

Isomerism in the Chemistry of Organogermanium Compounds (Part II)

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Abstract: The organogermanium chemistry covers huge fields, as shown by a survey covering the crystallographic and structural data of over four hundred and fifty examples. Over 10 percent of those compounds exist as distortion isomers (around 97 %) and ligand isomers (around 3 %). These are discussed in term of coordination around the Ge(II), Ge(IV) and Ge⁺³ atoms, and correlations are drawn between donor atoms, bond lengths and bond angles. Distortion isomers differ by degree of distortion in Ge – L distances and L-Ge-L angles. Interestingly, in the chemistry germanium coordination complexes besides configuration isomers, also distortion isomers dominate.

Keywords: Organogermanium, distortion, ligand isomerism, structure, analyse.

1. INTRODUCTION

Systematic studies in the field of stereoselectivity of complexes over the last 50 years have become of increasing interest. Isomers can be broadly classed into two main categories, structural and stereoisomers. The former can be divided into ionisation, hydrate, coordination number, linkage and polymerization sub-categories. The latter can be divided into geometric (cis – trans, fac-mer), optical and distortion isomerism.

Germanium exists in a range of oxidation states +1, +2, +4 and mixed valences. Oxidation state +4 is the most common. The large area of germanium organometallic compounds has recently been surveyed [1] with almost fifty isomeric examples noted. In this review we analyse and classify these examples.

Analyses of germanium coordination compounds showed [2] that there are at least two types of isomerism, i.e. distortion and configuration, from which the former, by far, prevails.

The system discussed have been sorted by nuclearity, and then subdivided according to the coordination number of the germanium atom. Within each coordination number, the compounds are listed in order of increasing covalent radius of the principle coordinating ligand atom and increasing complexity of coordination sphere.

2. DISTORTION ISOMERISM

The coexistence of two or more species differing only by degree of distortion of M-L bond distances and L-M-L bond angles is typical of the general class of distortion isomerism [3] There are almost fifty such examples in the chemistry of organogermanium compounds. The germanium oxidation states in these isomers are found to be Ge⁺³, +2 and +4 (the most common).

2.1. Monomeric Derivatives

The crystallographic and structural data for monomeric organogermanium distortion isomers are given in Table 1. There are two examples, yellow Ge(mes)(Bu¹){P(2,4,6-Bu¹₃C₆H₂)} [4] and colourless Ge(CPh)₄ [5,6], which exists in two isomeric forms.

In the former yellow example [4] both isomeric forms are monoclinic. In each isomer three different monodentate ligands, two C – donors and one P – donor ligand, create around each germanium (IV) atom a pyramidal environment (GeC₂P). The sum of all Ge-L bond distances (Ge-C(x2) plus Ge-P) is 6.124 Å in one isomer and 6.103 Å in another one. The L-Ge-L bond angles range from 110.9(5) to 134.7(4)^o and 110.7(6) to 137.2(5)^o, respectively.

Isomers of the Ge(CPh)₄ also differ by crystal class, one is tetragonal [5] and another one is orthorhombic [6,7]. Four unidentate C≡CPh ligands form a tetrahedral environment around each Ge(IV)atom (GeC₄).

There are twenty five derivatives which contain two crystallographically independent molecules within the same crystal (Table 1). Yellow Ge{2,3,5-(MeSi)₃C₅H₂}₂ [7] has a sandwich structure. The Ge-C (centroid distances and C(centroid)-Ge-C(centroid) angles are 2.256 and 2.261 Å with 169.48^o in molecule one and 2.250 and 2.252 Å with 171.77^o in molecule 2. The former molecule is somewhat less compressed than the latter one.

In orange Ge(frl)(mes)₂ [8] three unidentate C – donor ligands create a pyramidal arrangement around each germanium atom. Each molecule has one Ge = C bond of length 1.801 Å (molecule 1) and 1.806 Å (molecule 2). The other Ge-C bonds have a mean value of 1.937 Å.

The most common chromophore is GeC₄, created by four unidentate ligands [9-13], two uni- and one bidentate ligands [14,15]. In colourless Ge(Me)₃(η¹-pepp) [9] the sum of all four Ge-C bond distances are 7.98 Å (molecule 1) and 7.82 Å (molecule 2). In the former molecule deviation of the C-Ge-C bond angle from the ideal tetrahedral (109.5^o) is 10.2^o, which is much higher than that found in the latter molecule (4.5^o). This indicates that the former molecule is more distorted than the latter one.

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Table 1. Crystallographic and Structural Data for Monomeric Germanium Organometallic - Distortion Isomers^a

Compound (Colour)	Cryst. Cl. Space Gr. Z	a[Å] b[Å] c[Å]	α [°] β [°] γ [°]	Chromophore	Ge – L [Å]	L – Ge – L [°]	Ref.
Ge(mes)(Bu ^t) {P(2,4,6-Bu ^t ₃ C ₆ H ₂)} (yellow)	m C2/m 4	19.323(8) 15.216(8) 10.919(2)	103.7(2)	GeC ₂ P	mesC ^b 1.97(1) Bu ^t C 2.01(1) P 2.144(3)	C,C ^b 110.9(5) C,P 114.4(3) 134.7(4)	[4]
Ge(mes)(Bu ^t) {P(2,4,6-Bu ^t ₃ C ₆ H ₂)} (yellow)	m C2/m 4	19.352(1) 15.197(1) 10.927(2)	103.86(3)	GeC ₂ P	mesC 1.95(1) Bu ^t C 2.01(1) P 2.143 (4)	C,C 110.7(6) C,P 114.1(4) 135.2(5)	[4]
Ge(CCPPh) ₄ (colourless)	tg I-4 2	13.54 6.73		GeC ₄			[5]
Ge(CCPPh) ₄ (colourless)	or P2 ₁ nb 4	19.06 19.65 6.75		GeC ₄			[6]
Ge{2,3,5-(Me ₃ Si) ₃ - C ₃ H ₂ } ₂ (yellow)	tr P-1 4	11.377(3) 19.520(3) 20.780(3)	115.93(1) 97.43(21) 74.34(2)	GeC ₂ ^c GeC ₂ ^c	C ^c 2.256 2.261 C 2.250 2.252	C ^c ,C ^c 169.48 C ^c ,C ^c 171.77	[7]
Ge(frl)(mes) ₂ (orange)	tr P-1 4	12.115(4) 13.069(2) 16.539(2)	87.61(2) 77.19(2) 78.83(2)	GeC ₃ GeC ₃	frlC 1.801 mesC 1.937(-,7) frlC 1.806 mesC 1.937(-,7)	C,C not given C,C not given	[8]
Ge(Me) ₃ (η^1 -pepp) (colourless) (at 173 K)	tr P-1 2	11.049(4) 12.105(4) 20.510(7)	75.97(5) 78.97(5) 94.8(5)	GeC ₄ GeC ₄	MeC 1.92(2,3) 2.13(4) η^1 C 2.01(4) MeC 1.96(2,2) η^1 C 1.94(1)	C,C 109.5(9,10.2) C,C 109.5(9,4.5)	[9]
Ge(Et) ₃ (η^1 -pha) (colourless)	m P2 ₁ /n 8	9.468(4) 13.613(4) 20.971(5)	96.24(3)	GeC ₄ GeC ₄	EtC 1.94(6,3) 2.08(5) η^1 C 1.91(1) EtC 1.93(6,1) 2.13(5) η^1 C 1.93(4)	C,C 109.5(1.0,4.5) C,C 109.5(1.0,1.5)	[10]
Ge(Ph) ₃ (η^1 -pcpt) (colourless)	not given			GeC ₄ GeC ₄	PhC 1.941(4) 1.954(4,5) η^1 C 1.946(4) PhC 1.932(5) 1.961(5,8) η^1 C 1.958(4)	C,C 109.5(2,5.3) C,C 109.5(2,1.5)	[11]

