn)_2(\mu-nx)_3Fe](Et_2NH_2)Cl \cdot 2Pr^tOH$ (dark red)	m P2 ₁ /c 4	1056.5(2) 2541.3(5) 2019.8(4)	95.40(3)	$Sn^{IV}O_3Cl_3$ (x2)	μO_{ox} Cl	209.3(4,20) 239.9(2,18)	Fe 361.2(1)	O O 89.8(2,1.4) Cl Cl 94.1(1,2.9) O Cl 87.3(1,6.5) 174.0(1,2.1) N N 90.7(2,14.7) 161.7(2,3)	34
$(Ph_3Sn)_2(\mu-C_3H_4)_2Fe$ (dark orange)	tr P1 2	1086.0(2) 1149.7(3) 1586.8(3)	85.86(2) 81.56(2) 84.59(2)	$SnCl_4$ (x2) $FeCl_{10}$	μN_L C_m μC μC C	192.3(5,8) 213.7(4,8) 210.9(3,8) 206.4(3,6) 204.5(5,3)	Fe 374.4(-,2)	C C 109.4(1,3.7) C C 39.8(2)-170.5(2)	35
$(NEt_3)[(Cl_3Sn)_2Co(CO)_3]^+$ (orange-brown)	m P2 ₁ /a 4	1305.4(2) 963.9(3) 2175.0(3)	121.27(2)	$SnCl_3Co$ (x2) CoC_3 $SnCl_3Co$ (x2)	Cl OC Cl	235.1(1,24) not given 235.0(1,12)	Co 244.1(1) Co 244.4(1)	Cl Cl 99.2(1,5) Cl ₃ Sn 118.4(1,2.1) Sn Sn 178.9(1) Cl Cl 98.5(1,2.3) Cl Sn 118.6(1,1.6) Sn Sn 175.4(1) O O 83.5(4,7) Cl Cl 95.1(2,7) O Cl 88.0(4,2.2) 174.4(3,1.1) N N 90.4(5,10.5) 165.9(5,1)	36
$H[(Cl_3Sn)_2(\mu-dm)_3C_3] \cdot 2C_3H_6$ (yellow)	m C2/c 4	1465.7(3) 1382.3(3) 1683.7(3)	98.11(1)	CoC_3Sn $Sn^{IV}O_3Cl_3$ (x2) $Co^{III}N_6$	OC μO_L Cl μN_L	not given 210(1,1) 238.6(5,15) 190(1,2)	Co 244.1(1) Co 244.4(1)	O O 83.5(4,7) Cl Cl 95.1(2,7) O Cl 88.0(4,2.2) 174.4(3,1.1) N N 90.4(5,10.5) 165.9(5,1)	37
$(NBu_4)[(Br_3Sn)_2(\mu-dm)_3Co] \cdot H_2O$ (yellow)	or Pca2 ₁ 4	1627.1(3) 1533.7(3) 1857.2(4)		$Sn^{IV}O_3Br_3$ (x2) $Co^{III}N_5$	μO_3 Br μN_L	211.8(2,43) 253.8(7,50) 189.3(25,55)	Co 359.5(-,4)	O O 87.2(3,2.5) Br Br 96.3(2,2.1) O Br 88.1(3,4.0) 173.0(6,2.8) N N 90.3(10,9.9) 167.8(1,2.0)	38
$(NBu_4)[(Cl_3Sn)_2(\mu-nx)_3Co]$ (yellow)	or P2 ₁ 2 ₁ 2 ₁ 4	1656.6(4) 1655.1(4) 1656.0(4)		$Sn^{IV}O_3Cl_3$ (x2) $Co^{III}N_5$	μO_L Cl μN_L	211.2(13,25) 237.9(6,17) 191.3(14,9)	Co 361.5(-,6)	O O 88.5(4,3.9) Cl Cl 95.8(3,6) 172.4(1,5) N N 90.5(4,12.3) 164.5(6,9)	38
$[epi]Ni\{[Sn(NEt)_2]_2SiMe_2\}(\mu-ep)$ (brown black)	m P2 ₁ /c 2	1174.9(8) 988.6(4) 1656.7(19)	93.64(2)	$SnN(CN)$ (x2) $N C_3Sn$	N μC_{ep} C_p	not given 265.5(12,47) not given	N 232.6(2) 236.9(2) Sn 364.8(4)	N N 75.5(1) C N 114.6(2,2.1) Sn Sn 102.0(1)	39

[PPh ₃ (C ₆ H ₅) ₂] [Ni(μ-dto) ₂ (SnCl ₄) ₂] (blue)	m P2 ₁ /a 2	1448.7(5) 2633.4(8) 991.2(3)	124.74(4)	Sn ^{IV} Cl ₄ O ₂ (x2) μO _L	Cl 237.1(3,40) 221.1(5,7)	Cl/Cl 95.1(1,6,5) 165.6(1) 73.5(2) 86.8(2,6,7) 165.0(2,1,3) 92.6(1) not given N,N 77.8(7) C,C 89.6(9) N ₂ Sn 92.5(4,6) C ₂ Sn 87.7(5,1,6) Sn ₂ Sn 173.45(1) N,N 75.6(4)	40
[P(μ-dab)(CO) ₂ Ru (SnPh ₃) ₂ 3.5C ₃ H ₆ (pink)]	tr P1 2	1166.2(6) 1390.2(3) 1964.3(2)	71.24(2) 86.91(4) 77.89(3)	N ^{III} S ₄ SnC ₂ Ru (x2) RiN ₂ C ₂ OC	μS _L 218.2(2,1) C ₂ Sn not given N 204(2,4) OC 183(2,4)	not given Ru 268.8(2,3)	41
[P(Ph ₃) ₂ Rh {Sn(NBu) ₂ SiMe ₂ } ₂ (μ-Cl)], 2tol	m P2 ₁ /n 4	1345.9(7) 3310.0(17) 1631.4(8)	98.81(4)	Sn ^{IV} N ₂ ClRh (x2) RhP ₂ Sn	N 206(1) μCl not given Ph ₃ P not given	Rh 257.4(2,3)	42
(F ₃ Me) ₂ Pd(SnMe ₃) ₂ (ye'low) at 213K	or Pbca 8	1204.7(3) 3641.6(8) 9/6.8(3)		Sn ^{IV} C ₃ Pd (x2) PdP ₂ Sn	C _{Me} 218(1,4) P _{Me} 233.0(3,7)	Pf 260.5(1,2)	43
(PPh ₃) ₂ [Cl ₂ (NO) ₂ Os(SnCl ₃) ₃] (red)	m C2/c 4	1368.9(2) 1989.1(5) 2088.0(8)	99.54(2)	SnCl ₃ Os (x2) OsC ₃ N	Cl 235(5,1) Cl 237.5(4,11) ON 173.4(19)	Os 264.8(1)	44
(C ₆ H ₅) ₄ Os(SnPh ₃) ₂ (colourless)	m C2/c 8	4755(3) 931.3(7) 3197(2)	148.87(2)	SnC ₃ O ₃ (x2) OsC ₃ Sn	C _{Ph} no. given not given	Os 271.1(1,1)	45

$[(\text{dpm})_3(\text{CO})\text{Ir}(\text{SnCl}_3)_2][\text{Ir}_2(\text{SnCl}_3)_4]$ (red-green) at 130K	Ir^- Pt^- 2	1673.9(7) 1703.0(7) 2178.5(9)	79.61(3) 75.97(3) 67.78(3)	$\text{Sn}^{\text{II}}\text{Cl}_3\text{Ir}(\text{x}2)$ IrP_2CSn	Cl 238.4(12,39) P 231.6(6,25) OC 179(3)	Ir 258.0(3,12)	Cl_3Cl 95.7(4,14) Cl_3Ir 121.0(3,63) P-P 91.8(2) P ₃ C 87.1(3) 178.8(9) P ₃ Sn 124.6(2,12) C ₃ Sn 84.4(9,2.8) Sn ₃ Sn 103.7(2) Cl_3Ir 105.9(2,1) Ir_3Ir 146.1(1) P ₃ P 161.0(2,17) P ₃ C 92.3(10,1.1) P ₃ Cl 86.5(3,9) C ₃ Cl 172.6(8,1.8) P ₃ Sn 98.8(2,2.2) C ₃ Sn 98.7(8,1.3) C ₃ Sn 88.6(2,5) Cl_3Cl 98.55(7) Cl_3Pt 121.4(1,3,1)	45
$\{\text{FPt}_3(\text{CH}_2)_3\}$ $[\text{Cl}_2\text{Pt}(\text{SnCl}_3)_2]$ (yellow)	Ir^- Pt^- 1	1272.2(3) 1151.8(2) 1067.4(2)	110.73(1) 79.86(2) 114.39(1)	$\text{SnCl}_3\text{Pt}(\text{x}2)$ PtCl_3Sn	Cl 235.2(2,12) 278.6(2,19) Cl 229.6(2,3)	Pt 235.6(1,11)	Cl_3Cl 101.32(8) Cl_3Sn 73.6(1,8) Sn ₃ Sn 111.48(3) not given	47
$(\text{PmePh})_3$ $[\text{Cl}_2\text{Pt}(\text{SnCl}_3)_2]$ (yellow) (Net ₄) $[\text{Cl}_2\text{Pt}(\text{SnCl}_3)_2]$ (yellow)	m $\text{P}2_1/\text{n}$ 2 m $\text{P}2_1/\text{n}$ 4	1181.5(2) 1417.2(3) 1384.8(2) 1214.8(1) 1366.7(1) 1934.0(2)	96.56(1) 90.42(1)	$\text{SnCl}_3\text{Pt}(\text{x}2)$ PtCl_3Sn $\text{SnCl}_3\text{Pt}(\text{x}2)$ PtCl_2Sn	not given not given Cl 234.8(6,16) Cl 234.8(5,8)	Pt 248.9(1,6) Sn 375.3	not given Cl_3Cl 97.5(2,1.9) Cl_3Pt 119.7(1,5,3)	48
$(\text{FPt}_3)_2\text{Pt}\{\text{Sn}(\text{acac})_2\}_2$ (yellow)	or $\text{Pca}2_1$ 4	1932.7(5) 1281.1(2) 2197.8(2)		$\text{Sn}^{\text{II}}\text{O}_3\text{Pt}(\text{x}2)$ $\text{Pt}^3\text{F}_2\text{Sn}$	• not given P 226.1(4)	Pt 255.8(1)	Cl_3Cl 91.5(2) Cl_3Sn 85.4(2,2.0) Sn ₃ Sn 97.8(2) not given not given	49

50	{P(OPh) ₃ } ₂ (SnC ₃ H ₅) ₂ (yellow)	m P2 ₁ /n 2	1117.7(1) 1318.1(2) 1448.9(3)	98.52(1)	Sn ^{II} Cl ₃ Pt (x2) Pt ^{II} P ₂ Sn	Cl 234.2(6,10) P 227.2(3,0)	Pt 259.9(2)	Cl, Cl 99.5(2,3,1) C, Pt 118.2(2,3,3) P, P 180.0 P, Sn 91.3(1) S, Pt 110.6(1) S, S 108.9(1) S, Sn 92.74(9)
51	I(B ₁ ¹ ₂ bipy)(Me) ₂ Pt Sn(I, Me) ₂ (μ-S) ₂ SnMe ₂ [Me-C ₃] (yellow)	m P2 ₁ /n 4	1459.7(3) 1319.6(3) 1897.5(3)	104.41(1)	SnC ₂ SPt SnC ₂ S ₂ Pt ^{IV} N ₂ C ₂ SSn	C _{Me} not given μS 243.5(4) C _{Me} not given μS 238.5(4,31) N 217(1,4) C _{Me} 207(1,2) μS 243.9(3) C 226.2(3,5) μO 200.5(5)	Pt 255.2(1) S 100.1(1) S 108.2(1)	C, C 102.6(3) C, O 98.8(3,7,5) C, Pt 125.3(2,4,1) C, C 123.1(3) O, O 101.0(3) C, O 113.3(3,11,4) P, P 97.16(10) P, O 82.0(2,3,7) P, Sn 98.78(8) 164.00(6)
52	(PPh ₃) ₂ Pt-Sn(tfmp) (μ-O) ₂ -Sn(tfmp) ₂ 2tol (colourless)	tr P1 2	1445.8(12) 1773.9(15) 1940(2)	67.93(6) 73.62(7) 79.35(7)	SnC ₂ Opt SnC ₂ O ₂	C 222.3(9,10) μO 193.4(6,6)	Pt 262.8(1)	C, C 102.6(3) C, O 98.8(3,7,5) C, Pt 125.3(2,4,1) C, C 123.1(3) O, O 101.0(3) C, O 113.3(3,11,4) P, P 97.16(10) P, O 82.0(2,3,7) P, Sn 98.78(8) 164.00(6)
53	(thf) ₂ Yb(Sn ncp) ₂ (dark orange)	m C2/c 4	1372.6(6) 1815.4(7) 1998.9(8)	105.37(3)	SnC ₃ Yb (x2) Yb ^{II} O ₂	C not given • 234.5(7)	Yb 321.6(1)	not given O, O 102.4(2) O, Sr 104.6(2,2,0) S, Sn 132.34(3) C, C 97.0(7,1,2) C, Yb 119.8(7,10,0) O, O 89.8(4,3,7) 172.9(7) O, Sn 90.2(3,7,9) S, Sn 164.5(1)
54	(thf) ₄ Yb(SnPh ₃) ₂ (yellow)	m C2/c 4	1619.0(3) 1590.3(3) 1906.6(4)	98.91(3)	SnC ₃ Yb (x2) YbO ₁	C _{Ph} 216.8(18) 224.6(32,8) • 238.1(21,3) 242.2(14,0)	Yb 330.5(1)	C, C 97.0(7,1,2) C, Yb 119.8(7,10,0) O, O 89.8(4,3,7) 172.9(7) O, Sn 90.2(3,7,9) S, Sn 164.5(1)

[illegible]

57	[(F ^o O) ₃ Ti ₃ (μ-OP ^o) ₂ SnL] (yellow)	m P2 ₁ 2	1109.3(2) 1636.6(3) 1310.8(3)	100.70(3)	Sn ^{IV} O ₁₂	μO 208.2(5,24) I 278.1(1,2)	O 106.5(2,1,2)	O O 71.7(1,1) 93.8(2,5,9) 164.4(2) I I 97.23(3) O I 71.4(1,4) 98.7(3,13,2) 143.9(3,9,9)	
58	[(CH ₃ CH ₂) ₂ (CO) Nb} ₂ SnCl ₂] (red-orange)	?			Sn ^{IV} Cl ₂ Nb ₂	Cl 251.8(6) μO 209.0(5,51) O 178.6(6,28)	Nb 284.0(2)	Cl Cl 92.6(2) Cl Nb 103.5(1,4,1) Nb, Nb 140.69(5) C, Sn 90.3(6)	
58	[{cp ₂ (H)Nb} ₂ Sn(H)Cl] (orange)	?			NbC ₁₁ Sn SnCClNb ₂	OC 204(2) C _{op} 239(2,5) C _B 225(2) Cl 250.0(4)	Nb 286.2(1,6)	C Cl 89.8(5) C Nb 112.4(5,1,0) C Nb 101.3(1,3) Nb, Nb 129.44(5)	
59	[Ni(12-crown-4) ₂] [{(CO) ₅ Cr} ₂ Sn(8-OHqu)] (yellow)	m P2 ₁ /c 4	1433.6(5) 1065.8(5) 2819.1(9)	85.32(3)	Ni ^{IV} H ₂ cp ₂ Sn (x2) SnONCr ₂	H 167.5(2) O 209.9(3) N 227.1(4)	Cr 261.9(1,6)	O N 76.1(1) O Cr 106.0(1,5) N Cr 106.2(1,2,2) Cr, Cr 138.80(3) C C 91.5(2,1,8) C Sn 86.7(2) 175.8(2)	
59	(NBu ₄) ₂ [(CO) ₅ Cr] ₂ SnBr ₂ (yellow)	or Pna2 ₁ 4	3067(2) 1542.2(7) 1108.0(6)		CrC ₅ Sn (x2) SnBr ₂ Cr ₂	OC 185.2(5) 188.7(5) Br 260.6(3,2)	Cr 264.2(4,2)	Br, Br 92.3(1) Br, Cr 106.4(1,3,1) Cr, Cr 131.6(1) C C 91(1,3) C Sn 86.3(8) 175.0(8)	
59	(PPI ₄) ₂ [(CO) ₅ Cr] ₂ Sn(ac) ₂ (yellow)	m C2/c 4	2371.8(8) 1346.2(5) 1963.5(5)	111.47(1)	SnO ₂ Cr ₂ CrC ₅ Sn (x2)	O _{ac} 218.8(4,0) OC 182(2) 188(4) OC 183.9(7) 187.6(7)	Cr 268.4(1,0)	O O 8(3,2) O Cr 108.5(1,1,4) C, Cr 110.72(5) C C 91.7(3,1,9) C Sn 86.5(2) 173.7(2)	

$\{\text{cp}(\text{CO})_3\text{Cr}\}_2\text{SnCl}_2$ (orange)	m P2 ₁ /n 4	1031.4(12) 1564.6(20) 1222.3(12)	93.25(10)	SnCl ₂ Cr ₂	Cl 241.7(3.2)	Cr 269.7(2.4)	Cl Cl 95.0(1) Cl ₂ Cr 106.5(1.4,0) Cr ₂ Cr 130.2(1) C C 80.2(7.7) 116.3(6.1,7) C Sn 74.0(4.1,3) 129.9(5.1,0) C C 109.5(2.6,8)	60
$\{(\text{CO})_3\text{Cr}\}_2(\mu\text{-mes})$ SnMe ₂ (yellow)	m P2 ₁ /c 4	1551.4(2) 1302.6(2) 1570.9(2)	119.51(1)	SnC ₄ CrC ₉ (x2)	C _{Me} 214.9(4.8) μC 218.2(3.0) OC 183.3(4.9) C 221.9(4.25) μC 225.1(3.7) C _{Me} 216(2.1) μC 218(1.0) OC 187(3.13) C 217(2.16) μC 216(2.8)		61	
$\{(\text{CO})_3\text{Cr}\}_2(\mu\text{-Ph})$ SnMe ₂	or Pna2 ₁ 4	2563(2) 1032.0(8) 762.7(3)		SnC ₄ CrC ₉ (x2)	C _{Me} 216(2.1) μC 218(1.0) OC 187(3.13) C 217(2.16) μC 216(2.8)		62	
$\{\text{cp}(\text{CO})_3\text{Mo}\}_2\text{SnBr}_2$ (yellow)	or Pbca 8	1166.8(2) 1496.4(3) 2462.9(3)		Sn ^{II} Br ₂ Cr ₂ MoC ₃ (x2)	not given not given	not given	63	
$\{\text{cp}(\text{CO})_3\text{Mo}\}_2\text{SnI}_2$ (orange)	m P2 ₁ /c 4	1075.9(2) 1363.5(3) 1548.3(3)	90.05(3)	Sn ^{II} I ₂ Mo ₂	I 264.45(9) 277.90(8)	Mo 300.1(1.18)	I, I 94.23(3) I, Mo 105.4(1.4,5) Mo, Mo 113.9(3) C, Sn 70.9(3.3)	57
$(\text{PPh})_2[\{(\text{CO})_3\text{W}\}_2\text{SnBr}_2]$ SnBr ₂ (yellow orange)	tr P1 2	1171.6(6) 1370.8(7) 1869.3(9)	77.85(2) 78.93(2) 82.61(2)	MoC ₈ Sn (x2) SnBr ₂ W ₂ WC ₃ Sn (x2)	OC not given C _P 224.9(8.34) 242.2(9.78) Br 260.1(2.12)	W 280.9(2.0)	Br, Br 92.24(8) Br, W 106.8(1.4,7) W, W 130.62(4) C, C 91.3(7.1,6) C, Sn 87.1(4) 174.8(4)	59

$[(CO)_4W(\mu-Cl)_3W(SnCl_3)(CO)_3]$	or Pb _{2a} 8	1270.6(3) 1665.5(4) 1865.9(3)	$Sn^{IV}C_3W$ $W^{VI}C_3Cl_3Sn$	Cl O_2 μCl	232.4(5,10) 200.2(1) 253.3(3,43)	W W Cl	273.1(1) 352.5(1) 88.8(1,1,0)	Cl,Cl 102.0(2,9) Cl,W 116.1(1,1,8) C,C 76.1(6,2,3) Cl,Cl 107.3(5) C,Sn 75.9(1,1,2) C,Sn 70.2(4,1,5) 121.3(4) Cl,Sn 75.1(1) 114.4; 144.1(1) C,C 73.8(5,1,8) 116.1(6,3) Cl,Cl 77.0(1,1,1)	64
$[W(\eta^2-dedec)]_2$ ($\mu-CNEl_2$) ($\mu-S$) ($\mu-dedec$) {($\mu-S$) ₂ $Sn(CH_3)(SiMe_3)_2$ }} (blue)	tr P1 2	1209.2(5) 1272.5(5) 2188.8(15)	$Sn^{IV}C_2S_2$ $W^{VI}S_2CSn$ (x2)	not given S_L μS	256.3(9,42) 230.0(8,2) 242.3(8,85)	W S C	261.4(2) 69.3(2) 77.5(6)	C,S 106.2(6,6)	65
$[W(\eta^2-SCNM)_2]_2$ $W(3)\{(\eta^2-S$ $Sn(CH_3)(SiMe_3)_2\}$ ($\mu-M_2NCC(Me)_2$) ($\mu-S$) (emerald)	tr P1 2	1217.9(15) 1380.8(10) 1591.2(26)	$Sn^{IV}C_2S_2$ $W^{VI}S_4C$	C μS S μS C C S μS	215(5,6) 238(2,1) 214(2) 239(2,4) 203(4) 214(5) 252(2,6) 224	- 92.1(5,1) W 281.9(3) 75.8(5)	not given not given not given	not given	66
$\{Na(2,2,2-crypt)\}$ $\{(Me_3C_4H_4)(CO)_2$ $Mn\}_2$ SnCl at 213K $\{Na(2,2,2-crypt)\}$ $\{(Me_3C_4H_4)$ $(CO)_2Mn\}_2$ SnBr at 213K $\{N(2,2,2-crypt)\}$ $\{(Me_3C_4H_4)$ $(CO)_2Mn\}_2$ SnI at 213K	m P2 _{1/c} 4 m P2 _{1/c} 4 m P2 _{1/c} 4	1974.2(7) 838.9(4) 2415.4(9) 1952.5(3) 881.7(3) 2351.4(9) 1932.2(6) 889.2(2) 2362.8(6)	$Sn^{IV}ClMn_2$ $MnCl_7Sn$ (x2) $Sn^{IV}BrMn_2$ $MnCl_7Sn$ (x2)	not given not given B: not given I not given	250.1(3) 275.5(3) 298.5(1) not given	Mn Mn Mn Mn	245.8(2,8) 246.4(3,28) 246.8(2,26)	Cl,Mn 108.7(1,1,4) Mn,Mn 142.5(1) not given B,Mn 110.0(1,1,2) no: given I,Mn 109.7(1,1,5) no: given	67 67 67

{[cp(CO) ₂ Mn] ₂ Sn(phen)]}	m C2/c 8	1117.8(4) 3022.2(8) 771.9(2)	91.73(3)	Sn ⁰ N ₂ Mn ₂	N _{phen} 235.9(4.0)	Mn 247.1(1)	NN NM ₁ Mn ₁ Mn not given	70.3(2) 106.6(1) 141.5(1)	68
{[M(C ₃ H ₄) (CO) ₂ Mn] ₂ Sn(bpy)]}	or P ₆ ca 8	1372.8(9) 1253.2(9) 2899.0(2)	83.30(6) 67.96(7) 71.83(4)	MnC ₇ Sn (x2) Sn ⁰ N ₂ Mn ₂	OC 180(1.2) C _q 214.1(8.4) N _{bpy} 233.4(6.3)	Mn 247.4(2.3)	N ₁ N Mn ₁ Mn not given	69.1(2) 145.6(1)	69
{[Li(2,1,1-crypt)] [M(C ₃ H ₄ (CO) ₂ Mn] ₂ Sn(SBu ^t)}	tr PI 4	1164.7(8) 1205.6(5) 1533(1)	83.30(6) 67.96(7) 71.83(4)	MnC ₇ Sn (x2) Sn ⁰ S ₂ Mn ₂	not given S 247.4(3)	Mn 251.3(3.8)	S ₁ Sn Mn ₁ Mn not given	112.7(1.11.7) 134.4(1)	70
{(CO) ₃ Mn] ₂ SnCl ₂ }	m P2 ₁ /n 4	1414.4(5) 1222.3(4) 1030.3(4)	100.09(2)	Sn ^{IV} Cl ₂ Mn ₂	Cl 238.5(2.8)	Mn 263.5(1.15)	Cl ₁ Cl Cl ₂ Mn Mn ₁ Mn C C C Sn	95.80(7) 107.6(1.3.4) 126.25(4) 91.5(1.4.4) 86.9(8.4.3) 176.2(8.1.0)	71
{(CO) ₃ Mn] ₂ SnBr ₂ }	m P2 ₁ /c 4	1527.5(6) 765.0(3) 1685.5(6)	110.70(3)	SnBr ^{IV} ₂ Mn ₂	Br 254.8(2.10)	Mn 264.2(3.6)	Br ₁ Br Br ₂ Mn Mn ₁ Mn C C C Sn	98.44(8) 107.2(1.2.8) 125.88(9) 91.5(8.2.6) 86.9(8.3.3) 176.4(6)	71
{(MeNC)(CO) ₄ Mn] ₂ SnFh ₂ (ye low)}	m P2 ₁ /n 4	1858.7(27) 1414.7(14) 1058.6(13)	59.60(5)	SnC ^{IV} ₂ Mn ₂	C _{phen} 219.0(1.6)	Mn 271.2(1.1)	C C C Mn Mn ₁ Mn C C C Sn	100.5(1) 108.3(1.4.6) 121.9(1) 91.7(3.4.0) 86.3(2.4.1) 176.7(2.1.9)	72
{(CO) ₃ Mn(μ-C ₃ H ₄) ₂ SnCl ₂ }	or P2 ₁ 2 ₁ 4	691.2(4) 1196.4(10) 2335.1(15)		Sn ^{IV} C ₂ Cl ₂	μC 210.6(6.3) Cl 231.7(2.3)		C C Cl ₁ Cl C C C C	121.1(2) 102.0(1) 108.0(1.4) 92.1(1.1.2)	73

$\{(\text{CO})_4(\text{PPh}_3)_2\text{Re}\}_2$ SnBr_2 (colourless)	tr_- P1 2	989.6(5) 1340.4(5) 1803.1(6)	77.7(1) 85.2(1) 75.8(1)	$\text{Sn}^{\text{IV}}\text{Br}_2\text{Re}_2$ $\text{FeC}_4\text{P}_2\text{Sn}(\text{x}2)$	B: OC P_{Ph}	257.4(4,10) 200.4(9) 242.1(7,0)	Re 273.5(2,6)	B:Br 95.1(1) B:Re 108.2(1,4,7) R:Re 124.8(1) C:Re 90.2(4) C:P 93.4(8,4,7) C:Sn 86.8(9,10,0) P:Sn 173.1(2,1,6) C:Cl 94.7(7) R:Re 131.2(2) C:Re 106.1(5,1,4) NN 90.0(6,7) NC 90.0(5,6) not given	74a
$\{(\text{CO})_4\text{Re}\}_2$ (dark red)	m $\text{P2}_1/\text{n}$ 4	1085.6(9) 1238.0(5) 1432.5(9)	101.91(6)	SnCl_2Re_2	Cl	239.3(16,6)	Re 277.9(5,2)	C:Cl 94.7(7) R:Re 131.2(2) C:Re 106.1(5,1,4) NN 90.0(6,7) NC 90.0(5,6) not given	74b
$\{[(\text{CO})_3\text{Re}(\mu\text{-C})]\}_2$ $\text{Sn}(\text{tpp})$ $2(\text{o-Cl}_2\text{C}_6\text{H}_4)$	m $\text{P2}_1/\text{n}$ 2	1044(2) 1348(1) 2019(2)	110.8(1)	$\text{Sn}^{\text{IV}}\text{N}_2\text{C}_2$ $\text{ReC}_4(\text{x}2)$	N_{tpp} μC OC μC	207(2) 214 not given 175	138.5(8)	not given	75
$\{\text{cp}(\text{CO})_2\text{Fe}\}_2$ SnCl_2	m C2/c 4	1498(3) 763(2) 1518(3)	94.27(20)	$\text{SnC}_4^{\text{IV}}\text{Fe}_2$	Cl	243(1,0)	Fe 249.2(8)	C:Cl 94.1(6) C:Fe 107.2(3,2) Fe:Fe 128.6(3) CC 98.4(1,7) C:Sn 89.0(1,2) not given not given	76
$\{[\text{cp}(\text{CO})_2\text{Fe}\}_2$ $\text{Sn}(\text{OSO}_2\text{Ph}_2)]$	or $\text{P2}_12_12_1$ 4	1708 1224 1338		$\text{FeC}_2\text{Sn}(\text{x}2)$ SnOF_2 $\text{FeC}_2\text{Sn}(\text{x}2)$	OC C_{sp} O not given	176(4,0) 208(4,4) not given	Fe 249.8(-,9)	not given not given	77
$\{\text{cp}(\text{CO})_2\text{Fe}\}_2$ $\text{Sn}(\text{F})(\text{BF}_4)$ (orange)	m $\text{P2}_1/\text{n}$ 4	983.1(2) 1760.2(6) 1060.4(3)	104.28(2)	$\text{Sn}^{\text{IV}}\text{F}_2\text{Fe}_2$	F BF	203.0(6) 214.8(7)	Fe 250.0(2,4)	FF 85.0(3) F:Fe 107.2(2,1,5) Fe:Fe 132.7(1) not given	78
$\{\text{cp}(\text{CO})_2\text{Fe}\}_2$ $\text{Sn}(\text{F})(\text{BF}_4)$ (orange)	m $\text{P2}_1/\text{n}$ 4	1018.2(4) 1321.1(5) 1364.8(5)	104.96(4)	$\text{F}_2\text{C}_2\text{Sn}(\text{x}2)$ $\text{Sn}^{\text{IV}}\text{F}_2\text{Fe}_2$	OC C_{sp} F BF	178(1,5) 209(2,4) 204.1(4) 215.1(4)	Fe 250.6(1,0)	FF 83.3(2) F:Fe 106.3(1,2,9) Fe:Fe 135.7(1) not given	78

79	80	81	82	83	84
$\{\text{cp}(\text{CO})_2\text{Fe}\}_2\text{Sn}(\text{N}_3)_2$ (orange)	$\{\text{cp}(\text{CO})_2\text{Fe}\}\text{Sn}(\text{ah})$ (orange)	$\{\text{cp}(\text{CO})_2\text{Fe}\}_2$ SnBr (p-toyil) (pale red)	$\{\text{cp}(\text{CO})_2\text{Fe}\}_2$ SnONO ₂ (orange)	$\{\text{cp}(\text{CO})_2\text{Fe}\}_2\text{SnPh}_2$ (orange)	$\{\text{cp}(\text{CO})_2\text{Fe}\}_2\text{SnPh}_2$ (colourless)
m C2/c 4	m P2 ₁ /c 4	m P2 ₁ /c 4	m C2/c 4	or P2 ₁ 2 ₁ 2 ₁ 4	m C2/c 8
1737.5(3) 757.3(2) 1494.4(3)	1349.5(4) 1305.8(2) 1831.1(3)	964.3(1) 1201.6(2) 1920.5(4)	2025.5(4) 730(2) 1465(4)	1906(2) 1358(2) 870(1)	3458.0(3) 973.0(4) 1603.1(2)
113.34(3)	94.90(2)	98.68(1)	123.4(5)		111.91(1)
Sn ^{IV} N ₂ Fe ₂	FeC ₇ Sn (x2)	Sn ^{IV} CBrFe ₂	Sn ^{IV} O ₂ Fe ₂	Sn ^{IV} C ₂ Fe ₂	Sn ^{IV} C ₂ Fe ₂
N	OC C _{cp} O N	OC C _{cp}	O	C _{Ph}	C _{Ph}
215.8(7.0)	176.7(5.12) 208.8(3.26) 217.3(5.25) 224.7(4)	175.1(7.14) 209.6(7.27)	214(2.0)	217(2.1)	215.6(5.0)
Fe 250.4(1.0)	Fe 253.3(1.9)	Fe 253.9(1.4)	Fe 256.3(5.0)	Fe 257.0(3.3)	Fe 258.2(1.4)
N ₂ N N ₂ Fe FeFe not given	O O O, N O Fe N Fe Fe Fe C, C C, Sn C ₂ Sn C, Br C, Fe Br Fe F ₂ Fe C, C C, Fe	217.7(4) 257.3(1)	176.3(6.7) no: given	217(2.1)	173.2(6.16) no: given
92.8(4) 111.1(1) 127.2(1)	148.2(2) 56.6(1.6.1) 114.9(1.3.9) 129.38(3) 94.9(2) 87.7(2.3.7) 120.3(2.1) 98.0(1) 111.3(1.7) 104.8(1.1.3) 123.01(2) 92.4(3.7) 87.1(2.1.3)	253.9(1.4)	256.3(5.0)	257.0(3.3)	258.2(1.4)
79	80	81	82	83	84

50	$\{(\text{CO})_4\text{Co}\}_2\text{SnCl}_2$ (orange)	m $P2_1/c$ 4	1170.1(3) 1145.4(2) 1275.3(2)	108.47(2)	$\text{Sn}^{\text{IV}}\text{Cl}_2\text{Co}_2$	Cl 236.3(1,6) OC 180.3(6,16)	Co 253.1(1,1)	Cl ₂ Cl 101.2(1) Cl ₂ Co 105.8(1,8) Co ₂ Co 129.3(0) C-C 94.7(3,1,1) 119.3(3,3,2) C-Sn 85.3(2,1,2) 178.9(2,1)
91	$\{(\text{CO})_4\text{Co}\}_2\text{SnCl}_2$ (orange)	m $P2_1/c$ 4	1171.6(4) 1148.6(4) 1276.5(8)	108.42(3)	$\text{Sn}^{\text{IV}}\text{C}_2\text{Co}_2$	Cl 236.8(2,5)	Co 253.4(1,1)	Cl ₂ Cl 101.3(1) Cl ₂ Co 105.7(1,4,4) C ₂ Co 129.3(1) C-Sn 85.2(2,1,2) 178.6(2,1)
88	$\{(\eta^4\text{-C}_7\text{H}_3)(\text{CO})_4\text{Co}\}_2\text{SnPh}_2$ (dark red)	m $P2_1/c$ 4	931.0(11) 1727.9(27) 2022.9(30)	123.06(5)	$\text{CoC}_4\text{Sn (x2)}$ $\text{Sn}^{\text{IV}}\text{C}_2\text{Co}_2$	OC not given C _{Ph} 216.4(20,26)	Co 257.0(3,5)	C-C 99.6(1) C ₂ Co 118.3(1)
92	$(\text{CO})_7\text{Co}_2$ $\text{Sn}(\text{C}_2\text{H}_5\text{O}_2)_2$ (red)	or Pbca 4	1388(1) 2934(2) 1153(1)		$\text{Sn}^{\text{IV}}\text{O}_4\text{Co}_2$	OC 171.3(23,48) $\eta^4\text{C}$ 214.1(21,56) O 209(1,0) 213(1,2)	Co 257.7(3,14)	O ₂ O 83.6(4,6,1) 157.6(1) O-Co 101.3(3,3,7) 165.4(3,2,8) C ₂ Co 61.24(9) C-C 99(1,12) 147.6(9,5)
93	$[\text{cpCo}\{\mu\text{-}\eta^2\text{-P}(\text{OEt})_2\text{O}\}_3\text{Sn}]$ (lig'at yellow)	m $P2_1/a$ 4	1887.1(12) 2246.1(12) 1267.1(7)	92.53(5)	$\text{CoC}_4\text{Sn (x2)}$ $\text{Sn}^{\text{IV}}\text{O}_5$	μOC 187(2,2) OC 172(2,3) O 234(3,10) 276(3,7)	Co 437.2(8,7)	O ₂ O 79.0(11,8,6) 119.9(10,8,0) 152.1(11,1,7) P-P 91.9(6,1,8)
94	$(\text{C}_2\text{Co})_2(\mu\text{-dt})_2\text{Sn}^2$ (dark orange)	m C2/c 16	3086.0(5) 1341.7(2) 3118.3(5)	104.63(2)	$\text{CoC}_3\text{P}_3\text{(x2)}$ SnCB ₂	C _P 208(7,7) P 218(2,2) C 243 B 265(-,6) not given	not given	
95	$\{[\text{cp}(\text{P}(\text{Et})_3)\text{Ni}]_2\text{SnCl}_2$ (green)	or Pbca 8	1433.5(4) 1802.7(5) 2173.1(8)		CoC_2B_2 SnCl_2Ni_2	Cl 245.8(2,4)	Ni 246.6(1,2)	Cl ₂ Cl 91.4(1) Cl ₂ Ni 105.9(1,1,7) Ni ₂ Ni 133.8(1) not given

96	tr P1 2	[(CO) ₆ Ru ₂ Sn] {CH ₃ SiMe ₃ } ₂ (μ-dppm)] (pale yellow)	1133.8(2) 1362.6(4) 2073.9(2)	105.86(2) 97.67(1) 104.77(2)	SnC ₂ Ru ₂ RuC ₃ P ₂ Sn (x2)	C 223(2,0) OC not given P 236.6(4,8) C 218.8(5) 219.5(5) μS 245.8(2,4) OC 190.7(7,36) μS 243.1(2,16) Cl 235(1,1)	Ru 269.9(1) 271.5(1) Ru 295.4(2)	C,C 111.4(8) Ru,Ru 66.1(1) P,Ru 91.2(1,2) Sn,Ru 56.9(1,3) C,C 135.5(2) S,S 78.62(6) C,S 107.0(2,2,3) S,S 79.7(1,3) S,Ru 57.1(1,6) C,Cl 100.8(5,2,9) Cl,Fu 116.9(4,3,9) C,C 91(2) C,Cl 81.7(4,6) C,Cl 95(2,4) 174(1,1) C,C 88(2,7) C,Cl 83.5(4,7) C,Cl 92.0(1,7) 173(1,1)	97
98	tr P1 2	(CO) ₄ Ru ₂ (μ-S) ₂ Sn (tb) (tip)	1401.7(1) 188(1) 1292.5(6)	108.76(4) 90.06(4) 78.69(4)	Sn ^{IV} C ₂ S ₂ RuC ₃ S ₂ (x2) Sn ^{IV} C ₃ Ru RuCl ₃ C ₂	Ru 263.7(2) 65.7 Ru 256.5(4) Ru 315.7(4) 80.9(4,5)	C,C 135.5(2) S,S 78.62(6) C,S 107.0(2,2,3) S,S 79.7(1,3) S,Ru 57.1(1,6) C,Cl 100.8(5,2,9) Cl,Fu 116.9(4,3,9) C,C 91(2) C,Cl 81.7(4,6) C,Cl 95(2,4) 174(1,1) C,C 88(2,7) C,Cl 83.5(4,7) C,Cl 92.0(1,7) 173(1,1)	99	
100	m P2 ₁ /n 4	{(η ⁴ -cod) Rh} ₂ (μ-OE) ₄ Sn (OE) ₂ (pale yellow)	1029.6(5) 1562.8(7) 1296.0(3)	98.41(3)	Sn ^{III} Cl ₃ Rh Rh ^{II} P ₃ ClSn Sn ^{IV} O ₃	Cl 255.0(2,7) P _{Me} not given Cl 241.8(2,2) μO 208.9(4,14) 197.9(5,1)	Rh 271.6(1,5) Rh 510	C,Cl 92.28(9) Rh,Fh 142.52(3) P,Cl 159.04(9) P,Sn 100.81(6) O,O 73.5(2,2) 90.4(2)	101
101	m P2 ₁ /c 4	ClP ₃ (dppm) ₂ SnCl ₃ (red-orange)	1623.8(31) 1327.4(23) 2344.9(23)	108.28(12)	Rh ^{III} C ₂ O ₃ Sn ^{III} Cl ₃ Pd PdP ₂ Sn PdP ₂ Cl	η ⁴ C 207.3(6,1) μO 206.7(5,15) Cl 239.4(5,21) P 230.1(4,6) P 231.9(4,24) Cl 239.6(4)	Pd 264.4(2)	O,O 74.5(1,1) Cl,I 96.7(2,5,4) Cl,I ^d 120.1(1,5,8) P,P ₁ 84.9(1,6,9) P,S ₁ 96.5(1,2) Pd,S ₂ 165.8(1) P,Cl 94.1(1,7,9) P,P ₁ 86.6(1,3,9) Cl,I ^d 172.0(1)	100

