The structure of organic derivatives of hexacoordinated germanium. (O→Ge) chelated bis-(2-oxo-1-hexahydroazepinylmethyl)difluorogermane and bis-(2-oxo-1-hexahydroazepinylmethyl)fluorogermane tetrafluoroborate

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Two fluoro derivatives of hexacoordinated germanium containing chelated 2-oxo-1-hexahydroazepinylmethyl ligands were investigated by X-ray diffraction analysis. The coordination polyhedron of the Ge atom in difluoride **1** is a somewhat distorted octahedron with the following bond lengths (Å): Ge—F 1.799(2), Ge←O 2.185(3), and Ge—C 1.945(4). Tetrafluoroborate **2** has an ionic structure; the valence environment of the Ge atom is a distorted trigonal bipyramid open in the direction of the BF_4^- anion. The bond lengths in **2** are: Ge—F 1.792(8), Ge←O 2.001(4), and Ge—C 1.937(9) Å; the Ge...F(anion) distances are 3.43(1) and 3.68(1) Å. Analysis of the geometry of **1**, **2**, and related structures containing hexa-coordinated germanium shows that the parameters of their hypervalent moieties are related to each other by dependences similar to those observed in compounds of pentacoordinated Si and Ge.

Key words: derivatives of hexacoordinated germanium, hypervalent interaction, X-ray investigation.

We showed in the previous paper[1] that a hypervalent moiety in which a germanium atom is bound with two neutral (C) and four electronegative (X = O, Cl, I, etc.) atoms can be considered as a fragment involving two linear hypervalent X—Ge—X′ subsystems weakly affecting one another. The study of the mutual relationships between the geometric parameters of these subsystems is of both theoretical and practical interest, since, on the one hand, these parameters should essentially determine the reactivity of hypervalent compounds, and, on the other hand, they should correlate with the corresponding parameters of transition states involving hypervalent atoms in nucleophilic substitution reactions. In this paper we present the results of an X-ray structural investigation of two derivatives of hexacoordinated germanium, *viz.*, bis(2-oxo-1-hexahydroazepinylmethyl)difluorogermane (**1**) and bis(2-oxo-1-hexahydroazepinylmethyl)fluorogermanium tetrafluoroborate (**2**), which belong to the series of related (O→Ge) chelate compounds with a covalent (**A**) or ionic (**B**) structure being studied by us.

The main purpose of the present work has been to analyze the geometry of the hypervalent fragments in compounds **1**—**11** using the previously[1] suggested parametrization.

Experimental

The X-ray diffraction experiments for compounds **1** and **2** were carried out at 160 and 293 K, respectively, on a Siemens P3/PC diffractometer (λMoKα, graphite monochromator, θ/2θ-scanning, $2\theta_{max}$ = 52° (**1**) and 56° (**2**)).

Crystals of **1** are orthorhombic $a = 12.478(2)$, $b = 12.015(3)$, $c = 10.797(4)$ Å, $V = 1619(1)$ Å^3, $d_{calc} = 1.489$ g cm^{-3}, $Z = 4$ ($C_{14}H_{24}F_2GeN_2O_2$), space group *Pbcn*; the molecule is in a special position on the axis.

Crystals of **2** are orthorhombic $a = 14.371(4)$, $b = 11.285(3)$, $c = 11.043(4)$ Å, $V = 1791(1)$ Å^3, $d_{calc} = 1.598$ g cm^{-3}, $Z = 4$ ($C_{14}H_{24}BF_5GeN_2O_2$), space group *Aba2*; the molecule is in a special position on the axis.

