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Synthesis and molecular and crystal structures of new cation-anionic hypervalent germanium complexes with 1,1,3,3-tetrakis(O—Ge)chelato-1,1,3,3-tetra(lactamomethyl)-1,3-digermoxane dications

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The reaction of dichloride $(L^5)_2GeCl_2$ with $LiI \cdot H_2O$ under conditions, which did not exclude exposure to atmospheric oxygen, as well as hydrolysis of chloride triflate $(L^7)_2Ge(Cl)OTf$ in the presence of Et_3N and of perchlorate $(L^5)_2Ge(Cl)OClO_3$ by atmospheric moisture afforded cation-anionic complexes containing the digermoxane dications of the general formula $[(L^n)_2GeOGe(L^n)_2]^{2+}$ (L^n is a lactamomethyl *n*-membered bidentate C,O-coordinating ligand) with the triiodide, triflate, and perchlorate ions, respectively. According to the results of X-ray diffraction study, the digermoxane dications in these complexes contain two pentacoordinate Ge atoms each and occur as germylium ions stabilized by two O→Ge coordination bonds. In these complexes, the digermoxane dications are diastereomers in which the bischelate systems have opposite configurations.

Key words: hypervalence, germylium ions, pentacoordinate germanium, cation-anionic complexes, synthesis, X-ray diffraction study.

Beginning in 1993, pentacoordinate silylium cations stabilized by the intramolecular (intraionic) N→Si and O→Si coordination interactions[1,2] were extensively and systematically studied (see, for examples, the reviews,[3,4] papers,[5—9] and references cited therein). Their germanium analogs have been much less studied.[10] Examples are triflate $L_2Ge(H)OTf$ (L is the potentially bidentate 8-methoxynaphthyl ligand), in which (according to the results of X-ray diffraction analysis) the pentacoordinate germanium atom is weakly bound to the triflate anion, and its hydrate $[L_2GeH(H_2O)]^+OTf^-$ containing the hydrated germylium cation.[11a] The ionic structure of the triflate $L_2Ge(H)OTf$ in a solution in CH_2Cl_2 was confirmed by conductivity measurements. The $[LGeMe_2]^+Cl^-$ complexes, which contain the germylium cations stabilized by the tridentate monoanionic 2,6-bis(dialkylaminomethyl)-4-*tert*-butylphenyl N,C,N-chelating ligand L, were also synthesized.[11b]

Earlier,[12] we have found that the reactions of bis(lactamomethyl)dichlorogermanes $(L^n)_2GeCl_2$ (L is the bidentate lactamomethyl C,O-chelating ligand, *n* is the size of the lactam ring, 5—7) with LiX, AgX, or Me_3SiX (X = F, Br, I, OTf, or ClO_4) afforded two types of products depending on the nature of the nucleophile.[12] In the case of similar nucleofugicities of the entering (F or Br) and leaving (Cl) groups, both chlorine atoms are replaced by the nucleophile to give dihalides *cis*-$(L^n)_2GeX_2$ (X = F or Br). According to the results of X-ray diffraction analysis, the configurations of the coordination units in these dihalides are identical with those in the starting dichlorides, *i.e.*, the carbon atoms are in *trans* positions, whereas the coordinated O atoms and the Hal atoms are in *cis* positions with respect to each other. In the case of a substantial difference in the nucleofugicity of the entering (I, OTf, or $OClO_3$) and leaving (Cl) groups, only one halogen atom is replaced by a nucleophile to form monochlorides *trans*-$(L^n)_2Ge(Cl)X$ in which the C and O atoms and the monodentate ligands are *trans*-arranged with respect to each other. In the solid state, the monochlorides $(L^n)_2Ge(Cl)X$ occur as molecular hexacoordinate (5 + 1) germanium complexes with the Ge—Cl covalent bonds, whereas the X→Ge bonds are predominantly ionic in character. Compared to covalent dihalides $(L^n)_2GeX_2$, the latter compounds possess higher conductivity in CH_2Cl_2,

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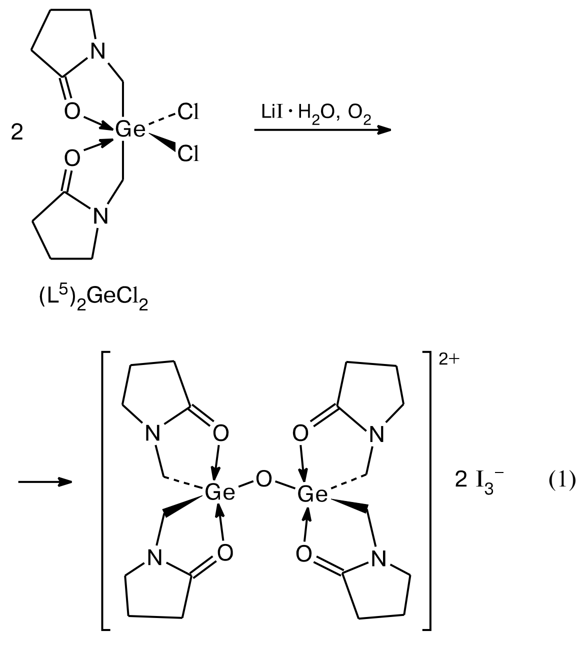
which suggests the presence of the germylium ions $[(L^n)_2Ge(Cl)]^+$ stabilized by two intraionic O→Ge coordination bonds in solutions of monochlorides $(L^n)_2Ge(Cl)X$.[12]

Analogous attempts to replace the chlorine atoms in bis(lactamomethyl)- and bis(amidomethyl)dichlorosilanes by performing the reactions in the presence of traces of moisture afforded exclusively the cation-anionic pentacoordinate silicon complexes $\{[(L^n)_2Si]_2O\}^{2+}X^{2-}$ and $\{[(MeCONMe)_2Si]_2O\}^{+}X^{2-}$ (X^{2-} = $2OTf^-$, $H_3O^+ \cdot 3Cl^-$, $HgCl_4^{2-}$, or $Hg_2Cl_6^{2-}$) containing disilylium dications stabilized by the intraionic O→Si coordination interaction.[9a,b] The ease of formation of such complexes was attributed to the thermodynamically favorable formation of the disiloxane bond and the possible additional stabilization of the cationic center by the adjacent lone electron pair of the oxygen atom of the disiloxane fragment. It should be noted that all these compounds were isolated using acidic reagents.