[$\{Cl(CO)Ir(\mu-dppp)\}_2 SnCl_2\}$ 2thf (green) at 130K	m C2/c 4	2740.6(15); 1702.6(6); 1541.0(9);	91.11(5)	$Sn^{II}C_2Ir_2$	Cl 245.9(9.0)	Ir 275.1(1.0)	102
(thf) $_3$ Yb(μ - 2 Ph) $_3$ Yb(thf) $_2$ SnPh $_3$ (dark ruby)	tr P1 2	1112.3(2); 1417.8(3); 1877.4(4)	101.94(2); 96.20(2); 109.85(2)	$Ir^{2+}Cl_2Sn$ (x2) $Sn^{II}C_3Yb$ $Yb^{II}C_3O_2$	P 23.10(8.1) OC 184(3) Cl 236.4(7) C $_3$ 222(1.1) μ C 253(1.3) O $_2$ 245.7(7.0)	Yb 337.9(1) Yb 322.6(1)	103
$\underline{Sn + M + M'}$ [cp $_2$ W(SnPh $_3$)HgI] (orange-red)	or Pb m 8	1646.1(3); 1780.1(3); 1788.7(3)		$Yb^{II}O_3C_3$	O $_2$ 245.8(8.24) μ C 263(1.2)		104
[MeGa(μ - η^2 -pz) $_3$ Mo(CO) $_4$ SnPh $_3$] (yellow)	m P2 $_1$ /c 4	1144.39(8); 1951.16(8); 1526.86(12)	111.370(3)	SnC_3W Wcp $_2$ Hg HgIW SnC_3Mo MoC $_3$ N $_3$ Sn	C $_3$ 215.8(3.8) OC 198.7(3.20) μ N $_3$ 224.2(2.3)	W 276.8(2) Hg 263.4(1) Mo 285.79(3)	105
(CO) $_4$ MoSn (μ -OBu) $_3$ Ti	m P2 $_1$ /n 4	995.2(8); 1759(1); 1511(1)	100.20(7)	Ga $_3$ N $_3$ C SnIIIO $_3$ Mo M $_3$ C $_3$ Sn TiO $_3$	C $_3$ 194.3(4) μ N $_3$ 192.5(3.6) μ O 201.7(9) OC not given μ O 255.7(15)	Mo 277.0(2) Ti 329.8(1)	106

107	$[(CO)_2Pt_2In(\mu, \eta^3-d)]$	tr	1291.1(5)	89.96(3)	SnC_3Mo	C_{2h}	211(4.2)	Mo 279.9(5)	C ₂ C	101(2.2)
	$(\mu-\eta^3-S_2Cl_2)_3Mo$	PI	1990.9(6)	116.85(3)	MoC_3S_2PSn	OC	195(5.6)	Mn 293.7(8)	C ₂ Mo	117(1.1)
	$(CO)_2SnPt_3, CH_2Cl_2$ (red)	2	1324.3(5)	91.18(3)		μS	244(1.1)		C ₂ C	159(1)
						P	235(1)		S ₂ S	70.0(4)
					MnC_3S_2PMo				C ₂ P	76(1.1)
						OC	179(6.6)		SP	117.1(5.168)
						η^3C	199(4)		S_2Mn	139.9(2)
						μS	236(1.2)		C ₂ C	101(2.12)
						P	216(2)		SS	72.8(4)
									C ₂ Mo	76(1)
108					SnC_3Mo					135(2.6)
									S ₂ Mo	53.5(3.1)
									P ₂ Mo	80.7(4)
					MoC_3S_2Sn	C_{2h}	not given	Mo 281.0(1)	not given	
						OC	196.7(5.23)	Mn 287.7(1)	C ₂ C	77.1(2.1.1)
						μS	245.8(1.6)			105.3(2)
					MnC_4S_2Mo				S ₂ S	70.20(6)
									C ₂ Sn	70.3(1.1.1)
										124.6(1)
					SnC_3MnCo	OC	179.3(5.12)		Sn_2Mn	134.96(6)
109						η^3C	202.9(4)		C ₂ C	106.5(2.3.7)
						μS	236.4(1.13)			153.7(2)
					SnC_3MnCo	C_{2h}	218(4.0)		S ₂ S	73.44(7)
								Mn 272.8(10)	C ₂ C	107.5(1.2)
								Co 265.7(10)	C ₂ Mn	111.0(9.2.0)
					MnC_3Sn				C ₂ Co	106.0(9.1.0)
						OC	184(4.1)		Mn_2Co	114.4(2)
							179(4)		C ₂ C	92.2(8)
					CoC_3Sn	OC	178(4.1)		C ₂ Sn	86.176
							171(4)		C ₂ C	108(2.18)
									C ₂ Sn	84(1.5)

498	[$(\text{CO})_3\text{Fe}\{\mu\text{-}\eta^2\text{-Si}(\text{OMe})_2\}(\mu\text{-dppm})$] PdSnPb ₃] 0.7 tol (deep red)	m P2 ₁ /c 4	1529(2) 2843(6) 1385(3)	116.19(7)	SnC ₃ Pd PdO ₂ FeSn	C _{Ph} not given P 218.78(9)	Pd 259.50(5) Fe 265.55(5)	not given O,P 174.79(7) O,Sn 94.51(6) P,Sn 90.20(3) Sn,Fe 169.34(2) P,Si 170.75(6) C,Pd 70.2(1.3,9) P,Pd 95.92(3) Si,Pd 75(0.3)	110
111	[$(\text{CO})_3\{\text{MeO}_2\text{Si}\}\text{Fe}(\mu\text{-dppm})\text{Sn}(\text{Cl})_2$] PbCl(PbEt ₃) CH ₂ Cl ₂ (bright yellow)	tr P1 2	1788.2(8) 1144.3(6) 1245.7(6)	79.79(2) 88.18(2) 72.25(2)	SnC ₃ FePt	Cl 241.3(3,14)	Fe 255.8(2) Pt 252.4(2)	Cl,Cl 89.6(1) Cl,Fe 110.3(1,7) Cl,Pt 113.3(1,8,1) Fe,Pt 115.8(1) C,C 97.4(3,2,5) C,P 95.1(2,4,5) C,Si 83.7(2,5,7) C,Sn 82.3(2,1,1) P,Si 91.5(1) Si,Sn 93.9(1) Cl,P 88.3(1,3,6) P,Sn 92.1(1,1,8)	111
	[$(\text{CO})_3\{\text{MeO}_2\text{Si}\}\text{Fe}(\mu\text{-dppm})\text{Sn}(\text{Cl})_2$] PbCl(PbEt ₃) CH ₂ Cl ₂ (bright yellow)	tr P1 2	1788.2(8) 1144.3(6) 1245.7(6)	79.79(2) 88.18(2) 72.25(2)	SnC ₃ FePt	Cl 241.3(3,14)	Fe 255.8(2) Pt 252.4(2)	Cl,Cl 89.6(1) Cl,Fe 110.3(1,7) Cl,Pt 113.3(1,8,1) Fe,Pt 115.8(1) C,C 97.4(3,2,5) C,P 95.1(2,4,5) C,Si 83.7(2,5,7) C,Sn 82.3(2,1,1) P,Si 91.5(1) Si,Sn 93.9(1) Cl,P 88.3(1,3,6) P,Sn 92.1(1,1,8)	111

Footnotes. a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Two crystallographically independent molecules present.

P (SnCl₂FePt), the platinum atom is square planar (PtP₂ClSn) and the iron atom is octahedrally coordinated (FeC₃PSiSn).

Table 1 shows that the tin atoms exist in oxidation states of zero, +2 and +4. The coordination geometry is predominantly tetrahedral, but also includes trigonal, pyramidal and octahedral examples. The most common ligands are carbon donors (phenyl and methyl) and the chlorine atom. The mean Sn-L bond distance in the pyramidally 3-coordinated Sn(0) derivatives increases in the order: 248 pm (SL) < 250 pm (CI) < 275.5 pm (Br) < 298.5 pm (F). For the other pyramidal derivatives the order is: 220.5 pm (CL), 250 pm (CI) < 260 pm (PL). For the tetrahedrally coordinated Sn(II) derivatives the Sn-L bond length increases in the order: 218.5 pm (CL) < 244 pm (CI). For the Sn(IV) tetrahedral derivatives the order is: 203.5 pm (F) < 218 pm (CL) < 239.5 pm (CI) < 257.5 pm (Br) < 271 pm (I). The mean Sn(IV)-L(bridge) bond distance increases in the order: 197 pm (μ-O), 241 pm (μ-S); and 211 pm (μ₃-N) < 252 pm (μ₃-S).

In heterodimeric tin compounds both non-transition and transition metals are represented. Of the former there are only 14 examples, the most common being Cd(II) [7,8,56]; Li [6,55]; Pb [7,11], Sr(II) [9], Ba(II) [10], Tl [106], Al(III) [57], Hg(II) [104] and Ga(III) [105]. The non-transition Sn-M distances are given in Table 1A, where the shortest is 301.3(11) pm for Sn-Li [55]. The remaining derivatives contain a transition metal.

There are several derivatives which contain two crystallographically independent molecules differing by degree of distortion in the M-L distances and bond L-M-L angles [6,10,24,27,36,56,86,94]. Such examples are typical of the general class of distortion isomerism [112].

Table 1A. Summary of Sn-M and M-M Distances in Heterotrimer Clusters.

M-M'	Cov. Radius of M [pm]	Shortest [ref]	Distances Longest [ref]	Average [pm]
M' = Non-Transition Metal				
Sn-Pb	131	336.1(4) [7]		
Sn-Li	134	301.3(11) [55]		
Sn-Cd	148	312.1(3) [7]		
Sn-Tl	152	329.8(1) [106]		
Sn-Ca	174	313.2(3) [7]	386.5(3) [56]	353
Sn-Sr	192	331.9(1) [9]		
M' = Transition Metal				
Sn-Ni	120	232.6(2) [39]	246.8(1) [95]	240.7
Sn-Fe	120	249.0(1) [77]	266.0(1) [30]	256.5
Sn-V	125	275.7(3) [19]	278.5(3) [19]	277.1
Sn-Co	126	244.1 [36]	259.1(3) [92]	252.5
Sn-Ru	126	256.5(4) [98]	271.5(1) [96]	266.0
Sn-Cr	127	254.9(1) [21]	270.1(2) [60]	264.0
Sn-Pt	128	234.3(1) [47]	262.8(1) [52]	253
Sn-Os	128	264.8(1) [44]	271.1(1) [45]	268
Sn-Pd	131	258.5(2) [101]	260.7(1) [43]	259.8
Sn-Ti	132	281.1(2) [12]	286.9(3) [13]	284.5
Sn-Rh	135	257.1(2) [42]	272.1(1) [99]	264.5
Sn-Ir	137	256.9(3) [46]	275.1(1) [102]	269
Sn-Nb	137	281.7(1) [20]	286.8(1) [58]	284.2
Sn-Mo	145	270.6(1) [24]	301.86(11) [57]	280.8
Sn-W	146	261.4(2) [65]	280.9(2) [59]	273.0
Sn-Mn	146	243.7(2) [67]	272.8(10) [109]	255.3
Sn-Zr	148	287.15(11) [16]	301.1(3) [17]	294.2
Sn-Hf	149	295.3(1) [18]		
Sn-Re	159	273.0(1) [74]	274.1(1) [26]	273.4
Sn-Sn		276.2(1) [32]	423.64 [16]	361.5
Fe-Fe		278.8(2) [86]	279.7(2) [86]	279.4
Co-Co		262.6(4) [92]	437.9(8) [93]	379.0
Ru-Ru		269.9(1) [97]	315.7(1) [98]	293.7
W-W		281.9(3) [66]	352.5(1) [64]	317.2
W-Hg		263.4(1) [104]		
Mo-Mn		287.7(1) [108]	293.7(8) [107]	290.7
Fe-Pd		266.55(6) REF???		

3. TETRAMERIC HETEROTIN COMPOUNDS

There are almost one hundred examples of tetrameric heterotin compounds for which the data are gathered in Table 2. These can be divided into five subgroups based on the number of different metals present. The most common subgroup contains two tin atoms and a pair of other metal atoms. The heterometals include both transition and non-transition metals.

3.1 Three Sn plus M

There are eleven derivatives which contain three tin atoms plus one other type of metal. Only two non-transition heterometal atoms are found in this subgroup. A yellow Sn_3Li derivative [113a] contains $\text{Li}(\text{thf})_4^+$ cations and $[(\text{BuN})(\text{imn})\text{Sn}_3\text{Li}(\text{thf})]^-$ anions together with free (thf) and toluene molecules. The heterometallic anion has a cubane structure $\text{Sn}_3\text{N}_4\text{Li}$ in which three $\text{C}_{10}\text{H}_7\text{N}^+$ imido ligands have similar environments. Each bridges the Li(I) centre with two Sn(II) centres within the cubane. The BuN^- group bridges all three tin atoms and is located at the corner opposite to the lithium atom. The coordination of the Li(I) by thf ensures that it adopts a typical pseudo-tetrahedral geometry. Each Sn(II) atom is 3-coordinate (SnN_3). In a colourless Sn_3In cluster [113] three SnMe_3 moieties and the InMe_3 unit are held together by a $\mu_4\text{-In}$ bridge. Each metal atom has a distorted tetrahedral environment (MC_3N).

A yellow derivative containing a Sn_3Zr cluster [114] has a $\mu_4\text{-Si}$ atom serving as a bridge between three SnMe_3 moieties and one Zrpc_2Cl unit. The tin atoms are all in distorted tetrahedral environments (SnC_3Si). The zirconocene cyclopentadienyl rings are eclipsed because of the incorporation of a Cl and a Si atom into the "sandwich" cavity. There are two crystallographically independent Sn_3Zr clusters, examples of distortion isomers.

Another pale yellow derivative has a Sn_3Cr cluster [115] in which 7-coordinate chromium is bonded to four terminal carbonyl groups and three triphenyltin units. The Sn-Cr bond distances range from 269.5(1) to 272.8(1) pm (average 271.4 pm). An orange Sn_3W cluster [116] has four units, three Me_3Sn and one $\text{W}(\text{CO})_5$, held together by a $\mu_4\text{-Si}$ atom. Distorted environments are found around all the metal atoms, tetrahedral for Sn and octahedral for W.

The structure of an orange Sn_3Ru cluster is shown in Figure 5, where it can be seen that the $(\text{Ph}_2\text{SnO}(\text{Me})\text{Sn}(\text{Ph}_2)\text{O}(\text{Me})\text{Sn}(\text{Ph}_2))_3$ occupies three coordination sites in a *mer* orientation around Ru. The terminal tin atoms are both tetrahedral (SnC_2ORu) and the central tin atom is in a distorted trigonal bipyramidal environment ($\text{SnC}_2\text{O}_2\text{Ru}$) with O atoms at apical positions ($\text{O-Sn-O} = 171.1^\circ$). The Sn(2)-Ru distance of 267.01(5) pm is about 6 pm longer than the remaining two Sn-Ru distances (260.72(5) and 261.02(5) pm). In a yellow Sn_3Pd cluster [118] three $\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Sn}$ moieties are held together by a $\mu_3\text{-Pd(0)}$ atom with Sn-Pd-Sn angles of $120.0^\circ (\pm 1.2^\circ)$ and a mean Sn-Pd bond distance of 253.0(1) pm. The Sn(II) atom has a trigonal planar environment (SnN_2Pd).

A yellow-orange Sn_3Os cluster [119] contains NMe_4^+ cations and $[(\text{Cl}_3\text{Sn})_3\text{OsCl}]^-$ anions. In the complex anion three Cl_3Sn moieties are directly bound to the OsCl unit with Sn-Os distances, one of 253 and two of 258 pm. Each metal atom has a distorted tetrahedral environment ($\text{Sn}^\text{II}\text{Cl}_3\text{Os}$) and ($\text{Os}^\text{VI}\text{ClSn}_3$).

Fig.5. Structure of $\text{Ph}_6\text{Sn}_3(\mu\text{-OMe})_2(\eta^2\text{-H}_2)(\text{CO})(\text{PPr}^3)\text{Ru}$ [117]

There are three Sn_3Pt clusters [120-122] in which three SnCl_3 moieties are directly bound to a Pt-L unit with Sn-Pt distances ranging from 253.5(1) to 264.3(2) pm (average 258.4 pm). Each Sn(II) atom has a distorted tetrahedral environment (SnCl_3Pt) with a mean Sn-Cl bond distance of 237 pm.

3.2 Two Sn plus Two M

3.2.1 Non-Transition Metal M

There are almost fifty clusters containing two pairs of metal atoms, two tin atoms and two of the same heterometal atoms. The latter include both transition and non-transition metal atoms. There are two Sn_2Li_2 clusters [123,124], the first has an imido Sn(II) dianion $[\text{MeNHSn}(\mu\text{-Nma})]_2^{2-}$ associated with two $[\text{Li}(\text{thf})_2]^+$ cations resulting in a z-shaped ladder arrangement in the core. The planar Sn_2N_2 core of the dianion is rhombic shaped. The second example contains a $\text{Sn}_2\text{O}_6\text{Li}_2$ cage which is constructed from two-semi norcubane $\text{Sn}_2\text{Li}_2\text{O}_3$ units sharing a Li_2O_2 four membered ring. A colourless Sn_2Na_2 cluster [121] is isostructural with the lithium example [124] and contains two independent molecules differing by degree of distortion. The Na-Na distance of 300 pm is about 40 pm longer than the Li-Li distance of 261 pm. This difference is identical with the differences between ionic radii of the four coordinate M^+ species, 59 pm (Li^+) and 99 pm (Na^+). Another colourless Sn_2Na_2 cluster [125] can be viewed as a twelve membered ring system where two Sn(II) and two Na(I) atoms are connected via four pyrazolyl functions. Two of the three pyrazol substituents at the tin atom are bridging to sodium and one is terminal. The Na(I) atoms are also coordinated to two (thf) units and one neutral pyrazol molecule.

There is a colourless Sn_2Mg_2 cluster [126] with a central $\text{Mg}_2(\text{OBU})_2$ four membered ring spirocyclically connected to two $\text{Mg}(\text{OBU})_2\text{Sn}$ rings through the common Mg atoms. The structure is completed by the coordination of an exocyclic tertiary-butoxy group to the terminal Sn(II) atoms. The Mg(II) atoms are therefore quasi-tetrahedrally coordinated while the Sn(II) atoms are in pyramidal three-fold Oxygen atom environments. The molecule displays a $\text{Sn}\cdots\text{Mg}\cdots\text{Mg}\cdots\text{Sn}$ one dimensional arrangement with Sn-Mg distance of 317(1) pm and Mg-Mg distance of 293.4(1) pm.

There are six colourless Sn_2Al_2 clusters [127-130]. One of these [127] has a central four membered Al_2O_2 ring with a SnPh_3 moiety bonded to each oxygen atom. The oxygen atoms are thus trigonal, linking three metal atoms, and the metal atoms have distorted tetrahedral environments ($\text{Sn}^+\text{C}_3\text{O}$ and $\text{Al}^+\text{O}_2\text{C}_2$, respectively). The Al-Al bond distance is 271.1(2) pm, but the Sn-Al distance is 347.3(1) pm indicating no direct heterometallic bond. In the next example [128] the Sn(II) centres are η^6 -bonded to two molecules of benzene. the two benzene planes are inclined to each other and form angles of 101.9° ($\text{Sn}(1)$) and 99.7° ($\text{Sn}(2)$), respectively. The two $(\eta^6\text{-C}_6\text{H}_6)_2\text{Sn}$ units of the dimer are linked by two direct chlorine bridges and two 1,3-bidentate AlCl_4 groups. The coordination of the Sn(II) centres is thus pseudo-octahedral, and the entire dimer approaches non-crystallographic C_{2h} symmetry. The remaining four derivatives [129,130] have a similar structure to that of the previous example [128]. The $[(\text{tol})\text{SnClAlCl}_4]_2$ derivative [130] exists in two triclinic isomeric forms (α - and β -) differing mostly by degree of distortion. Three Sn_2Ga_2 clusters [131-133] are colourless and contain four membered Ga_2N_2 [131,132] or Ga_2S_2 [133] rings. Each N or S is bonded to a SnMe_3 , SnMe_2 or SnCy_3 moiety. Each metal atom (Sn(IV) and Ga(III)) is quasi-tetrahedrally coordinated. A colourless $[\text{cy}_3\text{Sn}(\mu\text{-S})\text{InPh}_2]_2$ cluster [133] is isostructural with its Ga(III) analogue [133]. The Sn-In and In-In distances of 412.5(1) and 357.4(1) pm, respectively, rules out any metal-metal bonding.

In pale yellow Sn_2Ge_2 cluster [134] two heterodimers are connected by a nitrilimine group with a Sn-Ge-C-N-N-Ge-Sn arrangement. The nitrilimine linkage is almost linear ($\text{C-N-N} = 174.2(11)^\circ$), but the ends of the arrangement are bent ($\text{Sn-Ge-C} = 94.9(4)^\circ$ and $\text{N-Ge-Sn} = 100.9(3)^\circ$). The three methyl groups coordinated to each tin atom creates a quasi-tetrahedral environment (SnC_3Ge) with an average Sn-Ge bond distance of 265.0(2) pm. The environment about the Ge atoms is completed by η^1 -cyclopentadienyl plus $\text{CH}(\text{SiMe}_3)_2$ groups giving chromophores of GeC_3Sn and GeC_2NSn , respectively.

A black derivative [135] contains $\text{K}(2,2,2\text{-crypt})^+$ cations, $\text{Sn}_2\text{Bi}^{2-}$ anions and neutral ethylenediamine molecules. The anions have Sn and Bi in a disordered fashion over the four possible metal locations of the tetrahedral array, with bond distances ranging from 293.4(93) to 297.1(6) pm.

3.2.2 Transition Metal M

There are four coloured Sn_2Ti_2 clusters [136,137,15]. Two of them [136,137] contain four membered Ti_2N_2 rings. Each nitrogen atom is also bonded to a SnMe_3 unit. The nitrogen atoms are trigonal and the tin atoms quasi-tetrahedral. The skeleton structures of the other two derivatives [15] are very similar and exhibit a crystallographic centre of inversion with titanocene moieties in a staggered conformation. Two molecules of titanocene- (trimethylstannyl)-acetylide are linked by a π -bonding interaction between the titanium atom of one molecule and the acetylide group of the other. The dimeric titanium-acetylide skeleton is essentially planar. The Ti-Ti distances, 357.3(1) and 363.1(3) pm are considerably longer than the sum of the Ti

atom van der Waals radii (289.6 pm), suggesting no metallic bonding.

A yellow complex $(\text{Me}_3\text{SnNbcp}_2)_2(\mu\text{-O})$ [138] has a bridging oxygen atom on a crystallographic inversion centre. The linear Nb-O-Nb bridge has a Nb-O distance of 194.34(4) pm, and the two metals are linked by a Nb-Sn distance of 286.19(5) pm.

A blue Sn_2Cr_2 cluster [126] is isostructural with the Sn_2Mg_2 cluster in the same work and discussed previously [126]. The structure of a colourless Sn_2Mo_2 cluster [139] is composed of the $[(\text{Ph}_2\text{Sn})_2(\mu\text{-OH})_2(\mu\text{-MoOH})_2]^-$ anion, a tetrabutylammonium cation and dichloromethane solvent molecules. The two halves of the dimer are related by a crystallographic inversion centre. The complex anion contains a four membered $[\text{Sn-O(H)-Sn-O(H)}]$ ring with symmetric molybdate bridges between the tin atoms on either side of it. In addition, each Sn(IV) atom has bonds to two phenyl groups to complete a distorted octahedral *cis*- Ph_2SnO_4 coordination.

There are three Sn_2Mn_2 clusters [67,140,126]. In the first [67] two $\text{cp}(\text{CO})_2\text{MnSn}(\text{S}_2\text{C}_2\text{H}_4)$ dimers are connected by a $\text{SCH}_2\text{CH}_2\text{S}$ group in the manner $[\text{MnSnSCCSSnMn}]$, with mean Mn-Sn bond distance of 260.53(5) pm and Mn-Sn-S angles of $115.4(1)^\circ$. A second cluster [140] has a four membered Sn_2Mn_2 ring with Mn-Mn and Sn-Sn bond distances of 310.45(5) and 261.15(5) pm, respectively. The Mn-Sn-Mn and Sn-Mn-Sn bond angles are $72.94(2)$ and $106.93(2)^\circ$, respectively. Two phenyl groups on each tin atom complete a tetrahedral geometry about each tin atom (SnC_2Mn_2). A pseudo-octahedral environment about the Mn atoms is completed by a bridging $(\text{EtO})_2\text{POP}(\text{OEt})_2$ ligand (MnC_3PSn_2). The third pink cluster is isostructural with the aforementioned Cr and Mg analogues in the same publication [126]. The mean Sn-M and M-M distances increase in the order: 317(1) and 293.4(1) pm ($\text{M} = \text{Mg}$) < 326.7(2) and 306.6(1) pm (Cr) < 325.6(1) and 306.9(1) pm (Mn). A colourless Sn_2Re_2 cluster [141] shows two $\text{Re}(\text{CO})_4$ units directly bonded with a Re-Re bond distance of 328.9(3) pm. They are bridged by a μ -oxo-distannylene ($\text{Bu}_2\text{Sn-O-SnBu}_2$) group creating a five membered (Re-Re-Sn-O-Sn) ring with Re-Sn bond distances of 271.9(2) pm.

There are eight coloured Sn_2Fe_2 clusters [142-149]. Three of them [142-144] are characterised by a central lozenge shaped four membered Sn_2Fe_2 rings, with Sn-Fe bonds ranging from 263.1(11) to 267.4(1) pm (average 265 pm). The mean Sn-Fe-Sn and Fe-Sn-Fe bond angles are 77° and 103° , respectively. One of the derivatives has two crystallographically independent molecules present [142]. A red cluster [144] has two heterodimers, $\text{cp}(\text{CO})\text{FeSn}(\text{OSOPh})\text{Ph}$, linked by a dihydroxo-bridge with asymmetric Sn-O(H) bond distances (205.4(2) and 223.1(2) pm) and Sn-O-Sn bridge angles of $102.2(2)^\circ$. The Sn-Fe bond distance of 249.9(1) pm is the shortest in the series of tetrameric heterotin compounds. Each tin atom has a distorted trigonal-bipyramidal environment (SnO_3CFe) with the axis defined by O-Sn-O ($155.3(1)^\circ$). The structure of another red centrosymmetric Sn_2Fe_2 cluster [146] consists of a zigzag chain of four metal atoms (Fe-Sn-Sn-Fe) pseudo-tetrahedrally coordinated. The Sn-Fe and Sn-Sn bond distances are 260.5(2) and 299.1(2) pm, respectively. The Fe-Sn-Sn angles are equal at $114.9(1)^\circ$. A yellow example [148] consists of two ferrocene moieties linked through tin atoms in an eight membered metallocyclic central ring (Fe-C-Sn-C) $_2$. A pair of butyl groups about each tin atom completes a tetrahedral environment about the tin atoms (SnC_4). An orange derivative [149] is similar to the yellow cluster [148] having the same central metallocyclic ring structure. The Fe-Fe separation of 547 pm is similar to that found in the yellow derivative of 550 pm.

Two clusters contain Sn and Co [150,126]. The first is dark red and contains two crystallographically distinct molecules in the unit cell, each located astride a centre of inversion, but with no significant differences in molecular geometry [150]. Tin and cobalt atoms alternate around the four membered planar ring with angles at Co of 78° and at Sn of 102° . The mean Sn-Co, Sn-Sn and Co-Co distances in the two molecules are 254.1(5), 320.6(9) and 394.4(7) pm. This indicates that the Sn-Co is a real bond while the other two are not. Both tin atoms are in tetrahedral environments (SnC_2Co_2). The structure of the violet Sn_2Co_2 cluster is similar to those of the Mg, Cr and Mn clusters found in the same work [126]. The Sn-Co and Co-Co distances are 320.3(1) and 298.6(1) pm, respectively.

Three Sn_2Ni_2 clusters are reported [126,151]. The first is similar to the Co, Mg, Cr and Mn clusters in the same publication [126] and discussed previously. The Sn-Ni and Ni-Ni distances are 321.1(1) and 300.9(1) pm, respectively. The other two derivatives [151] consist of a planar Sn_2X_2 ring ($\text{X} = \text{S}$ or Se) with terminal $\{\text{cp}(\text{PPh}_3)\text{Ni}\}$ and Cl substituents in the *trans* arrangement. The Sn-Ni bond distances are 242.0(1) pm ($\text{X} = \text{Se}$) and 242.4(2) pm ($\text{X} = \text{S}$). Each tin atom has quasi-tetrahedral coordination (SnX_2ClNi).

A yellow Sn_2Ru_2 cluster has an almost linear central chain Sn-Ru-Ru-Sn [152]. The carbonyl ligands all lean slightly towards the outer SnMe_3 units with an eclipsed configuration. The Ru-Ru bond distance of 294.3(1) pm is about 25.2 pm longer than the Ru-Os bond length (269.1(1) pm).

The molecular core of red brown Sn_2Rh_2 cluster [153] is a bent Rh-Sn-Rh-SnCl $_3$ chain. The central tin atom resides within the cavity of the macrocycle (twelve membered $(\text{RhPCNCP})_2$), with coordination to two N atoms and two Rh atoms plus a terminal Cl atom. Each of the four metal atoms is in a unique environment. The central Sn(II) atom is square pyramidal ($\text{SnN}_2\text{Rh}_2\text{Cl}$) with Cl at the apex. The Sn-Rh bond distances are 258.8(2) and 260.1(2) pm. The outer Sn(II) atom is quasi-tetrahedral (SnCl_3Rh) with Sn-Rh bond distance of 258.7(3) pm.

pm. One Rh(I) atom is six coordinate ($\text{RhCl}_2\text{P}_2\text{CSn}$) and the other Rh(I) atom is trigonal-bipyramidal ($\text{RhP}_2\text{Sn}_2\text{C}$) with a Sn-Rh-C angle of $176.5(5)^\circ$.

A yellow osmium derivative [154] contains a planar tetrametallic core of alternate Sn and Os atoms (Sn_2Os_2). The Sn-Os distances are 275.8(1) and 276.8(1) pm, with Sn-Os-Sn angles of $75.32(3)^\circ$ and $104.68(3)^\circ$. A pair of methyl groups about each tin atom completes the quasi-tetrahedron (SnC_2Sn_2). The four CO groups about rhodium gives an octahedral environment (RhC_4Sn_2).

There are two coloured Sn_2Ir_2 clusters [155,156]. The first is bright green and contains a twisted tetrametallic chain of Sn-Ir-Ir-Sn with Ir-Ir-Sn bond angles of $92.9(1)^\circ$ and $164.2(1)^\circ$. Both Ir(II) atoms are bridged by a μ -S atom as well as by two dppm molecules. Pseudo-octahedral coordination is completed by a carbonyl group ($\text{IrP}_2\text{CSSnIr}$). Each Sn(II) atom is bonded to three Cl atoms to give a quasi-tetrahedral environment (SnCl_3Ir). The Ir-Ir bond distance of 287.8(1) pm is about 28.5 pm longer than the mean Sn-Ir bond distance of 259.3(1) pm. In the second derivative [156] two Ir centres are connected by a double bridge formed by a η^5 -pyrazolate group and a SBu^+ group linked through the S atom. This double bridge maintains and Ir-Ir bond distance of 272.21(6) pm. Each metal centre completes its coordination sphere by three terminal ligands, a carbonyl, a trimethyl phosphite and a trichlorostannate group (IrCNPSSnIr). The Sn-Ir-Ir-Sn chain is twisted with Sn-Ir-Ir angles of $108.7(1)^\circ$ and $153.0(1)^\circ$. The Sn-Ir bond distance of 261.4(1) pm is somewhat longer (2 pm) than that of the previous cluster [155].

Two yellow Sn_2Pt_2 clusters [157,158] are quite different from each other. The first consists of discrete di-chlorine bridged Pt dimers with each Pt atom bonded to SnCl_3 and PEt_3 moieties. These are *cis* to each other, but the entire molecule has a sym-trans geometry. The Pt atoms have distorted square planar environments (PtCl_2PSn) with a mean Pt-Sn bond distance of 248.2(3) pm. Each Sn atom is tetrahedrally coordinated (SnCl_3Pt). The second cluster [158] preserves the di-chlorine bridge but contains Pt-C=C-Pt units. The unique Pt atom has a geometry close to square planar, with the PtC_4Sn plane approximately normal (78.3°) to the other PtCl_2PC coordination plane. Each Sn(II) atom has a distorted tetrahedral environment (SnCl_3C).

3.3 Sn plus Three M

There are over thirty clusters which contain one tin atom with three identical heterometal atoms. The structural data for this group, which involves only transition metal atoms plus tin, is given in Table 2. A black SnCr_3 cluster [159] has a coplanar core of the four metal atoms with a mean Sn-Cr bond distance of 266.5(2) pm (maximum deviation 1.1 pm) and Cr-Sn-Cr angles all very close to 120° . The idealized geometry of the core is D_{3h} , with each chromium coordinated by five carbonyl groups. Two red SnMo_3 clusters [160,161] contain heterometallic cubane type $\text{Mo}_3\text{S}_4\text{Sn}$ cores with each metal atom six coordinate. The Sn-Mo and Mo-Mo distances range from 329.2 to 377.3 pm and 272.3 to 300.5 pm, respectively. There are two coloured SnW_3 clusters [162a,162b]. In the first the tin atom is central and coordinated to three W(CO)_5 units with Sn-W bond distances of 271.3(2), 279.0(2) and 279.4(2) pm. The fourth position about each tin atom is occupied by the O atom of a (thf) ligand resulting in a quasi-tetrahedral environment (SnW_3O). The structure of the second, dark brown, cluster is of a cubane type with a $\text{W}_3\text{S}_4\text{Sn}$ core similar to that of the molybdenum case discussed above [160]. Each metal atom is octahedrally coordinated, by three S and three N atoms for tungsten and by three S and three Cl atoms for tin. The mean W-W bond distance of 276.6(2) pm is about 3.6 pm longer than that of the shortest Mo-Mo bond distance in the Mo analogue [160].

There are four red SnMn_3 clusters [163-166] where the central atom is tin. In all four cases the Mn atoms are directly bonded to Sn with distances ranging from 244.5(1) to 275.8(2) pm (mean 267 pm). In a yellow orange SnRe_3 cluster [167] the asymmetric unit contains two similar but crystallographically independent molecules, examples of distortion isomerism. In each the three Re atoms define an approximate equilateral triangle, with the Sn atom bridging one edge essentially in the plane of the triangle. The Sn-Re bond distances are 266.6(3) and 287.4(4) pm in one molecule, 268.4(2) and 286.8(3) pm in the other. The Me_3Sn bridged Re-Re distances are 314.8(2) and 315.2(2) pm, respectively, and the mean value of the other Re-Re distances is shorter at 308 pm. Each rhenium atom has four terminal carbonyl groups.

There are two red SnFe_3 clusters [168,169] in which the four metal atoms form a core with a mean Sn-Fe bond distance of 254 pm (range from 252.7(1) - 255.6(1) pm). The Fe-Sn-Fe angles are all very close to 120° (maximum deviation 3.8°). One of them [169] contains two crystallographically independent clusters differing mostly by degree of distortion.

Three SnCo_3 clusters [90,170,171] may be described in terms of a central tin atom which carries a Br [170] or Cl [90,171] atom and three Co(CO)_4 moieties. The geometry about Sn is quasi-tetrahedral (SnXC_3), and the geometry about Co is distorted trigonal-bipyramidal with a mean Sn-Co bond distance of 260 pm (range from 258 to 262 pm). The mean Co-Sn-Co bond angle is $113.7(2)^\circ$.

The structure of the SnNi_3 cluster [95] is similar to that of the SnCo_3 clusters with a mean Sn-Ni bond distance of 252.59(1) pm (range 251.9(1) to 253.1(1) pm). The mean Ni-Sn-Ni angle of $113.7(1)^\circ$ is the same as

found in the SnCo_3 clusters.

There are four SnRu_3 clusters [172,173,97], the first is a yellow compound containing two independent molecules of essentially identical structure. The three Ru atoms are in a triangular cluster with only two metal-metal bonds which also have a bridging hydride ligand. A sulphide ligand bridges all three metal atoms together. Two of the Ru atoms carry three terminal carbonyl groups while the third has two carbonyls and a trichlorostannyl group which lies on the sulphur bridged side of the Ru_3 plane. The Ru-Sn distance is 257.1(1) pm in one molecule and 258.8(1) pm in the other. The ruthenium atoms differ in stereochemistry (Table 2) and the tin atom has a distorted tetrahedral arrangement (SnCl_3Ru). There are two dark red SnRu_3 isomers [173] which are isostructural, one of them being shown in Figure 6. The cluster consists of a triangular array of ruthenium atoms triply bridged by the (ampy) ligand, with two short edges (Ru-Ru = 287.8(1) pm and 269.5(1) pm). These are also bridged by hydrido and diphenylalkenyl ligands, respectively. The μ_3, η^1 -ampy ligand occupies three axial coordination sites, being linked to one Ru atom via the pyridinic nitrogen atom and to the other two Ru atoms by the exocyclic N atom. A SnPh_3 group is coordinated at an equatorial position to the first Ru atom being nearly cis to the hydride ligand. The cluster coordination shell is completed by seven terminal CO groups, three in axial sites *trans* to the (ampy) N atoms and four in equatorial sites. The final SnRu_3 cluster [97] is held by three μ_3 -bridging and one μ -bridging selenide atoms. The two μ_3 -Se atoms are bound to two Ru atoms and one Sn atom. The μ -Se atom links one Ru and one Sn atom. Two terminal C-donor ligands (tb and tip) complete a quasi-tetrahedral environment about the Sn atom (SnC_2Se_2). The Ru atoms differ from each other with chromophores of RuC_3Se_3 , RuC_3Se_2 and RuCSe_4 .

