Donor-Stabilized Germyl Cations. Stable Pentacoordinate Germanium Chloride [$PhGe(OCH_2CH_2NMe_2)_2$][Cl]

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Intramolecularly coordinated phenylbis[*N*-(dimethylamino)ethoxy]germanium chloride (**1**) has been prepared, and its structure has been investigated by ^{1}H and ^{13}C NMR spectroscopy in solutions and by X-ray diffraction analysis in the crystal. Compound **1** tends to ionize in hydrogen-bond-donor solvents, such as $CHCl_3$, with the formation of the ionic pentacoordinate form [$PhGe(OCH_2CH_2NMe_2)_2$][Cl] (**1b**) dominating over the neutral hexacoordinate form $PhGe(OCH_2CH_2NMe_2)_2Cl$ (**1a**). Crystals grown from $CHCl_3$ also represent the form **1b**. Salt **1b** is the first compound stable under ambient conditions containing a free germanium cation of the type $[RGeX_2]^+$ (R = Alk, Ar; X = substituent bonded to the germanium atom by a heteroatom: Hal, OR, NR_2) without bulky substituents at the germanium atom in the presence of the highly nucleophilic chloride anion.

Introduction

The ability of heavier main-group elements to accommodate more than eight electrons in their valence shells, thus forming so-called hypervalent or hypercoordinate compounds, is well-established, and the chemistry of such compounds in all its different facets has been regularly reviewed over the years. Group 14 elements are in the center of these investigations.[1]

Compounds containing intramolecularly coordinated ligands are prominent representatives of this class. We have recently reported the ability of the β-dimethylaminoethoxy ligand to stabilize thermodynamically divalent germanium and tin derivatives in the monomeric form under ambient conditions without involvement of any steric shielding of the E^{14} (E^{14} = group 14 element) atom.[2]

In this paper, we report on the use of the β-dimethylaminoethoxy ligand for the synthesis of a stable compound containing a pentacoordinate germyl cation, $[PhGe(OCH_2CH_2NMe_2)_2]^+$. The group 14 cations, i.e., silyl, germyl, or stannyl, stabilized by chelating ligands are of significant current interest.[3]

Three complementary strategies for the generation of stable silyl, germyl, or stannyl cations are available: (1) to reduce the probability of a nucleophilic attack at the cationic center by the use of counterions and solvents of very low nucleophilicity; (2) to hamper the approach of a nuclephile by sterically demanding substituents at the E^{14} center; (3) to stabilize the cations thermodynamically by introduction of auxiliary NR_2 or OR groups in the side chain, the electron lone pairs of which could, in principle, be capable of bonding to the empty p-orbital of the E^{14} center.

Stable group 14 salts of this kind with highly nucleophilic anions, such as chloride, can be prepared, as a rule, only in the presence of bulky ligands directly bonded to the E^{14} center.[3b,l,n,4] Nevertheless, recently, an X-ray diffraction study of the sterically unencumbered silicon complex [$(AcN(Me)CH_2)_2SiCl$][Cl][3j] containing a free silyl cation has been reported. The salt [PhGe($OCH_2CH_2NMe_2)_2$][Cl] (**1b**) considered in the present paper is the first stable compound containing (i) a cation of the type $[RGeX_2]^+$ (R = Alk, Ar; X = substituent bonded to Ge atom by a heteroatom: Hal, OR, NR_2) and (ii) a free germyl cation

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10.1021/om0600745 CCC: $33.50

without bulky substituents at the germanium atom in the presence of the chloride anion.

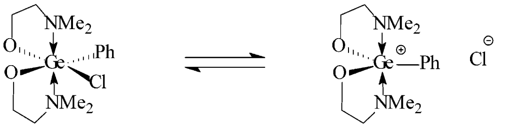
Results and Discussion

The compound $PhGe(OCH_2CH_2NMe_2)_2Cl$ (**1**) was prepared in high yield by the substituent exchange reaction of $PhGeCl_3$ with $Et_3GeOCH_2CH_2NMe_2$ using a 1:2 reagent ratio in THF (eq 1).

$$PhGeCl_3 + 2\ Et_3GeOCH_2CH_2NMe_2 \xrightarrow{THF} PhGe(OCH_2CH_2NMe_2)_2Cl + 2\ Et_3GeCl \quad (1)$$

Complex **1** is a white crystalline solid that is highly sensitive to traces of moisture. It is slightly soluble in THF and toluene, highly soluble in CH_2Cl_2 and $CHCl_3$, and insoluble in hexane and benzene.