In the present study, we report the synthesis and crystal structures of analogous cation-anionic hypervalent germanium complexes, which were prepared for the first time. The reactions giving rise to these complexes were carried out in the presence of water in a neutral or basic medium.

Results and Discussion

We found that the reaction of dichloride $(L^5)_2GeCl_2$ with $LiI \cdot H_2O$ in acetonitrile under conditions, which did not exclude exposure to atmospheric oxygen, afforded the cation-anionic digermoxane complex $[(L^5)_2GeOGe(L^5)_2]^{2+}2I_3^-$ (**1**) (reaction 1).



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In our opinion, the formation of the digermoxane fragment in compound **1** is associated with an increase in the basicity of the medium upon oxidation of an excess of the nucleophile (I^-) with atmospheric oxygen to give the triiodide ion.

$$6\,I^- + 2\,H_2O + O_2 \longrightarrow 2\,I_3^- + 4\,OH^- \qquad (2)$$

The reaction of dichloride $(L^7)_2GeCl_2$ with Me_3SiI in the presence of oxygen afforded the product of monosubstitution and oxidation, *viz.*, chloride triiodide $(L^7)_2Ge(Cl)I_3$.[13] This reaction did not give rise to compound **1**, apparently, because of the acidic character of the reagent used.

The first step of the reaction (1) giving rise to the final product **1** may involve hydrolysis of the dichloride $(L^5)_2GeCl_2$ in the presence of a base (OH^-) to form the digermoxane $[(L^5)_2Ge(Cl)]_2O$. Unlike the very strong Ge—Cl bond in the above-mentioned monochlorides *trans*-$(L^n)_2Ge(Cl)X$ (X = I, OTf, or $OClO_3$) containing (5 + 1)-coordinate germanium, this bond in the intermediate digermoxane should be a weaker component of the hypervalent Cl—Ge—O bond, because the Ge—Cl bond in the intermediate involves the anion of a stronger acid compared to the Ge—O bond. In other words, the digermoxane bond, like the disiloxane bond, is very inert in this process. As a result, the subsequent replacement of the chlorine atom by the triiodide ion becomes highly probable.

An alternative pathway of formation of complex **1** involves the transformation of the dichloride $(L^5)_2GeCl_2$

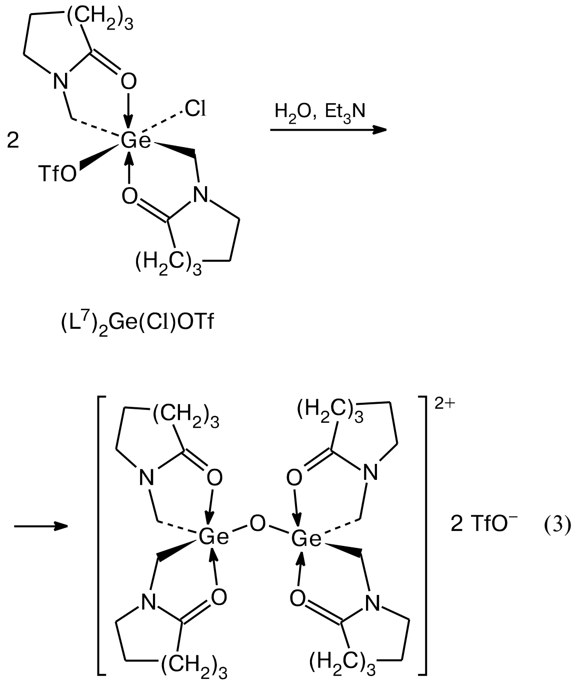

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Table 1. Bond lengths in the hypervalent fragments of the structures of **1**, **2**, and **4**

1a		**1b**		**2**		**4**	
Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
Ge(1)—O(1)	1.75(2)	Ge(3)—O(2)	1.77(2)	Ge(1)—O(1)	1.750(3)	Ge(1)—O(5)	1.752(3)
Ge(1)—O(11)	2.05(2)	Ge(3)—O(31)	2.06(2)	Ge(1)—O(2)	2.006(3)	Ge(1)—O(1)	2.048(3)
Ge(1)—O(12)	2.02(2)	Ge(3)—O(32)	2.03(2)	Ge(1)—O(3)	2.040(3)	Ge(1)—O(2)	2.017(3)
Ge(1)—C(11)	1.95(2)	Ge(3)—C(31)	1.95(2)	Ge(1)—C(1)	1.930(4)	Ge(1)—C(1)	1.959(5)
Ge(1)—C(16)	1.92(2)	Ge(3)—C(36)	1.94(3)	Ge(1)—C(8)	1.934(4)	Ge(1)—C(6)	1.937(5)
				Ge(1)...O(10)	3.539(5)	Ge(1)...O(13)	3.485(5)
Ge(2)—O(1)	1.74(2)	Ge(4)—O(2)	1.72(2)	Ge(2)—O(1)	1.751(3)	Ge(2)—O(5)	1.738(3)
Ge(2)—O(21)	2.06(2)	Ge(4)—O(41)	2.05(2)	Ge(2)—O(4)	2.060(3)	Ge(2)—O(3)	2.083(3)
Ge(2)—O(22)	2.02(2)	Ge(4)—O(42)	2.00(2)	Ge(2)—O(5)	1.993(3)	Ge(2)—O(4)	2.000(3)
Ge(2)—C(21)	1.99(2)	Ge(4)—C(41)	1.94(2)	Ge(2)—C(15)	1.941(4)	Ge(2)—C(11)	1.944(5)
Ge(2)—C(26)	1.93(2)	Ge(4)—C(46)	1.92(2)	Ge(2)—C(22)	1.931(4)	Ge(2)—C(16)	1.950(5)
Ge(2)...I(3)	4.438(5)	Ge(3)...I(4)	4.447(5)	Ge(2)...O(7)	3.553(5)		

into chloride iodide $(L^5)_2Ge(Cl)I$ and hydrolysis of the latter in the presence of a base (OH^-) to give digermoxane $[(L^5)_2Ge(Cl)]_2O$ followed by the replacement of the chlorine atom by the triiodide ion.