Fig.6. Structure of $[\text{Ru}_3(\mu\text{-H})(\mu, \eta^2\text{-ampy})\{\mu, \eta^1:\eta^2 \text{PhC}=\text{C}(\text{H})\text{Ph}\}(\text{SnPh}_3)(\text{CO})_7]$ [173]

There are eight coloured SnOs_3 clusters [174-178,97]. In an orange derivative [174] four metal atoms form a distorted tetrahedral array with Sn-Os bond distances of 264.1(4) and 264.2(4) pm, and Os-Os distances of 289.1(4) and 300.1(4) pm. Two Os atoms are bridged by a hydrido ligand. The cpy ligand is bonded via C and N atoms to Sn to give a distorted tetrahedral environment (SnNCOs_2). The cluster coordination shell is completed by ten carbonyl groups, three of them bound to the osmium atoms which are hydrido-bridged. The remaining four are coordinated to the third Os atom. A yellow cluster [175] crystallizes in the space group $P2_1/c$ with two independent but structurally similar molecules per unit cell. The cluster has a nearly planar butterfly structure with the Sn and one Os atom forming the hinge. The methylene ligand asymmetrically bridges two Os atoms with Os-O distances of 205(2) and 222(2) pm. Significant asymmetry also exists in the Os-Sn bond lengths with the Sn atom located 15.9 to 17.5 pm closer to one Os than the other two. The shorter Sn-Os distances are 264.192 pm in one molecule and 263.692 pm in the other. The Os-Os distances are 298.9(1) and 305.0(1) pm in one case and 298.5(1) and 305.7(1) pm in the other. The Sn atom has a distorted trigonal bipyramidal environment (SnCl_2Os_3). The coordination spheres of the Os atoms are all different (Table 2). In another cluster shown in Figure 7 [176] a bulky alkyl group originally attached to tin ends up on the carbon of an osmium attached CO ligand to form a η^2 -acyl group bridging the Os and Sn atoms. The (acyl) fragment spans the two metal atoms giving a basket-like configuration. Two pairs of Os atoms are each linked by hydride

bridges. The geometry about the Sn atom is trigonal planar (by C and two Os atoms) which is then capped by the O atom of the (acyl) bridge.

Fig.7. Structure of $\text{Os}_3\text{Sn}(\mu\text{-H})_2(\text{CO})_8\{\mu\text{-}\eta^2\text{-OCCH}(\text{SiMe}_3)_2\}\{\text{CH}(\text{SiMe}_3)_2\}$ [176]

The structure of another orange cluster [177] has a planar arachno-molecular metal framework with the bulky alkyl groups bonded essentially perpendicular to this plane. The yellow cluster [178] contains an open array of three Os atoms with a triply bridging sulphide ligand between them. There is also a triply bridging η^2 -thioformaldehyde ligand in which the sulphur atom bridges two of the Os atoms and the carbon atom links to the third. The SnMe_3 moiety is coordinated to one Os atom with an Os-Sn distance of 265.3(1) pm, with tin quasi-tetrahedral (SnC_3Os). Two yellow derivatives [97], one with S and the other with Se, are isostructural. The chalcogen atoms act as μ_3 -bridging ligands between all three Os atoms or between two Os atoms and one Sn atom. Eight terminal CO groups are distributed three to two Os atoms and two to the other Os atom. The cluster coordination shell is completed by two terminal C-donor ligands (tb and tip) which bond to the tin to complete a distorted tetrahedral environment (SnC_2XOs).

There are three coloured SnPt_3 clusters [179,180]. The first contains two crystallographically independent $[\text{Sn}\{\text{Pt}(\mu\text{-Cl})(\text{C}_6\text{F}_5)_2\}_3]$ anions. The inner platinum moiety can be described as a puckered Pt_3Cl_3 ring in which the Pt(II) atoms are interconnected by the Cl atoms and acts as a tridentate donor-acceptor ligand to the Sn(II) atom. Each Pt(II) atom has a square-pyramidal coordination ($\text{PtC}_2\text{Cl}_2\text{Sn}$) with a the Sn atom at the apex of each. A purple complex [180] has a SnPt_3 cluster cation with a PF_6^- anion. The cation contains an almost equilateral triangle of Pt atoms and a $\mu_3\text{-SnMe}_2(\text{PO}_2\text{F}_2)$ moiety. Two methyl groups, the PO_2F_2 moiety and three Pt atoms complete a roughly octahedral coordination about the Sn atom (SnC_2FPt_3). The Sn-Pt bond distances are 270.2(2), 273.9(2) and 276.6(2) pm. The Pt-Pt bond distances are shorter at 260.9(1), 261.5(1) and 263.5(1) pm.

3.4 Sn plus Two M and M'

There are five clusters of this type [106,168,181-183] with two identical heterometals plus one different, and their crystallographic and structural data are given in Table 2. Both transition and non-transition heterometal atoms are observed.

A dark purple derivative [181] contains a bent four metal atom unit $(\text{tpp})\text{SnMn}(\text{CO})_5\text{HgMn}(\text{CO})_5$ extended over the porphyrin ring with a $94.5(1)^\circ$ bend at Sn-Mn-Hg. The Mn-Hg-Mn link bends up away from the ring slightly ($164.4(1)^\circ$). The Sn atom is five coordinate in a square-pyramidal environment. The two Mn atoms are octahedrally coordinated by Co groups and metal atoms. The Sn-Mn, Mn-Hg and Hg-Mn bond distances are 255.4(3), 258.2(3) and 265.9(3) pm, respectively.

Four metal atoms are arranged nearly linearly, $(\text{CO})_5\text{Mo-Sn}(\text{m-OBu})_3\text{-In-Mo}(\text{CO})_5$ in another complex [106]. The intermetallic angles are 174.2° (Mo-Sn-In) and 178.8° (Mo-In-Sn). The metals are linked by single

TABLE 2. Crystallographic and Structural Data for Tetrameric Heterometallic Tin Clusters^a

COMPOUND (colour)	Crys. Cl Sp. Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo- phore	M-L [pm]	M-M [pm] M-L-M [°]	L-M-L [°]	Ref
3Sn + M								
[Li(thf) ₄]	tr ₋	1374.0(3)	73.97(3)	Sn ^{IV} N ₁	μ_3 N ^b 218	N ^b 99.3	NN ^b 80.4	113a
[(Bu ⁿ N)(imn) ₃]	P1	1451.6(3)	78.97(3)				87.1	
Sn ₃ Li(thf)[thf]·thf·tol (yellow)	2	1747.2(3)	77.99(3)	Li ⁺ N ₃ O	μ_4 N 210 O _{1H} 194(2)			
at 152(3)K								
(Me ₃ Sn) ₃ (μ ₄ -N) imn/Me ₃ (colourless)	c P2 ₁ 3 4	1305.7(1)		SnC ₃ N	C ₃ Me 214(2.1) μ_4 N ₁ 210.2(8) C ₃ Me 220(2.0) μ_4 N ₁ 239(3)	N 111.7(6)	CC 109.6(9.1.5) CN 109.3(9.1.4) CC 113.7(5) CN 104.8(6) not given	113b
[(OMe ₃ Sn) ₃ (μ ₄ -Si) Zr ₃ Cl ₂ Cl ^c] (yellow)	tr ₋ P1 4	1130.0(3) 1640.1(4) 1721.2(5)	104.15(2) 101.00(2) 92.12(2)	SnC ₃ Si Zr ₃ Cl ₂ SiCl	C ₃ Me not given μ_4 S 257.0(4.7) cp 219.1 μ_4 Si 277(2) Cl 241.7(4) μ_4 Si 256.8(4.9) cp 219.1 μ_4 Si 276.5(4) C 242.1(4) C ₃ H 216.9(6.14)	Si 102.8(1.3.2) Si 115.4(1.1.0) Si 101.7(1.2.5) Si 116.4(1.1.4) Cr 271.4(1.15)	cp cp 130.4(2) Si/Cl 93.6(2) not given cp cp 130.4(2) Si/Cl 94.9(1) C/C not given C/Cr 115.1(2.8.4) C/Cr 89.86(3) 126.5(1.2) C/Sn 77.0(2.7.3) 132.6(2) 162.6(2.2) not given	114
(NEt ₄) ₂ (Ph ₃ Sn) ₃ C ₃ (CO) ₄ (pale yellow)	tr ₋ P1 2	1437.1(4) 2056.0(10) 1073.0(5)	99.21(4) 105.07(3) 83.29(3)	SnC ₃ Cr				115
(NEt ₄) ₂ [(OMe ₃ Sn) ₃ (μ ₄ -Si)W(CO) ₅] (orange)	m P2 ₁ /m 4	1395.8(4) 1850.1(4) 1403.5(4)	94.96(2)	SnC ₃ Si WC ₃ Si	C ₃ Me not given μ_4 Si 256.9(4.12) OC 202.2(5) μ_4 Si 265.2(4)	Si 102.2(1.1.8) Si 116.0(1.2)	C/Si 88.0(5.2.2) 176.8(4)	116

$[\text{P}_2\text{H}_2\text{Sn}_3(\mu\text{-OMe})_2(\eta^2\text{-H}_2)(\text{CO})(\text{PtPr}_3)\text{Ru}]^0$ (colorless)	tr- P1^- 4	1170.5(1) 2012.9(2) 2273.9(2)	81.953(6) 81.181(6) 88.490(7)	$\text{SnC}_2\text{ORu}(x2)$ $\text{SnC}_3\text{O}_3\text{Ru}$	C_3H_3 not given $\mu\text{O}_3\text{M}_2$ 237.2(4.9) $\mu\text{O}_3\text{M}_2$ 228.3(2.18)	Ru 260.87(5.15) Ru 78.53(1) Ru 267.01(5) Ru 79.14(1) Ru 157.65(2)	not given C,C 107.2(2) O,O 171.5(1) R ₁ 126.2(2.63) C,C 171.5(2) P,Sn 176.59(3) N,N 90 Sn,Sn 120.0(1.12)	117
$\{(\text{Me}_3\text{Si})_2\text{N}\}_2\text{Sn}_3$ Pd (yellow) (NMe_2), $[(\text{Cl}_3\text{Sn})_3\text{OsCl}]$ (yellow-orange) $[\text{Pt}(\eta^3\text{-C}_4\text{H}_7)(\eta^4\text{-cod})][(\text{Cl}_3\text{Sn})_3\text{Pt}(\eta^3\text{-C}_4\text{H}_7)]$ (wine-red)	tr- P1^- 2	1395.3(5) 1386.898 1951.9(10) Not given	78.71(4) 87.23(4) 74.11(4)	RuC_2PSn_3 $\text{Sn}^{\text{II}}\text{N}_3\text{Pd}$ $\text{Pd}^{\text{II}}\text{Sn}_3$ $\text{Sn}^{\text{II}}\text{Cl}_3\text{Os}$	OC not given PPr not given LN not given Cl 237(2.6)	Pd 253.0(1.13)	N,N 90 Sn,Sn 120.0(1.12)	118
$(\text{As}^{\text{II}}\text{H}_4)[(\text{Cl}_3\text{Sn})_3\text{Pt}(\eta^4\text{-cod})]$ (yellow-brown)	tr- P1^- 2	1325.6(4) 1996.0(4) 861.5(3)	101.75(2) 104.69(2) 86.62(2)	$\text{Os}^{\text{II}}\text{C}_3\text{Sn}_3$ $\text{Sn}^{\text{II}}\text{C}_3\text{Pt}$ $\text{Pt}^{\text{II}}\text{C}_3\text{Sn}_3$	Cl not given Cl 238.8(4.52) C 217.6(12.14)	Os 253 258 (x2) Pt 254.1(1.7) 261.5(1) Pt 99.5(1.5.9)	Cl,Cl 94.2(2.46) Cl,O 122.1(2.65) Cl,Cl 96.6(1.22) Cl,Pt 120.2(1.89) C,Sn 106.9(3.19.0) 153.9(3.3.3)	119
$(\text{N}(\text{FPh})_2)[(\text{Cl}_3\text{Sn})_3\text{Pt}(\text{AsMe}_2)_2]$	m $\text{P2}/\text{m}$ 4	1544.5(2) 980.7(2) 3155.5(3)	97.71(1)	$\text{Sn}^{\text{II}}\text{C}_3\text{Pt}$ $\text{Pt}^{\text{II}}\text{C}_4\text{Sn}_3$ $\text{Sn}^{\text{II}}\text{C}_3\text{Pt}$ $\text{Pt}^{\text{II}}\text{As}_2\text{Sn}_3$	Cl 235.5(6) C_{cod} 223(2.0) 227(2) Cl 238.0(7.10) As 213.6(2.9)	Pt 255.7(2.11) 254.3(2) Pt 257.9(1) 261.3(2.1)	not given Sn,Sn 85.90(5) 94.3(1.5) not given As ₂ As 177.7(6) Sn,Sn 121.0(4.2.9) As,Sn 90.0(1.2.5)	121
$[\text{S}_3(\mu\text{-HfImes})(\mu\text{-Nm})_2]\text{Li}(\text{thD}_2)_2$ (yellow)	tr- P1^- 1	1108.0(7) 1172.0(7) 1056.1(5)	104.45(4) 99.70(5) 102.01(5)	$\text{Sn}^{\text{II}}\text{N}_3$ $\text{Li}^{\text{I}}\text{O}_2\text{N}_2$	μN 217.1(4.20) 225.7(4) O_{air} 198 μN 208(1.1)	N 101.2(2) N 89.5(3.7)	N,N 84.5(2.5.9) O,O 99.4(4) N,N 91.7(4) O,N 116.7	122
2Sn + 2M								

$[\text{Sn}(\mu\text{-OBu}^t)_2\text{Li}]_2$ (colourless)	m P2 ₁ /c 4	966.5(3) 1819(1) 1014(1)	107.1(1)	$\text{Sn}^{\text{II}}\text{O}_3$ Li^+O_4	μO 209.3(3,7) μO 192.9(8,4) 211.5(10,18)	O 97.1(3,3,2) Li 26.1(2) O 76.3(3)	O ₃ O 79.9(1,2) 97.6(1) O ₃ O 83.2(3,9) 105.7(3,2,0) 164.1(3)	124
$\text{Sn}(\mu\text{-OBu}^t)_2\text{Na}]_2^+$ (colourless)	tr P1 2	1041(1) 2046(1) 1033(1)	92.3(2) 118.6(1) 108.3(3)	$\text{Sn}^{\text{II}}\text{O}_3$ Na^+O_4	μO 209.5(3) 211.0(6,1) μO 227.3(6,3) 240.6(7,8)	O 101.0(2,2,5) Na 299 O 75.9(5)	O ₃ O 83.4(1,1) 93.5(2) O ₃ O 73.5(2,1) 105.1(2,3,0) 177.6(2)	124
$[(\text{pz})_2\text{Sn}(\mu\text{-pz})_2\text{Na}]$ (pzH) (thf) ₂ (colourless)	m P2 ₁ /c 2	1184.4(3) 1695.7(4) 1272.9(4)	92.57(3)	$\text{Sn}^{\text{II}}\text{O}_3$ Na^+O_4	μO 208.0(3) 210.0(5,0) μO 227.3(6,13) 242.4(7,22)	O 101.3(2,2,9) Na 300 O 76.5(5)	O ₃ O 83.3(2,0) 94.8(3) O ₃ O 72.6(2,0) 107.0(2,3,5) 178.1(2)	125
$[(\text{Bu}^t\text{O})$ $\text{Sn}(\mu\text{-OBu}^t)_2]_2$ $\{\text{Mg}(\mu\text{-OBu}^t)_2\}_2$ (colourless)	m P2 ₁ /n 2	1010.0(7) 1495.1(8) 1500.9(9)	97.30(6)	$\text{Sn}^{\text{II}}\text{O}_3$ MgO_4	μO 212.7(3,2) O 200.9(4) μO 196.4(3,6)	Mg 317.1(1) Mg 293.4(1)	O ₃ O 74.2(1) O 82.2(1,9)	126
$\{\text{Ph}_3\text{Sn}(\mu\text{-O})\}_2$ $\{\text{AlMe}_2\}_2$ (colourless)	tr P1 1	907.6(1) 973.3(2) 1308.4(3)	71.03(2) 74.22(1) 65.05(1)	$\text{Sn}^{\text{IV}}\text{O}_3$ $\text{Al}^{\text{III}}\text{O}_2\text{C}_2$	C_{H} 211.7(3,1) $\mu\text{-O}$ 198.4(4) $\mu\text{-O}$ 184.0(3,0) C_{H} 195.9(8,1)	Al 347.3(1) O 131.3(2) Al 271.1(2) O 95.1(2)	C 112.9(1,3,2) C 105.8(1,1,9) O ₃ O 84.9(1) C 118.6(1) O ₃ C 112.6(2,1,1) Cl 78.5(1,1) 167.8(1,1,3)	127
$[(\eta^5\text{-C}_6\text{H}_5)_2\text{SnCl}]$ $[\text{AlCl}_2]_2$ (colourless) at 273K	or Poca 8	1986.9(1) 1594.1(1) 2555.4(2)		$\text{Sn}^{\text{IV}}\text{C}_{12}\text{Cl}_4$ $\text{Al}^{\text{III}}\text{C}_4$	$\eta^6\text{C}$ 320(-,9) μCl 262.3(2,16) 291.2(3,74) Cl 210.5(4,11) μCl 216.9(4,8)	Cl 101.5(1,4)	Cl 119.1(1,3,5)	128

$[(C_{20}H_{14})SnCl(AICl_4)_2 \cdot 0.5C_6H_6]$ (colourless) at 213K	tr^- $P\bar{1}$ 1	1040.4(3) 1334.3(3) 1119.4(2)	98.63(2) 109.23(2) 105.77(2)	$Sn^{III}C_{12}Cl_3$ $Al^{III}Cl_4$	μCl 262.9(1,51) 293.9(1,139) not given	97.9(1)	$Cl-Cl$ 82.1(1) not given	129
$[(mes)SnCl(AICl_4)_2]$	m $P2_1/n$ 2	929.7(4) 1277.5(6) 1397.5(4)	95.57(3)	$Sn^{III}C_5Cl_3$ $Al^{III}Cl_4$	μCl 265.0(2,6) 3.11(-,13) Cl 209.0(3)		$Cl-Cl$ 78.3(1,11.5) 147.8(1) $Cl-Cl$ 109.5(1,3,6)	130
$\alpha-[(tol)SnCl(AICl_4)_2]$ (colourless)	tr^- $P\bar{1}$ 2	720.13(7) 866.25(7) 1132.9(1)	96.51(1) 93.23(1) 100.218(7)	$Sn^{III}C_5Cl_3$ $Al^{III}Cl_4$	μCl 265.3(1,13) 303(-,17) Cl 210.06(9)		$Cl-Cl$ 77.7(1,9,9) 146.39(4) $Cl-Cl$ 109.5(1,6,2)	130
$\beta-[(tol)SnCl(AICl_4)_2]$ (colourless)	tr^- $P\bar{1}$ 2	711.0(9) 942(1) 1156(1)	113.3(1) 99.5(1) 91.9(1)	$Sn^{III}C_5Cl_3$ $Al^{III}Cl_4$	μCl 215.1(1,42) μCl 262.9(1,23) 299.8(1,155)		$Cl-Cl$ 77.4(1,8,9) 148.62(6) $Cl-Cl$ 109.5(1,6,4)	130
$[Me_2Sn\{\mu-NP^t\}_2]Ga$ Me_2 (colourless)	m $P2_1/n$ 2	877.0(2) 1512.4(3) 962.2(1)	94.82(1)	$Sn^{IV}C_3N$ $Ga^{III}N_2C_2$	μN 211.2(4) μN 203.3(4,6) C_{Me} 197.9(5,5)	112.9(2,3) Ga 289.2(1)	not given	131
$[Me_2Sn(\mu-NEu)_2]Ga$ Me_2 (colourless)	m $P2_1/n$ 2	923.4(1) 1832.8(2) 972.9(1)	111.24(1)	$Sn^{IV}N_4C_2$ $Ga^{III}N_3C$	μN 208.2(4,65) C_{Me} 214.8(6,6)	93.6(2,4,5) 112.5(2)	NN 89.3(2) CC 110.0(3) NC 114.1(2,1,5) NN 83.3(1) CC 100.5(2)	132
$[cy-Sn(\mu-S)GaPh_2]_2$ (colourless)	tr^- $P\bar{1}$ 1	1082.5(2) 1146.5(3) 1361.5(3)	80.68(2) 77.95(2) 63.78(1)	$Sn^{IV}C_3S$ $Ga^{III}C_2S_2$	μN 189.1(3) 204.4(3,8) C_{Me} 198.1(6) C_{cy} 216(2,9) μS 240.5(3) C_{Ph} 196(1,0) μS 234.2(3)	93.9(1)	NN 87.6(2,1,5) CN 126.5(2)	133
$[cy-Sn(\mu-S)InPh_2]_2$ (colourless)	tr^- $P\bar{1}$ 1	1119.8(4) 1144.1(4) 1361.2(3)	80.15(2) 79.16(2) 62.36(2)	$Sn^{IV}C_3S$ $In^{III}C_2S_2$	C_{cy} 216.4(5,4) μS 244.6(2) C_{Ph} 214.5(7,4) μS 255.1(2)	In 412.5(1) 111.26(9) In 357.4(1)	CC 112.8(4,2,2) CS 105.8(3,8,8) CC 114.5(3) SS 93.5(1) CS 111.2(3,5,3) CC 112.6(3,2,8) CS 105.9(3,6,3) CC 116.3(2) SS 90.72(5) CS 110.4(2,4,1)	133

$\{[Me_3SnG=(p)]\}$ $\{CH(SiMe_3)_2\}_2$ (μ - η^3 -C-N-N) (pale yellow) at 173K	m P2 ₁ /c 4	946.3(4) 1904.1(5) 2984.0(9)	94.74(3)	SnC ₃ G ₂ GeC ₃ Sn GeC ₂ NSn	C _{Me} not given C 202.0(11,36) μ C _L 193.5(13) C 201.2(11,44) μ N _L 188.3(11) 13/Sn 295.7(6,23)	Ge 265.0(2,2)	not given C Sn 94.9(4) 118.4(3,4) C Sn 116.1(3,1,4) N Sn 100.9(3) Bi Bi 60.0(1,7) Bi ₂ Sn 60.0(1,7) Sn ₂ Sn 60.0(1,7) not given	134
$\{K(2,2,2\text{-crypt})\}_2$ [Sn ₂ Bi ₂] en (black) [Me ₃ Sn(μ -N)Ti cp(Cl)] ₂ (red)	m P2 ₁ 2 m P2 ₁ /n 4	1264.0(3) 2094.3(5) 1235.3(3) 1131.2(1) 1491.6(2) 2000.0(2)	118.97(1) 90.81(1)	SnBi ₂ Sn ^I BiSn ₂ Bi ^I Sn ^{IV} C ₃ N Tl ^{III} cp ₂ N ₂ Cl	295.7(6,23) 295.7(6,23) S ₂ /Bi 295.7(6,23) C _{Me} not given μ N 210.6(10,2) μ N 188.9(10,8) Cl 230.5(1,16) cp 211.3(5,3)	295.7(6,23) 128.1(5,2,2) Ti 278.6(3) 95.0(4,1)	not given Bi Bi 60.0(1,7) Bi ₂ Sn 60.0(1,7) Sn ₂ Sn 60.0(1,7) not given NN 84.7(4,1) NC 104.5(3,1,7)	135 136
[Me ₃ Sn(μ -N) Ti(C ₂ Me ₄ Et)F] ₂ (light red) at 150(2)K	m P2 ₁ /c 4	816.0(2) 1874.9(4) 2182.8(4)	99.48(3)	Sn ^{IV} C ₃ N Tl ^{III} cp ₂ N ₂ F	Me ₃ C not given μ N 206.7(3) μ N 190.7(3,4) F 183.6(2) cp 210.1(2)	127.1(2,2,0) 94.2(1,2)	not given NN 85.5(1,1) NF 106.02(11)	137
[Me ₃ Sn(μ - η^2 , η^1 C=C) Ti cp] ₂ (purple)	Or Pbca 4	1484.6(2) 1311.9(2) 1510.7(2)		Sn ^{IV} C ₄ Tl ^{III} cp ₂ C ₃	C _{Me} 212(1) μ C 212.0(5) μ C 205.5(5) 234.3(5,70) cp 211.5(9,3)	138.4(3) Ti 257.3(1) 105.6(2)	not given cp cp 129.2(3) C,C 30.6(2) 74.4(2)	15
[Me ₃ Sn(μ - η^2 , η^1 C=C) Ti(C ₂ H ₃ Me ₂) ₂ (dark purple)	m P2 ₁ /n 2	1078.9(3) 997.6(2) 1728.9(2)	98.98(1)	Sn ^{IV} C ₄ Tl ^{III} cp ₂ C ₃	C _{Me} 209(2) μ C 212.5(12) μ C 208.8(11) 235.5(12,69) cp 213.8(15,23) C _{Me} 216.6(6,2) 219.1(6)	142.0(6) Ti 363.1(1) 107.0(2)	not given cp cp 129.8(5) C,C 30.6(4) 73.0(4)	15
{Me ₃ SnNbcp ₂ } ₂ (μ -O) (yellow)	or Pbca 4	840.9(3) 2110.9(4) 1558.2(3)		Sn ^{IV} C ₃ Nb Nbcp ₂ OSn	cp 213.8(15,23) C _{Me} 216.6(6,2) 219.1(6) cp 212 μ O 194.34(4)	Nb 286.19(5) 179.99	not given cp cp 132.12 O cp 106 O ₂ Sn 87.52(2) O ₂ O 74.3(2)	138
{(Bu ^l O)Sn (μ -Bu) ₂ } {Cr(μ -OBu) ₂ } (blue)	n ^u P2 ₁ /c 2	1365.4(9) 1041.1(8) 1572.9(9)	103.27(8)	Sn ^{IV} O ₃ C ^{IV} O ₄	O 201.6(5) μ O 212.7(5,1) μ O 201.7(5,6) 204.5(5,7)	Cr 326.7(1) Cr 306.6(1)	O ₂ O 79.4(2,2,0)	126

(NBu ₄) ₂ [(Pb ₂ Sn) ₂] (μ-CH ₂) ₂ (μ-MrO) ₂] 4CH ₂ Cl ₂ (colourless)	or P _{bca} 4	1590.8(3) 2047.7(3) 2314.6(4)	Sn ^{IV} O ₄ C ₂	μHO 218.2(4.7) μO 212.2(5.7) C _{ph} 215.2(6.3)	111.2(2)	O,O 80.7(2,11.9) 164.4(2) C,C 109.2(2) O,C 93.4(2,2.7) 158.7(2.6) O,O 109.4(2,3.6)	139
{L ₂ [(2,1,1-crypt)] ₂ [(C ₄ H ₉ S) ₂ SnMn (cp*) ₂ (CO) ₂] {μ-S(CH ₂) ₂ S} [(CO) ₂ Mn] ₂ (μ-SnPh) ₂ (μ-tedip)]	m P ₂ /c 2	1486.9(5) 1497.8(5) 1714.0(3)	Mo ^{VI} O ₄ Sn ^{II} S ₃ Mn Mn ₂ C ₂ Sn	μO 181.8(4.3) O 1.722(4.4) S 247.9(3.5) not given	122.0(2.2) Mn 249.5(2)	S,Mn 115.4(1.7)	67
{(Bu ₄ O)Sn (μ-OBu) ₂] {Mn(μ-OBu) ₂] (pink)	m P ₂ /n 2	2309.5(4) 1038.5(1) 1843.9(5)	SnC ₂ Mn ₂ Mn ₂ C ₂ F ₂ Sn ₂	C _{ph} not given P 224.72(4)	Mn 2605.3(5) 261.78(6) Mn 310.45(5) 72.94(2) Mn 325.6(1)	C,C 98.6(1) Sn,Sn 106.93(2) P,Sn 91.49(3) O,O 75.2(3)	140
{(CO) ₂ ReSnBu ₂] (μ-O)] (colourless)	m C ₂ /c 4	1007.2(5) 1514.9(8) 1508.2(8)	Sn ^{II} O ₃ Mn ^{II} O ₄	O 199.4(9) μO 211.3(9.9) μO 203.7(7.8) 205.8(8,10)	Mn 306.9(1)	O,O 79.9(2.7)	126
		2067.2(2) 944.3(1) 1892.5(4)	SnC ₂ ORre	C _{ba} 215.2(3) μO 213.5(8)	Re 271.9(2)	C,C 109(1) C,O 99(1.1) C,Re 121(1.1) O,Re 100.9(5) C,C 91(1.9) 176(1)	141
			ReC ₄ Sn	OC 194(3.4)	Re 328.4(3)	C,Sn 92.0(8.2,4) 171.1(8) R ₂ ,Sn 91.7(5)	142
[M ₂ SnFe(CO) ₄] ₂ (yellow)	or Pham 4	1207.9(9) 1232.9(9) 1361.3(10)	Sn ^{IV} C ₂ Fe ₂ Fe ^{II} C ₄ Sn ₂ Sn ^{IV} C ₂ F ₂ Fe ^{II} C ₄ Sn ₂	C _{ba} 208(7.0) OC 174(7.0)	Fe 263.1(11) Sn 325.0(8) Te 413.9(15)	C,C 105(4) Fe,Fe 103.7(4) C,C 106.5(13) Sn,Sn 76.3(4) C,C 109(2) T ₂ ,Te 102.6(2) C,C 94(2) Sn,Sn 77.4(3)	

$[\text{Eu}_2\text{SnFe}(\text{CO})_3(\text{dppm})]$ (yellow)	tr P1^- 2	1139.9(2) 1559.8(3) 1086.9(3)	94.10(2) 100.56(2) 69.35(1)	$\text{Sn}^{\text{IV}}\text{C}_2\text{Fe}_2$ $\text{Fe}^{\text{II}}\text{C}_3\text{P}_2\text{Sn}_2$	C_{Ba} 217.7(6,6) O C 176.7(6) P 224.0(2)	Fe 265.9(1,15)	FeFe 103.77(3) P,Sn 104.08(5) Sn,Sn 76.23(3)	143
$[\text{Cp}_2\text{Sn}(\text{CO})_4]_2$ (deep red)	m C2/c 4	1980.3(4) 893.8(1) 1672.2(1)	103.91(1)	$\text{Sn}^{\text{II}}\text{C}_2\text{Fe}_2$	C_{ep} 222.0(5) 225.7(5)	Fe 266.0(1,10)	C, C 101.0(2) FeFe 102.04(3) C, Fe 113.4(1,5,1) C, C 96.1(2,3,3) C, Sn 86.3(2,5,4) 167.0(2,4,9)	144
$[\{\text{Ph}(\text{PhOSO})\text{SnFe}(\text{cp})(\text{CO})_2(\mu\text{-OH})\}_2]$ (yellow-orange)	m $\text{P2}_1/\text{c}$ 2	969.8(2) 1803.7(3) 1351.6(4)	123.44(3)	SnO_3CFe	O_L 220.6(2) μHO 205.4(2) 223.1(2)	Fe 249.9(1) Sn 349.3(1) 109.2(2)	Sn,Sn 77.96(2) O, O 78.1(1,7,4) 155.3(1) O C 95.7(1,11,8) O, Fe 99.7(1,1,3) 122.7(1)	145
$[\text{M}_2\text{Si}(\text{BuN})_2\text{SnFe}(\text{cp})(\text{CO})_2]_2$ (dark red)	m $\text{P2}_1/\text{n}$ 2	1054.7(7) 1994.4(11) 1136.6(7)	92.36(5)	$\text{SnN}_2\text{FeSn}^{\text{I}}$	OC 176.5(4,4) cp 171.3(2) N 209.9(4,2)	Fe 260.5(2) Sn 299.1(2)	C, Fe 129.0(1) C C 96.2(2) C Sn 88.4(1,6) N N 73.8(2) N, Fe 117.3(1,5) N Sn 113.6(1,4) Fe, Sn 114.9(1) C C 95.7(3) C Sn 88.2(2,3,2)	146
$[\text{Me}_2\text{SnFe}(\mu\text{-C}_3\text{H}_4)(\text{CO})_2]_2$ (yellow)	tr P1^- 2	774.9(2) 916.1(3) 1564.9(5)	91.35(3) 97.90(2) 103.67(3)	FeepC_2Sn SnC_3Fe FeepC_2Sn SnC_3F_2	OC 174.6(7,3) C_{ep} 203.1(9,14) C_{Me} 215.1(5,0) μC 216.5(5) OC 174.3(5,0) C_{Me} 216.5(6,0) μC 217.3(4) OC 174.3(5,0) C_{Ba} 216.0(4,7) μC 213.5(3,11) μC 205.2(3,11) C 214.3(3,8)	Fe 253.9(1) Fe 254.1(1)	C C 106.7(1) C, Fe 110.2(1) C C 92.7(2) C C 107.2(3) C, Fe 109.5(1) C C 92.0(2) C C 109.4(2,4,6)	147
$[\text{Bu}_2\text{Sn}(\mu\text{-C}_3\text{H}_4)_2\text{Fe}]_2$ (yellow)	tr P1^- 1	1021.7(3) 1074.8(4) 1017.3(3)	116.34(3) 90.21(2) 116.35(2)	FeepC_2Sn $\text{Sn}^{\text{IV}}\text{C}_4$ Feep2	μC 217.3(4) OC 174.3(5,0) C_{Ba} 216.0(4,7) μC 213.5(3,11) μC 205.2(3,11) C 214.3(3,8)	 	C C 106.5(2,2,0) 127.8(2,4,5) 117.9	148
$[\text{Bu}(\text{I})\text{Sn}(\mu\text{-C}_3\text{H}_4)_2\text{Fe}]_2$ (orange)	m $\text{P2}_1/\text{c}$ 2	1032.2(14) 1079.16(12) 1367.72(18)	94.080(12)	$\text{Sn}^{\text{IV}}\text{C}_3\text{I}$	C_{Ba} 214.9(5) μC 210.2(5,1) I 272.83(6)	 	cp, cp 117.9 C C 115.1(2,2,6) C I 103.0(1,3,5)	149

$[(CO)_2Rh_2Sn_2Cl_6]$ $\{\mu-2,6-(Fh_2P)_3py\}$ $2CH_2Cl_2$ (red brown)	or Pb_2 , a 4	1395.9(8) 1844.1(10) 2558.5(30)	$Sn^IVN_3Rh_2C_4$	N 252.1(10) Cl 242.1(5)	Rh 259.4(2,7)	N,N 171.4(9) N,Cl 94.2(5,6,2) Rh,Rh 151.7(1) N,Rh 89.2(5,4,5) Cl,Rh 104.1(1,5,1) Cl,Cl 94.5(2,5,2) Cl,Rh 124.2(2,2,6) C,Sn 74.6(1); 172.1(1) P,Sn 93.1(1,1,7) C,Sn 94.3(6) P,Sn 87.5(1,0) 111.3(1,5,7) C,Sn 90.8(5); 175.5(5) Sn,Sn 92.5(1)	153
			Sn^IVCl_3Rh	Cl 240.6(5,6)	Rh 258.7(3)		
			$Rh^IVCl_2P_2CSn$	Cl 243.8(6,51) P 233.9(5,10) OC 185(2)			
			$Rh^IVP_2Sn_2C$	P 229.6(6,8) OC 192(2)			
			$Sn^IVC_2Os_2$	Me C 214(1) 2.15(1)	Os 276.3(1,5)		154
	m $P2_1/n$ 2	9146.5(13) 1195.44(16) 981.2(1)	$O_3C_4Sn_2$	OC 193(1,1)			
$[M_2SnOs(CO)_4]_2$ (yellow)							
$[(CO)_2Ir_4(SnCl_3)_2]$ ($\mu-S$) ($\mu-dppm$) 1.5 CH_2Cl_2 (bright yellow)	m $P2_1/c$ 4	2235.7(6) 1569.5(8) 1832.0(7)	Sn^IVCl_3Ir	Cl 236.8(5,15)	Ir 259.3(1,18)	Cl,Cl 95.3(2,4,0) Cl,Ir 121.4(2,12,7) P,Sn 90.9(1,4,4) C,Sn 95.4(6,4,4) S,Sn 110.7(1) 144.3(1) 92.9(1) 164.2(1)	155
			Ir^IVP_2CSSn	P 235.1(5,18) OC 187.2(4) μS 235.9(5,33)	Ir 287.8(1) 75.2(1)		
$[(CO)_2Ir_4(SnCl_3)_2]$ ($\mu-pz$) ($\mu-SBu^t$) $\{P(O)Me_3\}_2$ (orange)	tr $P\bar{1}$ 2	1189.6(2) 1286.3(2) 1394.3(3)	$SnCl_3Ir$	Cl 235.7(5,17)	Ir 261.4(1,22)	Cl,Cl 98(1) Cl,Ir 119.5(3) C,Sn 90.3(5,3,2) N,Sn 92.8(2,2,8) P,Sn 92.0(1,6) S,Sn 101.2(1) 163.9(1) 108.7(1) 153.0(1)	156
			$IrCNPFSSn$	OC 186.3(10,3) μN_{pz} 207.8(9,10) μP 227.2(2,16) μS 239.0(3,17)	Ir 272.21(6)		

$[(PEt_3)_2Pt(SnCl_3)]_2$ (yellow)	m P2 ₁ /c 4	1059.3(6) 2347.3(8) 1243.2(6)	77.9(4)	$Sn^{III}Cl_3Pt$	Cl 232(2) μCl 235(1) P 2.19(1,1)	Pt 248.2(3.5) Pt 303.6(2)	not given Cl ₂ Cl 84.3(4.3) Cl ₂ P 94.1(4.0) Cl ₂ Sn 87.4(3.1) P ₂ Sn 94.3(3.6) Cl ₂ Cl 103.5(1.4) Cl ₂ C 107.9(2.5) 129.0(2)	157
$[(F_2Et)_2Pt(SnCl_3)]_2$ (orange-yellow)	tr P1 1	950.1(2) 1295.2(3) 926.3(2)	108.77(2) 106.99(2) 90.13(2)	$Sn^{III}Cl_3C$	Cl 229.9(2.11) μCl 212.7(6)			158
				$Pt^{IV}Cl_2CP$	μCl 240.5(2.10) μC_2 198.2(6) P ₂ 223.0(2)	94.9(1)		
Sn + 3M								
$(PP_2A)_2\{[(CO)_5Cr]\}_3$ (black, red) at 200 K	m P2 ₁ /c 4	1279.7(3) 1958.1(40) 2438.0(5)	103.42(2)	$SnCr_3$	OC 187.3(1.8)	Cr 266.592(6)	Cr, Cr 120.0(1.1.8) C ₂ Sn 85.0(1.9.5) S ₂ S 76.9(1.1.1)	159
$(Me_2NH_2)_6$ [(SCN) ₆ Mo ₃ S ₄ SnCl ₃] 0.5H ₂ O (red-purple)	m C2/c 8	4225.8(4) 1190.7(3) 2147.2(5)	94.449(9)	$Sn^{III}Cl_3S_3$ $Mo^{IV}N_3S_3$	Cl 246.0(4.14) μS 264.9(3.33) SCl ₄ 215.7(10.21) μS 234.3(3.13) S not given μS 252.7(5.39) S not given μS 234.8(5.24) O ₄ 229.2	Mo 373.2(-.41) 96.6(1.9) Mo 273.0(2.8) 71.2(1.8) Mo 329.2(5) 352.6(5.50) Mo 287.1(5.42) 305.2(5) W 271.3(2) 279.2(2.2)	SS 89.5(1.1.0) 108.0(1.6) SS 85.8(3.4.2) SS 91.6(3.1.9) 101.5(3.3.0) not given	160
$(Et_2PS)_2Mo_3S_4Sn$ (red)	or Pbca 8	2240(1) 2261(1) 2401(1)		$Sn^{IV}S_6$ $Mo^{IV}S_6$				161
$\{(CO)_5W\}_3(\mu_3-SnCl)$ (black)	m P2 ₁ /c 4	902.0(4) 1833.4(9) 1907.7(9)	121.84(3)	$SnOW_3$				162a
$(Me_2NH_2)_6$ [(SCN) ₆ W ₃ S ₄ SnCl ₃] 0.5H ₂ O (dark brown)	m C2/c 8	4279.2(10) 1198.8(2) 2172.5(3)	95.24(2)	WC_2Sn $Sn^{III}Cl_3S_3$ $W^{IV}N_3S_3$	OC not given Cl 250.2(9.10) μS 274.1(5.28) SCN 214.1(14.29) μS 234.3(4.30)	W 381.7(1.39) W 273.5(1.6)	S ₂ S 74.6(1.1.0) Not given	162b

