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ARTICLE TYPE

New oligogermane with five coordinate germanium atom: the preparation of 1-germylgermatrane

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The first example of oligogermanes, $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3\text{Ge}-\text{Ge}(\text{SiMe}_3)_3$ (**1**), containing hypercoordinate germanium atom was prepared and characterized by various methods (NMR, UV/vis, X-ray analysis). The electronic structure of the compound **1** was investigated by DFT calculations.

During the last three decades the compounds of the 14th Group elements (E= Si, Ge, Sn), containing element–element bonds, attract particular attention due to their unusual properties.¹ The delocalization of electrons of E–E bonds (σ -conjugation) is the distinctive feature of these compounds. Such conjugation results in appearance of a new unique properties (conductivity, luminescence, thermochromism, non-linear optical properties) typical for unsaturated hydrocarbons.² Thus, these compounds may be considered as “molecular conductors”. Broad interest to derivatives of this type may be caused by a construction of new prospective devices or an application for synthesis of unusual compounds.³ Many important features have been found for Si and Sn derivatives where E–E chain contains at least one hypervalent (hypercoordinate) 14th Group element. Several hypercoordinate Si complexes, mainly the chlorinated oligosilanes (**Ia–g**) and related compounds (**Ih, i, k**), have been prepared and studied by X-ray analysis (Chart 1, **Ia–l**).⁴ As it was found for the oligosilanes with additional intramolecular donor groups, as in **Id**,⁵ such intramolecular coordination leads to conformation of silicon chain where the electrons delocalization is capable, so hypercoordination may improve delocalization. The mono (**Ij**)⁶ or dianionic (**II**)^{6–7} complexes, containing hypercoordinate Si atoms, were obtained, too. Analogously, the related Sn derivatives have been prepared (Chart 2, **II**).^{8,9} However, no such Ge compounds (with Ge–Ge bond, where one germanium atom is hypercoordinate) have been prepared to date. According to the data published, the interaction of an external donor with oligogermanes, containing acceptor substituents, leads to decomposition of the oligogermane with Ge–Ge bond rupture.¹⁰ Thus, one can conclude that Ge–Ge bond is unstable towards additional donor interaction unlike Si–Si and Sn–Sn bonds. Only several digermanes with constrained additional interaction are reported to date (Chart 3, **IIIa–f**). First group includes compounds in which the Ge–Ge bond is stabilized against the rupture with special ligand structure where one acidic group

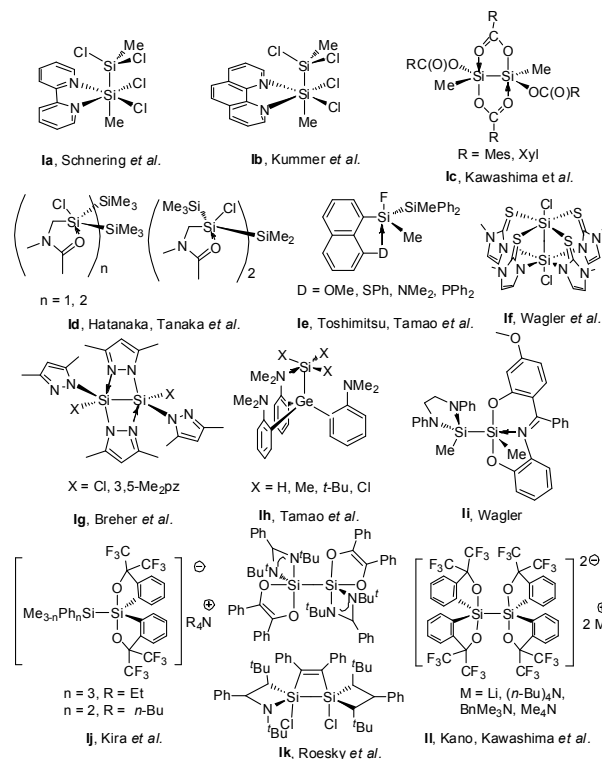


Chart 1 Molecular structures of hypercoordinate oligosilanes and related compounds (**Ia–l**).

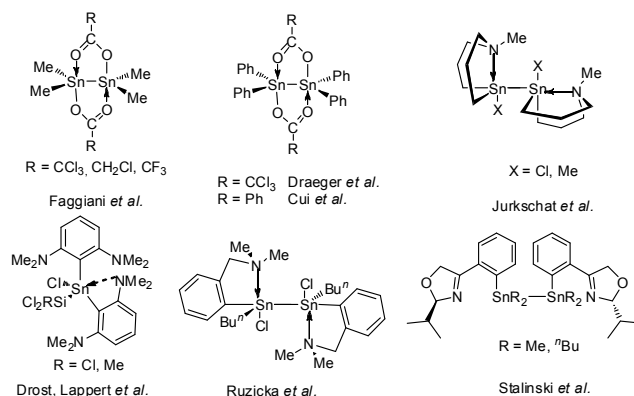


Chart 2 Molecular structures of hypercoordinate oligostannanes and related compounds (**II**).

