Isomers in the Chemistry of Germanium Coordination Compounds

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Abstract: The coordination chemistry of germanium covers quite bulk fields, as shown by a survey covering the crystallographic and structural data of over two hundred examples. About ten percent of those complexes exist as distortion isomers and are summarised. These are discussed in terms of the coordination around the germanium(I), germanium(II) and germanium(IV) atoms, and correlations are drawn between donor atoms, bond distances and interbond angles. Distortion isomers differing only by degree of distortion in Ge – L and L – Ge – L angles by far prevail. There is an example, which contains within one crystal distortion and coordination isomers, which is rarity.

Keywords: Germanium, complexes, distortion isomers, crystal structures.

1. INTRODUCTION

The largest use of germanium is in transistor technology, indeed transistor activity was first quantified in this element. While this use is now demisting, the transparency of germanium in the infrared is expanding of its use in optics for windows, prisms and lenses. The coordination chemistry of germanium covers a quite bulk field, as shown by a recent survey covering the crystallographic and structural data of almost two hundred examples [1]. About ten percent of these complexes exists as isomers and are summarised in this review. In this review we analyse and classify these examples. The aim of this presentation is to discuss the factors which could lead to a better understanding of stereochemical interactions within the coordination sphere. The systems discussed have been sorted by nuclearity and 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 principles coordinating ligand atom and increasing complexity of the coordination sphere.

2. DISTORTION ISOMERISM

The existence of two or more species, even within the same crystal, differing only by degree of distortion, is typical of general class of distortion isomerism [2].

2.1. Mononuclear Germanium Compounds

The crystallographic and structural data for mononuclear germanium distortion isomers are summarised in Table **1**. Purple $Ge(\eta^4\text{-}tpp)(MeO)_2$ is only example, which exists in two isomeric forms, monoclinic [3] and tetragonal [4] and in addition, the monoclinic contains two crystallographicaly independent molecules. A six coordinate environment around each Ge(IV) is created by one tetradentate tpp ligand (4 N) and two unidentate MeO ligands (GeN_4O_2). The

former ligand created a plane and the latter occupied axial positions. The structure exhibit a distorted geometry with a compressed tetragonal bipyramidal geometry around each Ge(IV) atom. The mean value of Ge – N (x4) and Ge – O (x2) bond distances elongated in the order: 11.700 Å (monoclinic, molecule 1) < 11.706 Å (monoclinic, molecule 2) < 11.778 Å (tetragonal).

There are seven derivatives which contains two crystallographically independent molecules within the same crystal. Three of them contain germanium in its +2 oxidation state and all belong to the monoclinic class [5-7]. Each Ge(II) atom is three coordinated.

The X-ray analysis of colourless $(NEt_3Bz)[GeCl_3]$ [5] and $(pi)[GeCl_3] .0.5\ H_2O$ [6] shows well separated complex $[GeCl_3]^-$ anion, NEt_3Bz^+ or pi^+ cation and water molecule. The isolated $[GeCl_3]^-$ anions have trigonal pyramidal structure with Cl – Ge – Cl angles in [5] with the mean values of 96.07 (3,78)° (molecule 1) and 96.04 (3, 2.63)° molecule 2; and in [6] 95.6 (5.3)° (molecule 1) and 96.5 (4,5)° (molecule 2). (The first number in parenthesis is e.s.d., and the second is maximum deviation from the mean). The mean Ge – Cl bond distances in [5] are 2.301 (2.3) and 2.299 (2.6) Å and in [6] 2.273 (7,5) and 2.278 (7,17) Å.

In yellow $GeI_2(PPh_3)$ [7] a trigonal pyramid around Ge(II) is created by two iodine atoms and one PPh_3 ligand (GeI_2P). The Ge – I and Ge – P bond distances of 2.635 Å (mean) and 2.503 Å in molecule 1 are somewhat shorter than those found in molecule 2 with the values of 2.653 Å (mean) and 2.510 Å, respectively. While the I– Ge -I bond angles are equal in the both molecules (99.0 (1)°), the mean I – Ge – P bond angles are different with the values of 91.7 (1, 1.3)° in the molecule 1 and 94.1 (1, 4)° in the molecule 2. The molecule 1 is somewhat more distorted than molecule 2.

