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Reactions of GeBr₄ with *N*,*N*-dimethyl-2-trimethylsiloxypropionamide (**2a**), (*S*)-2-trimethylsiloxypropionpyrrolidide ((*S*)-**2b**), and *N*,*N*-dimethyl-*O*-(trimethylsilyl)mandelamide (**2c**) afforded pentacoordinated neutral (O,O)-monochelates, *viz.*, *N*,*N*-dimethyl-2-tribromogermyloxypropionamide (**3a**), (*S*)-2-tribromogermyloxypropionpyrrolidide ((*S*)-**3b**), and *N*,*N*-dimethyl-*O*-(tribromogermyl)mandelamide (**3c**), respectively. X-ray diffraction study was performed for tribromides **3a**, (*S*)-**3b**, and **3c**, as well as for the *N*,*N*-dimethylmandelamide (**1c**) described earlier. According to the X-ray diffraction data, the Ge atom in tribromides **3a**, (*S*)-**3b**, and **3c** is pentacoordinated and has trigonal bipyramidal configuration with two halogen atoms and oxygen atom of the ether group in the equatorial positions and the halogen atom and the amide oxygen atom in the axial fragment, the bonds in which are somewhat longer as compared to the analogous bonds in tetracoordinated Ge compounds.

Key words: pentacoordinated germanium compounds, synthesis, X-ray diffraction study, quantum chemical calculations.

Hypercoordinated germanium compound attract attention of researchers by their structural features, reactivity, stereochemical nonrigidity in solutions, 1a,b as well as biological activity.1c Among them, penta- and hexacoordinated complexes containing (O,O)- and (S,S)-dianionic, (C,O)-, (C,N)-, and (O,N)-monoanionic chelate ligands are studied relatively well.^{1a} In particular, we developed convenient methods for the preparation of neutral and cation-anionic mono- and bis-chelate complexes of penta- and hexacoordinated germanium containing bidentate amidomethyl or lactamomethyl (C,O)-chelating ligands^{2,3} and studied their structure, reactivity, and behavior in solutions. At the same time, information on their structurally characterized (O,O)-chelate analogs is very scarce (see, for example, Refs 4a-c and references cited therein).

Recently, we have described the first representatives of neutral pentacoordinated germanium complexes contain-

ing (O,O)-monoanionic bidentate ligands based on 2-hydroxycarboxylic acid amides, (O \rightarrow Ge)-chelate *O*-[(chloromethyl)dichlorogermyl]mandelic^{4a} and *O*-trichlorogermyl-(*S*)-mandelic acid *N*,*N*-dimethylamides.^{4c} In continuation of this study, the present work is devoted to the synthesis, X-ray diffraction and quantum chemical studies of three representatives of monochelate tribromogermyl complexes with monoanionic bidentate (O,O)-chelating ligands based on 2-hydroxycarboxylic acid *N*,*N*-disubstituted amides, as well as X-ray diffraction analysis for the ligand described earlier,⁵ *viz.*, *N*,*N*-dimethylmandelamide.

Results and Discussion

Synthesis and structure. We have found that the reaction of GeBr₄ with O-trimethylsilyl derivatives of N,N-disubstituted 2-hydroxycarboxylic amides leads to pentaco-

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ordinated (O,O)-monochelate tribromogermyl complexes. *N*,*N*-dimethyl-2-hydroxypropionamide (**1a**), (*S*)-2-hydroxypropionpyrrolidide ((*S*)-**1b**), and *N*,*N*-dimethylmandelamide (**1c**) were used as the starting compounds, which were silylated with hexamethyldisilazane in the presence of a small amount of chlorotrimethylsilane to the corresponding *O*-trimethylsilyl derivatives **2a**, (*S*)-**2b**, and **2c** (Scheme 1). The reactions of the latter with GeBr₄ in an inert solvent, similarly to the analogous reaction involving GeCl₄^{4c} and independent on the ratio of reagents (see Experimental), leads to the isolation of the 1 : 1 reaction products, *viz.*, (O \rightarrow Ge)-chelate of *N*,*N*-disubstituted 2-(tribromogermyloxy)carboxylic amides **3a**, (*S*)-**3b**, and **3c**. The yields of the final products calculated from GeBr₄ were 70–80%.

Scheme 1



 $R^1 = Me, R^2 = R^3 = Me (a); R^1 = Me, R^2R^3 = (CH_2)_4 (b);$ $R^1 = Ph, R^2 = R^3 = Me (c)$

The structures of compounds (S)-1b, 2a-c, and 3a-c obtained in the present work and unknown earlier were inferred from the elemental analysis (except complex 3a), IR and NMR spectroscopic data. The structures of complexes 3a, (S)-3b, 3c, as well as dimethylamide 1c were confirmed by the X-ray diffraction study.

The IR spectra of *O*-trimethylsilyl derivatives 2a, (S)-2b, and 2c contain intensive absorption bands in the region 1700–1400 cm⁻¹, which are attributed to the asymmetric vibrations of the NCO fragment, v_{as} (NCO), at 1652, 1664, and 1648 cm⁻¹, respectively (which are accompanied by a band of weak intensity at 1620 cm⁻¹ assigned by us to the vibrations of the aromatic system). In the indicated region, the spectra of chelates 3a, (S)-3b, and 3c contain intensive absorption bands v_{as} (NCO) at 1630, 1639, and 1640 cm⁻¹, respectively, as well as additional bands of medium intensities for the symmetric vibrations of this fragment at 1485, 1464, and 1480 cm⁻¹, respectively. Note that the band for the asymmetric vibrations insignificantly shifts to the long-wave region when

going from *O*-trimethylsilyl to tribromogermyl derivatives, that was also noted^{4c} for N,N-dimethylamide Cl-3c.