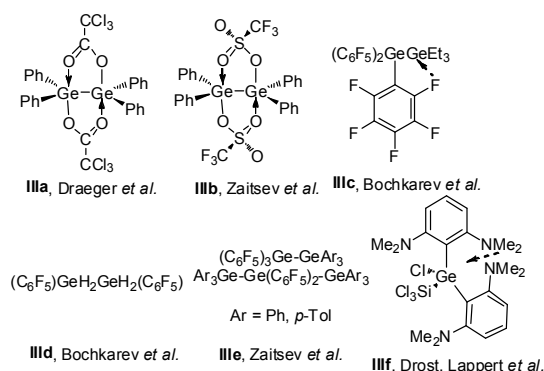


Chart 3 Molecular structures of hypercoordinate oligogermanes and related compounds (**IIIa-f**).

connected with both Ge atoms as in **IIIa**¹¹ and **IIIb**.¹² The others have very long additional contacts due to the ligand structure (Ge...F) and cannot be considered as compounds with any noticeable interaction (**IIIc**,¹³ **IIId**¹⁴) or related compounds (**IIIe**).¹⁵ A number of mixed (*o*-C₆H₄NMe₂)₃Ge-EX₃ derivatives (**II**) was obtained and investigated by XRD. The very weak N→E contacts were found in these compounds, too.¹⁶ The similar situation was found for **IIIf**.¹⁷ Thus, one can conclude that unusual type of substituents at Ge atoms may stabilize the Ge-Ge fragment with hypercoordinate Ge atom.

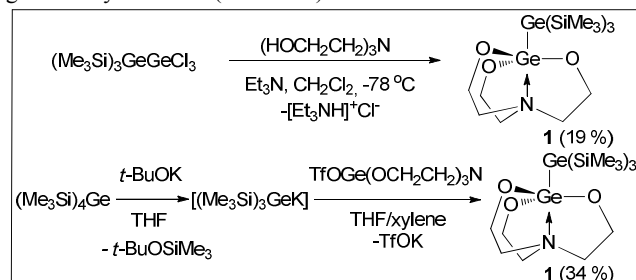
The structure and chemical behavior of metallatranes, N(CH₂CH₂O)₃M-X (**A**) – cyclic derivatives of trialkanolamines – have been extensively studied, and compounds of the elements have been reported all over the periodic table.¹⁸ These derivatives usually contain a transannular interaction between metal atom and the bridgehead nitrogen atom (exist in *endo* form).

Most of the previous works on metallatranes has been focused on the synthesis, properties and structural studies in order to confirm the supposed intramolecular N→M coordination. Moreover, many silatranes show biological activity.¹⁹ The main focus was to prepare the derivatives with different X and to answer on the question: «How the nature of substituent X does affects the strength of the transannular N→M bonding?» Now the conventional point of view is that for derivatives of Si and Ge the fragment N→M–X should be considered as three-center four-electron hypervalent interaction.²⁰ Thus, the substituent X with higher nucleophilicity lead to stronger interaction (the N→M distance is shortening). The derivatives with halogens, organyl radicals and different oxy substituents as X have been extensively studied to date. The other types of X are very rare. For example, several silatranes²¹ and stannatranes²² with transition metal as X have been prepared. According to the published data no derivatives of 14th Group elements with E (E = Si, Ge, Sn) containing substituent as X [N→Si(Ge,Sn)–Si(Ge,Sn)R₃] have been prepared to date. Before this work started we have suggested that *atrane* framework is the suitable ligand for the stabilization of hypercoordinate Ge atom in oligogermanes.

Here we present the synthesis, crystal structure, and electronic properties of the first Ge compound, N(CH₂CH₂O)₃Ge–Ge(SiMe₃)₃ (**1**), with non-constrained hypercoordination of germanium atom bounded to other Ge atom, which is unusual in terms of a chemical species prepared to date.

The compound **1** was obtained in the reaction of (Me₃Si)₃GeGeCl₃ with triethanolamine (Scheme 1). The low

yield of the product may be explained by competitive decomposition of intermediates with formation of colored insoluble precipitates, which possibly present the polygermanes. The similar chemical behavior was found earlier for the related Si derivatives in the presence of additional donors.²³ The alternative way to compound **1** includes the action of (Me₃Si)₃GeK (generated in situ using Marschner's procedure²⁴) on 1-germatranyl triflate²⁵ (Scheme 1).