(Table 1). Contd.....

Ge(Ph) ₃ (η ¹ -tm) (colourless)	m C2/c 8	16.916(8) 11.110(8) 24.217(16)	96.86(2)	GeC ₄ GeC ₄	PhC 1.943(6) 2.092(7) 2.215(6) η ¹ C 2.093(7) PhC 1.932(6) 2.057(7) 2.233(6) η ¹ C 2.114(6)	C,C 109.5(3,6,7) C,C 109.5(4,8,6)	[12]
Ge(Me) ₂ (η ¹ -pha). (η ¹ -adam) (colourless)	tr P-1 4	9.565 (2) 11.629 (3) 15.468 (2)	105.2 (1) 91.2 (1) 93.5 (2)	GeC ₄ GeC ₄	MeC 1.978(11,7) phaC 1.986(10) adamC 1.987(8) MeC 1.986(12,1) phaC 1.975(10) adamC 1.965(9)	C,C 109.5(5,4,1) C,C 109.5(6,3,7)	[13]
Ge(Me) ₂ (η ² -tphc) (colourless)	tr P-1 4	9.087(5) 14.154(7) 18.859(11)	85.74(4) 89.28(4) 83.97(4)	GeC ₄ GeC ₄	MeC 1.945(4,9) η ² C 1.950(3,1) MeC 1.942(5,2) η ² C 1.940(3,1)	C,C 89.9(1) ^d 109.2(2,4) 115.8(2,1.8) C,C 89.8(1) ^d 110.7(2,1) 114.8(2,2,3)	[14]
Ge(Et) ₂ (η ² -tphc) (colourless)	tr P-1 4	11.238(1) 12.855(2) 18.423(3)	107.20(1) 99.79(2) 90.72(2)	GeC ₄ GeC ₄	EtC 1.882(5,2) η ² C 1.925(5,3) EtC 1.883(6,2) η ² C 1.929(5,4)	C,C 90.9(2) ^d 106.5(2) 114.8(2,2,6) C,C 91.9(2) ^d 107.6(2) 114.2(2,2,0)	[15]
Ge(tdmp) ₃ (H) (colourless)	m P2 ₁ /n 8	35.046(5) 16.787(1) 8.907(2)	90.26	GeC ₃ H	C 1.959(8,0) H 1.58(8)	C,C 106.8(3) C,H 112(2)	[16]
Ge(Ph) ₃ {O(S)PPh ₂ } (colourless)	m P2 ₁ /c 8	19.515(8) 14.990(7) 20.889(7)	117.37(3)	GeC ₃ O GeC ₃ O	PhC 1.92(1,1) O 1.825(7) PhC 1.92(1,1) O 1.826(8)	C,C 112.5(6,2,3) C,O 106.2(4,6,2) C,C 113.1(6,9) C,O 105.5(4,6,9)	[17]
Ge(Ph) ₃ (OH) (colourless) (at 208 K)	tr P-1 16	15.408(6) 19.974(7) 23.264(11)	107.78(4) 103.54(4) 101.51(3)	GeC ₃ O	PhC 1.931(9,24) HO 1.791 (7,7)	C,C 107.1(4,2,4) C,O 111.7(4,2,7)	[18]
[Ge(mes) ₂ .{η ² -frl. (OCPh)}.0.5 C ₅ H ₁₂] (light yellow)	m P2 ₁ /c 8	22.807 (5) 17.713 (6) 18.425 (4)	102.64(2)	GeC ₃ O GeC ₃ O	mesC 2.00(2,4) η ² C 2.07(2) η ² O 1.83(1) mesC 1.97(3,1) η ² C 2.04(2) η ² O 1.82(1)	C,O 75(1) ^e C,O 75(1) ^e	[19]

(Table 1). Contd.....