An additional experiment confirmed that the reaction can actually follow this pathway and that H_2O and a base are necessary for the synthesis of cation-anionic digermoxane complexes. Thus, treatment of chloride triflate $(L^7)_2Ge(Cl)OTf$ with water and triethylamine in chloroform led to the formal cleavage of the more covalent Ge—Cl bond giving rise to the digermoxane ditriflate complex $[(L^7)_2GeOGe(L^7)_2]^{2+}\cdot 2OTf^-$ (**2**).

Taking into account that the leaving group X in the *trans*-$(L^n)_2Ge(Cl)X$ complexes is easily replaced by a nucleophile, the most probable sequence of steps through which the reaction (3) proceeds to give the final product can be represented as follows:

$$2\ (L^7)_2Ge(Cl)OTf \xrightarrow[-2\ [Et_3NH][OTf]]{a)\ H_2O,\ Et_3N}$$

$$\longrightarrow [(L^7)_2Ge(Cl)]_2O \xrightarrow[-2\ [Et_3NH]Cl]{b)\ 2\ [Et_3NH][OTf]} \mathbf{2} \qquad (4)$$

Early, we have demonstrated[12b] an analogous exchange in the course of the transformation of the chloride triflate $(L^7)_2Ge(Cl)OTf$ to chloride iodide $(L^7)_2Ge(Cl)I$ under the action of lithium iodide.

We have synthesized perchlorate $(L^5)_2Ge(Cl)OClO_3$ (**3**)* for the first time by treating the dichloride $(L^5)_2GeCl_2$ with lithium perchlorate according to the general scheme of the transformation of *cis*-dichlorides $(L^n)_2GeCl_2$ into *trans*-monochlorides $(L^n)_2Ge(Cl)X$.[12] Prolonged storage of perchlorate **3** under conditions, which did not exclude exposure to atmospheric moisture, afforded a product, from which the corresponding digermoxane diperchlorate **4** was isolated by recrystallization.

$$\underset{\mathbf{3}}{2\ (L^5)_2Ge(Cl)OClO_3} \xrightarrow[-2\ HCl]{H_2O}$$

$$\longrightarrow \underset{\mathbf{4}}{[(L^5)_2GeOGe(L^5)_2]^{2+}2OClO_3^-} \qquad (5)$$

It should be emphasized that the complex formed in this reaction contains the anion of strong acid. This is additional evidence that the oxygen atom of the germoxane fragment plays a stabilizing role in the formation of the cation-anionic digermoxane complexes under consideration.

Unlike the reaction (3), the reaction of the pentacoordinate triflates and iodides LGeH(R)X (X = OTf or I; R = Ph or L), which contain one or two potential C,O-coordinating 8-methoxynaphthyl ligands L, with an excess of H_2O/Et_3N gave rise to digermoxanes $[LGeH(R)]_2O$ with tetracoordinate germanium atoms.[11a] Apparently, this result is a consequence of a weaker O→Ge coordination in derivatives with the 8-methoxynaphthyl ligand compared to the cation-anionic digermoxane complexes synthesized by us. In particular, only one of two such ligands and the oxygen atom of the triflate group are rather strongly coordinated to the germanium atom in the above-mentioned triflate $L_2Ge(H)OTf$. The O—Ge distances are 2.36, 2.80 (with the oxygen atom of the uncoordinated methoxy group), and 1.99 Å. By contrast, each germanium atom in ditriflate **2** is equally strongly bound to the coordinated oxygen atoms of both lactamomethyl ligands (1.99—2.06 Å, see below), whereas the distance to the nearest oxygen atom of the triflate anion is 3.54 Å.

X-ray diffraction study demonstrated that the dications in complexes **1**, **2**, and **4** are complete analogs of the above-mentioned disiloxane dications.[2,9a,b] The bond

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* The crystal structure of this perchlorate will be described elsewhere.

Table 2. Bond angles in the hypervalent fragments of the structures of **1**, **2**, and **4**

1a		**1b**		**2**		**4**	
Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
Ge(1)—O(1)—Ge(2)	130(1)	Ge(3)—O(2)—Ge(4)	130(1)	Ge(1)—O(1)—Ge(2)	133.0(2)	Ge(1)—O(5)—Ge(2)	134.2(2)
O(11)—Ge(1)—O(12)	170.9(6)	O(31)—Ge(3)—O(32)	172.5(6)	O(2)—Ge(1)—O(3)	170.5(1)	O(1)—Ge(1)—O(2)	173.1(1)
O(1)—Ge(1)—C(11)	116.6(8)	O(2)—Ge(3)—C(31)	115.2(10)	O(1)—Ge(1)—C(1)	111.4(2)	O(5)—Ge(1)—C(1)	116.4(2)
O(1)—Ge(1)—C(16)	118.0(8)	O(2)—Ge(3)—C(36)	120.5(7)	O(1)—Ge(1)—C(8)	118.3(2)	O(5)—Ge(1)—C(6)	111.7(2)
C(11)—Ge(1)—C(16)	125(1)	C(31)—Ge(3)—C(36)	124(1)	C(1)—Ge(1)—C(8)	130.0(2)	C(1)—Ge(1)—C(6)	131.9(2)
O(11)—Ge(1)—O(1)	95.8(7)	O(31)—Ge(3)—O(2)	94.1(7)	O(2)—Ge(1)—O(1)	97.06(12)	O(1)—Ge(1)—O(5)	96.0(2)
O(11)—Ge(1)—C(11)	83.5(10)	O(31)—Ge(3)—C(31)	83.7(9)	O(2)—Ge(1)—C(1)	84.62(15)	O(1)—Ge(1)—C(1)	84.0(2)
O(11)—Ge(1)—C(16)	92.0(9)	O(31)—Ge(3)—C(36)	93.3(9)	O(2)—Ge(1)—C(8)	93.86(15)	O(1)—Ge(1)—C(6)	92.2(2)
				O(1)—Ge(1)...O(10)	174.3(5)	O(5)—Ge(1)...O(13)	154.6(5)
O(21)—Ge(2)—O(22)	172.3(6)	O(41)—Ge(4)—O(42)	173.0(6)	O(4)—Ge(2)—O(5)	172.0(1)	O(3)—Ge(2)—O(4)	171.0(1)
O(1)—Ge(2)—C(21)	116.7(9)	O(2)—Ge(4)—C(41)	120.8(8)	O(1)—Ge(2)—C(15)	116.5(2)	O(5)—Ge(2)—C(11)	110.7(2)
O(1)—Ge(2)—C(26)	119.8(7)	O(2)—Ge(4)—C(46)	116.3(9)	O(1)—Ge(2)—C(22)	113.9(2)	O(5)—Ge(2)—C(16)	121.0(2)
C(21)—Ge(2)—C(26)	123.5(9)	C(41)—Ge(4)—C(46)	123(1)	C(15)—Ge(2)—C(22)	129.6(2)	C(11)—Ge(2)—C(16)	128.3(2)
O(21)—Ge(2)—O(1)	93.3(7)	O(41)—Ge(4)—O(2)	95.4(8)	O(4)—Ge(2)—O(1)	94.8(1)	O(3)—Ge(2)—O(5)	94.1(1)
O(21)—Ge(2)—C(21)	84.5(8)	O(41)—Ge(4)—C(41)	84(1)	O(4)—Ge(2)—C(15)	83.17(14)	O(3)—Ge(2)—C(11)	83.5(2)
O(21)—Ge(2)—C(26)	94.5(9)	O(41)—Ge(4)—C(46)	91(1)	O(4)—Ge(2)—C(22)	90.41(15)	O(3)—Ge(2)—C(16)	93.5(2)
O(1)—Ge(2)...I(3)	171.8(4)	O(2)—Ge(4)...I(4)	166.3(4)	O(1)—Ge(2)...O(7)	163.7(5)		