Remaining four derivatives contain germanium in its + 4 oxidation state. In three of them, each Ge(IV) atom has a trigonal bipyramidal geometry and all but one of these exhibit a high degree of distortion due to the incorporation a tetradentate groups [8, 9] and terdentate group [10], which span the equatorial and axial position.

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Table 1.   Crystallographic and Structural data for Mononuclear Germanium Coordination Compounds – Distortion Isomers[a]

COMPOUND (COLOUR)	CRYST. CL. SPACE GR. Z	a[Å] b[Å] c[Å]	α[°] β[°] γ[°]	CHROMO-PHORE	Ge – L [Å]	L – Ge – L [°]	REF.
α-Ge(η⁴-tpp). (MeO)₂ (purple)	m P2₁/c 4	15.013(3) 14.441(5) 8.414(4)	91.85(2)	Ge^IVN₄O₂ Ge^IVN₄O₂	η⁴N_eq^b 2.010(4,0) 2.019(4,0) MeO_ax η⁴N_eq 1.821(3) 2.011(4,0) MeO_ax 2.020(4,0) 1.822(3)	N,N^b 89.1(2)^c N,O 91.5(2,2.6) N,N 90(1,2)^c N,O 91.5(2,2.6)	[3]
β-Ge(η⁴-tpp). (MeO)₂ (purple)	tg P4₂/n 4	19.413(2) 9.972(1)		Ge^IVN₄O₂	η⁴N_eq 2.022(3,0) 2.041(3,0) MeO_ax 1.826(3,0)	N,N 90.0(1,2)^c 180.0(1,0) O,O 180.0(1) N,O 90.0(1,3.4)	[4]
(NEt₃Bz)[GeCl₃] (colourless) at 203 K	m P2₁/c 8	25.706(3) 7.040(1) 20.037(2)	112.48(1)	Ge^IICl₃ Ge^IICl₃	Cl 2.301(2,3) Cl 2.299(2,6)	Cl,Cl 96.07(5,78) Cl,Cl 96.04(5,2.6)	[5]
(pi)[GeCl₃].0.5 H₂O (colourless)	m P2₁ 4	14.24 17.61 6.83	97.3	Ge^IICl₃ Ge^IICl₃	Cl 2.268(7) 2.276(8,1) Cl 2.261(7) 2.287(8,2)	Cl,Cl 95.6(5,6) Cl,Cl 96.5(4,5)	[6]
GeI₂(PPh₃) (yellow)	m P2₁/n 8	13.546(4) 10.415(5) 13.893(4)		Ge^III₂P Ge^III₂P	I 2.635(3,2) Ph₃P 2.503(4) I 2.653(3,8) Ph₃P 2.510(5)	I,I 99.0(1) I,P 91.7(1,1.3) I,I 99.0(1) I,P 94.1(1,4)	[7]
Ge{η⁴-N(CH₂CH₂O)₃}(OH) (colourless)	m P2₁/c 8	14.156(5) 11.002(3) 14.682(5)	112.63(2)	Ge^IVO₄N Ge^IVO₄N	η⁴O_eq 1.786(7,14) N_ap 2.166(6) HO_ap 1.767(6) η⁴O_eq 1.788(7,11) N_ap 2.185(6) HO_ap 1.763(8)	O,O 96.4(3,1.8) 118.8(3,4) O,N 83.6(3,6)^d 178.8(3) O,O 96.5(3,1.6) 118.8(3,1.1) O,N 83.6(3,2)^d 178.3(3)	[8]
Ge{η⁴-N(CH₂CH₂.O)₃}Br (not given)	or Pcab 16	11.953(5) 12.839(5) 24.167(6)		Ge^IVO₃NBr Ge^IVO₃NBr	η⁴O_eq 1.7876(17) 1.804(17,4) N_ap 2.090(20) Br_ap 2.360(4) η⁴O_eq 1.726(17) 1.786(16,6) N_ap 2.097(19) Br_ap 2.363(4)	O,O 119.4(8,1.2) O,N not given O,Br 94.5(6,1.4) N,Br 179.8(6) O,O 119.6(8,3) O,N not given O,Br 93.6(6,8) N,Br 178.9(5)	[9]
Ge{η³-O(CH₂.CH₂S)₂}Cl₂ (colourless)	or Pca2₁ 8	13.546(4) 10.415(5) 13.893(4)		Ge^IVCl₂S₂O Ge^IVCl₂S₂O	Cl_eq 2.179(4) η³S_eq 2.184(4,15) O_ap 2.36(1) Cl_ap 2.212(4) Cl_eq 2.131(6) η³S_eq 2.185(4,32) O_ap 2.39(1) Cl_ap 2.204(4)	Cl,Cl 101.0(2) S,S 130.7(2) Cl,S 104.1(2,9.9) Cl,O 85.3(3) 172.8(3) S,O 81.0(3,7)^d Cl,Cl 103.3(2) S,S 129.4(2) Cl,S 103.8(2,10.7) Cl,O 87.1(3) 169.3(3) S,O 81.0(3,1.3)^d	[10]
Ge(η⁴-tpp)(MeO)₂ (purple)	m P2₁/c 4	15.911(5) 14.441(5) 8.414(4)	91.85(2)	Ge^IVN₄O₂ Ge^IVN₄O₂	η⁴N_eq 2.010(4,0) 2.019(4,0) MeO_ax 1.821(3,0) η⁴N_eq 2.011(4,0) 2.020(4,0) MeO_ax 1.822(3,0)	N,N 89.1(2)^c N,O 92.8(2,6) N,N 90.5(1)^c N,O 91.5(2,2.6)	[3]

