The structure of organic derivatives of hexacoordinated germanium. (O→Ge) chelated bis(2-oxo-1-hexahydroazepinylmethyl)chlorogermane iodide and bis-(2-oxo-1-hexahydroazepinylmethyl)chlorogermane triiodide

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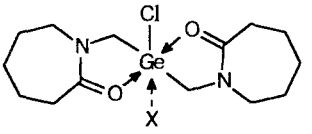
An X-ray structural study of the iodide and triiodide of bis-(2-oxo-1-hexahydroazepinylmethyl)chlorogermane (**1** and **2**, respectively; R = 0.033 and 0.031 on 3276 and 3093 reflections, respectively) attests to the essentially ionic structure of both compounds with weak I→Ge coordination: the I...Ge distances are 4.181(1)—4.219(2) Å, the Cl—Ge...I angles are 171.6(1)—180°, the coordination polyhedron of the Ge atom is a distorted trigonal bipyramid (without regard for the iodide ligands). A comparison of structures **1** and **2**, and other derivatives of penta- and hexacoordinated Ge shows that in certain cases, the electronic system of this atom with its coordination environment may be considered as containing a combination of two weakly interacting hypervalent X—Ge—X' moieties.

Key words: organic derivatives of hexacoordinated germanium; hypervalent bonds; solid angle Ω as a characteristic of a hypervalent fragment; simulation of pathways of S_N—Ge^V reactions.

Organic derivatives of hexacoordinated germanium, which we have systematically studied in recent years,[1—3] are of interest in two aspects. On the one hand, the Ge atom in these compounds exhibits mostly "metallic" properties and the structure of its coordination environment may be compared with that of transition and nontransition metals in analogous complexes. On the other hand, by analogy with compounds of pentacoordinated Si and Ge,[4,5] (5+1) and (4+2) type hexacoordinated structures (*i.e.*, with one or two bonds relatively lengthened) may be regarded as models of transition states of a pentacoordinated atom in nucleophilic substitution reactions. It is clear that to simulate the whole reaction, a series of structures with gradual variation of the coordination of the Ge atom from a trigonal bipyramid (TBP) to an octahedron are required. No such series has been obtained yet. In this work we present the results of an X-ray structural study of (O→Ge)-chelate bis(2-oxo-1-hexahydroazepinylmethyl)-chlorogermane iodide (**1**) and bis(2-oxo-1-hexahydroazepinylmethyl)chlorogermane triiodide (**2**), which as a whole have ionic structures with weak additional I→Ge coordination.



1: X = I
2: X = I_3

Experimental

The X-ray diffraction experiment for compounds **1** and **2** was carried out on a Syntex $P2_1$ diffractometer at 190 K (λMo-$K\alpha$, graphite monochromator, θ/2θ-scanning, $2\theta_{max}$ = 50°).

Crystals of **1** are orthorhombic, a = 28.961(2), b = 11.121(3), c = 22.041(4) Å, V = 7099(3) Å^3, d_{calc} = 1.824 g cm^{-3}, Z = 16 ($C_{14}H_{24}ClGeIN_2O_2$), space group *Pccn* (there are three crystallographically independent molecules in a cell; one of them is in a general position, the two others are on the 2 axes). The structure was solved by the direct method and refined by the block-diagonal least-squares method in the anisotropic approximation for nonhydrogen atoms. The H atoms were located in a difference synthesis and were included in the refinement with fixed C—H distances and isotropic thermal parameters U = 0.05 Å^2. The correction for absorption

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Table 1. The coordinates of nonhydrogen atoms in structure **1** ($\times 10^4$) and their equivalent isotropic thermal parameters ($Å^2 \times 10^3$)

