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Stereochemical rearrangements of dibromides of hexacoordinated germanium containing amidomethyl and lactamomethyl chelate ligands

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Abstract

For the first time a slow (on the NMR time scale) dynamic exchange between two diastereomers of hexacoordinated dibromogermanes containing two amidomethyl and lactamomethyl C,O-chelate ligands has been observed at room temperature in solution. The influence of temperature and solvent on the ratio of diastereomers was studied. At higher temperatures only one set of signals of the products were detected in the NMR spectra. Based on the dynamic NMR and quantum-chemical calculations (ab initio FR 3-21G), as well as on the structures determined for these compounds in the solid state, a *cis*-configuration of monodentate ligands was proposed for one of the diastereomers and an all-*trans*-configuration for the other. At low temperatures interconversion of enantiomers in the *cis*-diastereomer was observed. In the case of bis[(*N*-methylacetamido)methyl]dibromogermane the activation and thermodynamic parameters of enantiomerization ($\Delta G^{\#}_{298}$ 12.0±0.1 kcal mol^{-1}, $\Delta H^{\#}$ 10.7±0.3 kcal mol^{-1}, $\Delta S^{\#}$ −4.6±2.5 cal mol^{-1} K^{-1}) and diastereomeric exchange OcCtBrc$\rightleftharpoons$OtCtBrt ($\Delta G^{\#}_{298}$ 15.0±0.1 kcal mol^{-1}; $\Delta H^{\#}$ 0.1±0.8 kcal mol^{-1}; $\Delta S^{\#}$ − 50.0±5.8 cal mol^{-1} K^{-1}; ΔG°_{298} −0.2±0.1 kcal mol^{-1}; ΔH° −0.8±0.8 kcal mol^{-1}; ΔS° −2.6±1.0 cal mol^{-1} K^{-1}) were determined.

Keywords: Germanium; Hexacoordination; Stereochemical non-rigidity; Non-empirical quantum-chemical calculations

1. Introduction

One of the most interesting properties of the octahedral complexes of silicon, germanium and tin is their stereochemical non-rigidity (for example, see reviews [1–3] and references therein). Recently, studies of the dynamic stereochemistry of hexacoordinated derivatives of these elements with intramolecular coordination has mainly focused on silicon and tin with O,O–, O,N– and C,N-chelate ligands. For example, free energies of activation ($\Delta G^{\#}$) of stereodynamic process have been determined by the dynamic NMR (DNMR) method for acetylacetonate complexes of Si, Ge and Sn (12–17 kcal mol^{-1}) [4,5], bis(8-dimethylamino-1-naphthyl)silanes (**1**) (X = H, Y = F (14.7 kcal mol^{-1}), OMe (15.2 kcal mol^{-1}), Me (9.3 kcal mol^{-1}); X = Me, Y = Ph (12.7 kcal mol^{-1}) [6]), and 1,4-bis{2,6-bis[(dimethylaminomethyl)phenyl]dihydrosilyl}benzene (8.3 kcal mol^{-1}) [7]. The influence of solvent on the activation barrier of silicon complexes with *N*,*N*-dimethyl-*N*′-acylhydrazines (**2**) (X = F, Cl, R = Me, CH$_2$Ph, CF$_3$; Y = F, R = Ph) has also been studied [8,9]. The highest $\Delta G^{\#}$ values of the process (15–17 kcal mol^{-1}) were found in non-polar aprotic solvents (C_6D_6, $C_6D_5CD_3$, CCl_4). In π-acceptor solvents ($C_6D_5NO_2$, Me_2CO) the free energies of activation were ca. 2 kcal mol^{-1} lower, while the

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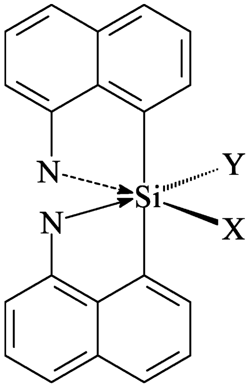
lowest barriers (10–12 kcal mol^{-1}) were detected in polar aprotic ($CDCl_3$, CD_2Cl_2) and donor (CD_3CN) solvents.



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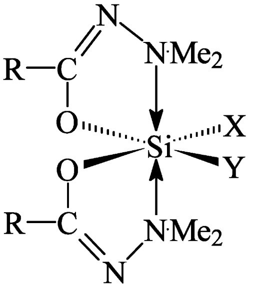

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Octahedral complexes L_2MHal_2 with D→M (M = Si, Ge, Sn; D = O or N atom in bidentate C,D-chelate ligand L) intramolecular coordination can exist a priori as five geometrical isomers. Their structures and symmetry space groups are shown in Fig. 1 (for example, DtCtXc means that the D atoms are in the *trans* position, C atoms in the *trans* position and X atoms in the *cis* positions relative to each other).

A dynamic equilibrium between the all-*trans* diastereomer (NtCtFt) and the NcCtFc diastereomer has been detected at low temperatures (below −50 °C) for the bis(3-dimethylamino)propyl) difluorostannane [10]. Up to now neutral complexes of hexacoordinated germanium and tin with a $MC_2D_2Hal_2$ coordination have been found to exist in the crystalline state generally as DcCtHalc (*cis*) or DtCtHalt (all-*trans*) diastereomers [2b].

Our recent investigations of stereochemical nonrigidity of hypercoordinated silicon, germanium and tin compounds have focused on the complexes with lactamomethyl and similar bidentate C,O-chelate ligands [2a]. In the present paper we report ^1H-DNMR studies of the stereodynamic processes in hexacoordinated dibromogermanes L_2GeBr_2, namely $(L^n)_2GeBr_2$ (**3a**–**c**) (L^n is a bidentate C,O-chelating *n*-membered lactamomethyl ligand; *n* = 5 (**a**), 6 (**b**), 7 (**c**)) and $[MeCON(Me)CH_2]_2GeBr_2$ (**4**).