(Table 1). Contd…..

Ge(η^4-tpp)(EtO)$_2$ (red violet) at 130 K	tr P-1 2	10.941(1) 11.212(1) 17.015	89.53(1) 73.77(1) 70.78(1)	Ge^{IV}N$_4$O$_2$	η^4N$_{eq}$ EtO$_{ax}$	2.013(3,0) 2.023(3,0) 1.865(3,0)	N,O	88.0(1,2)^c	[11]
				Ge^{IV}N$_4$O$_2$	η^4N$_{eq}$ EtO$_{ax}$	2.016(3,0) 2.029(3,0) 1.845(3,0)	N,O	90.0(1,2.5)^c	
(NMe$_4$)[GeCl$_3$] (colourless)	or Pna2$_1$ 4	13.096(2) 8.895(1) 9.115(1)		Ge^{II}Cl$_3$	Cl	2.262(8) 2.310(8,11)	Cl,Cl	95.2(3,6)	[12,13]
at 438 K	c Pm3m 1	6.522(2)		Ge^{II}Cl$_3$					[12]
at 190 K	or Pnam 4	13.083(6) 8.841(4) 9.027(4)		Ge^{II}Cl$_3$					[14]
at 160 K	m ? ?	13.068(6) 8.808(5) 8.962(6)	93.9(1)	Ge^{II}Cl$_3$	Cl	2.305(3,0)	Cl,Cl	95.2(1,1)	[14]

Footnotes:

[a]Where 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.

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

[c]The six-membered metallocyclic ring.

[d]The four - membered metallocyclic ring.

In Ge{η^4-N(CH$_2$CH$_2$O)$_3$}X (X – OH [8] or Br [9]), while three O atoms of tetradentate ligand occupied an equatorial position, and the N atom an axial position and the other axial position is occupy by X ligand. The mean values of Ge – L bond distances in molecule 1 vs molecule 2 in [8] are 1.786 (7, 14) vs 1.788 (7, 11) Å (Ge –O$_{eq}$); 2.166(6) vs 2.185(6)Å (Ge – N$_{ax}$); 1.767(6) vs 1.763(6)Å (Ge – OH$_{ax}$); and in [9] the values are 1.795(17, 19) vs 1.766(17, 40); 2.090(20) vs 2.097(19) Å, 2.369(4) vs 2.363(4)Å (Ge – Br$_{ax}$).

In Ge{η^3-O(CH$_2$CH$_2$S)$_2$}Cl$_2$ [10] two S atoms of terdentate ligand occupied an equatorial position and O atom axial position. One chlorine atom complete trigonal plane and the other one an axial. The Ge – L bond distances in molecule 1 vs molecule 2 are: 2.184(4, 15) vs 2.185(4, 32) Å (Ge – S$_{eq}$). 2.179(4) vs 2.131 (6)Å (Ge – Cl$_{eq}$), 2.36(1) vs 2.39(1)Å (Ge – O$_{ap}$) and 2.212(4) vs 2.204(4) Å (Ge – Cl$_{ap}$).

