

Isomers in the Chemistry of Germanium Heterometallic Clusters

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Abstract: Sixteen isomers of heterometallic germanium clusters have been analysed in this review. There are two types of isomerism, distortion ($\times 15$) and cis – trans ($\times 1$) and cis – isomer contains two crystallographically independent molecules. Distortion isomers, differing only by degree of distortion in Ge – L, Ge – M (M = metal) distances and L – Ge – L (L = ligand) angles. The data are discussed with these found in the isomerism of germanium coordination compounds as well as organogermanium derivatives. In the chemistry of germanium were found-seventy four derivatives as isomers. These are discussed and compared with those in tin (over two hundred and fifty examples) and lead (seventy examples) chemistry. This review and its precursors give the first overall survey of the structural data for the isomer complexes of the group IV metals.

Keywords: Germanium, heterometallic, clusters, isomers, crystal structures.

1. INTRODUCTION

The chemistry of germanium has been an active area of research in catalytic activity and reaction with organic species. Numerous structural studies have been carried out, including almost two hundred and fifty heterometallic germanium derivatives [1] with sixteen isomeric examples noted. In [2] we analysed and classified over twenty isomers in the chemistry of germanium coordination compounds. Another almost fifty isomeric examples in the chemistry of organogermanium compounds were also characterised and classified [3]. In this review we analyse and classify isomeric examples of germanium heterometallic derivatives to show a comprehensive view on the isomers in the chemistry of germanium.

2. DISTORTION ISOMERISM

The existence of two or more species differing by degree of distortion of M – L bond distances and L – M – L bond angles is typical of the general class of distortion isomers [4]. There are fifteen such examples in the chemistry of germanium heterometallic derivatives and their crystallographic and structural data are summarised in Table 1.

Yellow $\text{Cl}_3\text{GeAu}(\text{PPh}_3)_3$ [5] exists in two isomeric forms, both are monoclinic. In each of the derivative two non equivalent moieties, Cl_3Ge and $\text{Au}(\text{PPh}_3)_3$ are held together by a direct Ge – Au bond with the distances of 2.563(1) and 2.536(1) Å, respectively. Each M atom is a tetrahedrally coordinated (GeCl_3Au and AuP_3Ge). The isomers differ from each other by degree of distortion and are examples of distortion isomerism. The mean M – L bond distances of Ge – Cl = 2.240 (2) and Au – P = 2.425(1) Å in isomer 1 and 2.233(2) and 2.457(1) Å in isomer 2.

In GeCu dimer [6], which contains two crystallographically independent dimers, two non equivalent units (C_6F_5)₃Ge and $\text{Cu}(\text{PPh}_3)_2$ are also held together by a direct Ge – Cu bond with the lengths of 2.370(2) and 2.382(3) Å, respectively. While each Ge atom is tetrahedrally coordinated (GeC_3Cu) the Cu atoms have a trigonal planar environment (CuP_2Ge) the mean Ge – C bond distances are 2.015 and 2.008 Å, respectively. Six tetrahedral angles C – Ge – C(Cu) range from 95.7 (3) to 121.6(2) and 95.1(3) to 122.8(3)°, respectively. This indicates that the former is somewhat less distorted than the latter. Noticeable, the CuP_2Ge units follow the same trend (Table 1).

Another two dimers, GeMn [7] and GeSn [8] which also contain two crystallographically independent dimers, two non-equivalent units, $(\text{Ph})_3\text{Ge}$ and $\text{Mn}(\text{CO})_5$ [7] and $(\text{Me})_3\text{Ge}$ and $\text{Sn}(\text{Ph}_3)_3$ [8], are connected also by a direct Ge – M bonds, 2.53(2) and 2.54(2) Å (M = Mn) and 2.596(4) and 2.567(6) Å (M = Sn). These are also classical examples of distortion isomerism (Table 1). Structure of orange GeFe dimer [9] is shown in Fig. (1). Two non-equivalent moieties $(\text{Ph})_3\text{Ge}$ and $\text{Fe}(\text{cp})$ are held together by the $\text{C}_5\text{H}_4\text{CO}$ ligand via all six of the C atoms. It binds to Fe as $\eta^5\text{-C}_5\text{H}_4$, but as an acyl ligand to Ge, giving a sandwich complex geometry and a tetrahedral one, respectively. There are two crystallographically independent molecules. Unfortunately, the data are available only for one molecule (Table 1).