Scheme 1

The compound **1** was isolated as a colorless solid, readily soluble in common organic solvents. The molecular structure of the complex **1** was investigated in solid state by X-ray analysis (Fig. 1, Tables 1, S1) and in solution by multinuclear NMR (Table S2, Fig. S1-S3) and UV/vis (Fig. S4, S5) spectroscopy. In ¹H, ¹³C, ²⁹Si NMR spectra there are only one set of signals that corresponds to highly symmetric structure. The protons in OCH₂- or NCH₂-groups are magnetically equivalent that results in appearance of two triplets in ¹H NMR spectra.

The structure of **1** contains three crystallographically independent molecules. One of them occupies the general position while two others lie on the mirror planes. In all molecules atrane fragments and all SiMe₃ groups are disordered over two positions with occupancy ratios 0.5/0.5. The structure was checked for supercell and low-symmetry space groups. These possibilities were not confirmed. The compound **1** is a first example of oligogermanes containing Ge-Ge fragment with one hypercoordinate Ge atom. According to X-ray diffraction analysis data there are two different Ge atoms: the coordination polyhedron of pentacoordinate Ge atom may be described as distorted trigonal bipyramid, while tetracoordinate Ge atom possesses distorted tetrahedral geometry. The key parameter for neutral compound of pentacoordinate Ge, *viz.* Ge–Donor bond, is the longest Ge←N bond (see Table 1) among those previously found in germatranes (2.08–2.29 Å^{18b,c}). This fact is in agreement with *3c4e* theory due to the strong electron donor nature of (Me₃Si)₃Ge group which leads to decreasing of attraction of Ge center for dative bond formation in atrane framework. The length of Ge–Ge bond in **1** (2.41–2.42 Å) is close to that previously found for digermanes.^{2a} It should be noted that according to *3c4e* theory for pentacoordinate Ge atom apical bond (Ge(11)–Ge(12)) (Fig.1) in TBP (in *trans* position against donor atom) should be elongated in comparison with that for tetracoordinate atom (ordinary Ge–Ge bond).^{2a} However, the length of ordinary Ge–Ge bond in digermanes is very sensitive to steric volume of substituents at Ge atoms: Ph₃GeGeMe₃ (2.418(1) Å), Ph₃GeGeEt₃ (2.4253(7) Å), (*i*-Pr)₃GeGePh₃ (2.4637(7) Å), (Me₃Si)₃GeGe(SiMe₃)₃ (2.4787(7) Å), (*t*-Bu)₃GeGe(Bu-*t*)₃ (2.710(1) Å). So, the comparative weak transannular interaction does not affect significantly on length of Ge–Ge bond.

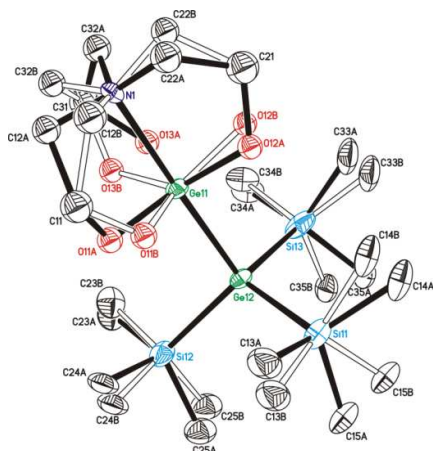


Fig. 1 Molecular structure of **1**. Molecule lies on general position; hydrogen atoms have been omitted for clarity. Disorder ratios are 0.5/0.5 for all sites (three independent molecules: A, B, C).

Table 1 Selected experimental (molecules A, B, C) and calculated bond lengths (Å) and angles (deg) for **1**

Value	Experimental			Calculated
	molecule A	molecule B	molecule C	
Ge←N	2.357(5)	2.423(7)	2.275(7)	2.570
Ge-Ge	2.4188(9)	2.415(1)	2.412(1)	2.458
Ge-O	1.780(8)- 1.837(8)	1.763(8)- 1.840(8)	1.801(7)- 1.812(8)	1.850
Ge-Si	2.362(2), 2.366(2), 2.369(2)	2.366(2), 2.366(2), 2.368(3)	2.366(3), 2.371(2), 2.371(2)	2.424
Ge-Ge-N	178.4(1)	179.9(2)	177.5(2)	176.5
Ge-Ge-Si	107.26(5), 105.85(5), 106.27(5)	105.97(5), 105.97(5), 104.78(7)	109.01(7), 107.34(5), 107.34(5)	106.0, 104.8, 106.9
Ge-Ge-O	99.8(3)- 101.7(3)	101.6(3)- 103.0(3)	98.2(3)- 101.4(3)	106.6, 102.9, 102.0
C-O-Ge	115.7(6)- 118.0(6)	119.9(7)- 123.5(14)	119.8(7)- 121.5(7)	121.2, 120.2, 121.9

