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Some Peculiarities of Structure, Stability and Reactivity of Compounds Containing Metal–Metal Bonds

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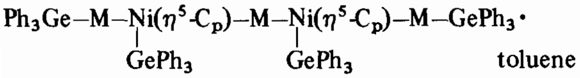
The complete X-ray analysis of bis(triphenylgermyl)mercury has been carried out. Hg–Ge bond lengths in the well-known structures of bi- and polynuclear organometallic compounds are shown to be covalent and change over a wide range. The influence of screening efficiency of central metal atom in bi- and polyorganometallic compounds upon their reactivity and thermal stability has been treated.

Introduction

Germyl derivatives of cadmium and mercury have been shown earlier to be convenient reagents for synthesis of various bi- and polynuclear compounds [1–3]. The compounds with chain containing nine metal atoms have been prepared [4, 5]:



$$Ph_3Ge{-}M{-}\underset{GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}C_p){-}M{-}\underset{GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}C_p){-}M{-}GePh_3\cdot\text{toluene}$$

M = Cd, Hg.

The preparation of such compounds extends our conceptions on possibility of existence of various compounds containing M–M bonds and allows us to reveal the influence of various factors upon these bonds.

Results and Discussion

The comprehensive data on correlation of stability of compounds and their reactivity are very useful in characterizing M–M bonds. It was interesting to compare reactivities of compounds such as R_2M, $(R_3E)_2M$ and more complicated organometallic polynuclear compounds (M = Zn, Cd, Hg, E = Si, Ge). The reactivity of R_2M compounds is known to be due to M–C bond polarity and increases in series: $R_2Hg < R_2Cd < R_2Zn$.

Unsymmetrical compounds such as RMX (X = Hal, OCOR and others) are more thermally stable and less reactive than symmetrical ones. Yet, the reactivity is determined not only by electronic effects, but also by steric factors. Dessi [6], who had also indicated this fact, made a conclusion that Kharasch [7] while investigating reactions of R–Hg–R′ with hydrogen chloride, studied practically a criterion of availability of central metal atom towards electrophilic attack, rather than electronegativity of radicals.

As far as thermal stability is concerned it decreases as a rule with increasing atomic weight of the metal, *i.e.* in the series: Zn > Cd > Hg, when R are equal. The average value of dissociation energy of M–C bond decreases in the same sequence [8].

The reactivity of $(R_3Ge)_2M$ compounds (M = Zn, Cd, Hg; R = Et, Ph) is much higher than that of corresponding R_2M compounds. Thus the former react easily with alkyl halides, carbonyl group, CO_2. Carbon derivatives of IIB group metals do not react in such a way. The reactivity of $(R_3Ge)_2M$ compounds depends strongly upon R (Alk, Ph, C_6F_5). The reactivity of $(R_3Ge)_2M$ compounds (M = Zn, Cd, Hg) is practically the same, if R = Me, Et. Under soft conditions these compounds react with 1,3-dibromethane, mercuric chloride, benzoyl peroxide, alkyl halides often at low temperature ($-20 \div -30$ °C). At R = Ph a considerable decrease in reactivity is noted for germyl derivatives of IIB group metals. Thus, if $(Et_3Ge)_2Hg$ reacts with 1,2-dibromethane with heat liberation at room temperature, the similar reaction of $(Ph_3Ge)_2Hg$ proceeds under harder conditions (3 hours at 100 °C). A similar phenomenon is observed in reactions of $(Et_3Ge)_2Hg$ and its Ph analogue with benzoyl peroxide, mercuric chloride and some other reagents.

The great difference in reactivity is observed when passing to C_6F_5– derivatives of germyl mercury. In contrast to $(Et_3Ge)_2Hg$ its analogues with C_6F_5–

TABLE I. Atomic Coordinates (×10^4 for Hg and Ge atoms ×10^5) and Their Anisotropic (Hg, Ge)– Isotropic (C) Thermal Factors $T = \exp[-\frac{1}{4}(B_{11}a^{*2}h^2 + \ldots + 2B_{23}b^*c^*kl)]$ in the Structure of $[(C_6H_5)_3Ge]_2Hg$.