Atom	x	y	z	U_{eq}
I(1a)[a]	7500	2500	7957.5(3)	34.3(2)
Ge(1a)[a]	7500	2500	6045.2(5)	19.0(3)
Cl(1a)[a]	7500	2500	5057(1)	26.1(8)
O(1a)	6815(2)	2723(4)	6112(2)	23(2)
N(1a)	6879(2)	842(5)	6463(2)	16(2)
C(1a)	7369(2)	922(7)	6385(3)	24(2)
C(2a)	6683(3)	−291(7)	6711(3)	26(2)
C(3a)	6488(2)	−151(7)	7352(3)	26(2)
C(4a)	6015(2)	403(7)	7362(3)	29(2)
C(5a)	5989(3)	1678(7)	7124(3)	27(2)
C(6a)	6118(2)	1838(7)	6460(3)	25(2)
C(7a)	6619(2)	1793(7)	6334(3)	21(2)
I(1b)[a]	7500	−2500	10468.4(3)	34.9(3)
Ge(1b)[a]	7500	−2500	8554.3(5)	19.8(3)
Cl(1b)[a]	7500	−2500	7564(1)	27.6(8)
O(1b)	6815(1)	−2299(4)	8638(2)	23(1)
N(1b)	6888(2)	−4167(5)	8991(2)	19(2)
C(1b)	7380(2)	−4101(7)	8869(3)	23(2)
C(2b)	6703(2)	−5297(7)	9247(3)	26(2)
C(3b)	6553(3)	−5197(7)	9903(3)	30(3)
C(4b)	6091(3)	−4580(8)	9985(3)	34(3)
C(5b)	6064(2)	−3308(7)	9750(3)	26(2)
C(6b)	6139(2)	−3191(7)	9062(3)	23(2)
C(7b)	6625(2)	−3228(7)	8882(3)	21(2)
I(1c)	5070.2(1)	−1017.7(5)	8620.7(2)	30.4(1)
Ge(1c)	5009.1(2)	2726.5(6)	8772.6(3)	20.9(2)
Cl(1c)	4999.9(6)	4713(2)	8842.3(8)	30.5(5)
O(1c)	4328(1)	2537(5)	8912(2)	23(1)
O(2c)	5692(1)	2624(4)	8625(2)	23(1)
N(1c)	4377(2)	1910(5)	7945(2)	20(2)
N(2c)	5658(2)	1815(6)	9548(2)	21(2)
C(1c)	4871(2)	2159(6)	7962(3)	24(2)
C(2c)	4174(3)	1419(6)	7378(3)	28(2)
C(3c)	4014(3)	131(7)	7433(4)	36(3)
C(4c)	3553(3)	−2(7)	7735(3)	33(3)
C(5c)	3546(3)	437(7)	8393(4)	33(3)
C(6c)	3634(2)	1785(7)	8458(3)	24(2)
C(7c)	4134(2)	2096(6)	8439(3)	18(2)
C(8c)	5155(2)	1979(7)	9542(3)	29(2)
C(9c)	5865(2)	1219(7)	10084(3)	28(2)
C(10c)	6031(3)	−55(7)	9964(4)	27(2)
C(11c)	6499(3)	−85(7)	9648(3)	29(2)
C(12c)	6490(3)	482(7)	9017(3)	28(2)
C(13c)	6396(2)	1826(6)	9009(3)	21(2)
C(14c)	5898(2)	2114(6)	9067(3)	20(2)

[a]The atom in a partial symmetry position on axis 2.

Table 2. The coordinates of atoms in structure **2** ($\times 10^4$, $\times 10^3$ for H atoms) and their equivalent isotropic (isotropic) thermal parameters ($\times 10^3$ Å^2, $\times 10^4$ Å^2 for H atoms)