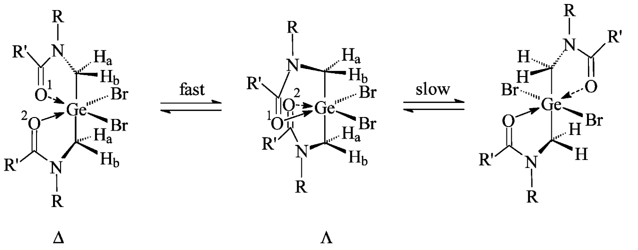
2. Results and discussion

The synthesis of compounds **3a**–**c** and their ^1H- and ^{13}C-NMR spectra in $CDCl_3$ has been reported earlier [11]. The dibromide **4** was prepared analogously by reaction of $(BrCH_2)_2GeBr_2$ with *N*-trimethylsilyl-*N*-methylacetamide (see Section 4).

In contrast to compounds of the type $(L^n)_2MX_2$ (M = Ge, X = Cl; M = Sn, X = Cl, Br) where only one set of signals corresponding to the *cis*-diastereomer was detected in the NMR spectra [3,12,13], the room temperature ^1H- and ^{13}C-NMR spectra of dibromides **3a**–**c** and **4** (Table 1) reveal the existence of two species with different integral intensities in $CDCl_3$ (86:14, 90:10, 64:36 and 55:45%, respectively).

Similar ratios were found in CD_2Cl_2 solutions while in CD_3CN only one set of signals was detected for all compounds. At higher temperatures (up to 50 °C) the signals of both species in $CDCl_3$ and CD_2Cl_2 coalesce into one set. A decrease in temperature leads to a reversible increase in the intensity of the minor set of signals. At −60 °C in $CDCl_3$ the ratios of intensity are 75:25 (**3a**), 82:18 (**3b**), 54:46 (**3c**) and 40:60 (**4**)%, respectively. In particular, for compound **4** the second set of signals at low temperatures becomes the most intense. Thus, the experimental results indicate a stereodynamic process leading to chemical exchange between two different species in solution.

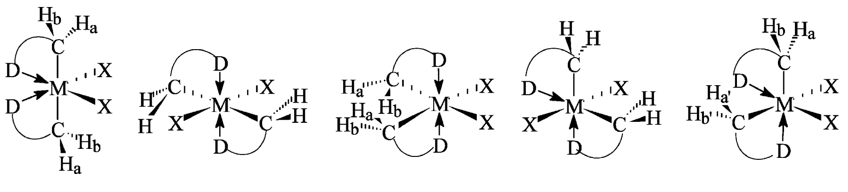
At lower temperatures a second exchange process was observed. The signals of the NCH_2Ge protons of the major species **M** broaden and at −60 °C ($CDCl_3$, CD_2Cl_2) appear as a quartet of an AB-system ($^1J_{HH}$ ~ 12 Hz). At the same time the corresponding signal of the minor species **m** retains its multiplicity.



cis-**3a**–**c**,**4** (OcCtBrc) all-*trans*-**3a**–**c**,**4** (OtCtBrt)

M **m**

3a, R,R' = $(CH_2)_3$; **3b**, R,R' = $(CH_2)_4$; **3c**, R,R' = $(CH_2)_3$; **4**, R = R' = Me



C_2, DcCtXc D_{2h}, DtCtXt C_2, DtCcXc C_{2v}, DcCcXt C_1, DcCcXc

Fig. 1. Possible diastereomers for octahedral intramolecular complexes with $MC_2D_2X_2$ coordination set.

Table 1
^{1}H, and ^{13}C chemical shifts (spin-coupling constants in hertz) of (O–Ge)-bischelate bis[lactamo(amido)methyl]dibromogermanes **3a**–**c**, **4**[a] in different solvents at room temperature