The structures were solved by the direct method and refined by the full-matrix least-squares method in the anisotropic approximation for nonhydrogen atoms. The H atoms located by the difference synthesis were refined isotropically

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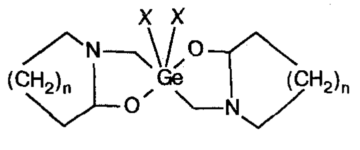
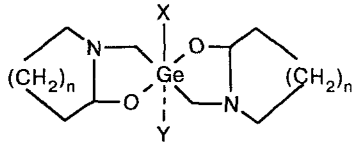


A

1: X = F; n = 3
3, **4**, **5**[2]: X = Cl; n = 1, 2, 3
6*: X = Br; n = 3



B

2: X = F; Y = BF_4; n = 3
7, **8**, **9**[3]: X = Cl; Y = OTf; n = 1, 2, 3
10, **11**[1]: X = Cl; Y = I, I_3; n = 3

(for structure **1**) or with fixed C—H distances and thermal parameters $U = 0.08$ Å^2 (for structure **2**). The BF_4^- anion in structure **2**, owing to its asymmetrical location with respect to the cation, is disordered over two positions connected by the crystallographic 2 axis (except for the B atom located on this axis). For this reason the populations of the positions of the atoms in this anion were taken to be 0.5. In order to obtain a realistic geometry for the anion, whose atoms undergo intense heat motion, it was refined according to a rigid tetrahedral model with equal B—F distances and F—B—F angles. Corrections for absorption in both structures (μ = 18.9 cm^{-1} (**1**) and 17.4 cm^{-1} (**2**)) were taken into account by the DIFABS program.[4] The final discrepancy factors in structure **1** were: R = 0.031, R_w = 0.032 over 1157 reflections with $I > 2\sigma(I)$; those in structure **2** were R = 0.045, R_w = 0.048 over 664 reflections with $I > 2\sigma(I)$. The coordinates and thermal parameters of the atoms in structures **1** and **2** are listed in Tables 1 and 2. All calculations were carried out on an IBM PC/AT computer using SHELXTL PLUS programs.[5]

Results and Discussion

The structures of molecules **1** and **2** (Figs 1 and 2), like those of other molecules of the **A** and **B** series studied, are determined by the set of electronegative substituents at the Ge atom. The halogen atoms in difluoride **1**, as in dichlorides **3**—**5**,[2] occupy the *cis*-position, *i.e.* the coordination unit of the Ge atom contains two identical (with a crystallographic accuracy, since they are connected by the 2 axis) O—Ge—F hypervalent fragments. The asymmetry of these fragments is slight, the O→Ge and Ge—F bonds are ~0.4 and ~0.15 Å longer than normal "tetrahedral" bonds (Table 3), therefore, the coordination of the Ge atom is close to octahedral: the CGeC angle has the maximum (~20°) deviation from the ideal value (180°) (Table 4).

Table 1. Coordinates of atoms (×10^4, or ×10^3 for H atoms) and their thermal parameters (Å^2×10^3) in structure **1**

Atom	x	y	z	$U_{eq}(U_{iso})$
Ge(1)[a]	5000	8995.9(3)	2500	20.1(1)
F(1)	6017(1)	10005(2)	2133(2)	39.0(6)
O(1)	6164(2)	7652(2)	2279(2)	26.4(7)
N(1)	6151(2)	7837(2)	4351(2)	21.1(7)
C(1)	5383(3)	8739(3)	4223(3)	25(1)
C(2)	6467(3)	7491(3)	5605(3)	31(1)
C(3)	6012(3)	6372(4)	5967(3)	39(1)
C(4)	6628(4)	5382(3)	5445(3)	40(1)
C(5)	6680(3)	5340(3)	4039(3)	31(1)
C(6)	7219(3)	6345(3)	3438(3)	27(1)
C(7)	6484(2)	7329(3)	3327(3)	22(1)
H(11)	480(2)	861(3)	466(3)	20(10)
H(12)	566(3)	939(3)	460(3)	30(10)
H(21)	724(2)	742(3)	563(3)	30(10)
H(22)	622(3)	809(3)	614(4)	50(10)
H(31)	609(3)	636(3)	676(4)	50(10)
H(32)	526(3)	636(4)	576(4)	50(10)
H(41)	733(3)	539(3)	585(4)	50(10)
H(42)	630(3)	470(3)	578(3)	40(10)
H(51)	704(3)	469(3)	380(3)	30(10)
H(52)	598(3)	524(3)	374(3)	30(10)
H(61)	784(3)	660(3)	388(3)	40(10)
H(62)	739(3)	615(3)	268(3)	20(10)

[a]The atom on the 2 axis.