The distinctive feature of oligogermanes in comparison with similar carbon analogs is a highly intensive absorption in UV/vis spectra ($\epsilon > 10^4 \text{ M}^{-1}\text{cm}^{-1}$). The main absorption band for **1** (221 nm in CH_2Cl_2 , $\sigma \rightarrow \sigma^*$ transition) is typical for Ge-Ge groups in digermanes. The presence of hypercoordination in **1** has a negligible effect on UV/vis absorption energy.¹²

The calculated at B3LYP/DGDZVP level of the theory distances and angles for **1** are close to experiment (Table 1; Fig. S6). The calculated at the BP86/TZ2P+ level in gas phase UV/vis spectra give the bands close to 234 and 225 (oscillator strengths are equal to 0.014 and 0.011, correspondingly) nm that indicates the $\sigma \rightarrow \sigma^*$ transitions. One can see from Fig. 2 that these transitions may be characterized as transition from HOMO (electron density is mainly located on the $[\text{Si}(\text{Me}_3)]_3$ with small contribution on the Ge-Ge bond) to LUMO+1 and LUMO+2 (anti-bonding Ge-Ge bond) orbitals.

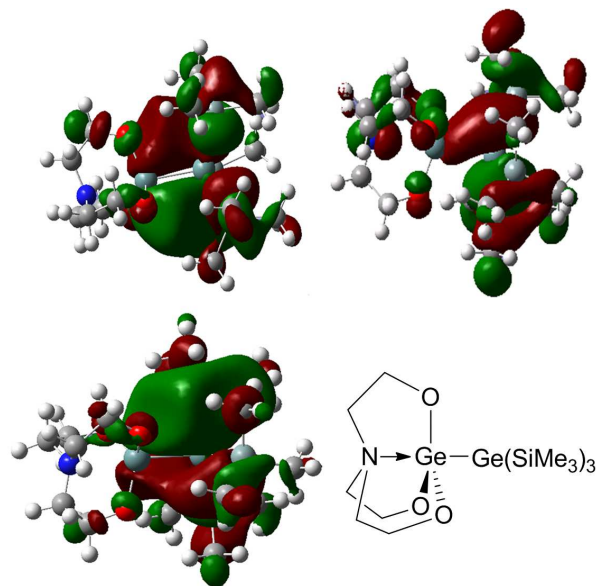
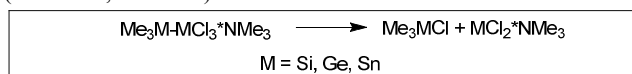


Fig. 2 Molecular orbitals of **1** (HOMO (left), LUMO + 1 (middle), LUMO + 2 (right)).

The population of the oxygen and nitrogen lone electron pairs less than 2 indicates that they interact with the anti-bonding Ge-O orbitals (Table S3, Fig. S7). Perturbation theory of 2nd order approximation of NBO indicates interaction between lone electron pairs of oxygen and nitrogen atoms and antibonding Ge-O orbitals. In fact the decrease the population of the lone electron pairs from 2e indicates that they are involved in the interaction, i.e. electron density is shifted from them. The total energy of these delocalization interactions is close to bond dissociation energy of Ge-Ge bond calculated at B3LYP/DGDZVP (60 kcal/mol) and at BP86/TZ2P+ (76 kcal/mol).

For clearing the stability of complexes of the elements of 14th Group with hypercoordinate element atom we performed calculations of decomposition reactions for related complexes, $\text{Me}_3\text{M}-\text{MCl}_3 \cdot \text{NMe}_3$ (M = Si, Ge, Sn). The complexes with NMe_3 decompose in accordance with the mechanism shown below (Scheme 2, Table S4).



Scheme 2

We have found that these three starting complexes are thermodynamic unstable and should decompose according to Scheme 2. However, the activation energy of decomposition of Ge complex is considerably less than analogous values for Si and Sn derivatives (Table S4). This fact is in accordance with the experimental data (see above), that Ge-Ge compounds with hypercoordinate Ge atom are the most unstable among 14th Group compounds.

In conclusion, in this work we presented the first example of oligogermane with hypercoordinate Ge atom. This investigation stimulated researchers in various science fields for novel more detailed investigation on oligo- and polygermane.

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- [†] Electronic Supplementary Information (ESI) available: synthetic methods and procedures, characterization data (experimental and calculated ¹H, ¹³C, ²⁹Si NMR spectra), computational data, and crystallographic data (CIF). CCDC 948962 contains the supplementary crystallographic data for compound 1. See DOI: 10.1039/b000000x/
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The first example of hypercoordinate oligogermanes was prepared and characterized.