Compound	Solvent	δ (ppm)						
		H(3) C(3)	H(4) C(4)	H(5) C(5)	H(6) C(6)	H(7) C(7)	NCH_2	C=O
3a[b]	$CDCl_3$	t, 2.53 (6.1)	q, 2.12 (6.1)	t, 3.60 (6.1)			br.s, 3.34	
		28.77	17.07	54.00			49.83	178.14
	CD_2Cl_2	t, 2.50 (6.1)	q, 2.10 (6.1)	t, 3.58 (6.1)			br.s, 3.26	
		29.37	17.66	55.27			50.54	177.62
	CD_3CN	t, 2.49 (6.0)	q, 2.07 (6.0)	t, 3.58 (6.0)			br.s, 3.22	
		29.29	17.75	55.65			50.71	178.17
3a[c]	$CDCl_3$	t, 2.77 (6.1)	q, 2.25 (6.1)	t, 3.79 (6.1)			br.s, 3.71	
		28.77	17.07	54.00			50.83	175.76
	CD_2Cl_2	t, 2.74 (6.1)	q, 2.27 (6.1)	t, 3.81 (6.1)			br.s, 3.80	
		29.16	17.00	54.72			52.44	174.99
3b[b]	$CDCl_3$	t, 2.50 (6.0)	m, 1.79	m, 1.92	t, 3.63 (6.0)		br.s, 3.43	
		28.27	19.45	21.94	49.94		43.18	174.38
	CD_2Cl_2	t, 2.41 (6.1)	m, 1.80	m, 1.89	t, 3.42 (6.1)		br.s, 3.41	
		29.65	20.82	22.92	58.36		50.23	175.57
	CD_3CN	t, 2.42 (6.1)	m, 1.78	m, 1.91	t, 3.47 (6.1)		br.s, 3.20	
		29.70	20.44	22.62	58.00		50.31	175.00
3b[c]	$CDCl_3$	t, 2.43 (6.0)	m, 1.80	m, 1.93	t, 3.56 (6.0)		br.s, 3.17	
		28.98	20.07	21.94	57.41		49.52	172.30
	CD_2Cl_2	t, 2.45 (6.1)	m, 1.80	m, 1.89	t, 3.55 (6.1)		br.s, 3.12	
		29.16	20.27	22.92	58.36		50.23	173.00
3c[b]	$CDCl_3$	t, 2.58 (6.3)	m, 1.70	m, 1.79	m, 1.98	t, 3.54 (6.3)	br.s, 3.38	
		29.78	21.79	25.89	33.49	59.53	51.58	180.08
	CD_2Cl_2	t, 2.57 (6.1)	m, 1.70	m, 1.72	m, 1.81	t, 3.53 (6.1)	br.s, 3.31	
		31.59	23.82	27.88	35.28	61.60	53.39	179.80
	CD_3CN	t, 2.60 (6.1)	m, 1.60	m, 1.73	m, 1.80	t, 3.61 (6.1)	br.s, 3.30	
		32.00	23.96	28.08	34.99	58.36	52.09	182.28
3c[c]	$CDCl_3$	t, 2.67 (6.3)	m, 1.71	m, 1.80	m, 1.97	t, 3.67 (6.3)	br.s, 3.88	
		29.60	21.78	25.54	32.98	52.57	47.60	177.85
	CD_2Cl_2	t, 2.57 (6.1)	m, 1.68	m, 1.72	m, 1.82	t, 3.54 (6.1)	br.s, 3.30	
		30.19	20.89	27.99	34.99	59.69	49.99	180.02

[a] ^{1}H-NMR ($CDCl_3$, δ, ppm): 3.20 s (NCH_3), 2.17 s ($CH_3C(O)$), 3.27 wide (NCH_2) (major diastereomer); 3.31 s (NCH_3), 2.28 s ($CH_3C(O)$), 3.73 wide (NCH_2) (minor diastereomer). ^{13}C-NMR ($CDCl_3$, δ, ppm): 37.91 (NCH_3), 18.36 ($CH_3C(O)$), 44.12 (NCH_2), 175.68 (C=O) (major diastereomer); 38.64 (NCH_3), 18.58 ($CH_3C(O)$), 58.47 (NCH_2), 172.93 (C=O) (minor diastereomer).

[b] The chemical shifts of the signals of the major diastereomer.

[c] The chemical shifts of the signals of the major diastereomer.

The only type of signal detected in CD_3CN is identical to the general shape of the **M** species. An increase in temperature restores the original spectrum. As an example, the ^{1}H-DNMR spectrum of **4** is shown below (Fig. 2).

The stereodynamic behaviour of the species **M** is similar to that of the dihalogenides $[L^{(n)}]_2MX_2$ (M = Ge, Sn; X = Hal) that exist in the crystal state as stereoisomers OcCtBrc with a *cis*-configuration of monodentate ligands [3]. Since no significant influence of temperature on the species **m** was found in the ^{1}H-NMR spectra, this suggests an absence of any elements of molecular asymmetry within their configurations. Only the OtCtBrt and OcCcBrt diastereomers comply with such a condition. It will be shown below that an exchange between diastereomers takes place at higher temperatures while enantiomerization is observed at lower temperatures.

2.1. Diastereomer interconversion

In order to estimate the relative stability of different diastereomers and select the best candidate between the above mentioned OtCtBrt and OcCcBrt diastereomers for the $\mathbf{M} \rightleftharpoons \mathbf{m}$ interconversion, we carried out a quantum-chemical analysis (ab initio FR 3-21G) of all