To assign the vibration frequencies more precisely, we performed calculations of the vibration spectra for the molecules 3a, (S)-3b, and 3c by the DFT method (mpw1pw91/6-311g(d,p)) in the framework of the Gaussian 03W program.⁵ Based on the calculations with allowance for the scaling factor⁶ (0.9567), the frequencies for asymmetric (1634, 1626, and 1636 cm⁻¹) and symmetric $(1505, 1473, and 1501 \text{ cm}^{-1})$ vibrations for the chelate NCO fragments were obtained, which were close enough to those observed in the experiment. In our view, the differences in the vibrational frequencies present can be attributed to the various phase states of the molecules in the experiment and calculations. Note that in contrast to $(O \rightarrow M)$ -chelate (M = Si, Ge) N-silylmethyl⁷ and N-germylmethyl⁸ amide and lactam derivatives, vibrational frequencies for the NCO fragment in the tribromides under study are less characteristic due to the small shift of the frequency with respect to the frequency of the starting O-trimethylsilyl derivatives for asymmetric vibrations and low frequencies for symmetric vibrations, whose bands overlap with vibrations for other fragments of the molecule.

The ¹H NMR spectra correspond to the suggested structures. The low-field shift of the signal in the ²⁹Si NMR spectra of the trimethylsilyl derivatives **2a** and (*S*)-**2b** (δ 16.1 and 15.7 ppm), as well as (*S*)-**2c** (δ 21.3 ppm)^{4c} indicates the absence of coordination interaction in them. This is also confirmed by the high-field shift (by 2–3 ppm) of the signal for the carbonyl group in their ¹³C NMR spectra as compared to pentacoordinated tribromogermyl complexes **3a**, (*S*)-**3b**, and **3c**. Analogous effect has been observed earlier^{2b,9} also for the C,O-chelate complexes with intramolecular coordination O \rightarrow M (M = Si, Ge) on their comparison with nonchelate model compounds.

X-ray diffraction study. General views of complexes **3a**, (*S*)-**3b**, and **3c**, as well as dimethylamide **1c** used as the starting compound, are given in Figs 1–4. Selected



Fig. 1. General view of molecule **3a** in representation of atoms by ellipsoids of thermal vibrations with 50% probability. Hydrogen atoms are not shown.



Fig. 2. General view of molecule (S)-3b in representation of atoms by ellipsoids of thermal vibrations with 50% probability. Hydrogen atoms are not shown.



Fig. 3. General view of molecule **3c** in representation of atoms by ellipsoids of thermal vibrations with 50% probability. Hydrogen atoms are not shown.



Fig. 4. Molecular structure of potential ligand **1c** in representation of atoms by ellipsoids of thermal vibrations with 50% probability. Average values of the main bond distances (Å) are: O(1)-C(3) 1.254(5), O(2)-C(4) 1.427(4), N(1)-C(3) 1.338(5), C(3)-C(4) 1.530(5).

structural parameters for complexes 3a, (S)-3b, and 3c are given in Table 1. The bond distances and bond angles in the structure of 1c agree with the values characteristic of 2-hydroxycarboxylic acid amides.¹⁰ In molecules 3a, (S)-3b, and 3c, the Ge atoms are pentacoordinated, the monoanionic ligands based on 2-hydroxycarboxylic acid amides are bidentate and form the O.O-chelate rings at the germanium atom. A special feature of complex 3c is spontaneous separation of the enantiomers (the structure crystallizes in the $P2_12_12_1$ chiral space group), which allowed us to assign the (S)-configuration of the asymmetric atom C(2). The absolute (S)-configuration of atom C(2) in complex (S)-3b is realized due to the use of enantiomer (S)-1b as the starting compound. It is impossible to assign absolute configuration for compound 3a (the space group is *P*-1).

In complexes **3a**, (*S*)-**3b**, and **3c**, the five-membered chelate ring corresponds to the envelope conformation with the atom C(2) coming out by 0.25, 0.12, and 0.28 Å, respectively. The coordination leads to the elongation of the C(1)–O(1) bond in the structure of **3c** by ~0.02 Å as compared to the analogous C(3)–O(1) bond in compound **1c** (see Fig. 4).

A coordination polyhedron of the germanium atom is of the highest interest, it corresponds to a distorted trigonal bipyramid. The Ge atom coming out of the plane of equatorial atoms Br(2), Br(3), and O(2) in complexes **3a**, (S)-**3b**, and **3c** toward Br(1) atom changes within narrow enough range of 0.12-0.15 Å. The bond distance Ge(1)-O(1) is low sensitive to the change in the nature of substituents on atoms C(1) and C(2) (see Table 1). This is true for the axial Ge(1)-Br(1) bond as well. Nevertheless, in complexes (S)-**3b** and **3c** the Ge(1)-O(1) bond is shorter than in **3a** by 0.02 Å. To sum up, the coordination

Table 1. The main bond distances (d) and bond angles (ω) in molecules **3a**, (S)-**3b**, and **3c** in crystals

Parameter	3a	(<i>S</i>)- 3 b	3c	
Bond distance		d∕Å		
Ge(1) - O(1)	2.036(4)	2.0134(19)	2.014(2)	
Ge(1) - O(2)	1.773(4)	1.7865(19)	1.787(2)	
Ge(1)-Br(1)	2.3956(9)	2.3956(4)	2.3971(5)	
Ge(1)-Br(2)	2.3008(9)	2.3192(4)	2.3016(5)	
Ge(1)-Br(3)	2.3154(9)	2.3047(4)	2.3082(5)	
C(1) - O(1)	1.277(7)	1.280(3)	1.271(4)	
C(1) - N(1)	1.311(7)	1.300(4)	1.308(4)	
$\Delta_{\rm Ge}^{*}$	0.147(2)	0.1213(9)	0.136(1)	
Angle		ω/deg		
O(1) - Ge(1) - Br(1)	171.46(12)	169.28(6)	174.03(7)	
C(1) - O(1) - Ge(1)	111.6(4)	110.69(18)	113.0(2)	

* The Ge atom coming out of the equatorial plane toward Br(1) atom.

center of the Ge(1) atom can be described as "rigid", similarly to that in complex Cl-3c studied earlier.^{4c}

The low sensitivity of geometric parameters of the coordination site to the ligand nature distinguishes the O,O-chelate complexes of trihalogermanes from the C,O-chelates containing the OGeC₃Hal (Hal = F, Cl, Br) coordination center, in which the interatomic Ge...O distance changes within a very wide range (for discussion on these structural regularities, see Refs 4c and 11).

