Organometallic Chemistry

Crystal and molecular structures of six-coordinate germanium difluorides and dibromides containing lactamomethyl C,O-chelating ligands

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The structures of (O—Ge)-bischelate bis(lactamomethyl)difluoro- and -dibromogermanes $[L^{(n)}]_2GeX_2$, where L is the bidentate lactamomethyl C,O-chelating ligand, n = 5—7 (the size of the lactam ring), and X = F or Br, were studied by X-ray diffraction analysis. The six-coordinate Ge atom in these compounds is involved in two hypervalent X—Ge—O bonds whose parameters are compared with the corresponding values in analogous dichlorides and five-coordinate Ge derivatives. On going from difluorides to dichlorides and then to dibromides, the coordination environment about the Ge atom approaches the ideal octahedron. An analogous effect is observed as the size of the lactam ring increases.

Key words: six-coordinate germanium compounds; synthesis; intramolecular coordination; X-ray diffraction study.

Organic derivatives of hypercoordinated germanium are studied to a much lesser extent than their Si and Sn analogs (for reviews, see Refs. 1 and 2 and references cited therein).[3] The majority of studies of hypercoordinated Si and Sn derivatives were devoted to compounds with N→M coordination bonds (M = Si or Sn). In the case of Ge, most of the studies concerned compounds with O→Ge coordination bonds.[4,5] In particular, six-coordinate germanium compounds containing lactamomethyl C,O-chelating ligands were used as models of transition states in S_N reactions involving the five-coordinate Ge atom.[6]

It should be noted that the series of bis(lactamomethyl) derivatives of six-coordinate germanium[6—8] and tin[9] studied by us previously fall into two groups of compounds markedly differing in structure. In dihalides of the general formula $[L^{(n)}]_2MX_2$ (L is the bidentate lactamomethyl C,O-chelating ligand; n = 5—7, which is the size of the lactam ring; M = Ge or Sn; X = Hal), the Hal atoms and the coordinating O atoms, which are involved in the nearly octahedral coordination environment about the M atom, are in *cis* positions, whereas the carbon atoms are in *trans* positions with respect to each other, *i.e.*, the M atom forms two identical linear

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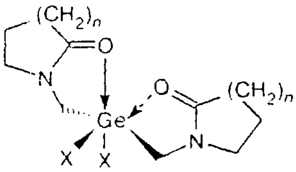
hypervalent X—M—O bonds. The replacement of one of the Hal atoms (except for I) by a better leaving group Y (OTf, BF_4, I, or I_3), which has been performed only in the case of Ge compounds, led to a change in the coordination of the Ge atom for (5+1). This coordination environment is intermediate between an octahedron and a trigonal pyramid with the C and O atoms and the monodentate ligands located in *trans* positions relative to each other. The hypervalent O--Ge—O and Hal—Ge—Y bonds differ substantially in properties. Thus, the former bond is virtually symmetrical, whereas the components of the latter bond can be considered as an actually covalent Hal—Ge bond and an essentially ionic Ge...Y bond located at a distance close to the sum of the van der Walls radii of the atoms.

In the present work, we consider and analyze the results of X-ray diffraction analysis of six-coordinate germanium derivatives containing lactamomethyl C,O-chelating ligands with the weakest O→Ge coordination bond, *viz.*, difluorides **1a—c**, and compounds with stronger O→Ge bonds, *viz.*, dichlorides **2a—c** and dibromides **3a—c**. Difluorides **1a,b** and dibromides **3a—c** are considered for the first time. Difluoride **1c**[8] and dichlorides **2a—c**[7] studied previously are also discussed because they complete the series of dihalides.



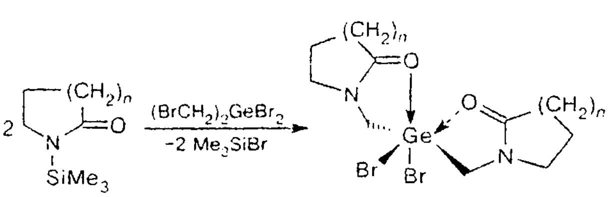
1a—c, **2a—c**, **3a—c**

X = F (**1**), Cl (**2**), Br (**3**); *n* = 1 (**a**), 2 (**b**), 3 (**c**)

Results and Discussion

Syntheses of difluorides **1a—c** and dibromide **3c** by the reactions of dichlorides **2a—c** with AgF and of dichloride **2c** with LiBr or Me_3SiBr, respectively, have been reported previously.[10] Dibromides **3a—c** under study were prepared by transmetallation starting from *N*-trimethylsilyllactams and bis(bromomethyl)dibromogermane taken in a ratio of 2 : 1 analogously to a procedure reported previously for the synthesis of dichlorides **2a—c** from the corresponding silyllactams and bis(chloromethyl)dichlorogermane[7] (Scheme 1).