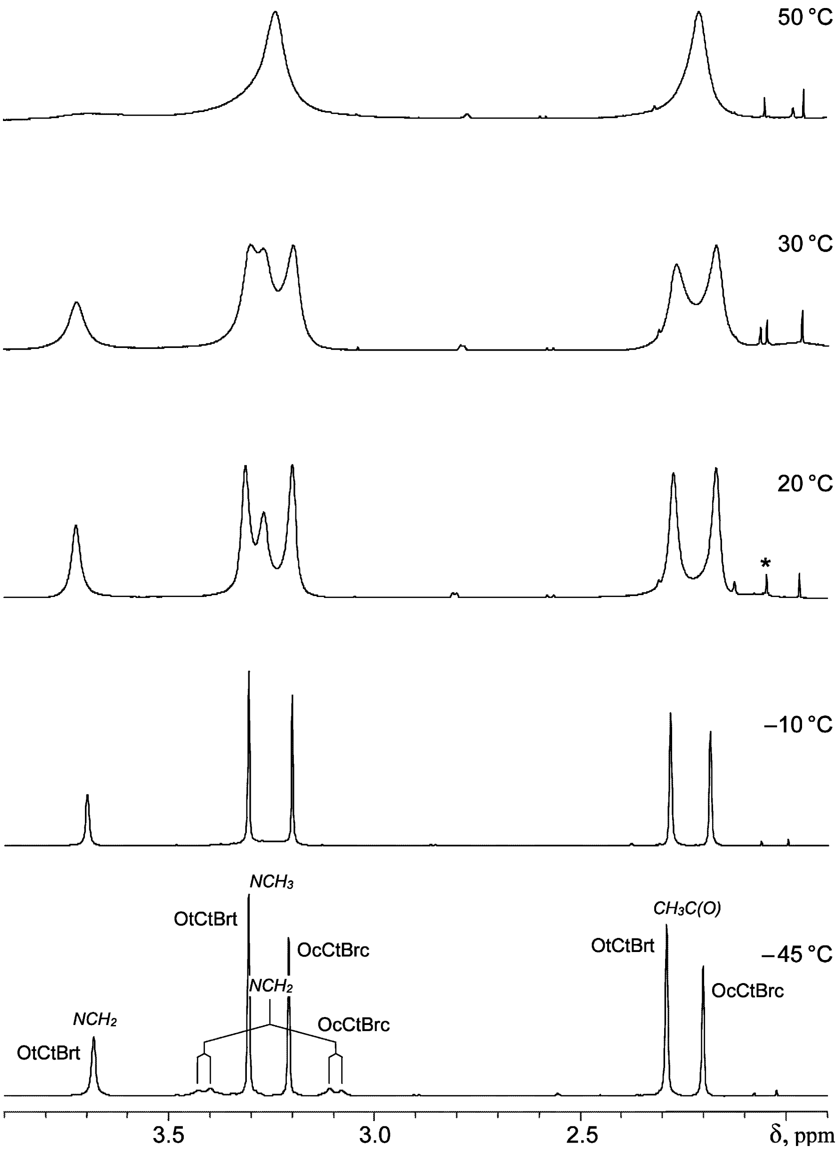


Fig. 2. ^{1}H-DNMR spectra of dibromide **4** ($CDCl_3$, ‘Varian VXR-400’).

possible diastereomers for an $(L^n)_2MHal_2$ complex (Fig. 1).

For the isolated molecule the calculated bond lengths in the hypervalent fragments of the OcCtHalc diastereomers of dibromides **3a**–**c** and **4** as well as the corresponding dichlorides, **3a**–**c-Cl$_2$** and **4-Cl$_2$**, are in agreement with the experimental values determined in the crystal by the X-ray method (Table 2).

The calculations represent adequately one of the most characteristic properties of hypervalent fragments in OcCtBrc diastereomers: that the shortening of one of the bonds in the fragment leads to an increase of the second distance.

According to X-ray data, the O → Ge bond lengths decrease from five to six and seven-membered lactams and also from dichlorides to dibromides. At the same time, the quantum-chemical calculations of the dependence of the O → Ge bond length in dihalogenides $(L^n)_2MHal_2$ on the lactam ring size (**3a** ≫ **3c** > **3b**; **3a-Cl$_2$** ≫ **3c-Cl$_2$** > **3b-Cl$_2$**) reflect not the X-ray data for the molecules in solid state but the relative basicity of the bidentate ligand (*N*-methylpyrrolidone, *N*-methylvalerolactam and *N*-methylcaprolactam) [14]. Thus, the protonation of the carbonyl group in the presence of heptafluorobutyric acid leads to a change in chemical shift of the corresponding carbon atom ($\Delta\delta_{C=O}$, ppm: 5.96, 6.86, 6.31, for *N*-methylpyrrolidone, *N*-methylvalerolactam and *N*-methylcaprolactam, respectively; the higher $\Delta\delta$ value corresponds to higher basicity) [14].

The relative energies (ΔE), selected bond lengths and effective atomic charges for diastereomers of the dibromide **4** are summarized in Table 3.

The lowest total energy was found for the OcCtBrc diastereomer. This is in accord with the fact that *cis*-

Table 2
Selected bond lengths in hypervalent fragments of the OcCtBrc diastereomers of studied (O–Ge)-bischelate bis[lactamo(amido)methyl]dihalogengermanes **3a**–**c**, **4**, **3a**–**c-Cl$_2$** and **4-Cl$_2$**, X-ray data [11–13] (ab initio FR 3-21G)

Compound	d(O–Ge) (Å)	d(Ge–X) (Å)
3a	2.141; 2.198 (2.024; 2.033)	2.460; 2.471 (2.540, 2.546)
3b	2.090; 2.111 (1.955; 1.955)	2.461; 2.520 (2.596; 2.598)
3c	2.087; 2.089 (1.965; 1.967)	2.506; 2.483 (2.567; 2.569)
4	(1.958; 1.958)	(2.596; 2.597)
3a-Cl$_2$	2.183; 2.329 (1.998; 1.998)	2.274; 2.284 (2.231; 2.231)
3b-Cl$_2$	2.093; 2.220 (1.966; 1.968)	2.280; 2.313 (2.395; 2.399)
3c-Cl$_2$	2.113; 2.137 (1.960; 1.961)	2.312; 2.324 (2.415; 2.416)
4-Cl$_2$	2.104; 2.116 (1.956; 1.957)	2.323; 2.325 (2.420; 2.421)

diastereomers were found both in the solid state and in solution of (O–M)chelate dihalogenides L_2MX_2 (M = Ge, X = F, Cl; M = Sn, X = Cl, Br, I) [3,12,13] as well as in the crystal of dibromides **3a**–**c** [11]. The OcCtBrc structure suggested earlier for the species **M** agrees with the temperature-dependent NMR spectra of compounds **3a**–**c**, **4** (Fig. 2). The total energy of the OtCtBrt diastereomer **4** is lower by about 4 kcal mol^{-1} than that in the OcCcBrt diastereomer (Table 3). Taking into account that the proportion of the species **m** increases at lower temperatures (which is probably a result of additional stabilization of the more polar complex by the solvent), we can suggest a dynamic equilibrium (on the NMR time scale) between the OcCtBrc and OtCtBrt diastereomers that takes place in solutions of dibromides **3a**–**c**, **4**.

The structures of the OtCtBrt diastereomers are somewhat similar to those of the bis(thiolactimo-S-methyl)dichlorogermanes which contain a $GeC_2Cl_2N_2$ coordination set [15]. According to X-ray data, these compounds exist as all-*trans*-diastereomers in the solid state.