The presence of the strong enough coordination Ge(1)-O(1) bond leads to a noticeable weakening of the axial Ge(1)-Br(1) bond as compared to the equatorial Ge-Br bonds. The differences between distances of the bonds under consideration are 0.08-0.09 Å, which is larger than those in complex Cl-3c.^{4c} This is not surprising, since the bond between the Br atom and the 14 group element is more polarizable than analogous bond with the Cl atom.¹²

With allowance for the weakening of the axial Ge(1)-Br(1) bond observed, it can be suggested that in polar solvents the molecular geometry of (S)-**3b** and **3c** is close to the experimental. This, in turn, allows one to consider a possibility of elimination of the axial Br(1) atom under mild conditions due to the formation of hydrogen bonds with the solvent. In such a case, elimination of the Br(1) atom can be one of the steps of the process for the formation of cyclic germylium cations, the structure and chemical properties of which will be a subject of our further studies. For the evaluation of the solvent influence on the electronic structure and strength of the bonds in the coordination site of the Ge(1) atom, we have performed quantum chemical calculations.

Quantum chemical calculations of complex 3a and its solvate clusters with MeCN. Earlier, 4c,11 during the study of hypercoordinated complexes containing the GeCl₃ fragment we have shown that stabilization of their cyclic form is favored by the intermolecular H...Cl contacts. Similarly, the presence of intermolecular H...Br interactions in solutions of polar solvents can promote elongation of the Ge(1)—Br(1) bond. For the quantum chemical simulation of the interaction of a solvent with compounds of pentacoordinated silicon, the methods describing solvate effects as the interaction with uninterrupted dielectric continuum or the system of point charges were used.^{13–15} Despite satisfactory description of the changes in molecular geometry depending on the solvent dielectric constant value, the impossibility to directly study strength of the intermolecular interactions in solution is an obvious disadvantage of these methods. Allowance for the solvent effect is important for the revealing abilities of the complex with the axial Ge—Br bonds to dissociate to the complex cation and Br⁻ anion, which is important for the understanding the mechanism of further transformations of compounds under consideration.

To analyze the solvent effect, we used an approach based on the (PBE0/6-311G(d,p)) quantum chemical calculation of systems including one molecule of a complex and a number of solvent molecules. Since the structures of the coordination sites of the Ge(1) atom in **3a**, (S)-**3b**, and **3c** are close, the quantum chemical calculations were performed for the most simple complex **3a**. Acetonitrile was chosen as a solvent, since it has no tendency to dissociation, has simple enough structure, and was used in the synthesis of compounds **3a**, (S)-**3b**, and **3c**. The general views of some calculated associates (solvate clusters) are given in Figs 5–7.

In the isolated molecule 3a, the Ge(1)-O(1) bond is elongated by 0.2 Å as compared to that in the crystal (Table 2).

Including two molecules of MeCN into the calculations is the reason for the significant shortening interatomic Ge(1)-O(1) distance and the corresponding increase in the interatomic Ge(1)-Br(1) distance. When the rest of the MeCN molecules are added, more monotonous change in the interatomic distances above occurs. Finally, the incorporation of the H₂O and HBr molecules into the solvate cluster, which are able to form strong H...Br bonds, does not lead to noticeable elongation of the Ge(1)-Br(1) bond. Dissociation of the axial Ge(1)-Br(1) bond proved possible on the interaction of the Br(1) atom with a strong proton donor, for which the cation H_3O^+ was used. Thus, the calculation shows that in the polar solvent the presence of only weak C-H...Br and C-H...O contacts is not enough for the elimination of the axial Br(1) atom.

Table 2. The bond distances (d/Å) of the coordination site in the isolated molecule and in the solvate clusters of **3a** with MeCN

Compound	Ge(1)-O(1)	Ge(1)-O(2)	Ge(1)-Br(1)	Ge(1)—Br(2)	Ge(1)—Br(3)
3a	2.213	1.799	2.344	2.322	2.325
3a · 2MeCN	2.138	1.800	2.377	2.321	2.326
3a · 4MeCN	2.075	1.793	2.388	2.339	2.339
3a · 6MeCN	2.040	1.797	2.411	2.340	2.333
$3a \cdot 6MeCN \cdot H_2O$	2.035	1.795	2.421	2.342	2.329
3a •6MeCN•HBr	2.018	1.796	2.442	2.332	2.328
$3a \cdot 6 MeCN \cdot H_3O^+$	1.845	1.757	4.573	2.251	2.260



Fig. 5. General view of associate $3a \cdot 6MeCN \cdot H_2O$. Hydrogen atoms are not shown.*



Fig. 6. General view of associate $3a \cdot 6MeCN \cdot HBr$. Hydrogen atoms are not shown.



Fig. 7. General view of associate $3a \cdot 6 \text{MeCN} \cdot \text{H}_3\text{O}^+$. Hydrogen atoms are not shown.