Structure of another orange GeFe dimer [10] is shown in Fig. (2). The N atom of the ferrocene amine base bonds to the capping Ge atom of the germanoborane. The Ge atom is unsymmetrical bonded to the atoms of the C_2B_3 face, slipping towards the boron side of the face to give distorted pentagonal-bipyramidal GeC_2B_4 cage. The unit cell contains two crystallographically independent molecules differing in the relative orientation of the carborane and ferrocene amine ligands. In one, the Ge – N bond (2.406(6) Å) is slightly rotated out of this plane.

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Table 1. Crystallographic and Structural Data for Germanium Heterometallic Compounds – Distortion Isomers^a

Compound (colour)	Cryst.cl. Space gr. z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M – L [Å]	M – M [Å]	L – M - L [°]	Ref.
Cl ₃ GeAu(PPh ₃) ₃ (yellow) at 250 K	m P2 ₁ /n 4	13.964(1) 23.578(1) 14.870(1)	92.84(1)	GeCl ₃ Au AuP ₃ Ge	Cl ^b 2.240(1,2) Ph ₃ P 2.425(1,12)	Au ^b 2.563(1)	Cl,Cl ^b not given P,P 111.0(1,1.6) 122.0(1) P,Ge 103.7(1,2.2)	[5]
Cl ₃ GeAu(PPh ₃) ₃ (yellow) at 205 K	m P2 ₁ /n 4	19.884(1) 20.040(1) 24.193(1)	91.39(1)	GeCl ₃ Au GeP ₃ Ge	Cl ^b 2.233(2,8) Ph ₃ P 2.457(1,8)	Au 2.536(1)	Cl,Cl not given P,P 113.4(1,2.4) P,Ge 105.6(1,6)	[5]
(C ₆ F ₅) ₃ GeCu(PPh ₃) ₃ (not given)	tr P-1 4	13.339(7) 19.575(9) 19.829(12)	98.2(4) 104.10(4) 94.62(4)	GeC ₃ Cu CuP ₂ Ge GeC ₃ Cu CuP ₂ Ge	C 2.015(8,15) P 2.263(3,7) C 2.008(9,14) P 2.273(3,1)	Cu 2.370(2) Cu 2.382(3)	C,C C,Cu 101.9(3,6.2) 109.8(2) 119.8(2,1.8) P,P 123.1(1) P,Ge 118.5(1,1.3) C,C 105.2(4,3.2) C,Cu 95.1(3) 121.7(3,1.1) P,P 123.1(7) P,Ge 118.4(1,3.3)	[6]
(PPh ₃) ₃ GeMn(CO) ₅ (not given)	tr P-1 4	11.38 11.66 17.17	105.0 97.8 91.2	GeP ₃ Mn MnC ₃ Ge GeP ₃ Mn	Ph ₃ P not given O ₃ C not given Ph ₃ P not given	Mn 2.53(2) Mn 2.54(2)	P,P not given P,P not given	[7]
(Me) ₃ GeSn(PPh) ₃ (colourless)	or Pna2 ₁ 4	20.741(3) 12.393(2) 8.064(1)		GeC ₃ Sn SnC ₃ Ge GeC ₃ Sn SnC ₃ Ge	MeC 1.985(7,6) PhC 2.095(7,4) MeC 1.982(8,1) PhC 2.091(7,0)	Sn 2.596(4) Sn 2.567(6)	C,C 107.1(8,1.5) C,Sn 111.8(7,2.2) C,C 108.4(8,1.7) C,C 111(2,2) C,Sn 108.6(4,2.0) C,C 106.8(2,4.5)	[8]
(PPh) ₃ Ge(μ-C ₅ H ₄ CO). Fe(η ⁵ -cp) (orange)	m P2 ₁ /n 8	14.765(4) 17.892(5) 17.963(4)	94.96(2)	GeC ₄ FeC ₁₀	μLC 2.016(9) C not given		C,C not given C,C not given	[9]
[{2,3-(Me ₂ Si) ₂ . C ₂ B ₄ H ₄ }Ge. {μ-N(Me) ₂ CH ₂ C ₅ H ₄ }. Fe(η ⁵ -cp)] (orange)	tr P-1 4	12.633(3) 14.146(2) 17.407(4)	102.65(2) 96.63(2) 110.65(2)	GeB ₂ C ₂ N FeC ₁₀ GeB ₂ C ₂ N FeC ₁₀	B 2.238(9,60) C 2.519(8,7) μLN 2.406(6) cpC not given B 2.247(8,39) C 2.448(6,5) μLN 2.496(6) cpC not given		not given not given	[10]
(Ph ₃ Ge) ₂ (μ-Hg) (not given)	tr P-1 4	7.660(2) 16.562(3) 19.220(4)	79.04(1) 81.65(2) 81.68(2)	GeC ₃ Hg HgGe ₂ GeC ₃ Hg HgGe ₂	PhC 1.957(13,16) PhC 1.954(13,28)	Hg 2.514(2,0) Hg 2.543(1,0)	C,C 108.1(5,1.5) C,Hg 110.2(4,2.1) Ge,Ge 178.65(5) C,C 106.9(5,1.6) C,Hg 111.9(4,4.1) Ge,Ge 180.0	[11]

(Table 1). Contd.....

