Translated from *Uspekhi Khimii*, **49**, 1651-1670 (1980) U.D.C. 547'13

Organometallic Compounds with Heteroatomic Chains

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Studies on the synthesis and chemical properties of organometallic compounds containing a chain of σ-linked atoms of heteroelements are surveyed and problems of the stability of such compounds are examined.
The bibliography includes 176 references.

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I. INTRODUCTION

In classifying the chemistry of organometallic compounds from the standpoint of composition, it is easy to identify the field in which compounds whose molecules contain a metal–metal group are studied. Such products are referred to as organobimetallic, organotrimetallic, etc. or the terminology adopted from inorganic chemistry is more frequently used nowadays, terms such as di-, tri-, ... poly-nuclear derivatives, in accordance with the number of heteroatoms in the molecule, being employed. The first representatives of this class were obtained in the 1920s but vigorous research has developed only in the last two decades. This took place in two main directions: (1) the search for and investigation of the properties of new combinations of heteroelements M–M′ in di- and tri-nuclear derivatives and (2) the synthesis and study of polynuclear compounds. The latter include typical clusters, i.e. substances whose molecules contain a three-dimensional or planar lattice of heteroatoms, as well as a variety of such compounds comprising substances with chains of σ-linked non-organogenic atoms, which can have a linear, branched, or cyclic form. It is noteworthy that, despite the significant difference between the kinds of M–M′ bonds in typical clusters and in σ-linked chains, these two types of substances are so close in their nature and structure that in some instances the assignment of a given compound to one class or the other is arbitrary.

The amount of literature information is by no means distributed uniformly between the above two fields of study. Whereas numerous original articles and reviews (see, for example, Vyazankin et al.[1] and Vahrenkamp[2]) have been devoted to the first area of the above studies, i.e. the investigation of di- and tri-nuclear compounds, data on polynuclear systems, particularly linear and cyclic compounds, are widely scattered and are incomplete; there is particularly little information about their reactivity. This can evidently be explained by serious technical difficulties of the synthesis of substances of this kind, their isolation in a pure state, and purification. At the same time, sufficient data exist on polynuclear compounds to make it necessary to survey them and arrange them systematically.

In the present review the first attempt is made to survey the available data on the synthesis and properties of organometallic compounds containing chains of four and more σ-linked atoms of heteroelements. The latter include all metals and metalloids with the exception of C, H, N, O and the halogens†. Sulphur-containing derivatives of the type $R_2\overset{\frown}{Sn-S-SnR_2-S}$, etc. are considered together with their scandium and tellurium analogues, despite the fact that sulphur belongs to organogenic elements. This approach is dictated by the similarity of the properties of all chalcogeno-derivatives and by the important role which organoelemental sulphides play in the chemistry of polynuclear compounds by virtue of the high stability of M–S compounds, their relative availability, and their likely practical usefulness.

In each section the data are arranged in accordance with the position of the heteroelements in Mendeleev's table. Initially data are presented on derivatives of non-transition elements in Groups ranging from I to VI, next mixed compounds are considered, i.e. compounds containing a non-transition element and a transition metal, and in the concluding part of the given section derivatives of transition metals are discussed.

For a more complete treatment of data on polynuclear linear and cyclic compounds, certain transition metal carbonyls and carbonyl halides are considered together with organometallic derivatives.

II. HOMOELEMENTAL COMPOUNDS

Organometallic oligomers containing chains of atoms of a single element were investigated before polyelemental compounds. This group of substances is related to inorganic crystalline polymers of the type $[K_2Pt(CN)_4Br_{0.3}.3H_2O]_x^3$ and $[Ir(CO)_3Cl]_x^4$, but they differ from them fundamentally by the absence of a crystalline columnar structure and also by the constant valence of the heteroatoms in the chain.

When diorganohalogenosilanes interact with alkali metals, cyclic polysilanes, $(R_2Si)_n$ are formed[5,6]. Together with low-molecular-weight products with $n \cong 6$, unstable polymers with $n \cong 55$ are obtained. The analogous reaction of diorganohalogenogermanes also leads to cyclic polygermanes but with a smaller number of heteroatoms in the chain ($n \leqslant 6$).[7,8] In the case of tin derivatives the first stage of the reaction of

† The terms "organoelements", "polyelemental", and similar ones imply that the atoms of any element other than those enumerated are present in the given compound.

R_2SnCl_2 with active metals (Li, Na) involves the formation of bivalent tin compounds R_2Sn. They polymerise in the course of several hours yielding 8–10-membered rings $(R_2Sn)_n$.[9–11] The formation of bivalent intermediates R_2M undoubtedly occurs also in the first two instances:

$$n\,R_2MX_2 + 2nM' \rightarrow 2n\,M'X + n\,[R_2M] \rightarrow (R_2M)_n\ ;$$
M=Si, Ge or Sn; M'=Li or Na; X=halogen .

In the reviews of Satge et al., devoted to germylenes[12], and Neumann[13], devoted to stannylenes, it was shown that polymerisation reactions and reactions involving insertion in metal–metal, metal–hydrogen, and metal–halogen bonds with formation of linear and cyclic oligomers and polymers are extremely characteristic of these highly reactive species.

The reactions of the monohalides R_3MX with alkali metals give rise to linear dimers. Thus the tetrasilane $R_3SiSiR_2SiR_2.SiR_3$ was obtained from R_2SiSiR_2Cl.[14,15] Cyclic stannanes $(R_2Sn)_n$ containing between 4 and 9 tin atoms in the ring are formed when diorganotin dihydrides are heated in the presence of amines[16]. In order to obtain homonuclear linear oligomers, Neumann and coworkers used the ring opening reaction of iodine[17,18]:

$$\begin{array}{l}Ph_2Ge{-}GePh_2\\ \quad|\quad\ |\\ Ph_2Ge{-}GePh_2\end{array} + I_2 \rightarrow I{-}GePh_2{-}[GePh_2]_2{-}GePh_2{-}I \xrightarrow{PhLi} Ph_3Ge{-}[GePh_2]_2{-}GePh_3$$

$$(Et_2Sn)_9 + I_2 \rightarrow I{-}SnEt_2{-}[SnEt_2]_7{-}SnEt_2{-}I\ .$$

A convenient method whereby one can sythesise Sn–Sn polymers as well as oligomers with a specified number of tin atoms has been developed[19,20]. The method consists in the hydrogenolysis of Sn–N bonds in amino- and amido-stannanes by organotin hydrides. This simple and convenient procedure for the formation of the metal–metal bond has come to be widely used also in the synthesis of two-element oligomers, examples of which are given in the next section.