Scheme 1



3a—c

These reactions were performed under conditions of thermodynamic control. Possible intermediates, which have been observed in particular in reactions of silyllactams with $(ClCH_2)_2GeCl_2$, *viz.*, *O*-germylmethylation products,[7] were not analyzed in the present study. Dibromides **3a—c** were obtained in 75—85% yields. The structures of the resulting compounds were confirmed by ^1H and ^{13}C NMR and IR spectroscopy and elemental analysis.

The IR spectra of dibromides **3a—c** (solutions in $CHCl_3$), like those of dihalides **1** and **2** described previously,[10] have two bands in the region of

Table 1. Chemical shifts in the ^1H and ^{13}C NMR spectra and the spin-spin coupling constants ($^2J_{HH}$) for (O--Ge)-bischelate bis(lactamomethyl)dibromogermanes **3a—c** (in $CDCl_3$)

Compound	δ ($^2J_{HH}$/Hz)						
	H(3); C(3)	H(4); C(4)	H(5); C(5)	H(6); C(6)	H(7); C(7)	NC$\underline{H}_2$Ge; N$\underline{C}H_2$Ge	C=O
3a	2.53 (t, *J* = 6.1); 28.77	2.12 (q, *J* = 6.1); 17.07	3.60 (t, *J* = 6.1); 54.00			3.34 (br.s); 49.83	176.81
3a*	2.77 (t, *J* = 6.1); 28.79	2.25 (q, *J* = 6.1); 16.07	3.79 (t, *J* = 6.1); 54.98			3.71 (br.s); 50.83	175.76
3b	2.50 (t, *J* = 6.0); 28.27	1.79 (m); 19.45	1.92 (m); 21.94	3.63 (t, *J* = 6.0); 49.94		3.43 (br.s); 43.18	174.38
3b*	2.43 (t, *J* = 6.0); 28.98	1.80 (m); 20.07	1.93 (m); 21.94	3.56 (t, *J* = 6.0); 57.41		3.17 (br.s); 49.52	172.30
3c	2.58 (t, *J* = 6.3); 29.78	1.70 (m); 21.79	1.79 (m); 25.89	1.98 (m); 33.49	3.54 (t, *J* = 6.3); 59.53	3.38 (br.s); 51.58	177.85
3c*	2.67 (t, *J* = 6.3); 29.60	1.71 (m); 21.78	1.80 (m); 25.54	1.97 (m); 32.98	3.67 (t, *J* = 6.3); 52.57	3.88 (br.s); 47.60	180.08

* The chemical shifts of the signals of the second stereoisomer.

1700—1500 cm^{-1} belonging to strongly coupled ν(C=O) and ν(C=N) stretching vibrations of the amide fragments (a medium intensity low-frequency band and a strong high-frequency band). Their positions and intensities are virtually independent of the nature of the halogen atom.

The ^{1}H and ^{13}C NMR spectra of dibromides **3a—c** ($CDCl_3$) have two sets of signals with different integral intensities (Table 1). At –20 °C, their ratios were as follows (%): 86 : 14 (**3a**), 90 : 10 (**3b**), and 64 : 36 (**3c**). In the ^{1}H NMR spectra, the signals of the NCH_2Ge groups in both sets are observed as broadened singlets.

At low temperature, the broadened signal for the protons of the NCH_2Ge group in the major set is transformed into a quartet of an AB system. This temperature dependence of the signals for the above-mentioned protons has been observed previously for dihalides $[L^{(n)}]_2MX_2$ (M = Ge or Sn; X = Hal[11]; in the crystalline state, these compounds occur as stereoisomers with *cis* arrangement of the monodentate halogen ligands). This dependence was attributed to the fact that solutions contain the same stereoisomer in which the above-mentioned protons are diastereotopic due to the presence of the chiral center (the central atom) in the molecules of these dihalides. An increase in the temperature is accompanied by broadening and subsequent coalescence first of the signals of the quartet of the AB system and then of the signals of the identical groups in both sets. These data suggest that both the diastereomer with the *cis* arrangement of the Br atoms and the diastereomer with the *trans* configuration of the like ligands are present in solutions (this suggestion will be discussed in detail elsewhere).