A six coordinate environment around Ge(IV) in red violet Ge(η^4-tpp)(EtO)$_2$ [11] is created by one tetradentate tpp and two unidentate EtO ligands (GeN$_4$O$_2$). The mean Ge – N$_{eq}$ and Ge – O$_{ax}$ bond distances are 2.018(3,5) and 1.865(3,0) Å in molecule 1 and 2.022(3,7) and 1.845(3,0) Å in molecule 2. Each Ge(IV) atom has a compressed tetragonal bipyramidal environment with a different degree of distortion (Table **1**).

Colourless (NMe$_4$)[GeCl$_3$] [12-14] has been studied at different temperatures. At 424 K the modification is cubic [12], at 293 K is orthorhombic [12, 13], at 190 K is also orthorhombic [14] and at 160 K is monoclinic [14]. Each Ge(II) has a trigonal pyramidal environment (GeCl$_3$) with the mean Ge – Cl bond distance in the orthorhombic case of 2.294(8, 32) Å which is somewhat shorter than that found in the monoclinic case (2.305(3, 0)Å) (Table **1**).

The data in Table **1** shows the mean Ge(II) – L bond distance increases with the atomic size of L in the sequence:

2.285 Å (Cl, 0.99Å) < 2.507 Å (P, 1.06Å) < 2.644Å (I, 1.33Å) in 3-coordinate derivatives. In Ge(IV) – L mean bond length, the following trends are apparent:

5-coordinate: 1.765Å (OH$_{ax}$) < 2.155Å (Cl$_{eq}$) < 2.2O8Å (Cl$_{ax}$) < 2.361Å (Br$_{ax}$) (unidentate); 2.185Å (S$_{eq}$) < 2.375Å (O$_{ax}$) (terdentate 2S + O); 1.784Å (O$_{eq}$) < 2.135Å (N$_{ax}$) (tetradentae 3O + N).

Both electronic and steric factors affect the bonding of the chelated ligands as can be seen in the opening of the L – Ge(IV) – L bond angle of the respective metallocycles. The mean L – Ge(IV) – L bond angle opens in the order of the respective metallocycles: 81.0° (-OCS-) < 83.6° (-OCN-) < 90.0° (-NC$_3$N-).

2.2. Di – and Oligonuclear Germanium Compounds

There are eight derivatives which contain two crystallographicaly independent molecules (Table **2**). Three of them are binuclear. Yellow [Ge(SiMeiPr$_2$)$_2$]$_2$ [15] shows near planar geometry around the Ge = Ge bond enforced by the triallylsilyl derivatives. The geometry of the complex is trans-bent with averaged bonding angle of 6.5°. No twisting was observed. The complex contains two crystallographically independent binuclears with Ge = Ge bond lengths of 2.266(1) and 2.268(2) Å and mean Ge – Si bond lengths of 2.403(2) and 2.400(2)Å, respectively.

In colourless [Ge(μ-O){N(SiMe$_3$)$_2$}$_2$]$_2$ [16] distorted edge-shared tetraedra are joined by two O atoms which serve as bridges. Two crystallographically independent binuclears are differing from each other by degree of distortion. The Ge – Ge, Ge –μO and Ge – N bond distances (molecule 1 vs molecule 2) are 2.606(2) vs 2.608(2) Å, 1.805(9) vs 1.805(9) Å, and 1.919(11) vs 1.826(11) Å, respectively. The Ge – O-Ge, μO – Ge –μO and N – Ge – N bond angles are: 91.8(4) vs 93:2(4)°, 88.1(5) vs 86.7(5) and 115.3(5) vs 114.7(5)°.