An interesting Sn–Sn oligomer containing a cyclopentadienyltricarbonyltungsten substituent $\{Sn^{IV}[W(CO)_3Cp]_2\}_n$ have been obtained[21] by the reaction of $(CH_3C_5H_4)_2Sn^{II}$ with $HW(CO)_3Cp$. Unfortunately the value of n was not given for this compound, although it is apparently low:

$$(CH_3C_5H_4)_2\,Sn^{II} + 2HW(CO)_3\,Cp \xrightarrow{-CH_4C_5H_5}$$
$$\rightarrow \{Sn^{II}[W(CO)_3\,Cp]_2\} \rightarrow 1/n\,\{Sn^{IV}[W(CO)_3\,Cp]_2\}_n\ .$$

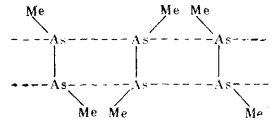
Silicon, germanium, and tin oligomers are viscous liquids, or, in rare cases, amorphous solids sparingly soluble in organic solvents. The solubility decreases with increase of molecular weight and the substances acquire a colour ranging from yellow to dark-red. Their thermal stability decreases on passing from silicon to germanium and tin and their reactivities increase in the same sequence.

Apart from Group IVB elements, homonuclear polymers are formed by phosphorus, arsenic, and antimony. Cyclic tetra-, penta-, and poly-phosphines are synthesised by the reaction of primary phosphines RPH_2 with dichlorophosphines[22,23]. The reaction of methylphosphine and methylarsine with dibenzylmercury results in the formation of the five-membered rings $(MeE)_5$ only[24]:

$$5MeEH_2 + 5\,(PhCH_2)_2Hg \rightarrow (MeE)_5 + 10PhMe + 5Hg$$
E = P or As.

The opening of rings of this type with the aid of RX leads to the formation of linear oligomers with the corresponding number of atoms of the heteroelement in the chain[25].

Penta- and hexa-nuclear formations are most typical for cyclic polyarsines, while in the linear oligomers the number of arsenic atoms can reach 50.[26,27] An X-ray diffraction study of the polymer $(MeAs)_n$, obtained by the reaction of $MeAsH_2$ with halogenoarsines or by the catalytic rearrangement of the cyclic pentomer $(MeAs)_5$, led to the conclusion that this compound has an unusual "ladder" structure[26]:



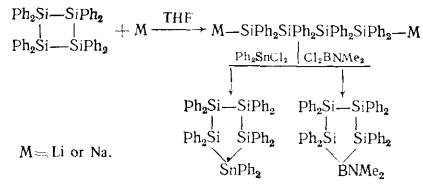
It was established that the length of the longitudinal As–As bonds (2.9 Å) appreciably exceeds the length of the transverse As–As bonds (2.4 Å) and the sum of the covalent radii (2.42 Å). On this basis, the authors[28] suggested that the aresenic atoms are linked to one another along the chain by "incomplete" bonds. In the determination of their physical properties it was found that the polymer is a semiconductor with a very low conductivity of 4.8×10^{13} cm Ω^{-1} (at 300 K).[28]

An analogous structure has been postulated for polymethylstibine $(MeSb)_n$, formed as a dark-red solid by the reaction of $MeSbH_2$ with dibenzylmercury[24]. The silylated polystibine $(Et_3SiSb)_n$ has been obtained together with ethylene and bromotriethylsilane by the reaction of $(Et_3Si)_3Sb$ with 1,2-dibromoethane[29].

III. TWO-ELEMENT COMPOUNDS

In the case of polynuclear compounds under consideration, the commonest are those whose molecules contain chains of atoms of two heteroelements. In the vast majority of cases the heteroatoms include those of silicon, germanium, or tin. The longest of the polynuclear derivatives whose existence has been demonstrated at the present time includes 11 heteroatoms: $Ph_3SiS{-}S_7{-}SSiPh_3$.[30] However, this nonasulphide should really be included among monoelemental compounds, since virtually the entire chain consists of sulphur atoms alone. The octanuclear cyclic cadmium ferrate $[-Fe(CO)_4-Cd-]_4$ should therefore be regarded as the two-element oligomer with the longest chain[31]. Several polymers are known whose molecular weights have not been determined owing to their poor solubility or low thermal stability, for example $[-Zr(SnPh_3)_2{-}SnPh_2-]_n$,[20] $[-Ge(C_6F_5)_2{-}Ge(C_6F_5)_2-Hg-]_n$,[32] and $(EtAlSe)_n$.[33,34] However, bearing in mind the considerable tendency of heteroatomic oligomers towards cyclisation, it is difficult to expect that n in these compounds exceeds 3–4. Furthermore, a more complex structure can be ruled out for the Zr–Sn polymer.

Derivatives of alkali metals with $M{-}(Si)_n{-}M$ chains (M = Li or Na; n = 4 or 5) have been obtained by the reaction of lithium or sodium and cyclic tetrasilane or pentasilane[35]. The products readily interact with organometallic halides[36,37] and are therefore suitable for the synthesis of other polynuclear compounds:



By allowing Ph_2GeH_2 to react with diethylmercury, Neumann and coworkers obtained the polymer $[-GePh_2{-}Hg-]_n$ in the form of a viscous yellowish resin[38,39]. However, this polymer cannot be regarded as an individaul compound, because its synthesis is accompanied by the liberation of metallic mercury and hence the formation of side products. It is impossible to

separate them from the polymer in view of the lability of the –Ge–Hg–Ge–Hg– chain. On heating or ultraviolet irradiation, the compound is readily demercurated with formation of polygermanes $[Ph_2Ge]_n$. The analogous silicon oligomer $[-SiMe_2-Hg-]_n$ has been synthesised by the reaction of dibromodimethylsilane with sodium amalgam[40].