Atom	x	y	z	U_{eq} (U_{iso})
I(1)	1143.6(5)	3654.4(5)	7664.5(2)	58.7(2)
I(2)	1789.7(4)	3469.1(4)	6452.1(2)	37.1(1)
I(3)	2475.1(5)	3405.3(3)	5236.0(2)	41.2(2)
Ge(1)	5561.3(6)	3626.4(5)	8309.3(3)	26.0(2)
Cl(1)	7768(2)	3834(1)	8727.8(7)	41.0(5)
O(1)	4752(4)	4753(3)	8880(2)	32(1)
O(2)	5969(4)	2447(3)	7668(2)	34(1)
N(1)	3955(5)	2860(4)	9152(2)	27(1)
N(2)	5596(5)	4259(4)	7142(2)	26(1)
C(1)	4575(6)	2285(5)	8669(3)	30(2)
C(2)	3200(7)	2032(6)	9524(3)	35(2)
C(3)	1578(6)	2220(6)	9426(3)	35(2)
C(4)	1090(6)	3415(6)	9727(3)	37(2)
C(5)	1644(6)	4659(6)	9513(3)	37(2)
C(6)	3295(6)	4777(6)	9652(3)	32(2)
C(7)	4038(5)	4111(5)	9212(3)	28(2)
C(8)	5184(7)	4857(5)	7671(3)	30(2)
C(9)	5578(7)	5032(5)	6598(3)	34(2)
C(10)	7037(7)	5127(6)	6396(3)	37(2)
C(11)	7429(7)	3970(6)	6061(3)	41(2)
C(12)	7591(6)	2742(6)	6416(3)	33(2)
C(13)	6211(6)	2314(5)	6637(3)	35(2)
C(14)	5918(5)	3031(5)	7163(3)	28(2)
H(11)	535(7)	163(5)	892(3)	4(2)
H(12)	376(6)	178(5)	834(3)	2(1)
H(21)	369(6)	219(6)	995(3)	4(2)
H(22)	344(5)	122(5)	950(2)	1(1)
H(31)	103(9)	143(8)	956(4)	8(3)
H(32)	136(6)	223(6)	899(3)	4(2)
H(41)	165(6)	340(5)	1023(3)	4(2)
H(42)	−3(7)	338(5)	974(3)	4(2)
H(51)	129(5)	527(5)	974(2)	1(1)
H(52)	161(8)	489(7)	906(4)	7(2)
H(61)	366(6)	448(5)	1003(3)	2(1)
H(62)	338(6)	581(6)	961(3)	3(1)
H(81)	571(6)	560(6)	778(2)	2(1)
H(82)	405(8)	505(7)	756(3)	6(2)
H(91)	542(6)	597(6)	674(2)	3(1)
H(92)	484(6)	462(6)	633(3)	3(1)
H(101)	773(5)	524(4)	673(2)	1(1)
H(102)	691(5)	581(5)	614(2)	1(1)
H(111)	844(8)	413(7)	591(3)	6(2)
H(112)	675(5)	387(4)	570(2)	1(1)
H(121)	832(8)	265(7)	680(3)	6(2)
H(122)	797(6)	204(6)	617(3)	3(1)
H(131)	618(5)	135(5)	674(2)	1(1)
H(132)	514(5)	246(5)	632(2)	2(1)

(μ = 35.8 cm^{-1}) was taken into account by the DIFABS program.[6] The final discrepancy factors: $R = 0.033$, $R_w = 0.036$ on 3276 reflections with $I > 3\sigma(I)$.

Crystals of **2** are monoclinic, $a = 9.436(2)$, $b = 10.468(2)$, $c = 22.666(5)$ Å, $\beta = 99.03(2)°$, $V = 2211(1)$ Å^3, $d_{calc} = 2.226$ g cm^{-3}, $Z = 4$ ($C_{14}H_{24}ClGeI_3N_2O_2$), space group $P2_1/n$. The structure was solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms and in the isotropic approximation for the H atoms located in the difference synthesis. The correction for absorption (μ = 54.6 cm^{-1}) was taken into account by the DIFABS program.[6] The final discrepancy factors: $R = 0.031$, $R_w = 0.036$ on 3093 reflections with $I > 3\sigma(I)$.

The coordinates and thermal parameters of the atoms in structures **1** and **2** are given in Tables 1 and 2. The calculations were carried out on an IBM PC/AT computer by SHELXTL PLUS programs.[7]

Results and Discussion

A virtually ionic structure of the compounds **1** and **2** (Figs 1 and 2) is indicated by the fact that the shortest I...Ge distances equal 4.181(1)—4.219(2) Å (Tables 3 and 4), which is close to the sum of the van der Waals radii of these atoms (4.0—4.2 Å, according to various estimations[8]). However, the ionic character of the bonding does not mean that there is no covalent component. In fact, even in such an ionic crystal as KI, the degree of the ionic character of the bonds (determined from the effective charges on the atoms) is only ~70 %.[8] The complete transfer of the electrons of a bond to the anion apparently occurs only when the cation-anion distance noticeably exceeds the sum of their radii, which occurs, for example, in the case when the bond is shielded by other atoms. Thus, the Ge atoms in compounds **1** and **2** may be considered to be (5+1)-hexacoordinated.