To study the electronic structure of the isolated molecule **3a** and its solvate clusters, we performed topological analysis of the calculated function of the electron density distribution in the framework of the "Atoms in the molecules" theory (AM).¹⁶ The critical points (CT) (3, -1) are localized for all chemical bonds, as well as for weak intermolecular interactions. The topological parameters of the bonds formed by the Ge atom are given in Table 3 (the electron density values ($\rho(r)$), its Laplacian ($X^2\rho(r)$), the local energy density ($H^e(r)$), and the potential energy density ($V^e(r)$) in the CT (3, -1)).

Similarly to the complexes studied earlier, ^{4c} which contain the GeCl₃ fragment, the bonds formed by the Ge atom in molecule **3a** and its associates correspond to the interactions of the intermediate type in the framework of the AM theory (the values $X^2\rho(r) > 0$, whereas the values $H^e(r) < 0$ in the CT (3, -1)). From Table 3, it follows that for the antibatic change of the Ge(1)-O(1) and Ge(1)-Br(1) bond distances, the changes of the $\rho(r)$ and $V^e(r)$ values bear the same character. Quantitative evaluation of the change in the bond strength in the coordination environment of the Ge atom was performed based on the correlational dependence suggested by Espinosa, Molins, and Lecomte (EML).¹⁷ The Ge-O and Ge-Br bond energies are given in Table 3.

An increase in the number of MeCN molecules leads to the strengthening of the axial Ge(1)-O(1) bond by ~14 kcal mol⁻¹, with the weakening the axial Ge(1)-Br(1)bond being much less (~5 kcal mol⁻¹). The Ge(1)-O(1)bond in the isolated molecule **5a** is somewhat stronger than those in the isolated molecules of the complexes with the $GeCl_3$ fragment.¹¹ The change in the Ge(1)-O(1)and Ge(1)-Br(1) bond distances when the number of MeCN molecules is increased is accompanied by the formation of weak H-bonds C-H...Br, C-H...N, and C-H...O both between the solvent and complex **3a** and between MeCN molecules.

Molecules of H_2O and HBr are bound to MeCN and complex **3a** by the weak O—H...Br and O—H...Br hydrogen bonds. When a number of solvent molecules increases, not only weak hydrogen bonds are formed, but interactions of the type "ledge—cavity" emerge as well, which correspond to the orientational interactions between lone electron pairs on the N or Br atoms and regions of local rarefaction of electron density (the central C atom of the acetonitrile molecule or the N atom of the dimethylamino group). Such bonds in the framework of the AM theory correspond to the interactions of the closed shell type.

The EML correlation scheme was used for the calculation of energies for all weak interactions between molecules of the solvent and **3a**. The overall value of these interactions (E_{solv}) regularly increases with the increase of a number of the solvent molecule, in the limit it can be described as the solvation energy at 0 K. In the case of solvate clusters **3a** · 2MeCN and **3a** · 4MeCN, the contri-

^{*} Figures 5—7 are available in full color in the on-line version of the journal (http://www.springerlink.com).

Compound	Ge(1)-O(1)	Ge(1)—O(2)	Ge(1)-Br(1)	Ge(1)-Br(2)	Ge(1)-Br(3)			
	$ ho(r)/e \text{\AA}^{-3}$							
3a	0.37	0.90	0.59	0.61	0.61			
3a · 2MeCN	0.43	0.90	0.55	0.61	0.61			
3a · 4MeCN	0.50	0.92	0.55	0.59	0.59			
3a · 6MeCN	0.53	0.91	0.52	0.59	0.60			
$3a \cdot 6MeCN \cdot H_2O$	0.54	0.92	0.51	0.59	0.61			
3a •6MeCN•HBr	0.56	0.92	0.49	0.60	0.61			
$3a \cdot 6MeCN \cdot H_3O^+$	0.82	1.02	_	0.69	0.70			
-		$ abla^2 ho(r)/e \mathrm{\AA}^{-5}$						
3a	3.25	12.29	0.67	0.58	0.63			
3a · 2MeCN	3.86	12.19	0.77	0.51	0.63			
3a · 4MeCN	4.53	12.60	0.80	0.65	0.67			
3a · 6MeCN	5.01	12.36	0.84	0.65	0.65			
$3a \cdot 6MeCN \cdot H_2O$	5.09	12.40	0.86	0.67	0.64			
3a •6MeCN•HBr	5.41	12.40	0.92	0.64	0.63			
$3a \cdot 6MeCN \cdot H_3O^+$	10.54	14.49	_	0.40	0.48			
			$E^{\rm e}(r)/{\rm e}{\rm \AA}^{-3}$					
3a	-0.08	-0.34	-0.27	-0.28	-0.28			
3a · MeCN	-0.11	-0.35	-0.24	-0.28	-0.28			
3a · MeCN	-0.15	-0.36	-0.23	-0.27	-0.27			
3a · MeCN	-0.17	-0.36	-0.22	-0.27	-0.28			
$3a \cdot MeCN \cdot H_2O$	-0.17	-0.36	-0.21	-0.27	-0.28			
3a · 6MeCN · HBr	-0.18	-0.36	-0.19	-0.28	-0.28			
$3a \cdot 6 MeCN \cdot H_3O^+$	-0.30	-0.43	—	-0.36	-0.35			
	$V^{\rm e}(r)/{\rm au}$							
3a	-0.06	-0.23	-0.09	-0.09	-0.09			
3a · 2MeCN	-0.07	-0.23	-0.08	-0.09	-0.09			
3a · 4MeCN	-0.09	-0.24	-0.08	-0.09	-0.09			
3a · 6MeCN	-0.10	-0.23	-0.07	-0.09	-0.09			
$3a \cdot 6MeCN \cdot H_2O$	-0.10	-0.24	-0.07	-0.09	-0.09			
$3a \cdot 6 MeCN \cdot HBr$	-0.11	-0.24	-0.07	-0.09	-0.09			
$3a \cdot 6MeCN \cdot H_3O^+$	-0.20	-0.28	—	-0.11	-0.11			
	$E_{\rm b}/{ m kcal}~{ m mol}^{-1}$							
3a	18.2	72.2	27.3	28.2	28.2			
3a · 2MeCN	22.9	72.5	24.8	28.6	28.2			
3a · 4MeCN	28.6	74.7	24.2	27.3	27.3			
3a · 6MeCN	32.0	73.4	22.6	27.0	27.6			
$3a \cdot 6 MeCN \cdot H_2O$	32.4	74.2	22.0	26.9	28.0			
3a · 6MeCN · HBr	34.4	74.2	20.7	27.7	28.4			
$3a \cdot 6 MeCN \cdot H_3O^+$	62.5	87.1	—	34.7	34.1			