The germylmercury chain becomes stable when the mercury atoms are in the γ-positions relative to one another. Thus the hexanuclear oligomer and the polymer have been obtained by the hydride method using 1,2-dihydro[tetrakis-(pentafluorophenyl)]digermane[32]:

$$(C_6F_5)_2Ge(H)-Ge(H)(C_6F_5)_2 \xrightarrow[-EtH]{EtHgGe(C_6F_5)_3} (C_6F_5)_5GeHgGe(C_6F_5)_2Ge(C_6F_5)_2HgGe(C_6F_5)_3$$

$$(C_6F_5)_2Ge(H)-Ge(H)(C_6F_5)_2 \xrightarrow[-(Me_3Si)_2NH]{[(Me_3Si)_2N]_2Hg} [-Ge(C_6F_5)_2-Ge(C_6F_5)_2-Hg-]_n .$$

Both products are thermally and hydrolytically stable and are not oxidised in air. In terms of its chemical properties and solubility, the former compound resembles $[(C_6F_5)_3Ge]_2Hg$.[41] The polymer $[-Ge(C_6F_5)_2Ge(C_6F_5)_2Hg-]_n$ is virtually insoluble, as a result of which it exhibits a lower reactivity (for example, in oxidative addition reactions) than the above hexanuclear compound of bis[tris(pentafluorophenyl)germyl]-mercury.

Polynuclear substances having the general formula $[RMX]_n$, where M = Al, Ga, or In and X is a chalcogen, are formed in reactions of sulphur or hydrogen sulphide with R_3M [42,43] and also in the thermal decomposition of the unstable products of the interaction of hydrogen chalcogenides of the type Et_3GeSeH with triethylaluminium, triethylgallium, or triethylindium[33,34]. It has been suggested that the association of the M–X units in these substances,

$$(Et_3MX)_2M'Et \xrightarrow{\Delta} (Et_3M)_2E + 1/n\,(EtM'E)_n ;$$
M=Si or Ge; E=S, Se or Te; M'=Al, Ga or In

takes place via coordinate and not covalent bonds[34]. However, this hypothesis is based solely on a qualitative estimate of their solubility and requires additional confirmation. Analogous boron compounds (borasulphols) are known to exist as σ-heterocycles BR–S–RR–S–Br–S.[44]

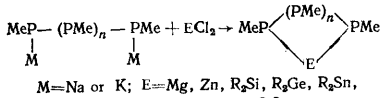
The method involving the hydrogenolysis of the Sn–N and Ge–N bonds by tin and germanium hydrides is extremely convenient for the formation of tin–germanium chains[19,20,45]:

$$2R_3GeNR'_2 + 2R_2SnH_2 \rightarrow 2R_3Ge-SnR_2H \xrightarrow[R'_2NH]{\Delta} R_3Ge-SnR_2-SnR_2-GeR_3 + H_2 ;$$

$$n\,R_2Sn(NR'_2)_2 + n\,R_2GeH_2 \rightarrow [-SnR_2-GeR_2-]_n + 2n\,R'_2NH$$
R = alkyl, aryl .

Compounds with the linear groups $Ge-(Sn)_3-Ge$, $Ge-(Sn)_4-Ge$, and GeSnGeSnGe have also been obtained by this method. In terms of their physical properties, they differ little from polygermanes and polystannanes, while in terms of their reactivity, they occupy an intermediate position.

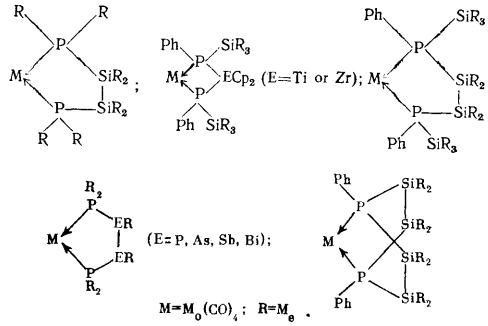
Group VB elements form a large series of polynuclear compounds. When phosphorus-containing rings $[RP]_n$ (n = 4 or 5) are opened under the influence of alkali metals, the products are linear polyphosphines containing Li, Na, and K atoms as the end-groups[46]. Their interaction with metal halides and organometallic halides yields penta- and hexanuclear heterocyclic products[46,47]:



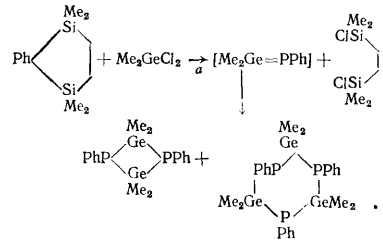
M=Na or K; E=Mg, Zn, R_2Si, R_2Ge, R_2Sn, S or Cp_2Ti; n=2.3 .

In certain cases the reactions under consideration are accompanied by the formation of polymers.

The high reactivity of alkali metal organophosphides is also used to synthesise linear silylpolyphosphines $R_3Si-(PR)_4-SiR_3$,[47] $Me_3Si-PPh-PPh-SiMe_3$,[48] $(Me_3Si)_2P-P(SiMe_3)_2$,[49,50] and $(Me_3Si)_2P-SiMe_2-P(SiMe_3)_2$.[51] The phosphorus atoms in these compounds, like those in the usual organophosphines, are capable of forming a coordinate bond with transition metal atoms. This made it possible to synthesise a series of unusual molybdenum complexes with phosphorus-containing heteroelemental polynuclear ligands[51–53]:



The cyclic trimers $[-SiPh_2-PPh-]_3$ and $[-GePh_2-PPH-]_3$ have been obtained by the reaction of $PhPK_2$ with dichlorodiphenylsilane and $PhP(GeClPh_2)_2$ respectively[54]. Dimers and trimers with Ge–P units are also formed in reactions of dichlorodimethylgermane with phenylphosphine[55] and 2,5-disilaphospholan[56]. It has been shown[56] that in the latter case extremely active germaphosphimines $[R_2GePR']$, containing the Ge=P double bond, are formed at an intermediate stage:

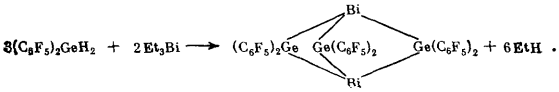


This reaction (stage *b*) is extremely characteristic of organometallic monomers. Resembling outwardly the polymerisation of olefins, it differs from the latter by the fact that it yields tetra-hexa-nuclear rings and not long linear chains.