The I→Ge interaction is manifested as a distortion of the coordination polyhedron of the Ge atom, which is a TBP with the O atoms in axial positions and the C and Cl atoms in equatorial positions. Additional coordination by the I atom occurs in the equatorial plane of the TBP, so that the CGeC angles are increased by 15—19° with respect to the ideal value (120°), and the ClGeC angles are correspondingly decreased (Fig. 1, Tables 5 and 6). A similar "opening" of the coordination polyhedron (tetrahedron) in the direction of a "readily leaving" group has already been observed in the structures of (4+1)-pentacoordinated derivatives of Si and Ge. This deformation has been described by the corresponding decrease (Δ) of the deviation of the central atom from the plane of the three equatorial substituents.[4] However, in the case of (5+1)-hexacoordination such as a simple parameter is not applicable. We suggest that the distortion of the coordination polyhedron of the hypervalent fragment be characterized by the deviation ($\Delta\Omega$) of the solid angle (Ω), which is formed by the directions of the equatorial valent bonds (in the octahedron or TBP) and encloses the "leaving" axial substituent, from the ideal value ($\Omega_0 = 2\pi$). In the case of (4+1)-pentacoordination, an additional interaction would alter $\Delta\Omega = \Omega_0 - \Omega$ from $2\pi - \pi = \pi$ (an ideal tetrahedron, no additional interaction) to 0 (an ideal TBP). In the case of (5+1)-hexacoordination, an additional interaction would alter $\Delta\Omega = \Omega_0 - \Omega$ from $2\pi - \frac{4}{3}\pi = \frac{2}{3}\pi$ (an ideal TBP, no additional interaction) to 0 (an ideal octahedron). These values for the I→Ge bond in structures **1** and **2** lie within a narrow interval, 0.57π—0.59π, which is noticeably less than the ideal value (0.67π) for an initial undistorted TBP.

Table 3. The main bond lengths in structure **1**

Bond	*d*/Å	Bond	*d*/Å
Ion pair **1a**		Ion pair **1b**	
Ge(1a)...I(1a)	4.215(2)	Ge(1b)...I(1b)	4.219(2)
Ge(1a)—Cl(1a)	2.178(3)	Ge(1b)—Cl(1b)	2.182(3)
Ge(1a)—O(1a)	2.006(4)	Ge(1b)—O(1b)	2.006(4)
Ge(1a)—C(1a)	1.946(8)	Ge(1b)—C(1b)	1.942(8)
O(1a)—C(7a)	1.277(9)	O(1b)—C(7b)	1.289(9)
N(1a)—C(1a)	1.432(8)	N(1b)—C(1b)	1.454(8)
N(1a)—C(7a)	1.328(9)	N(1b)—C(7b)	1.314(9)
Ion pair **1c**			
Ge(1c)...I(1c)	4.181(1)	O(1c)—C(7c)	1.284(8)
Ge(1c)—Cl(1c)	2.215(2)	O(2c)—C(14c)	1.275(8)
Ge(1c)—O(1c)	2.006(4)	N(1c)—C(1c)	1.456(8)
Ge(1c)—O(2c)	2.006(4)	N(1c)—C(7c)	1.312(8)
Ge(1c)—C(1c)	1.937(6)	N(2c)—C(8c)	1.468(8)
Ge(1c)—C(8c)	1.935(7)	N(2c)—C(14c)	1.312(8)

Table 4. Bond lengths in structure **2**

Bond	*d*/Å	Bond	*d*/Å
I(1)—I(2)	2.913(1)	N(2)—C(8)	1.458(8)
I(2)—I(3)	2.929(1)	N(2)—C(9)	1.472(7)
Ge(1)...I(1)	4.195(1)	N(2)—C(14)	1.321(7)
Ge(1)—Cl(1)	2.160(2)	C(2)—C(3)	1.524(8)
Ge(1)—O(1)	1.990(4)	C(3)—C(4)	1.531(9)
Ge(1)—O(2)	1.991(4)	C(4)—C(5)	1.511(9)
Ge(1)—C(1)	1.934(6)	C(5)—C(6)	1.545(8)
Ge(1)—C(8)	1.929(6)	C(6)—C(7)	1.480(9)
O(1)—C(7)	1.276(7)	C(9)—C(10)	1.521(9)
O(2)—C(14)	1.292(7)	C(10)—C(11)	1.507(9)
N(1)—C(1)	1.449(8)	C(11)—C(12)	1.512(9)
N(1)—C(2)	1.470(8)	C(12)—C(13)	1.534(9)
N(1)—C(7)	1.318(7)	C(13)—C(14)	1.472(8)