Table 2. **Crystallographic and Structural Data for Bi- and Oligonuclear Germanium Coordination Compounds – Distortion Isomers**

Compound (colour)	Cyst.cl. Space gr. z	a [Å] b [Å] c [Å]	α [°] β [°] γ [°]	Chromo-phore	Ge – L [Å]	Ge – Ge [Å] Ge–L–Ge [°]	L – Ge - L [Å]	Ref.
[Ge(SiMeiPr$_2$)$_2$]$_2$ (yellow) at 150 K	tr P-1 2	11.948(3) 16.352(4) 11.168(4)	104.73(3) 117.79(2) 81.88(2)	GeSi$_2$Ge GeSi$_2$Ge	Si[b] 2.405(2,5) Si 2.400(2,2)	2.266(1) 2.268(1)	Si,Si[b] 117.0(0) Si,Ge 121.1(0,3) Si,Si 118.2(0) Si,Ge 120.7(0,2.8)	[15]
[{Ge-(μ-O){N(SiMe$_3$)$_2$}$_2$]$_2$ (colourless)	or Pbca 16	27.687(4) 18.105(9) 35.742(11)		GeO$_2$N$_2$ GeO$_2$N$_2$	μO 1.805(9) N 1.819(11,17) μO 1.805(9) N 1.826(11,13)	2.606(2) 91.8(4,4) 2.608(2) 93.2(4,3)	O,O 88.1(5) N,N 115.3(5,0) O,O 86.7(5) N,N 114.7(5,1)	[16]
[Ge{μ-NSi(OCMe$_3$)$_3$}(η^2-Me$_2$en)]$_2$	tr P-1 2	9.674(5) 14.626(4) 16.813(4)	85.36(5) 89.49(4) 74.27(5)	GeN$_4$ GeN$_4$	μN 1.839(4,4) η^{2}N 1.770(12,1) μN 1.847(4,6) η^{2}N 1.810(4,1)	2.659(1) 92.6(2) 2.677(1) 92.9(2)	N,N 87.4(2) 89.3(5)[c] 120.9(4,1.2) N,N 87.1(2) 92.3(2)[c] 120.1(2,4.2)	[17]
Ge$_4$(SitBu$_3$)$_4$ (red) at 203 K	m ? 8	18.1997(2) 16.8809(2) 25.0074(4)	97.94(4)	GeSiGe$_3$	Si 2.383(4,5)	2.441(2,10)	Ge,Ge 60.00(7,3.8) Si,Ge 143.8(1,12.9)	[18]
(Nme$_4$)$_4$[Ge$_4$(μ-S)$_6$(S)$_4$] (colourless)	c P4-3n 8	19.5490(4)		GeS$_4$ GeS$_4$	μS 2.23(1,1) S 2.14(1) μS 2.23(1,0) S 2.22(1)		S,S 109.5(9,3.2) S,S 109.5(9,0)	[19]
(dpa)[Ge$_4$(μ-S)$_6$(S)$_3$] (yellow)	m P2$_1$/n 4	13.718(2) 10.7789(9) 20.350(4)	103.382(8)	GeS$_4$ (x3) GeS$_3$	μS not given S not given μS not given			[20]
(2,2,2-cryptr-K)$_6$ (Ge$_9$)(Ge$_9$)0.5en (brown) at 233 K	tr P-1 2	14.397(1) 19.765(2) 28.898(2)	87.485(9) 79.168(9) 85.415(8)	GeGe$_8$ GeGe$_8$	Ge 2.572-2.817(2) 2.562-2.853(2) Ge	2.642 (average) 2.641 (average)	Ge,Ge not given Ge,Ge not given	[21]
(2,2,2-cryptr-K)$_6$ (Ge$_9$)(Ge$_9$)0.5en (deep red) at 233 K	tr P-1 2	14.503(1) 19.924(2) 28.935(2)	87.43(1) 80.85(1) 85.92(1)	GeGe$_8$ GeGe$_8$	Ge 2.527-2.837(2) 2.562-2.904(2) Ge	2.633 (average) 2.637 (average)	Ge,Ge not given Ge,Ge not given	[21]
GeCl$_3$(NPMe$_3$) (colourless)	tr P-1 2	12.49(2) 12.54(3) 6.66(1)	100.96(10) 91.45(14) 102.77(15)	GeCl$_3$N (monomer) GeCl$_3$N (dimer)	Cl 2.139(3,5) N 1.737(8) Cl 2.173(2,3) 2.345(3) μN 1.837(7) 1.972(1)	2.915(1) 99.8(3)	Cl,Cl 104.6(1,1.0) Cl,N 114.0(3,4.8) Cl,Cl 88.2(1,1) 116.6(1) N,N 80.2(2) Cl,N 94.5(2,1.7) 121.6(3,9) 176.4(1)	[22]

Footnotes:
[a]Where 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.
[b]The chemical identity of the coordinated atom or ligand is specified in the columns.
[c]The five -membered metallocyclic ring.