The stannylphosphines $[-SnPh_2PPh-]_3$ and $[-SnPh_2-P(SnPh_3)-]_3$ are obtained by the reactions of triphenylstannyl-lithium with dichlorophenylphosphine[57].

Silyl-, germyl-, and particularly stannyl-phosphorus oligomers are readily hydrolysed and oxidised. In contrast to their phenyl analogues, the thermal stability of alkylstannylphosphines is low and they cannot be obtained by the above methods.

A surprisingly stable germylbismuth compound has been obtained recently by the reaction of $(C_6F_5)_2GeH_2$ with triethylbismuth[58]. An X-ray diffraction study failed to confirm the structure proposed initially for this product. It was established that its heteroelemental framework is made up of three germanium atoms and two bismuth atoms and has the form of a trigonal bipyramid[59]:

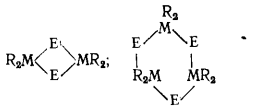


In contrast to $(C_6F_5)_3GeBiEt_2$ and $[(C_6F_5)_3.Ge]_2BiEt$, this product is not oxidised in air either in the crystalline state or in

solution. At the same time, it exhibits a higher reactivity with respect to compounds such as, for example, $Pt(PPh_3)_3$.

The interaction of the silyl sulphide $(Me_2SiS)_3$ with dichlorophenylphosphine[60] and dichlorophenylarsine[61] leads to pentanuclear cyclic oligomers $(PhMS)_3$, where M = P or As. The reaction of $(PhPS)_3$ with $(PhP)_5$ gives rise to cyclotetraphosphine sulphide PPh–PPh–S–PPh–PPh. A further twelve methods of synthesis of this substance have been published[62].

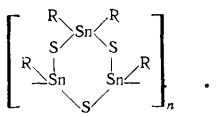
A cyclic structure is also most characteristic of oligomers with chains made up of atoms of Group IVB and VIB elements:



R = alkyl or aryl; E = S or Se; M = Si[63,64] or Ge[65–70]; Sn[71–76] or Pb[68].

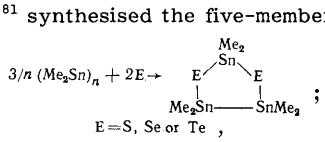
These compounds are usually obtained by the reaction of the dihalides R_2MHal_2 with a sodium chalcogenide or hydrogen sulphides in the presence of an amine. When sulphur or selenium is heated with tetra-alkyl(aryl)germanes and the corresponding stannanes, the dihydride $(C_6F_5)_2GeH_2$, or bis-(triphenylstannyl) sulphide to 100–150 °C, the same products are formed. In the majority of the reactions quoted compounds of the type of the germathione $[R_2Ge{=}S]$, whose polymerisation gives rise to tetra- or hexa-nuclear heterocycles, are apparently formed. This process has been established fairly reliably in relation to diethylgermathione in equilibrium with the cyclic trimer $(Et_2GeS)_3$.[77] The insertion of the stannathiones R_2SnS in the Sn–X bond in $R_{4-n}.SnX_n$ (X = Cl, Br, SCN, or OMe) yields a linear Sn–S oligomer[78].

The formation of linear intermediates of the type $R_3M-(Se)_n-SeR$ has been postulated in reactions of S or Se with R_4M.[68,72] In the presence of an excess of the chalcogen and for M = Sn this process leads to a product having the composition $R_4Sn_3S_4$, for which the authors postulate the polymeric cyclolinear structure[79]



One should also note the formation of cyclic and linear germyl and stannyl chalcogenides by the reaction of the sulphide $Ph_2Ge(SNa)_2$ [65] or the selenides $R_3SnSeLi$ [74] with halogeno-derivatives of the type Ph_2GeBr_2. The formation of the polymer $ClR_2Ge-(Se-GeR_2)_n-Se-GeR_2Cl$ together with the cyclic trimer has been noted in the reaction of Me_2GeCl_2 with Na_2Se,[66] but the number of Se–Ge units in the chain was not determined.

Mathiasch[80,81] synthesised the five-membered heterocycles



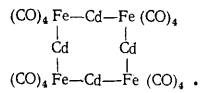
E = S, Se or Te,

by the oxidation of polymeric dimethyltin with chalcogens. Their stability decreases appreciably in the sequence S > Se > Te.

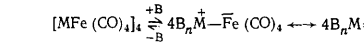
Chains having the composition Ge–S–S–Ge and $Si-S_n-Si$ (n = 5, 7, 9) are known. The former have been obtained by the interaction of triphenylgermanethiol or sodium triphenylgermyl sulphide with iodine[65,82] and the latter have been synthesised by the reaction of sodium triphenylsilyl sulphide with the dichloropolysulphides S_mCl_2 (m = 3, 5, 7).[30]

All compounds with chains consisting of Si(Ge, Sn) and sulphur atoms are colourless liquids (with R = alkyl) or crystalline solids (with R = aryl), which are stable in air. Selenium derivatives are less stable, decomposing rapidly in moist air with liberation of selenium. Both sulphur and selenium derivatives with a linear structure as a rule disproportionate on heating to 150–200 °C, forming four-membered hexanuclear heterocyles $(-MR_2-X-)_n$. X-Ray diffraction studies showed that the latter have the boat configuration and can exist in two crystalline modifications—tetragonal and monoclinic[83–85].

Compounds with chains comprising transition and non-transition metal atoms have been synthesised as some of the first polynuclear compounds. Thus cadmium and mercury carbonylferrates $[MFe(CO)_4]_4$ (M = Cd or Hg) have been obtained by the reactions of $Fe(CO)_5$ with cadmium and mercury salts[86,87]. An interesting method for the reversible degradation of such compounds under the influence of Lewis bases, which has been proposed recently, made it possible to obtain $[CdFe(CO)_4]_n$ in a crystalline form and to determine its structure[31]. It was found that the compound is a planar virtually square eight-membered heterocycle:



The reversible degradation method (involving the homolysis of M–M bonds) is important, because it makes it possible to solve one of the most difficult problems in the chemistry of polynuclear compounds—the purification of sparingly soluble and involatile substances with a high molecular weight. The crude polymer is depolymerised by simple dissolution in a basic organic solvent. The resulting solution of monomeric units solvated by solvent molecules, $[MFe(CO)_4].B_n$, is purified by the usual procedures and repolymerised by the gradual elimination of the solvent *in vacuo*[31,88,89].