lengths and bond angles in the hypervalent fragments of the digermoxane dications are given in Tables 1 and 2, respectively. The three-dimensional structures of these complexes in the crystals are shown in Figs. 1—3.

A comparison of the structural parameters led us to some conclusions about the properties of the three-center linear hypervalent bond of the general type X—Ge—Y. In the complexes under consideration, the hypervalent fragments contain the symmetrical hypervalent O—Ge—O bond. These fragments are positively charged. In each cation—anion pair in the structure of **1**, the distances from one of the Ge atoms (Ge(2) or Ge(3)) to the nearest I atom of the anion are in the range of 4.44—4.45 Å (see Table 1), which is only slightly larger than the sum of the van der Waals radii of these atoms (4.2 Å).[14] On the whole, the structure of one-half of dication **1**, *viz*., —OGe$(L^5)_2$, with the adjacent I_3^- anion is very similar to the structure of the $[ClGe(L^7)_2]^+I_3^-$ complex studied by us earlier.[13] In the latter complex, the corresponding Ge...I distance is 4.195(1) Å. An analogous structural similarity was observed for complexes **2** and **4** and chloride triflates $[(L^n)_2Ge(Cl)]^+OTf^-$.[12] In the latter compounds, the

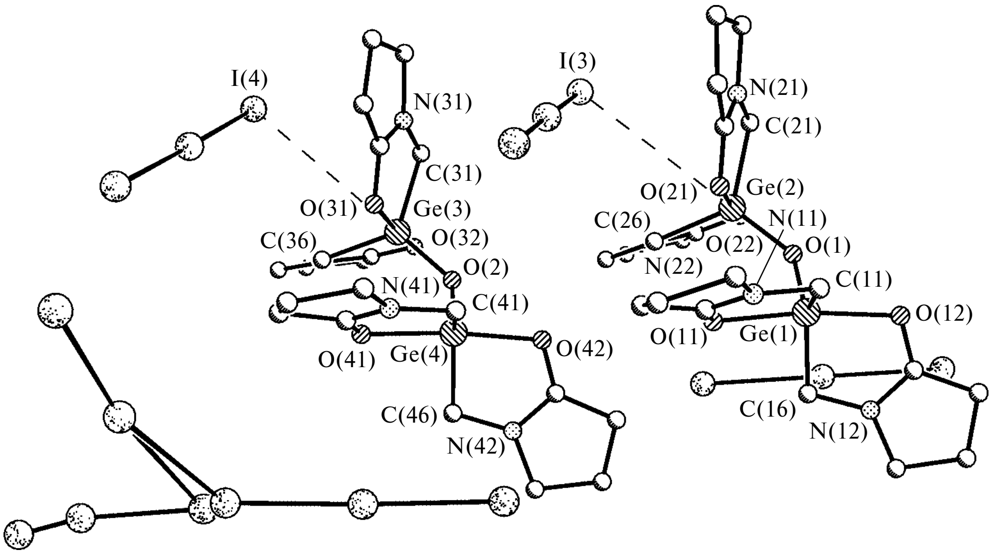

Fig. 1. Crystallographically independent cation-anionic complexes **1** in the crystal. Only atoms coordinated to the hypervalent Ge atoms are shown. The H atoms are omitted. The occupancies of the positions of the iodine atoms in the disordered anion vary from 0.25 to 0.7.