Table 2. Coordinates of atoms (×10^4) and their thermal parameters (Å^2 ×10^3) in structure **2**

Atom	x	y	z	U_{eq}
Ge(1)[a]	5000	5000	0	40.3(2)
F(1)[a]	5000	5000	−1623(7)	62(1)
O(1)	3609(3)	4951(4)	66(10)	48(1)
N(1)	3938(4)	3135(5)	754(6)	38(1)
C(1)	4913(5)	3409(7)	649(9)	50(1)
C(2)	3671(6)	1973(7)	1277(9)	54(1)
C(3)	3208(6)	2073(8)	2509(8)	55(1)
C(4)	2187(6)	2393(8)	2446(10)	56(1)
C(5)	1996(5)	3625(7)	1905(9)	57(1)
C(6)	2300(5)	3761(7)	600(9)	52(1)
C(7)	3326(5)	3946(6)	439(7)	38(1)
B(1)[a]	5000	5000	3692(6)	64(1)
F(2)[b]	5714(4)	5276(6)	2955(9)	85(1)
F(3)[b]	4191(3)	5285(7)	3150(10)	128(1)
F(4)[b]	5014(5)	3829(3)	3927(10)	126(1)
F(5)[b]	5082(6)	5607(7)	4736(7)	155(1)

[a]The atom on the 2 axis, the population of the position is 0.5.
[b]The population of the position is 0.5.

The ionic structure of compound **2** is similar to those of compounds **7**—**11**,[1,3] which also belong to the **B**

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* The complete data of the X-ray structural investigation of dibromide **6** will be published in a separate communication.

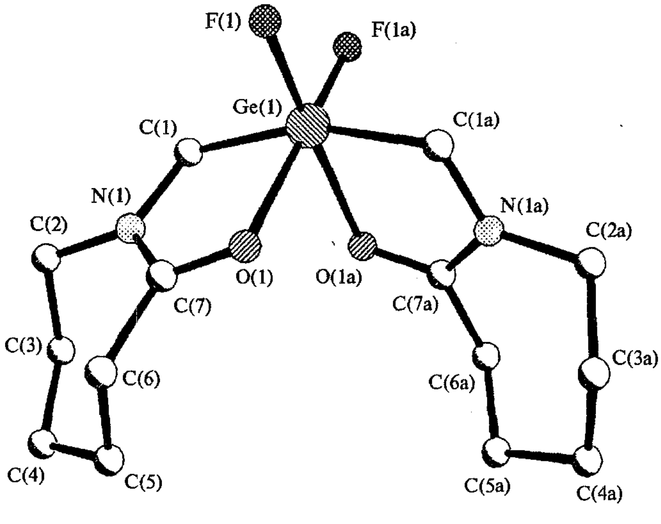

Fig. 1. The general view of molecule **1** in the crystal. The H atoms are not shown.

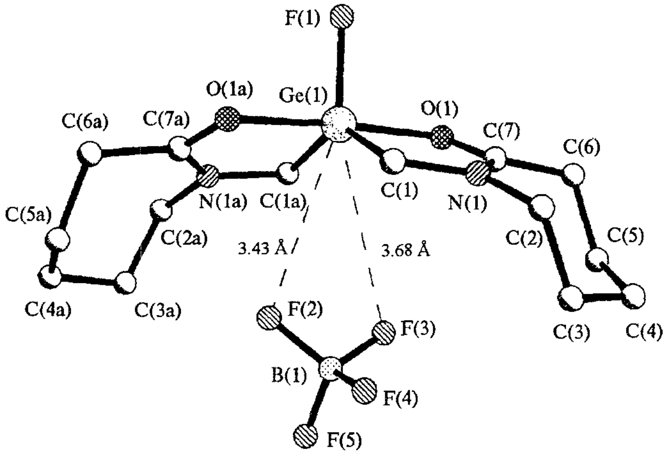

Fig. 2. The cation-anion pair in the crystal of **2**. The H atoms are not shown.