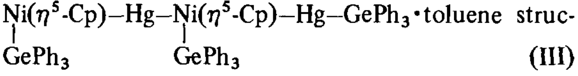
Atom	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Hg(1)	50000	50000	50000	5.88(4)	6.47(5)	3.80(4)	−2.10(4)	0.43(3)	−0.28(4)
Hg(2)	79677(7)	−16023(4)	82963(3)	4.95(3)	5502(4)	4.64(3)	−1.08(2)	0.22(2)	−0.16(2)
Ge(1)	30419(2)	42630(9)	60402(8)	4.74(7)	4.92(9)	3.35(8)	−1.19(6)	0.02(6)	−0.49(7)
Ge(2)	62813(2)	−24829(9)	93046(8)	4.44(7)	3.82(8)		−0.94(6)	−0.14(6)	−0.20(6)
Ge(3)	97074(2)	−7434(9)	72851(8)	4.36(7)	4.04(8)	3.95(8)	−0.85(5)	−0.08(6)	−0.35(6)
Atom	x	y	z	B_{iso}, Å^2	Atom	x	y	z	B_{iso}, Å^2
C(1)	1809(15)	3422(8)	5828(8)	5.1(3)	C(11)	6646(17)	3894(9)	7568(8)	6.0(4)
C(2)	2674(16)	2749(8)	5490(8)	5.4(3)	C(12)	5569(16)	4243(8)	7047(8)	5.3(3)
C(3)	1779(18)	2151(9)	5331(9)	6.7(4)	C(13)	1170(15)	5053(8)	6445(7)	4.5(3)
C(4)	−35(18)	2178(10)	5507(9)	6.9(4)	C(14)	50(18)	5589(10)	5979(9)	7.2(4)
C(5)	−938(17)	2809(9)	5837(9)	6.6(4)	C(15)	−1361(20)	6105(10)	6270(10)	8.1(4)
C(6)	−46(16)	3420(9)	5998(8)	5.6(3)	C(16)	−1631(18)	6134(9)	6957(9)	6.8(4)
C(7)	4526(13)	3742(8)	6795(7)	4.2(4)	C(17)	−538(17)	5652(9)	7426(8)	6.3(4)
C(8)	4671(15)	2914(8)	7058(8)	5.2(3)	C(18)	870(15)	5103(8)	7152(7)	4.8(3)
C(9)	5788(17)	2564(9)	7584(8)	6.1(4)	C(19)	5268(15)	−3314(8)	8942(7)	4.5(3)
C(10)	6755(16)	3074(8)	7833(8)	5.3(3)	C(20)	4139(17)	−3062(9)	8399(8)	6.4(4)
C(21)	3398(18)	−3668(10)	8145(9)	7.4(4)	C(38)	6631(16)	370(9)	6794(8)	5.8(3)
C(22)	3724(19)	−4472(10)	8416(9)	7.6(4)	C(39)	5523(18)	768(10)	6291(9)	6.9(4)
C(23)	4866(18)	−4734(9)	8926(9)	6.7(4)	C(40)	5911(18)	685(10)	5598(9)	7.0(4)
C(24)	5618(15)	−4150(8)	9190(8)	5.1(3)	C(41)	7370(118)	166(10)	5377(9)	6.9(4)
C(25)	7866(14)	−3096(8)	9982(7)	4.4(3)	C(42)	8496(16)	−261(9)	5873(8)	5.5(3)
C(26)	9438(16)	−3529(8)	9719(8)	5.6(3)	C(43)	11596(15)	−1448(8)	6807(7)	5.03(3)
C(27)	10623(18)	−3971(9)	10216(9)	6.9(4)	C(44)	11189(17)	−2131(9)	6563(8)	6.4(4)
C(28)	10241(19)	−3936(10)	10912(9)	7.6(4)	C(45)	12500(19)	−2655(10)	6216(10)	8.3(5)
C(29)	8730(9)	−3522(10)	11175(9)	7.9(4)	C(46)	14180(19)	−2486(10)	6148(9)	7.9(4)
C(30)	7516(17)	−3091(9)	10714(8)	6.1(4)	C(47)	14668(18)	−1847(10)	6369(9)	7.4(4)
C(31)	4400(15)	−1844(8)	9823(7)	4.7(3)	C(48)	13388(17)	−1291(9)	6705(8)	6.0(3)
C(32)	2612(17)	−1972(9)	9877(8)	6.2(4)	C(49)	10798(14)	72(8)	7644(7)	4.5(3)
C(33)	1301(18)	−1499(10)	10276(9)	7.2(4)	C(50)	10493(16)	9190(9)	7399(8)	5.5(3)
C(34)	1718(18)	−897(10)	10590(9)	7.4(4)	C(51)	11301(17)	1461(9)	7699(9)	6.5(4)
C(35)	3450(18)	−761(10)	10566(9)	7.1(4)	C(52)	12349(17)	1145(9)	8233(9)	6.8(4)
C(36)	4740(17)	−1232(9)	10168(8)	6.1(4)	C(53)	12677(17)	340(10)	8474(9)	6.9(4)
C(37)	8184(15)	−155(8)	6582(7)	6.4(3)	C(54)	11885(16)	−220(9)	8189(8)	5.8(3)

radical do not react with EtBr, CF_3COOH and reactions with $HgCl_2(C_6H_5COO)_2$, HCl do not proceed readily on heating for a long time. Depending upon R the same regularity in changing reactivity is found also for germyl cadmium compounds.