Quantum-chemical analysis suggests a shorter O–Ge bond in the **4**-OtCtBrt diastereomer compared to the **4**-OcCtBrc diastereomer (Table 3). This agrees with the NMR data where the ^{13}C-NMR signals of the carbon atom of the carbonyl groups of the all-*trans*-diastereomers for dibromides **3a**–**c**, **4** are shifted by 2–3 ppm to higher frequency from the signals of the *cis*-complexes (see Ref. [11] and Table 1).

The thermodynamic parameters of the equilibrium OcCtBrc$\rightleftharpoons$OtCtBrt calculated from the NMR spectra for **4** are as follows: ΔG°_{298} -0.2 ± 0.1 kcal mol^{-1}; ΔH° -0.8 ± 0.8 kcal mol^{-1}; ΔS° -2.6 ± 1.0 cal mol^{-1} K^{-1} ($n = 10$; $r = 0.997$).

The activation parameters of exchange between the two diastereomers has been calculated for **4** using line-shape analysis of the $CH_3C(O)$ singlets ($\Delta\nu$ 37 Hz) to give the following results: $\Delta G^{\#}_{298}$ 15.0 ± 0.1 kcal mol^{-1}; $\Delta H^{\#}$ 0.1 ± 0.8 kcal mol^{-1}; $\Delta S^{\#}$ -50.0 ± 5.8 cal mol^{-1} K^{-1} ($n = 15$; $r = 0.997$). We believe that these data agree with a dissociative mechanism of diastereomeric exchange in hexacoordinated dibromogermanes (Scheme 1). The high negative value of $\Delta S^{\#}$ indicates a highly ordered and compact transition state (species **A**, **B**) [16].

Another possible path includes a nucleophilic attack by the non-dissociated dibromide molecule from the opposite side of the germacenium ion (**A**), which leads to formation of intermediate **C** (Scheme 1).

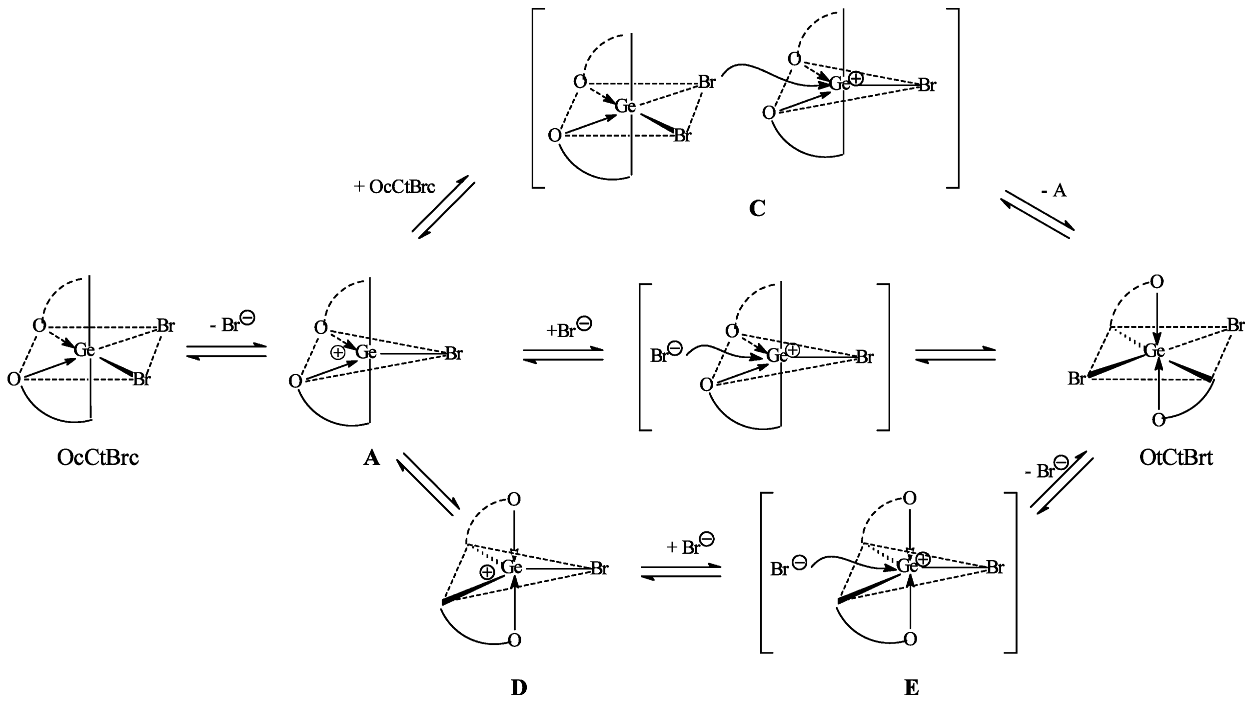
2.2. *Enantiomer interconversion*

Based on the dihalogenides L_2MX_2 (M = Ge, F, Cl; M = Sn; X = Cl, Br, I) mentioned earlier, the low-temperature stereodynamic process for compounds **3a**–**c**, **4** is likely to be an enantiomerization $\Delta C_2 \rightleftharpoons \Lambda C_2$. The values of the barriers of enantiomerization for the dibromides **3a**–**c** and **4** in different solvents are by ca. 0.4–0.6 kcal mol^{-1} lower than the $\Delta G^{\#}$ values for the corresponding dichlorides [3,17] (Table 4). The data for **4** indicate that an increase in temperature from 250 to 298 K slightly affects the $\Delta G^{\#}$ value, which increases by about 0.2 kcal mol^{-1}.