The geometric parameters of the valence environment about the Ge atom in the structures of **1a—c** and **3a—c** (Tables 2 and 3) and in dichlorides **2a—c** reported previously[7] reflect pronounced regularities associated with a change in the size of the lactam ring and the replacement of the halogen ligands. As a result of an increase in the size of the ring and a change from fluorides to chlorides and then to bromides, the coordination environment about the germanium atom approximates an octahedron, which, for example, followed from an increase in the C—Ge—C angles. Moreover, this regularity is manifested in the $d(\Delta\Omega)$ dependences,[6] where d are the lengths of the components of the hypervalent bonds and $\Delta\Omega$ are the deviations of the solid angle Ω (which involves these components and is determined by the directions of the pseudoequatorial bonds of the Ge atom) from the ideal value (2π) corresponding to the symmetrical X—Ge—O hypervalent bond.

In molecules **1a—c**, **2a—c**, and **3a—c**, the $\Delta\Omega$ values are 52°, 42°, 37°, 43°, 42°, 30°, 38°, 30°, and 26°, respectively (the average values for two virtually identical hypervalent bonds in each molecule are given). The typical correlation $d_{Ge—O}(\Delta\Omega)$ is shown in Fig. 1.

Table 2. Bond lengths (d) in the hypervalent fragments of molecules **1** and **3** (X = F (**1**) or Br (**3**))

Bond	d/Å					
	1a	**1b**	**1c***	**3a**	**3b**	**3c**
Ge—X(1)	1.754(4)	1.798(6)	1.799(1)	2.458(1)	2.520(2)	2.506(1)
Ge—X(2)	1.754(4)	1.790(7)	1.799(2)	2.472(1)	2.461(2)	2.483(1)
Ge—O(1)	2.265(4)	2.232(7)	2.185(3)	2.203(6)	2.090(7)	2.089(4)
Ge—O(2)	2.265(4)	2.187(6)	2.185(3)	2.139(6)	2.111(5)	2.087(4)
Ge—C(1)	1.967(5)	1.887(8)	1.945(4)	1.965(7)	1.958(9)	1.965(6)
Ge—C(y)**	1.967(5)	2.001(6)	1.945(4)	1.983(7)	1.952(9)	1.9396)

* According to published data.[8]

** The atom is generated from the basis atom by symmetry operations: y = 1a* (**1a,c**), 6 (**2a**), 7 (**b**), and 8 (**2c**).

Table 3. Principal bond angles (ω) in the hypervalent fragments of molecules **1** and **3** (X = F (**1**) or Br (**3**))

Angle	ω/deg					
	1a	**1b**	**1c** [8]	**3a**	**3b**	**3c**
X(1)—Ge—X(2)	98.2(3)	94.6(3)	95.3(1)	96.23(5)	95.1(1)	96.4(1)
X(1)—Ge—O(1)	171.3(2)	174.3(3)	172.2(1)	172.1(2)	173.4(2)	174.1(1)
X(1)—Ge—O(2)	90.2(2)	91.5(2)	90.3(1)	91.2(2)	90.0(2)	88.1(1)
X(2)—Ge—O(1)	90.2(2)	90.4(3)	90.3(1)	90.8(2)	88.7(2)	88.1(1)
X(2)—Ge—O(2)	171.3(2)	171.5(3)	172.2(1)	172.3(2)	173.1(2)	173.4(1)
X(2)—Ge—C(1)	99.2(2)	98.3(3)	98.3(1)	97.6(3)	100.0(3)	94.1(2)
O(1)—Ge—O(2)	81.4(2)	83.8(3)	84.7(1)	81.9(2)	86.7(3)	87.7(2)
C(1)—Ge—C(y)*	155.6(3)	157.4(2)	161.7(2)	162.7(4)	163.8(3)	168.0(3)

* The atom is generated from the basis atom by symmetry operations: y = 1a* (**1a,c**), 6 (**2a**), 7 (**b**), and 8 (**2c**).