As a rule, the compounds with C_6F_5– radicals are more oxidation stable than the compounds with hydrocarbon radicals [9]. Thermal stability of Ge–Hg and Ge–Cd compounds increases when passing from compounds with R = Me and Et to compounds containing Ph and Ph^f radicals. $(Et_3Ge)_2Hg$ begins to decompose slowly at 190 °C, $(Ph_3Ge)_2Hg$ melts without Hg formation at 215 °C, and its analogue with Ph^f-radical melts at 230 °C. A similar phenomenon is observed also for germyl cadmium compounds. If $(Ph_3Ge)_2Cd$ decomposes with Cd formation at 105 °C, $(Ph^f_3Ge)_2Cd$ melts at 220 °C.

The chemical properties of germyl derivatives of IIB group metals are investigated in detail, yet the data on structures of these compounds are absent (with an exception of recently determined structure of $[(C_6F_5)_3Ge]_2Hg$ [10]).

As it was interesting to clear up whether the Hg–Ge bond length remains the same in



$$Ph_3Ge{-}Hg{-}\underset{GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Hg{-}\underset{GePh_3}{\underset{|}{Ni}}(\eta^5\text{-}Cp){-}Hg{-}GePh_3\cdot\text{toluene} \qquad \text{(III)}$$

structure, investigated earlier [5], and which is similar to that in $(Ph_3Ge)_2Hg$, X-ray analysis of $(Ph_3Ge)_2Hg$ was carried out.

The latter indicated that an unit cell contains two independent molecules I and II; molecule I is in the centre of symmetry with coordinates (0.5, 0.5, 0.5), the second one is in a general position. The general view of molecule I with numbering of atoms is given in Fig. 1. Bond lengths and valent angles in molecules I and II are listed in Tables II and III, respectively. Hg atoms in both molecules are coordi-

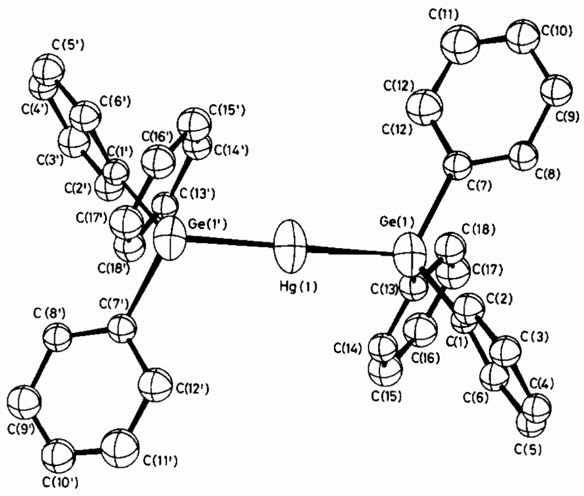


Fig. 1. The general view of molecule I with numbering of atoms.

TABLE II. Bond Lengths (Å) in the Molecules I and II.

Bond Length	Å	Bond Length	Å
C(19)–C(20)	1.42(2)		
C(20)–C(21)	1.41(2)	$\mathrm{C{-}C_{av.}}$	1.39(2)
C(21)–C(22)	1.34(2)		
Hg(1)–Ge(1)	2.543(1)	C(22)–C(23)	1.38(2)
Hg(2)–Ge(2)	2.514(2)	C(23)–C(24)	1.40(2)
Hg(2)–Ge(3)	2.514(2)	C(24)–C(19)	1.38(2)
Ge(1)–C(1)	1.926(13)	C(25)–C(26)	1.39(2)
Ge(1)–C(7)	1.964(12)	C(26)–C(27)	1.44(2)
Ge(1)–C(13)	1.973(13)	C(27)–C(28)	1.34(2)
Ge(2)–C(19)	1.944(13)	C(28)–C(29)	1.34(2)
Ge(2)–C(25)	1.946(13)	C(29)–C(30)	1.40(2)
Ge(2)–C(31)	1.973(13)	C(30)–C(25)	1.40(2)
Ge(3)–C(37)	1.958(13)	C(31)–C(32)	1.40(2)
Ge(3)–C(43)	1.958(13)	C(32)–C(33)	1.41(2)
Ge(3)–C(49)	1.961(13)	C(33)–C(34)	1.36(2)
		C(34)–C(35)	1.37(2)
$\mathrm{Ge{-}C_{av.}}$	1.95(13)	C(35)–C(36)	1.40(2)
		C(36)–C(31)	1.39(2)
C(1)–C(2)	1.43(2)	C(37)–C(38)	1.43(2)
C(2)–C(3)	1.38(2)	C(39)–C(39)	1.39(2)
C(3)–C(4)	1.38(2)	C(39)–C(40)	1.35(2)
C(4)–C(5)	1.37(2)	C(40)–C(41)	1.38(2)
C(5)–C(6)	1.40(2)	C(41)–C(42)	1.40(2)
C(6)–C(1)	1.41(2)	C(42)–C(37)	1.39(2)
C(7)–C(8)	1.36(2)	C(43)–C(44)	1.40(2)
C(8)–C(9)	1.40(2)	C(44)–C(45)	1.41(2)
C(9)–C(10)	1.39(2)	C(45)–C(46)	1.34(2)
C(10)–C(11)	1.35(2)	C(46)–C(47)	1.33(2)
C(11)–C(12)	1.38(2)	C(47)–C(48)	1.42(2)
C(12)–C(7)	1.42(2)	C(48)–C(43)	1.41(2)
C(13)–C(14)	1.42(2)	C(49)–C(50)	1.38(2)
C(14)–C(15)	1.40(2)	C(50)–C(51)	1.42(2)
C(15)–C(16)	1.32(2)	C(51)–C(52)	1.37(2)
C(16)–C(17)	1.38(2)	C(52)–C(53)	1.33(2)
C(17)–C(18)	1.42(2)	C(53)–C(54)	1.41(2)
C(18)–C(13)	1.36(2)	C(54)–C(49)	1.40(2)