Table 3
Quantum-chemical calculations (ab initio FR 3-21G) for diastereomers of dibromide **4**

Diastereomer	Effective charges			Bond lengths (Å)		ΔE [a] (kcal mol^{-1})
	Ge	O	Br	Ge–O	Ge–Br	
OcCcBrt	1.732	−0.731; −0.731	−0.610; −0.610	1.894; 1.894	2.660; 2.660	5.6
OtCcBrc	1.764	−0.729; −0.729	−0.525; −0.529	1.932; 1.933	2.594; 2.605	18.6
OcCcBrc	1.717	−0.721; −0.740	−0.513; −0.538	1.913; 1.979	2.546; 2.580	13.2
OcCtBrc	1.690	−0.749; −0.749	−0.563; −0.563	1.958; 1.958	2.596; 2.597	0
OtCtBrt	1.731	−0.745; −0.745	−0.615; −0.630	1.916; 1.916	2.667; 2.701	1.4

[a] $\Delta E = E_{OxCxBrx} - E_{OcCtBrc}$.



Scheme 1. Dissociative mechanism of diastereomeric exchange in hexacoordinate germanium dibromides.

The low solubility of the dibromides **3a–c**, **4** in aprotic low-polar solvents (in particular, $C_6D_5CD_3$) along with the relatively high melting point of CD_3CN and the possibility of reaction with deuterated alcohols significantly reduced our ability to vary the nature of the solvent. Nevertheless, it is clear that the barriers in aprotic polar solvents ($CDCl_3$, CD_2Cl_2) are the same as in solvents with significant donor ability (CD_3CN). At the same time the $\Delta G^{\#}$ values remain virtually constant in the concentrations range used ($\sim$0.2–0.6 M). These facts suggest a predominantly intramolecular character for the rate-controlling stage of the enantiomerization process.

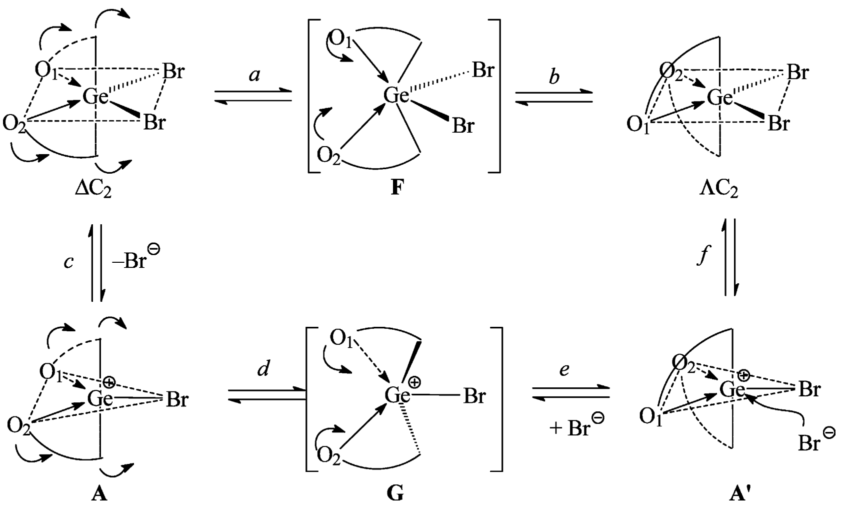
Scheme 2 illustrates the possible regular (non-dissociative) and non-regular (involving dissociation of halide-ion) mechanisms of the enantiomerization $\Delta C_2 \rightleftharpoons \Lambda C_2$.

The regular mechanism (Scheme 2, **a**) includes the formation of a bicapped tetrahedral intermediate with four covalent C–Ge and Br–Ge bonds and two coordination O→Ge bonds (**F**) and subsequent exchange of chelate ligands (**b**) (the arrows indicate the directions of atom movements). The bicapped tetrahedral structure of the intermediate **F** is similar to the neutral bis-chelate complexes of silicon **1** (X = Y = H, F) with relatively weak N→Si coordination (with distances 2.6–2.8 Å) [6,7]. In certain cases a bicapped tetrahedral configuration is more favorable than the octahedral configuration and undoubtedly may be stable enough to be an intermediate in the exchange reactions, or at least a reasonably low-energy transition state. Recently, a similar intramolecular mechanism for the (O,O′)-1,2 shift of *cis*-equatorial ligands has been proposed for stereodynamic processes in neutral com-

Table 4
Enantiomerization barriers in (O–Ge)-bischelate bis[lactamo(amido)methyl]dibromo- and -dichlorogermanes **3a–c**, **4**, **3a–c-Cl₂** and **4-Cl₂**

Compound	Solvent	$\Delta G^{\#} \pm 0.1$ (kcal mol^{-1}) (T_c, K)	Compound	Solvent	$\Delta G^{\#} \pm 0.1$ (kcal mol^{-1}) (T_c, K)
3a	$CDCl_3$	10.2 (218) [3]	**3c**	$CDCl_3$	12.9 (274) [3]
	CD_2Cl_2	10.3 (220)		CD_2Cl_2	13.1 (274)
	CD_3CN	10.3 (220)		CD_3CN	13.1 (276)
3b	$CDCl_3$	12.1 (258) [3]	**4** [a]	$CDCl_3$	11.8 (250)
	CD_2Cl_2	12.2 (256)	**3a-Cl₂**	$CDCl_3$	10.6 (225) [3]
	CD_3CN	12.1 (259)	**3b-Cl₂**	$CDCl_3$	12.8 (269) [3]
			3c-Cl₂	$CDCl_3$	13.6 (268) [3]
			4-Cl₂	$CDCl_3$	12.1 (256) [16]

[a] $\Delta G^{\#}_{298}$ 12.0 kcal mol^{-1}, $\Delta H^{\#}$ 10.7 ± 0.3 kcal mol^{-1}, $\Delta S^{\#}$ −4.6 ± 2.5 cal mol^{-1} K^{-1} ($CDCl_3$).