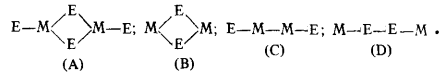


M = Cd or Hg; B = Acetone, THF, amine, etc.

We may note that in the given case polymerisation leads to cyclic oligomers and not linear macromolecules.

Compounds with chains comprising aluminium (gallium, indium) and transition metal atoms have apparently not been obtained hitherto#. However, the extremely stable Ir–Tl bond in the complexes $[(RCO_2)_2Tl-Ir(O_2CR)ClPPh_3]$ (R = alkyl)[91] showed that such oligomers can be entirely stable.

Group IVB elements form linear, cyclic, and mixed linear-cyclic polynuclear compounds with Mn, Fe, Ru, Os, Co, and Pt. The (A),[92–98] (B),[89,99–115] (C),[116–124] and (D)[125–132] structures are commonest (E is a Group IVB element and M is a transition metal):



(A) (B) (C) (D)

Six-membered Co–Sn and Fe–Ge heterocycles[133] and the linear nonanuclear compound $[(Ph_3Sn)_3Zr]_2SnPh_2$ [20] are also known. X-Ray diffraction data and measurements of the magnetic susceptibility showed that in certain compounds with structures (A) and (B) there is a direct M–M bond[93–95]. It has been suggested that deformations of rings (B) can lead to the cleavage of the M–E bonds and the formation of linear structures of the type $R_2E \rightarrow M-M \leftarrow ER_2$.[134] However, this has not been confirmed[115].

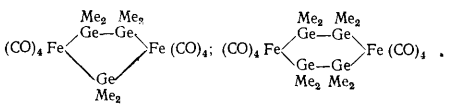
The gallium (indium)–manganese carbonyl complexes, described by Preut and Haupt[90] belong to the series of typical clusters and are therefore outside the scope of this review.

The principal methods for the synthesis of oligomers (A) and (B) include the reactions of metal carbonyls with organogermanium and organotin hydrides and halides. There is an interesting reaction of dicyclopentadienyltin with $Fe_2(CO)_9$ leading to the formation of the ring $[Cp_2SnFe(CO)_4]_2$ containing the Cp–Sn σ-bond, while the initial stannane has a "sandwich" structure[89]. The interaction of the hydrides R_3EH (E = Si or Ge) with the carbonyls $M_3(CO)_{12}$ leads to linear compounds (B). One or several carbonyl groups in the latter can be substituted by other ligands, for example, cyclopentadiene[119-121]. Chains with structure (D) are formed on alkylation with a Grignard reagent of halogeno-derivatives of the type $Cp(CO)_2Fe–GeCl_3$ when dicyclopentadienyltin interacts with metal carbonyls and in reactions of the dihalides R_2GeBr_2 with an anion of the type $(CO)_5Mn^-$.

The reaction involving the insertion of the zero-valent triphenylphosphine complex of platinum in the Ge–H bond of 1,2-dihydrodigermane has been proposed for the synthesis of a germylplatinum chain[132]:

$$\begin{array}{l}(C_6F_5)_2Ge—H\\ |\\ (C_6F_5)_2Ge—H\end{array} + Pt(PPh_3)_3 \rightarrow \begin{array}{l}(C_6F_5)_2Ge—Pt(PPh_3)_2—H\\ |\\ (C_6F_5)_2Ge—Pt(PPh_3)_2—H\end{array} + 2PPh_3 .$$

The reaction of 1,2-dichlorogermane with disodium iron tetracarbonyl leads to penta- and hexa-nuclear heterocycles[135]:



It has been suggested[136] that the interaction of tin tetrachloride with $Ru_3(CO)_{12}$ leads to the formation of a compound with the $Cl–Ru(CO)_4–Ru(CO)_4–Ru(CO)_4–SnCl_3$ chain. In contrast to fairly stable compounds having the structures (A), (B), (C), and (D), this oligomer is rapidly converted into the dinuclear complex $(CO)_4Ru(Cl)SnCl_3$ on heating. $Os_3(CO)_{12}$ reacts analogously[137].

On interaction with NH_4S_5, dicyclopentadienyltitanium dichloride forms compounds containing a heterocycle made up of five sulphur atoms and a titanium atom: $Cp_2\overline{TiSSSSS}$.[138] The conformational transformations of this product have been investigated[139].

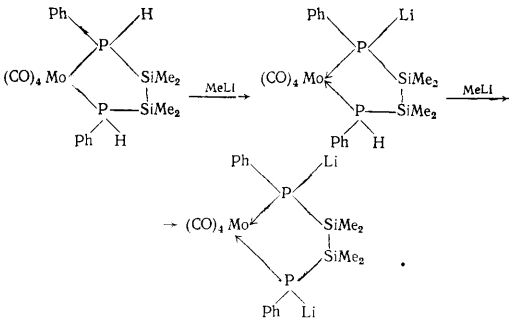
The complexes $[CpM(CO)_3M']_n$, where M = Mo or W and M′ = Cu or Ag, are examples of two-element polynuclear compounds whose skeleton is made up only of transition metal atoms[140]. They are obtained by the reaction of cyclopentadienyltricarbonyl-molybdenum or -tungsten anions with copper(I) and silver salts respectively. The complexes $[Co(CO)_4Ag]_n$, $[Co(CO)_4Cu(NH_3)_4]_n$, and $[(PhO)_3PFe(CO)_2.NOAg]_n$ have been synthesised similarly. On the basis of the stretching vibration frequencies of the CO groups in the infrared spectra, the authors postulate the presence of covalent M–M′ bonds in these compounds. The determination of n for the complex $[(Bu_3P)Co(CO)_3Ag]_n$ in various solvents showed that the degree of its polymerisation varies with the basicity of the solvent. Thus $n = 4$ in benzene and $n = 3$ in chloroform. Pyridine and other strong Lewis bases decompose these cyclic oligomers to monomeric units of the type $Co(CO)_4Ag.L$ (L is a solvent molecule). All the complexes decompose in the light and are oxidised in air.

The formation of an unstable intermediate with the linear Os–Os–Os–Au chain in the reaction of $Os_3(CO)_{12}$ with $ClAuPPh_3$ has been suggested[141].