TABLE III. Bond Angles (degree) in the Molecules I and II.

Angle	Degree	Angle	Degree
Ge(2)Hg(2)Ge(3)	178.65(5)	Ge(1)C(7)C(8)	123(1)
Hg(1)Ge(1)C(1)	116.0(4)	Ge(1)C(7)C(12)	118(1)
Hg(1)Ge(1)C(7)	108.5(4)	C(7)C(8)C(9)	121(1)
Hg(1)Ge(1)C(13)	111.2(4)	C(8)C(9)C(10)	119(1)
C(1)Ge(1)C(7)	107.8(5)	C(9)C(10)C(11)	121(1)
C(1)Ge(1)C(13)	105.3(5)	C(10)C(11)C(12)	121(1)
C(7)Ge(1)C(13)	107.7(5)	C(11)C(12)C(7)	120(1)
		C(8)C(7)C(12)	119(1)
Hg(2)Ge(2)C(19)	110.1(4)		
Hg(2)Ge(2)C(25)	110.7(4)	Ge(1)C(13)C(14)	119(1)
Hg(2)Ge(2)C(34)	112.3(4)	Ge(1)C(13)C(18)	123(1)
C(19)Ge(2)C(25)	106.6(5)	C(13)C(14)C(15)	119(1)
C(19)Ge(2)C(31)	109.2(5)	C(14)C(15)C(16)	122(2)
C(25)Ge(2)C(31)	107.8(5)	C(15)C(16)C(17)	122(2)
		C(16)C(17)C(18)	118(1)
Hg(2)Ge(3)C(37)	111.0(4)	C(17)C(18)C(13)	122(1)
Hg(2)Ge(3)C(43)	110.5(4)	C(14)C(13)C(18)	118(1)
Hg(2)Ge(3)C(49)	110.3(4)		
		Ge(2)C(19)C(20)	120(1)
C(37)Ge(3)C(43)	108.1(5)	Ge(2)C(19)C(24)	122(1)
C(37)Ge(3)C(49)	108.4(5)		
C(43)Ge(3)C(49)	108.4(5)	C(19)C(20)C(21)	119(1)
		C(20)C(21)C(22)	121(1)
Ge(1)C(1)C(2)	124(1)	C(21)C(22)C(23)	120(2)
Ge(1)C(1)C(6)	122(1)	C(22)C(23)C(24)	120(1)
		C(23)C(24)C(19)	122(1)
C(1)C(2)C(3)	123(1)	C(20)C(19)C(24)	118(1)
C(2)C(3)C(4)	120(1)		
C(3)C(4)C(5)	119(1)	Ge(2)C(25)C(26)	118(1)
C(4)C(5)C(6)	121(1)	Ge(2)C(25)C(30)	123(1)
C(5)C(6)C(1)	122(1)		
C(2)C(1)C(6)	114(1)	C(25)C(26)C(27)	119(1)
C(26)C(28)C(29)	120(1)	C(40)C(41)C(42)	120(1)
C(27)C(28)C(29)	122(2)	C(41)C(42)C(37)	121(1)
C(28)C(29)C(30)	120(2)	C(38)C(37)C(42)	118(2)
C(29)C(30)C(25)	Ge(3)		
C(25)C(26)C(30)	119(1)	Ge(3)C(43)C(44)	120(1)
		Ge(3)C(43)C(48)	122(1)
Ge(2)C(31)C(32)	122(1)		
Ge(2)C(31)C(36)	122(1)	C(43)C(44)C(45)	122(1)
		C(44)C(45)C(46)	117(2)
C(31)C(32)C(33)	120(1)	C(45)C(46)C(47)	124(2)
C(32)C(33)C(34)	121(1)	C(46)C(47)C(48)	121(2)
C(33)C(34)C(35)	121(2)	C(47)C(48)C(43)	118(1)
C(34)C(35)C(36)	117(1)	C(44)C(43)C(48)	118(1)