Table 3. The topological characteristic and the bond energy values formed by the Ge atom in the isolated molecule **3a** and its solvate clusters

bution of intermolecular C–H...Br interactions into the values E_{solv} (3.3 and 9.3 kcal mol⁻¹) is 2.2 and 3.8 kcal mol⁻¹. In solvate clusters of more complicated structure, the contribution of C–H...Br yet decreases, whereas the value E_{solv} significantly increases (for **3a** · 6MeCN · **H**₂O, and **3a** · 6MeCN · HBr it is 15.6, 18.4, and 19.7 kcal mol⁻¹, respectively).

Almost in all solvate clusters, interactions between the Br atoms and MeCN molecules are weak, their overall value does not exceed 6.0 kcal mol⁻¹ (in **5a** · 6MeCN), despite a large number of such interactions (6–11). Incorporation of an H₂O molecule into the solvate cluster **3a** · 6MeCN resulted only in insignificant increase (to 6.3 kcal mol⁻¹) of the overall energy of the interactions involving bromine atoms. The part of the intermolecular interactions is illustrated by the dependence between the relative strengthening the Ge(1)–O(1) bond (as compared to **3a**) and the value E_{solv} . This dependence can be de-



Fig. 8. The change of the bond distances $(\Delta_{\text{Ge}-\text{O}})$ versus solvation energy values (E_{solv}) calculated using the EML correlation, ¹⁷ the line obeys the equation $\Delta_{\text{Ge}-\text{O}} = 0.05 + 0.0744E_{\text{solv}}$.

scribed as linear with the correlation coefficient equal to 0.96 (Fig. 8).

The change of the Ge(1)-Br(1) and Ge(1)-O(1)bond energies is a consequence of redistribution of electron density in the axial O(1)-Ge(1)-Br(1) fragment. Analysis of the charges calculated in the framework of the AM theory (Table 4) showed that the largest changes are observed for the Ge(1) atoms and the axial Br(1) atoms. The increase of the positive charge on the Ge atom and the negative charge on the Br(1) atom indicate polarization of the axial Ge(1)-Br(1) bond. The largest positive charge on the Ge bond is observed in the case of full dissociation of the Ge(1)-Br(1) bond. Charges on the rest of the atoms are virtually unchanged on the shortening of the Ge(1)-Br(1) bond.

According to the concept of the donating bond formulated for silatranes,¹³ transition of the electron density occurs from the lone electron pair on the N atom to the region of the Si—X bond (X is the exocyclic substituent). The same notions were also used for the explanation of a chemical bond in various monochelates with pentacoordinated Si atom.^{18,19} The use of charges calculated in the framework of the AM theory allows one to draw conclusion on the fact that transition of the electron density occurs from the Ge(1) and Br(1) atoms toward the O(1) atom. Thus, transition of electron density in the structure of **3a** occurs in the opposite direction as compared to compounds containing pentacoordinated silicon atom. This agrees with the results of the work²⁰ devoted to the quantum chemical calculations of halogermatranes.

Interaction of molecules **3a** and the solvent makes possible redistribution of the electron density between them. Analysis of atomic charge values allowed us to establish the value and direction of the electron density transition. It turned out that on the interaction of molecule **3a** with the solvent molecule, it acquires a small negative charge (from -0.03 to -0.04 e) that indicates a certain outflow of electron density from the solvent molecules.

In conclusion, the coordination Ge–O bond in complexes **3a**, (S)-**3b**, and **3c** proved stronger than in analogous complexes with the GeCl₃ fragment studied earlier.^{4c,11} The influence of a polar solvent leads to a noticeable strengthening of the Ge–O bond and the corresponding weakening the Ge–Br bond, which is accompanied by the increase in polarization of these bonds.

Experimental

IR spectra were recorded on a Specord IR-75 spectrometer in KBr and Bruker IR-20 IR Fourier in 0.1-mm CaF₂ cuvettes for ~5% solutions of compounds. ¹H and ¹³C NMR spectra of compounds studied in different solvents (C_6D_6 , CDCl₃, CD₃CN, DMSO-d₆) were recorded on a Bruker Avance 400 and Varian VXR-400 spectrometers (400 and 100 MHz, respectively) with Me₄Si as an internal standard.

Specific rotation of optically active compounds was measured on a VNIIKIProdmash 1-EPO polarimeter in 0.5-dm cuvettes.*

Commercial methyl (*S*)-2-hydroxypropionate ((*S*)-4) (Acros), $[\alpha]_D^{22}$ -8.1° (*c* 2.00, CH₂Cl₂) was used in the work.

5-Methyl-1,3-dioxolan-4-one $(5)^{21}$ and 5-phenyl-1,3-dioxolan-4-one $(6)^{22}$ were obtained according to the procedures described earlier.

* The authors are grateful to V. M. Dem yanovich and E. Yu. Smirnova for the measurement of specific rotation.