$(\text{NEt}_4)_2 [\{(\text{CO})_4\text{Fe}\}_3 (\mu_3\text{-}\eta^5)\text{I}^{\text{r}} (\text{red})]$	m P2 ₁ /c 8	1091.0(4) 4045(1) 1746.1(5)	98.00(2)	Sn ^{IV} Fe ₃ FeC ₄ Sn Sn ^{IV} Fe ₃	OC no. given	Fe 254.8(3,9) Fe 254.9(3,8)	Fe ₂ Fe 120.0(1,1.8) no. given Fe ₂ Fe 120.0(1,1.2)	169
$[\{(\text{CO})_4\text{Co}\}_3 (\mu_3\text{-}\eta^5\text{Er}) (\text{dark red})]$	hx P6 ₃ 2	1020(1) 1181(2)		Sn ^{IV} BrCo ₃ CoC ₄ Sn	Br 252.0(5) O ₂ 175.6(6)	Co 260.2(6) Co 432	Br ₂ Co 104.8(2) Co ₂ Co 112.5(2) C ₂ Sn 87(3,2) 176(4)	170
$[\{(\text{CO})_4\text{Co}\}_3 (\mu_3\text{-Sn})\text{Cl}]$	m P2 ₁ /c 4	836(1) 1606(1) 1620(1)		Sn ^{IV} C Co ₃	Cl 254(1)	Co 258.5(10,5) 262(1)	Cl ₂ Co 104.0(5) Co ₂ Co 84.0(3) 114.0(3)	171
$[\{(\text{CO})_4\text{Co}\}_3 (\mu_3\text{-Sn})\text{Cl}]$	m P2 ₁ /n 4	813.1(4) 1624.0(4) 1627.1(4)	104.05(3)	CoC ₄ Sn Sn ^{IV} ClCo ₃ CoC ₄ Sn	O ₂ 177(3) Cl 239.4(1) O ₂ 179.5(4,22)	Co 250.4(1,1) 251.0(1)	C ₂ Sn 84.2(9,4,5) Cl ₂ Co 103.8(0,1,5) Co ₂ Co 114.5(0,5) C ₂ Sn 85.4(1,2,5) 178.0(1,2)	90
$[\{\text{cp}(\text{PEt}_3)\text{Ni}\}_3 (\mu_3\text{-Sn})\text{Cl}]$	or P2 ₁ 2 ₁ 2 ₁ 4	1144.6(1) 1632.1(1) 2129.4(1)		Sn ^{IV} ClNi ₃ Ni ^{cp} P ₃ Sn	Cl 252.7(2) C _{sp} 213(1,8) P ₃ 213.6(3,8)	Ni 252.5(1,6)	Cl ₂ Ni 104.7(1,1,0) Ni ₂ Ni 113.7(1,1,2) P ₃ Sn 98.4(1,9)	95

(μ-H) ₂ (μ ₃ -S)(μ-Cl) Ru ₁₃ (CO) ₈ (SnCl ₃) ₂ (yellow)	tr P1 4	1009.3(2) 1334.6(2) 1683.2(3)	110.20(1) 91.13(2) 91.61(1)	SnCl ₃ Ru	Cl 235.5(2,9)	Ru 257.1(1)	C ₁ Cl 100.0(1,2,4) Cl ₁ Ru 118.0(1,1,9) C ₂ Sn 89.4(3,1,0) H ₁ Sn 176(2) Cl ₂ Sn 87.24(5)
RuC ₃ HSClSn				RuC ₃ H ₂ S	OC 185(1,5) μH 175(6) μ ₃ S 240.4(2) μCl 246.9(2)	Ru 293.1(10) H 115(3,3) S 76.0(1,6) 92.31(7)	C ₁ Ru 104.7(3,1,1,7) 151.5(3) H ₁ Ru 23, 92(2) S ₁ Ru 31.81(3) C ₂ Ru 105.0(3,1,1,9) H ₂ Ru 32(2) S ₂ Ru 31.60(5) C ₃ Ru 88.78(5) C ₄ Cl 99.9(1,1,3) C ₅ Ru 117.9(1,3,0)
RuC ₃ HSCl				RuC ₃ H ₂ S	OC 189(1,4) μH 164(6) μ ₃ S 239.1(2) μCl 245.0(2)	Ru 345.8(1)	C ₁ Ru 92.8(3,3,2) H ₁ Sn 176(2) S ₁ Sn 91.78(2) C ₂ Sn 86.42(5) C ₃ Ru 103.1(3,1,3,2) 149.5(3) H ₂ Ru 28, 91(2) S ₂ Ru 53.01(3) C ₄ Ru 104.5(2,14,1) 148.4(3) H ₃ Ru 37(2) S ₃ Ru 51.17(2) C ₅ Ru 89.31(6)
SnCl ₃ Ru				RuC ₃ H ₂ S	OC 186.7(9,34) μH 178(6) μ ₃ S 241.1(2) μCl 246.2(2)	Ru 292.4(1) H 111(3,3) S 75.8(1,3) 92.42(7) Ru 294.2(1)	C ₁ Sn 92.8(3,3,2) H ₁ Sn 176(2) S ₁ Sn 91.78(2) C ₂ Sn 86.42(5) C ₃ Ru 103.1(3,1,3,2) 149.5(3) H ₂ Ru 28, 91(2) S ₂ Ru 53.01(3) C ₄ Ru 104.5(2,14,1) 148.4(3) H ₃ Ru 37(2) S ₃ Ru 51.17(2) C ₅ Ru 89.31(6)
RuC ₃ HSCl				RuC ₃ H ₂ S	OC 189(1,5) μH 151(6) μ ₃ S 241.1(2) μCl 244.3(2)	Ru 348.1(1)	C ₁ Sn 92.8(3,3,2) H ₁ Sn 176(2) S ₁ Sn 91.78(2) C ₂ Sn 86.42(5) C ₃ Ru 103.1(3,1,3,2) 149.5(3) H ₂ Ru 28, 91(2) S ₂ Ru 53.01(3) C ₄ Ru 104.5(2,14,1) 148.4(3) H ₃ Ru 37(2) S ₃ Ru 51.17(2) C ₅ Ru 89.31(6)

[Ru ₃ (μ-H) (μ ₃ ,η ² -a-η ² y)(SnPh ₃) {μ,η ¹ :η ² -PhC=C(H) Ph}(CO) ₇] · 6C ₆ D ₆ (dark red)	m P2 ₁ /c 4	1103.2(6) 3700.6(6) 1216(1)	109.19(5)	SnC ₃ Ru RuC ₂ HNSn RuC ₄ NH RuC ₄ N	C _{ph} not given OC not given μH 20(1) N 213.6(8) OC not given C _L 223(1) μC 220(1) μH 200(1) N 215.0(8) OC not given μC 217(1) N 220.4(7)	Ru 262.3(1) R ₁ 273.2(1) 293.6(1) Ru 276.2(1) C 78.5(3)	no given Sn,Ru 102.80(1) 160.80(1) Ru,Ru 58.20(1) μC,Ru 50.2(3) 114.6(3) C,Ru 76.3(3) 125.5(1) Ru,Ru 64.60(1) μC,Ru 51.2(3) 108.2(3) Ru,Ru 57.20(1) not given Sn,Ru 100.30(1) 155.90(1) Ru,Ru 55.70(1) μC,Ru 51.4(2) 109.2(3) C,Ru 76.3(3) 138.6(3) Ru,Ru 62.40(1) μC,Ru 52.3(3) 109.5(3) Ru,Ru 61.90(1)	173
[Ru ₃ (μ-H)(μ ₃ ,η ² - ampy)(SnPh ₃) {μ,η ¹ :η ² - PhC=C(H)Ph}(CO) ₇] (dark red)	tr P1 2	1108.6(7) 1275(1) 1906.0(7)	74.14(7) 86.6(1) 67.46(1)	SnC ₃ Ru RuC ₂ HNSn RuC ₄ NH RuC ₄ N	C _{ph} not given OC not given μH 2.0(1) N 223.5(8) OC not given C _L 227(1) μC 220(1) μH 160(1) N 213.5(9) OC not given μC 217.0(9) N 213.3(9)	Ru 266.2(1) Ru 287.8(1) 289.3(1) Ru 269.5(1)	not given Sn,Ru 100.30(1) 155.90(1) Ru,Ru 55.70(1) μC,Ru 51.4(2) 109.2(3) C,Ru 76.3(3) 138.6(3) Ru,Ru 62.40(1) μC,Ru 52.3(3) 109.5(3) Ru,Ru 61.90(1)	173

(CO) ₇ Ru ₃ Se ₄ Sn (tip) (tb)	tr ⁻ P1 2	1557.8(4) 2312.3(5) 1019.5(2)	98.16(2) 98.11(2) 94.51(2)	SnC ₂ Se ₂	C ₆ C _{6p} μ ₃ Se μ ₃ Se OC μ ₃ Se OC μ ₃ Se OC μ ₃ Se μ ₃ Se	218(4) 217(4) 251.7(6) 254.0(6) 139(5,12) 2574(5,28) 174(6) 196(6,3) 248.9(7,15) 187(6) 255.8(7) 255.9(7,23)	μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se	93.7(2) 90.5(2) 115.9(2)	Ru Ru Ru Ru Ru Ru Ru Ru Ru Ru	278.4(6) 67.0(2.5) 96.4(2.6)	μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se	81.5(2.8)	μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se μ ₃ Se	89.6(2,2.9) 164.6(2) 82.1(2,5.3) 129.0(2) 55.4(2,2) 124.7(2)

$(\text{CO})_{10}\text{Os}_3(\mu\text{-H})$ $\text{Sn}(\eta^5\text{-cpy})$ (orange)	m $\text{P2}_1/\text{n}$ 4	1079.6(3) 1929.6(1) 1539.6(2)	90 016(6)	SnNCOs_2	N_{py} 223.5(4) C 223.9(16)	Os 264.1(4,1)	not given	174
$\text{Os}_3\text{SnCl}_2(\text{Cl})_{11}$ $(\mu\text{-CH}_2)^e$ (yellow)	m $\text{P2}_1/\text{c}$ 8	1865.5(3) 1366.8(3) 1704.2(3)	90 926(15)	OsC_4 $\text{OsC}_3\text{H}_2\text{Sn}$ (x2) SnCl_2Os_3	μH 187(3,8) Cl 239.2(8,1)	Os 289.1(4) 300.1(4) Os 264.1(2) 280.0(2) 286.8(2)	not given Cl ₂ Cl 104.7(3) Os Os 65.8(2,2.3) 131.7(1) Cl Os 104.3(2,7.6) 126.3(2,2.6) Sn Os 58.4(1) Sn Os 56.4(1,2.9) Os Os 112.7(1) Sn Os 57.7(1,7) Cl ₂ Cl 103.0(3) Os Os 65.7(1,2.5) 131.4(1) Cl ₂ Os 104.6(2,7.4) 127.3(2,3.8) Sn Os 53.6(1)	175
				OsC_3Sn OsC_3Sn OsC_5 SnCl_2Os_3	OC not given μC 205(2) μC 222(2) Cl 238.0(9,3)	Os 305.0(1) Os 298.9(1) 88.8(9) Os 263.6(2) 281.1(2) 288.6(2)		
				OsC_4Sn	OC not given	Os 305.7(1)		
				OsC_4Sn	μC 205(3)	Os 293.5(2) 88.7(1,2)	Sn Os 56.4(1,3.2) Os Os 112.8(1) Sn Os 57.2(1)	
				OsC_5 $\text{Sn}^{\text{II}}\text{OCO}_2$ $\text{OsC}_3\text{H}_2\text{Sn}$ $\text{OsC}_3\text{H}_2\text{Sn}$ OsC_4 SnC_2Os_2 OsC_3Sn OsC_3Sn OsC_3O	μC 222(2) O 211.7(5) C not given μH 171(9,9) μH 191(9) C 214.0(7) C not given μC 214.7(13) μC 213.4(18) O 216.1(10)	Os 265.8(0) Os 304.1(3.41) Os 289.5(0) Os 267.6(1) 2.816(1)	not given not given not given not given not given	176
$[\text{Os}_3\text{Sn}(\mu\text{-H})_2(\text{CO})_9\{\mu\text{-}\eta^2\text{-OCCH}(\text{SiMe}_3)_2\}\{\text{CH}(\text{SiMe}_3)_2\}]$	not given							
$[\text{Os}_3\text{Sn}(\text{CO})_9\{\mu\text{-C}(\text{CO}_2\text{Me})\text{CH}_2\text{CO}(\text{OSiMe}_3)\}\{\text{CH}(\text{SiMe}_3)_2\}]$ (red)	not given							

$[\text{Os}_3\text{Sn}(\mu\text{-H})_2(\text{CO})_{10}\{\text{CH}(\text{SiMe}_3)_2\}_2]$ (orange)	m P2 ₁ /c 4	961.7 2134.2 1946.1	102.31	SnC ₂ Os ₂	C not given	Os 264.5(3) 285.5(3) Os 294.3(3,41)	Sn, Sn 64(1)	177
$\text{H}_2\text{Os}_3(\mu_3\text{-S})(\mu_1\text{-}\eta^2\text{-S}\square\text{H}_2)(\text{CO})_7$ (P1,fc ₂ Ph) (SnMe ₃) (yellow)	m P2 ₁ /c 4	1042.6(2) 1142.1(2) 2456.3(4)	95.41(2)	OsC ₃ Os OsC ₃ Os OsC ₃ Os	C _{3v} 214.5(14.3) OC 184.5(9.5) $\mu_3\text{S}$ 238.2(2,11)	Os 265.3(1) Os 294.2(1)	O ₃ Os 50.1(1) S ₁ Os 58.1(4) C C 95.2 C C 106.7(5,2,6) C Os 112.2(4,1,2) C Sn 37.5(3,1,0) S Sn 103.1(6,2,0) S ₁ Os 144.8(2) C Os 115.9(3,9) S Os 54.0(1,2) C Os 85.2(3,14,4) 140.9(3,16,5) S ₁ Os 51.6(1,6); 73.94(5) P ₁ Os 122.6(1,14,6) Os ₃ Os 87.05(1) C Os 97.4(3,19,2) 147.2(3) S ₁ Os 53.6(5,6)	178
				OsC ₂ S ₂ P	OC 187.8(9,2) $\mu_3\text{S}$ 246.8(2,7)	Os 295.0(1,8)		
				OsC ₄ S	OC 189.0(9,41) C 216.6(9) $\mu_3\text{S}$ 242.8(2) C 216.5(9) 219.3(8) $\mu_3\text{S}$ 248.9(3)	Os 266.2(2) 64.63(8) 120.1(1)	C C 128.7(3) C S 106.5(3,2,3) C Os 115.3(2,2,3) S Os 57.7(7) S Sn 57.65(8); 91.45(8) 136.5(8) S ₁ Os 144.2(4) not given not given	97
(fb) (tip) SnSO ₃ (CO) ₈ S ₂ (yellow)	tr P1 2	1331(1) 2406.9(4) 1205.1(3)	94.57(2) 1113.75(3) 99.58(5)	SnC ₂ SO ₃	OC 188(1,1) $\mu_3\text{S}$ 244.9(3,4) 249.1(3) OC 190(1,4) $\mu_3\text{S}$ 245.6(3,25) OC 189(2,2) $\mu_3\text{S}$ 240.3(3,16)	Os 274.5(3) 81.91(9)		
				OsC ₂ S ₃ Sn				
				OsC ₃ S ₃				
				OsC ₃ S ₂				

[(tb) (tip) SnSeOs ₃ (CO) ₆ Se ₂] (yellow)	tr P ⁻ 2	1682.1(5) 1826.0(6) 1350.8(4)	106.22(3) 107.09(2) 75.37(3)	SnC ₂ SeOs	C 218(2,0) μ ₃ Se 260.8(3)	Os 267.2(2) 61.6(8) 118.4(1)	C C 127.7(3) C Se 106.1(2,6) C Os 115.9(4) S ₂ O ₃ 52.13(7) S ₂ Sr 52.13(7) 91.38(7) 138.58(7) Sn ₂ Os 144.16(5) not given not given	97
(NBu ₄) [Sn{Pt(μ-Cl) (C ₆ F ₅) ₂ }] ⁺ (yellow)	m Cc 8	1939.66(12) 1518.82(17) 4148.03(25)	93.799(5)	Sn ^{IV} Pt ₃ Pt ^{IV} C ₂ Cl ₂ Sn	OC 188.3(2) μ ₃ Se 257.4(3,8) 260.6(3) OC 183(3,3) μ ₃ Se 257.5(3,30) OC 191(3,6) μ ₃ Se 252.5(3,13)	Pt 270.4(2) 273.7(3,5)	Pt ₃ Pt 87.7(30) not given not given	179
[{(μ-dp)(m)Pt} ₃ Sn(vie ₂) (P O ₂ F ₂)] PF ₆ (purple)	m C ₂ 4	2480.8(5) 1213.6(3) 2689.0(6)	105.64(2)	Pt ^{IV} C ₂ C ₂ Sn SnC ₂ Pt ₃ PtP ₂ Pt ₂ Sn	C 193.7(27,61) Cl 241.1(7,35) C _{Me} 212(3,5) F 212(2) P not given	Pt 270.2(2) 275.2(2,14) Pt 261.2(1,3) 263.5(1)	not given not given not given not given	180
{Pt ₃ (μ ₃ -Sn) ₃ (μ ₃ -O) (μ ₃ -ppm) ₃ [PF ₆]} _{0.75} {P ₃ (μ ₃ - SnF ₃)(μ ₃ -Cl) (μ-dppm) ₃ } _{0.25} (orange)	c P43n 8	2524.2(5)		SnF ₃ Pt ₃ PtCP	F 196(3) OC 216(5) P not given	Pt 280.5(2) Pt 263.9(3)	not given not given	180

[illegible]

$\text{Sn} + \text{M} + \text{M}' + \text{M}''$	m	$(\text{CO})_5\text{CrS}_n(\mu\text{-OBu})_3$ $\text{InMo}(\text{CO})_5$	1051(1) 3030(2) 10748(7)	107.36(7)	$\text{Sn}^{\text{II}}\text{O}_3\text{Cr}$ InO_4Mo CrC_3Sn MoC_3In $\text{Sn}^{\text{IV}}\text{ClFe-}$ CoNi	μO 207(1) μO 221(1) OC not given OC not given Cl 245.28(22)	Cr 263.6(3) In 308.7(2) Mo 273.4(2)	O O 76.6(5)	106
$\{[\text{cpF}\equiv(\text{CO})_2]\}$ $\{\text{cpNi}(\text{CO})_2\}$ $\{\text{Co}(\text{CO})_4\}$ $(\mu_3\text{-SnCb})]$	m P _{2,1/c} 4	1615.9(3) 861.8(2) 1623.0(4)	109.91(2)				Fe 254.41(12) Co 265.06(12) Ni 249.31(11)	Cl ₂ Fe 103.70(7) Cl ₂ C ₉ 99.58(6) Cl ₂ Ni 105.49(6) FeC ₉ 117.35(4) FeNi 119.32(4) Co ₂ Ni 108.55(4) CC 93.7(5) CSn 90.6(3,1,1) cp ₃ Sn 120 CSn 81.7(3,1,6) 177.8(4) CSn 91.7(3) cp ₃ Sn 126	184
					FcpC ₂ Sn	cp 171.4 OC 174.1(12,11)			
					CoC ₄ Sn	OC 178.8(15,14)			
					NicpC	cp 172.7 OC 174.1(13)			

Footnotes. a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Two crystallographically independent molecules present.

bonds. 274.2(1) pm (Mo-In), 276.1(1) pm (Mo-Sn), and 307.8(1) pm (Sn-In).

In a red cluster [168] two $\text{cpFe}(\text{CO})_2$ units and a $\text{Cr}(\text{CO})_4$ unit are directly bonded to Sn with Fe-Sn bond distances of 255.0(2) and 257.0(1) pm, and Sn-Cr distance of 262.4(1) pm. The Fe-Sn-Fe bond angle is $115.74(4)^\circ$, and the mean Fe-Sn-Cr angle is $121.6(1)^\circ$.

A purple SnFe_2Mo cluster [182] has a tin atom in the central position bonded to two $\text{cpFe}(\text{CO})_2$ and one $\text{cpMo}(\text{CO})_3$ moieties. The Sn-Fe bond distances are 259.3(7) and 259.8(7) pm, and a Sn-Mo distance of 289.1(5) pm. The relevant bond angles are $115.6(1)^\circ$ (Fe-Sn-Fe) and $116.8(2)^\circ$ (Fe-Sn-Mo, mean). A Cl atom on Sn(IV) completes the a distorted tetrahedral arrangement (SnClFe_2Mo). A related cluster SnFe_2Co [183] again has all three moieties, two $\text{cpFe}(\text{CO})_2$ and one $\text{Co}(\text{CO})_4$ bound directly to Sn(IV). A Cl atom completes the distorted tetrahedral environment of the tin (SnClFe_2Co). The structure contains two crystallographically independent clusters differing mostly by degree of distortion.

3.5 Sn plus M and M' and M"

Two clusters contain four different metal atoms are summarised in Table 2. The first [106] contains a $(\text{CO})_5\text{Cr-Sn}(\mu\text{-OBu})_3\text{In-Mo}(\text{CO})_5$ array, with Cr-Sn, Sn-In and In-Mo distances of 263.693, 308.7(2) and 273.4(2) pm, respectively. Only the first and the last represent actual metal-metal bonds.

In a SnFeCoNi cluster [184] a central Sn(IV) atom has an almost perfect tetrahedral geometry even though bonded to three different moieties, $\text{cpFe}(\text{CO})_2$, $\text{cpNi}(\text{CO})$ and $\text{Co}(\text{CO})_4$, and a terminal Cl atom. The Sn-M bond distances increase in the order: 249.31(11) pm (Sn-Ni) < 254.419(12) pm (Sn-Fe) < 265.61(11) pm (Sn-Co). The M-Sn-M' bond angles open in the order: $108.55(4)^\circ$ (Co-Sn-Ni) < $117.35(4)^\circ$ (Co-Sn-Fe) < $119.32(4)^\circ$ (Ni-Sn-Fe).

The data in Table 2 shows atoms in oxidation states 0, +2 and +4, but there are several clusters without distinguishable oxidation states assigned to the metal atoms. The tin atoms are three, four, five and six coordinate, with distorted tetrahedral being the most common. The most common C-donor ligand is the methyl group, usually with a Cl atom co-donor. However, in the three coordinate Sn(II) derivatives, the most common donor atom is O (usually from the OBu^+ moiety). In these latter cases the Sn(II)-L bond distances are longer for N-donors than O-donors, the values being 217.5 pm versus 203 pm for terminal ligands and 226 pm versus 211 pm for bridging ligands, respectively. The mean Sn(II)-L versus Sn(IV)-L bond distances for tetrahedrally coordinated species are: 217 versus 216.5 pm (CL) and 248 versus 237 pm (Cl).

About 18% of the heterotetrameric tin compounds contain non-transition elements. A summary of the non-transition Sn-M and M-M distances are given in Table 2A. Only three derivative to Hg, Ge or Bi can be considered to exhibit a metal-metal bond. The remainder of the examples (about 80%) contain transition metals in clusters with tin, a rich and complex chemistry. A summary of these Sn-M and M-M distances is given in Table 2B. The shortest bond is the Sn-Ni bond at 242.0(1) pm [151]. The mean Sn-M bond distance increases with the covalent radius of the heterometal atom, with the exceptions of Pd, Rh and Ir. The length of the Sn-M bond varies markedly with the electronegativity of the groups attached to the Sn atom, as does the deviation from tetrahedral shape. The shortest Sn-M bond distances are found in the heterotrimeric clusters (Table 1A), except for three cases. These are: 264.8(1) pm (tri-) versus 253 pm (tetra-) for Sn-Os; 258.5(2) versus 251.7(1) pm for Sn-Pd; and 273.6(1) pm versus 266.6(3) pm for Sn-Re. The mean Sn-M distances are also generally shorter in the trimeric than the tetrameric derivatives, but again there are exceptions. These are: 266.0 pm (tri) versus 262.8 pm (tetra) for Sn-Ru, 259.8 pm versus 253.0 pm for Sn-Pd; 264.5 pm versus 259.2 pm for Sn-Ir; and 280.8 pm versus 278.6 pm for Sn-Mn. One example [130] is found in two isomeric forms. Several examples [114,117,124,142,147,150,167, 169,172,179,183] contain two crystallographically independent molecules which represent examples of distortion isomerism [113].

Table 2A. Summary of Sn-M and M-M Distances in Heterotetrameric Clusters (Non-Transition)

M-M'	Cov. Radius of M [pm]	Distances	
		Shortest [ref]	Longest [ref]
Sn-Al	118	347.3(1) [127]	
Sn-Ge	122	264.8(2) [134]	265.0(2) [134]
Sn-Ga	126	392.6(1) [133]	
Sn-Mg	130	317.1(1) [126]	
Sn-In	144	307.8(1) [106]	412.5(1) [133]
Sn-Bi	146	293.4(6) [135]	297.1(6) [135]
Sn-Hg	151	258.3(3) [181]	
Al-Al		271.1(2) [127]	
Ga-Ga		289.2(1) [131]	320.3(1) [133]
Mg-Mg		293.4(1) [126]	
In-In		357.4(1) [133]	

Table 2B. Summary of Sn-M and M-M distances in Heterotetrameric Clusters (Transition)

M-M'	Cov. Radius of M [pm]	Distances [pm]			Distances > 300 pm
		Shortest [ref]	Longest [ref]	Average	
Sn-Ni	120	242.0(1) [151]	253.1(1) [95]	248.5	321.1(1) [126]
Sn-Fe	120	249.9(1) [146]	267.4(1) [169]	257.7	
Sn-Co	126	253.8(5) [150]	268.1(2) [183]	260	
Sn-Ru	126	257.1(1) [172]	269.1(1) [152]	262.8	
Sn-Cr	127	263.6(3) [106]	272.8(1) [159]	267.5	326.7(1) [126]
Sn-Pt	128	247.8(2) [157]	280.5(2) [180]	264.7	
Sn-Os	128	253 [119]	285.5(2) [177]	270.4	
Sn-Pd	131	251.7(1) [118]	254.0(1) [118]	253.0	
Sn-Rh	135	258.7(2) [153]	260.1(2) [153]	259.2	
Sn-Ir	137	257.5(1) [155]	263.8(1) [156]	260.4	
Sn-Nb	137	286.19(5) [138]			
Sn-Mo	145	276.1(1) [106]	281.1(3) [182]	278.6	329.2 – 357.6 [161]
Sn-W	146	271.3(2) [162a]	279.4(2) [162a]	276.5	377.8, 385.6 [162b]
Sn-Mn	146	244.5(1) [163]	275.8(2) [166]	264.7	325.6(1) [126]
Sn-Re	159	266.6(3) [167]	287.4(3) [167]	276.2	
Sn-Sn		299.1(2) [146]			319.1(5) [150] – 349.3(1) [145]
Ni-Ni					300.9(1) [126]
Fe-Fe					413.1(19), 413.9(15) [142]
Co-Co					392.9(7), 396.7(7) [150]
Ru-Ru		269.5(1) [173]	296.9(1) [172]	286.5	345.8(1), 348.1(1) [172]
Cr-Cr					306.6(1) [126]
Pt-Pt		260.9(1) [180]	263.9(3) [180]	262.5	303.6(2) [157]
Os-Os		274.5(3) [97]	298.9(1) [175]	290.4	304.1, 305.7 [175]
Ti-Ti		278.6(3) [136]			357.3(1), 363.1(1) [115]
Ir-Ir		272.2(1) [156]	287.8(1) [155]	280	
Mo-Mo		272.3(2) [160]	291.1(2) [161]	278.7	305.2(2) [161]
W-W		273.0(1) [162b]	274.1(1) [162b]	273.5	
Mn-Mn		261.78(6) [140]			306.4(2) [163] - 310.45(5) [140]
Mn-In		273.4(3) [106]	274.19(1) [106]		
Mo-Hg		265.9(3) [181]			
Re-Re					3013(2) - 328.4(3) [141]

4. PENTAMERIC HETEROTIN COMPOUNDS

4.1 Four Sn plus M

There are almost thirty heteropentameric tin compounds summarised in Table 3. Seven clusters contain four tin plus one other metal, of which the only non-transition example is Sn_4Al [185]. This molecule approaches 3m point symmetry and incorporates a $\text{Sn}_4\text{N}_3\text{O}$ cage in a distorted cube arrangement. This can be viewed as two differently sized interpenetrating concentric tetrahedra of Sn and N plus O atoms. The N atoms carry tert-butyl groups while the O atom becomes a donor to the AlMe_3 moiety attached to a corner of the cube. The Sn-Sn distances range from 332.0(1) to 337.8(1) pm, which excludes any direct metal-metal bond.

Two purple Sn_4M clusters [186], where M is Zr or Hf, are isostructural (MSn_4C_4) with a dodecahedron of D_{2d} symmetry. This can be viewed as two interpenetrating tetrahedra of carbonyl and triphenylstannyl groups. The Ph_3Sn units form an elongated tetrahedron (A sites) while the CO groups form a quite flattened tetrahedron (B sites). The Sn-M distances are 308.6(1) pm for Zr and 306.3(1) pm for Hf.

A pale yellow compound [187] consists of discrete NMe_4^+ cations and Sn_4W cluster anions. The latter contain a central seven coordinate tungsten atom bonded to three terminal CO groups, two Ph_3Sn groups and two Ph_2Sn of the bidentate ligand $(\text{Ph}_2\text{Sn})_2\text{OPr}^+$. The Sn-W bond distances range from 276.0(2) to 281.1(2) pm (average 278 pm). The seven donor atoms are in an approximate 4:3 piano stool arrangement about the central tungsten (WSn_4C_3). Each Sn atom has a quasi-tetrahedral environment with either SnC_2OW or SnC_3W chromophores.

There are two Sn_4Ni clusters, dark red [188] and green-black [189]. In the former a central Ni(0) atom is almost tetrahedrally surrounded by $\text{Sn}(\text{NBu})_2\text{SiMe}_3$ moieties. The SnN_2Si groups are skewed with respect to each other and degrade the three-fold symmetry of a regular tetrahedron (NiSn_4) giving rise to severe distortions. However, the Sn-Ni bond distances are remarkably constant at a mean value of 239.4(1) pm (maximum deviation 0.6 pm), which is about 17 pm smaller than the sum of the covalent radii of Sn and Ni. This implies considerable double bond character which may be due to $\sigma\pi$ - $\pi\sigma$ back donation in the Sn-Ni bond [188]. The second derivative has the central Ni atom in a cavity of the $(\text{pz})_8$ macrocyclic ligand, coordinated by four N

atoms in a square planar arrangement. The four SnBu^+ moieties are located around the macrocycle in a star fashion. Each Sn atom is coordinated to two thiolates of different pyrrole rings and also to the meso nitrogen of a porphyrazine. A nearly square-pyramidal geometry about each tin is completed by two tert-butyl groups, one being at the apex. Two independent tin atoms are adjacent and lie 73 pm and 54 pm above the plane of the planar porphyrasineoctathiolate ligand. The other two tin atoms are related by inversion and lie below this plane, resulting in a quasi-chair conformation.

A pale yellow Sn_4Pt cluster [190] has a hexacoordinate Pt(IV) species with four Sn-Pt bonds. Two of these are to $\text{Sn}(\text{p-MeC}_6\text{H}_4)_2(\mu\text{-OMe})$ moieties, one is to $\text{Sn}(\text{p-MeC}_6\text{H}_4)_3$ and one to a neutral $\text{Sn}^{\text{II}}(\text{P-MeC}_6\text{H}_4)$ unit. The Sn-Pt bond distances range from 258.591 to 264.5(1) pm (average 261.3 pm). The mean Sn-Pt-Sn angles are 80.6° and 95.6° .

4.2 Three Sn plus Two M

A colourless Sn_3Li_2 cluster [191] shown in Figure 8 is a trigonal prismatic unit built up from three stacked triangular units on top of one another. The central triangle is Sn_3O in which the O atom bridges all three Sn atoms. The local symmetry about each Sn atom is distorted trigonal bipyramidal, with O atoms of the cyclometallated alkoxide groups being in mutually *trans* axial positions. These are also bonded to a lithium atom in the top and bottom LiO_3 triangles of the cluster core.

Fig.8. Structure of $[\{\text{Sn}(\text{phpr})_2\}_3\text{Li}_2\text{O}]$ [191]

The structure of a deep orange Sn_3Pt_2 cluster [49] consists of a trigonal bipyramid with the Pt atoms separated from one another by 259.3(1) pm and with bond angles of 118.9° (P-Pt-Sn) and 98.6° (Sn-Pt-Sn). The two apical coordination positions at Pt are occupied by PPh_3 molecules, while the three equatorially bridging ligands are symmetrically disposed with a Pt-Sn distance of 268.0(1) pm and Pt-Sn-Pt angle of $57.87(3)^\circ$. This geometry represents face sharing of two distorted PPTSn_3 fragments. Two chelated (acac) groups complete an octahedral coordination about each Sn(II) atom (SnO_4Pt_2).

4.3 Two Sn plus Three M

An orange brown complex [36] contains a cobalt cation $[\text{Co}\{\text{pz}\}_3\text{BH}_2]^+$ with a Sn_2Co_3 cluster anion $[\{(\text{CO})_5\text{CoSn}(\text{Cl})_2\}_2\text{Co}(\text{CO})_3]^-$. The anion has a planar central $\text{Co}(\text{CO})_5$ unit with two $\text{SnCl}_2\{\text{Co}(\text{CO})_5\}$ units bonded in a trans arrangement [$\text{Co}(2)\text{-Sn}(1)\text{-Co}(1)\text{-Sn}(1')\text{-Co}(2)$]. The $\text{Sn}(1)\text{-Co}(1)$ bond distance of 246.891 pm is shorter than that of $\text{Sn}(1)\text{-Co}(2)$ at 256.2(1) pm. The $\text{Sn}(1)\text{-Co}(1)\text{-Sn}(1')$ angle is almost linear ($176.5(1)^\circ$). The other two $\text{Co}(1)\text{-Sn}(1)\text{-Co}(2)$ angles are bent at $127.5(1)^\circ$.

There are two isostructural Sn_2M_3 clusters [192], one with ruthenium and one with osmium. The structures show a planar array of five metal atoms, with Sn atoms bridging two edges of the M_3 triangle, the third edge being bridged equatorially by a carbonyl group. The mean Sn-Ru and Sn-Os distances are 273.592 and 273.7(0) pm, respectively. The Ru-Ru distance of 293.1(2) pm is smaller than the Os-Os distance of 294.7(0) pm as expected.

The yellow Sn_2Pd_3 cluster [193] has a distorted propeller shaped Pd_3Sn_2 frame composed of three triangles, Pd_3 and two Pd_2Sn with a mutual Pd-Pd edge. There are two short Pd-Pd bonds (270.8(1) and 272.0(1) pm) with the Pd atoms linked by slightly asymmetrical CO bridges. The Pd-Sn bond lengths are 267.9(1) to 272.1(1) pm with a mean value of 269.7(1) pm. The Sn(II) atoms are pseudo-octahedrally

coordinated (SnO_4Pb_2).

An amber Sn_2Os_3 cluster [194] contains an osmium triangle with three different Os-Os distances, 304.8(2), 285.4(2) and 290.9(2) pm. The Os-Os-Os angle deviates from $60(+/-3.8)^\circ$. Each of the two $\text{Sn}\{\text{CH}(\text{SiMe}_3)_2\}$ moieties is bound to two Os atoms, sharing one, with distances of 287.3(3) and 264.9(3) pm and 286.6(3) and 265.1(2) pm. The structure of a colourless Sn_2Os_3 cluster consists of an Os_3 triangle, two edges of which are bridged by hydrogen ligands. The bridged edges are longer (302.1(3) and 307.0(2) pm) than the unbridged edge (289.6(3) pm). Two SnMe_3 moieties are bonded to one Os atom with distances of 272.6(5) and 269.6(4) pm.

There are two coloured Sn_2Pt_3 clusters [196,197]. The first is a red derivative [196] consisting of a triangle of Pt atoms each coordinated to a η^3 -cycloocta-1,5-diene ring and capped above and below by SnCl_3 moieties. The average distances are 258(1) pm for three Pt-Pt distances, 280(1) pm for six Pt-Sn distances and 239(2) pm for six Sn-Cl distances. The mean bond angles are 60.0° for Pt-Pt-Pt, 54.9° for Pt-Sn-Pt and 62.5° for Pt-Pt-Sn. The orange cluster [197] also contains a Pt triangle (Pt-Pt distances 260.9(2), 262.2(1) and 263.9(1) pm) with the edge of the triangle bridged by a μ -dppm ligand and each face bridged by a μ_3 - SnF_3 moiety. Thus the Pt_3Sn_2 cluster adopts a slightly distorted trigonal bipyramidal geometry, with two apical μ_3 - SnF_3 moieties in an eclipsed orientation with respect to each other. The Sn(II) atom has an approximately octahedral environment (SnF_3Pt_3). The Sn-Pt bond distances range from 269.9(2) to 283.0(2) pm (average 278 pm).

The structure of a colourless SnCu_4 cluster [198] is shown in Figure 9. A C_{3v} symmetry hypohexagonal metal core is linked by a combination of N, S and N, i-S-chelating (mit) ligands to form a cage-like molecule. The Sn(II) atom is bonded to the N-centres of three (mit) ligands. Three symmetry related ligands form bridges between the Sn atom and each of the equatorial Cu(I) ligands of the core ($\text{S-Cu} = 226.6(2)$ pm) with the remaining mit ligands N, i-S-chelating the three available Cu_3 faces of the Cu_4 pyramid. The Cu-Sn distances are 272.7(2) and 290.2(1) pm. The Cu-Cu distances range from 267.1(2) to 313.2(2) pm.

Fig.9. Structure of $[\text{Sn}(\text{mit})_4\text{Cu}_4]$ [198]

Crystals of a SnRe_4 cluster [199] reveals two Re_2P_4 units forming an elongated tetrahedron about the central tin atom. The resulting metallo-spiropentane displays a curious distortion about the tin, as demonstrated by the Sn-Re distances ranging from 262.7(2) to 279.3(2) pm.

There are two SnFe_4 clusters [86,200]. The former [86] contains two triangles of the metal atoms which share the tin atom. There are two pairs of Sn-Fe bond distances, one of 254.6(4) pm and the other of 255.7(4) ± 0.2 pm. The Fe-Fe edges are equal with a distance of 289.0(5) pm. Each iron atom is also bonded to four terminal carbonyl groups. The latter cluster [200] exhibits a distorted tetrahedral configuration around the central Sn(IV) atom, with two $\text{Fe}(\text{CO})_4$ groups (Sn-Fe = 258.8(3) and 258.9(3) pm) and one $[\text{Fe}_2(\text{CO})_8]^-$ unit (Sn-Fe = 272.5(3) and 273.4(3) pm). Two iron atoms in the latter unit are bridged by two carbonyl groups with Fe-Fe bond distance of 260.5(3) pm.

Red $\text{SnCo}_4(\text{CO})_{16}$ was studied by two groups [201,202] and their data correspond well. The tetrahedral Sn atom sits on a site of 23 symmetry and is surrounded by four trigonal bipyramidal $\text{Co}(\text{CO})_4$ groups with equal bond distances, 266.9(1) pm [201] and 267.03(14) pm [202]. The structure of $\text{Ph}_2\text{Sn}\{(\mu-\eta^5\text{-C}_2\text{H})\text{Co}_2(\text{CO})_8\}_2$ [203] is shown in Figure 10. A tetrahedral arrangement about the central tin atom is built up from two $\{(\mu-\eta^5\text{-C}_2\text{H})\text{Co}_2(\text{CO})_8\}$ moieties with symmetrically Sn-C bond distances (212.2(7) and 212.3(7) pm). The Co-Co bond distances in the respective two moieties are 247.8(2) and 248.7(2) pm.