{Me ₃ Ge} ₂ . Mg(η ² -dme) ₂ (colourless)	tr P-1 4	9.375(1) 16.809(5) 17.769(3)	116.47(1) 99.85(1) 98.25(2)	GeC ₃ Mg MgO ₄ Ge ₂ GeC ₃ Mg MgO ₄ Ge ₂	MeC 1.78(4,4) 2.00(3,3) η ² O 2.22(1,4) MeC 1.96(3,4) η ² O 2.115(2,1) 2.28(2,4)	Mg 2.715(6,3) Mg 2.722(7,5)	C,C 98(1,4) O,O 73.0(5,6) ^c 85.1(5,4,7) 154.5(5) O,Ge 95.8(4,6,6) Ge,Ge 166.9(4,1,2) 99.4(2) C,C 98(1,3) O,O 74.2(6,3) ^c 82.1(6,3,8) 151.8(6) O,Ge 96.5(5,6,1) 169.1(5,1) Ge,Ge 99.2(2)	[12]
[{η ⁵ -cp*}(CO) ₂ . Mn] ₂ (μ-Ge)] ^d (orange)	m C2/c 16	21.878(11) 21.931(10) 21.900(12)	104.70(5)	GeMn ₂ MnC ₇ Ge	OC 1.71(9,0) η ⁵ C 2.20(4)	Mn 2.18(2)	Mn,Mn 179(1) C,C 88(7) C,cp 124(5) C,Ge 89(5) cp,Ge 127(1)	[13]
[Me ₃ GeRu(CO) ₂ . (μ-C ₈ H ₆)(CO) ₂ . RuGeMe ₃] (pale yellow)	m P2 ₁ 4	9.395(3) 22.555(9) 10.984(5)	96.93(7)	GeC ₃ Ru RuC ₇ Ge GeC ₃ Ru RuC ₇ Ge	MeC 1.92(6,9) OC 1.77(4,3) C 2.35(4,23) MeC 1.88(5,16) OC 1.84(4,6) C 2.33(4,25)	Ru 2.481(5,5) Ru 3.056(4) Ru 2.487(5,5) Ru 3.060(4)	C,C 107(2,3) C,Ru 112(2,3) C,C 93.5(2,3) C,Ge 83.0(2,1.1) C,Ru 90.9(3,1.4) Ge,Ru 171.0(2,1.2) C,C 107(2,7) C,Ru 112(2,3) C,C 90.6(6,1.2) C,Ge 83.7(10,1.0) C,Ru 90.4(10,1.5) Ge,Ru 171.3(2,4)	[14]
(CO) ₄ Fe] ₄ (μ ₄ -Ge) (red)	m Pc 4	9.704(2) 11.932(3) 20.901(4)	99.32(2)	GeFe ₄ FeC ₄ GeFe GeFe ₄ FeC ₄ GeFe	OC not given OC not given	Fe 2.394(2,6) 2.425(2,14) Fe 2.827(3,11) 4.371(8,17) Fe 2.378(2) 2.419(2,19) Fe 2.820(3,10) 4.391(8,11)	Fe,Fe 72.0(1,1) 130.9(1,7) C,C 108.2(7) Ge,Fe 54.0(1,7) Fe,Fe 71.7(1,3) 131.0(1,2,5) C,C 108.2(7) Ge,Fe 54.2(1,7)	[15]
(η ⁵ -cp)Co(CO) ₂ Co. (η ⁵ -cp)(GeCl ₂) ₂ Fe(CO) ₄ (black)	or P2 ₁ ,2 ₁ s	39.26(2) 12.161(8) 9.82(1)		GeCl ₂ CoFe CoC ₇ GeCo' FeC ₄ Ge ₂	Cl 2.22(2) μOC 1.87(3) cpC 2.10(3) OC 1.81(4)	Co 2.341(9) Fe 2.438(4) Co 2.439(5) C 95(1)	Cl,Cl 98.7(12) Co,Fe 123.6(8) C,Ge 87.6(10) Ge,Co' 102.0(8) C,C 93(3) Ge,Ge 88.2(2)	[16]
(NEt ₄)[{CO} ₁₂ . (μ-CO) ₄ Co ₅](μ ₅ -Ge) (red black)	or Pn2 ₁ 8	12.014(1) 36.938(4) 15.249(2)		GeCo ₅ CoC ₄ GeCo' GeCo ₅ CoC ₄ GeCo'	μOC 1.63-2.04 OC 1.54-2.03	Co 2.35(1) 2.47(1,4) Co 2.54(1,2) Co 2.33(1) 2.46(1,2) Co 2.52(1,2)	Co,Co 62.5(-,5) Co,Co 60(-,1) Ge,Co 59(-,1) Co,Co 63(-,1) Co,Co 60 Ge,Co 59.5(-,5)	[17]

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

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

^cFive-membered metallocyclic ring.