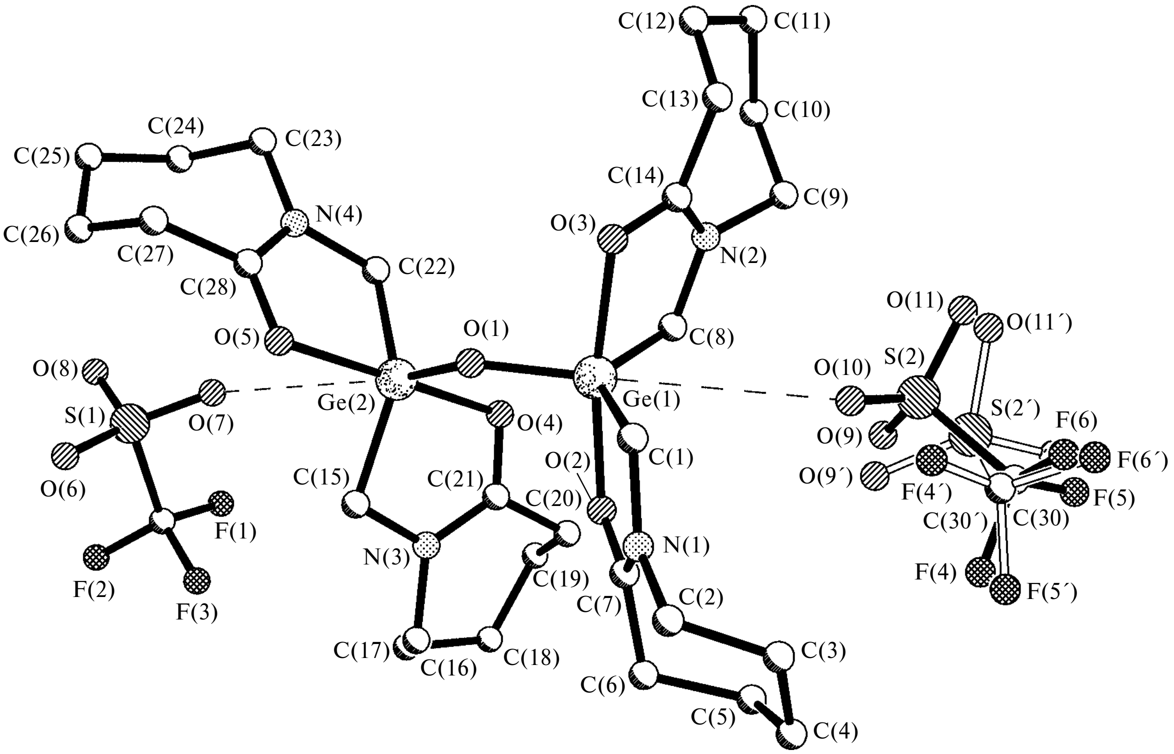

Fig. 2. Molecular structure of complex **2** in the crystal. The H atoms are omitted. Two possible orientations of one of the anions with the occupancies of 0.7 and 0.3 are presented.

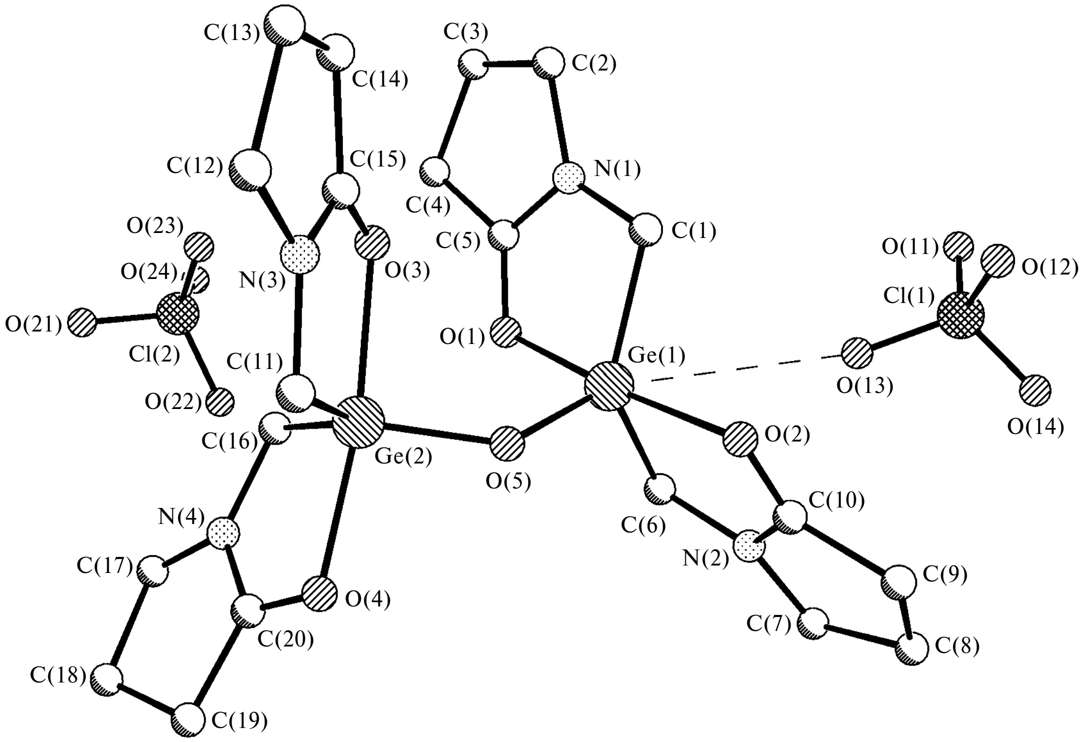

Fig. 3. Molecular structure of complex **4** in the crystal. The H atoms are omitted.

distances between the Ge atoms of the cations and the O atoms of the OTf$^-$ anions are in the range of 3.02—3.36 Å (the sum of the van der Waals radii of the Ge and O atoms is 3.5 Å [14]). In complexes **2** and **4**, the Ge...O(Tf) and Ge...O(ClO$_3$) distances are in the range of 3.49—3.55 Å. This is indirect evidence in favor of our earlier assumption[12b,13] that weak X$^-$→Ge coordination (X = OTf, I$_3$, or OClO$_3$) occurs in such structures. The more "rigid" Ge—O bond (compared to the Ge—Cl bond) in the digermoxane fragment is responsible also for a weakening of the *trans*-arranged Ge...X bond, *i.e.*, for the longer Ge...X distances in complexes **1**, **2**, and **4**, in which, nevertheless, weak coordination interactions should persist.

This conclusion was also confirmed by analysis of the bond angles at the hypercoordinated Ge atoms. Strengthening of the X$^-$→Ge coordination interaction is accompanied by "opening" of the coordination polyhedron of the Ge atom toward the ligand X, *i.e.*, by an increase in the solid angle Ω formed by the directions of the bonds between the Ge atom and the ligands in the *cis* positions with respect to X.[15] In the complexes under consideration, these are two O—Ge bonds and two C—Ge bonds, the first two bonds being involved in the nearly linear symmetrical hypervalent O—Ge—O bond. Therefore, the angle Ω can in fact be increased only due to an increase in the C—Ge—C bond angle. This is actually observed by comparing the hypervalent fragments in which an additional (sixth) coordination bond of the Ge atoms is either present or absent. In the structures of **1** and **4**, the above-mentioned weak coordination is observed only for one Ge atom of the two atoms present in each cation. By contrast, all germanium atoms in the structure of **2** have a coordination number of (5 + 1). It is particularly correct to compare the geometry of the hypervalent fragments present in the same structure (**1** and **4**) because in this case the differences between the intra- and intermolecular steric interactions, which have a strong effect on weak coordination bonds, are of much less importance. In the structure of **2**, the C—Ge—C bond angles at both Ge atoms are equal to within the experimental error (130.0(2) and 129.6(2)°; see Table 2). In the structure of **4**, these angles are 131.9(2) and 128.3(2)° in the presence and absence of the Ge←O(ClO$_3$) interaction, respectively, *i.e.*, this angle is noticeably smaller in the latter case. For complex **1**, the above-mentioned effect is masked by a low accuracy of determination of the crystal structure due to the presence of a large number of strongly absorbing iodine atoms and their disorder.