Table 4. The charges on the germanium atom and bound to it atoms calculated in the framework of the AM theory

Compound	Ge(1)	O(1)	O(2)	Br(1)	Br(2)	Br(3)
3a 3a • 2MeCN 3a • 4MeCN 3a • 6MeCN 3a • 6MeCN • H ₂ O	1.82 1.83 1.85 1.86 1.86	-1.17 -1.17 -1.17 -1.18 -1.18	-1.13 -1.14 -1.12 -1.13 -1.13	-0.45 -0.49 -0.50 -0.52 -0.51	-0.46 -0.42 -0.44 -0.44 -0.44	$-0.46 \\ -0.43 \\ -0.44 \\ -0.43 \\ -0.43$
$3a \cdot 6MeCN \cdot HBr$ $3a \cdot 6MeCN \cdot H_3O^+$	1.86 1.93	-1.18 -1.15	-1.13 -1.10	-0.51 -0.29	-0.44 -0.33	$-0.43 \\ -0.35$

N, N-Dimethyl-2-trimethylsiloxypropionamide (2a). Dioxolan-4-one 5 (80.1 g, 0.78 mol) (see Ref. 21) was added dropwise to a 30% aqueous dimethylamine (180 mL, 54 g, 1.2 mol) with stirring. The reaction mixture was stirred for 1.5 h, then kept for 2 days at ~20 °C, and fraction distilled to obtain N, N-dimethyl-2-hydroxypropionamide (1a) (32.6 g, 36%), b.p. 130–132 °C (40 Torr), $n_{\rm D}^{20}$ 1.4580 (*cf.* Ref. 23: b.p. 78.6–79.6 °C (4 Torr), $n_{\rm D}^{25}$ 1.4571). Hexamethyldisilazane (80 mL, 61.9 g, 0.53 mol) and Me₃SiCl (10 mL, 8.6 g, 0.08 mol) were added to the obtained dimethylamide 1a (32.6 g, 0.277 mol). The reaction mixture was refluxed for 1.5 h and fraction distilled to yield dimethylamide 2a (39.7 g, 75%), b.p. 96-98 °C (14 Torr), *n*_D²⁰ 1.4310. Found (%): C, 50.45; H, 10.13; N, 7.50. C₈H₁₉NO₂Si. Calculated (%): C, 50.75; H, 10.11; N, 7.40. IR (CHCl₃), v/cm⁻¹: 1630 (C=O). ¹H NMR (CDCl₃), δ: 0.07 (s, 9 H, SiMe₃); 1.31 (d, 3 H, C<u>H</u>₃CH, ${}^{3}J_{H,H} = 6.9$ Hz); 2.87, 3.06 (both s, 6 H, 2 NCH₃); 4.51 (q, 1 H, C<u>H</u>CH₃, ${}^{3}J_{H,H} =$ = 6.9 Hz). ${}^{13}C$ NMR (CDCl₃), δ : -0.22 (SiMe₃); 20.88 (CH<u>C</u>H₃); 35.71, 36.44 (NMe₂); 68.62 (<u>C</u>HMe); 172.58 (C=O). ²⁹Si (CDCl₃), δ: 16.1.

 $(O \rightarrow Ge)$ -Chelate *N*,*N*-dimethyl-2-tribromogermyloxypropionamide (3a). Germanium tetrabromide (7.86 g, 0.02 mol) was added dropwise to a solution of dimethylamide 2a (3.78 g, 0.02 mol) in hexane (35 mL) with stirring, which was continued for another 2 h, then the reaction mixture was kept for 1 day at ~20 °C. Crystals formed were filtered off and washed with hexane to yield tribromide 3a (6.1 g, 71%), m.p. 117–120 °C (in a capillary tube). A part of the compound was refluxed in MeCN. The structure of oily crystals of tribromide 3a formed was confirmed by X-ray diffraction analysis (see Fig. 1).

Attempted purification of the crystals from the oil by recrystallization from acetonitrile or reprecipitation from the solution in hot benzene by addition of hexane again led to oily crystals. IR (CHCl₃), v/cm⁻¹: 1630 (NCO). ¹H NMR (CDCl₃), δ : 1.47 (br.d, 3 H, C<u>H</u>₃CH, ³J_{H,H} = 6.9 Hz); 3.23–3.40 (br.m, 6 H, 2 NMe); 4.92 (br.q, 1 H, C<u>H</u>Me, ³J_{H,H} = 6.9 Hz).

(*S*)-2-Hydroxypropionpyrrolidide ((*S*)-1b) was obtained from methyl ester (*S*)-4 and pyrrolidine according to the procedure described for the synthesis of racemic 1b.²⁴ The yield was 60%, b.p. 95–97 °C (1 Torr), n_D^{20} 1.4890 (*cf.* Ref. 24 for racemate: b.p. 134–135 °C (7 Torr), n_D^{20} 1.4900), $[\alpha]_D^{22}$ –53.6° (*c* 2.23, CH₂Cl₂). Found (%): C, 58.52; H, 9.00; N, 9.87. C₇H₁₃NO₂. Calculated (%): C, 58.74; H, 9.09; N, 9.79. IR (neat), v/cm⁻¹: 1654 (C=O). ¹H NMR (C₆D₆), δ : 1.24 (m, 4 H, CH₂CH₂); 1.28 (d, 3 H, CH₃CH); 2.65, 2.72 (both m, 2 H, NCH₂); 3.24, 3.35 (both m, 2 H, NCH₂); 4.17 (q, 1 H, MeCH). ¹³C NMR (C₆D₆), δ : 20.6 (<u>C</u>H₃CH); 23.5, 25.6 (both s, CH₂); 45.2, 45.9 (both s, NCH₂); 65.4 (MeCH); 173.4 (C=O).