The ^1H and ^{13}C NMR spectra of **1** in $CDCl_3$ at room temperature reveal the association–dissociation equilibrium between the neutral hexacoordinate form $PhGe(OCH_2CH_2NMe_2)_2Cl$ (**1a**) and the ionic pentacoordinate form $[PhGe(OCH_2CH_2NMe_2)_2][Cl]$ (**1b**) (eq 2).



1a **1b** (2)

The ionic form **1b** dominates over the neutral form **1a** in a 6.5:1 ratio. The form **1b** is manifested as two singlets of the diastereotopic methyl groups of the nitrogen atom at 2.00 and 2.57 ppm, two multiplets of the diastereotopic protons of the CH_2N groups centered at 2.75 and 3.02 ppm, and a multiplet of the CH_2O protons centered at 3.97 ppm in the ^1H NMR spectrum. In the ^{13}C NMR spectrum, the same chemical groups give rise to two singlets at 43.37 and 44.15 ppm, a singlet at 56.09 ppm, and a singlet at 57.84 ppm, respectively. In contrast, three signals both in the ^1H (a singlet at 2.47 ppm and two multiplets centered at 2.95 and 3.80 ppm) and the ^{13}C (three singlets at 41.78, 54.80, and 58.05 ppm) NMR spectra, corresponding respectively to NMe_2, CH_2N, and CH_2O groups, belong to the neutral form **1a**. All signals are significantly broadened. The general shape of the spectra points to the fact that **1a** is characterized by a fast exchange of the NMe_2 groups (on the time scale of NMR), while the interconversion between **1a** and **1b** proceeds at a moderate rate. A more detailed variable-temperature NMR study of **1** will be the subject of further investigations.

The structure of **1b** was studied by X-ray diffraction analysis. Single crystals of **1b** suitable for X-ray crystallography were obtained from a $CHCl_3$ solution. The form **1b** crystallizes as a solvate with two chloroform molecules. The crystal structure of $\mathbf{1b}\cdot 2CHCl_3$ is shown in Figure 1 along with the atomic numbering scheme and selected bond lengths and angles.

The X-ray diffraction study clearly confirms the ionic nature of **1b** with its well-separated pentacoordinate $[PhGe(OCH_2CH_2NMe_2)_2]^+$ cations and chloride anions. The closest Ge···Cl distance is 4.668(2) Å, which decisively excludes any bonding interactions. This is one of the longest $Ge^+\cdots A^-$ (A = anion) distances among those reported in the literature.[4,5] Longer $Ge^+\cdots Hal^-$ distances were observed only in (a) a sterically encumbered germanium complex, in which the pentacoordinate germyl cation is stabilized by the 2,6-bis(dialkylaminomethyl)-4-(*tert*-butyl)phenyl tridentate ligand (**2**)[4] (the closest Ge···Cl distance is 4.977(7) Å) and (b) the $[MamxGe(Me)(Bu^t)][I]$ (Mamx = 2,4-di-*tert*-butyl-6-(*N*,*N*-dimethylaminomethyl)phenyl) (**3**)[5e] and $[MamxGe(Me)(Tip)][I]$ (Tip = 2,4,6-$^iPr_3C_6H_2$) (**4**)[5g] complexes with the tetracoordinate germanium atoms also bearing bulky substituents, in which the Ge···I distances are equal to 4.887(1) and 5.160(3) Å, respectively.

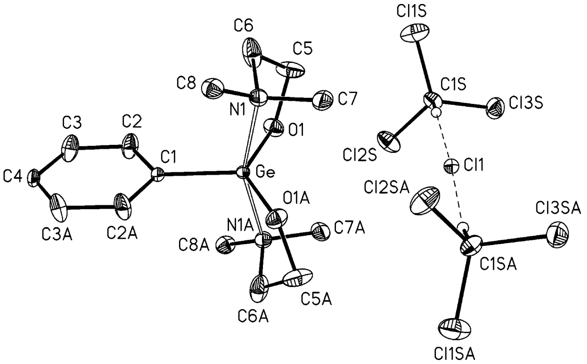


Figure 1. Crystal structure of $\mathbf{1b}\cdot 2CHCl_3$ with 40% probability ellipsoids (most H atoms are omitted for clarity). The label A denotes symmetrically equivalent atom relative to the 2-fold axis. The coordination Ge←N bonds are shown by double lines and the H-bonds are shown by dashed lines. Selected bond lengths (Å) and angles (deg): Ge–O1 1.780(3), Ge–C1 1.912(4), Ge←N1 2.092(4), Ge···Cl1 4.668(2), O1–Ge–C1 113.8(2), O1–Ge←N1 85.3(2), N1→Ge–C1 101.1(1), O1–Ge–O1^i 132.5(3), N1→Ge←N1^i 157.8(2), O1–Ge←N1^i 85.8(2). Symmetry operation i: $1 - x, y, 1.5 - z$.