The hypervalent O—Ge—O bonds in the dications in the complexes under consideration are symmetrical from the chemical standpoint. However, the O—Ge distances are somewhat different for different Ge atoms. In the structure of **4**, this difference is as large as 0.08 Å. In the more accurate structures of **2** and **4**, these differences are also significant (vary from 10 to 25σ). This asymmetry is typical of both germanium-containing cations[12b] and silicon-containing dications[2,9a,b] of this class. This effect is not observed only in the crystal structures in which the hypervalent atom is located on a twofold axis.[13,16] It is not inconceivable that in the latter case, the crystallographic symmetry masks an insignificant difference in the lengths of the components of the hypervalent bond, which corresponds to the conformational energy minimum of the molecule (cation). This distortion of the symmetry is not associated with the properties of the hypervalent bond as such because the deviation of the Ge atom from the plane of the equatorial substituents does not correlate with the O—Ge distances. Actually, if this correlation were true, the hypervalent atom M would deviate from the above-mentioned plane toward the shorter component of the hypervalent X—M—X fragment.[17] However, small deviations of the Ge atoms from this plane in the dications of complexes **1**, **2**, and **4** occur toward either the shorter component of the hypervalent bond (Ge(1) and Ge(4) atoms in the structure of **1** and both Ge atoms in the structure of **2**) or the longer component (Ge(2) and Ge(3) atoms in the structure of **1** and both Ge atoms in the structure of **4**).

It is known[9a,b] that the (L$_2$SiOSiL$_2$)$^{2+}$ dications can occur as different diastereomers due to chirality of the hypervalent fragment. Unlike their silicon analogs, all the germanium dications under consideration are formed as diastereomers of one type because the bischelate systems involved in these dications differ in chirality (ΛΔ type according to the accepted notations[18]). The O—Ge...Ge—O pseudotorsion angles determining the relative rotation of the bischelate systems are in the range of 55—65°, like in analogous silylium dications. By contrast, the Ge—O—Ge angle is somewhat smaller (130—134°) than the Si—O—Si angle in the silicon analogs (~145°).

Although compounds **1**, **2**, and **4** crystallize in different space groups, the packing of the complexes in all crystal structures is characterized by the presence of channels extended along one of the crystallographic axes (Figs. 4 and 5). These channels are occupied by the anions. The transverse sizes of the channels in the structures of **1** and **2** allow for disorder of the anions. In the crystal of **2** (for strong disorder of the anions in the structure of **1**, see the Experimental section), one of the OTf$^-$ anions is disordered over two positions with the occupancies of 0.7 and 0.3 (see Fig. 2). Presumably, this disorder is favored by different orientations of the seven-membered lactam rings at the Ge(1) atom with respect to the planes of the chelate rings. The folding of the second lactam ring along the C(9)...C(13) line away from the triflate anion increases the cross-section of the channel occupied by this anion and crystallographically equivalent anions.

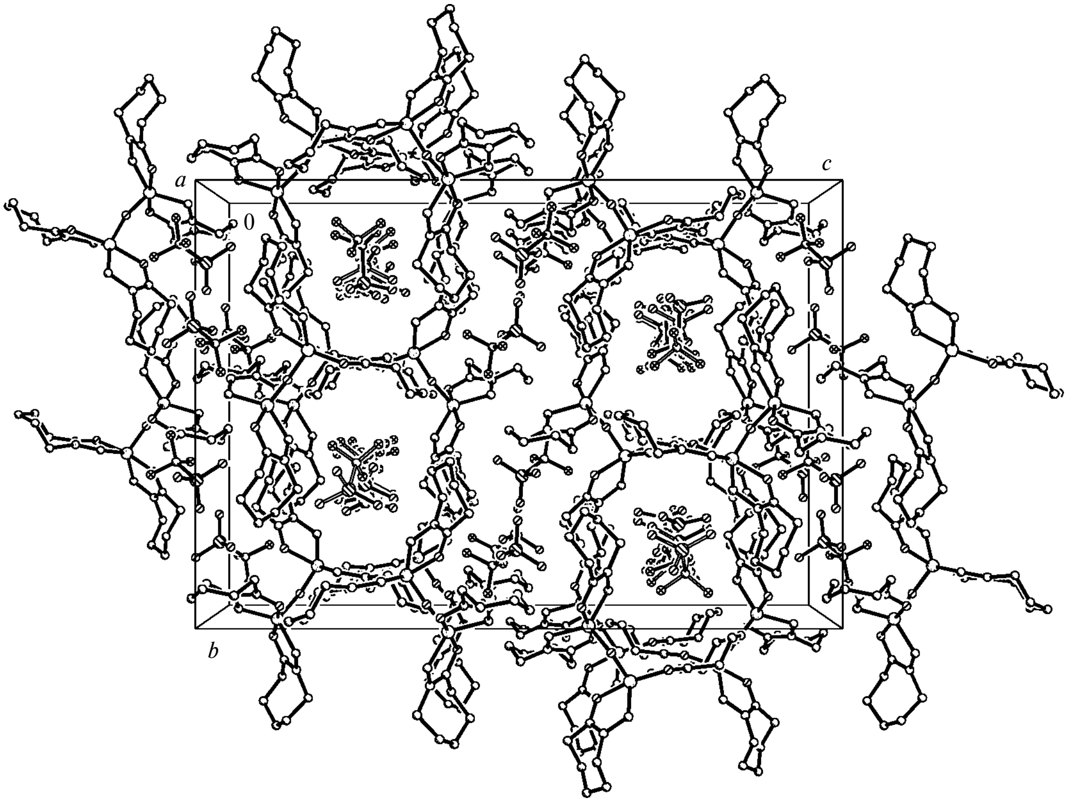

Fig. 4. Crystal structure of **1** projected along the direction of the channels containing the disordered anions.