Scheme 2. Regular and non-regular mechanisms of the enantiomerization in coordination sets of hexacoordinate germanium dibromides without rupture of O → Ge bond.

plexes **2** of hexacoordinated silicon [8,9]. Each of these processes can transform one diastereomer into another diastereomer.

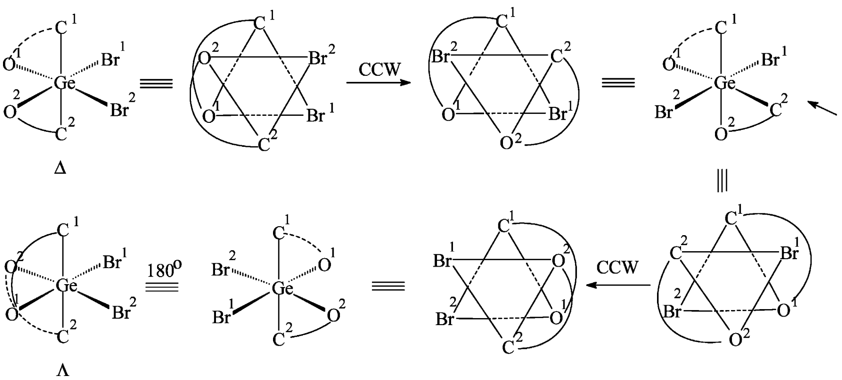
Within the non-dissociative mechanisms two well-known exchange processes are the Bailar [18] and Ray–Dutt [19] twist mechanisms. It should be noted that each of these processes can transform one diastereomer into another. So, a single twist may be ruled out as a possible enantiomerization mechanism. However, it is possible to perform a combination of two consecutive twists which is the stereochemical equivalent of an (O,O′)-1,2 shift [9] (see Scheme 2). Thus, the twist mechanism could not be ruled out completely (Scheme 3).

However, the strongest arguments in favor of the direct (O,O′)-1,2-shift are the single-stage character of the process and the high stability of the bicapped tetrahedral configurations in the solid state of hexacoordinated silicon compounds. The alternative twist mechanisms must include a strained trigonal prismatic transition state (Scheme 3).

According to Table 4 and Fig. 3, the highest barrier among the dibromides **3a**–**c** was found for **3c**, i.e. for the compound with the strongest O → Ge coordination.

Higher $\Delta G^{\#}$ values for **3c** and **3c-Cl$_2$** are probably the result of high steric hindrance in the transition state **F** (Scheme 2). The decrease of $\Delta G^{\#}$ values in the series of **3c** > **3b** ≫ **3a** (Table 4) may be assigned either to a decrease of steric strain of the coordination set due to larger O → Ge distances or to the (O,O′)-1,2 shift reversible rupture of the O → Ge coordination bond (Scheme 4).

A similar dependence was observed for the dichlorides **3a**–**c-Cl$_2$** (Fig. 3). At the same time, compound **4-Cl$_2$** falls far from the main curve. The lower than expected barrier indicates the possibility of different mechanism of enantiomerization for the *N*-methylacetamide derivatives **4** and **4-Cl$_2$**. According to X-ray and quantum-chemical data (Table 2), the average O → Ge bond in the compounds **4-Cl$_2$** and **4** is the shortest known for dihalogenogermanes L_2GeHal_2 discussed, while the



Scheme 3. Regular mechanism of the enantiomerization in coordination set of hexacoordinate germanium dibromides through two consecutive twists.

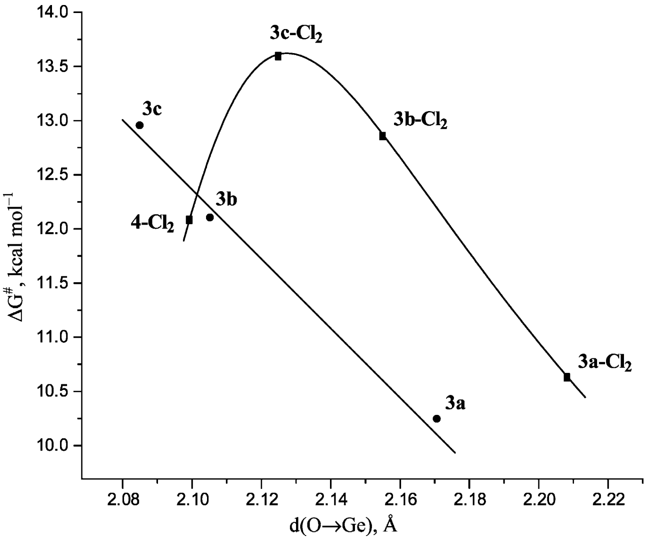
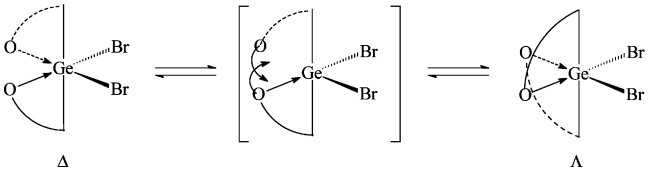


Fig. 3. Dependence of the average O–Ge distance on the free energy of activation ($\Delta G^{\#}$ in $CDCl_3$) of the enantiomerization in hexacoordinated germanium dibromides and dichlorides.