Table 3. Bond lengths (d/Å) and angles (ω/deg.) in structure **1**

Bond	d	Bond	d
Ge(1)—F(1)	1.799(2)	N(1)—C(7)	1.330(4)
Ge(1)—O(1)	2.185(3)	C(2)—C(3)	1.511(6)
Ge(1)—C(1)	1.945(4)	C(3)—C(4)	1.524(6)
O(1)—C(7)	1.260(4)	C(4)—C(5)	1.521(5)
N(1)—C(1)	1.453(4)	C(5)—C(6)	1.527(5)
N(1)—C(2)	1.470(4)	C(6)—C(7)	1.502(5)

Angle	ω	Angle	ω
F(1)—Ge(1)—F(1a)	95.3(1)	C(1)—N(1)—C(7)	117.9(2)
F(1)—Ge(1)—O(1)	90.3(1)	C(2)—N(1)—C(7)	123.6(3)
F(1)—Ge(1)—O(1a)	172.2(1)	Ge(1)—C(1)—N(1)	111.8(2)
F(1)—Ge(1)—C(1)	98.3(1)	N(1)—C(2)—C(3)	112.9(3)
F(1)—Ge(1)—C(1a)	94.0(1)	C(2)—C(3)—C(4)	114.2(3)
O(1)—Ge(1)—O(1a)	84.7(1)	C(3)—C(4)—C(5)	114.7(3)
O(1)—Ge(1)—C(1)	79.8(1)	C(4)—C(5)—C(6)	114.6(3)
O(1)—Ge(1)—C(1a)	86.7(1)	C(5)—C(6)—C(7)	112.8(3)
C(1)—Ge(1)—C(1a)	161.7(2)	O(1)—C(7)—N(1)	120.4(3)
Ge(1)—O(1)—C(7)	109.9(2)	O(1)—C(7)—C(6)	120.5(3)
C(1)—N(1)—C(2)	118.4(2)	N(1)—C(7)—C(6)	119.0(3)

Table 4. Bond lengths (d/Å) and angles (ω/deg.) in structure **2**

Bond	d	Bond	d
Ge(1)—F(1)	1.792(8)	C(3)—C(4)	1.51(1)
Ge(1)—O(1)	2.001(4)	C(4)—C(5)	1.54(1)
Ge(1)—C(1)	1.937(9)	C(5)—C(6)	1.51(1)
O(1)—C(7)	1.273(9)	C(6)—C(7)	1.50(1)
N(1)—C(1)	1.439(9)	B(1)—F(2)	1.347(9)
N(1)—C(2)	1.48(1)	B(1)—F(3)	1.346(7)
N(1)—C(7)	1.316(9)	B(1)—F(4)	1.347(4)
C(2)—C(3)	1.52(1)	B(1)—F(5)	1.35(1)

Angle	ω	Angle	ω
F(1)—Ge(1)—O(1)	92.1(3)	C(2)—C(3)—C(4)	113.7(8)
F(1)—Ge(1)—C(1)	111.7(3)	C(3)—C(4)—C(5)	114.0(7)
F(1)—Ge(1)...F(2)	161.8(3)	C(4)—C(5)—C(6)	114.2(7)
O(1)—Ge(1)—C(1)	84.0(3)	C(5)—C(6)—C(7)	114.3(7)
O(1)—Ge(1)—O(1a)	175.8(7)	O(1)—C(7)—N(1)	119.4(6)
O(1)—Ge(1)—C(1a)	94.4(3)	O(1)—C(7)—C(6)	118.5(6)
C(1)—Ge(1)—C(1a)	136.6(6)	N(1)—C(7)—C(6)	121.9(6)
Ge(1)—O(1)—C(7)	110.8(4)	F(2)—B(1)—F(3)	109.5(7)
C(1)—N(1)—C(2)	118.3(6)	F(2)—B(1)—F(4)	109.4(5)
C(1)—N(1)—C(7)	118.7(6)	F(3)—B(1)—F(4)	109.4(5)
C(2)—N(1)—C(7)	123.0(6)	F(2)—B(1)—F(5)	109.5(5)
Ge(1)—C(1)—N(1)	107.0(5)	F(3)—B(1)—F(5)	109.5(6)
N(1)—C(2)—C(3)	113.3(6)	F(4)—B(1)—F(5)	109.4(7)