TABLE 3. Crystallographic and Structural Data for Pentameric HeteroTin Clusters^a

COMPOUND (colour)	Crys. cl Sp. Grp	a [pm] b [pm] c [nm]	α [°] β [°] γ [°]	Chromo- phore.	M-L [pm]	M-M [pm] M-L-M [°]	L-M-L [°]	Ref
[Me ₃ Al(μ -O)] Sn(μ -NCMe ₃) (colourless)	m P2 ₁ /c 4	1017.4(5) 1488.5(7) 1748(1)	91.5(1)	SnN ₂ O (x3)	μ -O ^o 220.3(4.9) μ -N 218.9(6.17)	Sn 334.8(1.78) O 100.2(2.9) N 98.8(2.2.4)	O ₃ N ^b 79.0(2.7) N N 81.9(2.4)	185
(NPr ₄) ₂ [(Ph ₃ Sn) ₄ { μ -Zr(CO) ₄ }] (purple)	tg ₋ P4 ₂ /c 2	1533.9(3) - 1504.5(3)		SnN ₃ AlC ₃ O SnC ₃ Zr ZrC ₃	μ -N 220(6.4) μ -C 199.6(9.29) μ -O 189.5(5) C _{Ph} 222(2) OC 223.2(5)	O 117.9(2.8) Zr 308.6(1)	N N 80.7(2.1.1) C C 114.6(3.1.3) C O 103.6(3.1.3) n: t given C ₃ Sn 67.1(1.1.1) 89.4(1) 142.0(1) Sn Sn 80.3;	186
(NPr ₄) ₂ [(Ph ₃ Sn) ₄ { μ -Hf(CO) ₄ }] (purple)	tg ₋ P4 ₂ /c 2	1532.2(2) - 1904.2(3)		SnC ₃ Hf HfC ₃	C _{Ph} 222(1) OC 216.2(12)	Hf 306.3(1)	not given C ₃ Sn 67.4(3.8) 88.1(3) 143.3(3) Sn Sn 80.5; 125.6(1)	186
(NMe ₄)[(Ph ₃ Sn) ₂ {(Ph ₃ Sn) ₂ (-OPr ⁱ) W(CO) ₃ }] (pale yellow)	m P2 ₁ /c 4	2258.0(10) 1416.2(4) 2307.0(10)	114.21(4)	SnC ₂ OW (x2) SnC ₃ W (x2) WC ₃ Sn ₁	C _{Ph} 211(3.11) μ -O 215(2.1) C _{Ph} 217(3.8) OC 196(3.2)	W 276.6(2.6) O 96.9(6) Sn 322.1(3) W 279.7(2.14) Sn 349.4(3.14)	C ₃ C 103(1.2) C ₃ O 99(1.3) C ₃ W 126.0(7.4.9) O ₃ W 95.7(4.14) C ₃ C 101(1.2.6) C ₃ W 113.9(5.3.8) 122.4(6.2.6) C ₃ Sn 77.8(7.9.1) 96.2(8.7.5) 140.3(7.1.7) Sn ₃ Sn 75.6(7.4.4)	187

$[\{Me_2S(Bu^iN)_2Sn\}_4]$ (dark red)	tr PI 2	1391(1) 1390(1) 1981(2)	72.97(9) 88.37(9) 61.14(9)	$Sn^{II}Ni$ Ni^0Sn	N 205.5(9)	Ni 239.4(2.6)	not given Sn_3Sn 103.6(1.5.5)	188
$[Bu^i_2Sn]_4$ $\{Ni(pz)S_8\}$ (green-black)	m C2/c 4	2191.1(3) 2126.5(2) 1488.2(3)	94.44(2)	SnC_2S_2N	C_{Eu} 219.9(5.5) S 258.7(1.8) N 231.1(3.7)		121.9(1.1.1) C,C 122.6(2.4) S,S 145.3(1.1.8) C,S 97.8(1.5.7) C,N 96.2(2.1.7) 141.2(2.1.3) S,N 76.9(1.4) N,N 90.3(1.2) 180.0	189
$[Ph_2Sn(Ph_2Sn)_3]$ (-ONe) ₂ (m- ⁱ Pr(H) PEt ₃) (pale yellow)	tr PI 2	1278.4(2) 1391.7(2) 2186.1(2)	79.74(1) 74.33(1) 67.78(1)	$Sn^{II}C_2O_3Pt$	C_{Ph} not given O 227.6(7) 234.4(7)	Pt 262.6(1)	C,C 106.9(4) O,O 171.3(2) C,Pt 126.5(4.4.4) not given	190
$[\{Sn(phen)_2\}_3L_2O]$ 2phenH (colourless)	m P2 ₁ /n 2	1113.0(1) 1315.7(7) 2307.7(2)	95.68(1)	$Sn^0O_3C_1$	O 209.1(3.1) C 210.7(5.6) O 209.4(4.6)	msO 120.0(2.5)	Sn_3Sn 80.6(1.3) 95.6(1.1.3) O,O 83.7(1.5) 167.6(2.3) C,C 125.5(3.5) O,C 81.0(2.1) 104.6(2.6) 117.2(2.4)	191
$[\{acac\}_2Sn]_3$ $\{Pt(pPh_3)\}_2$ (deep orange) $[CO\{(pz)_3BH\}_2]$ $[\{(CO)_3CoSn(Cl)_2\}_2]$ Co (CO) ₃ (orange brown)	trg R3c 2 m C2/c 4	1726.0(6) 2409.1(7) 732.5(4) 3254.4(8)	60.56(2) 118.52(9)	$Li^I O_3$ $Sn^{II}O_4Pt_2$ $Pt^I PSn_3Pt$ $SnCl_2Co_2$ CoC_3Sn	O 188(1.1) O 234.2(9) O not given P 222.4(4) Cl 239.7(2.4) OC not given	O 103.9(3) O 89.8(3.3) Pt 268.0(1) Pt 259.3(1) Co 246.8(1) 256.2(1)	Pt,Pt 57.87(3) P,Sn 118.9 Sn,Sn 98.6 Cl,Cl 98.6(1) Cl,Co 106.7(1.4.4) Co,Co 127.5(1) Sn,Sn 176.5(1)	49 36

$[R_{10}\{ \dots Sn(C^H(SiMe_3)_2) \} \{ CO_{10} \}]$	tr P1 2	1631.1(4) 1188.4(2) 1861.0(4)	105.62(2) 66.18(2) 108.48(2)	SnC ₂ Ru ₂	C 220.1(31,28)	Ru 273.5(2,2)	C, C 108.0(9,2.7) C, Ru 119.5(6,6.2) Ru, Ru 65.4(1,2) 38.7(6,6)	192
				RuC ₄ SnRu ₂ (x2)	OC 192.7(16.48) OC 212.3(17.9)	Ru 288.1(2) 295.6(2,7)	C, Sn 93.9(4,12.0) mC, Sn 165.2(5.5) Sn, Ru 57.2(4,1) 118.0(4,3)	
				RuC ₃ Sn ₂ Ru ₂	OC 186.2(1.4) 192.5(15,4)		C, Sn 91.1(5,4,2) Sn, Sn 172.57(4) Sn, Ru 57.47(4) 115.5(1,1)	
$Pd_3Sn_2(acac)_4(CO)_2$ (PPH ₃) ₃ (yellow)	m P2 ₁ /n 4	1578.1(2) 2846.9(2) 1664.7(1)	93.09(1)	SnO ₄ Pd ₂	O 210.7(9.19) 225.1(9.38)	Pd 258.3(1,4) 2.710(1,11)	O, O 81.0(3,8.5) 149.4(3,1.2) Pd, Pd 62.0(0,5) O, Pd 102.5(2,10.2)	193
				PtCPSn ₂ Pd ₂ (x2)	OC 209(1,2) P _{Ph} 229.3(3,21)	Pt 271.4(1,5) 279.8(1)	C, Sn 121.0(3,2,1) P, Sn 108.2(1,5,1) Sn, Sn 99.2(1,2) Sn, Pd 8.7(1,6)	
				PdC ₂ PPd ₂	OC 209(1,2) P _{Ph} P 229.9(3)		91.1(1,9,0) Pd, Pd 55.0(1,1) C, Pd 49.8(3,5) 110.8(3,8) P, Pd 145.9(1,1,0) Pd, Pd 62.07(5)	

$[\text{Os}_3\{\text{--Sn}(\text{CH}(\text{SiMe}_3)_2)_2(\text{--dipm})(\text{C})_2\text{a}](\text{amber})$	tr P1 2	1160.7(6) 1731.6(12) 2416.5(16)	110.83(5) 91.94(5) 92.48(5)	SnC ₂ Os ₂ OsC ₂ PSnOs ₂ OsC ₃ PSnOs ₂ OsC ₂ Sn ₂ Os ₂	C not given P 229.7(8) P 235.6(8)	Os 265.0(3,1) 286.9(3,4) Os 288.1(2,28) Os 304.8(2)	C,C 105.0(12,5,6) Os O ₃ 54.4(1,2,4) Os O ₃ 53.8(1) Os O ₃ 59.0(1) Os O ₃ 57.2(1)	194
$[\text{Os}_3\{\text{--Sn}(\text{CH}(\text{SiMe}_3)_2)(\text{CO})_2\}(\text{colourless})$	m P2 ₁ /c 4	1670 2235 1967	110	SnC ₂ Os ₂ OsC ₄ SnOs ₂ (x2) OsC ₃ Sn ₂ Os ₂	C not given Os 273.7(7,16) Os 289.3(0) Os 297.4(0,7)	not given	192	
$[\text{Os}_3(\text{--H})_2(\text{CO})_{10}(\text{SnMe}_3)](\text{colourless})$	m P2 ₁ /n 4	945.6(2) 2257.5(4) 1312.4(4)	95.40(2)	SnC ₃ Os OsC ₃ H ₃ Sn	C _M : 207(5,2) 214(6,1) OC 192(4,3)	C ₂ C 107(2,3) C ₂ O ₃ 112(2,4) C ₂ Sn 35.1(16,2,4) Sn ₂ Os 102.99(10) 159.65(10) Os ₂ O ₃ 48.8(1,1,9) C ₂ Sn 91.0(15,10,2) Sn ₂ Os 111.20(9) 173.65(10) Os ₂ O ₃ 62.48(6)	195	
$(\text{cod})_2\text{Pt}_2(\text{SnCl})_2(\text{red})$	m P2 ₁ /a 4	1797(3) 1816(3) 1023(2)	111.4(2)	OsC ₄ H SnCl ₃ Pt PtC ₂ Sn ₂ Pt ₂	OC 178(6) 193(4,1) Cl 239(2) B, 215	Pt 280(1) Pt 258(1)	Pt,Pt 54.9 Pt ₂ Sn 62.5 Pt ₂ Pt 60.0	196
$[\text{Pt}_2(\mu\text{--Sn}(\text{CH}_2)_2(\mu\text{--dipm}))_3][3\text{CH}_2\text{Cl}_2](\text{orange})$	tr P1 2	1300.2(3) 1502.7(3) 2174.4(5)	83.05(2) 77.29(2) 78.30(2)	SnF ₃ Pt ₃ PtPt ₂ Sn ₂ Pt ₂	F 195(1,4) P 227.8(5) 230.6(5,7)	Pt 272.2(2,23) 279.2(2,9) 281.9(2,11) Pt 262.3(1,16)	F,F 90.0(6,1,9) F,Pt 104.7(4,6,6) 158(4,5,6) Pt,Pt 36.3(1,1,2) P ₂ Sn 108.7(2,6,9) Sn,Pt 61.7(1,2,5) P ₂ Pt 95.5(2,2,2) 155.1(2,2,3) Pt,Pt 60.0(1,6) Sn ₂ Sn 113.9(1,1,8)	197

[Sn(mi)-Cu ₄ -4thf (colourless) at 173(2)K	rh ₃ R3 6	1605.38(6)	Sn ^{II} NiCu	N 220.2(6)	Cu 272.7(2) 250.2(1) Cu 268.3(1)	N N 90.0(2)	198
		3900.1(3)	Cu ^I Sn ₂ NSnCu (x2)	μS 230.0(2) S 226.6(2) N 196.7(6)	Cu 267.1- 313.2(2)	S S 113.78(5) S, Sn 104.72(7)	199
			Cu ^I Sn ₂ Cu ₂ (x2)	μS 231.5(2)	Re 261.6(21) 214.2(2.10) 219.3(2)	Re, Re 56.0(1.4)	
			SnRe ₄		Re 255.1(2.5) Fe 251.6(4.10) 255.7(4.2)	not given Fe, Fe 58.9(1.1)	86
			ReP ₂ SnR ₂ Sn ^V Fe ₄	P 233.5(7.9)	Fe 289.0(4) Fe 253.8(3.1) 273.0(3.5)	Sn Fe 55.3(1.1) Fe, Fe 57.0(7) 117.5(1.5.1)	200
			FeC ₄ SnFe Sn ^V Fe ₄	OC not given		C, Sn 85.8(6.4.8) 178.3(8.1.0)	
			FeC ₄ Sn(x2)	OC 168-181(2)		C, Sn 86.3(5.5.9) 175.8(7.4)	
			FeC ₆ SnFe	OC 199(2.6) OC 168-181(2)	Fe 260.5(3) 81.8(7.9)	Sn, Fe 61.5(1.2) not given	201
			SnCo ₄		Co 266.9(1)		
			CoC ₄ Sn	OC 177.6(7) 181(1)		C, Sn 86.5(2) 180.0	202
			SnC ₁₀ CoC ₄ Sn	OC 177.2(13) 182.1(16)		Co, Co 109.47 C, Sn 87.5(4) 180.0	203
			SnC ₄	Ph C 213.0(7.0) μC 212.3(7.1)		C, C 109.5(3.2.4)	
			CoC ₂ Co	OC not given μC 107.2(7.28)	Co 247.8(2) 248.7(2)	not given	
Sn{Re ₂ H ₆ (PM ₂ Ph) ₄ } ₂ (at 118K)	m P2 ₁ /a 4	2380.2(15) 1371.51(8) 2553.4(16)					
Sn{Fe ₂ (CO) ₉ } ₂	not given						
(NEt ₄) ₂ [Sn{Fe ₂ CO ₉ } ₂]{Fe(CO) ₅ } ₂]	m Cc 4	1157.2(6) 2246(1) 1704.9(4)					
SnCo ₄ (CO) ₁₆ (burnt orange)	c ₂ F43c 8	1725.5(2)					
SnCo ₄ (CO) ₁₆ (red)	c ₂ F43c 8	1730.1(3)					
Ph ₂ Sn{(μ-O ² -C ₂ H) Co ₂ (CO) ₈ } ₂	or Pbca 8	1946(1) 1599.2(7) 2010(1)					

Me ₃ SnOs ₄ (μ-X(CO)) ₁₄ (red)	tr ₁ P1	792.9(1) 1207.2(2) 1473.9(2)	80.82(1) 81.60(1) 75.46(1)	SnC ₃ O ₃	C _M : 202(3,2) 219(3)	Os 269.7(2)	C ₃ C C ₃ Os C ₃ Sn	not given 13.1(9,1,9) 87.7(7)	204
	2			OsC ₃ HSn Os ₂	OC 185(2,4) μH 180	Os 280.7(1) 205.0(1)	Sn ₂ Os Os ₂ Os	108.86(4) 58.16(4)	
				O ₃ C ₃ HOs ₃	OC 183(2,1) μH 182	H 102 Os 280.8(1,2) 287.5(10)	Os ₂ Os C ₃ Os Os ₂ Os	130.2(5) 64.93(3)	
				OsC ₄ Os ₂ (x2)	OC 186(2,3)	Os 285.1(1)	C ₃ O ₃	125.12(3) 75.6(6) 109.6(7)	
							Os Os	58.7(1,2,3) 15.21(3)	
[Os ₃ (CO) ₁₂ Cl (SnCl ₂)(μW(CO)) ₃] 0.5 Cl ₂ Cl ₂	tr ₁ P1 ?	850(1) 1336.8(9) 1831.1(12)	110.74(4) 92.93(3) 103.82(4)	SnCl ₃ OsW	Cl not given	Os 263.6(5) W 275.6(7)	Os W	132.8(2)	205
				OsC ₄ SnOs	OC not given	Os 290.7(4)	Sn Os	175.8(2)	
				OsC ₄ Os	OC not given	Os 286.2(4)	Os Os	175.9(2)	
				OsC ₃ Os	OC not given				
				Wq ₁ C ₃ Sn	OC not given				
{(CO) ₄ Fe} ₂	m	1427.3(8)		Sn ₂ O ₃ Fe	μO 199.2(7)	F ₂ 247.6(1)	O O	14.9(4,2,0)	206
{Sn(μ-OEt) ₃ } ₂ Pb (gold yellow)	C2/c 4	1627.8(9) 2015.8(9)	102.1(10)	FeC ₄ Sn Pb O ₃	202.9(7,2) OC not given μO 252.4(7,42) 273.0(7)	Pb 332.7(1)	O Fe C Sn O O	128.6(4,2,0) 171.6(5) 63.2(1)	
								113.5(1,6,0) 164.8(1,8)	

Footnotes : a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

Fig.10. Structure of $\text{Ph}_2\text{Sn}\{(\mu\text{-}\eta^2\text{-C}_2\text{H})\text{Co}_2(\text{CO})_3\}_2$ [203]

In a red SnOs_4 cluster [204] the osmium atoms adopt a planar butterfly arrangement with Os-Os distances of 280.7(1), 287.5(1), 281.0(1), 305.0(1) and 285.1(1) pm. The Sn atom lies approximately in the Os_4 plane attached to one of the "wingtip" Os atoms (Sn-Os = 269.7(2) pm, and cis to the neighbouring Os atom). Three methyl groups complete the distorted tetrahedral configuration about the tin atom.

Table 3A. Summary of Sn-M and M-M Distances in Pentameric heterotin Clusters

M-M'	Cov. Radius of M' [pm]	Distances [pm]		Average	Distances > 300 pm
		Shortest [ref]	Longest [ref]		
Sn-Al	118				332.0 – 337.891 [185]
Sn-Zr	148				308.6(1) [186]
Sn-Hf	149				306.1(1) [186]
Sn-Pb	131				332.7(1) [206]
Sn-Sn					322.1(3) – 350.7(3) [187]
Sn-Ni	120	239.3(2) [188]	239.9(2) [188]	239.4	
Sn-Fe	120	247.6(1) [206]	273.4(3) [200]	259.0	
Sn-Co	126	246.8(1) [36]	267.0(1) [202]	259.2	
Sn-Ru	126	273.3(2) [192]	273.7(2) [192]	273.5	
Sn-Pt	128	258.5(1) [190]	283.0(2) [197]	272.0	
Sn-Os	128	263.6(6) [205]	286.6(3) [194]	272.8	
Sn-Pd	131	267.9(2) [193]	272.1(2) [193]	269.6	
Sn-Cu	138	272.7(1) [198]	290.2(1) [198]	281.4	
Sn-W	146	275.6(7) [205]			
Sn-Re	159	262.6(1) [199]	279.3(2) [199]	272.6	
Fe-Fe		260.5(3) [200]	289.0(4) [200]	274.7	
Co-Co		247.8(2) [203]	248.7(2) [203]	248.2	
Ru-Ru		288.1(2) [192]	296.3(2) [192]	292.5	
Pt-Pt		258(1) [196]	259.3(1) [49]	277	
Os-Os		270.7(4) [205]	298.1(2) [192]	286.8	302.1(3) – 307.0(3) [195]
Pd-Pd		270.8(1) [193]	279.8(1) [193]	274.2	
Cu-Cu		260.3(1) [198]	268.3(1) [198]	264.3	313.2(2) [198]
Re-Re		255.5(2) [199]	256.6(2) [199]	256.0	

A SnOs_3W cluster [205] has a linear tri-osmium backbone (Os-Os-Os = 175.9(2)°). The $\text{SnCl}_2(\text{cpW}(\text{CO})_3)$ occupies an axial position on one terminal osmium, also making a linear Os_3Sn chain (Os-Os-Sn = 175.8(2)°, and Os-Sn = 263.6(6) pm). The tungsten is bonded to tin (Sn-W = 275.6(7) pm) to give a

hetero-pentametallic chain with no bridging ligands. The Os-Sn-W angle is $132.8(2)^\circ$.

A gold yellow $\text{Sn}_2\text{Fe}_2\text{Pb}$ cluster [206] has a crystallographic twofold axis passing through the Pb(II) atom. The metal atoms are coupled one-dimensionally, $(\text{CO})_4\text{Fe-Sn}(\mu\text{-OBu})_3\text{Pb}(\mu\text{-OBu})_3\text{Sn-Fe}(\text{CO})_4$, with equal Sn-Fe bond distances of 247.6(1) pm. Each Sn(II) atom has a quasi-tetrahedral environment (SnO_3Fe). The central Pb(II) atom has a quasi-octahedral environment (PbO_6).

The data in Table 3 shows six categories of the pentameric derivatives, Sn_4M (7 examples), Sn_3M_2 (2 examples), Sn_2M_3 (8 examples), SnM_4 (8 examples), $\text{SnM}_3\text{M}'$ (1 example) and $\text{Sn}_2\text{M}_2\text{M}'$ (1 example). The most common environment about tin is distorted tetrahedral. A summary of the Sn-M and M-M distances in the pentameric derivatives is found in Table 3A. The shortest bond distance is Sn-Ni at 239.3(2) pm [188]. Notably, the mean Sn-M bond distances in the pentameric derivatives are generally longer than those in the tri- and tetrameric derivatives, except for Sn-Ni and Sn-Re.5.

HEXAMERIC HETEROTIN COMPOUNDS

Crystallographic and structural data for over forty hexameric heterotin clusters are summarised in Table 4. There are six subgroups based on the metal content ratios: Sn_5M (5 examples); Sn_4M_2 (10 examples); Sn_3M_3 (7 examples); $\text{Sn}_2\text{M}_3\text{M}'$ (1 example) and $\text{Sn}_2\text{M}_1\text{M}'_2$ (2-examples).

5.1 Five Sn plus M

The bright orange Sn_5Ru cluster [207] has a central Ru(II) atom coordinated to five SnCl_3 moieties and a Cl atom. The Sn-Ru bond distance ranges from 255.3(2) to 258.6(1) pm (average 257.4 pm). Each Sn atom is quasi-tetrahedral (SnCl_3Ru) while the Ru atom is six coordinate (RuClSn_5). In a dark red Sn_5Rh cluster [42] the central Rh(I) atom is bonded by only the five $\text{Sn}\{(\text{NBu})_2\text{SiMe}_2\}$ moieties. Two Sn(II) atoms are non-symmetrically bridged by a chlorine atom ($\text{Sn-Cl} = 258.5(3)$ and $273.8(3)$ pm, respectively). The mean Sn-Rh distance for these two Sn atoms is about 3 pm longer than the mean Sn-Rh distance for the remaining three Sn(II) atoms (254.1 pm). The Rh(I) atom has almost ideal trigonal-bipyramidal geometry (RhSn_5). There are two pairs of Sn(II) atoms, one in a Y-shaped environment (Sn_2Rh) and the other a distorted tetrahedron (Sn_2ClRh). Two crystallographically independent molecules are found in a yellow-orange Sn_5Os cluster with identical configurations differing by degree of distortion. Each Os atom is octahedrally coordinated (OsClSn_5). The Sn-Os bond distance ranges from 253.1 to 260.0 pm. Each Sn(II) atom has a quasi-tetrahedral environment (SnCl_3Os). Another yellow Sn_5Os cluster [209] is isostructural with the previous structure [208] and also contains two crystallographically independent molecules. In the red Sn_5Pt cluster the $[\text{Pt}(\text{SnCl}_3)_5]^-$ anion is a regular trigonal bipyramid with average axial Sn-Pt bond length of 255.30(7) pm, a little shorter than the equatorial Sn-Pt value of 257.22(10) pm. The Sn(II) atoms are pseudo-tetrahedrally coordinated (SnCl_3Pt). This subgroup of the hexameric heterotin clusters contains tin only in the oxidation state of two, Sn(II).

5.2 Four Sn plus Two M

The Sn_4M_2 clusters have ten examples, the first of which is a non-transition metal derivative shown in Figure 11 [211]. This consists of a central Li_2Br_2 four membered ring with a crystallographic inversion centre, with each Li(I) atom coordinated to two tert-butylamine ligands ($\text{Li-N} = 204.5(5)$ pm). Almost in the plane of the Li_2Br_2 ring, two $\text{Sn}_2\text{Br}_2\{(\text{NBu})_2\text{H}\}_2$ moieties are linked through Br-Sn bonds, forming a layer of Sn, Li and

Fig.11. Structure of $\text{Sn}\{(\text{H})\text{NBu}\}_2\text{Br}_2 \cdot 2\text{Li}_2\text{Br}_2(\text{BuNH}_2)_4$ [211]

Br atoms. A colourless Sn_4Al_2 cluster [212] contains a central Sn_4N_4 cube ($\text{Sn-Sn} = 323.6(2)$ pm). Two of the Sn(II) atoms are bonded to an AlCl_3 group ($\text{Sn-Al} = 278(1)$ pm), giving two types of Sn(II) environment, SnN_3 and SnN_3Al . Two colourless Sn_4In_2 clusters [213] are isostructural with a central In_2N_2 ring, with each In atom coordinated also to a Cl atom and a methyl or ethyl group. The N atoms also carry SnMe_3 groups (average $\text{Sn-N} = 213$ pm), and each Sn atom is quasi-tetrahedral (SnC_3N). A colourless Sn_4Sb_2 cluster [213] has the Sb atoms bonded at $287.6(1)$ pm, and each carries two SnMe_3 moieties with an average Sn-Sb bond distance of $279.7(1)$ pm. This cluster was studied by other workers [214] and at both room temperature and $153(3)$ K. There are also transition metal derivatives, for example colourless Sn_4Re_2 cluster [215] which contains three four member rings that form a ladder-type structure (Sn_4O_4). Here, two $\mu_3\text{-O}$ and μOH groups serve as bridges between Sn(II) atoms. Each OREO_3 unit is bonded to outer Sn(IV) atoms, which carry two terminal phenyl groups to complete a distorted trigonal bipyramidal geometry. The Re^{IV} atoms have distorted tetrahedral geometry. The structure of a green Sn_4Ni cluster [216] contains a six membered ring $[\text{NiCNSnOSnNC}]_2$ with a OH group acting as a bridge between a pair of Sn(IV) atoms. Each Sn(IV) atom is also coordinated to three methyl groups creating a distorted trigonal-bipyramidal geometry (SnC_3ON) with O and N atoms at the apices. The Ni(IV) atoms each carry CN groups to complete NiC_4 stereochemistry. In yellow Sn_4Ru_2 cluster [217] two $(\text{Me}_3\text{Sn})_2\text{Ru}(\text{CO})_3$ groups are linked by two bridging Me_3Sn groups. The Ru_2Sn_3 bridge plane contains a crystallographic centre of symmetry. Each Ru atom is bonded to six atoms (RuC_3Sn_3) and the two octahedra share an edge to form the dimeric unit. The Sn-Ru distances are $263.8(2)$, $268.6(2)$ and $269.4(2)$ pm. The Ru-Ru distance is $311.6(3)$ pm. Two pairs of Sn atoms, SnC_2Ru_2 and SnC_3Ru , have a quasi-tetrahedral arrangement. A dark green Sn_4Rh_2 cluster [218] consists of two edge shared octahedral rhodium centres linked by two bridging SnCl_2 groups. The octahedral coordination about each rhodium is completed by three terminal 2,6-xylyl isocyanate ligands (average $\text{Rh-C} = 199(1)$ pm and one terminal SnCl_3 group *trans* to the SnCl_2 bridges. The Sn_4Rh_2 arrangement of metal atoms is approximately planar. A crystallographic centre of inversion is found in the centre of the Rh_2Sn_3 rhombus. The shorter Sn-Rh bond length to the SnCl_3 ligand is $261.6(1)$ pm, and the longer to the SnCl_2 bridge is $264.5(1)$ pm. This reflects a greater degree of Sn-Rh π -bonding in the former. The Sn atoms have quasi-tetrahedral geometry. All of the results are comparable

5.3 Three Sn plus Three M

The Sn_3M_3 core is found in eight clusters, all with transition metal atoms. The structure of Sn_3Mn_3 cluster [219] has a six membered metallocycle of alternate Sn and Mn atoms with average Sn-Mn bond distances of $258.8(5)$ pm. The endocyclic ring angle at Mn is $90.5(2)^\circ$ and at Sn is $141.6(2)^\circ$. A yellow Sn_3Fe_3 cluster [220] contains a bicyclic Sn_3Se_4 framework with Sn-Se-Sn angles of $94.6(1)^\circ$ (four membered ring) and $110.5(1)^\circ$ (six membered ring). Each Sn(II) atom also carries an $\text{Fe}(\text{CO})_2\text{cp}$ moiety with an average Sn-Fe bond distance of $249.2(2)$ pm. Each tin atom is quasi-tetrahedral, SnSe_3Fe and SnSe_2ClFe . There are two red and one orange Sn_3Ru_3 clusters [96] which are isostructural. The Ru triangle and three Sn atoms form a planar array with average Sn-Ru bond distance of 271 pm ($288.7(2)$ to $297.7(2)$ pm). One of the clusters contains two crystallographically independent molecules, differing by degree of distortion (Table 4). In all clusters the Sn atoms are quasi-tetrahedral (SnC_2Ru_2). In one Sn_3Pd_3 cluster [221] the metal atoms form a planar array similar to the previous cases [96]. The mean Sn-Pd bond distance of 262 pm is about 9 pm shorter than that found in Sn_3Ru_3 clusters [96]. Each Sn atom is in a distorted tetrahedral environment SnN_2Pd_2 . The remaining Sn_3M_3 clusters ($\text{M} = \text{Os}$ [154] or Pt [221]) are isostructural with the Ru and Pd analogues discussed above. The mean Sn-Os and Sn-Pt bond distances are 267 and 262 pm, respectively. The mean Os-Os distance is $297.4(1)$ pm, and mean Sn-Pt distance is $276.3(1)$ pm. In this subsection, six examples are isostructural [96,154,221] with a triangle of M atoms and the three Sn atoms forming a planar array. The mean Sn-M bond distance increases in the order: 262 pm (Pd,Pt) < 267 pm (Os) < 271 pm (Ru). The mean M-M bond distance increases in the order: 276 pm (Pt) < 281 pm (Pd) < 294 pm (Ru) < 297 pm (Os).

5.4 Two Sn plus Four M

The Sn_2M_4 clusters contain a non-transition metal example where M is aluminium [222]. This has an eight membered ring $\text{Al}_2\text{Sn}_2\text{Cl}_4$ with two Sn(II) centres linked by two AlCl_4 moieties. Each Sn(II) atom is η^6 -bonded to a hexamethylbenzene ring at a distance of 245 pm.

The other Sn_2M_4 clusters all involve transition metal heterometal atoms. Five of these ($\text{M} = \text{Mo}$ [223], Fe [223,230], Co [232]) clusters contain planar Sn_3X_2 rings ($\text{X} = \text{Te}$ [223], Se [230,232] or S [237]. Four $\text{Mcp}(\text{CO})_2$ [223,230] or $\text{Co}(\text{CO})_4$ moieties [232] are connected in pairs to Sn atoms to complete a quasi-tetrahedral environment (SnX_2M_2). As the covalent radius of M increases so does the mean value of the Sn-M distance, for example: $258.7(2)$ pm (Fe , 120 pm) < $259.2(2)$ pm (Co , 126 pm) < 288.7 pm (Mo , 145 pm).

There are two orange Sn_2W_4 clusters [224,225] which contain $[\text{Sn}_2(\text{WX}_4)_4]^{4-}$ anions ($\text{X} = \text{S}$ [224] or Se

[225]). The anion contains two central SnY_6 octahedra coupled via a common edge. These octahedra are bonded to four non-equivalent WY_4 tetrahedra via common edges. Two of the WY_4^{2-} anions are coordinated as bidentate ligands to the Sn(II) atom and retain two free S atoms. The other WY_4^{2-} anions coordinate as tridentate ligands with only one free S atom. These tridentate WY_4 ligands contain a triply bonded S atom.

There are six Sn_2Mn_4 clusters [166,226-229]. Molecules of $\text{H}_2\text{Sn}_2\{\text{Mn}(\text{CO})_5\}_4$ [226] have C_2 symmetry with a tin-tin axis ($\text{Sn-Sn} = 289.4(5)$ pm). The manganese atoms are in an octahedral environment comprised of five CO groups and one Sn atom. Each tin atom is in a distorted tetrahedral environment ($\text{SnMn}_2\text{Sn}''$) with the Sn-Mn bond distances of 267.5(5) pm and 273.0(5) pm, respectively. Another two Sn_2Mn_4 clusters [166,227] are isostructural. The central fragment contains a planar Mn_2Sn_2 rhombus with a Mn-Mn bond (309.1(1) pm [166] and 308.6(1) pm [227] across the ring, and Sn-Mn bond distances of 262.0(1) and 262.7(1) pm [166] or 262.5(1) and 263.0(1) pm [227]. The Sn(IV) atoms each have a terminal bond to Cl [166] or Br [227], and a $\text{Mn}(\text{CO})_5$ ligand ($\text{Sn-Mn} = 262.6(1)$ pm [166] or 263.4(1) pm [227]), to create a distorted tetrahedral environment. Two red-brown Sn_2Mn_4 clusters [228] are isostructural and composed of an Sn_2^{2-} moiety coordinated linearly end-on to two $\text{Mn}(\text{CO})_5$ units. In addition, the tin centres are bridged by two $\mu\text{-Mn}(\text{cp}'(\text{CO})_2)$ units and a $\mu\text{-Cl}$ ligand. The resulting structure thus resembles a [1.1.1] propellane scaffolding with a mean Sn-Sn distance of 285.2(2) pm. The Sn-Mn bond distances range from 250.8(14) to 276.0(3) pm. A dark red Sn_2Mn_4 cluster [229] has a central Sn-Sn (288.5(1) pm) unit, with each Sn tetrahedrally surrounded by two $\text{Mn}(\text{CO})_5$ groups and one Br atom. The average Sn-Mn bond distance is 273 pm, and the Sn-Sn-Mn angles range from 113.26(3)° to 117.26(3)°.

There are three coloured Sn_2Fe_4 clusters [223,230,231], two of which are isostructural and have been discussed above [223,230] together with corresponding Sn_2Co_4 structures [232]. The third [231] contains a centrosymmetric Sn_2O_2 dimer with unsymmetrically bridged OH groups ($\text{Sn-O} = 202(1)$ and $223(1)$ pm). Each tin carries two ($\mu\text{-C}_5\text{H}_5\text{-2-CH}_2\text{NMe}_3$)Fcnp moieties and a terminal OH group, completing a distorted trigonal-bipyramidal arrangement (SnO_3C_2) with two of the O atoms at apical positions ($\text{O-Sn-O} = 158.4(5)$ pm).

Two yellow Sn_2Re_4 clusters [233,234] are also isostructural. The central fragment contains a planar Re_2Sn_2 rhombus with a *trans*-annular Re-Re bond of 316.0(2) pm [233] or 317.6(1) pm [234]. A Cl [233] or I [234] plus a $\text{Re}(\text{CO})_4(\text{PPh}_3)$ moiety are bonded to Sn(IV) in *trans* positions with respect to the ring plane. The mean Sn-Re bond distances are almost equal at 274 and 275 pm, respectively. Each Sn(IV) atom is quasi-tetrahedrally coordinated, SnXR_3 .

A gold-yellow Sn_2Au_4 cluster [235] consists of a tetrahedral Au core with opposite edges bridged by SnCl_3 groups. The molecule has a crystallographically imposed C_2 symmetry axis. The Au-Au bond angles range from 263.4(5) to 281.28(5) pm, the shorter values being those where the Au atoms are edge-bridged by the SnCl_3 groups. The Au-Au-Au bond angles range from 56.34(9)° to 62.72(1)°, showing a slight departure from regular tetrahedral geometry. The Sn-Au bond lengths are 281.5(7) and 297.3(8) pm. Each Sn atom has a pseudo-trigonal bipyramidal arrangement (SnCl_3Au).

5.5 Sn plus Five M

The structure of a green SnFe_5 cluster [236] consists of a SnFe_2 triangle linked to an Fe_3 triangle via a spiro Sn atom. The mean Fe-Fe distance on the unbridged sides (270.8(1) pm) is about 5 pm longer than the bridged side at 265.8(1) pm. The Fe-Fe bond of the $\text{Fe}_2(\text{CO})_8$ group is longest at 287.8(2) pm, and the Sn-Fe bond distances range from 253.5(1) to 259.0(1) pm.

5.6 Two Sn plus 4(M + M')

There are three examples which have two heterometal atoms present with tin. A bright orange $\text{Sn}_2\text{Os}_3\text{Pt}$ cluster [237] contains a tetrahedral array of two Os, one Pt and one Sn atom. One of the Os atoms bears three CO groups while the other carries two CO groups and a trichlorostannate(II) ligand. The Pt atom carries a tricyclohexyl phosphine group and a CO ligand. The tin atom is bonded to a Cl atom and a molecule of diethyl ether. An $\text{Os}(\text{CO})_4$ unit bridges the Sn atom and the $\text{Os}(\text{CO})_3$ moiety, resulting in an overall edge-bridged tetrahedral metal core. The separations between Os and Sn range from 260.8(4) to 305.8(5) pm. A brown $\text{Sn}_2\text{W}_2\text{Fe}_2$ cluster [238] contains half of the metal atoms, a sodium ion, two diethyl ether molecules and half of a dioxane molecule. The cluster dianion is a centrosymmetric dimer built around a planar Sn_2Fe_2 core. Each of the $\text{W}(\text{CO})_5$ moieties is bound to the Sn atom of this core. The SnFe_2W unit is nearly planar with the tSn atom only 55.4(4) pm out of the Fe_2W plane. The Sn-Fe bond distances of 268.1(1) and 269.4(2) pm are shorter than the Sn-W bond distance of 279.9(1) pm. The third cluster $\text{Sn}_2\text{Fe}_2\text{Co}_2$ [126] has six metal atoms arranged in a one dimensional chain, $(\text{CO})_4\text{FeSn}(\mu\text{-OBU})_2\text{Co}(\mu\text{-OBU})_2\text{Co}(\mu\text{-OBU})_2\text{SnFe}(\text{CO})_4$. Each Sn atom is also coordinated to a terminal OBU group. The Sn-Fe bond distance is 248.0(1) pm, the Co-Co distance is 297.7(3) pm, but the Co-Sn distance of 316.5(1) pm indicates no metal-metal bond.