(*S*)-2-Trimethylsiloxypropionpyrrolidide ((*S*)-2b). Hexamethyldisilazane (1.74 g, 0.011 mol) and Me₃SiCl (0.1 g, 0.001 mol) were added to compound (*S*)-1b (2.00 g, 0.014 mol), the mixture was refluxed for 3 h with vigorous stirring, unreacted reagents were evaporated *in vacuo*. Fraction distillation of the residue gave pyrrolidide (*S*)-2b (2.05 g, 57%), b.p. 97–99 °C (1 Torr), n_D^{20} 1.4608, $[\alpha]_D^{22}$ –20.4° (*c* 2.16, CH₂Cl₂). Found (%): C, 55.88; H, 10.05; N, 6.74. C₁₀H₂₁NO₂Si. Calculated (%): C, 55.77; H, 9.83; N, 6.50. IR (neat), v/cm⁻¹: 1664 (C=O). ¹H NMR (CDCl₃), δ : 0.24 (s, 9 H, Me₃Si); 1.34, 1.39 (both m, 4 H, CH₂CH₂); 1.45 (m, 3 H, Me); 3.23, 3.29 (both m, 2 H, NCH₂); 3.43, 3.45 (both m, 2 H, NCH₂); 4.49 (s, 1 H, MeC<u>H</u>). ¹³C NMR (CDCl₃), δ : 0.4 (Me₃Si); 20.5 (Me); 23.5 (CH₂); 26.3

(CH₂); 45.7, 46.1 (both s, NCH₂); 69.7 (Me<u>C</u>H); 170.6 (C=O). ²⁹Si (C₆D₆, δ: 15.7.

 $(O \rightarrow Ge)$ -Chelate (S)-2-tribromogermyloxypropionpyrrolidide ((S)-3b). A (the ratio of reagents 2 : 1). Germanium tetrabromide (0.43 g, 0.001 mol) was added to a solution of pyrrolidide (S)-2b (0.47 g, 0.002 mol) in hexane (6 mL), which was accompanied by immediate formation of a light pink crystalline precipitate. The reaction mixture was stirred for 1 h, the precipitate was filtered off, washed with hexane, dried *in vacuo* of an oil pump to yield pyrrolidide (S)-3b (0.31 g, 30%), m.p. 162.5 °C (MeCN).

B (the ratio of reagents 1 : 1). Pyrrolidide (*S*)-**3b** was obtained similarly to the preceding experiment from pyrrolidide (*S*)-**2b** (1.00 g, 0.005 mol) and GeBr₄ (1.82 g, 0.005 mol). The yield was 1.70 g (81%), m.p. 162 °C (with decomp.), $[\alpha]_D^{22}$ –59.8° (*c* 1.85, CH₂Cl₂). The IR and ¹H and ¹³C NMR spectra of the samples synthesized in experiments *A* and *B* were identical. Found (%): C, 18.63; H, 2.89; N, 3.10. C₇H₁₂Br₃GeNO₂. Calculated (%): C, 18.50; H, 2.66; N, 3.08. IR (CH₂Cl₂), v/cm⁻¹: 1639 (NCO). ¹H NMR (C₆D₆), & 0.83, 0.93 (both m, 4 H, CH₂CH₂); 1.14 (d, 3 H, Me); 2.06, 2.14 (both m, 2 H, NCH₂); 2.75, 2.85 (both m, 2 H, NCH₂); 4.16 (q, 1 H, MeC<u>H</u>). ¹³C NMR (CD₃CN), & 19.2 (Me); 23.4 (CH₂); 25.1 (CH₂); 47.7, 48.8 (both s, NCH₂); 68.5 (MeC<u>H</u>); 173.3 (C=O).

N,N-Dimethylmandelamide (1c).* A solution of dioxolan-4one (6)²² (10.5 g, 0.064 mol) in diethyl ether (10 mL) was added dropwise to a solution of anhydrous dimethylamine (10.2 g, 0.226 mol, 15 mL) in anhydrous diethyl ether (20 mL) with stirring and cooling to -5 °C. The reaction mixture was stirred for 1 h at cooling and for another 20 min at ~20 °C. A precipitate formed was filtered off and dried *in vacuo* to yield dimethylamide 1c (11.4 g, 99%), m.p. 152–153 °C (hexane) (*cf.* Ref. 25: m.p. 141–143 °C (ethyl acetate)). IR (Nujol), v/cm⁻¹: 1632 (C=O), 1620 (Ph). ¹H NMR (CDCl₃), δ : 2.76, 3.01 (both s, 6 H, NMe₂); 4.77 (br.s, 1 H, OH); 5.2 (s, 1 H, MeCH); 7.3–7.37 (m, 5 H, Ph). ¹³C NMR (CDCl₃), δ : 36.3, 36.4 (NMe₂); 71.6 (MeCH); 127.5, 128.5, 129 (Ph); 141.3 (*C_i*, Ph); 172.4 (C=O).

N,N-Dimethyl-*O*-trimethylsilylmandelamide (2c). A mixture of dimethylamide 1c (11.5 g, 0.065 mol), hexamethyldisilazane (7.1 g, 0.044 mol), and Me₃SiCl (0.1 g, 0.001 mol) was refluxed with vigorous stirring for 3 h, during which dimethylamide 1c was dissolved. Unreacted reagents were evaporated *in vacuo*, fraction distillation yielded dimethylamide 2c (14 g, 86%), b.p. 93–94 °C (1 Torr). The compound solidified on standing, m.p. 56–58 °C (*cf.* Ref. 4c: b.p. 154–155 °C (9 Torr), n_D^{20} 1.4971). Found (%): C, 62.45; H, 8.39; N, 5.35. C₁₃H₂₁NO₂Si. Calculated (%): C, 62.11; H, 8.42; N, 5.57. IR (CHCl₃), v/cm⁻¹: 1648 (C=O), 1620 (Ph). ¹H NMR (CDCl₃), δ : 0.13 (s, 9 H, Me₃Si); 2.82, 2.85 (both s, 6 H, NMe₂); 5.48 (s, 1 H, MeC<u>H</u>); 7.19–7.41 (m, 5 H, Ph). ¹³C NMR (CDCl₃), δ : –0.28 (MeSi); 35.53, 36.20 (NMe₂); 76.53 (Me<u>C</u>H); 125.3, 127.47, 128.32 (Ph); 140.7 (*C*_i, Ph); 171.41 (C=O).

