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Modelling of Hexacoordinated Transition States of Germanium Based on the Crystal Structures of Germanium-substituted Bis(lactamo-*N*-methyl)germanes L_2GeX_2 and L_2GeXY (X, Y = Hal, OTf, BF_4, I_3)

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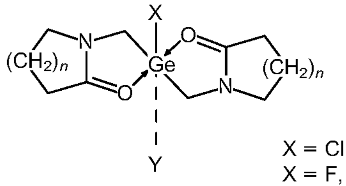
X-Ray structural data on the investigation of hypervalent organogermanium compounds testify to the absence of essential differences in the structural parameters between the series of penta- and hexacoordinated compounds, regarded as models for S_N-Si reactions.

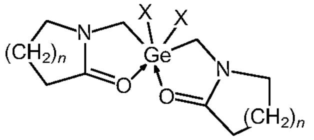
The modelling of inter- and intramolecular processes of the nucleophilic substitution type or the alteration of substituent positions on atoms with labile coordination environments (metals, Si, Ge) by means of a series of static structures possessing a higher coordination of these atoms has been known for a long time[1,2] and is now a common approach.[3,4] In a recent paper[5] on the structural modelling of S_N2 reactions at the tetracoordinated Si atom some essential methodological conclusions were made. In particular, it was shown that the displacement Δ of the M atom out of the plane of the equatorial substituents R in the axial symmetrical hypervalent fragment $X–MR_3–X'$ may be considered as a geometric parameter which adequately reproduces the state of the pentacoordinated atom M. The dependences between the d_{M-X} ($d_{M-X'}$) bond lengths in hypervalent fragments and Δ in the case of high homogenity of the model structure series represent smooth quasi-hyperbolic functions whose specific forms are determined by the nature of X and, to some extent, by the steric conditions of the M–X component (for instance, whether it is involved in the chelate ring).

Experimental modelling of S_N2 reactions with a hexacoordinated reaction centre has previously been considered only as a theoretical possibility, but our recent synthesis and X-ray structural studies[6–9] of hexacoordinated organogermanium compounds **1**–**11** including those with 5 + 1 coordination (*i.e.* with a strongly elongated sixth bond) allowed us to begin a practical realization of such modelling.



L_2GeXY
trans-(5 + 1)

X = Cl, Y = OTf, *n* = 1(**1**), 2(**2**), 3(**3**)[6]
X = F, Y = BF_4, *n* = 3(**5**)[7]
X = Cl, Y = I, *n* = 3(**6**)[8]
X = Cl, Y = I_3, *n* = 3(**7**)[8]



L_2GeX_2
cis-(2 + 4)

X = F, *n* = 3(**4**)[7]
X = Br, *n* = 3(**8**)[8]
X = Cl, *n* = 1(**9**), 2(**10**), 3(**11**)[7]

The uniform series of models **1**–**11** studied includes molecules with a 5 + 1 coordination of the Ge atom [distorted trigonal bipyramid (TBP) and long sixth bond] and with a distorted 2 + 4 coordination (two covalent Ge–C and four coordination Ge–X bonds). The identical monodentate substituents at the Ge atom in the bis(lactamo-*N*-methyl)germanes studied take a *cis*-configuration while in the case of the different substituents (X≠Y) both chelate rings and monodentate ligands are in a *trans*-orientation. In addition to the similarity of the chelate rings, an essential feature of the molecules considered is the presence of two hypervalent fragments (O–Ge–O and X–Ge···Y in the first and two O–Ge–X in the second group); the Ge–O distances reach 2.0–2.3 Å in the O–Ge–O fragments and 3.35 Å in the case of Ge–OTf groups, while the usual Ge–O bond lengths in tetrahedral Ge are *ca.* 1.75 Å.[10]

If hypervalent fragments of the hexacoordinated atom are considered independently, a "natural" parameter defining its state (intermediate between TBP and octahedral coordination) is a solid angle Ω, confined within the directions of four pseudo-equatorial bonds and containing an axial ligand. For a symmetrical description of coordination states relative to the ideal octahedron we proposed[7] to use a value of

$= -2\pi$, similar, with respect to the symmetrization relation, to the parameter Δ for **TBP** (Fig. 1). In the case of pentacoordination with axial symmetry along a hypervalent fragment the values of Δ and $\Delta\Omega$ are related almost linearly.