IV. THREE-ELEMENT COMPOUNDS

The number of known compounds whose chains are made up of atoms of three different heteroelements is much smaller than that of two-element systems.

The only compound of this type, containing alkali metal atoms, has apparently been obtained by Johannsen and Stelzer[53], who metallated a bidentate phosphine ligand in a molybdenum complex:



A mercury derivative, with the Ge–Si–Hg–Si–Ge chain has been synthesised by the hydride method using the germylsilane $Et_3GeSiEt_2H$ as the starting material[142].

A large series of chalcogen-containing pentanuclear compounds have been obtained on the basis of the organoelemental hydride chalcogenides R_3MEH (M = Si, Ge, or Sn; E = S, Se, or Te). Their interaction with metals[143], metal alkyls[33,34,144,145], and organodielemental derivatives[146,147] proceeds readily and yields the required products with high yields as a rule

$$2(RO)_3SiSH + M \rightarrow (RO)_3SiSMSSi(OR)_3 + H_2 ;$$
$$M = Ca, Sr \text{ or } Ba$$
$$2Et_3SiSeH + Et_2M \rightarrow Et_3SiSeMSeSiEt_3 + 2EtH ;$$
$$M = Zn \text{ or } Cd$$
$$2Et_3SiSH + Et_3M \rightarrow (Et_3SiS)_2MEt + 2EtH ;$$
$$M = Al, Ga \text{ or } In$$
$$2Et_3SiTeH + (Et_3Ge)_2Hg \rightarrow Et_3SiTeHgTeSiEt_3 + 2Et_3GeH .$$

Zinc, cadmium, and mercury derivatives are stable under normal conditions and consist of colourless or pale-brown crystalline substances. The low solubilities and high melting points (decomposition temperatures) of the zinc and cadmium compounds apparently indicate their association. Chains based on Group IIIB metals have a very low thermal stability. In all cases, with the exception of $(Et_3SiS)_3AlEt$, they decompose fully in the course of the reaction. The reactions of triethylaluminium, triethylgallium, and triethylindium with an excess of the hydride chalcogenide lead to compounds of the $(Et_3SiTeAlTe)_n$ series[34], for which there is a possibility of both σ-linked Te–Al chains and associated coordination compounds with Te → Al bonds. These substances are evidently the products of the decomposition of unstable intermediates of the type $(Et_3GeSe)_3Al$. However, one should note that thermal decomposition of the analogous boron derivative $(Me_3SiS)_3B$ leads to products of another composition[148].

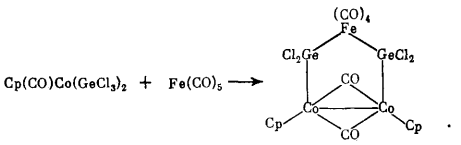
The tetranuclear organoelemental cadmium and mercury sulphides and selenides, for example, $(C_6F_5)_3GeSHgGe(C_6F_5)_3$, are obtained by the insertion of elemental chalcogens in the Ge–Hg, Ge–Cd, or Si–Hg bonds[70,149-151]:

$$(R_3Ge)_2Hg + 1/8\,E_8 \rightarrow R_3Ge—E—Hg—GeR_3 ;$$
$$E = S \text{ or } Se .$$

The insertion of a second chalcogen atom with formation of a pentanuclear chain of the type Ge–S–Hg–S–Ge is uncharacteristic of these reactions and is observed only on interaction of germylcadmium with sulphur. In contrast to the symmetrical pentanuclear compounds described above, all the tetranuclear chalcogen-containing substances decompose rapidly at room temperature (with the exception of the stable C_6F_5 derivative).

The condensation of $Cp_2Ti(SH)_2$ with dichlorodimethylsilane and similar compounds in the presence of an amine and also with dimethylsiloxane leads to cyclic products with the SiSTiSSi groups[152]. Ring closure takes place via the oxygen atom or siloxane groups.

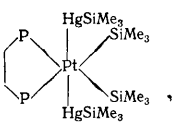
A stable heterocyclic compound incorporating the atoms of two transition metals has been synthesised via the reaction[133]



Metal carbonyl anions are frequently used in the synthesis of three-element oligomers. For example, the reaction of the anion $Me_3SiOs(CO)_4^-$ with $Me_3SiRu(CO)I$ gives rise to a compound with the SiOsRuSi group[153]. An unexpected pentanuclear linear complex $[Me_3GeRu(CO)_4]_2Hg$ has been isolated in the reaction of $Me_3GeRu(CO)_4^-$ with the iodide $CpFe(CO)_2I$.[96] The authors explain the formation of the mercury derivative by the fact that sodium amalgam was used to synthesise the anion.

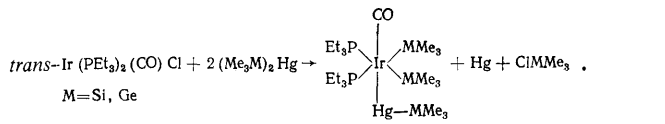
Frequent attempts have been made to employ carbonyl anions and dianions as well as carbonyl hydrides in polycondensation reactions with organometallic halides, for example, R_2SnCl_2, in order to form linear polymeric structures[118,154]. However, in most cases the reactions terminated by the formation of four-membered heterocycles. Collman and coworkers, who were the first to undertake an extensive search for methods of synthesis of organometallic polymers, were able to synthesise two linear pentanuclear complexes[154,155]. The first of these $(CO)_5Re-SnBu_2-Os(CO)_4-SnBu_2-Re(CO)_5$, was obtained by the reaction of *trans*-$(ClBu_2Sn)_2.Os(CO)_4$ with rhenium pentacarbonyl hydride. The second, $(CO)_5Mn-GePh_2-Fe(CO)_4-GePh_2-Mn(CO)_5$ were synthesised by treating $Fe_2(CO)_9$ with two moles of $(CO)_5MnGePh_2H$. The iron derivative has the *trans*-configuration, which the authors believe gives grounds for the hope of obtaining longer chains.