^dThere are three crystallographically independent molecules.

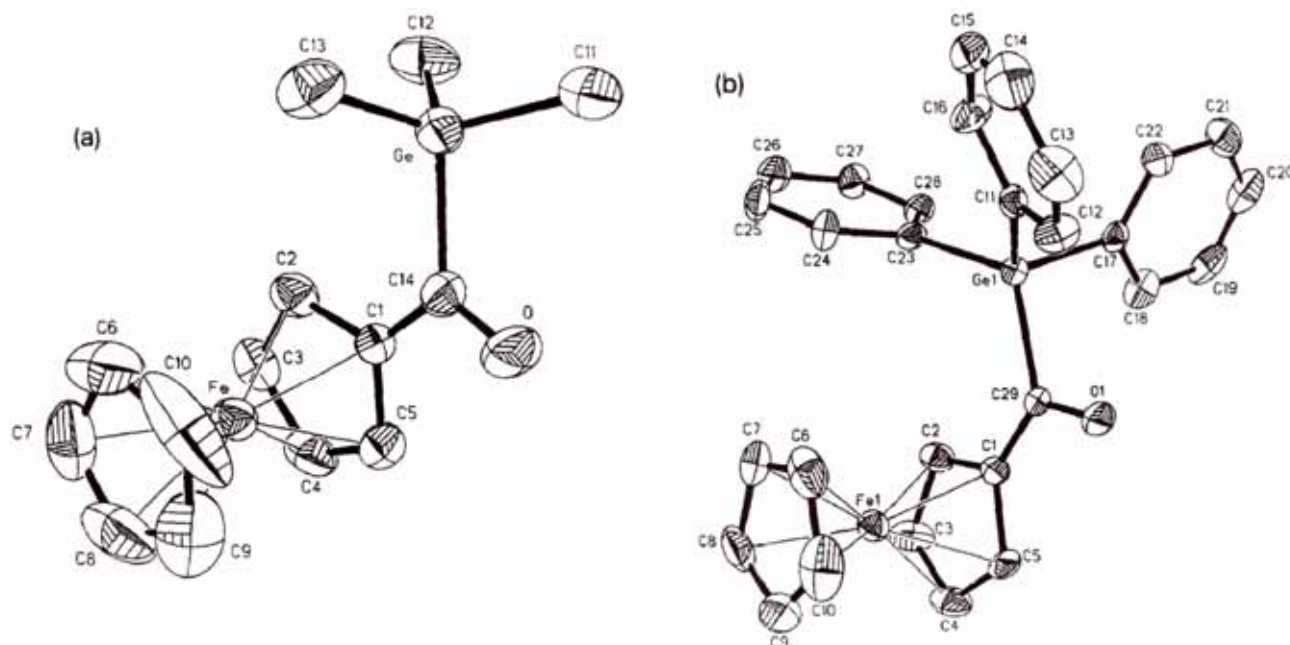


Fig. (1). Structure of two independent molecules of $[(PPh_3)Ge(\mu-C_5H_4CO)Fe(cp)]$ [9].

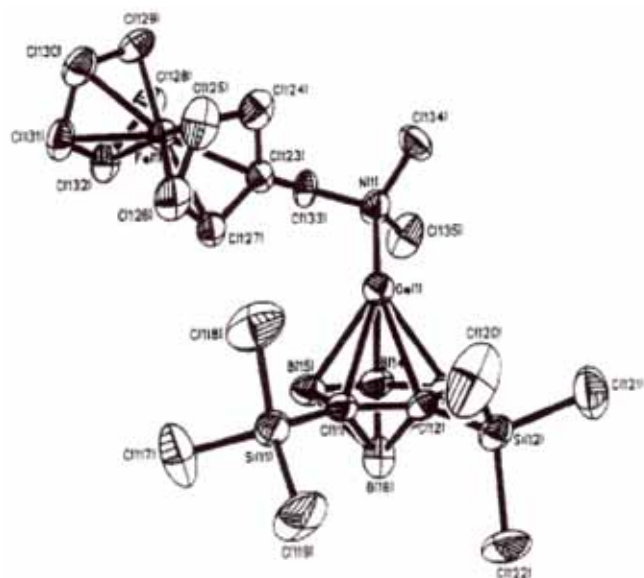


Fig. (2). Structure of $[(Me_3Si)_2C_2B_4H_4}\{Ge\{N(Me)_2CH_2C_5H_4\}Fe(cp)]$ [10].