(continued overleaf)

TABLE III. *(continued)*

Angle	degree	Angle	degree
C(35)C(36)C(31)	125(1)	Ge(3)C(49)C(50)	123(1)
C(32)C(31)C(36)	116(1)	Ge(3)C(49)C(54)	118(1)
Ge(3)C(37)C(38)	120(1)	C(49)C(50)C(51)	119(1)
Ge(3)C(37)C(42)	122(1)	C(50)C(51)C(52)	119(1)
		C(51)C(52)C(53)	123(2)
C(37)C(38)C(39)	120(1)	C(52)C(53)C(54)	119(1)
C(38)C(39)C(40)	121(1)	C(53)C(54)C(49)	120(1)
C(39)C(40)C(41)	121(1)	C(54)C(49)C(50)	119(1)

nated linearly, yet Ge(2)–Hg(2)–Ge(3) angle, 178.68(3)°, in molecule II is slightly distorted and differs from an ideal value of 180°. Hg–Ge bond lengths in molecules I and II differ considerably, they being 2.543(1) Å in molecule I and 2.514(2) Å in molecule II, respectively, the first one being much more than the second. Such a considerable difference of Hg–Ge bond lengths in independent molecules is probably due to packing effects only, as the only difference between molecules I and II is their different packing in crystal (see Fig. 2). The value of Hg–Ge bond in molecule I is close to this bond value 2.534(3) Å, which was obtained for Ph$_3^f$Ge–Hg–Pt(PPh$_3$)$_2$–SnPh$_3^f$ [11], in molecule II it coincides with the value 2.516(3) Å, which was obtained earlier in structure III [5] and is close to the sum of covalent radii in Hg and Ge atoms 2.52 Å (r_{Hg} = 1.30 Å [12], r_{Ge} = 1.22 Å [13]). At the same time Hg–Ge bond length values in molecules I and II are significantly greater than the length of this bond, 2.483(1) Å, in (Ph$_3^f$Ge)$_2$Hg structure [10]. This seems to confirm the validity of the assumption of shortening Hg–Ge bond in the latter at the expense of Hg···F intramolecular interaction [10].

Thus, Hg–Ge bond length values obtained in four structures mentioned above are within the broad range between 2.483(1) and 2.543(1) Å; this seems to be indicative of the 'looseness' of the Hg–Ge bond and the dependence upon external factors (additional intramolecular interaction, steric factors).

Ge atoms have a distorted tetrahedral coordination. The average values of Hg–Ge–C angle in molecules I and II are equal to 111.9(4) and 110.8(4)°,