series and have readily leaving groups at the Ge atom. The C_2 crystallographic symmetry of the cation corresponds to that of the O→Ge←O hypervalent fragment, the bond lengths in which, as well as the other bond lengths in the cation (Table 4), are close to the corresponding bond lengths in structures **7—11**. The distortion of the trigonal-bipyramidal (TBP) coordination of the Ge atom in the equatorial plane (the CGeC angle is 136.6(6)°; Table 4) is also of the same order as that observed in the **B** series of compounds. It is caused by the weak coordination interactions F(2)→Ge(1) and F(3)→Ge(1) at the distances of 3.43(1) and 3.68(1) Å, which are close to the sum of the van der Waals radii of these atoms (~3.4 Å).[6] In the given case, additional interaction of this sort is natural, since the small size of the anion does not hamper the participation of the two identical F atoms in this interaction. The slight difference between the Ge...F distances is obviously due to the fact that this orientation of the anion is energetically favorable.

The results of the X-ray structural study of compounds **1—11** allow one to make a first attempt at

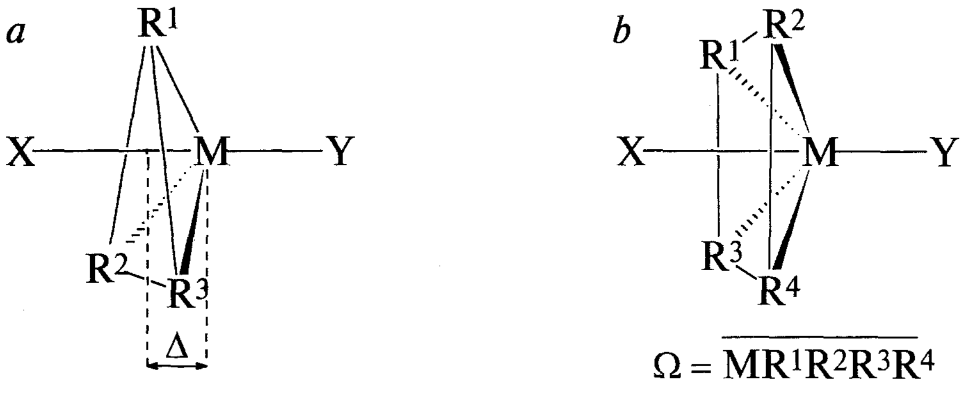

Fig. 3. For defining the Δ and Ω parameters: the penta- (*a*) and the hexacoordination (*b*) of the M atom.

identifying the relationships between the geometric parameters of the linear hypervalent X—M—X′ fragments in the case of a hexacoordinated M atom. We suggested[1] that the deviation ΔΩ of the solid angle (Ω) between the valent bonds nearest the axial substituent X from the value $\Omega_0 = 2\pi$, which corresponds to identical effects of the axial substituents on the central atom, be used as the parameter determining the state of these fragments. The ΔΩ parameter is analogous to the deviation (Δ) of the pentacoordinated M atom from the plane of equatorial substituents (Fig. 3), which is generally used as the characteristic parameter, and in the case of a TBP with a fixed equatorial environment these parameters are related by an unambiguous monotonic dependence. For a hexacoordinated unit, the Δ value is not the determining parameter, since the four "equatorial" (with respect to the linear X—M—X′ fragment) substituents are by no means necessarily located in one plane. In addition, the use of Δ does not allow one to compare TBP units with different equatorial environments (Δ depends substantially on the lengths of the equatorial bonds). Therefore, in the case of pentacoordination, the ΔΩ parameter should also be considered to be more universal.