Several methods, frequently used to synthesise three-element compounds, are based on the use of a series of compounds $(R_3M)_2Hg$, where M = Si, Ge or Sn, as the initial organoelemental mercury derivatives for the synthesis of three-element compounds. These methods include exchange reactions with halogen-containing transition metal complexes, oxidative addition reactions with zero-valent transition metal complexes, and a combination of these reactions. Thus the photochemical reactions of $Fe(CO)_5$ and $Fe_2(CO)_9$ with $(Me_3Si)_2Hg$, which lead to the pentanuclear compound [*cis*-$Fe(CO)_4SiMe_3]_2Hg$, are regarded as oxidative addition of the $Fe(CO)_4$ species to the Si–Hg bond[156]. By allowing bis(trimethylsilyl)mercury to react with $Cl_2Pt(Ph_2PCH_2)_2$, Glockling and Pollock[157] obtained a pale-red substance to which they attributed the following structure on the basis of spectroscopic data:



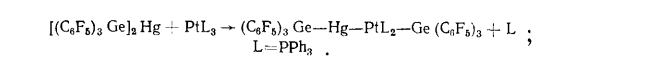
However, elemental analysis of this product was not carried out and, bearing in mind the very low stability of the analogous germanium groups $R_3Ge-Hg-Pt-GeR_3$, where R = alkyl[158], the proposed structure appears doubtful.

A similar combination of the exchange method and the method involving oxidative addition to a metal in a low-valence state obtains also in the reaction[159]



It is of interest to note that the Hg–Ir bond is chemically the most inert in the Si(Ge)–Hg–Ir–Si(Ge) chain formed.

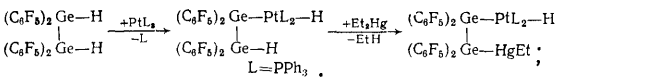
It was observed in 1976 that the triphenylphosphine complexes of zero-valent platinum and palladium are readily inserted in the M–M′ bond in compounds of the type $R_3Ge-Hg-GeR_3$.[160] The tetranuclear products formed proved to be entirely thermally stable in the case of $R = C_6F_5$:



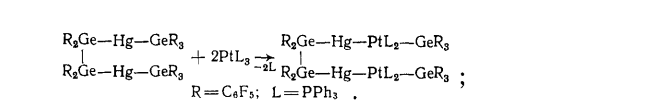
This made it possible to obtain a series of compounds with a wide variety of chains: GeHgPdGe, SnHgPtSn, GeCdPtGe, and GeZnPtGe.[158,160] The reaction involving $Ni(PPh_3)_4$ apparently leads to the analogous nickel derivatives, but they could not be isolated in a pure state.

X-Ray diffraction and ^{31}P NMR data have shown that the Pt–Hg complexes have a square planar *cis*-structure probably with a small admixture of the *trans*-isomer. In the palladium analogue both isomers are present in approximately equal proportions. Qualitative comparison established that their thermal and chemical stabilities decrease in the sequences Hg > Cd > Zn, Pt > Pd > Ni, and Ge > Sn. When $(C_6F_5)_3Ge.HgPtL_2Ge(C_6F_3)_3$ reacts with reagents such as Br_2 and hydrogen chloride, the Ge–Hg and Hg–Pt bonds are the first to be cleaved. The complexes are colourless or pale-yellow crystalline substances readily soluble in benzene, acetone, and tetrahydrofuran (THF).

The complex $(Ph_3Ge)_2CdPd(PPh_3)_2$, which the authors also believe to contain the metal chain GeCdPdGe, has been obtained similarly[161]. It has been established that a second PtL_2 species is not inserted in the remaining Ge–Hg bond in chains of the type GeHgPtGe, which can be explained both by steric hindrance and by changes in the nature of the Ge–Hg bond after the addition of platinum to the Hg atom. 1,2-Dihydro-1,1,2,2-tetrakis(pentafluorophenyl)digermane and a mercury derivative based on it have therefore been used to synthesise compounds with a longer chain. The product of the insertion of PtL_2 in one of the Ge–H bonds in $HGe(C_6H_5)_2-Ge(C_6F_5)_2H$ was made to react with Et_2Hg. Despite the excess of hydride, this results in the evolution of only one equivalent of ethane and a tetranuclear compound is formed[132]:

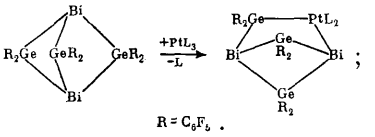


In the oligomer $(C_6F_5)_3GeHgGe(C_6F_5)_2Ge(C_6F_5)_2HgGe(C_6F_5)_3$ the atoms are separated by the Ge–Ge group and the reaction of this compound with a platinum complex leads to the addition of two equivalents of $Pt(PPh_3)_2$, as was to be expected[162]:



The resulting diplatinum octanuclear compound is entirely stable. Its reactivity, solubility, and infrared and ultraviolet spectra are similar to those of the tetranuclear complex $(C_6F_5)_3GeHgPtL_2Ge(C_6F_5)_3$. The great length of the polymetallic chain is manifested only by the appearance of broadened low-intensity bands in the long-wavelength part of the electronic absorption spectrum. It is easy to show by calculation that not less than nine steric (*cis*-, *trans*-) and structural isomeric forms can exist for this product (PtL_2 is not inserted in the Ge–Ge bond under the conditions adopted)[158]. This finding clearly demonstrates the feature characteristic of all the polyelemental oligomers, which consist in the fact that the difficulties associated with the identification and study of the reactivities of these compounds increase sharply after even a slight increase of the length of the heteroelement chain.

The triphenylphosphine complexes of zero-valent platinum are also inserted in the Ge–Bi bond of the tricyclic compound $R_2\overline{GeBiGeR_2BiGeR_2}$:[59]



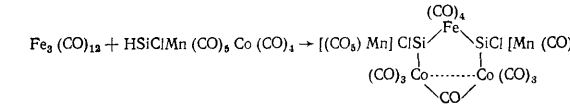
$R = C_6F_5$.

It is of interest that the second equivalent of PtL_2 is not inserted despite the presence of several Ge–Bi bonds remote from the platinum involved in the addition process. The structure of the product isolated from benzene in the form of dark cherry-red crystals was established by X-ray diffraction. The molecule of the complex contains the nonplanar heterocycle $\overline{PtGeBiGeBi}$ with the $(C_6F_5)_2Ge$ bridging group.