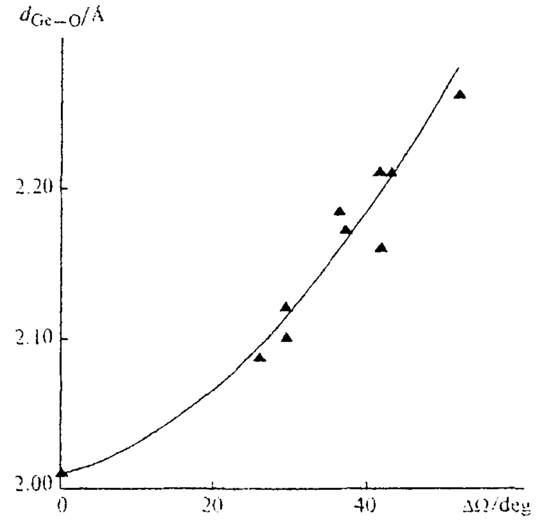


Fig. 1. Correlation dependences of the hypervalent bond length (d_{Ge-O}) on the solid angle (ΔΩ) for compounds **1**—**3**. The value of 2.01 Å at ΔΩ = 0° was taken as the average in a series of analogous structures.[8,12,13]

The point with ΔΩ = 42° and d_{Ge-O} = 2.16 Å corresponds to dichloride **2b** containing six-membered lactam rings. The unit cell of compound **2b**, unlike those of all other compounds, contains a *p*-xylene molecule of solvation. This accounts for the fact that the former structure drops out of the common series. The above point was ignored in the construction of the correlation curve.

It is noteworthy that only slight shortening of the Ge—O bonds is observed on going from a five-membered lactam ring to six- or seven-membered rings. The range in which the average Ge—O bonds vary in the structures of **1**—**3** is 0.08 Å, whereas this range in analogous lactamomethyl five-coordinate Ge monochlorides[14,15] is 0.12 Å, the Ge—O bond lengths being approximately the same. However, it should be noted that dihalides **1**—**3** under consideration, unlike five-coordinate Ge monochloride, contain O and Hal atoms (the second O—Ge—Hal hypervalent bond) instead of one of the C atoms. Previously,[16] we have already mentioned that the presence of electron-withdrawing substituents leads to the formation of a more rigid hypervalent bond. Apparently, this accounts for the fact that the Ge—Br bonds in structures **3a**—**c** are noticeably shorter (2.46—2.52 Å) than that in *N*-(dimethylbromogermylmethyl)-*N*-[(*S*)-1-phenylethyl]acetamide,[17] in which the lengths of the components of the O—Ge—Br hypervalent bond are 2.138(5) and 2.558(1) Å, respectively. Therefore, the specific mutual effect of the hypervalent bonds in the molecules under consideration is absent and only electronic effects of individual atoms are observed. Previously, an analogous conclusion was drawn[6] for the symmetrical O—Ge—O hypervalent bonds. Hence, the hypervalent bonds in the structures with five-coordinate (a trigonal-bipyramidal environment) and six-coordinate (an octahedral environment) atoms can be considered using common parametrization taking, of course, into account the difference in the ranges in which the ΔΩ values vary, *viz.*, π and 2/3π for a tetragonal bipyramid and an octahedron, respectively.[6]