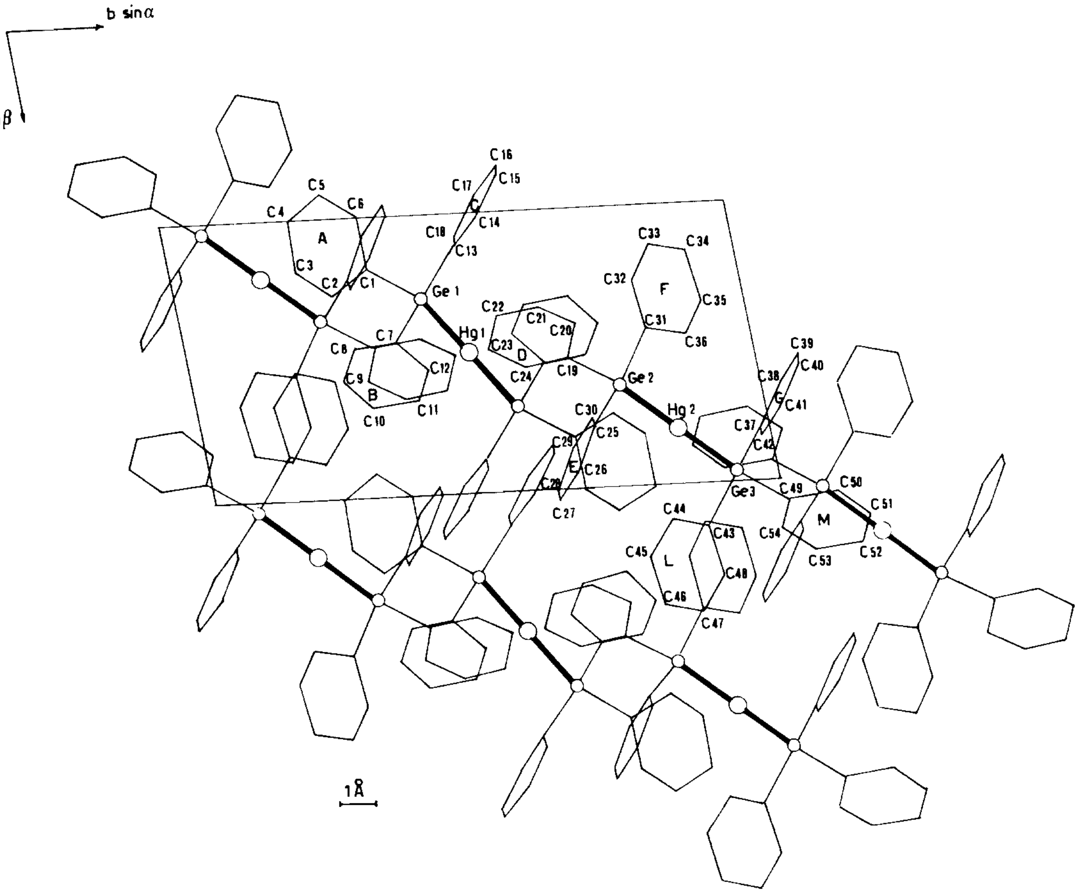


Fig. 2. Crystal packing of molecules I and II. The projection is along the C axis (Hg–Ge bonds are printed by thick lines).

respectively, *i.e.* they are somewhat greater in comparison with an ideal value of 109.5°. Ge–C bond lengths in molecules I and II vary between 1.93(1) and 1.97(1) Å, the average value coinciding with this bond length 1.959(9) Å in (Ph$_3^f$Ge)$_2$Hg molecule [10]. Phenyl rings are planar (the maximum deviation of atoms from mid-planes or Ph- rings is 0.02 Å). The average values of C–C bond lengths and C–C–C angles in molecules I and II are the same and equal to 1.39(2) Å and 120(2)°, respectively. Dihedral angles between Ph-rings are equal to: 66.8(AB), 73.4(AC), 70.2(BC), 70.9(DE), 67.7(DF), 67.7(GL), 64.4(GM), 66.1(LM) (see Fig. 2). Ge atoms are slightly outside the scope of Ph-ring planes: deviations lie within the range between $-0.05 \div 0.05$ Å (exclusive of Ge(1) atom being outside the scope of C-ring in molecule I at a distance of -0.11 Å).

It is of interest that the difference between two exocyclic Ge–C–C angles at carbon ipso- atoms of Ph-rings in molecules I and II is not so great as that found at ipso-carbons of two C_6F_5-rings in (Ph$_3^f$Ge)$_2$Hg molecule. The maximum difference of these angles in molecules I and II is equal to 5° [(Ge(1)–C(7)–C(8) 123(1)° and Ge(1)–C(7)–C(12) 118(1)°], yet in (Ph$_3^f$Ge)$_2$Hg molecule these angles differ greatly: 128.4(7) and 116.7°, 126.5(7) and 118.2(7)°.

It should be noted that (Ph$_3$Ge)$_2$Hg monocrystals are rather stable in the air (do not change during several days), whereas fine-powdered (Ph$_3$Ge)$_2$Hg as well as its solutions are easily oxidized by air oxygen. This stability is probably explained by the fact that Hg atoms in a crystal (due to stepwise molecule position relative to each other) are screened not only by Ph$_3$Ge-fragments bonded directly with them, but also by Ph$_3$Ge fragments of the neighbouring molecules (see Fig. 2). This prevents the approach of oxygen molecules to Hg atoms.

The change of substituents in the series Alk, Ph and Ph^f results in increasing $\mathrm{Ge}^{\delta-} \leftarrow \mathrm{M}^{\delta+}$ (M = Cd, Hg) bond polarity. It should facilitate reactions proceeding through heterolytic mechanisms (reactions with RHal, RCOOH, HgCl$_2$). This phenomenon is confirmed and illustrated by many examples of reactions between R$_2$Hg and acids, though it lacks any general nature. As was mentioned earlier the reverse phenomenon is observed for germylmercury derivatives with Ph and Ph^f substituents.

Steric factors, such as the extent of screening a central metal atom, are supposed to play a large part in case of (R$_3$Ge)$_2$Hg (R = Alk, Ph and Ph^f).

The projection of a molecule on the unit radius cylinder, the axis of which coincides with the line connecting M–M′ atoms (see Fig. 3a) is a striking feature of the extent of screening a central metal atom in molecules, such as R$_3$M–M′–MR$_3$. In this case the atoms of the molecule represent hard spheres with van der Waals radii. We have composed a FORTRAN program for computer aided calculation of such cylindrical projections for arbitrary molecules using symmetry and parameters of the elementary cell and atomic coordinates of the molecule as well. The developments of such cylindrical projections for (R$_3$Ge)$_2$Hg with R = Me, Ph and Ph^f are given in Fig. 3b. (The projection of (Me$_3$Ge)$_2$Hg molecule was constructed on the basis of (Ph$_3$Ge)$_2$Hg crystal structure). While computing the following values of van der Waals radii were used: $r_c = 1.59$ Å and $r_o = 1.36$ Å [14]. Hydrogen atoms were not taken into account. These projections show an extent of screening a central Hg atom in the molecule and therewith allow to estimate a possibility of an approach of other molecules (oxygen, water and others) to Hg atom.