 $(O \rightarrow Ge)$ -Chelate *N*,*N*-dimethyl-*O*-tribromogermylmandelamide (3c). *A*. Dimethylamide 2c (1.26 g, 0.005 mol) was added dropwise to a mixture of GeBr₄ (1.96 g, 0.005 mol) and hexane (5 mL) with stirring. The reaction mixture was stirred for 3 h and kept for 1 day. Crystals formed were filtered off and washed with hexane (10 mL) to obtain tribromide 6a (1.87 g, 76%), m.p. 185–188 °C (MeCN). Found (%): C, 24.35; H, 2.41; N, 2.81.

^{*} With participation of N. S. Ivanov.

Parameter	1c	3 a	(<i>S</i>)- 3 b	3c
Molecular formula	C ₁₀ H ₁₃ NO ₂	C ₅ H ₁₀ Br ₃ GeNO ₂	C ₇ H ₁₂ Br ₃ GeNO ₂	C ₁₀ H ₁₂ Br ₃ GeNO ₂
Molecular weight	179.21	428.46	454.50	490.53
Space group	$P2_1/c$	PĪ	$P2_{1}2_{1}2_{1}$	$P2_{1}2_{1}2_{1}$
Temperature/K	100	120	100	100
a/Å	20.959(5)	6.6228(11)	8.5569(5)	7.4248(4)
b/Å	6.1085(15)	9.5629(17)	11.6449(7)	10.7590(6)
c/Å	14.648(4)	9.7359(17)	12.5983(8)	17.6215(10)
α/deg	90.00	102.421(3)	90.00	90.00
β/deg	109.849(7)	104.602(3)	90.00	90.00
γ/deg	90.00	96.943(3)	90.00	90.00
$V/Å^3$	1763.9(7)	572.63(17)	1255.35(13)	1407.67(14)
Ż	8	2	4	4
$d_{\rm calc}/{\rm g}{\rm cm}^{-3}$	1.350	2.485	2.405	2.315
μ/cm^{-1}	0.9	131.1	119.7	106.8
Crystal size/mm ³	$0.20 \times 0.20 \times 0.05$	$0.1 \times 0.1 \times 0.3$	0.23×0.14×0.11	0.10×0.05×0.05
Diffractometer	«Bruker APEX II»	«Bruker Smart 1000»	«Bruker APEX II»	«Bruker APEX II»
$T_{\rm min}/T_{\rm max}$	0.981/0.995	0.085/0.462	0.150/0.263	0.415/0.617
Total number of reflections	14134	8229	18695	16748
Number of independent	3377	3306	4377	3629
reflections (R_{int})	(0.089)	(0.063)	(0.049)	(0.044)
Number of reflections with $I > 2\sigma(I)$	1919	2279	3948	3441
$\theta_{\rm max}/{\rm deg}$	26.0	30.1	32.0	28.7
Divergence factors				
$R[I \ge 2\sigma(I)]$	0.073	0.043	0.025	0.022
wR_2	0.189	0.095	0.047	0.052
GOF	0.98	0.99	1.00	1.00
Number of refined parameters	239	113	128	156
Residual electron density/e $Å^{-3}$,	0.56/-0.27	1.46/-2.17	0.70/-0.58	0.52/-0.84
$\Delta \rho_{max} / \Delta \rho_{min}$ The Flank parameter	_	_	0.022(11)	0.010(12)

Table 5. The main parameters of the X-ray diffraction experiment and crystallostructural data for compounds 1c, 3a, (S)-3b, and 3c

C₁₀H₁₂Br₃GeNO₂. Calculated (%): C, 24.49; H, 2.47; N, 2.86. IR (MeCN), ν/cm^{-1} : 1640 (NCO). ¹H NMR (CDCl₃), δ : 2.77, 3.16 (both s, 6 H, NMe₂); 5.76 (s, 1 H, CH); 7.35–7.53 (m, 5 H, Ph). ¹³C NMR (DMSO), δ : 39.9 (NMe₂); 73.5 (CH); 127.6, 129.5, 138.9 (Ph); 175.18 (C=O).

B. A mixture of dimethylamide 2c (0.93 g, 3.7 mmol), GeBr₄ (0.73 g, 1.85 mmol) in hexane (5 mL) was stirred for 2.5 h. The following day, crystals formed were filtered off to obtain tribromide 3c (1.37 g, 75.5%), m.p. 182–185 °C (MeCN).

X-ray diffraction study of compounds 1c, 3a, (S)-3b, and 3c. Monocrystals of 1c for X-ray diffraction analysis were obtained by recrystallization of a sample from hexane, of pyrrolidide (S)-3b and dimethylamide 3c, from acetonitrile; monocrystals of dimethylamide 3a were selected from the reaction mixture.

The structures of **1c**, **3a**–**c** were solved by the direct method and refined in the full-matrix anisotropic approximation from F^2 . Hydrogen atoms were calculated from geometric considerations and refined isotropically with imposing analogous restrictions. All the calculations were performed using the SHELXTL PLUS program package.²⁶

The main bond distances and bond angles in the structures studied are given in Table 1 and Fig. 4 Captions, the main crystallostructural data, in Table 5.

Quantum chemical calculations. All the quantum chemical calculations for the isolated molecule **3a** and its associates were performed with the full optimization of geometry using the PC-GAMESS/FIREFLY 7.1.F program,²⁷ partially based on the GAMESS-US program code.²⁸ To confirm that the optimized structures belong to the local minima, calculation of the hessian matrix was performed. Topological analysis and calculation of charges were performed using the AIMALL program.²⁹

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