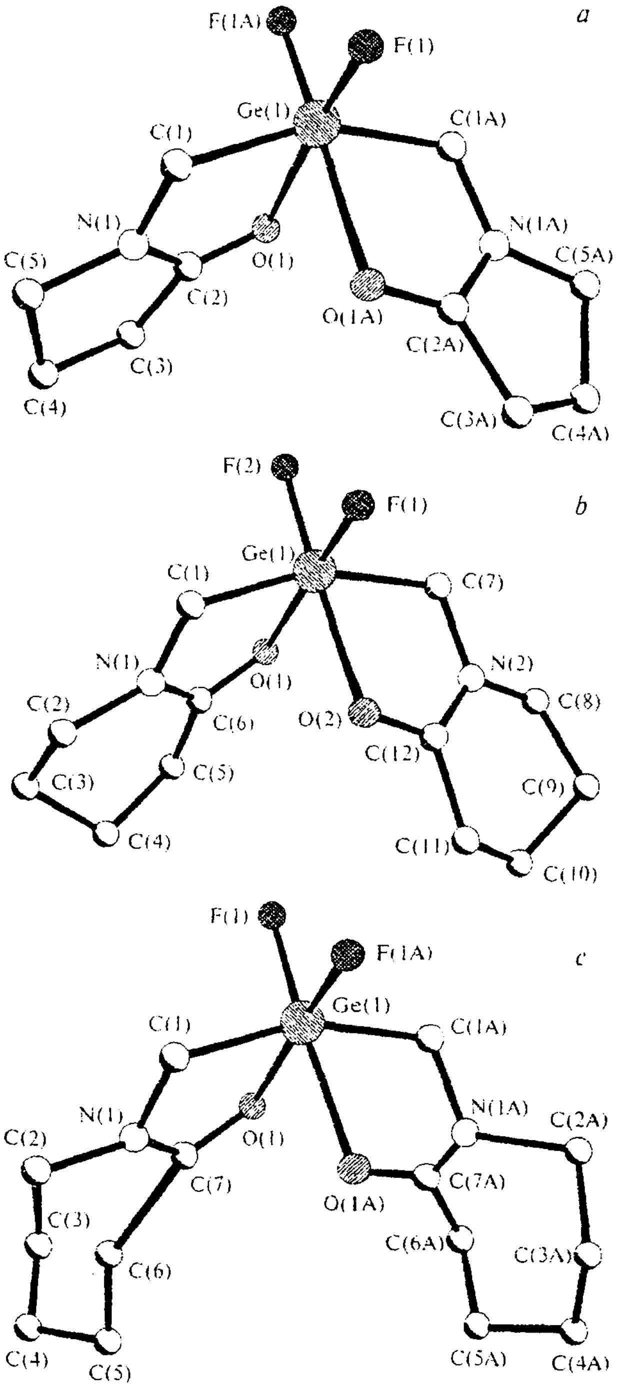


Fig. 2. Molecular structures of **1a** (*a*), **1b** (*b*), and **1c** (*c*) in crystals. The H atoms are omitted.

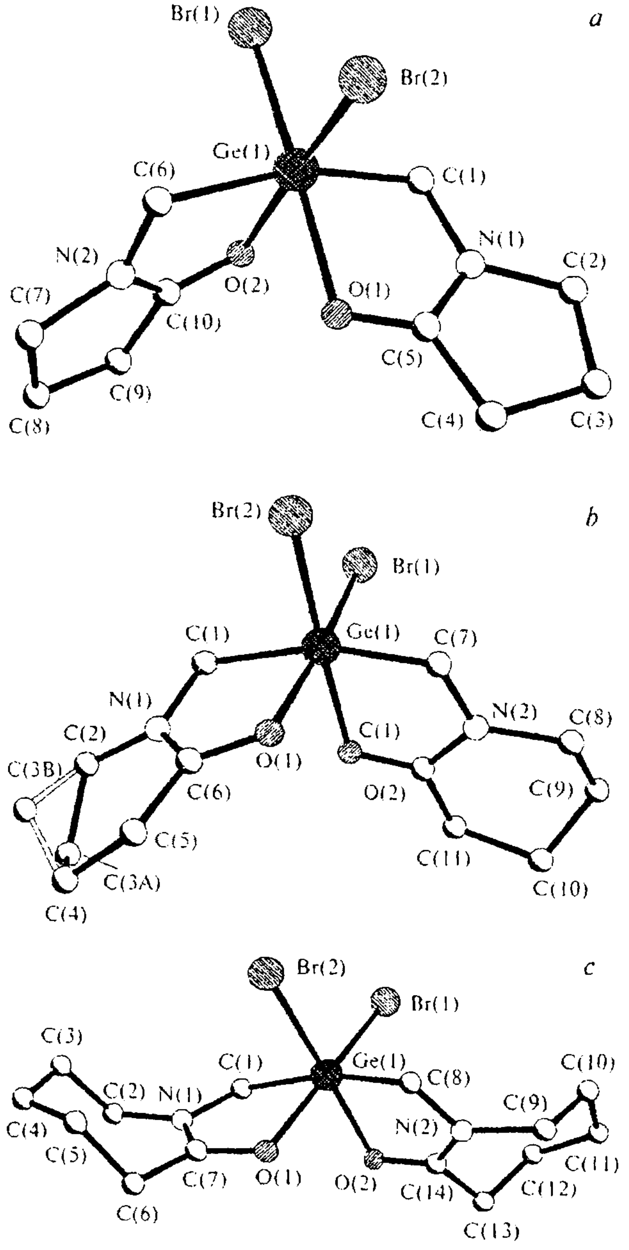


Fig. 3. Molecular structures of **3a** (*a*), **3b** (*b*), and **3c** (*c*) in crystals. The H atoms are omitted.