There are three trimers, a colourless Ge_2Hg [11], Ge_2Mg [12] and orange $GeMn_2$ [13], while the Ge_2Hg and Ge_2Mg [11, 12] contains two, the $GeMn_2$ three crystallographically independent molecules (Table 1). In Ge_2Hg [11] two equivalent Ph_3Ge moieties are held together by a direct $Ge - Hg$ bond distances with the mean values of 2.514 Å in molecule one and 2.543 Å in another one. The three metal atoms form a linear chain, $Ge - Hg - Ge$, 178.65(5) and 180.0°, respectively. Structure of the Ge_2Mg trimer [12] contains a $Ge - Mg - Ge$ chain with different degrees of distortion from the linearity. The mean $Ge - Mg$ bond distances are 2.715 and 2.722 Å, respectively. Each Ge atom is tetrahedrally coordinated (GeC_3Mg) and Mg is octahedrally (MgO_4Ge_2).

Structure of $GeMn_2$ trimer [13] contains a $Mn - Ge - Mn$ chain with the mean $Ge - Mn$ bond distance of 2.18(2) Å and $Mn - Ge - Mn$ angle of 179(1)°. Unfortunately, the data are available only for one trimer.

The structure of a pale yellow Ge_2Ru_2 tetramer [14] (Fig. 3) shows a pentalene ligand bonded to a nearly linear $Ge - Ru - Ru - Ge$ spine. The two C atoms common to both rings are bonded to both Ru atoms in the form of a trans verge bridge. The remaining two groups of three C atoms of the pentalene are each bonded to individual $\eta - allyl$ interannular unit to one Ru atom. The trimethylgermyl groups adopt an eclipsed configuration with respect to the bond axis. The two CO groups attached to each Ru atom are likewise eclipsed and mutually orthogonal. There are two crystallographically independent tetramers differing by degree of distortion. The $M - M$ distances are $Ge - Ru$ 2.481 Å, (mean) and $Ru - Ru$ 3.0546(4) Å in one tetramer, and 2.487 Å (mean) and 3.060(4) Å, in another one. Each Ge atom has a tetrahedral arrangement (GeC_3Ru) and Ru atom is a semisandwich with two additional C (CO) atoms and Ge (RuC_7Ge) (Table 1).

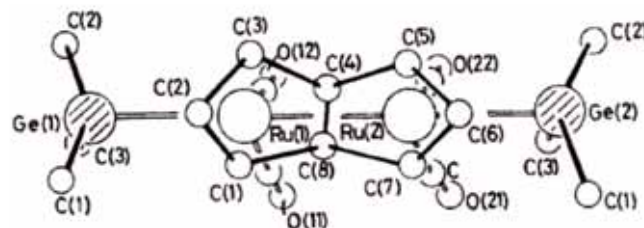


Fig. (3). Structure of $[(Me_3GeRu(CO)_2}_2(\mu-C_8H_6)]$ [14].

The structure of red $\{(CO)_4Fe\}_4(\mu_4-Ge)$ pentamer [15] contains a $GeFe_4$ skeleton with two $Fe - Fe$ single bonds. There are two crystallographically independent clusters with the mean $Ge - Fe$ and $Fe - Fe$ bond lengths of 2.405(2) and 2.827(3) Å in one; and 2.409(2) and 2.820(3) Å in the other.

Noticeably, the sum of all six M – M bond lengths in the two independent clusters is almost the same 15.275 and 15.268 Å. Each Ge atom has a tetrahedral arrangement (GeFe₄) and Fe atoms are six-coordinated (FeC₄GeFe') (Table 1).

Structure of black {(cp)(CO)Co}₂(GeCl₂)₂Fe(CO)₄ pentamer [16] is shown in Fig. (4). The structure contains a planar five membered Co-Ge-Fe-Ge-Co heterometal ring with the following bond distances: Co-Ge, 2.341(9) Å, Ge-Fe, 2.438(4) Å, Co-Co, 2.439(5) Å. The M – M – M bond angles close up in the order: Co – Ge – Fe, 123.6(8)° > Ge – Co – Co', 102(8)° > Ge – Fe – Ge, 88.2(2)°. There are two crystallographically independent clusters, but only for one data are available.