Ge(Me) ₃ { η^1 -N. (SO ₂ Me) ₂ (colourless) (at 178 K)}	tr P-1 4	7.717(2) 12.041(4) 13.884(5)	66.75(3) 84.12(3) 74.15(2)	GeC ₃ N GeC ₃ N	MeC 1.926(3,5) η^1 N 1.982(2) MeC 1.929(3,7) η^1 N 1.985(2)	C,C 110.9(1,1.0) 115.7 (1) C,N 106.2(1,2.5) C,C 109.3(1) 114.7(1,1.4) C,N 105.9(1,3.0)	[20]
Ge(Ph) ₃ { η^1 -SCOPr [†] (colourless)}	tr P-1 2	14.386(7) 18.598(6) 9.223(3)	102.85(3) 94.58(3) 108.1(3)	GeC ₃ S GeC ₃ S	PhC 1.94(1,1) η^1 S 2.251(5) PhC 1.94(1,0) η^1 S 2.256(5)	C,C 111.8(6,1.3) C,S 99.4(3) 110.8(4,2.4) C,C 111.5(6,2.2) C,S 100.8(3) 110.5(4,2.2)	[21]
Ge(mes) ₂ { η^2 -at (colourless)}	m P2 ₁ /n 8	24.277 (5) 10.789 (1) 18.832 (2)	98.70(1)	GeC ₃ S GeC ₃ S	mesC 1.957(4,1) η^2 C 1.973(5) η^2 S 2.222(1) mesC 1.961(5,8) η^2 C 1.970(5) η^2 S 2.222(1)	C,C 116.1(1,8) 126.2(1) C,S 52.9(1) ^f 114.6(1,4.5) C,C 114.4(1,1.0) 128.6(1) C,S 52.8(1) ^f 115.4(1,3.2)	[22]
Ge{CH(SiMe ₃) ₂ } ₂ . (η^2 -PCBu [†]) (yellow)	m P2 ₁ /n 8	23.074(5) 12.548(3) 23.235(5)	118.74 (2)	GeC ₃ P GeC ₃ P	C not given η^2 C 1.932(1) η^2 P 2.298(4) C not given η^2 C 1.928(1) η^2 P 2.291(4)	C,P 45.2 (3) ^f C,P 45.9(3) ^f	[23]
Ge(mes) ₂ { η^2 -dbtp (white)}	tr P-1 4	10.950(9) 16.921(12) 17.299(13)	110.23(7) 91.70(7) 90.61(6)	GeC ₃ P GeC ₃ P	mesC 1.976(7,1) η^2 C 1.962(9) η^2 P 2.354(3) mesC 1.991(10,0) η^2 C 1.953 (8) η^2 P 2.369 (3)	C,C 115.9(4,4.0) C,P 75.6(3) ^e 115.8(3,6.0) C,C 115.9(4,3.4) C,P 75.2(3) ^e 116.0(3,5.0)	[24]
Ge(Ph) ₃ Br (not given)	m P2 ₁ /c 8	18.770(4) 9.662(3) 18.467(4)	106.84(8)	GeC ₃ Br GeC ₃ Br	PhC 1.934(10,7) Br 2.318(2) PhC 1.936(10,5) Br 2.322(3)	C,C 112.4(4,2.5) C,Br 106.4(4,5) C,C 112.5(4,1.6) C,Br 106.3(4,9)	[25]
GeCl ₃ { η^1 -pce (colourless)}	tr P-1 4	8.450(4) 11.730(5) 14.718(6)	104.50(3) 103.71(4) 69.20(3)	GeCl ₃ C GeCl ₃ C	Cl 2.118(2,18) η^1 C 1.949(9) Cl 2.116(2,9) η^1 C 1.952(7)	Cl,Cl 107.1(2,4) Cl,C 111.7(2,1.0) Cl,Cl 106.8(2,5) Cl,C 112.0(2,2.5)	[26]
[Ge(η^1 -S ₂ COPr [†]) ₃ . (Me)] _{0.5} CS ₂ (colourless) (at 245 K)	tr P-1 4	14.81(1) 14.82(1) 14.04(1)	93.01(7) 114.19(5) 60.09(4)	GeS ₃ C GeS ₃ C	η^1 S 2.247(5,10) MeC 1.91(1) η^1 S 2.250(5,9) MeC 1.92(1)	S,S 102.3(2,3) S,C 115.9(5,5) S,S 102.4(2,7) S,C 115.9(5,1.0)	[27]

(Table 1). Contd.....

Ge(Et) ₂ { η^2 -P ₂ (Bu ^t) ₂ (colourless) (at 113 K)	m C2/c 12	51.935(11) 9.786(3) 10.137(3)	100.02(2)	GeC ₂ P ₂ GeC ₂ P ₂	EtC 1.958(8,0) η^2 P 2.301(2,0) EtC 1.960(9,4) η^2 P 2.298(2,2)	P,P 58.0(1) ^f P,P 58.0(1) ^f	[28]
Ge(Me)(Ph). (η^2 -dmamp)Cl (colourless)	m P2 ₁ /n 8	7.540(2) 13.461(4) 12.876(1)	96.56(1)	GeC ₃ NCl GeC ₃ NCl	C _{eq} not given N _{ax} 2.479(11) Cl _{ax} 2.327(5) N _{ax} 2.508(11) Cl _{ax} 2.301(4)	C,N 77.3(4) ^d N,Cl 174.0(2) C,N 76.6(4) ^d N,Cl 173.8(3)	[29]
GeCl ₃ (η^2 -mba) (colourless)	m P2 ₁ /c 8	13.883(3) 11.582(4) 17.773(7)	107.02(3)	GeCl ₃ OC GeCl ₃ O	Cl _{eq} 2.140(3,8) η^2 C _{eq} 1.98 (1) η^2 O _{ax} 2.080 (7) Cl _{ax} 2.252 (3) Cl _{eq} 2.145(3,5) η^2 C _{eq} 1.97(1) η^2 O _{ax} 2.092(7) Cl _{ax} 2.239(3)	Cl,Cl 95.6(1,1.4) 111.7(2) Cl,O 86.9(2,1.4) 174.5(2) Cl,Cl 93.5(3); 123.1(3,4.9) O,C 82.3(4) ^d Cl,Cl 95.5 (4,1) 113.0(1) Cl,O 86.4(2,4) 176.5 (2) Cl,Cl 95.6 (1) 122.1 (4,6) O,C 81.2 (4) ^d	[30]
Ge(Me) ₂ (η^2 -S ₂ . CNMe ₂)Br (not given)	m P2 ₁ 4	9.471(4) 10.777(5) 11.383(4)	106.99(3)	GeC ₂ S ₂ Br GeC ₂ S ₂ Br	MeC _{eq} 1.96(2,0) η^2 S _{eq} 2.222(4) η^2 S _{ax} 2.840(5) Br _{ax} 2.418(3) MeC _{eq} 1.89(2,1) η^2 S _{eq} 2.252(4) η^2 S _{ax} 2.817(5) Br _{ax} 2.430(5)	C,C 119.4(2) S,S 69.8(1) ^e C,S 88.8(6,1.9) 117.9(5,2.7) C,Br 101.0 (6,5) S,Br 89.4;159.1(1) C,C 120.8(9) S,S 69.2 (2) ^e C,S 87.9(6,3) 116.6(6,1.9) C,Br 101.2(5,1.1) S,Br 91.5;161.1(1)	[31]
[GeF ₅ (η^1 -mbach)]. H ₂ O (colourless) (at 173 K)	tr P-1 4	7.5228(11) 12.174(2) 12.304(2)	73.74(2) 82.44(2) 74.76(1)	GeF ₅ C GeF ₅ C	F 1.796(2,9) 1.848(1,19) η^1 C 1.977(2) F 1.810(2,21) 1.849(2,3) η^1 C 1.978(2)	F,F 88.79(7,3.68) 174.60(7,39) F,C 92.26(9,2.38) 176.19(9) F,F 88.49(7,3.14) 174.12(7,60) F,C 92.84(9,1.32) 177.13(9)	[32]

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

^bThe chemical identity of the coordination atom or ligand is specified in these columns.

^cThe ring centroid.

^dFive membered metallocyclic ring.

^eFour membered metallocyclic ring.

^fThree membered metallocyclic ring.

In another colourless $\text{Ge}(\text{Et})_3(\eta^1\text{-pha})$ [10] the sum of all four Ge-C bond distances and deviation of the C-Ge-C bond angles from the ideal (109.5°) are 7.87 \AA and 4.5° (molecule 1) and 7.92 \AA and 1.5° (molecule 2).