The Ge–S(Se) and Hg–Fe groups proved to be inactive with respect to $Pt(PPh_3)_3$. In reactions with $(C_6F_5)_3GeXH$ (X = S or Se) platinum adds to the X–H bond with the simultaneous formation of a small amount of the pentanuclear compounds $[(C_6F_5)_3GeX]_2Pt(PPh_3)_2$ as side products[132]. In the interaction of $(ClHg)_2Fe(C_5H_5N)$ with PtL_3 the Hg–Cl bond is attacked. The platinum derivatives formed in the intermediate stages are unstable and are rapidly demercurated[163].

V. FOUR-ELEMENT COMPOUNDS

So far as we are aware, only five compounds whose chains contain the atoms of four heteroelements of different kinds have been synthesised at the present time. The first of these was obtained in the form of dark-green crystals by the reaction[164]



The labile compounds $Et_3SiXHgGeEt_3$ (X = S, Se, or Te) were synthesised by the protodegermylation of bis(triethylgermyl)mercury by the chalcogenide hydrides Et_3SiXH.[147]

In the interaction of tris(triphenylphosphine)platinum with $(C_6F_5)_3GeHgSn(C_6F_5)_3$ the PtL_2 species is evidently inserted in both Ge–Hg and Hg–Sn bonds with formation of the isomers GeHgPtSn and GePtHgSn, which cannot be separated[158]. There are virtually no data on the reactivities of these compounds.

Five-element chains have apparently not been obtained hitherto.

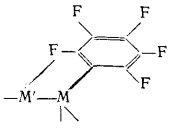
VI. THE STABILITY OF POLYMETALLIC GROUPS

One of the main conditions for the successful synthesis of organometallic compounds with chains comprising atoms of heteroelements is the stability of the resulting M–M bonds. The stability of the products is determined, like that of the usual mononuclear organometallic compounds[165], by quantum-chemical, thermodynamic, and kinetic factors. The first of these is manifested by the distinct dependence of the stability of polynuclear compounds on the positions in the Periodic Table of the heteroelements making up the chain. The stability of the oligomers incorporating atoms of *d* elements as a rule increases in each subgroup with increase of the atomic weight of the metal. The opposite variation of the stability of the M–M bond with the atomic weight of the element can be seen for *p* elements; the IIIB subgroup is intermediate in this respect.

The thermodynamic aspect is understood as the fulfilment of the condition $G_1 - G_2 > 0$ for stable compounds, where G_2 is the free energy of the oligomer system and G_1 the free energy of the system formed after the dissociation (spontaneous or under the influence of the attacking reagent) of the weakest or most reactive M–M bond. Presumably, in polymerisation and polycondensation reactions of organometallic compounds, the thermodynamic factor determines primarily the formation of small rings and not long linear molecules as in the case of *C*-derivatives. The possibility of the formation of conjugated groups as well as resonance effects lead to an appreciable energy gain for heterocycles compared with macrochains of the same elements.

The kinetic parameters constitute a no less important factor governing the stability of organopolymetallic compounds. The high activation energy for the initial decomposition reaction can lead to the stabilisation of thermodynamically unstable compounds or compounds with a low stability. Organic substituents at the heteroatoms play an important role in this respect. It is known that the presence of groups such as neopentyl-, t-butyl, trimethylsilylmethyl, etc. increases sharply the stability of the polymetallic compound[166-168]. For mononuclear compounds, the same effect has been explained[165] by the steric shielding of the metal atoms by bulky substituents from direct attack in collisions and also by the decrease of the efficiency of energy transfer to the M–C bond (which determines the stability of these compounds) in consequence of the distribution of energy among the vibrational levels of the substituents themselves. All these factors are equally applicable to compounds containing heteroelement chains§.

Evidently another cause leads to the stabilisation of pentafluorophenyl derivatives[158,169,170], because the bulk of the C_6F_5 ring is only slightly greater than that of the phenyl group. It has been suggested[59] that the stability of the compounds is achieved in this case by virtue of the intramolecular coordination of the unshared electron pairs of the *ortho*-fluorine atoms to the vacant orbitals of the heteroatom M′ in the β-position relative to the C_6F_5 substituent.



§ However, one cannot agree with the view[165] that polychloromethyl and the lower perfluoroalkyl groups are sterically hindered.

The spatial disposition of the o-F and M′ atoms favours such coordination[158,171]. We may note that, for this reason, i.e. by virtue of the molecular geometry, the coordination of o-F to the α-M atom, postulated for certain compounds $(C_6F_5)_n$ M (see. for example, Razuvaev et al.[172]), appears less probable. Evidently the coordination involving the β-heteroatom is impossible for compounds where M′ has no suitable vacant orbitals, for example, S, Se, Te, and Bi. In such cases the introduction of C_6F_5 substituents does not stabilise the polyelement groups[59,173]. On the other hand, if M′ is strongly electrophilic, then a rapid redistribution of bonds with liberation of the metal fluoride takes place in the five-membered coordination ring formed. Nor can one exclude the possibility of the dissociation of such compounds at the M–M′ bond with formation of highly reactive nucleophilic species of the type of $(C_6F_5)_3Ge^-$, which vigorously attack the C_6F_5 rings of the neighbouring molecules. For this reason, in the series of compounds with active M′ (Li, Pr, Nd) [174,175] the pentafluorophenyl derivatives are less stable than their H-analogues. On the other hand, in compounds with less active M′ (Zn, Cd, Hg, Pt) [158,169,170,176] intramolecular coordination increases the stability of the oligomer, formally increasing the energy of the M–M′ bonds in the M′–M–C_6F_5 fragments.

The chemistry of polynuclear organometallic compounds with linear and cyclic structures clearly exhibits the characteristic features of both the chemistry of the usual organometallic compounds and of carbochain polymers. At the same time oligomers and polymers with heteroelement chains have a number of specific properties, which require the development of fundamentally new methods of synthesis of such compounds and method for their investigation. These difficulties greatly inhibit studies on the field under consideration. However, virtually unlimited potential possibilities of varying the properties of organopolymetallic compounds (by selecting a wide variety of combinations of heteroatoms in the chains and their ligand environment) make substances of this class extremely attractive as convenient models for the solution of a number of theoretical problems in chemistry and physics. For the same reasons, the above compounds are extremely promising in the context of applied problems (high-temperature superconductivity, ferromagnetism, catalysis, etc.). There is no doubt that studies on organometallic polymers will develop vigorously in the immediate future.

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