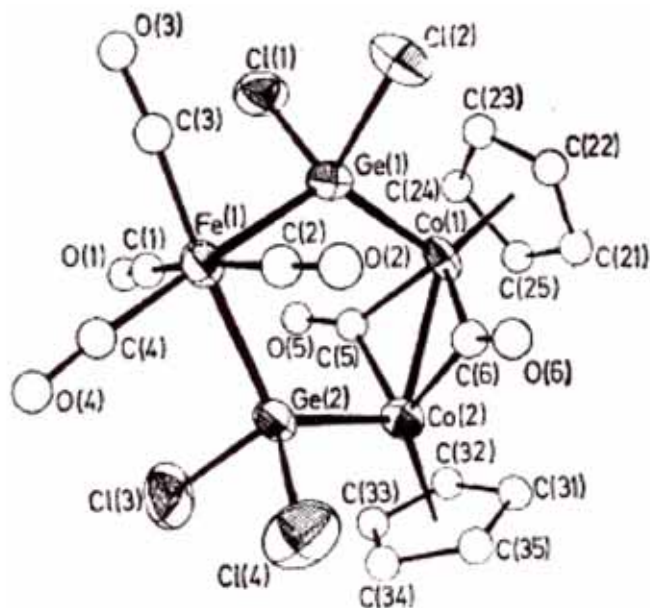


Fig. (4). Structure of {(cp)(CO)Co}₂(GeCl₂)₂Fe(CO)₄ [16].

Finally, there is a red black GeCo₅ clusters [17], which contains NEt₄⁺ cation and [(CO)₁₂(μ-CO)₄Co₅](μ₅-Ge)⁻ anion. Structure of the cluster anion is shown in Fig. (5). The anion has a GeCo₅ skeleton consisting of a GeCo₂ triangle and a GeCo₃ tetrahedron sharing a common apex at the Ge atom, which is thus involved in five Ge-Co bonds. These range in length from 2.35-2.51(1) Å in one cluster and 2.33-2.48(1) Å in another one. The Co – Co bonds range from 2.52-2.56(1) Å and 2.50-2.54(1) Å, respectively. Both Co atoms of the GeCo₂ fragment are bonded to three carbonyl groups, one of them acting as a bridge between them. The Co atoms of the GeCo₃ unit each have two terminal carbonyl groups, with an additional CO ligand along each edge of the Co₃ triangle. The Ge atom has a square pyramidal environment (GeCo₅) with the mean Ge – Co bond distances in plane 2.47 Å in one cluster and 2.46 Å in another one, which are somewhat longer than that of the Ge – Co (apical) bond distances of 2.35 and 2.33 Å, respectively. These two crystallographically independent clusters are examples of distortion isomerism (Table 1).

Inspection of the data in Table 1 reveals that there are three types of crystal classes: monoclinic (x 6), triclinic (x 5) and orthorhombic (x 3). In the series of distortion isomers,

coordination numbers about Ge are: GeMn₂ [13], GeC₄ [9], GeCl₃Au [5], GeC₃M (M = Cu [6], Mn [7], Sn[8], Mg [12] and Ru [14]), GeFe₄ [15], GeCl₂CoFe [16], GeB₂C₂N [10], and GeCo₅ [17]. Coordination numbers about M are HgGe₂ [11], CuP₂Ge [6], AuP₃Ge [5], SnC₃Ge [8], MnC₅Ge [7], MgO₄Ge₂ [12], FeC₄Ge₂ [16], FeC₄GeFe [15], CoC₄ GeCo [17], MnC₇Ge [13], RuC₇Ge [14], CoC₇GeCo [16], and FeC₁₀ (sandwich) [9, 10].

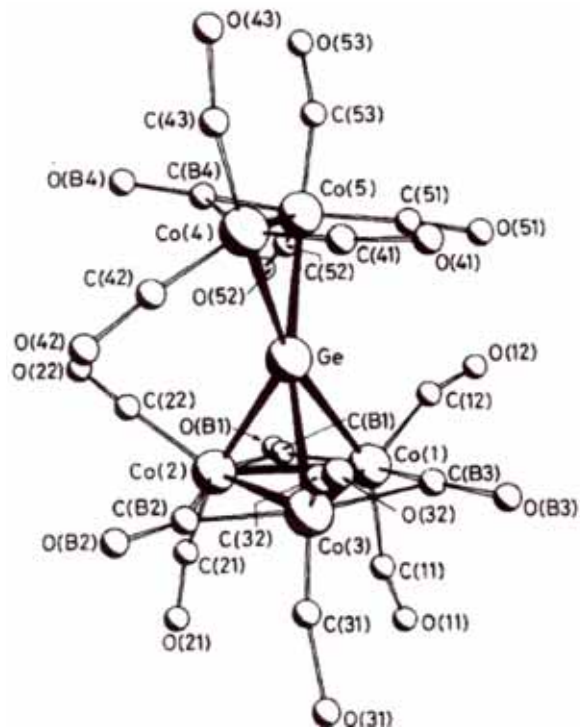


Fig. (5). Structure of [(CO)₁₂(μ-CO)₄Co₅](μ₅-Ge) [17].