The characteristic features of the structures, which are not associated with the hypervalence of the Ge atoms, are the disorder of one of the lactam rings in dibromide **3b** and a sharp difference in the molecular conformation in the crystals of **1c** and **3c** (Figs. 2 and 3, respectively). Apparently, these characteristic features result from substantial flexibility of the six- and seven-membered lactam rings adopting a particular conformation in the course of crystallization, which provides a thermodynamically favorable molecular packing.

It is noteworthy that dibromide **3b** containing the six-membered lactam rings crystallizes in the chiral space group $P6_1$, *i.e.*, only one enantiomer with a particular configuration of the bischelate $Ge[L^{(6)}]_2$ system is present in the crystal. One enantiomer was also observed in the crystals of dichlorostannane[9] $[L^{(6)}]_2SnCl_2$; however, the bischelate system in the latter adopts an opposite configuration. To the contrary, analogous dichlorogermane **2b**[4] and difluorogermane **1b** studied in the present work crystallized as racemates. Since a particular energy barrier (10.5—14 kcal mol^{-1}, see Ref. 11) should be overcome to change the configuration of the bischelate system in this type of molecules, two questions arise: Why are the enantiomorphic structures typical only of compounds containing six-membered lactam rings and what are the reasons for crystallization of the dihalides under consideration either in chiral or achiral space groups? Taking into account that the dynamic ^1H NMR spectra are indicative of interconversion of the enantiomers of the *cis* diastereomer in solution,[11] it can be suggested that the enantiomers are separated at the stage of crystallization.

Experimental

The IR spectra of ~5% solutions of the compounds in $CHCl_3$ were measured on a Specord IR-75 instrument in KBr cells.

The ^1H and ^{13}C NMR spectra of solutions of the compounds in $CDCl_3$ (C = ~0.5 M) were recorded on a Varian XL-400 spectrometer (at 400.1 and 100.6 MHz, respectively) in the pulsed mode followed by the Fourier transform and ^2H stabilization of the resonance conditions. The chemical shifts were measured relative to the internal standard (tetramethylsilane).

The starting *N*-trimethylsilyllactams were synthesized according to procedures reported previously.[18]

(O—Ge)-Bischelate bis[(2-oxopyrrolidino)methyl]dibromogermane (3a). A solution of *N*-trimethylsilyl-2-pyrrolidone (1.57 g, 10 mmol) and $(BrCH_2)_2GeBr_2$ (2.1 g, 5 mmol) in *o*-xylene (15 mL) was refluxed for 2 h. The solvent was removed *in vacuo* and compound **3a** was obtained in a yield of 1.5 g (74%), m.p. 226—227 °C (from toluene). IR ($CHCl_3$), ν/cm^{-1}: 1605 (s), 1515 (w) (NCO). Found (%): C, 27.76; H, 3.61; N, 6.68. $C_{10}H_{16}Br_2GeO_2N_2$. Calculated (%): C, 28.02; H, 3.76; N, 6.54.

(O—Ge)-Bischelate bis[(2-oxopiperidino)methyl]dibromogermane (3b). Compound **3b** was prepared from *N*-trimethylsilyl-2-piperidone (1.37 g, 8 mmol) and $(BrCH_2)_2GeBr_2$ (1.7 g, 4 mmol) according to an analogous procedure in a yield of 1.65 g (85%), m.p. 215—216 °C (from toluene, melting was started at 202—203 °C). IR ($CHCl_3$), ν/cm^{-1}: 1585 (s), 1505 (m) (NCO). Found (%): C, 31.23; H, 4.26; N, 6.20. $C_{12}H_{20}Br_2GeO_2N_2$. Calculated (%): C, 31.56; H, 4.41; N, 6.13.

(O—Ge)-Bischelate bis[(2-oxohexahydroazepino)methyl]dibromogermane (3c). Compound **3c** was prepared from *N*-trimethylsilylhexahydroazepin-2-one (3.7 g, 20 mmol) and $(BrCH_2)_2GeBr_2$ (4.2 g, 10 mmol) according to an analogous procedure in a yield of 3.6 g (83%), m.p. 257—258 °C (from MeCN). IR ($CHCl_3$), ν/cm^{-1}: 1580 (s), 1500 (m) (NCO) (*cf.* Ref. 10).