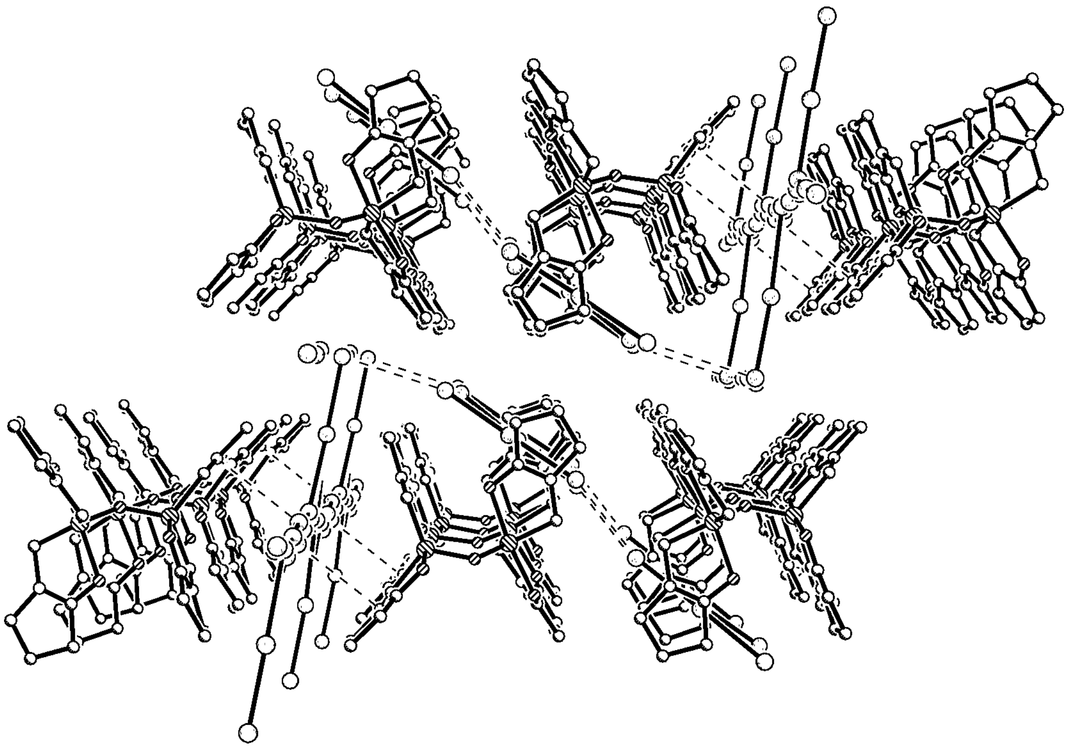

Fig. 5. Crystal structure of **2** projected along the axis *a*.

Experimental

The IR spectra of ~5% solutions of the compounds were recorded on a Specord IR-75 instrument in cells with KBr windows. The ^{1}H and ^{13}C NMR spectra were measured on a Varian XL-400 spectrometer (400.1 and 100.6 MHz, respectively) with Me_4Si as the internal standard.

The starting bis(lactamomethyl)dichlorogermanes[19] and bis[(2-oxoperhydroazepinyl)methyl]chlorotrifluoromethanesulfonylgermane[12a] were synthesized according to procedures described earlier.

1,1,3,3-Tetrakis(O—Ge)chelato-1,1,3,3-tetra[1-(2-oxopyrrolidinyl)methyl]digermoxane di(triiodide) (1). A solution of bis(2-oxopyrrolidinomethyl)dichlorogermane (1.0 g, 3 mmol) and $LiI \cdot H_2O$ (7.5 g, 50 mmol) in MeCN (20 mL) was refluxed for 4 h. Then the reaction mixture was concentrated to dryness *in vacuo* and the residue was extracted with *o*-xylene (3×15 mL). The solvent was distilled off *in vacuo* to prepare compound **1** in a yield of 0.9 g (47%), m.p. 180—182 °C (dioxane—MeCN, 10 : 1). IR ($CHCl_3$), ν/cm^{-1}: 1580 (s), 1500 (w). Found (%): C, 18.80; H, 2.54; N, 4.16. $C_{20}H_{32}Ge_2I_6N_4O_5$. Calculated (%): C, 18.26; H, 2.45; N, 4.26.

1,1,3,3-Tetrakis(O—Ge)chelato-1,1,3,3-tetra[(2-oxoperhydroazepinyl)methyl]-1,3-digermoxane di(triflate) (2). A solution of bis[(2-oxoperhydroazepinyl)methyl]chlorotrifluoromethanesulfonylgermane (0.6 g, 0.001 mol), water (0.018 g, 0.001 mol), and Et_3N (0.101 g, 0.001 mol) in $CHCl_3$ (10 mL) was stirred at ~20 °C for 24 h and then water (2 mL) was added. The organic layer was separated and the water layer was extracted with chloroform (2×4 mL). The combined organic layers were dried over $CaCl_2$ and the solvent was distilled off. The residue was triturated with heptane (5 mL) to prepare complex **2** in a yield of 0.5 g (47%), m.p. 198—200 °C (THF—CH_3CN, 20 : 1). IR ($CHCl_3$), ν/cm^{-1}: 1617, 1500. ^{1}H NMR ($CDCl_3$), δ: 1.60 (m, 8 H, H(4)); 1.67 (m, 8 H, H(5)); 1.94 (m, 8 H, H(6)); 2.68 (m, 8 H, H(3)); 3.02 and 3.58 (d, 8 H, $GeCH_2$, $^2J_{H,H}$ = 13.8 Hz); 3.64—3.80 (m, 8 H, H(7)). ^{13}C NMR ($CDCl_3$), δ: 29.36 (C(3)); 22.01 (C(4)); 25.53 (C(5)); 33.14 (C(6)); 52.59 (C(7)); 40.99 (NCH_2); 182.03 (C=O). Found (%): C, 37.64; H, 5.27; N, 5.56. $C_{30}H_{48}F_6Ge_2N_4S_2O_{11}$. Calculated (%): C, 37.37; H, 5.018; N, 5.81.