The data in Table 4 shows that the Sn atom in the hexameric compounds is mostly in a quasi-

TABLE 4. Crystallographic and Structural Data for Hexameric Hetero Tin Clusters^a

COMPOUND (colour)	Crys. cl Sp. Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo- phore.	M-L [pm]	M-M [pm] M-L-M [°]	M-L-M [°]	Ref
5 Sn + M (NMe ₂) ₄ [Ru SnCl ₃] ₅ Cl] (orange)	or P2 ₁ /ca 4	1979.6(5) 1388.2(2) 2477.2(2)		Sn ^{IV} Cl ₃ Ru	Cl ^b 238.8(5,27)	Ru 257.4(1,21)	Cl ₃ Cl 94.8(2,2.9) Cl ₃ Ru 121.7(1,9.0) Cl ₃ Sn 87.0(1,5.6) 179.5(1) Sn ₃ Sn 92.5(1,6.4) 173.0(1,6.0) not given	207
[Rh{Sn(NBu) ₂ SiMe ₂ } ₅ Cl] tol (dark red)	or Cmc2 ₁ 4	1655(2) 2233(2) 2263(2)		Sn ^{III} N ₂ Rh (x3) Sn ^{III} N ₂ ClRh (x2)	N not given ;Cl 258.5(3) 2 768(3)	Rh 252.6(1) 254.9(1,0) Rh 257.1(1,3)		42
(Nm ₂) ₄ [Os (SnCl ₃) ₅ Cl] ^c (yellow-orange)	m P2 ₁ /n 8	1194.1(3) 2047.5(4) 3959.7(8)	90.27	Rh ^I Sn ₃ Sn ^{IV} Cl ₃ Os Os ^{II} Cl ₃ Sn ₃	Cl 237(-,6) Cl 236(-,5)	Os 253.1-260.0	Sn Sn 92.2(1,4.9) 121.3(1) 178.1(1) Cl Cl 94.2(-,4.6) Cl Os 122.1(-,6.7) Cl Cl 91 - 97.5 Cl ₃ Sn 118 - 128 Cl Cl 94.2(-,3.0) Cl Os 112.1(-,4.5) Cl ₃ Sn 86.6(-,1.0) 176.9 Cl Cl 94.3(-,4.3) Cl Os 122.2(-,6.3)	208
(NH ₄) ₄ {Os (SnCl ₃) ₅ Cl} ^c (yellow-orange)	m P2 ₁ /n 8	1194.1(3) 2047.5(4) 3959.7(8)	89.73(3)	Sn ^{IV} Cl ₃ Os Os ^{II} Cl ₃ Sn ₃ Sn ^{IV} Cl ₃ Os Os ^{II} Cl ₃ Sn ₃	Cl 237(2,6) Cl 242(2) Cl 238(2,5)	Os 253.0(5) 257.7(5,1) 258.9(5) Os 253.0(5) 257.1(5,7) 259.4(5,4)		209
(Ph ₃ Pme) ₃ [Pt(SnCl ₃) ₅] (red)	trg- R3 2	1589.7(1)	82.02(1)	Sn ^{IV} Cl ₃ Pt Pt ^{IV} Sn ₅	Cl 245(2) C 236.3(5,19)	Pt 255.14(7,0) 255.45(6,0) 257.22(10)	Cl Sn 87.1(-,3.0) 178.7 Cl Cl 97.4(2,2.7) Cl Pt 119.8(1,2.5) Sn Sn 90.0(1,2)	

$[(Me_3Sn)_2Sb]_2$ (colourless)	m P2 ₁ /c 2	674.7(2) 1821.8(4) 1262.3(3)	124.02(2)	SnC ₃ Sb SbSn ₂ Sb	C _{Me} 214(1,2)	Sb 279.8(1,1) Sb 288.2(1)	C, C 107.8(5,2.8) C, Sb 111.0(3,2.7) Sn, Sb 91.3(3) 95.99(3)	214
at 153(3)K	m P2 ₁ /c 2	666.5(1) 1800.2(3) 1248.5(2)		SnC ₃ Sb SbSn ₂ Sb	C _{Me} 214.8(9,16)	Sb 279.7(1,1) Sb 286.58(9)	C, C 108.0(4,1.9) C, Sb 110.9(2,1.7) Sn, Sb 90.86(2) 95.42(2)	
$[O_3ReO(Ph)_2SnO$ (Ph) ₂ SnOH] ₂ (colourless)	or Pbca 4	1784.4(3) 1444.8(2) 1983.7(4)		Sn ^{IV} C ₃ O ₃	C _{Ph} 210.8(8,8) μ ₃ O 202.2(5,14) 213.3(4,0) μHO 214.1(5,28) O 169.6(7,15) μO 174.4(5)	3 108.8(2,2.3) 142.3(2) : 102.3(2) 169.0(3)	O O 73.4(2,1.0) 81.6(2) 150.7(2,1.9)	215
$(NBu)_2\{[(\mu-CH)$ (Me ₃ Sn) ₂] ₂ [(μ-NC) ₂ N(CN) ₂] ₂ (yellow)	m P2 ₁ /c 2	892.0(2) 1896.4(4) 2245.7(5)	99.83(1)	Re ^{VII} O ₄ Sn ^{IV} C ₃ ON N ^{IV} C ₄	C _{Me} 211(1,3) μHO 214.9(4) μCN 252.9(6) μNC 186.8(7,4) NC 186.0(7,10)	134.6(2)	O O 109.5(4,1.4) C O 94.6(3,1.6) O N 174.4(1)	216
$[(Me_3Sn)_2Ru(CO)_3]_2$ (yellow)	m P2 ₁ /c 2	1122(2) 922(2) 1439(2)	105.3(1)	SnC ₂ Ru ₂ (x2) SnC ₃ Ru (x2) Ru ^{III} C ₃ Sn ₃	C _{Me} 216(2,4) C _{Me} 210(4) 216(3,1) OC 186(2) 190(2,0)	Ru 263.8(2) 259.4(2) Ru 268.6(2) Ru 311.6(3)	C, C 109(1) Ru, Ru 71.50(6) C, Ru 117.9(5,5.0) C, C 107(1,1) C, Ru 108(1,1) 12(1) C, Sn 87.3(6,7.5) Sr, Sn 97.1(1,11.4) 165.69(6)	217

$[(C_8H_5N)_3Rh(SnCl_3)(\mu-SnCl_2)_2]$ (dark green)	m $P2_1/n$ 2	1400.5(3) 1279.6(4) 1938.9(3)	104.96(2)	$SnCl_2Rh_2$ (x2)	Cl 235.8(3,8)	Rh 261.6(1) 264.5(1)	Cl, Cl 98.7(1) Rh, Rh 104.63(3) Cl, Ru 113.4(1,3,2) Cl, Cl 99.3(1,1,9) Cl, Ru 114.4(1,2) 125.5(1) C, Sn 90.4(3,4,4) 170.2(3) Sn, Sn 88.3(1,11,0) 174.55(4)	218
3 Sn + 3 M $[(CO)_4MnSnCl(dmf)]_3$	or Pbca 8	1187.8(3) 2020.5(4) 3187.4(6)		$Sn^II OClMn_2$	O_{hmf} 227.2(23,23) Cl 241.9(9,20) O C not given	Mn 258.8(5,10)	O Cl 90.9(7,1,3) Mn, Mn 141.6(2,2,1) Cl, Mn 106.8(3,2,5) Sn, Sn 86.2(2,5) 95.1(2)	219
$[{\{cp(CO)_2Fe\}_3 ClSn_3Se_4}]$ (yellow-orange)	m $P2_1/n$ 4	1435.2(7) 1124.4(4) 1972.2(12)	94.59(4)	$SnSe_3Fe(x2)$ $SnSe_2ClFe$	μSe 256.6(2,19) μSe 254.8(2,9) Cl 242.8(3)	Fe 249.4(2,1) 82.2(1,1) Fe 248.8(2) 100.5(1,1,5)	Se, Se 102.0(1,7,5) Se, Fe 116.3(1,10,8) Se, Se 112.4(1) Se, Fe 95.8(1,2,2) Se, Fe 117.3(1,4,9) Cl, Fe 106.2(1) not given	220
$[(CO)_3Ru_3\{\mu-Sn(CH_3SiMe_3)_2\}_2\{\mu-Sn(tip)_2\}]$ (red)	tr $P1$ 2	1498.6(5) 1514.3(5) 2303.5(5)	107.99(6) 89.75(6) 119.99(6)	$FeCr_2C_2Sn$ SnC_2Ru_2	OC 176(1,2) C_{cp} 207(1,3) C 213(2,3)	Ru 264.8(2,7) 269.0(2,1) 272.4(2,5)	C, C 103.3(9,2,5) Ru, Ru 65.5(1,6)	96
$(CO)_3Ru_3\{\mu-Sn(tip)_2\}_3$ (red)	m $P2_1/c$ 6	3160(4) 1721(2) 3447(4)	104.31(14)	RuC_3Sn_2 SnC_2Ru_2 RuC_3Sn_2	OC not given C 221(2,4) OC not given	Ru 288.7(2) 291.7(2,2) Ru 272.6(2,9) Ru 294.8(2,12)	Sn, Ru 57.2(1,1,5) Ru, Ru 60.0(1,7) C, C 95.4(7,1,7) Ru, Ru not given Sn, Ru 57.3(1,3) Ru, Ru 60.0(1,4) C, C 99.7(8,1,0) Sn, Ru 57.4(1,2) Ru, Ru 60.0(1,5)	96

(CO) ₃ Ru ₃ {μ-Sn CH ₃ (SiMe ₃) ₂ } [μ-Sn(tip) ₂] (orange)	hx P6 ₃ 6	1973.5(2) 4943.1(8)	SnC ₃ Ru ₂	C 222(1,2)	Ru 270.6(2,1) 272.1(2) 275.0(2,20) Ru 296.3(2,20)	C, C 97.6(5,1,2) Ru ₃ Ru 65.9(1,0)	96
[(CO) ₃ Pd{μ-Sn (N(SiMe ₃) ₂) ₂ }] ₃	m P2 ₁ /n 4	1166.3(2) 2360.9(4) 2743.2(5)	RuC ₃ Sn ₂ Sn ₃ N ₂ Pd ₂ PdCSn ₃	OC not given N 203(-,8) OC not given	Pd 262.2(3,7) Pd 281.4(3,23) Os 267.0(1,3)	Sn ₃ Ru 57.0(1,7) Ru ₃ Ru 60.0(1,7) N ₃ N 105(1) Pd ₃ Pd 64.32(8) Sn ₃ Pd 57.92(8) Pd ₃ Pd 60.71(1) C ₃ C 106.4(5) Os ₃ Os 67.6(2) C ₃ Os 119.8(2,1) C ₃ C 89.6(2) C ₃ Sn 90.0(2,0) 94.7(3) Sn ₃ Sn 172.31(2)	221
[(CO) ₃ Os(μ-SnMe ₂) ₃] (yellow)	hx P6 ₃ /m 2	1100.7(2) 1281.8(2)	SnC ₂ Os ₂ OsC ₃ Sn ₂	C ₃ Os 214.1(7) OC 191(1,3)	Os 297.4(1)		154
[(CO)Pt{μ-Sn N(SiMe ₃) ₂ }] ₃	m P2 ₁ /n 4	1168.8(1) 2358.2(2) 2742.6(2)	SnN ₃ Pt ₂ PtCSn ₃	N 205(2) OC not given	Pt 262.0(1,6) Pt 276.3(1,12)	N ₃ N 103(1) Pt ₃ Pt 63.31(3) Sn ₃ Pt 58.48(3) Pt ₃ Pt 60.43(2)	221
2 Sn + 4 M [(η ⁶ -C ₆ Me ₆) Sn(AlCl ₄) ₂] 3C ₆ H ₆ (colourless)	tr ⁻ P1 ⁻ 1	1185.2(1) 1183.7(1) 1203.1(1)	Sn ^{IV} C ₃ Cl ₄ A ^{III} Cl ₄	μCl 252.0(1) 306.1(1,36) η ⁶ 245 Cl 210.9(1,34) μCl 216.0(2,18) μTe 232.0(2,1)	Cl ₃ Cl 69.9(1,1,6) 131.5(1,2,9) C ₃ Cl 109.5(1,3,7)		222
{[cp(CO) ₂ Mo] ₄ Sn ₂ Te ₂] to (yellow) at 233K	tr ⁻ P1 ⁻ 1	935.3(5) 1001.2(5) 1348.0(7)	SnTe ₂ Mo ₂ MocpC ₂ Sn	OC 196(1,2) cp C 235(1,2)	Mo 287.7(2) 289.8(2) 87.4(1)	Te ₃ Te 92.5(1) Te ₃ Mo 109.8(1,8,1) Mo ₃ Mo 120.5(1) not given	223

$(\text{Ph})_4[\text{Sn}_2(\text{WSe}_4)_4]$ (orange)	tr P1 1	146.2(3) 1424.0(3) 1289.5(9)	94.79(4) 99.28(4) 106.08(2)	$\text{Sn}^{\text{II}}\text{Se}_6$	μS 271.0(8)– 304.7(8) $\mu_3\text{S}$ 295.6(6)– 309.3(6) S 215.8(1,10) μS 220.8(3,31) $\mu_3\text{S}$ 227.2(5)	W 350.8(6) Sn 464.7(2)	not given	224
$(\text{FPh}_4)_1[\text{Sn}_2(\text{WSe}_4)_4]$ (orange) at 153 K	tr P1 1	1298.1(3) 1441.2(6) 1464.4(7)	105.26(4) 99.79(3) 94.56(3)	$\text{Sn}^{\text{II}}\text{Se}_6$ $\text{W}^{\text{VI}}\text{Se}_4$ SnMn_2Sn	S 215.8(1,10) μS 220.8(3,31) $\mu_3\text{S}$ 227.2(5)		not given	225
$[\text{Sn}_2(\text{Mn}(\text{CO})_5)_4\text{I}_2]$	m C2/c 4	1571(5) 1718(5) 1251(5)	107.3(2)	MnC_2Sn	OC 182(4,9)	Mn 267.5(5) Sn 273.0(5) Sn 289.4(5)	Sn,Mn 107.7(1) 121.9(1) Mn,Mn 119.8(1) C Sn 85.5(12,12) 174.6(10,4)	226
$[\text{Mn}_2(\text{CO})_8\{\mu\text{-Sn}(\text{Cl})\text{Mn}(\text{CO})_5\}_2]$	m P1 ₁ /c 2	873.3(2) 1230.0(2) 1546.4(2)	115.98(10)	$\text{Sn}^{\text{IV}}\text{ClMn}_3$	Cl 240.3(1)	Mn 262.4(1,4)	Cl,Mn 106.4(1,3,8) Mn,Mn 72.17(2) 132.75(2) C Sn 86.0(2,8,8) 17.3(1,1,9) Sn,Sn 107.83(2) C Sn 87.3(2,3,1) 176.86(16)	166
$[\text{Mn}_2(\text{CO})_8\{\mu\text{-Sn}(\text{Br})\text{Mn}(\text{CO})_5\}_2]$	M P2 ₁ /m 2	881.7 1237.6 1551.1	63.54	$\text{Sn}^{\text{IV}}\text{BrMn}_3$	Br 255.4(1)	Mn 263.0(1,5)	Br,Mn 106.5(1,3,8) Mn,Mn 71.91(2) 132.22(3) C Sn 86.0(2,8,6) 173.0(2,1,5) C Sn 87.4(2,3,0)	227
$[\{(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}\}_4(\mu\text{-Sn}_2\text{Cl})]$ 0.5 Et ₂ O (medium brown)	m C2/c 4	2632.5(10) 1380.5(5) 1879.7(9)	121.47(2)	$\text{MnC}_2\text{Sn}_2(\text{x}2)$ $\text{Sn}^{\text{O}}\text{ClMn}_3$	OC 183.1(6,28) μCl 2/4,9(3,5)	Mn 273.8(3) 275.8(3,2) Sn 285.3(2) 62.5(1)	C Sn 87.4(2,3,0) Cl,Mn 92.1(1) 105.5(1) Mn,Mn 102.3(1) 126.4(1,2,5) Sn Sn 62.4(1,2) Cl,Mn 91.5(3) 106.7(3) Mn,Mn 102.9(3) 126.1(3,1,6) Sn Sn 62.6(3,0)	228
$[\{(\text{C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}\}_4(\mu\text{-Sn}_2\text{Cl})]$ Na ₂ (thf) ₄] C ₂ H ₄ O (red brown)	or Pbca 8	1781(20) 1971(2) 3395(20)		MnncpC_2Sn $\text{Sn}^{\text{O}}\text{ClMn}_3$	not given μCl 2/4,3(10)	Mn 250.8(14) 274.2(11,8) Sn 285.1(17) 62.6(3)	Sn Sn 62.4(1,2) Cl,Mn 91.5(3) 106.7(3) Mn,Mn 102.9(3) 126.1(3,1,6) Sn Sn 62.6(3,0)	228

{Mn(CO) ₅ SnBr ₂ (dark red)	m P2 ₁ /c 4	1659.1(5) 1245.5(2) 1721.4(8)	108.10(3)	SnBr ₂ Mn ₃	Br 257.6(1)	Mn 270.6(1.3) 274.7(1.4) Sn 288.5(1)	B: Mn 103.6(1.3,4) Mn, Mn 119.2(1.5) Sn, Mn 115.1(1.2,2) Br, Sn 95.5(1.7) C, Sn 87.3(3.4,1) 177.3(3.2,7)	229
{cp(CO) ₂ Fe ₄ Sn ₂ Se ₂ (orange) (at 180K)	m P2 ₁ /n 4	1136.8(6) 2464(1) 1267.9(7)	115.26(4)	SnSe ₂ Fe ₂	μSe 259.5(3.13)	Fe 257.9(2.9) 85.8(1.4)	Se, Se 94.1(1.3) Se, Fe 110.8(1.1,9) Fe, Fe 118.1(1.8) not given	230
{cp(CO) ₂ Fe ₃ Sn ₂ Te ₂ (red brown) at 193K	m P2 ₁ /n 2	732.5(5) 2315.2(18) 1027.8(11)	109.19(7)	Fe ₃ cpC ₂ Sn SnTe ₂ Fe ₂	OC 210(1.3) C _{cp} 174(1.2) μTe 281.4(3.3)	Fe 259.5(3.2) 86.4(1)	Te, Te 93.6(1) Te, Fe 111.2(1.6,5) Fe, Fe 116.3(1) not given	223
{[cpFe(μ-C ₃ H ₃ -2- CH ₂ NMe ₂) ₂ Sn(OH) ₂ ·2CHCl ₃ (orange)]	tr P1 1	1300(2) 1109(1) 1313(1)	73.4(1) 75.9(1) 81.4(1)	Fe ₃ cpC ₂ Sn SnO ₂ C ₂	OC 173(1.2) cp, C 210(1.1) μHO 202(1) 223(1) HO 212(1) μC 214(2.2)	HO 108.4(8)	O, O 71.6(5) 86.7(5) 158.4(5) C, C 115.2(7) O, C 96.7(6.4,7) 121.2(6.3,6)	231
{(CO) ₄ Co ₃ Sn ₂ (yellow)	or Fddd 8	1239.0(8) 2109.6(13) 2163.3(14)		Fe ₃ cp ₂ SnS ₂ Co ₂	no: given μS 243.9(2)	Co 259.1(2) 85.9(1)	S, S 94.2(1) Co, Co 115.9(1) S, Co 112.2(1) C, Sn 144.5(2.2,0) 175.7(3)	232
{(CO) ₄ Co ₃ Sn ₂ Se ₂ (red-brown)	or Fddd 8	1255.8(7) 2137.1(15) 2171.6(12)		SnSe ₂ Co ₃	μSe 256.3(1)	Co 259.3(1) 84.3(4)	Se, Se 95.7(1) Co, Co 115.7(1) Se, Co 111.8(1) C, Sn 84.5(4.2,0) 176.8(4)	232
{[Re ₂ (CO) ₈ {μ-Sn(Cl) Re(CO) ₄ (PPh ₃) ₃ }] (yellow)	or Pbcn 4	1918.9(6) 1603.4(6) 1904.2(5)		Sn ^{IV} ClRe ₁ ReC ₃ Sn ₂ (x2) ReC ₄ PnSn(x2)	Cl 243(1) OC 180(4) OC 172(5) P _{th} 242.4(9)	Re 269.5(3) 276.2(3.2) Fe 331.6(2)	Cl, Re 105.9(3.1,0) Re, Fe 69.78(6) 132.2(1.3) S ₃ , Sn 110.2(8) C, Sn 81(2.7) P, Sn 93(2)	233

$[\text{Re}_2(\text{CO})_8\{\mu\text{-Sn}(\text{I})\text{Re}(\text{CO})_2(\text{PPh}_3)_2\}]_2$ (yellow)	m P2 ₁ /c 2	909.6(7) 2927.1(9) 1129.1(7)	93.73(5)	$\text{Sn}^{\text{IV}}\text{Re}_3$ $\text{Re}_2\text{C}_3\text{Sn}_2$ (x2) $\text{ReC}_4\text{P}_2\text{Sn}$ (x2) $\text{SnC}_{13}\text{Au}_2$	I OC not given P_{1h} 243.0(4) Cl 236.6(3) 238.5(4.2)	Re 271.4(1) 277.2(1.4)	I ₂ Re 106.9(1.2.5) Re ₂ Re 69.89(3) 130.8(1.1.5) Sn ₂ Sn 110.11(3) P ₂ Sn 177.03(9) Cl ₂ Cl 96.4(1.2) Cl ₂ Au 101.5(1.10.1) 135.4(1.8.8) Au ₂ Au 54.06(1) P ₂ Sn 120.0(1.2.7) P ₂ Au 115.0(1.1.8) 176.2(1.1.1) Sn ₂ Au 63.0(1.3.0) 116.5(1.4.3) Au ₂ Au 60.0(1.3.7)	234
$(\text{PPh}_3)_4\text{Au}_4(\mu\text{-SnCl}_3)_2$ (golden yellow)	m C2/c 4	1985.8(4) 1987.7(6) 2012.7(3)	97.06(2)	AuPSn_2	P 231.8(2.3)	Au 263.4(5) 276.9(6.4) 281.3(5)	Sn ₂ Sn 110.11(3) P ₂ Sn 177.03(9) Cl ₂ Cl 96.4(1.2) Cl ₂ Au 101.5(1.10.1) 135.4(1.8.8) Au ₂ Au 54.06(1) P ₂ Sn 120.0(1.2.7) P ₂ Au 115.0(1.1.8) 176.2(1.1.1) Sn ₂ Au 63.0(1.3.0) 116.5(1.4.3) Au ₂ Au 60.0(1.3.7)	235
Sn + 5 M $\text{SnFe}_4(\text{CO})_{19}$ (dark green)	tr P1 2	917.9(2) 1082.5(3) 1656.5(4)	78.67(2) 78.22(2) 68.75(75(2))	SnFe_4 FeC_4Sn (x2) FeC_4Sn (x2) FeC_4Fe_2	OC not given OC not given μOC 198.9(8.6) OC not given	Fe 255.0(1.16) 259.8(1.2) Fe 287.8(2) Fe 265.8(1) 83.8(8) Fe 270.8(2.3)	Fe ₂ Fe 65.2(1.3.5) 128.0(1.2) 141.3(1.4) Sn ₂ Fe 55.6(1.6) Sn ₂ Fe 59.1(1.1) 99.0(1.1) Fe ₂ Fe 60.6(1.1) Fe ₂ Fe 58.8(1)	236

Three Types of M

$\text{Os}_3\text{PtSn}(\mu_3\text{-H}_2)$
 $(\text{CO})_9(\mu_3\text{-Cl})(\text{OEt}_2)$
 $(\text{SnCl}_3)(\text{P}^i\text{C}_3)$
 (bright orange)

m	1888.7(8)	$\text{Sn}^{\text{II}}\text{OC}(\text{Os}_3\text{Pt})$	Os^{II} 249(4) Cl 240.0(15)	Os 262.5(5,19) Pt 297.5(5)	O, Os 104.0(9,14) Os, Os 150.9(9) O, Pt 144.8(9) Cl, Os 109.1(4) Cl, Pt 83.9(4) Os, Os 64.3(1,1.3) Os, Pt 58.1(1,3,2) Cl, Os 109.8(2) Cl, Os 114.9(6,4) P, Os 131.1(4) P, Os 114.4(4) S, Os 58.5(1,5,6) C, Sn 90.3(2,7,7) C, Os 159.2(15) C, Os 88.1(19,6,2) Sn, Os 162.7(15) Sn, Os 65.2(1) Sn, Pt 61.0(1) Sn, Os 51.0(1,8) Pt, Os 58.1(1) Os, Os 105.3(1) Os, Os 95.2(1) Sn, Os 64.2(2) Pt, Os 105.4(2) Pt, Os 55.5(1)
$\text{P}2_1/\text{m}$ 4	1259.7(8) 2047.5(8)	$\text{Sn}^{\text{II}}\text{C}_3\text{Os}$	Cl 236(3,1)	Os 261.2(5)	
		PtHCP Os_2Sn	μH not given OC 204(17) P_{cy} 238.8(14)		
		OsC_4SnOs	OC 173(6) 191(6,4)	Os 300.3(3)	
		$\text{OsC}_3\text{H}_2\text{Sn} \cdot \text{PtO}_2$	OC 192(7,5)	Os 309.2(3)	
		$\text{OsH}_2\text{C}_2 - \text{Sn}_2\text{PtOs}$	OC 188(6,2)		

[W(CO) ₅ SnClFe (CQ) ₂] ₂ [N ₃ (OE _{1/2}) ₄ (C ₆ H ₅ O ₂)] (brown)	tr P ₁ 1	991.9(2) 1265.5(3) 1313.1(4)	67.72(2) 77.65(4) 70.67(2)	Sn ^{II} ClFe ₂ W	Cl 250.5(3)	Fe 268.7(1,7) W 279.9(1)	Cl ₂ W 100.8(1) Cl ₂ Fe 102.2(1,8) W ₂ Fe 123.7(1,1,3) F ₂ Fe 100.3(1) C ₂ Sn 88.0(4,2,1) 178.2(3) C ₂ Sn 85.0(4,5,3) 169.2(4,4) Sn ₂ Sn 79.7(1)	238
[C ₂ Sn ₂ (CBu) ₈ F ₂ (CO) ₄] (wine red)	tr P ₁ 2	1078.6(7) 1102.9(7) 2401.7(9)	87.04(9) 87.94(9) 79.45(9)	SnO ₂ Fe	O 195.7(1) μO 205.7(5,0) μO 195.0(6,1) 200.5(6,2) OC 175.4(9)	Fe 248.0(1) Co 297.7(3) Sn 316.5(1)	O O 75.4(2) O O 77.7(2) 80.6(3)	126

Footnotes a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Two crystallographically independent molecules present.

tetrahedral environment, with some in distorted tetrahedral or pseudo-octahedral situations. The most common ligands for Sn are the methyl group or a Cl atom. There are three hexameric clusters which contain two crystallographically independent molecules, differing mostly by degree of distortion [96,208,209], and which belong to the general class of distortion isomers [113]. The metal-metal distances in the hexamers are listed in Table 4a. The Sn-Fe bond distance of 248.0(1) [226] is the shortest in the series of hexameric heterotin clusters.

Table 4A. Summary of Sn and M-M Distances in Hexameric Heterotin Clusters

M-M'	Cov. Radius of M' [pm]	Shortest [ref]	Longest [ref]	Average	Distances > 300 pm
Sn-Al	118	278(1) [212]			
Sn-Fe	120	248.0(1) [126]	269.4(2) [238]	257.5	
Sn-Co	126	259.1(1) [232]	259.3(1) [232]	259.2	316.5(1) [126]
Sn-Ru	126	255.3(1) [207]	275.0(1) [96]	268.6	
Sn-Pt	128	255.1(1) [210]	297.5(5) [237]	265.2	
Sn-Os	128	253.0(5) [209]	267.3(1) [154]	259.2	305.8(5) [237]
Sn-Pd	131	261.4(3) [221]	262.8(3) [221]	262.1	
Sn-Rh	135	252.6(1) [42]	264.5(1) [218]	258	
Sn-Sb	140	278.9(1) [213]	280.5(1) [213]	279.5	
Sn-Au	143	281.5(8) [235]	297.3(8) [235]	289.4	
Sn-Mo	145	287.7(2) [223]	289.8(2) [223]	288.7	
Sn-W	146	279.9(1) [283]			350.8(6) [224]
Sn-Mn	146	250.8(3) [228]	275.9(3) [228]	265.7	
Sn-Re	159	269.5(3) [233]	277.6(1) [234]	274.6	
Sn-Sn		285.1(2) [228]	289.4(5) [226]	287.0	323.6(2) [212] – 464.7(2) [224]
Fe-Fe		265.8(2) [236]	287.8(2) [236]	273.8	
Co-Co		297.7(3) [126]			
Mn-Mn					308.6(1) [227]; 309.1(1) [166]
Re-Re					316.0(2) [233]; 317.6(1) [234]
Ru-Ru		288.7(1) [96]	297.7(1) [96]	294.0	311.6(3) [217]
Pt-Pt		275.3(1) [221]	277.5(1) [221]	276.3	
Os-Os		297.4(1)			300.3(3) – 309.2(3) [237]
Pd-Pd		279.5(2) [221]	283.4(1) [221]	281.4	
Sb-Sb		287.6(1) [213]	288.6(1) [213]	288.0	
Au-Au		263.4(1) [235]	281.3(5) [235]	274.6	

6. HEPTAMERIC HETEROTIN COMPOUNDS

There are thirteen heptameric heterotin clusters summarised in Table 5 and referenced in order of decreasing number of tin atoms, without sub-headings. Only transition heterometal atoms are found in this series.

The structure of an orange-yellow Sn_6Fe cluster is shown in Figure 12. The central part of the molecule contains a ball framework of SnO_6 . The $\text{Fe}(\text{CO})_4$ moiety is directly bound to a Sn atom with the Sn-Fe bond distance of 247.2 pm.

An orange Sn_2Mn_4 cluster [240] has a cubane-like $\text{Sn}_3\text{S}_4\text{Mn}$ cage. Each Sn(II) atom is bonded to a $\text{Mn}(\text{cp}(\text{CO})_2)$ moiety and completes a quasi-tetrahedral environment about each Sn(II) atom (SnS_3Mn) with the Sn-Mn bond distance of 245.5(1) pm. A pale brown Sn_3Fe_4 cluster [230] contains a tricyclic $\text{Sn}_3\text{S}_4\text{Fe}$ cage. Two rings are five membered $\text{Sn}_2\text{S}_2\text{Fe}$ and the other is four membered Sn_2S_2 , requiring that two Sn atoms and one S atom belong to all three rings. Each Sn atom is also bonded to an $\text{Fe}(\text{cp}(\text{CO})_2)$ moiety. The ring Fe is also coordinated to a terminal CO group and a cyclopentadienyl ligand. The Sn-Fe bond distances range from 250.3(2) to 257.0(2) pm (average 252.3 pm). Each Sn atom is quasi-tetrahedral, two with the chromophore SnS_3Fe and one with SnS_2Fe_2 . Dark green $\text{Me}_4\text{Sn}_3\text{Fe}_4(\text{CO})_{16}$ [241] contains almost exactly planar Sn_2Fe_2 rings, causing the compression of the average Sn-Fe-Sn angle to 77.9° . The Fe-Sn-Fe angles within the ring are at 105.2° at the terminal Sn atom and 98.8° at the central Sn atom. Each Sn atom is tetrahedrally coordinated, the central tin bonded to four $\text{Fe}(\text{CO})_4$ groups (average Sn-Fe = 274.7 pm), and the terminal tin to two $\text{Fe}(\text{CO})_4$ groups (average Sn-Fe = 262.5 pm) and two methyl groups.

The molecule of a green cluster [242] can be described as a hexametallc Ir_4Sn_2 planar "raft" surmounted by a $\mu_4\text{-RSnO}_3$ "sail". The geometry about the capping tin of the sail is that of a highly distorted trigonal bipyramid (SnO_3ClIr) with Sn-Ir bond distance of 263.7(6) pm. The remaining Sn atoms are quasi-tetrahedral (SnC_2Ir_2) with Sn-Ir bond distances of 267.6(6) and 268.0(6) pm.

The structure of a black Sn_2Fe_3 cluster [243] consists of an equatorial $\text{Fe}_3(\text{CO})_9$ triangular cluster capped

TABLE 5. Crystallographic and Structural Data for Heptameric Hetero Tin Clusters^a

COMPOUND (color)	Crys.cl Sp.Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo- phore.	M-L [pm]	M-M [pm] M-L-M [°]	L-M-L [°]	Ref
$[\text{Fe}(\text{CO})_4\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OSiMe}_3)_4]$ (orange-yellow)	m P2 ₁ /n 4	1340.4(2) 1696.4(3) 1776.6(2)	90.384(12)	SnO ₄ Fe	$\mu_3\text{O}$ 200.5(-15) $\mu_3\text{OR}$ 233.5(-62)	Fe 247.2	O ^b _R 77.8(-15) O _O 100.1 O ₃ O _R 141.4 O ₂ O _R 75.1(-1.5) O _O 92.5(-.4) O ₃ O _R 136.3(-.7) C ₃ C 94.7(-1.9) 111.0, 163.1	239
$[\{(\eta^5\text{-CO})_2\text{MnSn}\}_3(\mu_3\text{-S})_3\mu_3\text{Mn}(\text{thf})_3]$ (orange) (at 208K)	rh R3 2	1408.9(7)	71.36(4)	SnO ₃ (x5) F ₂ C ₄ Sn	$\mu_3\text{O}$ 208.7(-23) $\mu_3\text{OR}$ 244.8(-39) OC 176.8(-42)	Mn 245.5(1) S 89.1(1.1,4) 89.0(1.3)	S _S 91.9(12.0) S _S 88.2(1)	240
$[\text{CF}_3(\text{CO})_7\text{Fe}_2\text{S}_3(\mu_3\text{-S})(\mu\text{-S})_3\text{thf}]$ (pale brown) (at 210K)	tr P1 2	1215.5(5) 1226.1(9) 1563.8(8)	76.00(5) 71.23(3) 61.24(5)	SnS ₂ Fe ₂ SnS ₃ Fe(x2) FeepCSSn FeepC ₃ Sn (x3)	μS 251.2(3,9) μS 242.2(3,31) $\mu_3\text{S}$ 251.5(3,17) C _p 208(1,4) OC 175(1,1) $\mu_3\text{S}$ 227.9(3)	Fe 251.3(2) S 257.0(2) S 98.3(1,1) Fe 250.4(2.1) μS 86.2(1) $\mu_3\text{S}$ 83.3(1) - 113.5(1,5)	S _S 103.8(1) F ₂ Fe 129.0(1) SFe 106.4(1,9) S _S 100.5(1,9.1) SFe 117.0(1,3.4) S ₃ Sn 87.9(1)	230

$\text{Me}_4\text{Sn}_3\text{Fe}_4(\text{CO})_{16}$ (dark green)	m $\text{P2}_1/\text{c}$ 4	1104(2) 1636(1) 1909(1)	108.5(2)	SnFe_4 $\text{Sn}_2\text{C}_2\text{Fe}_2(\times 2)$ FeC_4Sn_2	C_{48} OC	Fe 273.3(10.1) 276.0(10.6) Fe 261.4(5.9) 263.6(5.3)	FeFe 98.8(5.7) 115.0(5.1.2) C-C 106(4) FeFe 105.2(5.8) C-Fe 111(2.3) C-Sn 83(2.3) 106(2.3) 168(2.9)	241
$[\text{Ir}_4\text{Sn}_2(\text{CO})_8\{\text{CH}(\text{SiMe}_3)_2\}_2\text{O}_3]$ (green)	tr P1 2	1209.5(9) 1551.1(11) 2251(2)	82.48(5) 87.86(5) 75.56(5)	SnO_2ClIr $\text{Sn}_2\text{C}_2\text{Ir}_2(\times 2)$ $\text{IrC}_2\text{Sn}_2\text{Ir}_3$ $\text{IrC}_2\text{OSnIr}_2(\times 3)$ SnFe_{124}	μO 230.8(26) 219.3(25.1) OC not given μO 212.0(26) 213.2(26.2)	Ir 263.7(6) Ir 267.8(6.2)	C-Ir 150.1(11) not given not given	242
$[\{\text{cpFe}(\text{CO})_2\}_2\text{Sn}_2\text{Fe}_2(\text{CO})_8]$ (black)	m $\text{P2}_1/\text{c}$ 4	1985.9(15) 1093.8(12) 1568.7(12)	119.83(3)	$\text{FeC}_3\text{SnFe}_3(\times 3)$ $\text{Feq}(\text{C}_2\text{Fe})(\times 1)$ SnClC_3	OC not given Cl 241.8(2)	Fe 247.1(5) 2.57(4) Fe 179.2(6)	FeFe 64.5 140.5 not given not given	243
$[\text{Co}\{\text{HB}(\text{pz})_3\}_2]$ $[\text{Sn}_2\text{Co}_3\text{Cl}_2(\text{CO})_{19}]$	m C2/c 4	2732.5(4) 951.6(1) 2331.6(8)	113.51(2)	CoC_3Sn_2 $\text{CoC}_4\text{Sn}(\times 4)$	OC 175(1.2) OC 175(1.2)	Co 250.8(1) 256.2(1.6)	Cl_2Co 104.4(1.4.3) Co_2Co 114.0(1.3.7) C-Sn 89.5(3.0) Sn-Sn 179.1(1) C-Sn 84.8(3) 178.2(3)	244
$[\{\text{SnEu}_2\}(\text{Nb}_6\text{Cl}_{19})\{\text{PhC}_4\}_3]_2$ (brown black) at 193K	m C2/c 8	3525.0(7) 2404.8(2) 2795.6(6)	102.74(2)	SnC_3Cl_2 $\text{NbCl}_6\text{Nb}_2(\times 3)$ $\text{NbCl}_5\text{C}_4(\times 3)$	C_{84} 214.8(20.48) μCl 274.6(4.4) μCl 245.3(5.72) $\mu_3\text{Cl}$ 243.7(4.15) Cl 237.0(4.71) μCl 261.1(4.124) O^4C 235.1(16.26)	Nb 286.6(2.17) μCl 73.0(1.3) $\mu_3\text{Cl}$ 72.0(1.7)	C-C 120.0(7.3.4) Cl_2Cl 179.5(1) C-Cl 90.0(5.5.5) Cl_2Cl 89.5(1.17.9) 163.8(2.4.3) Nb-Nb 60.0(1.6) Cl_2Cl 73.6(1) - 155.5(2) Cl_2C 77.7(4) 158.3(4)	245

$[(\text{H}_2\text{O})_9\text{Mo}_3\text{S}_3\text{SnS}_4]$	tr	1449.9(4)	105.16(3)	$\text{Sn}^{\text{II}}\text{S}_6$	$\mu_3\text{S}$ 251.3(3,3)	Mo 373.9(1)	S,S not given	246
$\text{Mo}_3(\text{H}_2\text{O})_9$	P1	1851.7(6)	119.92(2)		265.9(3)			
$\text{Me}(\text{C}_6\text{H}_4\text{SO}_3)_8$	1	1374.6(5)	72.59(3)	MoO_3S_3	H_2O 217.7(-20)	Mo 268.8(2.8)	not given	
$\cdot 26\text{H}_2\text{O}$					$\mu_3\text{S}$ 234.0(3,4)			
(dark brown)	rh	2079.2(6)	44.80(1)	$\text{Sn}^{\text{II}}\text{S}_3\text{Mn}$	$\mu_3\text{S}$ 247.6(4,23)	Mn 247.0(2)	S,S 94.1(2,5.9)	240
$\{\text{Na}(2,2,2)\text{cryptan}\}$	R3				256.5(3,14)	88.9(1,2.5)		
$\{[\text{cp}](\text{CO})_2\text{MnSn}\}_3$	2			$\text{Mn}(\text{C}_2\text{Sn})$	$\mu_3\text{S}$ 300.8(7)	90.4(1,1)	S,S 78.6(2)	
$\{\text{Na}(\text{thf})_3\}$				NaO_3S_3	$\mu_3\text{S}$ 298.2(6)	89.6(1,2)	S,S 79.3(3)	
(orange)								
at 208K								
$(\text{NEt}_4)_2\{(\text{CO})_4\text{FeSn}\}$	m	1043.1(1)		SnCl_2Fe_2	Cl 242.8(3,0)	Fe 249.6(1)	not given	247
$\text{Cl}_2\text{Fe}(\text{CO})_3\text{Hg}$	P2 ₁ /n	1331.4(2)	93.55(3)	HgFe ₂		255.3(1)	not given	
(orange)	4	1836.6(5)		FeC_4HgSn	OC 179.0(11,13)	Fe 257.1(1)	not given	
				FeC_4Sn	OC 176.1(11,3)		not given	
$\{[\text{SnMn}(\text{CO})_5]_2\text{Fe}_3$	m	956.5(2)		$\text{S}_3^{\text{IV}}\text{Fe}_3\text{Mn}$	not given			248
$(\text{CO})_9\}$	P2 ₁ /n	1132.2(2)	96.05(1)	$\text{FeC}_3\text{Sn}_2\text{Fe}_2$				
	4	2773.1(5)		MnC_5Sn				
$[\text{Fe}_3(\text{CO})_9\{\mu_3\text{-SnRe}$	m	972.5(2)		SnFe_3Re		Fe 254.3(3,49)	Fe,Fe 67.0(1,2)	746
$(\text{CO})_3\}$	P2 ₁ /n	1148.3(3)	96.89(2)			Re 2.726(2,14)	Fe,Re 140.4(1,1)	
(dark red)	4	2793.6(7)		$\text{FeC}_3\text{SnFe}_2$	OC 171.0(29)	Fe 283.7(4)	C,C 97.9(11)	
				ReC_5Sn	OC 194.6(29)		not given	

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parentheses is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

on both sides by $\text{SnFe}(\text{CO})_2\text{cp}$ fragments. All carbonyl groups in the molecule are terminally bonded. Three of them are approximately in the equatorial plane, which roughly defines a non-crystallographic mirror plane for the molecule. The average distances in the core of the molecule are: $\text{Sn-Fe}(\text{terminal})$ 247.1(5) pm; $\text{Sn-Fe}(\text{equatorial})$ 253.7(4) pm; Fe-Fe 279.2(6) pm.