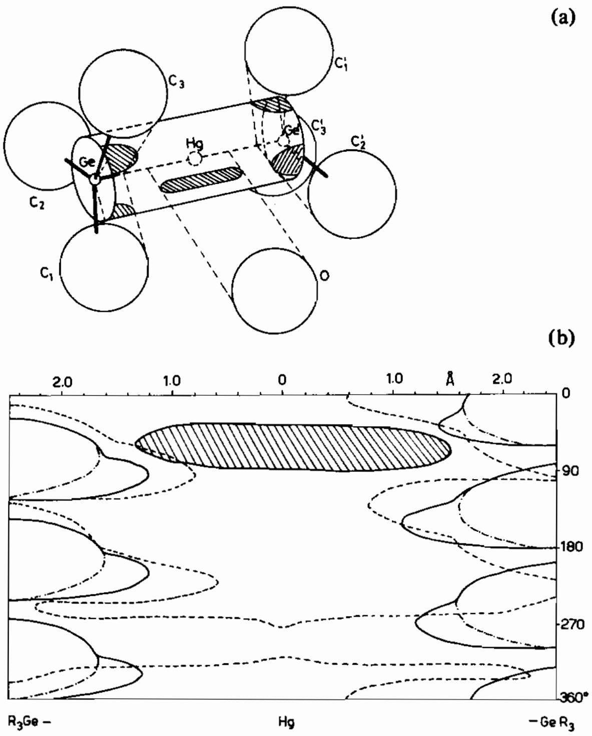


Fig. 3. The scheme illustrating the construction of a cylindrical projection of (Me$_3$Ge)$_2$Hg (a) molecule. The developments of cylindrical-projections (Ge–Ge is an axis of the cylinder) of (Me$_3$Ge)$_2$Hg (–·–·–), (Ph$_3$Ge)$_2$Hg (———) and (Ph$_3^f$Ge)$_2$Hg (-------) molecules. The shaded area is a projection of an oxygen atom (from a molecule of oxygen), located at a distance of 3 Å from the Hg atom (b).

For comparison, an oxygen atom located at the distance of 3 Å from the Hg atom was projected on the same cylinder (see Fig. 3). It is seen (Fig. 3) that in case of Me-substituents the minimum distance between terminal points of Me-groups bound to different Ge-atoms in (Me$_3$Ge)$_2$Hg molecule is equal to 3.3 Å, *i.e.* Me-groups shield slightly the

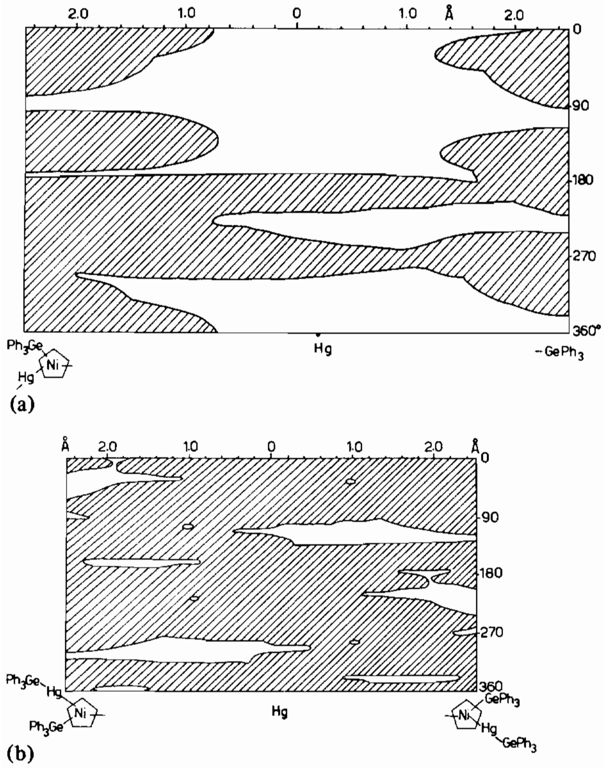


Fig. 4. Developments of a cylindrical projection (a projection of a molecule is a shaded area) of the symmetrically independent part of molecule III: $Ph_3Ge{-}Hg{-}\underset{GePh_3}{Ni}(\eta^5\text{-}C_p){-}Hg{-}\underset{GePh_3}{Ni}(\eta^5\text{-}C_p){-}Hg{-}GePh_3\cdot$toluene (Ni–Ge(2) is an axis of the cylinder) (a) and of the whole molecule III (Ni–Ni is an axis of the cylinder) (b).