Two colourless $\text{Ge}(\text{Ph})_3(\eta^1\text{-CL})$ (CL = pcpt [11] or tm [12]), follow the same trend with the values in the former of 7.795 \AA and 5.3° (molecule 1) and 7.812 \AA and 1.5° (molecule 2). The values of the latter [12] are 8.343 \AA , 6.7° (molecule 1), and 8.336 \AA , 8.6° (molecule 2). The mean Ge-C bond distance in the series elongates in the sequence: 1.795 \AA (Me) < 1.992 \AA (Et) < 2.015 \AA (Ph), which follows bulky ligands.

In $\text{Ge}(\text{Me})_2(\eta^1\text{-pha})(\eta^1\text{-adam})$ [13] three different unidentate C – donor ligands create a tetrahedral environment around each germanium atom with different degree of distortion.

In two colourless $\text{Ge}(\text{CL})_2(\eta^2\text{-tphc})$ (CL = Me [14] or Et [15]) a tetrahedral environment around each Ge(IV) atom is built up by two unidentate CL and one bidentate tphc ligand, which form one five – membered metallocyclic ring. Distortions of the coordination polyhedra from the regular tetrahedral geometry differ from each other (Table 1).

A tetrahedral arrangement around each Ge(IV) atom in $\text{Ge}(\text{tdmp})_3(\text{H})$ [16] is created by three unidentate C – donor tdmp ligand and hydrogen (GeC_3H). Unfortunately only mean values are given in original paper.

There are three derivatives, $\text{Ge}(\text{Ph})_3\{\text{O}(\text{S})\text{PPh}_2\}$ [17], $\text{Ge}(\text{Ph})_3(\text{OH})$ [18] and $\text{Ge}(\text{mes})_2\{\eta^2\text{-fri}(\text{OCPh})\}$. $0.5 \text{ C}_5\text{H}_2$ [19], in which Ge(IV) atom has a tetrahedral arrangement (GeC_3O). While the two derivatives [17, 19] contain two crystallographically independent molecules, the $\text{Ge}(\text{Ph})_3(\text{OH})$ [18] contains eight such molecules. Unfortunately, only mean values are given in original paper. While in [17, 18] the GeC_3O chromophore is built up from unidentate ligands, in [19] it is made of two unidentate mesityl ligands and one hetero-bidentate (O+C) ligand. The tetrahedra differ by degree of distortion (Table 2).

In colourless $\text{Ge}(\text{Me})_3\{\eta^1\text{-N}(\text{SO}_2\text{Me})_2\}$ [20] a tetrahedral arrangement around Ge(IV) atom is created by three C donor atoms of methyl groups and a unidentate N- donor $\text{N}(\text{SO}_2\text{Me})_2$ ligand (GeC_3N). The sum of all four Ge – C(x3) and Ge-N(x1) bond distances are 7.76 \AA (molecule 1) and 7.77 \AA (molecule 2). The six “tetrahedral angles” fall in the narrow range $103.7(1) - 115.7^\circ$ and $102.9(1) - 116.1(1)^\circ$, respectively. This indicates a somewhat higher degree of distortion in molecule 2 than in molecule 1 (Table 1).

There are two colourless derivatives, $\text{Ge}(\text{Ph})_3(\eta^1\text{-SCOPr}^i)$ [21] and $\text{Ge}(\text{mes})_2(\eta^2\text{-at})$ [22] in which each Ge(IV) atom has a tetrahedral arrangement (GeC_3S). In the latter a tetrahedral geometry is created by two unidentate C – mesityl ligands and one heterobidentate C + S donor, 3-(2-adamantyl)-thia ligand. Five of the six “tetrahedral angles” fall in the narrow range $110.1(1) - 126.2(1)^\circ$ (molecule 1) and $113.2(1) - 128.6(1)^\circ$ (molecule 2), while the angle which is part of the three – membered metallocycle (-CS-) is significantly smaller ($52.9(1)$ and $52.8(1)^\circ$), respectively.

In another two derivatives, yellow $\text{Ge}\{\eta^1\text{-CH}(\text{SiMe}_3)_2\}_2(\eta^2\text{-PCBu}^t)$ [23] and white $\text{Ge}(\text{mes})_2(\eta^2\text{-dbtp})$

[24], a tetrahedral environment around each Ge(IV) atom is built up by two C – donor $\text{CH}(\text{SiMe}_3)_2$ ligands with a bidentate (C + P) donor PCBu^t ligand in the former and by two mesityl ligands (C donor) with a bidentate (C + P donor) dbtp ligand in the latter. All tetrahedral arrangements are much distorted, because a part of the three – in the former and the four – membered metallocycles are significantly smaller (Table 1).

In $\text{Ge}(\text{Ph})_3\text{Br}$ [25] a tetrahedral environment around each Ge(IV) atom is created by three phenyl ligands with the values (molecule 1 vs. molecule 2): Ge – C = $1.934(10,7)$ and $1.936(10,5) \text{ \AA}$ and Ge – Br = $2.318(2)$ and $2.322(3) \text{ \AA}$ and the L-Ge-L bond angles range from $105.9(4)$ to $114.9(4)^\circ$ and from $105.4(4)$ to $114.4(4)^\circ$, respectively.

In colourless $\text{GeCl}_3(\eta^1\text{-pce})$ [26] three Cl atoms and C – donor atom of pce ligand form a distorted tetrahedral arrangement around each Ge(IV) atom (GeCl_3C). Six tetrahedral angles fall in the narrow range $106.7(2) - 112.7(2)^\circ$ (molecule 1) and $106.3(2) - 114.5(2)^\circ$ (molecule 2), which indicates a somewhat higher degree of distortion in the molecule 2.

In another colourless $[\text{Ge}(\eta^1\text{-S}_2\text{COPr}^i)_3(\text{Me})]$. 0.5 CS_2 [27] three unidentate S – donor S_2COPr^i ligands with a methyl group create a tetrahedral arrangement around each Ge(IV) atom. The molecules are differing from each other by degree of distortion (Table 1).

Two ethyl groups with a bidentate – P donor atoms $\text{P}_2(\text{Bu}^t)_2$ in [28] create also a tetrahedral environment around each Ge(IV) atom (GeC_2P_2). The tetrahedron are much distorted, because a part of the tree membered metallocycle with the P-Ge-P bond angle of $58.0(1)^\circ$.