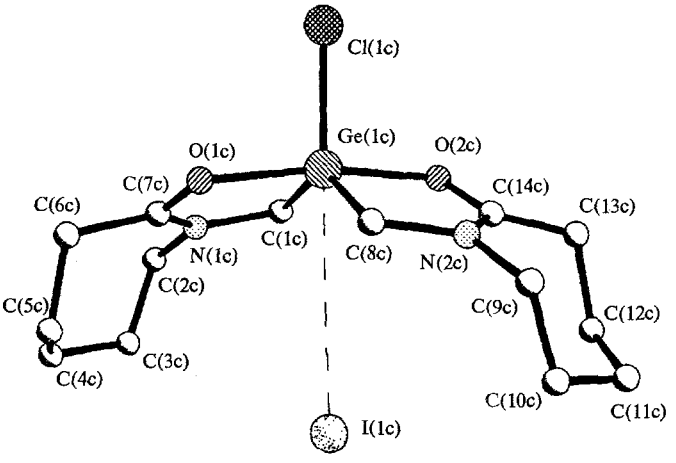


Fig. 1. The general view of one of the symmetrically independent cation-anion pairs **1c** in the crystal of **1**. The **1a** and **1b** pairs located on crystallographic 2 axes have the same configuration. The numbering of the atoms in the symmetrically independent halves of the **1a** and **1b** pairs correspond to that shown for the left half of the **1c** pair.

Table 5. The main bond angles in structure **1**

Angle	ω/deg	Angle	ω/deg
Ion pair **1a**		Ion pair **1b**	
I(1a)...Ge(1a)Cl(1a)	180.0	I(1b)...Ge(1b)Cl(1b)	180.0
I(1a)...Ge(1a)O(1a)	85.8(1)	I(1b)...Ge(1b)O(1b)	84.7(1)
I(1a)...Ge(1a)C(1a)	67.3(2)	I(1b)...Ge(1b)C(1b)	69.1(2)
Cl(1a)Ge(1a)O(1a)	94.2(1)	Cl(1b)Ge(1b)O(1b)	95.3(1)
Cl(1a)Ge(1a)C(1a)	112.7(2)	Cl(1b)Ge(1b)C(1b)	110.9(2)
O(1a)Ge(1a)O(1aa)	171.5(3)	O(1b)Ge(1b)C(1b)	83.8(2)
O(1a)Ge(1a)C(1a)	83.7(2)	O(1b)Ge(1b)O(1ba)	169.4(3)
C(1a)Ge(1a)O(1aa)	93.1(2)	C(1b)Ge(1b)O(1ba)	92.4(2)
C(1a)Ge(1a)C(1aa)	134.7(4)	C(1b)Ge(1b)C(1ba)	138.1(4)
Ge(1a)O(1a)C(7a)	111.5(4)	Ge(1b)O(1b)C(7b)	111.8(4)
C(1a)N(1a)C(7a)	119.0(6)	C(1b)N(1b)C(7b)	119.6(6)
Ge(1a)C(1a)N(1a)	107.2(5)	Ge(1b)C(1b)N(1b)	106.7(5)
O(1a)C(7a)N(1a)	118.4(5)	O(1b)C(7b)N(1b)	117.8(6)
Ion pair **1c**			
I(1c)...Ge(1c)Cl(1c)	178.2(1)	O(2c)Ge(1c)C(1c)	92.0(2)
I(1c)...Ge(1c)O(1c)	87.1(1)	O(2c)Ge(1c)C(8c)	84.4(2)
I(1c)...Ge(1c)O(2c)	83.6(1)	C(1c)Ge(1c)C(8c)	135.5(3)
I(1c)...Ge(1c)C(1c)	67.1(2)	Ge(1c)O(1c)C(7c)	110.3(4)
I(1c)...Ge(1c)C(8c)	68.5(2)	Ge(1c)O(2c)C(14c)	111.2(4)
Cl(1c)Ge(1c)O(1c)	94.7(2)	C(1c)N(1c)C(7c)	118.5(5)
Cl(1c)Ge(1c)O(2c)	94.6(1)	C(8c)N(2c)C(14c)	119.1(5)
Cl(1c)Ge(1c)C(1c)	112.7(2)	Ge(1c)C(1c)N(1c)	106.7(4)
Cl(1c)Ge(1c)C(8c)	111.7(2)	O(1c)C(7c)N(1c)	119.9(6)
O(1c)Ge(1c)O(2c)	170.7(2)	Ge(1c)C(8c)N(2c)	106.1(4)
O(1c)Ge(1c)C(1c)	84.5(2)	O(2c)C(14c)N(2c)	118.9(6)
O(1c)Ge(1c)C(8c)	92.0(2)		