Scheme 4. Non-regular mechanisms of the enantiomerization in coordination sets of hexacoordinate germanium dibromides with rupture of the O→Ge bond.

average Ge–X bond is the longest. The slightly negative $\Delta S^{\#}$ value for **4** does not disagree with the non-regular dissociative mechanism, that involves dissociation of the monodentate ligand and formation of a germacenium ion (Scheme 2).[1]

The possible non-regular processes include the dissociation of the monodentate ligand (**c**) followed by formation of a pentacoordinate germacenium ion (**A**), exchange of chelate ligand positions (**d**, **e**) and subsequent frontal nucleophilic attack of bromide-ion at the Ge atom (**f**) (Scheme 2). Taking into account the higher electroconductivity of the dibromides **3a**–**c** and **4** in comparison with the corresponding dichlorides [3], this mechanism seems more probable for the complex **4** in comparison with both **4-Cl₂** and **3a**–**c**. The activation barrier of **4** is significantly lower than the values found earlier for $[L_2Ge(Cl)]Y$ complexes (> 20 kcal mol^{-1}) [3] that are obviously capable of dissociation in solution to give germacenium ions of the type of $L_2Ge(Cl)^+$.

The mechanism of enantiomerization involving the dissociation of the O→Ge coordination bond followed by a Berry pseudorotation [20] in the pentacoordinated intermediate seems to be unlikely for the dibromides **3a**–**c**, **4** which has significantly lower activation energies than the corresponding dichlorides (Scheme 5).

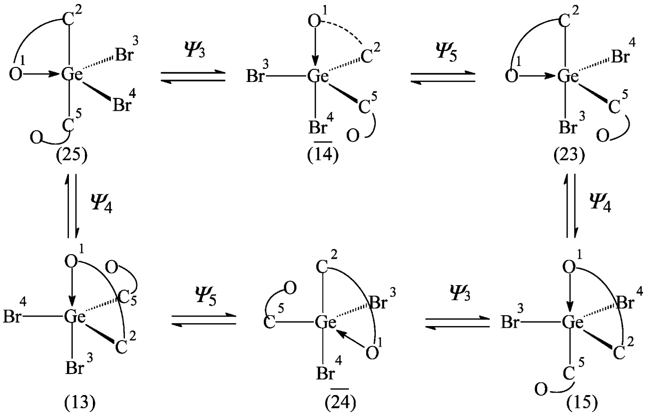
Such a mechanism must involve the formation of topomers with a diequatorial chelate ligand that requires the distortion of the O–Ge–C angle in the five-membered ring from ca. 120 to 90 °. Thus, the monodentate substituents can be the only ‘pivot’ ligands, and the process does not lead to equivalence of the oxygen atoms.

3. Conclusion

We found that in solutions of hexacoordinate dibromogermanes **3a**–**c** and **4** two exchange processes take place. One of them is a dynamic equilibrium between two diastereomers, OcCtBrc and OtCtBrt. The process proceeds at higher temperatures with an activation energy of about 15 kcal mol^{-1}. At lower temperatures the equilibrium shifts toward the OtCtBrt species.

On the basis of the influence of temperature on the isomer ratios, DNMR data and quantum-chemical calculations we suggest that the diastereomerization process proceeds via the sequence: (i) Ge–Br dissociation; (ii) nucleophilic attack of the Ge atom by a Br anion or neutral dibromide opposite to the leaving group.

The second process is an enantiomerization of the diastereomers with a *cis*-configuration of monodentate ligands. The activation energy of the process is lower (10–12 kcal mol^{-1}). In accordance with DNMR data, the dependence of the activation energy of enantiomerization on the O→Ge bond length (both experimental and calculated) indicates that a regular non-dissociative



Scheme 5. Mechanism for site exchange of acyclic ligands by pseudo-rotation in the pentacoordinate intermediate without inversion at germanium (ψ indicates Berry pseudo-rotation or similar process).

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[1] The very recent studies give higher $\Delta S^{\#}$ values for the **3a**–**c** complexes (by ~3–5 cal mol^{-1} K^{-1}) that is still in agreement with the discussed mechanism.

mechanism involving the formation of a neutral bicapped intermediate is dominant in solutions of the dibromides. Gradual lengthening of the Ge–Br bond due to the increase of the O → Ge coordination bond strength in some of the dibromides may lead to a predominant role of non-regular mechanisms involving a dissociation of halide-ion.

4. Experimental

4.1. NMR spectroscopy

The ^{1}H, and ^{13}C-NMR spectra of the compounds studied in $CDCl_3$, CD_2Cl_2 and CD_3CN were recorded on a 'Varian VXR-400' instrument (400.1 and 100.6 MHz, respectively). ^{1}H and ^{13}C chemical shifts were measured using tetramethylsilane as the internal reference.

Temperature calibrations were performed using the distances between the non-equivalent protons of methanol (-90 to $+30$ °C) and ethylene glycol ($+30$ to $+85$ °C) [21]. Activation parameters of the stereodynamic processes were calculated using DNMR-SIM software [22].

Non-empirical quantum-chemical calculations were performed on a FR 3-21G basis on a Silicon Graphics workstation using SPARTAN 5 software [23].

*4.2. Bis(O–Ge)chelate bis[(N-methyl)acetamidomethyl]dibromogermane (**4**)*

A solution of bis(bromomethyl)dibromogermane (1.7 g, 4 mmol) in *o*-xylene (8 ml) was added dropwise to a solution of *N*-trimethylsilyl-*N*-methylacetamide (1.18 g, 8 mmol) in *o*-xylene (8 ml). The reaction mixture was refluxed over a period of 2.5 h and then stirred for 16 h while cooling to room temperature The crystalline precipitate was filtered, washed with toluene and dried in vacuo to give 1.1 g (2.72 mmol, 68%) of the dibromide **4**.

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