A distorted trigonal bipyramidal geometry is found in another three derivatives $\text{Ge}(\text{Me})(\text{Ph})(\eta^2\text{-dmamp})\text{Cl}$ [29], $\text{GeCl}_3(\eta^2\text{-mba})$ [30] and $\text{Ge}(\text{Me})_2(\eta^2\text{-S}_2\text{CNMe}_2)\text{Br}$ [31]. In [29] the distorted trigonal bipyramidal is made from two unidentate C – donor ligands (Me and Ph) and one heterobidentate (N + C donors) dmamp ligand and Cl atom. In this the axial sites are occupied by N and Cl atoms. Three Cl atoms which occupy the equatorial plane with one heterobidentate (O + C donors) mba ligand spanning the axial sites has been found in [30]. In [31] a S – bidentate, N,N-dimethyldithiocarbamate ligand spans an axial and equatorial position. The other axial position carries the Br atom and the two methyl groups are located in the equatorial plane ($\text{GeC}_2\text{S}_2\text{Br}$) (Table 1).

Finally there is colourless derivative, $[\text{GeF}_5(\eta^1\text{-mbach})]\cdot\text{H}_2\text{O}$ [32] in which Ge(IV) atoms are six coordinated (GeF_5C) (Table 1).

Inspection of the data in Table 1 reveals that the germanium is predominantly found in the oxidation state + 4, with one example [7] in which Ge(II) atom is sandwiched (GeC_2). The germanium (IV) atoms are found in distorted trigonal planar (GeC_3 , GeC_2P), tetrahedral (by far prevails) (GeC_4 , GeC_3X (X = H, O, N, S, P or Br), GeCl_3C , GeS_3C and GeC_2P_2); trigonal bipyramidal (GeC_3NCl , GeCl_3OC and $\text{GeC}_2\text{S}_2\text{Br}$) and pseudo-octahedral (GeF_5C).

Two derivatives, $\text{Ge}(\text{mes})(\text{Bu}^t)\{\text{P}(2,4,6\text{-Bu}^t_3\text{C}_6\text{H}_2)\}$ [4] and $\text{Ge}(\text{CCPh})_4$ [5, 6] exist in two isomeric forms, one de-

Table 2. Crystallographic and Structural Data for Di- and Oligomeric Germanium Organometallics -Distortion Isomers^a

Compound (Colour)	Cyst. Cl. Space Gr. Z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromophore	Ge – L [Å]	Ge – Ge [Å] Ge–L–Ge [°]	L – Ge - L [Å]	Ref.
Ge ₂ (Ph) ₆ (colourless)	tr P-1 2	8.849(6) 9.744(5) 10.465(4)	97.43(6) 106.34(12) 113.64(3)	GeC ₃ Ge'	PhC ^b 1.958(13,10)	2.437(2)	C,C ^b 108.1(6,1.1)	[33]
Ge ₂ (Ph) ₆ (colourless)hx	hx P6 ₃ 22 3	17.43 (3) 8.47 (1)		GeC ₃ Ge'				[33]
{(Ph) ₃ Ge} ₂ (μ -S) (colourless)	or P2 ₁ 2 ₁ 2 ₁ 4	9.617(2) 17.345(3) 18.408(3)		GeC ₃ S	PhC 1.943(7,12) μ S 2.234(2,7)	110.7(1)	C,C 109.9(3,1.2) C,S 108.5(2,7.2)	[34]
{(Ph) ₃ Ge} ₂ (μ -S) (colourless) (at 143 K)	m P2 ₁ /c 4	11.020(3) 15.473(3) 18.606(3)	106.92(2)	GeC ₃ S	PhC 1.945(4,26) μ S 2.237(1,25)	111.2(1)	C,C 110.2(2,2.9) C,S 109.6(1,6.8)	[34]
Ge ₂ (Bu ¹) ₆ (colourless)	or Iba2 ₁ 8	16.406(4) 11.419(3) 29.648(3)		GeC ₃ Ge' GeC ₃ Ge'	Bu ¹ C 2.060(8,25) Bu ¹ C 2.092(7,44)	2.705 (1) 2.714 (1)	C,C 107.9(3,1.6) C,Ge' 111.8(3,1.7) C,C 106.4(3,1.1) C,Ge' 112.4(3,2.5)	[35]
Ge ₂ (μ - η^2 -SCC- (Bu ²) ₂ (Ph) ₄) (colourless)	tr P-1 4	11.355(1) 14.519(1) 19.070(3)	93.76(1) 90.3(2) 101.36(1)	GeC ₃ Ge' GeC ₂ SGe' GeC ₃ Ge' GeC ₂ SGe'	PhC not given η^2 C 2.020(15) PhC not given η^2 S 2.242 (6) η^2 C 2.018 (17) η^2 S 2.240 (6)	2.406(2) 2.408(3)	C,Ge' 85.6(4) S,Ge' 78.7 (2) C,Ge' 84.5 (5) S,Ge' 78.3 (2)	[36]
{(Ph) ₂ Ge(μ - η^2 -CH=CH)} ₂ (colourless)	tr P-1 2	11.54(3) 10.93(3) 10.24(3)	97.5(1) 106.0(1) 99.5(1)	GeC ₄ GeC ₄	μ C 1.95 PhC 1.955(-,15) μ C 1.95 PhC 1.98		C,C 109.5(-,4.5) C,C 109.5(-,2.5)	[37]
(Me ₂ Ge) ₂ . (μ - η^2 -tcs) (colourless)	m P2 ₁ /b 4	17.990 15.729 10.021	115.71	GeC ₄	tcsC 1.975(-,3) MeC 1.950(-,5)		C,C not given	[38]
{[η^4 -N(CH ₂ CH ₂ - O) ₃]Ge} ₂ (μ -CH ₂) (colourless)	m P2 ₁ /b 8	14.235(5) 13.554(5) 17.949(10)	93.78(6)	GeO ₃ NC GeO ₃ NC	μ C 1.96(2,1) η^4 O 1.79(1,2) η^4 N 2.29 μ C 1.95(2,6) η^4 O 1.79 (1,1) η^4 N 2.29	122.3(8) 119.0(9)	O,O 117.4(7,4.3) O,C 100.1(8,5.2) C,N 174(1,2) O,O 117.4(7,4.8) O,C 98.5(8,6.1) C,N 176(1,3)	[39]
(Cl ₃ Ge) ₂ { μ -1,4- (Me ₂ Si) ₂ CPPC-(SiMe ₃) ₂ } (yellow)(at 143 K)	tr P-1 2	9.003(3) 9.108(3) 22.898(5)	88.63(2) 82.73(2) 61.84(2)	GeCl ₃ C	Cl 2.142(2,0) μ LC 1.936(5)		not given	[40]

tameric (x 2) and nonameric (x 1). Colourless $\text{Ge}_2(\text{Ph})_6$ [33] exists in three isomeric forms, triclinic, hexagonal and rhombohedral. Unfortunately, only structural data of the triclinic form are available. Two equivalent GeC_3 moieties are held together by a direct Ge-Ge bond (Ge-Ge = 2.437(2) Å). Another colourless derivative, $\{(\text{Ph})_3\text{Ge}\}_2(\mu\text{-S})$ [34] exists in two isomeric forms, both are monoclinic. In each single S atom acts as a bridge between two Ge(IV) atoms. The bridge angle Ge-S-Ge is 100.7(1)° (molecule 1) and 111.2(1)° (molecule 2). Each Ge(IV) atom is in a tetrahedral environment (GeC_3S) with the sum values (Ge-C (x 3) + Ge-S (x 1)) of 8.063 Å (molecule 1) and 8.072 Å (molecule 2). The six tetrahedral angles range from 101.3(2) to 115.7(2)° in molecule 1 and from 102.8(1) to 115.4(2)° in molecule 2. This indicates that the former molecule is somewhat less crowded with some higher degree of distortion.