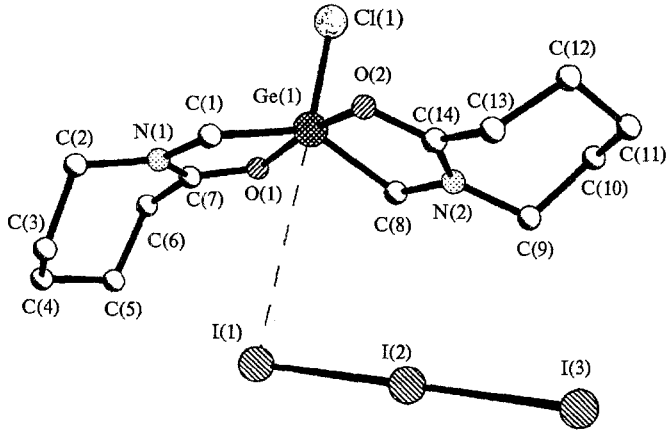


Fig. 2. The general view of the cation-anion pair in the crystal of **2**.

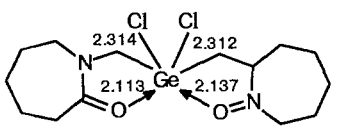
Table 6. Bond angles in structure **2**

Angle	ω/deg	Angle	ω/deg
I(1)I(2)I(3)	177.4(1)	C(8)N(2)C(9)	118.9(4)
I(1)...Ge(1)Cl(1)	171.6(1)	C(8)N(2)C(14)	118.5(4)
I(1)...Ge(1)O(1)	76.1(1)	C(9)N(2)C(14)	122.6(5)
I(1)...Ge(1)O(2)	92.6(1)	Ge(1)C(1)N(1)	107.2(3)
I(1)...Ge(1)C(1)	68.6(2)	N(1)C(2)C(3)	113.9(5)
I(1)...Ge(1)C(8)	71.2(2)	C(2)C(3)C(4)	113.9(5)
Cl(1)Ge(1)O(1)	95.6(1)	C(3)C(4)C(5)	114.7(6)
Cl(1)Ge(1)O(2)	95.7(1)	C(4)C(5)C(6)	113.1(5)
Cl(1)Ge(1)C(1)	112.5(2)	C(5)C(6)C(7)	113.2(5)
Cl(1)Ge(1)C(8)	108.3(2)	O(1)C(7)N(1)	119.5(5)
O(1)Ge(1)O(2)	168.7(2)	O(1)C(7)C(6)	119.9(5)
O(1)Ge(1)C(1)	84.1(2)	N(1)C(7)C(6)	120.7(5)
O(1)Ge(1)C(8)	92.7(2)	Ge(1)C(8)N(2)	106.8(3)
O(2)Ge(1)C(1)	91.1(2)	N(2)C(9)C(10)	113.3(5)
O(2)Ge(1)C(8)	84.3(2)	C(9)C(10)C(11)	113.9(5)
C(1)Ge(1)C(8)	139.2(2)	C(10)C(11)C(12)	115.3(5)
Ge(1)O(1)C(7)	111.2(3)	C(11)C(12)C(13)	113.7(5)
Ge(1)O(2)C(14)	111.7(3)	C(12)C(13)C(14)	113.1(5)
C(1)N(1)C(2)	118.6(4)	O(2)C(14)N(2)	118.0(5)
C(1)N(1)C(7)	117.7(5)	O(2)C(14)C(13)	119.4(5)
C(2)N(1)C(7)	123.6(5)	N(2)C(14)C(13)	122.6(5)