Fig.12. Structure of $[\text{Fe}(\text{CO})_4\text{Sn}_6\text{O}_4(\text{OSiMe}_3)_4]$ [239]

The structure of $[\text{Co}\{\text{HB}(\text{pz})_3\}_2]^+ [\text{Sn}_3\text{Co}_5\text{Cl}_2(\text{CO})_{19}]^-$ [244] consists of discrete cations and anions. the latter consists of two $\text{Sn}(\text{Cl})\{\text{Co}(\text{CO})_4\}_2$ groups bonded *trans* to each other about the planar $\text{Co}(\text{CO})_3$ fragment. Within these groups the $\text{Co}(\text{CO})_4$ moieties have a trigonal bipyramidal geometry (CoC_3Sn_2) with average Sn-Co bond distance of 266.2(1) pm. Both tin atoms are tetrahedrally coordinated (SnClCo_3) with the $\text{Sn-Co}(\text{central})$ bond of 250.8(1) pm, which is about 15.4 pm shorter than the remaining two Sn-Co bond distances (average 266.2(1) pm).

A brown-black SnNb_6 cluster [245] contains a central Nb_3 cluster plus three outer Nb atoms bonded to η^4 -tetraphenylcyclobutadiene ligands. The Bu_3Sn unit has an effectively trigonal-planar structure with Cl atoms occupying axial positions to complete a trigonal-bipyramid. The entity consists of a central triangular $\text{Nb}_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3$ cluster with $\text{Cl}_3\text{NbCl}_2(\eta^4\text{-C}_4\text{Ph})$ units. A dark brown SnMo_6 cluster [246] contains a heterometal double cubane type $\text{Mo}_3\text{S}_4\text{SnS}_4\text{Mo}_3$ core with the mean Mo-Mo distance of 268.8(2) pm, with a six coordinate Sn(II) atom (SnS_6).

The structure of an orange $\text{Sn}_3\text{Mn}_3\text{Na}$ cluster [240] is similar to that of the Sn_3Mn_4 cluster [240] in which the Mn atom is substituted by Na to give a $\text{Sn}_3\text{S}_4\text{Na}$ core. Each Sn(II) atom is also bonded to a $\text{Mn}(\text{CO})_2\text{cp}$ moiety, giving a quasi-tetrahedral arrangement about each Sn(II) atom (SnS_3Mn) with Sn-Mn bond distance of 247.0(2) pm. An orange $\text{Sn}_2\text{Fe}_4\text{Hg}$ cluster [247] contains the unbridged FeSnFeHgFeSnFe skeleton with metal-metal bonds of value: Hg-Fe 257.1(1) pm; $\text{Sn-Fe}(\text{outer})$ 249.6(1) pm and $\text{Sn-Fe}(\text{inner})$ 259.3(1) pm.

Table 5A. Summary of Sn-M and M-M Distances in Heptameric Heterotin Clusters

M-M'	Cov. Radius of M [pm]	Distances [pm]		
		Shortest [ref]	Longest [ref]	Average
Sn-Fe	120	247.1(5) [243]	259.3(1) [247]	254.8
Sn-Co	126	250.8(1) [244]	266.8(1) [244]	261.1
Sn-Ir	137	263.7(6) [242]	268.0(6) [242]	266.4
Sn-Mn	146	245.5(1) [240]	247.0(2) [240]	246.2
Sn-Re	159	271.2(2) [74b]	274.0(2) [74b]	272.6
Fe-Fe		273.1(5) [241]	280.7(4) [74b]	276.4
Fe-Hg		257.1(1) [247]		
Nb-Nb		284.9(2) [245]	288.2(2) [245]	286.6

The data in Table 5 show tin to be predominantly tetrahedral in these derivatives, with some examples of trigonal-bipyramidal and octahedral coordination with varying degrees of distortion. The most common heterometal atom is iron, and there are only four donor ligand atoms, O, S, Cl and C. The metal-metal bond distances are summarised in Table 5A, where it can be seen that the shortest is Sn-Mn at 245.5(1) pm.

7. OCTAMERIC HETEROTIN COMPOUNDS

The data for twelve octameric heterotin compounds are given in Table 6. The structures are listed and discussed in order of decreasing number of tin atoms. The heterometal atoms include both transition and non-transition metals.

The highest number of tin atoms is exhibited in an orange red Sn_6Fe_2 cluster [239] which has a structure similar to that of a previous Sn_6Fe cluster shown in Figure 12 [239]. In the octamer an additional $\text{Fe}(\text{CO})_4$ moiety is bonded to the Sn(6) atom with an Sn-Fe bond distance of 246.3(1) pm, shorter by 0.9 pm than that found in the heptamer. There are two sets of Sn atoms, one with distorted trigonal-bipyramidal geometry (SnO_4Fe) and the other with distorted tetrahedral geometry SnO_4 .

A red Sn_4Li_4 cluster [113a] contains a fourteen membered $\text{Sn}_4\text{P}_6\text{Li}_4$ core. The molecule consists of an association between the $[\text{Sn}_2(\text{Pcy})_2]^-$ anion and four $[\text{Li}(\text{thf})_4]^+$ cations. The anion can be viewed as constructed of two puckered $\text{Sn}_2(\text{Pcy})_2$ dimer rings linked by two dimer bridging Pcy groups. The four Li^+ cations are bonded to the P centres of the $\text{Sn}_2(\mu\text{-Pcy})_2$ dimer units and to the P centres of the dimer in the equatorial position of the anion. The Sn(II) atom is tricoordinate (SnP_3). A colourless Sn_4Al_4 cluster [249] has a central $\text{O}_2\text{Sn}_4\text{Cl}_2$ core of approximately D_{2h} symmetry, with four coordinate $\mu_4\text{-O}$ and $\mu_4\text{-Cl}$ atoms. The $(\text{PrO})_2\text{Al}_2$ dimers are connected with the central core by $\mu_4\text{-O}$ and $\mu\text{-OPr}$ bridged groups. Each metal atom has a distorted trigonal-bipyramidal environment (SnO_3Cl_2 and AlO_4Cl). Another colourless Sn_4Al_4 cluster [250] is shown in Figure 13. It is composed of dimeric units $[(\eta^6\text{-C}_6\text{Me}_6)\text{SnCl}(\text{AlCl}_4)]_2$ containing crystallographically non-equivalent monomers. These dimers are cross-linked to form centrosymmetrical tetramers. The molecular unit of the white Sn_4Cd_4 cluster [251] includes a planar eight membered ring of four Cd atoms linked in pairs by single O atoms of two acetate anions. Each of these is also chelated to one of the Cd atoms being bridged. The ring is completed by two oxo-groups, each linking a pair of Cd atoms on opposite sides of the ring. Pairs of Sn atoms are also bonded to the oxo-groups, making them four coordinate.

Fig.13. Structure of $[(\text{C}_6\text{Me}_6)\text{SnCl}(\text{AlCl}_4)]_4$ [250]

The structure of a deep red Sn_4Mo_4 cluster [223] consists of an adamantane-like Sn_4Te_6 framework. Each Sn atom is bonded to a $\text{Mo}(\text{CO})_2\text{cp}$ unit with average Sn-Mo bond distance of 280.2(3) pm. Each Sn atom has a quasi-tetrahedral environment (SnTe_3Mo). A Sn_4W_4 cluster [252] contains two structurally similar but symmetry independent molecules in a unit cell. Each has a crystallographically imposed centre of symmetry located in the middle of the sixteen membered ring, which is formally a $[\text{-O-Wcp}(\text{O})\text{-O-SnMe}_3\text{-}]_4$ tetramer. The interplanar angle between the Sn_4 and W_4 planes in one molecule is 11° and in the other is 14° . Each Sn atom has a trigonal bipyramidal arrangement (SnC_3O_2), and each W atom has a typical three legged piano-stool geometry. There are two orange [230] and one yellow [253] Sn_4Fe_4 clusters, all isostructural with an adamantane-like cage Sn_4X_6 ($\text{X} = \text{S}$ [253] or Se [230]). Each of four $\text{Fcpc}(\text{CO})_2$ moieties is coordinated to the Sn atom giving a quasi-tetrahedral environment (SnX_3Fe). The mean Sn-Fe bond distances are 250.4 pm [253] and 252.6 pm [230].

TABLE 6. Crystallographic and Structural Data for Octameric Hetero Tin Clusters^a

COMPOUND (colour)	Crys.cl Sp. Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo- phore.	M-L [pm]	M-M [pm]	L-M-L [°]	Ref		
[Fe(CO) ₄] ₂ Sn ₆ (μ ₃ -O) ₄ , (μ ₃ -OSiMe ₃) ₄ 0.5C ₆ H ₆ (orange red)	m	1180.4(2)		SnO ₄ Fe (x3)	μ ₃ O' 202.5(-.17)	Fe 246.3(1)	O O 97.9(-.4)	239		
	P2 ₁ /n	1748.9(3)	97.146(9)		μ ₃ Or 234.0(-.41)		O O ₂ 76.8(-1.5)			
	4	2322.2(2)		SnO ₄ (x3)	μ ₃ O 219.4(-.18)		Or ₂ Or 139.3(1)			
					μ ₃ Or 241.4(-.84)		O O 92.5(-.8)			
[Sn ₂ (Pcy) ₃] ₂ Li ₄ (thf) ₄ 2thf (red) at 155(2)K	m	2915.9(5)		FeC ₄ Sn	OC 176.9(-.29)		O ₂ Or 134.3(-.1)	113a		
	C2/c	1498.1(2)	115.253(9)	Sn ^{II} P ₃	μ ₄ P 260.6(4) -		C C 92.4(-.14)			
	4	1923.5(3)		Li ^I P ₃ O	μ ₄ P 251.2(-.24(2)		114.2(-.43)			
					O _{thf} 192		170.9(-.25)			
[{(C ¹⁸ O) ₈ Cl ₂ Al ₂ }] ₂ O ₃ Sn ₄ Cl ₂ (colourless)	or	1925.5(9)		SnO ₄ Cl ₂	μ ₄ O 207.4(2.1)		P P 88.4(1) -	113a		
	Pbca	1445.7(8)			μ ₄ O 224.2(4.12)		100.1(1)			
	4	2036.7(9)			μ ₄ Cl 302.9(2.31)	μ ₄ O 127.4(2)	108.6		249	
					321.1(2.8)	μ ₄ Cl 75.71(11)				
[O ⁵ -C ₃ Me ₆] ₂ SnCl (AlCl ₄) ₂ 1.5PhCl (colourless) at 238K	tr ₋	1248.1(2)	100.77(1)	AlO ₂ Cl	μ ₄ O 191.5(4.3)		O O 67.9(1.5)	250		
	P1	1474.9(2)	93.62(1)		μ ₄ O 182.3(4.26)		56.0(1.5)			
	1	1289.9(2)	100.98(1)		Cl 219.5(3.1)		Cl ₂ Cl 66.2(1.4)			
						μ ₄ O 97.2(2)	O ₂ Cl 74.0(1.12)			
[O ⁵ -C ₃ Me ₆] ₂ SnCl (AlCl ₄) ₂ 1.5PhCl (colourless) at 238K	tr ₋	1248.1(2)	100.77(1)	SnC ₆ Cl ₅ (x2)	μ ₄ O 191.5(4.3)		85.9(1.44)			
	P1	1474.9(2)	93.62(1)		μ ₄ O 182.3(4.26)		137.6(1.13)			
	1	1289.9(2)	100.98(1)		Cl 219.5(3.1)		O O 80.5(2.6)			
						μ ₄ O 97.2(2)	117.3(2,18.0)			
[O ⁵ -C ₃ Me ₆] ₂ SnCl (AlCl ₄) ₂ 1.5PhCl (colourless) at 238K	tr ₋	1248.1(2)	100.77(1)	SnC ₆ Cl ₆ (x2)	μ ₄ Cl 312.5(1)		O ₂ Cl 99.7(2.65)	250		
	P1	1474.9(2)	93.62(1)		μ ₄ Cl 261.5(1.29)		175.7(2.22)			
	1	1289.9(2)	100.98(1)		349.5(2,130)	μ ₄ O 102.0(2)	not given			
					μ ₃ Cl 338.0(1)	S ₁ 389.3(3)				
[O ⁵ -C ₃ Me ₆] ₂ SnCl (AlCl ₄) ₂ 1.5PhCl (colourless) at 238K	tr ₋	1248.1(2)	100.77(1)	AlCl ₄ (x2)	μ ₄ Cl 274.0(1.68)		μ ₄ Cl 73.4(1)			
	P1	1474.9(2)	93.62(1)		336.8(1,129)		μ ₄ Cl 94.2(1.9)			
	1	1289.9(2)	100.98(1)		μ ₃ Cl 216.6(2)					
					μ ₄ Cl 212.8(2.8)					
[O ⁵ -C ₃ Me ₆] ₂ SnCl (AlCl ₄) ₂ 1.5PhCl (colourless) at 238K	tr ₋	1248.1(2)	100.77(1)	AlCl ₄ (x2)	μ ₄ Cl 217.0(2.22)					
	P1	1474.9(2)	93.62(1)		Cl 210.9(2.5)					
	1	1289.9(2)	100.98(1)							

$\text{Cd}_4\text{Sn}_4(\mu_4\text{O})_2(\text{ac})_{10}$ ($\text{Br}^-\text{CH}_3\text{O})_{10}$ (white)	m C _{2/c} 4	2531.6(15) 1507.6(7) 2822.1(10)	98.16(4)	SnO_5	$\mu_4\text{O}$ not given $\mu_4\text{O}$ 236.9(16,35) O_{25} 212.5(17,61) O 195.5(19)	$\mu_4\text{O}$ 103.4(7) $\mu_4\text{O}$ 97.7(7)	O O 87.5(6)	251
				CdO_5	$\mu_4\text{O}$ not given $\mu_4\text{O}_{\text{ac}}$ 225.6(20) O_{ac} 230.1(20) $\mu_4\text{O}$ not given $\mu_4\text{O}_{\text{ac}}$ 234.6(18) O_{ac} 231.0(18)	$\mu_4\text{O}$ 124.5(1) $\mu_4\text{O}$ 90.3(7)	O O 166.8(5)	
				CdO_7	$\mu_4\text{O}$ not given $\mu_4\text{O}_{\text{ac}}$ 234.6(18) O_{ac} 231.0(18)		O O 54.7(7) 82.4, 106.4 148.9(6)	
$[\{\text{cp}(\text{CO})_2\text{Mo}\}_4\text{Sn}_4\text{Te}_6]$ 2.5 to 1 (deep red) at 200K	m $\text{P}2_1/\text{m}$ 4	1324.2(7) 2498.8(14) 2058.8(15)	91.38(5)	SnTe_3Mo	$\mu_4\text{Te}$ 275.2(2,12)	Mo 280.2(3,5) 105.9(1,2,2)	TeTe 111.1(1,3,3) TeMo 107.7(1,5,7) not given	223
$[\text{M}(\text{Fe}_3\text{Sn})_4]$ $\{\text{cp}^*\text{W}(\text{O})\}_4(\mu-\text{O})_8]^2$	tr $\text{P}\bar{1}$ 2	1440.3(3) 1505.1(4) 1608.4(4)	86.18(3) ? 86.88(3)	MoepC_2Sn $\text{Sn}^{\text{IV}}\text{C}_3\text{O}_2$ WepO_3	OC 200(2,3) C_{ep} 232(2,6) C_{Me} no. given $\mu_4\text{O}$ 224.5(12,36) O 172.2(15,13) $\mu_4\text{O}$ 177.3(15,11) cp not given $\mu_4\text{O}$ 222.9(14,6) O 173.4(14,4) $\mu_4\text{O}$ 178.2(14,30) $\mu_4\text{S}$ 242.0(9,23)	147.2(7,8,2)	O, O 178.2(5,4) O O 105.5(6,1,0)	252
				$\{\text{Sn}^{\text{IV}}\text{C}_3\text{O}_2\}$ WepO_3	$\mu_4\text{O}$ 222.9(14,6) O 173.4(14,4) $\mu_4\text{O}$ 178.2(14,30) $\mu_4\text{S}$ 242.0(9,23)	146.6(6,5,6)	O, O 177.8(5,4) O, O 104.7(7,1,1)	
$[\{\text{cp}(\text{CO})_2\text{Fe}\}_4\text{Sn}_4\text{S}_6]$ $2\text{CH}_2\text{Cl}_2$ (yellow)	m $\text{P}2_1/\text{m}$ 2	1144.2(2) 1952.8(5) 1152.1(1)	98.73(2)	SnS_3Fe	not given $\mu_4\text{S}$ 254.4(4,20)	Fe 249.9(7,0) 251.3(5,0)	S S 109.2(4,1,9) S_4Fe 109.9(2,1,5)	253
$[\{\text{cp}(\text{CO})_2\text{Fe}\}_4\text{Sn}_4\text{Se}_6]^2$ (orange-red) at 180K	tg $\text{P}4_2/\text{mnc}$ 12	2277(2) - 3362(2)		FeepC_2Sn SnSe_3Fe	not given $\mu_4\text{Se}$ 254.4(4,20)	Fe 250.0(6,5) 253.0(6) 107.9(1,9)	SeSe 110.3(1,2,0) SeFe 108.7(1,1,8)	230
				FeepC_2Sn	O, C 177(3,3) C_{ep} 234 - 226(6) $\mu_4\text{Se}$ 254.2(4,6)	Fe 249.0(5) 253.3(4) 107.2(1,3)	SeSe 110.7(1,7) SeFe 108.3(1,1,9)	
				SnSe_3Fe	no. given			
				FeepC_2Sn	no. given			

$[\text{Os}_4(\mu_3\text{-O})_2(\text{SnMe}_2)_4(\text{CO})_{14}] \text{ tol}$ (yellow)	m $P2_1/a$ 2	1389.5(2) 1255.0(2) 1405.3(2)	113.56(1)	SnC_2OOs	C_{46} 214(1,3) $\mu_3\text{O}$ 204.2(8,9)	Os 266.9(1,4) 127.3(4)	C 109.0(6,3,5) C, O 102.5(4,1,8) C, O 117.5(4,6,4) O, O 104.2(2,7,8)	154
				OsC_3OSnOs	OC 191(1,3) $\mu_3\text{O}$ 215.8(7) OC 194(2,2)	Os 297.02(8) 125.0(4)	O, Sn 98.5(2) O, Os 85.5(2) Sn, Os 72.40(3)	
$\text{Sn}_2\text{Fe}_6(\text{CO})_{23}$ (dark brown) at 183K	tr $P1$ 2	822.1(1) 1255.1(3) 1644.4(5)	95.65(2) 104.53(2) 100.83(2)	SnFe_4		Fe 255.1(5,22) 259.1(4,21) Fe 273.4(5)	Fe, Fe 66.2(2,2,1) 134.7(2,8,2) Sn, Sn 91.6(1,8) Sn, Fe 57.9(1,1,2) Sn, Fe 55.8(1,4)	254
				$\text{FeC}_4\text{Sn}_2\text{Fe}$ (1:2) μOC not given $\text{FeC}_4\text{Sn}_2\text{Fe}$ (1:4)	OC not given μOC not given OC not given	Fe 285.7(6) 286.2(7)	not given not given not given	
$[\text{Pt}_6(\mu_3\text{SnBr}_3)_2(\mu\text{-CO})_6(\mu\text{-dppm})_3]$	m $P2_1/c$ 4	1683.1(3) 1858.8(3) 3357.5(6)	90.20(2)	SnBr_3Pt_3	Br not given	Pt 274.5(3) 295.0(3)	not given	255
				$\text{PtC}_2\text{SnPt}_3$	not given	Pt 266.8(2,13) 293.7(2,9)	not given	

Footnotes : a Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

c. Two crystallographically independent molecules.

A yellow Sn_4Os_4 cluster [154] has a crystallographic 2-fold axis that passes through the centre of an $\text{Os}_2\text{Sn}_2\text{O}_2$ ring. Four membered, essentially planar, Os_2SnO rings share OsO edges with the central ring. The dihedral angle between the planes is 1.5° . The central ring has a boat conformation, with dihedral angle of 46.4° . Each tin atom has a quasi-tetrahedral environment (SnC_2OOs) with average Sn-Os bond distance of 266.9(1) pm.

A dark brown $\text{Sn}_2\text{Fe}_6(\text{CO})_{23}$ cluster [254] contains four SnFe_2 triangles, as shown in Figure 14. Two triangles with a common edge have a dihedral angle of $73.1(1)^\circ$ at one Sn atom and 83° at the other. The butterfly angle between the two central triangles is $115.8(1)^\circ$. The Sn-Fe bond distance ranges from 252.9(5) to 261.2(4) pm (average 256 pm), while the Sn-Sn separation is essentially non-bonding at 369 pm. A Sn_2Pt_6 cluster [255] is shown in Figure 15. The molecule has approximately D_{3h} symmetry, and the metal core can be described as a trigonal prism of Pt atoms, with each triangular face capped by a SnBr_3 group. Thus both the Pt_3 triangles and the SnBr_3 groups are eclipsed. The Pt-Pt bond length within each triangle ranges from 265.6(2) to 294.6(2) pm. The Pt-Sn distances are in the range 274.5(3) to 295.0(3) pm.

Fig.14. Structure of $\text{Sn}_2\text{Fe}_6(\text{CO})_{23}$ [254]

Fig.15. Structure of $[\text{Pt}_6(\mu_3\text{-SnBr}_3)_2(\mu\text{-dppm})_3]$ [255]

The data in Table 6 indicate the most favoured cluster is Sn_4M_4 (nine out of twelve). The most common donor atom is oxygen. Despite the few examples, tin was found in all its commonest coordination environments, tetrahedral, trigonal planar, trigonal bipyramidal and octahedral. Distorted tetrahedral was found to be the most common geometry. The metal-metal bond distances are summarised in Table 6A for the octameric derivatives. The shortest value was observed for Sn-Fe at 246.3(1) pm [239].

Table 6A Summary of Sn-M and M-M Distances in Octameric Heterotin Clusters

M-M'	Covalent Radius of M' [pm]	Distances [pm]		Average
		Shortest [ref]	Longest [ref]	
Sn-Fe	120	246.3(1) [239]	261.2(5) [254]	253.3
Sn-Os	128	266.6(1) [154]	267.3(1) [154]	267
Sn-Pt	124	274.5(3) [255]	295.0(3) [255]	not given
Sn-Mo	145	279.7(3) [223]	280.7(3) [223]	280.2
Fe-Fe		273.4(5) [254]	286.2(7) [254]	281.8
Os-Os		297.02(8) [154]		
Pt-Pt		265.6(2) [255]	294.6(2) [255]	not given

8. OLIGOMERIC DERIVATIVES

The data for almost twenty oligomeric derivatives are given in Table 7. The structures are listed in order of increasing nuclearity, and secondarily by decreasing number of tin atoms, without sub-headings. All classes of heterometal atom are represented in this series.

Two anions, TiSn_8^- and TiSn_9^- exhibit an unusual 50:50 occupational disorder in a single anionic site, with seven atoms coincident in both species of this red brown cluster [256]. The former has a tricapped trigonal-

prismatic configuration, while the latter has a bicapped square-antiprismatic geometry. The average Sn-Tl distance of 306.3 pm in the former is about 55 pm shorter than that found in the latter (311.8 pm). The Sn-Sn distance in the former ranges from 287.9(4) to 330.1(5) pm, and in the latter from 286.2(4) to 325.3(4) pm.

There are three coloured Sn_8Ln ($\text{Ln} = \text{Sm}$ or Yb) isostructural clusters [257]. The Yb derivative exists in two isomeric forms, orthorhombic and tetragonal. The molecules of the clusters have a distorted octahedral structure in which the central Ln atom is bonded to four O atoms of (thf) molecules equatorially and two Sn(II) atoms of two $\text{Sn}(\text{SnMe}_3)_3$ moieties axially. The Sn-Ln bond angles are $178.8(1)^\circ$ ($\text{Ln} = \text{Sm}$), $178.5(1)^\circ$ (Yb, orthorhombic) and $176.2(1)^\circ$ (Yb, tetragonal). The average Ln-Sn distances are 339.4(4) pm (Sm), 329.4(5) pm (Yb, orthorhombic) and 330.0(4) pm (Yb, tetragonal). Two Sn(II) atoms in each cluster contain the SnLnSn_3 chromophore with average Sn-Sn distances of 277.8(6), 278.6(6) and 280.0(4) pm, respectively. The remaining six Sn(II) atoms in each of the respective clusters contain the SnC_3C chromophore.

A red cluster [258] contains $[\text{Au}_8(\text{PPh}_3)_7(\text{SnCl}_3)]^+$ cations and $[\text{SnCl}_6]^-$ anions. The structure of the cation is shown in Figure 16. The gold atoms in the structure are arranged in a centred ring, all bonded to a central Au atom. The central Au to peripheral Au atom distances lie in the range 263.3(2) to 267.9(2) pm. In contrast, the Au-Au bond lengths for the peripheral atoms lie in the range 284.7(2) to 296.5(3) pm. The SnCl_3 moiety is coordinated exclusively to the central Au atom with Sn-Au distance of 262.5(3) pm.

Fig.16. (a) Structure of $[\text{Au}_8(\text{PPh}_3)_7(\text{SnCl}_3)]^+$.

(b) Phenyl Rings omitted [258]

A black cluster contains $\text{K}[(\text{cyp})]^+$ cations and $\text{closo-}[\text{Sn}_9\text{Cr}(\text{CO})_3]^{4-}$ anions [259]. There are two crystallographically independent anions in the unit cell that are structurally identical and reveals a virtually undistorted bicapped square antiprismatic shape. The formation of the cluster can be viewed as the insertion of a neutral $\text{Cr}(\text{CO})_3$ fragment into the open square face of a nido- Sn_9^{4-} ion. The $\text{Cr}(\text{CO})_3$ fragment occupies a capping position in the bicapped square antiprism, with average Sn-Cr bond length of 287.1(6) pm. The Sn-Sn distances within the square planes are 306(2) and 316(3) pm. The distances between the two square planes average at 299(2) pm.

An orange Sn_8Mo_2 cluster [262] has virtual C_{2h} symmetry with six metal atoms (Sn, Sn, Mo, Mo, Sn, Sn) lying in a plane. The Mo-Mo distance of 220.1(2) pm indicates triple bonding. The average Sn-Mo and Sn-Sn bond distances are 277.8(2) and 277.49(2) pm, respectively. All eight tin atoms are quasi-tetrahedral, two as SnMoSn_3 and six as SnC_3Sn chromophores.

A Sn_6Ni_3 cluster [261] contains a polycyclic Sn_6Se_9 cage enclosing a central cpNi_2 unit. Each of the remaining three $\text{cp}(\text{PPh}_3)\text{Ni}$ moieties coordinate to a Sn atom, completing a distorted tetrahedral geometry about these three Sn atoms (SnSe_3Ni) with average Sn-Ni bond distance of 243.5(3) pm. Another three Sn atoms have a trigonal bipyramidal arrangement (SnSe_3Ni_2) with average Sn-Ni bond length of 252.9(3) pm.

There are red and yellow Sn_6Cr_6 clusters [262,22b], and the structure of the former is shown in Figure 17. The six Sn atoms form an almost regular octahedron with Sn-Sn distances from 293.0(1) to 296.0(1) pm. Each Sn atom is coordinated through its lone pair of electrons to one $\text{Cr}(\text{CO})_3$ fragment. The Sn-Cr bond vectors radiate outwards with Sn-Cr bond lengths of 260.8(2) and 261.3(2) pm. The deviations from ideal Sn-Sn-Cr

angle (135°) result from spatial requirements of the bulky $\text{Cr}(\text{CO})_5$ groups (Figure 17), but overall are quite small. The yellow cluster [22b] contains $[\text{Na}(12\text{-crown-}4)]^+$ cations and $\{(\text{CO})_5\text{CrSn}\}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4\}^-$ anions. The $\text{Sn}_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ cage of the anion has a rhombododecahedral structure. Each Sn(II) atom acts as a ligand towards $\text{Cr}(\text{CO})_5$ via the stereochemically active lone pair electrons, and each is five coordinate (SnO_4Cr) with average Sn-Cr bond distance of 253.8 pm. A similar structure is observed for an orange Sn_6Mn_6 cluster [240], with the $\text{Cr}(\text{CO})_5$ "ligands" replaced by $\text{cp}^*(\text{CO})_2\text{Mn}$ units, with average Sn-Mn bond lengths of 243.7 pm.

Fig.17. Structure of $[\text{Sn}_6\{\text{Cr}(\text{CO})_5\}_4]^{2-}$ [262]

In Sn_4Pt_8 cluster [263] the Pt_8 metal core consists of three stacked edge-sharing tetrahedra of Pt atoms which generate four concave butterfly surfaces, each linked to one SnCl_2 group. The whole Pt_8Sn_4 metal framework can be considered as the layering of two outer, symmetry related, Pt(I)-Pt(I) edges with two inner, symmetry related, Pt(2)-Pt(2)-Sn planar rhombuses. The chlorine atoms are essentially coplanar with the Pt_2Sn_2 rhombuses. Of the ten CO ligands eight are terminally bonded to the eight Pt atoms, and two double bridge the outer Pt(1)-Pt(1) edges. The Pt tetrahedra are significantly elongated along the 4 axis, with average Pt-Pt bond lengths of 266.5(1) pm (intra-layer) and 292.5(1) pm (interlayer). The intra-layer Pt-Sn distance of 295.0(1) pm is longer than the average interlayer value of 260.4(1) pm.

There are two Sn_2W_9 clusters [264] and the structure of one of them is shown in Figure 18. The anion has nominal C_{3h} symmetry, with three WO_6 octahedra of the β -Keggin anion replaced by three PhSnO_5 groups.

Two red-brown $\text{Sn}_2\text{Ni}_{11}$ clusters [256] contain the $[\text{PPh}_3\text{Me}]^+$ cation and $[\text{Ni}_{11}(\text{SnR}_2)(\text{CO})_{18}]^-$ anions ($\text{R} = \text{Me}$ or Bu), plus (thf) molecules in the methyl derivative. The structure of the anion shows a Ni-centred $\text{Ni}_{10}\text{Sn}_2$ icosahedral cage of pseudo- D_{5d} symmetry surrounded by a polyhedral array of 18 CO groups and two R groups attached to Sn. The methyl derivative has ten terminal, four doubly and four triply bridged CO groups. the butyl derivative has ten terminal, six doubly and two triply bridged CO groups. Despite this difference, the corresponding mean inter-atomic distances in the Ni centred $\text{Ni}_{10}\text{Sn}_2$ cages of the clusters are within 1 pm of each other. The pentagonal antiprism of ten surface Ni atoms, with an interstitial Ni and two capping Sn atoms has the following mean bond lengths: Ni(central)-Sn, 235.1(1) pm; Ni(central)-Ni(surface), 258 pm; Ni(surface)-Sn, 272 pm. The intra-pentagonal distance is Ni(surface)-Ni(surface), 279 pm, and the intra-pentagonal distance is Ni(surface)-Ni(surface), 251 pm.

The metal framework of $[\text{Ni}_{12}(\mu_{12}\text{-Sn})(\text{CO})_{12}(\mu\text{-CO})_6(\mu_3\text{-CO})_4]^{2-}$ [266] consists of an icosahedron of Ni atoms slightly elongated along one pseudo- C_5 axis with an interstitial Sn atom. The average interatomic distances in the cluster are: Ni-Ni(intra), 260.6 pm; Ni-Ni(inter), 295.6 pm; Ni-Ni(cap) 264.1 pm; Sn-Ni(1-5/1'-5'), 257.5 pm and Sn-Ni(6/6), 274.5 pm.

There are two white clusters [267] of Sn_3W_{15} and Sn_3W_{18} . The $[(\text{PhSn})_3(\text{P}_2\text{W}_{15}\text{O}_{39}\text{H}_4)]^{5-}$ anion is shown in Figure 19. It has the expected C_{3v} Dawson structure with three capping $\{\text{WO}\}^{*4}$ units replaced by $\{\text{SnPh}\}^{*3}$.

The $[(\text{PhSnOH})_2(\text{PhSnOH}_2)(\text{PW}_9\text{O}_{34})_2]^{11-}$ [267] anion consists of two PW_9 anions linked by three Ph_3Sn groups into an assembly of virtual D_{3h} symmetry. The PW_9 groups are formed by removal of three adjacent corner-shared WO_6 octahedra. The Sn atoms, which act as the filler in a double PW_9 sandwich, have slightly distorted octahedral coordination (SnO_5C). Each Sn atom is displaced by 25 pm out of the plane of the four bridging O atoms in the direction of the phenyl group.

TABLE 7. Crystallographic and Structural Data for Oligomeric HeteroTin Clusters^a

COMPOUND (colour)	Crys c] Sp. Grp Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo- phore	M-L [pm]	M-M [pm] M-L-M [°]	L-M-L [°]	Ref
{K(2,2,2-crypt)} ₃	tr ₋	1514.1(4)	98.72(2)	SnTlSn ₄ (x4)		Tl ^b 306.3(-10)	Tl,Sn ^b not given	256
(TlSn ₈ TeSn ₃) 0.5en (red-brown)	P1	2219.5(5) 1411.3(3)	101.04(2) 89.44(2)			Sn 296.0(-17) 309.8(-10) 314.9(-10) Sn 290.1(-22) 296.0(-17) 330.1		
				SnSn ₄₅ (x4)				
				SnTlSn ₄ (x4)		Tl 311.8(-46) Sn 292.0(-67) 326.8(-54)		
				SnSn ₁₄ SnSn ₁₅ (x4)		Sn 306.3(-10) Sn 292.0(-67) 326.8(-64) 314.1(-32)		
{(Me ₃ Sn) ₃ Sn} ₂ Sm(thf) ₁₄ (dark green) at 173K	or Pca2 ₁ 4	2151.1(2) 1321.5(3) 2064.0(4)		Sn ^{II} SnSn ₃ (x2) Sn ^{II} C ₃ Sn (x6) Sm ^{III} O ₂ Sn ₂ Sn ^{II} YbSn ₃ (x2)	C _{4h} 213	Sn 339.4(4,8) Sn 277.8(6,22) Sn 277.8(6,22) O _{4h} 251(4,3) Yb 329.4(5,5)	Sm Sn 117.4(1)- 123.7(1) not given Sn Sn 178.8(1) Yb,Sn 117.9(2)- 124.2(2) not given	257
{(Nle ₃ Sn) ₃ Sn} ₂ Yb(thf) ₁₄ (light yellow) at 173K	or Pca2 ₁ 4	2153.4(3) 1315.8(2) 2061.6(4)		Sn ^{II} C ₃ Sn (x6) Yb ^{III} O ₂ Sn ₂ Sn ^{II} YbSn ₃ (x2)	C _{4h} 216 O _{4h} 236(-,2)	Sn 278.6(6,32) Sn 278.6(6,32)		257
{(Nle ₃ Sn) ₃ Sn} ₂ Yb(thf) ₁₄ (light yellow) at 173K	tg ₋ I42d 8	2085.1(4) 2631.1(5)		Sn ^{II} C ₃ Sn (x6) Yb ^{III} O ₂ Sn ₂	C _{4h} 216 O _{4h} 236(-,2)	Yb 330.0(4) Sn 280.0(4,3) Sn 280.0(4,3)	Sn Sn 178.5(1) Yb Sn 113.8(1)- 128.9(1) not given Sn Sn 176.2(1)	257

$[Au_2(\eta^3-Ph)_3(\eta^5-SnCl_3)_2]$ $[SnCl_6]$ (red)	m C2/c 4	4823.0(14) 1683.1(7) 3224.0(10)	96.50(3)	$SnCl_3Au$ $AuSnAu_7$	Cl 241(1,1) 246(1)	Au 252.5(3) Sn 262.5(3) Au 265.4(2,25)	Cl_2Cl 96.2(4,9) Cl_2Au 120.7(3,2,9) $SnAu$ 80.3(1,2,2) 102.8(1,4,1) 119.56(9) 150.1(1)	258
$[K(cryp)]_4$ $[Sn_2Cr(CO)_3]^+$ (black)	m P2/c 8	2039.8(4) 4970.5(11) 2410.8(4)	91.55(2)	$SnCrSn_4(x4)$ $SnSn_4$ $SnSn_5(x4)$	P 229(1,2)	Au 290.7(2,60) Cr 287.1(6,19) Sn 299.2 306(3) Sn 294.2 Sn 299.2 316(3)	P_2Au 127.3(3,14,3) 170.1(3,8,9) not given	259
$[Mo_2\{Sn(SnMe_3)_3\}_2]$ $(NMe_2)_4$ (orange) at 111K	or $Pbn2_1$ 4	1460.0(4) 3173.7(13) 1354.5(4)		CrC_3Sn_4 $SnMoSn_1(x2)$ $SnC_3Sn(x6)$	OC 166(1) 171(1,0)	Mo 277.8(2,5) Sn 277.4(2,6)	Sn,Sn 101.6(1,4,1) Sn,Mo 111.3(1,2,8) 125.5(1,3)	260
				$MoN_2S_{11}Mo$	C_{Me} 209.1(24) 215.4(25,11) 219.8(25,5) N 195.2(13,31)	Mo 220.1(2)	N,N 125.0(7,1) N,Sn 108.8(5,3,4) N,Mo 105.3(6,2,3) $S_{11}Mo$ 100.6(10,1)	

$\text{cp}_4(\text{PP}_{13})_3\text{Ni}_5$ Sn_6Se_9 at 183K	m Cc 4	1630(1) 2584(1) 2078(2)	92.36(5)	$\text{SnSe}_3\text{Ni}_2(\times 3)$	$\mu_3\text{Se}$ 251.2(3) - $\mu_2\text{Se}$ 270.3(3)	Ni 250.1(3,7) 255.8(3,5) 82.0(1,1,3) 97.0(1,4)	Se,Se 92.8(1,1,4) Ni,Ni 63.8(1,1)	261
				$\text{SnSe}_3\text{Ni}(\times 3)$	$\mu_3\text{Se}$ 251.2(3) - $\mu_2\text{Se}$ 270.3(3)	Ni 243.5(3,5) 97.0(1,4)	Se,Se 105.9(1) - 113.3(1)	
				$\text{NiSe}_3\text{Sr}_3\text{Ni}$	$\mu_2\text{Se}$ 270.3(3) $\mu_3\text{Se}$ 242.2(4,5)	Ni 267.3(4)	Se,Se 99.4(1,9) Se,Sn 66.4(1,3) Se,Ni 118.6(1,5) Sn,Ni 59.1(1,2) Sn,Sn 93.3(1,1,0) Sn,Ni 57.1(1,2)	
				NiopSn_3		Sn 255.8(3,5) Ni 267.3(4) Sn 243.5(3,5)	not given	
				$\text{NiopPSn}(\times 3)$	C_{ep} 210(2,6) P_{th} 2.139(5,8)			262
$\{\text{K}(2,2,2\text{-crown})\}_2$ $[\text{Sn}_6\{\text{Cr}(\text{CO})_5\}_6]$ (deep red)	tr P1 1	1350.1(9) 1376.4(7) 1574.9(10)	83.93(5) 65.60(5) 74.99(5)	SnCrSn_4		Cr 261.0(2,3) Sn 294.5(1,15)	Cr,Sn 121.1(1) 134.5(1,4,6) 148.0(1)	
				$\text{Cr-C}_3\text{Sn}$	OC not given			
$\{\text{Na}(12\text{-crown-4})_2\}_2$ $[\{\text{CO}_5\text{CrSn}\}_6]$ $(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ 3tif (yellow)	m P2 ₁ /n 4	1163.2(6) 2961(2) 1980(1)	88.87(4)	$\text{Sn}^{\text{II}}\text{O}_4\text{Cr}$	$\mu_2\text{O}$ 205(-,10) $\mu_2\text{HO}$ 234(-,18)	Cr 253.8(-,8)	O,O 74(-,3) 95(-,1,6) 133.1(-,7) O,Cr 113(-,10) 130(-,2)	22b
$[\{\text{cp}^*(\text{CO})_2\text{MnSn}\}_6]$ $(\mu_3\text{-O})_4(\mu_3\text{-OH})_4$ (orange) at 233K	tr P1 2	1445.8(6) 1483.2(5) 2237.6(9)	89.17(3) 72.23(3) 83.05(3)	$\text{Cr-C}_3\text{Sn}$ $\text{Sn}^{\text{II}}\text{O}_4\text{Mn}$	OC not given $\mu_2\text{O}$ 206(-,1) $\mu_2\text{HO}$ 234(-,7)	Mn 243.7(-,8)	O,O 74.0(-,1,4) 94.4(-,7) 131.7(-,3) O,Mn 114(-,6) 132(-,3)	240
$(\text{PPh})_2[\text{Pt}_6(\text{SnCl}_2)_4]$ $(\text{CO})_{10}$	tg I42m 2	1455.0(3) - 1822.0(4)		$\text{Mn}^{\text{II}}\text{Sn}$ $\text{SnCl}_2\text{Pt}_2(\times 3)$	OC not given Cl 235.6(4)	Pt 260.4(1,9) 295.0(1) Pt 267.4(1) 289.9(1) Pt 265.6(1) 297.7(1)	Cl,Cl 98.1(3) Pt,Pt 120.1(1)	263

$C_{54}H_{54}[PnSn]_3$ (SiW ₉ O ₃₄), 8H ₂ O at 173K	m C2/c 8	4891(2) 1211.1(3) 2033.4(9)	102.30	SnO ₃ C	μO 208(3,6) 278(2,4) C _{Ph} 206(6,11) μO 174(4,4) 189(4,7) 242(3,9)	not given	264
$C_{59}H_{59}(BuSnOH)_3$ (SiW ₉ O ₃₄) ₂ , 36H ₂ O	tg P42 ₁ m 4	2900.5(4) - 1341.2(4)		SnO ₃ C	μO 205(3,10) μHO 193(5,7) C _{Bu} 242(8,9) μO 171(3,5) 188(3,14) 227(3,7)	not given	264
$(PPh_3)_2Me_2[Ni_{11}]$ (SnMe ₂)(CO) ₈ , thf (red brown)	m C2/c 4	2661.3(4) 1205.4(2) 2256.2(3)	102.17(1)	SnC ₂ Ni ₅	C _{Me} not given	Ni 235.1 272	265
$(PPh_3)_2Me_2[Ni_{11}]$ (SnBu ₂) ₂ (CO) ₁₈ (red brown)	m P2 ₁ /c 2	1420.2(6) 1892.5(6) 1445.2(5)	115.18	NiC _x Ni _x SnC ₂ Ni ₅ NiC _x Ni _x	OC not given C _{Bu} not given OC not given	Ni 251 - 279 Ni 235.1(1) 272 Ni 251 - 279	265
$(PPh_4)_2$ [Ni ₁₂ Sn(CO) ₂₂] (red brown)	m P2 ₁ /n 2	1182.9(3) 1503.8(8) 2123.8(6)	96.28(2)	SnNi ₁₂ NiSnNi _x NiNi _x		Ni 257.5(x5) 274.5 Ni 260.6 264.1 295.6	266
$K_3H_4[PnSn]_3$ P ₂ W ₁₅ O ₅₉ , 6H ₂ O (white) at 203K	tg I4/m 8	3009.6(4) 2219.6(5) 2010.5(6)		SnO ₃ C	μO 205(2,3) 2.41(2,2) C _{Ph} 2.10(3,5) μO 167 - 139(2) μO 205(4,13) C _{Ph} 2.10(6,7) μO 170 - 244(2)	not given	267
$K_{11}H_{11}[PnSnOH]_3$ (FVW ₉ O ₃₄) ₂ , 16H ₂ O (white) at 203K	tg I4/amd 16	3552.2(5) - 3324.3(7)		WO ₆ SnO ₃ C WO ₅		not given	267

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the e.s.d., and the second is the maximum deviation from the mean.

b. The chemical identity of the coordinated atom or ligand is specified in these columns.