The X-Ray analysis of colourless $\text{Ge}_2(\text{Bu})_6$ [35] shows that there are two crystallographically independent molecules, which differ by degree of distortion. In each molecule two GeC_3 moieties are held together by a direct Ge-Ge bond, with the Ge-Ge values of 2.705(1) and 2.714(1) Å, respectively. The mean Ge-C bond distance of 2.060(8) Å in molecule 1 is about 0.032 Å shorter than that in molecule 2 (2.092(7) Å). The six tetrahedral angles range from 106.9(3) to 113.5(3)° and from 105.3(3) to 114.9(3)° (Table 2).

X-Ray analysis of molecule $\text{Ge}_2(\mu\text{-}\eta^2\text{-SCCBu}^1)(\text{Ph})_4$ [36] shows that it contains also two crystallographically independent molecules, differing mostly by degree of distortion. The four membered ring of Ge(1)Ge(2)SC(1) has a puckered structure (Fig. 1) in which the dihedral angle formed by the Ge(1)Ge(2)S plane and the Ge(1)SC(1) plane averages by 15.4° between the two molecules. The Ge(1)-Ge(2) bond length is 2.406(2) and 2.408(3) Å, respectively (Table 2).

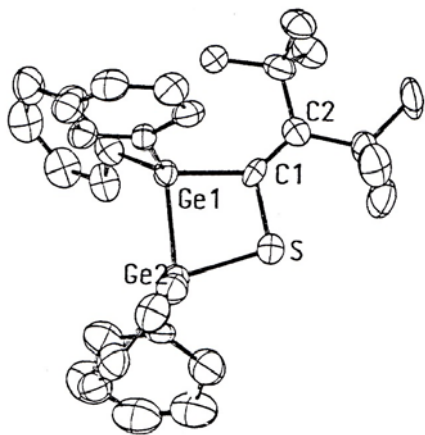


Fig. (1). Structure of $\text{Ge}_2(\mu\text{-}\eta^2\text{-SCCBu}^1)(\text{Ph})_4$ [36].

Another colourless $\{(\text{Ph})_2\text{Ge}(\mu\text{-}\eta^2\text{-CH=CH})\}_2$ [37] contains a six membered metallocyclic ring $\text{C}_2\text{Ge}_2\text{C}_2$. The six membered $\text{C}_2\text{Ge}_2\text{C}_2$ skeleton is almost planar. The absence of significant $d\pi - p\pi$ interaction between the Ge atoms and the double bond of the heterocycle is indicated by the equality of the endo- and exocyclic Ge-C bond lengths (Table 2). Each Ge(IV) atom is a tetrahedrally coordinated GeC_4 with the average $\{\text{Ge-C}(x4)\}(x2)$ bond distance of 15.62 Å (in one dimer) and 15.72 Å (in the other one). The former dimer is somewhat more distorted than the latter (Table 2).

A tetracyclic ring system has been found in $[(\text{Me}_2\text{Ge})_2(\mu\text{-}\eta^2\text{-tcs})]$ [38]. The central six membered ring Ge(1)C(2)Si(2)O(1)Si(1)C(1) has a somewhat distorted chair conformation. The satellite eight membered tetrasiloxane rings, arranged in the centre of symmetry, have a non-planar conformation. The atoms O(1) and O(2) deviate from the plane of the four Si atoms in one direction, and the atoms O(1) and O(2) deviate in the other direction. Each germanium atom is tetrahedrally coordinated (GeC_4) (Table 2).

In $\{[\eta^4\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3]\text{Ge}\}_2(\mu\text{-CH}_2)$ [39] a single ligand ($\mu\text{-CH}_2$) acts as a bridge between two $\{\eta^4\text{-N}(\text{CH}_2\text{CH}_2\text{O})_3\}\text{Ge}$ moieties, with Ge-C-Ge bridge angle of 122.3(8)° in molecule 1 and 119.0(9)° in molecule 2. Each Ge(IV) atom is a trigonal bipyramidally coordinated (GeO_3NC). The three O atoms create a trigonal plane and N with C donor atoms occupy axial positions with the mean $\mu\text{C-Ge-N}$ bond angles of 174(1) and 176(1)°, respectively (Table 2).

In yellow $(\text{Cl}_3\text{Ge})_2\{\mu\text{-}1,4\text{-}(\text{Me}_3\text{Si})_2\text{CPPC}(\text{SiMe}_3)_2\}$ [40] two Cl_3Ge units are bridged by $\mu\text{-}1,4\text{-}(\text{Me}_3\text{Si})_2\text{CPPC}(\text{SiMe}_3)_2$ giving a GeCl_3C chromophore around both Ge(IV) atoms. There are two crystallographically independent dimers, but data for only one of them are available.

There are two trimer derivatives [41, 42] which contain two crystallographically independent trimers (Table 2). Colourless $\text{Ge}_3(\text{Ph})_6\text{Cl}_2$ [41] contains the Cl-Ge-Cl chain with the mean Ge-Ge bond distances of 2.418(2) and 2.420(2) Å respectively. The Ge-Ge-Ge angles are 116.7(1) and 110.4(1)°, respectively. Each trimer has a central Ge atom with chromophore GeC_2Ge_2 , and satellite Ge atoms with GeC_2ClGe . The tetrahedral angles range from 105.8 to 116.7(1)° in one trimer and from 104.4 to 119.9(1)° in another one.

Structure of $(\text{Me}_3\text{Ge})_3(\mu\text{-}\eta^2\text{-popch})$ [42] is shown in Fig. (2). Here the 1-(p-phenoxyphenyl) cyclohexane moiety serves as a bridge between the three GeMe_3 units. Each Ge(IV) has a distorted tetrahedral geometry, GeC_4 (Table 2).