1,1,3,3-Tetrakis(O—Ge)chelato-1,1,3,3-tetra[1-(2-oxopyrrolidinyl)methyl]digermoxane di(perchlorate) (4). A solution of bis(2-oxopyrrolidonomethyl)dichlorogermane (1.53 g, 4.5 mmol) and $LiClO_4 \cdot 3H_2O$ (7.1 g, 20 mmol) in MeCN (15 mL) was refluxed for 1 h. Then the solution was concentrated to 1/3 of the initial volume and extracted with hot toluene (4×12 mL). The solvent was distilled off *in vacuo* to prepare crude (O—Ge)-bischelate bis[1-(2-oxopyrrolidinyl)methyl]chlorogermanium perchlorate (**3**) in a yield of 0.8 g (44%), m.p. 207—208 °C (toluene), t.decomp. 255—257 °C. IR ($CHCl_3$), ν/cm^{-1}: 1615 (s), 1510 (m). ^{1}H NMR ($CDCl_3$), δ: 2.23 (m, 4 H, CCH_2C); 2.72 (t, 4 H, $COCH_2$); 3.20, 3.70 (dd, 4 H, $GeCH_2$); 3.85 (t, 4 H, NCH_2). A solution of compound **3** (0.3 g, 1 mmol) in a 20 : 1 toluene—MeCN mixture (20 mL) was stored under conditions, which did not exclude exposure to atmospheric mois-

Table 3. Principal details of X-ray diffraction study and crystallographic characteristics of compounds **1**, **2**, and **4**

Compound	1	2	4
Molecular formula	$C_{40}H_{64}N_8O_{10}Ge_4I_{12}$	$C_{30}H_{48}F_6Ge_2N_4O_{11}S_2$	$C_{20}H_{32}Cl_2Ge_2N_4O_{13}$
T/K	190	110	163
a/Å	13.707(2)	12.743(2)	11.562(3)
b/Å	15.224(3)	20.732(4)	14.611(4)
c/Å	21.408(4)	29.834(5)	17.481(9)
α/deg	92.31(2)	90	90
β/deg	108.38(2)	90	106.82(5)
γ/deg	116.50(2)	90	90
V/Å^3	3707(4)	7882(2)	2827(2)
d_{calc}/g cm^{-3}	2.356	1.625	1.768
Space group,	$P\bar{1}$	*Pbca*	$P2_1/n$
Z	2	8	4
Diffractometer	Syntex $P2_1$	Siemens Smart PLATFORM	Syntex $P2_1$
Radiation	Mo-Kα	Mo-Kα	Mo-Kα
$2\theta_{max}$/deg	48	60	50
Scanning technique	θ/2θ	ω/2θ	θ/2θ
Number of measured reflections	9574	62001	4947
Number of reflections in least-squares	5528	11442	4687
Number of parameters in least-squares	712	568	498
Absorption coefficient/cm^{-1}	67.23	17.20	23.87
$R_1(I > 2\sigma(I))$	0.071[a]	0.059	0.048
wR_2 (for all reflections)	0.071[b]	0.122	0.130

[a] $I > 3\sigma$ for **1**.

[b] R_w for **1**.

ture, for 18 months, after which compound **4** was obtained as colorless single crystals in a yield of 0.1 g (27%).

Single crystals suitable for X-ray diffraction study were prepared by recrystallization of **1** from a 10 : 1 dioxane—MeCN mixture, recrystallization of compound **2** from THF, and recrystallization of compounds **3** and **4** from a 20 : 1 toluene—MeCN mixture.

X-ray diffraction study of compounds 1—4. The crystallographic parameters and the main characteristics of X-ray diffraction experiments for compounds **1**, **2**, and **4** are given in Table 3. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The H atoms in the structures of **1** and **4** were placed in calculated positions and refined using the riding model with fixed thermal parameters $U = 0.04$ Å^2 for **1** and $U = 1.2U_C$ for **4** (U_C is the equivalent thermal parameter of the corresponding carbon atom). The positions of the H atoms in the structure of **2** were revealed from a difference electron density synthesis and refined isotropically. For the structure of **1**, the absorption correction was applied using the DIFABS program.[20] The unit cell of the crystal of **1** contains two independent formula units. In the case of **1**, the structure solution and refinement revealed strong disorder of one of the four anions. The corresponding electron density peaks form a T-shaped configuration (see Fig. 1) in the vicinity of the crystallographic inversion centers. These peaks were refined as iodine atoms with reasonable thermal parameters only assuming the occupancies of 0.25—0.7. On the whole, the scattering centers in the crystal structure occupy channels, which are extended along the axis *b* and have branches. The distances between these centers (2.8—3.0 Å) correspond to the standard I—I bond length in the anions. The shape of the channels (see Fig. 4, the branches are located in a single plane perpendicular to the direction of the channels) and the arrangement of the possible positions of the I atoms in these channels indicate that a part of the crystallographic positions are occupied by the I_5^- anions with an angular structure. However, it is difficult to construct an unambiguous model taking into account also substantial dynamic disorder (thermal vibrations). Hence, the best reproducible intense electron density peaks in the above-mentioned channels in the structure of **1** were formally refined as I atoms with anisotropic thermal parameters and occupancies lower than unity with the aim of reducing the *R* factor and errors of the determination of the geometric parameters for the ordered portion of the structure to reasonable values.

In the course of refinement of the structure of **2**, the disorder of one of the anions over two positions with different orientations of the axes was revealed (see Fig. 2). The occupancies of these positions were taken equal to 0.7 and 0.3 (weak O→Ge coordination was observed in a more probable orientation). In this case, the thermal parameters of the atoms are characterized by minimum differences for two possible positions of the anion.

All calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS program package (versions 4.0 and 5.0).[21,22] The bond lengths and bond angles in the hypervalent fragments in the structures of **1**, **2**, and **4** are given in Tables 1 and 2, respectively. All other geometric parameters and atomic coordinates were deposited with the Cambridge Structural Database.[23]

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