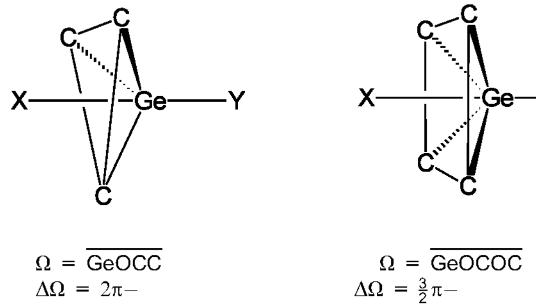


Fig. 1 Ω and $\Delta\Omega$ evaluation for TBP and octahedral configurations.

The dependence of $d_{\mathrm{O-Ge}}$ on $\Delta\Omega$ for the structures **1**–**11** is shown in Fig. 2. It should be noted that the O→Ge bonds, both involved and not involved in chelate rings and so having opposite signs of $\Delta\Omega$, are not distinguished here, which results in additional scattering of the $d(\Delta\Omega)$ points relative to the regression curve. One more reason for the scattering mentioned consists of large errors in the calculation of $\Delta\Omega$ in those cases for which the long sixth bond is considered as equatorial, *viz*. for O–Ge–O hypervalent fragments. The positions of such ligands as I, I_3, BF_4 and OTf, whose interaction with the Ge atom is predominantly ionic, is very sensitive to the influence of the surroundings, which is reflected in the symmetry distortions of the Ge atom coordination polyhedron. Therefore, in Fig. 2 the area of $d_{\mathrm{O-Ge}}$ around 2.0 Å is shown as a whole, without specifying the positions of individual points. This area contains the points corresponding to O–Ge distances in hypervalent fragments O–Ge–O with O atoms involved in lactamo-*N*-methyl ligands of *trans*-L_2GeXY compounds.

Despite the drawbacks mentioned above and a scarcity of available data, the $d(\Delta\Omega)$ correlation for O→Ge bonds of hexacoordinated germanium is sufficiently clear-cut. It is of interest to compare it with similar relations for pentacoordination. Unfortunately, contrary to the structures of pentacoordinated silicon, such a complete and uniform series of similar organogermanium structures have still not been studied. Nevertheless, the data summary in ref. 11 allow us to construct approximate $d_{\mathrm{O-Ge}}(\Delta)$ curves for two cases of the equatorial surrounding of Ge atoms (GeC_3 and $GeCCl_2$).

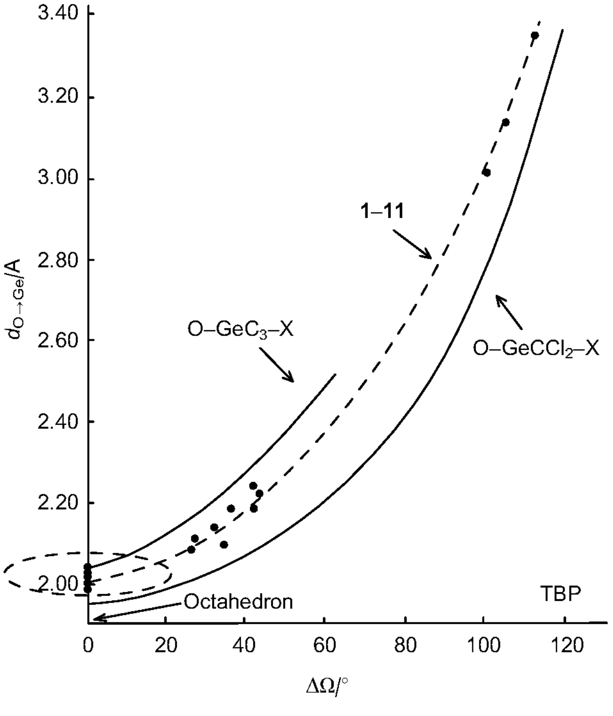
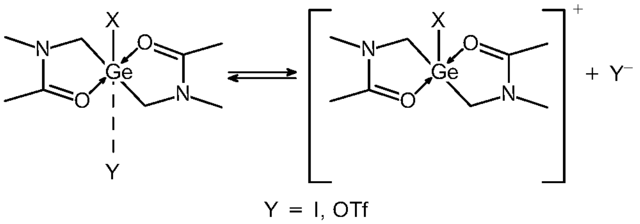


Fig. 2 Correlation curves $d(\Delta\Omega)$ for hypervalent fragments in compounds of hexa- (dashed line) and pentacoordinated germanium.