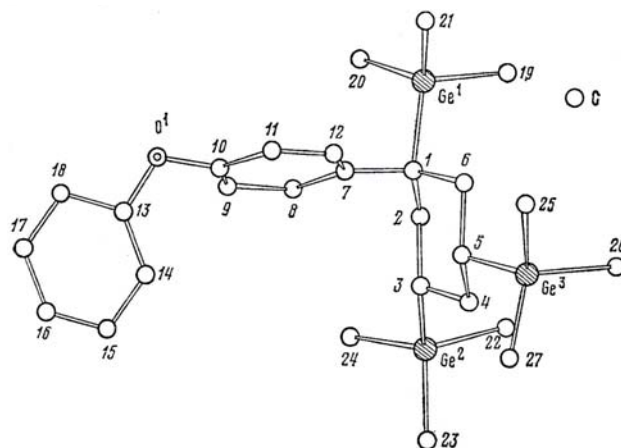


Fig. (2). Structure of $(\text{Me}_3\text{Ge})_3(\mu\text{-}\eta^2\text{-popch})$ [42].

Structure of colourless $\text{Ge}_5(\text{Ph})_{10}$ [43] is shown in Fig. (3). As it can be seen, the structure contains the five membered Ge_5 ring with a conformation in between C_5 and C_2 . The mean Ge-Ge bond distances are 2.456(2) Å in pentamer

1 and 2.450(2) Å in pentamer 2. Each Ge atom has a GeC_2Ge_2 chromophore with the mean Ge-C(Ph) bond distances of 1.973 and 1.969 Å, respectively. The tetrahedral angles fall in the narrow range 105.5- 119.1° (pentamer 1) and 103.4 – 117.8° (pentamer 2). This indicates that former is somewhat more distorted than the latter.

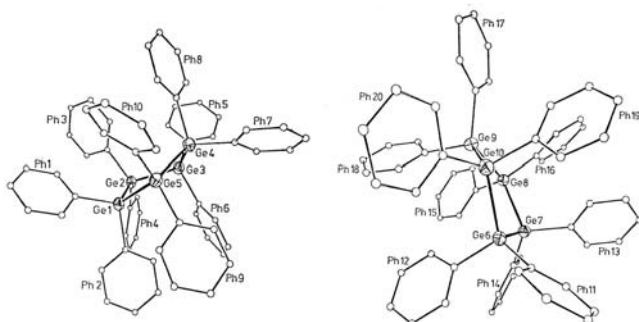


Fig. (3). Structure of $\text{Ge}_5(\text{Ph})_{10}$ [43].

The symmetric units of another colourless pentamer [44] contain two bicyclic $\text{Ge}_5\text{O}_6\text{Ph}_8$ cages and one distorted acetone molecule of crystallisation. The structure of them is disordered and one of them is shown in Fig. (4). The total symmetry of both molecules is near to D_3 , the symmetry of the individual eight membered ring $(\text{GeO})_4$ is near to C_2 . Each of O atoms serves as a bridge between two Ge atoms. The central Ge atoms have GeO_2C_2 chromophores, and the terminal Ge atoms GeO_3C . The Ge...Ge separations in two independent pentamers range from 3.165 to 4.420(2) Å and 3.176 to 4.506(2) Å, respectively, effectively excludes any metal – metal bonds.

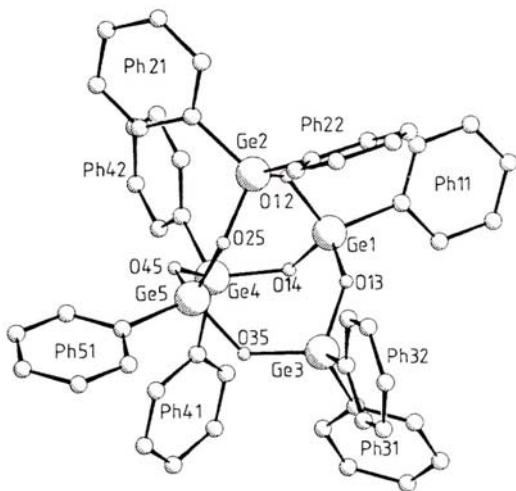


Fig. (4). Structure of $\text{Ge}_5(\text{O})_6(\text{Ph})_6$ [44].

There is one example with nine Ge atoms [45] and its structure is shown in Fig. (5). There are two independent molecules in the unit cell. The inner Ge-Si distances (average 2.398(4) Å) are somewhat longer than the outermost one (average 2.384(4) Å, probably because of the steric repulsion of the dendrite arms. Although the geometries at the branching points are nearly tetrahedral, the bond angles at the spacers ($\text{Si1} - \text{Ge3} - \text{Si2} = 116.9(2)^\circ$, $\text{Si1} - \text{Ge2} - \text{Si3} = 115.2^\circ$, $\text{Si1} - \text{Ge3} - \text{Si4} = 114.3(1)^\circ$), showing a decreasing trend.

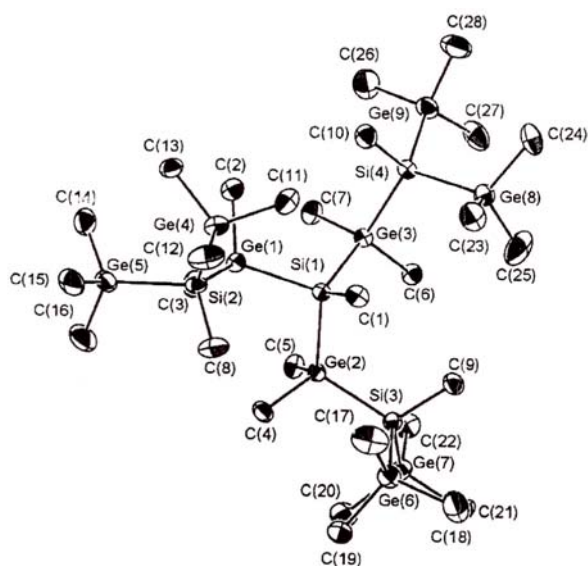


Fig. (5). Structure of $\text{Ge}_9(\text{Me})_{24}(\text{SiMe}_3)_4$ [45].

Inspection of the data in Table 2 reveals that the derivatives belong to the following crystal classes: triclinic (x 7) > monoclinic (x 5) > orthorhombic (x2) > hexagonal and rhombohedral (each x 1). One derivative is yellow [40] and remainders are colourless. Germanium is found in the oxidation states Ge^{+3} , Ge(II), Ge(IV) and one example contains mixed valences (Ge(II) – Ge(IV) – Ge(II)). Only in one derivative [39] each Ge(IV) atom has a trigonal bipyramidal environment (GeO_3NC), remainders are tetrahedrally coordinated with following chromophores: Ge_2^{+3} ($\text{GeC}_3\text{Ge}'$ [33, 35, 36]), Ge(IV) (GeC_3S [34], GeC_4 [37, 38, 42], GeCl_3C [40] and GeC_3Si [45]); Ge(II) (GeC_2Ge_2 [43] and GeO_2C_2 plus GeO_3C [44]) and mixed valences 2 Ge(II) plus Ge(IV) ($\text{Ge(II)C}_2\text{ClGe(IV)}$ and $\text{Ge(IV)C}_2\text{Ge}_2(\text{II})$ [41]). The mean Ge-Ge bond distances elongated in the sequence: 2.417 Å (Ge_2^{3+}) < 2.423 Å (Ge(II) - Ge(IV)) < 2.453 Å (Ge(II) – Ge(II)).