Hg atom thus allowing an oxygen atom to approach it freely. With more bulky Ph-substituents, *i.e.* in the case of more effective Hg atom shielding, such a possibility of approaching is yet substantially restricted, as the minimum distance between Ph-groups at different Ge atoms is 2.2 Å. With Ph^f substituents Hg atom shielding is still further increased. Anomalies in arrangement of two Ph^f-rings in $(Ph_3^fGe)_2Hg$ molecule (Fig. 3b) are caused by its specific structural features, *viz.* by intramolecular secondary Hg•••F and Ge•••F interactions [10]. The influence of this interaction and the steric shielding of Hg atom in the molecule on its stability and reactivity is discussed in the present paper.

The projections given show that the extent of shielding a central Hg atom in $(R_3Ge)_2Hg$ (R = Me, Ph, Ph^f) molecules correlates well with the data mentioned above on reactivity and thermal stability for these compounds, *i.e.* with increasing the extent of shielding a central metal atom, the reactivity decreases and thermal stability of these compounds increases.

When comparing compounds such as $(R_3Ge)_2M$ and $Ph_3Ge{-}M{-}\underset{GePh_3}{Ni}(\eta^5\text{-}C_p){-}M{-}\underset{GePh_3}{Ni}(\eta^5\text{-}C_p){-}M{-}GePh_3$ (M = Cd, Hg), a sharp increase of thermal stability should be observed when passing from $(Ph_3Ge)_2Cd$ (dec. T. 105 °C) to $Ph_3{-}Cd{-}\underset{GePh_3}{Ni}(\eta^5\text{-}C_p){-}Cd{-}\underset{GePh_3}{Ni}(\eta^5\text{-}C_p){-}Cd{-}GePh_3$ compound (dec. T. 195 °C). X-ray analysis was carried out for all these compounds earlier [4, 5]. The cylindrical projection (Ni–Ge(2) is an axis of the cylinder) of a symmetrically independent part of $Ph_3Ge(2){-}Hg(2){-}\underset{Ge(1)Ph_3}{Ni}(\eta^5\text{-}C_p){-}Hg(1){-}\underset{Ge(1)Ph_3}{Ni}(\eta^5\text{-}C_p){-}Hg(2){-}Ge(2)Ph_3$ (the whole of the molecule is centrosymmetrical) is given in Fig. 4a, which indicated that Hg(2) atom in this fragment is substantially shielded from access from outside. On cylindrical projection of the whole of the molecule (Fig. 4b) (Ni–Ni is an axis of the cylinder) the Hg(1) central atom in this molecule proves to be completely closed. The similar phenomenon is observed for the Cd-analogue.

Thus, covalent M–M bonds in the above mentioned polynuclear organometallic compounds are strongly shielded by all ligands from external influences and form a metallic 'skeleton' inside an 'organic case' which seems to be responsible for an increased stability of polymetallic chains.

It is interesting to note that in the reaction between $(Et_3Ge)_2Cd$ and $(\eta^5\text{-}C_p)_2Ni$ we have not succeeded in isolating polynuclear organometallic compounds, perhaps because of weakly shielding M–M bonds by ethyl substituents.

Experimental

X-ray analysis was performed with an automatic diffractometer 'Syntex $P2_1$' (λMoKα, 4555 independent reflections with $I > 2\sigma$, $2\theta/\theta$ scan in the range of I $\leqslant 20 \leqslant 50°$). Intensities were corrected for absorption (μ/MoKα) = 70.3 cm^{-1}) taking into account the real shape of a crystal according to [15].

The crystals of $(Ph_3Ge)_2Hg$ are triclinic at 20 °C, a = 7.660(2), b = 16.562(3), c = 19.220(4) Å, α = 79.04(1), β = 81.65(2), γ = 81.68(2)°, d_{meas} = 1.69, d_{calc} = 1.71 g cm^{-3}, Z = 4. Space group P I.

The structure was solved by the heavy atom method. Hg atoms were localized in the Patterson function, the other nonhydrogen atoms were revealed by subsequent electron density syntheses. H atoms were placed into positions calculated on geometrical ground (C–H 1.0 Å, C–C–H 120°), but their positional and isotropic thermal parameters (assumed B_{iso} = 5.0 Å) were not refined. The structure was refined by a least squares technique in block-diagonal approximation with anisotropic thermal factors for Hg and Ge atoms and with isotropic ones for C atoms. The final values of discrepancy factors are R = 0.065 and R_{Ge} = 0.045. Atomic coordinates and their anisotropic-isotropic thermal factors are given in Table I. All calculations were performed with an Eclipse S/200 mini-computer using EXTL programs.

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