Fig.18. Structure of $[(\text{PhSn})_3(\beta\text{-SiW}_9\text{O}_{37})]^{7-}$ [264]
[267]

Fig.19. Structure of $[(\text{PhSn})_3(\text{P}_2\text{W}_{15}\text{O}_{59}\text{H}_4)]^{5-}$

The data in Table 7 shows clusters of nine Sn_9M ($\text{M} = \text{Tl}$ [256], Sm or Yb [257]) and SnAu_8 [258]; ten Sn_9M ($\text{M} = \text{Tl}$ [256] or Cr [259]) and Sn_8Mo_2 [260]; eleven Sn_6Ni_5 [261]; twelve Sn_6M_6 ($\text{M} = \text{Cr}$ [262] or Mn [240]), Sn_4Pt_8 [263] and Sn_3W_9 [264]; thirteen $\text{Sn}_3\text{Ni}_{11}$ [265] and SnNi_{12} [266]; eighteen Sn_3W_{15} [267], and twenty one Sn_3W_{18} [267]. The nonanuclear Yb derivative [257] has two isomeric forms, orthorhombic and tetragonal, which are isostructural. One example [259] contains two crystallographically independent molecules within the same crystal. Both of these systems are examples of distortion isomerism [113]. The metal-metal distances found in the oligomers are given in Tabel 7A. The Sn-Mo triply bonded distance of 220.192 pm [260] is the shortest in the chemistry of heterometallic tin compounds.

Table 7A. Summary of Sn-M and M-M Distances in Oligomeric Heterotin Clusters.

M-M'	Cov. Radius of M' [pm]	Shortest [ref]	Distances [pm] Longest [ref]	Average	Distances > 300 pm
Sn-Tl					305.5 – 307.3 [256]
Sn-Ni	120	235(1) [265]	274.5 [266]	258	
Sn-Cr	127	252.7 [22b]	289.0(6) [259]	267	
Sn-Pt	128	259.5(1) [263]	295.0(1) [263]	272	
Sn-Au	143	262.5(3) [258]			
Sn-Mo	145	277.4(2) [260]	278.3(2) [260]	278	
Sn-Mn	146	242.9 [240]	244.8 [240]	244	
Sn-Sm					338.6 – 340.2(4) [257]
Sn-Yb					328.9 – 330.0(4) [257]
Sn-Sn		268.2(4) [256]	296.0(1) [262]	285	
Ni-Ni		251 [265]	294.6 [266]	268	
Pt-Pt		265.6(1) [263]	297.7(1) [263]	280	
Au-Au		263.3(2) [258]	267.9(2) [258]	265	
Mo-Mo		220.1(2) [260]			

9 POLYMERIC HETEROTIN COMPOUNDS

Crystallographic and structural data for almost thirty polymeric heterotin compounds are gathered in Table 8. Both transition and non-transition heterometal atoms are involved in these complexes.

A helical polymer with a Sn(IV) atom in the centre of a trigonal bipyramid of tert-butoxy groups linked by two structurally different atoms has been observed in colourless $[\text{KSn}(\text{OBu})_3(0.5\text{tol})]$ [268]. Another colourless complex $\text{KSn}(\text{OBu})_3$ [124] is a one dimensional polymer of distorted trigonal bipyramidal SnO_3M cages aligned to give the central metal atoms a five fold coordination (MO_5), as shown in Figure 20. The Sn(II) atoms have trigonal pyramidal coordination, with fairly constant Sn-O bond lengths of 206.7 pm. The K-O distances range from 256.495 to 318.8(6) pm. A white $\text{Ca}[\text{Sn}(\text{ac})_3]_2$ complex [269] has a three dimensional network structure. The Ca(II) atom is in distorted octahedral sites. The Sn(II) atom is at the apex of a regular trigonal pyramid with three equal Sn-O bond distances of 214.0(7) pm and three equal O-Sn-O angles of

83.5(2)°.

Fig.20. Structure of $\text{KSn}(\text{OBu})_3$ [124]

There are three colourless isostructural (aryl) ClSnAlCl_4 complexes [170,271]. All contain the $\text{Sn}_2\text{Cl}_2^{+2}$ unit as an integral feature. The structures are composed of these dimers interconnected by bridging AlCl_4 groups to form an infinite chain structure in [001] directions. Another colourless $[(\text{C}_6\text{H}_5\text{Sn}(\text{AlCl}_4)_2)\text{C}_6\text{H}_6]$ complex [272] is described as $\text{Sn}(\text{II})$ units bonded to two Cl atoms from three different AlCl_4 units to form a linear chain propagating in approximately the [101] direction. In a colourless gallium derivative [273] layers are built up from $\{\text{C}_6\text{H}_5\text{SnCl}(\text{GaCl}_4)\}_2$ subunits. These consist of a $\text{Sn}_2\text{Cl}_2^{+2}$ four membered ring, two GaCl_4 tetrahedra on opposite sides of the ring, and two benzene molecules η^6 -bonded to the Sn atoms in a distorted fashion. Colourless $\text{Tl}_2\text{Sn}(\text{OEt})_6$ [274] exists as a one dimensional polymer of octahedral $\text{Sn}(\text{IV})$ atoms (SnO_6) and distorted trigonal bipyramidal $\text{Tl}(\text{I})$ atoms with the lone pair electrons in the equatorial plane. There are two types of ethoxide group, one with a triply bridging O atom (between Sn and two Tl), and one with a doubly bridging O atom (between Sn and Tl).

A structural study of $(\text{Bu}^n)_4\text{N}(\text{Et}_3\text{Sn})_2\text{Cu}$ [275] confirmed the formation of negatively charged, three dimensional, host framework with wide parallel interior channels occupied by well ordered Bu^n_4 cations. In the supramolecular aggregate each $\text{Sn}(\text{IV})$ atom has a distorted trigonal bipyramidal environment (SnC_3N_2), and the $\text{Cu}(\text{I})$ atoms have a distorted tetrahedral one (CuCl_4).

There are two yellow $[(\text{Me}_3\text{Sn})_4\text{M}(\text{CN})_8] \cdot 2\text{thf}$ isostructural polymers ($\text{M} = \text{Mo}$ or W) [276]. Every $\text{M}(\text{CN})_8$ group is connected through Me_3Sn bridges to eight other $\text{M}(\text{CN})_8$ groups to form the corners of a body-centred tetragonal unit cell. In another colourless polymer [277] octahedra of $\text{trans-Me}_2\text{SnO}_4$ and tetrahedra of MoO_4 share apices to form a three dimensional structure. Another related system [278] contains tetrahedral MoO_4 and trigonal bipyramidal Me_3SnO_2 units in which definitive three dimensional structural networks are not found.

Two Me_3SnMO_4 polymers ($\text{M} = \text{Te}$ [279] and Re [280]) show differences between each other. Both have a zig-zag chain structure, but the perrhenate complex has a crystallographic mirror axis while the pertechnetate does not. In both compounds the $\text{Sn}(\text{IV})$ atom forms the centre of a trigonal bipyramidal coordination geometry, with two O atoms in apical sites and three methyl groups in the equatorial plane. Both $\text{Te}(\text{VII})$ and $\text{Re}(\text{VII})$ atoms have a distorted tetrahedral environment.

Two colourless Sn/Fe complexes [281,282] have an infinite, three dimensional, network of two different non-linear chains. These are, A: $-(\text{Sn}-\text{N}-\text{C}-\text{Fe}-\text{N}-\text{Sn}-\text{N}-\text{C}-\text{Fe}-\text{C}-\text{N})-$; and B: $-(\text{Sn}-\text{O}-\text{O}(\text{solvent})\text{O}-\text{O}-\text{Sn}-\text{N}-\text{C}-\text{Fe}-\text{C}-\text{N})-$, where the solvent is H_2O [281] or 1,4-dioxane [282]. The $\text{Me}_3\text{Sn}(\text{NC})_2$ units of chain A (average $\text{Sn}-\text{N} = 232.0$ pm [281] and 233 pm [282]) are essentially trigonal bipyramidal. The $\text{Me}_3\text{Sn}(\text{NC})\text{O}$ units of chain B are also trigonal bipyramidal. The $\text{Fe}(\text{II})$ atoms are all six coordinate (FeO_6). An orange polymer [283] contains an extensively porous, three dimensional, host framework of corner sharing $[\text{Fe}(\mu\text{-CN})_6]$ and trigonal bipyramidal $\text{SnMe}_3(\mu\text{-NC})_2$ units. Alternatively, the structure could be viewed as a network of two unique infinite chains, A (non-linear) and B (quasi-linear). An orange-red complex [284] has five coordinate, trigonal

bipyramidal, Sn(IV) atoms with equatorial vinyl groups and two apical O atoms from bridging carboxylate groups from a cyclopentadienyl derivative $C_5H_4COO^-$. There is another cyclopentadienyl ring present, C_5H_5 , and the result is a linear polymer. Both cyclopentadienyl rings are planar and π -bonded to the Fe(II) atom, which is equidistant from these planes.

Distorted $Co(CNSn)_6$ fragments and trigonal bipyramidal configured N_2SnMe_3 units are found within the three-dimensional network of a white complex [285]. The structure of a brick red complex $(Me_3Sn)_3Ru(CN)_6$ [287] is similar to that of its cobalt analogue [286].

The architecture of red $(Me_3Sn)_3Rh(SCN)_6$ is strongly reminiscent of "super-Prussian blue" systems. There is a three dimensional framework involving $\{Rh_8\}$ pseudo-cubes as the basic building blocks, with Rh(III) atoms held apart by non-linear $\{SCN-SnMe_3-NCS\}$ spacers. The Rh(III) atoms have a quasi-octahedral geometry (RhS_6). The Sn(IV) atoms have quasi-trigonal bipyramidal format (SnC_3N_2) with N atoms in apical positions.

The structure of $KSn(dto)_3Cu(Ptol)_2$ [289] is shown in Figure 21. The Sn(IV) atom has a distorted octahedral environment of two O atoms and four S atoms from two S,S-chelated and one O,O-chelated dithiooxalate ligands. The O,O-chelated ligand bridges, via the S,S-chelating side, to the bis(tritolylphosphine)copper(I) moiety. The coordination of the Cu atom is that of a distorted tetrahedron (CuS_2P_2). The potassium coordination geometry is an irregular polyhedron formed by seven O atoms, five from the dithiooxalate ligands and two from acetone molecules. The K(I) atoms bind the $Sn(dto)_3Cu(Ptol)_2$ moieties into dimeric pairs which are further linked in chains along the x-axis by the K-O linkages.

Fig.21. Structure of $KSn(dto)_3Cu(Ptol)_2$ [289].

A black compound [290] contains linear chains of composition $\{Au(Ag_{1-x}Au_x)_2Sn_2Te_9\}^{-4}$ separated by EN_4N^+ cations. The closest inter-chain Te-Te contact is 700 pm. The Au atom has distorted planar coordination ($AuTe_4$), whereas the Sn and mixed Au/Ag site show tetrahedral and trigonal planar coordination, respectively. A dark red complex [291] contains a mixed metal, one-dimensional, chain with alternating $\{In(en)_2Te_2\}$ octahedra and $\{SnTe_4\}$ tetrahedra. For the final Sn(II)-Fe(III) polymer [292] only unit cell dimensions are available.

The data in Table 8 indicate tin in both Sn(II) and Sn(IV) oxidation states, with the latter more common. The Sn(II) atoms are found in pyramidal-planar, trigonal bipyramidal (most common), and seven coordinate geometries. The Sn(IV) atoms are found in tetrahedral, trigonal bipyramidal (again most common) and pseudo-octahedral geometries. The most common ligand donor atoms are O and N (as NC). There are no examples with a metal-metal bond, and one and three dimensional chains are the most common.

10 CONCLUSIONS

There are over three hundred and eighty heterometallic tin compounds in this review. Of these 130 are trimers, 100 tetramers, 30 pentamers, 45 hexamers, 15 heptamers, 12 octamers, 20 oligomers and 30 polymers. There are about two hundred and forty dimeric derivatives [5], giving a rich chemistry of over six hundred heterometallic derivatives. In these the Sn atom is found in oxidation states of 0, +2 and +4, with geometries including trigonal planar, tetrahedral, trigonal bipyramidal, octahedral and seven coordinate, with varying degrees of distortion. Of these the first only exhibits Sn(0) and Sn(II) and the last only Sn(II) oxidation states. Tetrahedral geometry is by far the most common.

Two clusters [130,257] exist in two isomeric forms with similar stereochemistry, differing by degree of

TABLE 8. Crystallographic and Structural Data for Polymeric Hetero Tin Clusters^a

COMPOUND (colour)	Crys. sys. Z	a [pm] b [pm] c [pm]	α [°] β [°] γ [°]	Chromo- phore.	M-L, [pm]	M-M [pm] M-L-M [°]	L-M-L [°]	Ref
[KSn(Obu) ¹ 5] 0.5 to 1 (colourless)	or Fddd 32	2514.9(11) 2965.8(13) 3255.8(21)		Sn ^{IV} O ₅	O ^p 197.5(7) μ O 200.5(8.3) 205.7(7) μ O 254.9(8.7) 280.8(7.6)	K 378.1(1.72) 104.9(3.52)	O ₂ O 78.8(3) 93.6(3.51) 127.9(3.85) 166.7(3) O O 61.0(3.28) 130.9(5.10.1) 153.5(6.9.3)	268
K ₂ Sn(Obu) ¹ ₃ (colourless)	or P2 ₁ /2 ₁ / ₂ ₁ 4	1907(1) 1060(1) 896(1)		Sn ^{IV} O ₃	μ O 206.1(5) μ_3 C 207.0(6.4)	μ O 102.5(2) μ_3 O 85.6(2.1.5) 100.4(2.1.0) μ_3 O 97.3(3.2.0)	O O 81.5(2) 91.3(2.6)	124
Ca[Sn(ac) ¹] ₂ (white)	trg P3 1	831 - 849		Sn ^{IV} O ₃ C ₃ ^{IV} O ₆	μ O 256.4(5) μ_3 O 283.8(5.33) 313.1(6.57) O 214.0(7.0)	Sn 425.0(5) Ca 624.8(9)	O O 57.8(2.6.7) 123.0(2.6.0) 175.5(2.2.4) O O 83.5(2.0)	269
(C ₃ F ₅)ClSnAlCl ₄ (colourless)	m P2 ₁ /n 4	1962.4(6) 953.1(1) 709.9(1)	93.65(1)	Sn ^{IV} C ₆ Cl ₅ Al ^{III} Cl ₄	cor ^p 250(2) μ Cl 232(-.40) Cl 237.7(6) μ Cl 214.6(6.42) cor ^p 277	99.7(1)	O ₂ O 90.0(2.5.4) 183.0 Cl ₂ Cl 78.7(1.10.3)	270
(cp-Me ₂ C ₆ H ₄)ClSn AlCl ₄ (colourless)	m I2/c 8	1897.0(7) 1090.3(4) 1547.0(4)	107.33(1)	Sn ^{IV} C ₆ Cl ₅ Al ^{III} Cl ₄	cor ^p 271 μ Cl 293(3.31) Cl 209.1(5) μ Cl 215.0(5.30)	Sn 407.7(2)	Cl ₂ Cl 109.4(3.6.5) Cl ₂ Cl 78.8(1.11.9)	270
(me ₃)ClSnAlCl ₄ (colourless)	m P2 ₁ /n 4	929.3(1) 1265.4(1) 1377.0(1)	95.76(1)	Sn ^{IV} C ₆ Cl ₅ Al ^{III} Cl ₄	cor ^p 271 μ Cl 232(1.29) Cl 210.6(1) μ Cl 214.5(1.28)	100.7(1)	Cl ₂ Cl 78.2(1.10.6) 112.1(1.8.6) 147.0(1.1.0)	271

$[(C_2H_5)_4Sn(AlCl_4)_2]$ C_2H_6 (colourless)	m $P2_1/n$ 4	1128.2(3) 1731.7(8) 1264.6(6)	110.08(1)	$Sn^{III}C_3Cl_6$ $Al^{III}Cl_4$	ν_{C-Cl} 274(1) μ_{Cl} 300(2,28) μ_{Cl} 201.5(3,7) μ_{Cl} 218.2(3,17) μ_{Cl} 212.6(4,15) μ_{Cl} 244.2(2,1) μ_{Cl} 276.9(2,38) 336.8(2,27) μ_O 226.1(2,13) 243.0(3,11) μ_O 174.5(3,20) μ_{Cl} 332(2,23) μ_{Cl} 252.7(4,34) 291.6(6,36) 322.8(5,41)	95.5(1)	Cl_4Cl 74.6(1,6,7) Cl_4Cl 109.5(2,5,2)	272
$Al(OPr^i)_3Sn_2Cl_3$ (colourless)	m $P2_1/c$ 4	1349.8(7) 899.1(5) 1834.8(9)	90.98(4)	$Al^{III}Cl_4$ $Sn^{IV}C_3O_2$	μ_{Cl} 212.6(4,15) μ_{Cl} 244.2(2,1) μ_{Cl} 276.9(2,38) 336.8(2,27) μ_O 226.1(2,13) 243.0(3,11) μ_O 174.5(3,20) μ_{Cl} 332(2,23) μ_{Cl} 252.7(4,34) 291.6(6,36) 322.8(5,41)	93.4(1,1,5)	Cl_4Cl 109.5(1,3,4) Cl_4Cl 68.5(4,1,2) 77.6(5,5) 83.7(5,2)	249
$\{(C_6H_5)_4SnCl\}$ $(GaCl_4)_2$ (colourless)	or $Pca2_1$ 8	2098.0(4) 915.5(2) 1407.7(3)		$Al^{III}O_4$ $Sn^{IV}C_6Cl_5$	μ_O 174.5(3,20) μ_{Cl} 332(2,23) μ_{Cl} 252.7(4,34) 291.6(6,36) 322.8(5,41)	115.9(2) 124.5(3)	O_2O not given C_2Cl 75.9(1,4,6) 87.8(1,6,9) 160.7(1,10,3)	273
$Tl_2Sn(OEt)_6$ (colourless)	m $c2$ 2	648.7(3) 1683.1(9) 929.3(5)	101.88(4)	$Ga^{III}Cl_4$ $Sn^{IV}O_5$ $Te^{IV}O_4$	μ_{Cl} 217.0(6,46) μ_{Cl} 238(1,3) μ_O 220.3(3) μ_O 253(4,3) μ_{Cl} 270(3,1) C_{Br} not given μ_{CN} 233.3(8,7) μ_{NC} 196.6(9,1)	106.2(2,1,2)	Cl_4Cl 109.4(3,4,7) O_2O 83 - 96	274
$(Bu_4N)(Et_3Sn)_2$ $Cu(CN)_4$	tg $I4_322$ 8	1436.0(2) - 4000.3(6)		$Sn^{IV}C_3N_2$ $Cu^{II}Cl_4$	μ_{Cl} 217.0(6,46) μ_{Cl} 238(1,3) μ_O 220.3(3) μ_O 253(4,3) μ_{Cl} 270(3,1) C_{Br} not given μ_{CN} 233.3(8,7) μ_{NC} 196.6(9,1)		O_2O 63.5(9,5) 155(1,2) NN 1/8.4(6,4)	275
$(Me_3Sn)_4Mo(CN)_8$ 2thf (yellow) at 223K	tg $I4_322$ 2	1319.1(2) - 1144.8(2)		SnC_3N_2 MoC_3 SnC_3N_2	C_{Me} not given μ_{CN} 233.5(5) not given C_{Me} not given μ_{CN} 232(1) not given C_{Me} 211(2,1) μ_O 220(1,3) 234(1)		CC 106.3(6,1,2) 123.8(4) not given	276
$(Me_3Sn)_4W(CN)_8$ 2thf (yellow) at 223K	tg $I4_322$ 2	1319.2(2) - 1143.4(2)		$W^{VI}C_8$ $Sn^{IV}O_4C_2$	μ_{CN} 232(1) not given C_{Me} 211(2,1) μ_O 220(1,3) 234(1)		CC 106.3(6,1,2) 123.8(4) not given	276
Me_2SnMoO_4 (colourless)	tg $P4_3/mbc$?	1370.5(2) - 727.1(1)		$W^{VI}C_8$ $Sn^{IV}O_4C_2$	μ_{CN} 232(1) not given C_{Me} 211(2,1) μ_O 220(1,3) 234(1)	166.8(5) 178.7(5)	O_2O 90.6(4,5,3) 174.3(3,3,8) CC 172.7(6) OC 89.7(5,5,7) OO 109.4(4,1,0) OO 179.8(4) OC 90.0(2,1) OO 109.4(1,2,0)	277
$(Me_3Sn)_2MoO_4$ (colourless)	tg $I4_1/amd$ 4	739.0(2) - 2593.6(5)		$Mo^{VI}O_4$ $Sn^{IV}C_3O_2$ $Mn^{VI}O_4$	μ_O 175(1,1) C_{Me} 212.1(18,25) μ_O 226.8(9) μ_O 177.0(8)	143.6(4)		278

$\text{Me}_3\text{SnTcO}_4$ (colourless)	m $\text{P2}_1/\text{c}$ 4	961.6(9) 764.5(6) 1150.1(7)	91.16(7)	$\text{Sn}^{\text{IV}}\text{C}_3\text{O}_2$ $\text{Tc}^{\text{VII}}\text{O}_4$	C_{Me} 210(2,3) μO 231(1,2) O 165(2,1) μO 171(1,0)	152.6(7) 175.6(8)	279
$\text{Me}_3\text{SnReO}_4$ (colourless)	or Pnma 4	1195.3(2) 954.1(2) 767.8(1)		$\text{Sn}^{\text{IV}}\text{C}_3\text{O}_2$ $\text{Re}^{\text{VII}}\text{O}_4$	C_{Me} 207.8(7,0) 214.4(10) μO 229.7(8,5) μO 167.6(7,0) μO 171.9(2,8) C_{Me} 211.6(1,19) μCN 232.0(4,0)	157.7(5) 180.1(4)	280
$[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_5(\text{H}_2\text{O})_4]$ (colourless)	or Cmca 4	1705.4(2) 1853.4(2) 1158.6(1)		$\text{Sn}^{\text{IV}}\text{C}_3\text{N}_2$ $\text{Fe}^{\text{II}}\text{C}_5$ $\text{Sn}^{\text{IV}}\text{C}_3\text{NO}$	μNC 189.8(4) C_{Me} 211.6(9,9) μCN 228.1(7) H_2O 235.0(7) μNC 188.6(6) C_{Me} not given μCN 228.5(9) 237.4(8) μNC 192.0(9,3) μCN 216.0(9) H_2O 245.1(8) μNC 192.3(10) C_{Me} not given μCN 233.3(6,2,9) μNC not given μCN 230.2(6) μNC not given C 210(2,0) 216(2) O 212(2) 242(2) C_{ep} 201(1,1)	CC 119.4(3) NN 178.7(2) CN 90.5(1,10) CC 89.0(2,4) CC 118.2(2) CN 92.5(3,13) CO 87.1(3,5) ON 178.9(3) not given CN 89.5	281
$[(\text{Me}_3\text{Sn})_4\text{Fe}(\text{CN})_6(\text{H}_2\text{O})_2(\text{dio})]$ (colourless)	m $\text{P2}_1/\text{h}$ 2	1324.2(2) 1139.6(2) 1332.2(3)	101.37(1)	$\text{Fe}^{\text{II}}\text{C}$ $\text{Sn}^{\text{IV}}\text{C}_3\text{N}_2$ $\text{Fe}^{\text{II}}\text{C}_6$ $\text{Sn}^{\text{IV}}\text{C}_3\text{NO}$	μNC 192.0(9,3) μCN 216.0(9) H_2O 245.1(8) μNC 192.3(10) C_{Me} not given μCN 233.3(6,2,9) μNC not given μCN 230.2(6) μNC not given C 210(2,0) 216(2) O 212(2) 242(2) C_{ep} 201(1,1)	not given CN 94.2 CO 85.8 not given CC 120.0(4,2,6)	282
$[(\text{Me}_3\text{Sn})_3\text{Fe}(\text{CN})_6(\text{Cocp})_2]$ (orange)	m C2/c 4	1799.5(2) 1557.0(3) 1236.0(2)	92.60(2)	$\text{Fe}^{\text{II}}\text{C}_6$ $\text{Sn}^{\text{IV}}\text{C}_3\text{N}_2$ $\text{Fe}^{\text{II}}\text{C}_6$ $\text{Sn}^{\text{IV}}\text{C}_3\text{N}_2$ $\text{Fe}^{\text{II}}\text{C}_6$ $\text{Sn}^{\text{IV}}\text{C}_3\text{O}_2$	μNC 192.0(9,3) μCN 216.0(9) H_2O 245.1(8) μNC 192.3(10) C_{Me} not given μCN 233.3(6,2,9) μNC not given μCN 230.2(6) μNC not given C 210(2,0) 216(2) O 212(2) 242(2) C_{ep} 201(1,1)	CC 120.0(7,5,6) OO 178.6(4) OO 109.4(7,7,2)	283
$(\text{CH}_2=\text{CH})_3\text{Sn}(\text{OCCCH}_3)\text{Feep}$ (red orange)	m $\text{P2}_1/\text{h}$ 4	1510.5(5) 1003.0(4) 1140.2(4)	104.06(4)	$\text{Fe}^{\text{II}}\text{C}_6$ $\text{Sn}^{\text{IV}}\text{C}_3\text{O}_2$ $\text{Fe}^{\text{II}}\text{C}_6$ $\text{Sn}^{\text{IV}}\text{C}_3\text{O}_2$	μNC 192.0(9,3) μCN 216.0(9) H_2O 245.1(8) μNC 192.3(10) C_{Me} not given μCN 233.3(6,2,9) μNC not given μCN 230.2(6) μNC not given C 210(2,0) 216(2) O 212(2) 242(2) C_{ep} 201(1,1)	CC 91.8(3) CC 120.0(5,2,3) CC 180.0(1) CC 115(1,1) 127(1) OO 172.5(2) CO 90(1,16) not given	284

(Me ₃ Sn) ₃ Co(CN) ₆ (colourless)	m P2 4	1685.7(6) 1294.1(7) 1466.4(15)	106.99(3)	Sn ^{IV} C ₃ N ₂ Co ^{III} C ₆ Sn ^{IV} C ₃ N ₂	C _{Me} 208.3 (x2) 215(3) μCN 235(1) μNC 187(2) C _{Me} , not given μCN 22.9(4.7)	C ₂ C 120.0(1,6.7) N ₂ N 173.5(7)	285
(Me ₃ Sn) ₃ Co(CN) ₆ (colourless)	m P2 ₁ /c 4	1685.7(6) 1294.1(7) 1466.4(5)	106.99(1)	Sn ^{IV} C ₃ N ₂ Sn ^{IV} C ₃ N ₂ Co ^{III} C ₆ Sn ^{IV} C ₃ N ₂	μCN 22.7(4.7) μCN 24.1(4.13) μNC no: given C _{Me} no: given μCN not given μNC not given C _{Me} 208(3.3) μSCN 235(2.1)	C ₂ C 50.2(8) N ₂ N 175(1) N ₂ N 170(1) N ₂ N 175(1)	286
(Me ₃ Sn) ₃ Ru(CN) ₆ (brick red)	or Pmna 4	1124.8(1) 1645.9(2) 1754.8(3)		Ru ^{II} C ₆ Sn ^{IV} C ₃ N ₂	μNC no: given C _{Me} no: given μCN not given μNC not given		287
(Me ₃ Sn) ₃ Rh(SCN) ₅ (red)	rh R3c 6	1344.1(2) - 3055.7(6)		Rh ^{III} S ₃ Sn ^{IV} S ₂ O ₂	μNC 238.5(6.34) S 247.0(2.20) O 215.7(4.2)	C ₂ C 120.0(9.5.0) N ₂ N 175.5(6) C ₂ N 90.7(3.1.9) S S not given S S 94.3(1.9.2) O O 74.47(1.7) S O 84.8(1) 166.1(2.1.6)	288
KSn(dto) ₃ Cu (PtoI ₃) ₂ .2Me ₂ CO	tr P1	1098.1(2) 1113.6(2) 2633.7(6)	106.69(2) 99.97(2) 78.39(2)	Rh ^{III} S ₃ Sn ^{IV} S ₂ O ₂	μNC 238.5(6.34) S 247.0(2.20) O 215.7(4.2)	S S not given S S 94.3(1.9.2) O O 74.47(1.7) S O 84.8(1) 166.1(2.1.6)	289
(NEt ₄) ₄ [Au(Ag _{1-x} Ag _x) ₂ Sn ₂ Te ₂] (black)	or Pmna 4	2044.8(4) 2431.5(7) 1154.0(3)		Cu ^I S ₂ P ₂ K ^I O ₇	S 232.0(2.5) P 227.7(2.5) O 269.9(7.70) 303.9(6.98) μTe 271.1(4.5) 275.0(10.10)	S S 91.5(1) P P 118.3(1) O O 54.4(2) 78.1(2)	290
KIn(en) ₂ SnTe ₄ 1.5en (dark red)	or Cmca 8	2606.9(3) 1527.8(4) 1497.2(4)		SnTe ₅ AuTe ₁ AgTe ₁ SnTe ₁ InN ₄ Te ₂	μTe 259.9(3) 266.6(4) μTe 261.5(3.6) 272.4(5) Te 265.1(2) μTe 276.6(2) N 231(2.4) μTe 282.7(2.0)	T ₂ Te 109.5(1.4.5) N ₂ N 75.5(5) 86.9(7.3) 154.6(8) Te ₂ Te 85.32(7) N T ₂ 94.2(4) 171.3(4)	291

292

Na₁₂Sn₄Fe₃H₇
(cit)₉.38H₂O)
(red)

m
C2/c

2300
1300
1450

119

Footnotes: a. Where more than one chemically equivalent distance or angle is present, the mean value is tabulated. The first number in parenthesis is the s.d., and the second is the maximum deviation from the mean.
b. The chemical identity of the coordinated atom or ligand is specified in these columns.
c. Centroid of the ring

147,150,167,169,172,179,183,208,209,230,252,259] which exhibit distortion isomerism [113], in that they contain two crystallographically independent molecules within the same crystal, differing only by degree of distortion.

The heterometal atoms include the transition and lanthanide metals along with the non-transition metals. The shortest Sn-M(non-transition) bond distances are found mostly in the dimeric derivatives [5], with values: 253.7(6) pm (Sn-Ge); 263.4(1) pm (Sn-Zn); 277.6(4) pm (Sn-Li); and 280.9(2) pm (Sn-Pb). In the tetramers the values are: 258.3(3) pm (Sn-Mg); 264.8(2) pm (Sn-Ge); and 293.4(6) pm (Sn-Bi). In the hexamers the values are: 278(1) pm (Sn-Al); and 278.9(1) pm (Sn-Pb). There is a much richer chemistry with the transition metals, for which the details have been discussed within each sub-section. Only Sn-M distances less than 250 pm are shown in the summary Table 9.

Table 9. Summary of Sn-M Bond Distances In Heterometallic Tin Clusters

Sn-M	Dimers [5]	Trimers	Tetramers	Pentamers	Hexamers	Heptamers	Octamers	Oligomers
Sn-Ni	238.7(1)	232.6(2)	242.0(1)	239.3(2)	-	-	-	235(1)
Sn-Fe	240.8(1)	249.0(1)	249.9(1)	247.6(1)	248.0(1)	247.1(5)	246.3(1)	-
Sn-Co	243.8(1)	244.1(1)	-	246.8(1)	-	-	-	-
Sn-Pt	248.6(3)	234.3(1)	247.8(2)	-	-	-	-	-
Sn-Pd	247.3(6)	-	-	-	-	-	-	-
Sn-Rh	245.0(1)	-	-	-	-	-	-	-
Sn-Mn	-	243.7(2)	244.5(1)	-	-	245.5(1)	-	242.9

Although Sn(IV) is formally considered to be "hard" while Sn(II) is borderline "soft", both are found bonded to a variety of "hard" and "soft" heterometal atoms. However, Table 9 indicates that, generally, only the iron subgroup elements generate a direct metal-metal bond with distances less than 250 pm. A comparison of shortest Pb-M bond distances [293] with Sn-M bond distances are given in Table 10. As expected, the Pb-M distances are mostly longer than the corresponding Sn-M distances, corresponding to the covalent radii of the two Group IV elements (141 pm (Sn) and 147 pm (Pb)). However, at 280.9(2) pm the Sn-Pb bond distance is actually shorter than the sum of the respective radii.

Table 10. Summary of the Sn-M and Pb-M [293] bond distances in Heterometal Derivatives.

M-M'	Dimers [pm] [5]	Trimers [pm]	Tetramers [pm]	Pentamers [pm]
Sn-Ge	253.7(6)			
Pb-Ge	259.9(2)			
Sn-Fe		249.0(1)	249.9(1)	247.6(1)
Pb-Fe		270.6(5)	262.0(4)	260.5(3)
Sn-Pt	248.6(3)	234.3(1)		
Pb-Pt	269.8(8)	276.9(2)		
Sn-Li	277.6(4)			
Pb-Li	285.2(5)			
Sn-Ir		256.9(3)		
Pb-Ir		283.1(2)		
Sn-V	275.7(2)			
Pb-V	293.6(5)			
Sn-Mo		270.6(1)		
Pb-Mo		280.8(1)		
Sn-Mn	250.8(3)	243.7(2)	244.5(1)	
Pb-Mn	261.7(3)	246.3(1)	249.0(1)	
Sn-Co				246.8(1)
Pb-Co				273.8(5)
Sn-Pb	280.9(2)			

This overview, together with its precursors [1-5], has surveyed nearly three thousand tin compounds, serving to focus attention on area in the rich chemistry of tin which could use additional study. Correlations have been drawn which may assist in prediction of the behaviour of tin in a variety of industrial, biological and environmental situations. In collecting the data it was evident that some data is already irretrievable, some is transparent to data retrieval searches and some is difficult to locate. In a few cases incorrect information has been promulgated in the literature. Where possible these problems have been corrected in this review. Other reviews in this series include magnesium and aluminium, the subgroups of titanium, vanadium, manganese, copper and

zinc, all of which are referenced in the later reviews of lead [293,294]. Also currently underway is a full review of the coordination, organometallic and heterometallic compounds of germanium to complete Group IV non-transition metals.

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