Normalization of these dependences to the curve based on the parameters of structures **1**–**11** is rather simple: an almost linear relation between Δ and $\Delta\Omega$ in TBP is to be used with alteration of the $\Delta\Omega$ scale, since the range of this parameter variation for pentacoordination (180°) is 1.5 times greater than for hexacoordination (120°). The renormalized curves for the pentacoordinated Ge atom are also shown in Fig. 1. Agreement between all three curves looks impressive. In fact, if the mutual influence of hypervalent fragments in the structures **1**–**11** can be ignored,[7] the $d(\Delta\Omega)$ correlation curve has to correspond to the curve for a pentacoordinated Ge atom with two C atoms and <u>one</u> electronegative atom (intermediate in character between atoms participating in the second hypervalent fragment) in the equatorial surroundings. Thus, an intermediate position of the $d_{\mathrm{O-Ge}}(\Delta\Omega)$ curve for the hexacoordinated Ge atom which fits well with such an assumption implies the absence of not only a *qualitative* but, in fact, a *quantitative* difference in the structural parameters between the penta- and hexacoordinated Ge atom relative to the selected hypervalent fragment, at least in the series of compounds considered.

It should be noted that in the ionic fluorotetrafluoroboride **5** and nearly ionic (in the crystal state) iodide **6** and triiodide **7**, coordination polyhedra of the Ge atom constitute a distorted **TBP** with axial hypervalent fragment O–Ge–O, two C atoms and substituent X in equatorial positions, so it may be considered as a germacenium cation with pentacoordinated Ge atom, stabilized by intramolecular coordination. Considerable elongation of one of the pseudo-axial bonds with non-chelate monodentate ligands in mixed bis-chelate compounds *trans*-$L_2Ge(X)Y$ (L-chelate lactam ligand) allows us to suggest the possibility of dissociation of these compounds in sufficiently polar solvents with formation of the corresponding $[L_2GeX]^+$ cations. Such an assumption is confirmed by conductometric measurements (Table 1). Electroconductivity of *cis*-dichlorides **9**–**11** in CH_2Cl_2 turned out to be rather low, as in the cases of penta- and tetracoordinated Ge chlorides. On substitution of one halogen atom in dichlorides **9**–**11** for an iodine or triflate group electroconductivity is increased by *ca*. an order of magnitude and becomes close to the electroconductivity of fluorotetrafluoroborate **5**, which has an apparently ionic structure in the crystalline state. Thus, the present data testify to the reality of existence in solution of the germacenium cations with a pentacoordinated Ge atom stabilized by intraionic coordination:



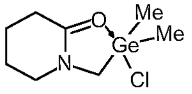
Y = I, OTf

In conclusion, it should be noted that the existence of stable compounds of hexacoordinated germanium testifies to the authenticity of an *associative mechanism* with formation of intermediates with an hexacoordinated Ge atom in S_N reactions of pentacoordinated Ge compounds with such relatively poor leaving groups as chloride.

In turn, a *dissociative mechanism* is very probable for reactions of hexacoordinated Ge compounds $L_2Ge(X)Y$ with intermediate formation of germacenium ions $[L_2GeX]^+$ stabilized by intraionic coordination.

Table 1 Electroconductivity Λ of solutions of hypervalent organogermanium compounds in CH_2Cl_2 at 25 °C.

Compound	Concentration/mmol dm^{-3}	Λ/mSm cm^2 $mmol^{-1}$
2	5.7	1550
5	1.4	4040
8	1.9	1200
10	6.7	93
12	18.9	6.4
13	7.8	358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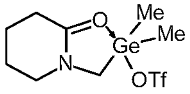
13

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