Structure of colourless [Ge{μ-NSi(OCMe$_3$)$_3$}(η^2-Me$_2$en)]$_2$ [17] contains two edge-shared tetrahedral which are joined by two N-donor NSi(OCMe$_3$)$_3$ ligands which serve as bridges. Chelated Me$_2$en ligand completed a tetrahedral environment around each germanium atom (GeN$_4$). The Ge – Ge bond distances which differ from each other with the values of 2.659(1) Å (molecule 1) and 2.677(1)Å (molecule 2). The sum of Ge – N bond distances of 7.218Å in molecule 1 is about 0.096Å smaller than that found in molecule 2 (7.314Å). This indicates that the former molecule is somewhat more crowded than the latter one.

There are three tetranuclear derivatives [18-20] which contain two crystallographically independent molecules. In

red $Ge_4(SitBu_3)_4$ [18] four germanium atoms form almost a regular tetrahedron with Ge – Ge bond distances from 2.431(2) Å to 2.447(2) Å and Ge – Ge – Ge angles from 59.62(7)° to 60.10(7)°. Each Ge(I) atom carries a terminal $SitBu_3$ group with mean Ge – Si bond distance of 2.383(4) Å.

The remaining tetranuclear derivatives [19, 20] contain $Ge_4S_{10}^{-4}$ [19] or $Ge_4S_9^{-2}$ [20] anions, which posses an adamantane-like structure. Structure of $Ge_4S_{10}^{-4}$ anion is shown in Fig. (**1**). The tetrahedral anions are composed of nearly regular tetrahedral Ge(IV) centres, each having one terminal S and three doubly bridging S atoms (Table **2**).
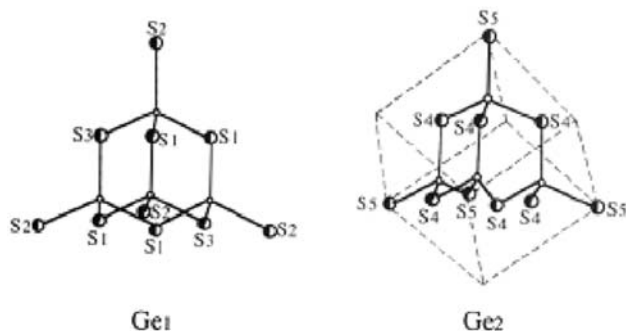
Fig. (1). Structure of $[Ge_4(\mu\text{-}S)_6(S)_4]^{4-}$.

There are two oligonuclear derivatives, brown (2,2,2-crypt-K)$_6$(Ge$_9$)(Ge$_9$).0.5 en [21] and deep red (2,2,2-crypt-K)$_6$ (Ge$_9$)(Ge$_9$).1.5 en [21] which are isostructural and contains two the Ge$_9^{-3}$ clusters. The structure of a Ge$_9^{-3}$ unit is shown in Fig. (**2**). It is depicted as a tricapped non-regular trigonal prism. In brown derivative the Ge – Ge bond distances range from 2.572(2) to 2.817(2) Å in one Ge-Ge$_8$ cluster and from 2.562 to 2.853(2) Å in the other one GeGe$_8$ cluster. In deep red derivative the values are (2.527(2) – 2.837(2)Å and 2.562(2) – 2.904(2) Å respectively (Table **2**).
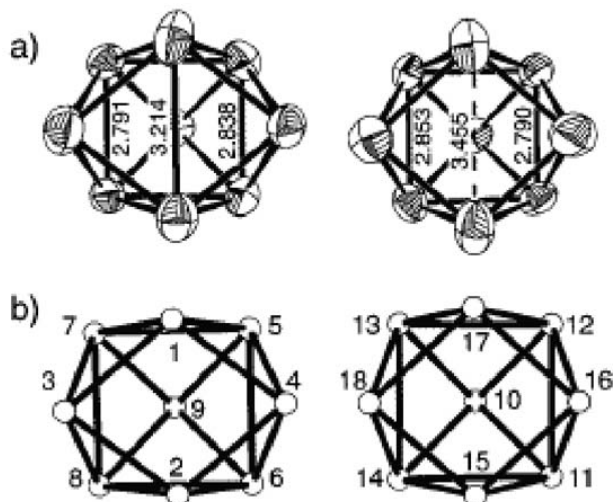