The mean values of Ge-C bond distances elongated in the sequences:

$$\text{Ge}_2^{+3}: 1.96\text{Å} (\text{L} = \text{Ph}) < 2.075\text{Å} (\text{Bu}^t) < 2.241\text{Å} (\text{LS});$$

$$\text{Ge(II)}: 1.75\text{Å} (\mu\text{-O}) < 1.94\text{Å} (\text{Ph}) < 2.192\text{Å} (\text{Cl});$$

$$\text{Ge(IV)}: 1.94\text{Å} (\text{Me}) < 1.95\text{Å} (\text{Ph}; \text{C}^2\text{L}) < 1.975\text{Å} (\text{C}^3\text{L}) < 2.142\text{Å} (\text{Cl}) <$$

$$2.235\text{Å} (\mu\text{-S}) < 2.390\text{Å} (\mu_3\text{S}).$$

3. LIGAND ISOMERISM

There are two colourless derivatives, $\text{Ge}(\text{o-tolyl})_4$ [46] and $\text{Ge}(\text{p-tolyl})_4$ [47] which are examples of ligand isomerism. The former is triclinic and the latter is monoclinic. The derivatives are isostructural, four tolyl ligands create around each Ge(IV) atom a tetrahedral environment (GeC_4). The mean Ge-C bond distance of 1.966(3) Å in the former is around 0.018 Å longer than in the latter (1.948(4) Å (Table 3)).

4. CONCLUSIONS

An analysis over four hundred and fifty organogermanium compounds shows that some 10 % of them exist in

Table 3. Crystallographic and Structural Data for Monomeric Germanium Organometallics – Ligand Isomers^a

Compound (Colour)	Cryst. Cl. Space Gr. Z	a[Å] b[Å] c[Å]	α [°] β [°] γ [°]	Chromophore	Ge – L [Å]	L – Ge – L [°]	Ref.
Ge(o-tolyl) ₄ (colourless)	tr P-1 2	8.245(2) 8.210(2) 17.072(6)	79.48(2) 84.20(2) 91.55(2)	GeC ₄	C ^b 1.966(3,0)	C, C ^b not given	[46]
Ge(o-tolyl) ₄ (colourless)	m Pc 2	9.997(1) 10.498(1) 11.934(3)	109.04(1)	GeC ₄	C 1.948(4,10)	C, C 109.5(2,2,0)	[47]

Footnotes: ^aIf more than one chemically equivalent distance or sample is present, the mean value is tabulated. The first member in parentheses is the e.s.d., and the second one is the maximum deviation from the mean.

^bThe chemical identity of the coordinated atom or ligand is specified in these columns.

isomeric forms [1]. Organogermanium compounds are the most part colourless, but some of them are white, yellow and even orange. The lowest and highest coordination number found in the organogermanium isomers is three and six respectively. The frequency of occurrence increases in the order: six < five < three < four coordinate. The most common are four coordinate examples with variously distorted tetrahedral arrangement. Consideration of the nuclearity of the isomers shows a range of possibilities: mono – (x 32) > di – (x 11) >> tri – and penta – each (x 2) > nonamer (x 1) derivatives.

There are two types of isomerism – distortion (x 44) and ligand (x 2). The Ge₂(Ph)₆ [33] occur in three isomeric forms (triclinic, hexagonal and rhombohedral). Three derivatives, Ge(mes)₂(Bu^t)₂{P(2,4,6-Bu^t₃C₆H₂)₂} (both monoclinic [4], Ge(CCPH)₄ (tetragonal [5] and orthorhombic [6]), and {Ph₃Ge}₂(μ-S) (orthorhombic and monoclinic) [34] exist in two isomeric forms. In Ge(Ph)₃(OH) [18] eight crystallographically independent molecules has been found. Remainers (Tables 1 and 2) contain two crystallographically independent molecules. All these isomers as well as independent molecules differ by degree of distortion involving both Ge – L distances and L – Ge – L angles. The existence of two or more species, differing by degree of distortion, is typical of the general class of distortion isomerism [3].

Two derivatives, Ge(o-tolyl)₄ [46] and Ge(p-tolyl)₄ [47] are example of ligand isomerism. In the chemistry of germanium coordination compounds, at least two types of isomerism were observed [2], distortion and configuration isomerism. The former by far prevails. In general, one can say that the distortion isomerism in both germanium coordination compounds as well as organogermanium compounds dominates. The corresponding study of germanium heterometallic compounds are currently in progress.

ACKNOWLEDGEMENTS

The authors wish to thank those who gave permission for reproduction of original figures and the Ministry of Education of the Slovak Republic, VEGA 1/0353/08 and APVV-20-005504 grants for financial support.

ABBREVIATIONS

at = 3-(2-adamantyl)-thia

Bu ^t	= tert-butyl
2,4,6-Bu ^t ₃ C ₆ H ₂	= 2,4,6-tris-tert-butylphenyl
CCPh	= phenylacetylidene
cp	= cyclopentadienyl
dbtp	= 2,4-di(tert-butyl)phenylphosphine
dmamp	= N,N-2-(dimethylamino)methylphenyl
Et	= ethyl
frl	= fluorenylidene
hx	= hexagonal
mba	= methyl-N-methyl-p-methylbenzamide
mbach	= 4-methyl-1,4-bisazoniacyclohex-1-yl-methyl
mes	= mesityl
or	= orthorhombic
pcpt	= 6-phenyl-4H-cyclopenta[6]thiophen-4-one
pepp	= 1-(phenethyl)-4-propioanilidopiperidine
Ph	= phenyl
pha	= propinhydroxamic acid
Pr ⁱ	= iso-propyl
popch	= 1-(p-phenoxyphenol)cyclohexane
rh	= rhombohedral
tes	= tricyclic carbosiloxane
Tdmp	= tris-{2-(dimethylamino)methyl}phenyl
tg	= tetragonal
tm	= p-tolylthiomethyl
tphc	= 2,3,4,5-tetraphenylcyclopentadienyl
tr	= triclinic

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Received: June 12, 2008

Revised: July 03, 2008

Accepted: July 06, 2008

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