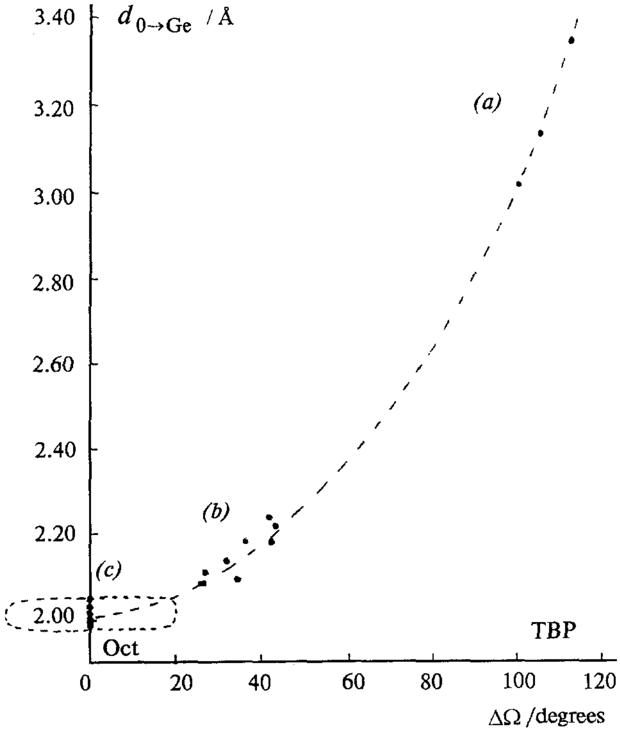

Fig. 4. The correlation dependence of the O→Ge bond length on ΔΩ in compounds **1—11**. The region of the spread in the points corresponding to strong O→Ge interactions in the compounds with a weak second hypervalent bond is marked.

In the compounds **1—11** under consideration, only the O→Ge bond lengths vary over a fairly wide interval, which makes it possible to reveal the $d_{O\to Ge}(\Delta\Omega)$ correlation similar to the $d_{M-X}(\Delta)$ dependences obtained earlier[7,8] for compounds of pentacoordinated Si and Ge. These results are summarized in Fig. 4, where three groups of points ($d_{O\to Ge}$, ΔΩ) can be distinguished. The first group (*a*) corresponds to weak TfO→Ge hypervalent bonds in compounds **7—9** and apparently properly describes the desired correlation. The second group (*b*) (ΔΩ = 20—50°) reflects the correlations of the parameters in dihalides **1—6** in which the coordination of the Ge atom is close to octahedral. The rather large spread in these points may be due to the low accuracy of the structures of dichlorides **3—5**.[2] In fact, slight (about 1°) variations in the RGeR bond angles can result in considerable (up to 10°) changes in ΔΩ. However, in this case, the possibility of substantial interference of the two hypervalent fragments cannot be ruled out, and to judge this with confidence, a greater number of fairly accurate structures is needed. Finally, all of the third group (*c*) points associated with the strongest O→Ge interactions in the coordination units containing weak second hypervalent bonds (the **B** series compounds) were intentionally placed on the $\Delta\Omega = 0$ axis. The problem is that the location of the fourth "equatorial" substituent (OTf, I, I_3, etc.) is subjected to noticeable influences of steric and van der Waals interactions, since the coordination of this substituent with the central atom is weak. Therefore, in this case, the observed $\Delta\Omega$ values, which lie in the interval ±20°, have especially great errors, which can be estimated just by the deviation from $\Delta\Omega = 0$. A typical example is structure **11** in which the deviation of the I(1) atom from the equatorial plane of the TBP cation can be as great as 0.6 Å for equal O→Ge bond lengths, and the $\Delta\Omega$ values for these bonds are ±10°. Taking into account the approximately uniform distribution of the points of the third group over the $d_{O\to Ge}$ interval 1.98—2.05 Å and $\Delta\Omega$ ±20°, one may conclude that $\Delta\Omega = 0$ corresponds to O→Ge bond length of ~2.01 Å. Notice that this value is close to the corresponding value in structures containing a pentacoordinated Ge atom.[8]

Thus, the transition from a neutral to a positively charged TBP hypervalent fragment insignificantly affects the lengths of the hypervalent bonds, at least, in the region of small distortions of the TBP coordination. The general $d(\Delta\Omega)$ dependences for penta- and hexacoordinated hypervalent chelates are undoubtedly different, if for no other reason than that the intervals in which $\Delta\Omega$ varies are in these cases 2π and $4/3\pi$, respectively. It should be emphasized that there are not enough structural data on hexacoordinated Ge compounds with two hypervalent fragments to make possible a detailed discussion of the $d(\Delta\Omega)$ dependences: even the data on the O→Ge bond describe, to a large extent qualitatively, only the part of the curve with $\Delta\Omega > 0$. However, the results of the analysis performed indicate that this approach to the study of the structure of hypervalent fragments with a hexacoordinated central atom is promising.

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