The shortest Ge – M (M = group A or group B) bond distance here is for Ge – Hg, 2.514(2)Å [11] and Ge – Mn 2.18(2) Å [13].

3. CIS – TRANS ISOMERISM

White (Cl₃Ge)₂Ru(CO)₄ [18] is only example, which exists in two isomeric forms, cis- and trans-, and the former contains two crystallographically independent molecules (Table 2). Both geometric isomers are monoclinic. The three metal atoms form an unsymmetrical triangle with the mean Ge-Ru bond lengths in cis isomer of 2.469 Å (molecule 1) and 2.478 Å (molecule 2), and 2.477(1) Å in trans- isomer. The Ge – Ru- Ge angles are 90.5(1) and 91.5(2)° in cis- isomer. Each Ge atom is a tetrahedrally coordinated (GeCl₃Ru) and Ru atom is an octahedrally coordinated (RuC₄Ge₂) (Table 2).

4. CONCLUSIONS

Sixteen isomers of heterometallic germanium clusters have been included in this review. There are two types of isomerism – distortion and cis- trans. The former by far prevails (x 15). A yellow Cl₃GeAu(PPh₃)₃ [5] exists in two isomeric forms. An orange {(cp*)(CO)₂Mn}₂(μ-Ge) [13] contains within the same crystal three independent molecules.

Table 2. Crystallographic and Structural Data for Germanium Heterometallic Compounds - Cis-Trans Isomers^a

Compound (colour)	Cryst.cl. Space gr. z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo- phore	M – L [Å]	M – M [Å]	L – M - L [°]	Ref.
cis- (Cl ₃ Ge) ₂ Ru (CO) ₄ (white)	m P2 ₁ 4	9.759(5) 12.608(10) 12.878(9)	91.57(10)	GeCl ₃ Ru RuC ₄ Ge ₂ GeCl ₃ Ru RuC ₄ Ge ₂	Cl ^b 2.15(1,2) OC 1.93(4,2) Cl 2.14 (1,4) OC 1.99 (4,6)	Ru ^b 2.469(5,8) Ru 2.478(5,1)	Cl,Cl ^b 102.3(4,1.6) Cl,Ru 115.9(9,3.6) C,C 93(2,3) 174(2) C,Ge 88(1,1) 178(1,1) Ge,Ge 90.5(1) Cl,Cl 102.7(5,3.6) Cl,Ru 115.5(4,6.6) C,C 93(1,2) 173(1) C,Ge 87(1,3) 178(1,0) Ge,Ge 91.5(2)	[18]
trans- (Cl ₃ Ge) ₂ . Ru (CO) ₄ (white)	m P2 ₁ /n 2	9.152(1) 10.025(1) 8.399(1)	94.84 (1)	GeCl ₃ Ru RuC ₄ Ge ₂	Cl 2.153(2,8) OC 1.978(6,2)	Ru 2.477(1)	Cl,Cl 103.2(1,2.0) Cl,Ru 115.15(5,1.85) C,C 88.9(2) C,Ge 89.9(1,1)	[18]

Footnotes: ^aWhere more than one chemically equivalent distance or angle 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.

Remainders contain two such molecules. Also cis- {Cl₃Ge}₂Ru(CO)₄ [18] contains two such molecules. All are examples of distortion isomerism.