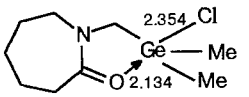
The similarity of the geometries of the hypervalent fragments in the four molecules under consideration (three crystallographically independent molecules in structure **1** and one molecule in structure **2**) does not allow one to identify the correlations between their parameters, as was done for the series of analogous compounds of pentacoordinated Si and Ge.[5,9] Nevertheless, some conclusions on the effect of the nature of the additional ligand on the parameters of the hypervalent fragment may be drawn. For (4+1)-coordination we previously[9] found that with the same types of atoms in the axial positions of the hypervalent TBP fragment (and with an invariable equatorial environment of the central atom), the lengths of the axial bonds are unambiguous functions of the Δ parameter, if one ignores the insignificant steric and electrostatic effects of the environment of this moiety. The wide variation of the lengths of hypervalent bonds in the series of compounds of pentacoordinated Si and Ge studied was achieved by using N—C=O→, Ar—C(=O)O⁻, and other groups in which, for the same type of coordinating atom (O), the degrees of electron delocalization were substantially different, which, in its turn, strongly affected their coordination interaction with the Si and Ge atoms. One might suggest that the polarizability of the additional ligand is one of the main parameters determining the length of the hypervalent bond. However, the coincidence of the I...Ge distances found in structures **1** and **2** is inconsistent with this suggestion. In fact, the polarizability of I_3^- should be much greater than that of I^- (for, example, according to the published data,[10] the polarizability of

Br_2 is 1.7-fold greater than that of Br^-), and, therefore, a substantial difference between the Ge...I and Ge...I_3 interactions should have been expected. However, this discrepancy is possibly illusory and is caused by two factors: 1) the absence of electron delocalization in I_3^- prevents the electron density in molecule **2** from flowing to the I→Ge bond, though I_3^- possesses greater polarizability than I^-; 2) steric interactions of the bulky I_3^- group counteract shortening of the I...Ge distance in molecule **2**. The significance of the former factor is rather evident; the latter is difficult to judge definitely. In our opinion, the transoid orientation of the cation in structure **2** (Fig. 2) is due to the fact that this conformation is favorable to the observed arrangement of I_3^- with respect to the coordination polyhedron, which is impossible with a cisoid relative conformation of the chelate rings in compound **2**. However, there are no steric restrictions to the other orientation of I_3^- with retention of the I...Ge distance observed in structure **2**. Therefore, the influence of steric factors on the I→Ge interaction in **2** should be comparable to the effects of the changing the packing. In structures with pentacoordinated Si, these effects noticeably change the lengths of the weak coordination bonds (by ~0.1 Å at O→Si distances of 2.6—2.7 Å).[11]

A comparison of the structures of iodides **1** and **2** and *cis*-dichloride **3**, which has a similar "spirocyclic" system, leads[1] to the somewhat unexpected conclusion that the type of coordination and the geometric parameters of the coordination environment of the Ge atom in the latter compound are in some respects closer to those in the analog **4**,[5] than to those found in iodides **1** and **2**.



3



4

In fact, owing to the *cis*-arrangement of the Cl substituents in molecule **3**, two O—Ge—Cl linear hypervalent fragments with the distribution of bond lengths close to that observed in **4** are realized. Moreover, the deviations Δ of the Ge atoms from the planes of the substituents perpendicular to the axes of the hypervalent fragments, in molecules **3** and **4** are close: 0.14 and 0.12 Å in **3** and 0.15 Å in **4**. The interference of the hypervalent fragments in **3** results in mutual shortening of their bonds, similar to that observed for the interference of the M—X polar bonds in the MX_nR_m coordination units or when the valency of the metal in these units increases.[8] The main hypervalent fragment, OGeO, in structures **1** and **2** is symmetrical and its parameters ($\Delta = 0$, O→Ge ≈ 2.00 Å) correspond well to the $d_{Ge-O}(\Delta)$ dependence obtained[5] for a number of type **4** compounds. Therefore, it is only slightly affected by the second hypervalent fragment I→Ge—Cl.

Thus, the presence of two "rigid" covalent bonds (Ge—C) at the penta- or hexacoordinated Ge atom in compounds **1—3** makes it possible that the other electronegative substituents form one or two relatively weakly interfering hypervalent linear systems X—Ge—X′, whose geometric parameters are described by similar dependences for both penta- and hexacoordination. This conclusion allows one to apply a method of analysis similar to that offered previously for compounds of pentacoordinated atoms[9] for the analysis of compounds of hexacoordinated Si and Ge (the uncertainty of the correlation parameter Δ for high coordination of the hypervalent atom is removed when Δ is replaced by ΔΩ).

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