Fig. (2). View of the Ge$_9^{3-}$ anions: (**a**) Cluster A (left) and B (right) With thermal ellipsoids shown at 50 % probability level, atom labels see (**b**). (**b**) The same clusters shown as parallel projection emphasizing the different Shapes of the two polyhedra.

Structure of colourless GeCl$_3$(NPMe$_3$) [22] shows that in the unit cell are two symmetry related monomers containing

tetracoordinated germanium (GeCl$_3$N), and one crystallographically centrosymmetric dimer with a planar four membered (GeN)$_2$ ring exhibiting trigonal bipyramidal configuration around each Ge(IV) atom(GeCl$_3$N$_2$). The very short Ge – N bond length of 1.737(8) Å in the monomer is indicative of the involvement of a pπ – dπ component. At least two types of isomerism exist in the example, distortion (monomer) and configuration isomerism (four coordinate monomer and pentacoordinated dimer) (Table **2**).

3. CONCLUSIONS

This review summarises the crystallographic and structural data for twenty coordination compounds of germanium which are distortion isomers. Another one [22] contains two types of isomerism, distortion and configuration. Remainders [4-21] contain two crystallographic independent molecules differ mostly by degree of distortion.

Germanium exists in an oxidation states + 1, + 2 and + 4, including non-integral Ge$_9^{3-}$. Of these + 4 oxidation state is the most common. The isomers are mostly colourless, yellow, but there are some red examples. The nuclearity of isomerism is mono-, di-, tetra – and nanonuclears.

The α- and β-Ge(η^4-tpp)(MeO)$_2$ [3,4] isomers are different not only by degree of distortion, but also by crystal class, α- being monoclinic and β- tetragonal. In additional α- contains two crystallographically independent molecules. There are six derivatives [5-8, 11, 18, 20] which are monoclinic, six [15, 17, 21, 22] are triclinic, three [9, 10, 16] are orthorhombic and one [9] is cubic. Colourless (NMe$_4$) [GeCl$_3$] at 424 K is cubic [12] is orthorhombic at 293 K and 190 K [12-14] and is monoclinic at 160 K [14].

There is a variety of inner coordination spheres around the germanium atom. In Ge(1) complex is tetrahedral (GeSiGe$_3$). In Ge(II) complexes are trigonal planar with varied degrees of distortion: GeCl$_3$,GeI$_3$, GeI$_2$P and GeSi$_2$Ge; and tetrahedral GeN$_4$. The environment around Ge(IV) are tetrahedral: GeS$_4$, GeO$_2$N$_2$; trigonal bipyramidal: GeO$_4$N, GeO$_3$NBr and GeCl$_2$S$_2$O, and compressed tetragonal bipyramidal GeN$_4$O$_2$. Most axial positions are occupied by O donor atom ligands.

This review, together with its precursors [23, 24] represents the first overall survey of the structural data of isomers for the non-transition sub-group (Ge – Sn – Pb). Interesting while in lead complex chemistry exists several types of isomers included distortion (60 %) ligand (20 %), coordination (12 %) and polymerization (8 %) [24], in tin coordination chemistry distortion (96.5 %) and cis – trans (3.5 %) [23], in the germanium coordination chemistry distortion isomerism with one example which contains in the same crystal distortion and coordination isomers, and it is rarity. Generally, the distortion isomerism in this sub-group by far prevails.

ABBREVIATIONS

tBu   = terc-butyl

Bz   = benzyl

cryp   = cryptate

c   = cubic

en   = ethylendiamine

Et   = ethyl

EtO   = ethoxy

m   = monoclinic

Me$_2$en = N,N-dimethylethylenediamine

MeO   = methoxy

or   = orthorhombic

pi   = pilocarpine

PPh$_3$ = triphenylphosphine

iPr   = isopropyl

tg   = tetragonal

tpp   = tetraphenylporphinato

tr   = triclinic

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