Summary of germanium – metal bond distances found in the series of distortion isomers are given in Table 3. Although germanium is classified as a soft, class B metal atom,

Table 3. Summary of the Ge-M Bond Distances in Heterometallic Germanium Clusters – Distortion Isomers

Ge-M	Isomers [Å]		Ref.
	I.	II.	
Ge-Au	2.561 (1)	2.536 (1)	[5]
Ge-Cu	2.370 (2)	2.382 (3)	[6]
Ge-Mn	2.53 (2)	2.54 (2)	[7]
Ge-Sn	2.596 (6)	2.567 (6)	[8]
Ge-Hg	2.514 (2)	2.543 (2)	[11]
Ge-Mg	2.715 (6,3) ^a	2.722 (6,5) ^a	[12]
Ge-Mn		2.18 (2) ^b	[13]
Ge-Ru	2.481 (5,5) ^a	2.487 (5,5) ^a	[14]
Ge-Fe	2.394 (2,6) ^a	2.378 (2,0) ^a	[15]
	2.425 (2,14) ^a	2.419 (2,10) ^a	
Ge-Co		2.341 (9) ^b	[16]
Ge-Fe		2.438 (4) ^b	[16]
Ge-Co	2.41 (1,6) ^a	2.39 (1,7) ^a	[17]
Ge-Ru	2.469 (5,8) ^a	2.478 (5,1) ^a	[18]

^aThe mean values are tabulated. The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean.

^bOnly the mean value was given in original paper.

it is apparent that it binds to both soft B and hard class A heterometal atom. The shortest Ge – M (M = group A or group B) bond distances here is for Ge – Hg, 2.514(2) [11] and for Ge – Mn, 2.18(2) Å [13].

The mean Ge – Ru bond distances of 2.469 Å in cis-(Cl₃Ge)₂Ru(CO) [18] is about 0.008 Å shorter than that in trans-(Cl₃Ge)₂Ru(CO)₄ [18] (2.477 Å).

This review and its precursors [2, 3] give the first overall survey of the structural data for the isomers of germanium complexes. In the chemistry of germanium coordination compounds [2] two types of isomers were found: distortion (twenty examples) and configuration (two examples). In the chemistry of organogermanium derivatives [3] were also found two types of isomers: a distortion (over forty examples) and ligand isomers (two examples). In general, in the chemistry of germanium complexes by far prevails a distortion isomerism, while cis-trans configuration and ligand isomerism are not so frequent.

This review and its precursors [2, 3, 19-23] give the first overall survey of the structural data for isomer complexes of the group IV metals.

In the chemistry of the group IV metal complexes exists four hundred as isomers, with the seventy four examples in the chemistry of germanium [2, 3 and present review], two hundred and fifty six of tin [19-22] and seventy of lead complexes [23]. The isomers exists in the following crystal classes: monoclinic (x 38) > triclinic (x 27) > orthorhombic (x 7) > tetragonal and cubic, each (x 1) in the chemistry of germanium; monoclinic (x 125) > triclinic (x 75) > orthorhombic (x 38) > tetragonal (x 12) > trigonal (x 3) > hexagonal (x 2) and cubic (x 1) in the chemistry of tin; and monoclinic (x 31) > triclinic (x 23) > orthorhombic (x 8) > tetragonal (x 4) > trigonal (x 2) > hexagonal and cubic, each (x 1) in the chemistry of lead. One can see that the monoclinic (48 %) and triclinic (31.25 %) by far prevail in the chemistry of isomers of the respective the group IV metals.

Structural data of all four hundred isomers showed that stereoisomers dominate in the chemistry of the group IV metals. Included are distortion (x 68) > ligand, cis-trans and configuration, each (x 2) isomerism, in the chemistry of germanium; distortion (x 238) > ligand (x 12) > cis-trans (x 5) > polymerisation (x 1) isomerism in the chemistry of tin; and distortion (x 44) > ligand (x 12) > coordination (x 9) > polymerisation (x 5) isomerism, in the chemistry of lead. In general, the number of isomers in the group IV metal complexes increases in the order: distortion (x 350, 87.5 %) > ligand (x 26, 6.5 %) > coordination (x 9, 2.35 %) > cis-trans (7, 1.75 %) > polymerisation (x 6, 1.5 %) > configuration (x 2, 0.5 %). Only two types of isomerism (configuration and polymerisation) belong to the structural class, remainders are stereoisomers. Distortion isomerisation is far more common with two crystallographically independent molecules within the same crystal.

Interestingly, that in the chemistry of transition elements like for example copper Cu(II) [4], Cu(I) [24] and platinum [25]) also distortion isomers with a monoclinic class dominate.

It is hoped that such a review will help to focus attention on areas of transition as well as non transition chemistry that

could be enhanced by further study and assist in allowing comparative behaviour of the respective metal atoms in the situation which can arise from the widespread use of metals.

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6. ABBREVIATIONS

C ₆ F ₅	=	pentafluorophenyl
cp	=	cyclopentadienyl
cp [*]	=	pentamethylcyclopentadienyl
dme	=	1,2-dimethoxyethane
Et	=	ethyl
m	=	monoclinic
Me	=	methyl
or	=	orthorhombic
Ph	=	phenyl
PPh ₃	=	triphenylphosphine
tr	=	triclinic

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