Table 4. Principal details of X-ray data collection and crystal-structural data for compounds **1a,b**, and **3a—c**

Parameter	**1a**	**1b**	**3a**	**3b**	**3c**
Molecular formula	$C_{10}H_{16}N_2O_2GeF_2$	$C_{12}H_{20}N_2O_2GeF_2$	$C_{10}H_{16}N_2O_2GeBr_2$	$C_{12}H_{20}N_2O_2GeBr_2$	$C_{14}H_{24}N_2O_2GeBr_2$
Diffractometer	Syntex $P2_1$	Siemens P3/PC	Siemens P3/PC	Syntex $P2_1$	Syntex $P2_1$
Radiation (T/K)	Mo-Kα, 180	Mo-Kα, 160	Mo-Kα, 293	Mo-Kα, 200	Mo-Kα, 190
Scanning technique ($2\theta_{max}$/deg)	θ/2θ (60)	θ/2θ (57)	θ/2θ (48)	θ/2θ (50)	θ/2θ (50)
a/Å	14.598(6)	17.852(2)	15.593(2)	9.759(2)	6.412(2)
b/Å	22.741(9)	7.674(3)	7.892(2)	9.759(3)	18.684(3)
c/Å	7.194(2)	12.763(4)	11.749(2)	27.883(4)	14.858(4)
α/deg	90	90	90	90	90
β/deg	90	129.29(2)	100.83(1)	90	100.72(2)
γ/deg	90	90	90	120	90
V/Å^3	2388(1)	1353(1)	1420.2(4)	2300(2)	1749(1)
d_{calc}/g cm^{-3}	1.706	1.644	2.005	1.979	1.841
Space group (Z)	$Fdd2$ (4)	Cc (4)	$P2_1/c$ (4)	$P6_1$ (6)	$P2_1/n$ (4)
Number of measured reflections	3559	1908	2242	3250	3121
Number of reflections used in least-squares	749 ($I > 3.5\delta(I)$)	1468 ($I > 2\delta(I)$)	1233 ($I > 2\delta(I)$)	1225 ($I > 2\delta(I)$)	2021 ($I > 2.5\delta(I)$)
Number of parameters in the refinement	77	170	154	181	286
Absorption coefficient (cm^{-1})	12.9	22.9	77.8	72.1	63.3
R_1($I > 2\sigma(I)$)	0.043 ($I > 3.5\sigma(I)$)	0.032	0.0504	0.036	0.034 ($I > 2.5\sigma(I)$)
R_w (wR_2 for **2a**, $I > 2\sigma(I)$)	0.051 ($I > 3.5\sigma(I)$)	0.034	0.1034	0.028	0.033 ($I > 2.5\sigma(I)$)

Single crystals suitable for X-ray diffraction analysis were prepared by repeated recrystallization of the compounds from a 1 : 1 dioxane—heptane mixture (**1a**), a 1 : 1 dioxane—*o*-xylene mixture (**1b**), toluene (**3a**), a 7 : 1 toluene—heptane mixture (**3b**), or acetonitrile (**3c**).

X-ray diffraction study of compounds 1a,b and 3a—c. The crystal-structural data and the principal details of X-ray data collection for compounds **1** and **3** are given in Table 4. The structures were solved by the direct method and refined by the full-matrix least-squares method with anisotropic thermal parameters for nonhydrogen atoms. The H atoms in the structures of **1a,b** and **3a,b** were placed in calculated positions and refined using the riding model with fixed thermal parameters (U = 0.04 Å^2 for **1a**, U = 0.05 Å^2 for **1b** and **3b**, 1.2U_c for **3a**, where U_c is the equivalent thermal parameter of the corresponding C atom). The molecule of compound **1a** occupies a special position, *viz.*, a twofold axis. The absolute structure of compound **3a** was determined using the Hamilton test. In the structure of **3b**, the C(3) atom is disordered over two positions (the occupancies are 0.38 and 0.62). In the structure of **3c**, the positions of the H atoms were located from the difference electron density synthesis and refined isotropically. The absorption corrections were applied using the DIFABS program.[19] All calculations were carried out on an IBM PC/AT computer using the SHELXTL PLUS program package[20,21] (versions 4.0 and 5.0). The principal bond lengths and bond angles are given in Tables 2 and 3, respectively. The remaining geometric parameters and atomic coordinates were deposited with the Cambridge Structural Database.

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