The chloride anion is bonded to the chloroform solvate molecules by hydrogen bonds $C{-}H\cdots Cl^-$ (Cl1···C1S 3.363(3) Å, Cl1···H1S 2.38 Å, Cl1···C1S–H1S 167°) (Figure 1).

It is of interest that in (aza(14)annulene-methylthiolato)germanium iodide (**5**) and (aza(14)annulene-methylselenolato)germanium iodide (**6**) complexes,[5d] despite the presence of iodide counterions, the shortest intermolecular Ge···X (X = any atom of anion or solvent molecules) distances are those between the germanium atom and the chlorine atoms of one of the solvate chloroform molecules equal to 4.143(2) and 4.357(2) Å in **5** and 4.170(5) and 4.381(5) Å in **6**. The germanium atoms in complexes **5** and **6** adopt square pyramidal (SP) geometries.

Complex **1b** has intrinsic C_2 symmetry and occupies a special position on the 2-fold axis in the crystal structure. Compound **1b** is chiral. The enantiomers cocrystallize in the centrosymmetric space group *C*2/*c*.

The geometry of complex **1b** corresponds to a distorted trigonal bipyramid (TBP) with the two β-dimethylaminoethoxy ligands coordinated in chelating fashion. Two oxygen and one carbon atom occupy the equatorial positions, whereas two nitrogen atoms are in the axial positions. This is the most typical geometry for pentacoordinate bis-chelates with two nitrogen-donor ligands.[6] The distortions are manifested in a deviation of

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(i) the $N\rightarrow Ge\leftarrow N$ angle (157.8(2)°) from the ideal value of 180° and (ii) the equatorial O−Ge−O and C−Ge−O angles from the ideal value of 120°. Interestingly, the deviation from TBP geometry for crystal **1b** is very similar to that in related pentacoordinate silicon complexes, as evident from the O−Si−O and $N\rightarrow Si\leftarrow N$ angles, which are in the ranges 134.0−137.0° and 155.0−157.0°, respectively. These values correspond to a substantial distortion of TBP along the TBP→SP coordinate, as calculated from the difference between the $N\rightarrow E^{14}\leftarrow N$ and $O-E^{14}-O$ angles [$\%TBP = 100(NE^{14}N - OE^{14}O)/60$].

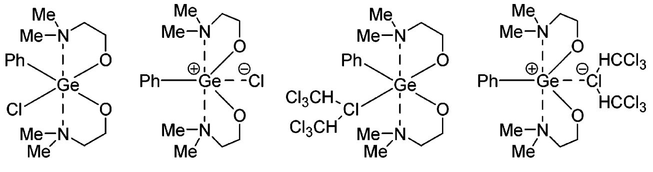
Although the Ge···Cl distances considerably exceed the sum of the van der Waals radii of Ge and Cl (∼3.70 Å),[7] the chloride anions apparently induce widening of the O−Ge−O angles (Figure 1).

The intramolecular $Ge\leftarrow N$ coordination bonds in the germyl cation of **1b** (2.092(4) Å) are very close in length to those in the related neutral hexacoordinate complexes (2.069(4)−2.132(4) Å).[8] However, they are considerably shorter than the $Ge\leftarrow N$ bonds in the sterically hindered pentacoordinate germyl cation stabilized by the 2,6-bis(dialkylaminomethyl)-4-(*tert*-butyl)phenyl tridentate ligand (2.31(2) and 2.36(2) Å).[4]

In addition, the covalent bonds to germanium in the germyl cation of **1b** are generally shorter than the corresponding bonds in the related neutral hexacoordinate complexes, which might be expected in positively charged species.

Theoretical DFT Study

Theoretical calculations at the density functional level of theory (PBE/TZ2p)[9] have been performed for covalent **A** and ionic **B** forms of molecule $Ph\text{-}Ge(OCH_2CH_2NMe_2)_2Cl$ (for calculation details, structures, and energetic parameters, see the Supporting Information). Covalent **C** and ionic **D** forms of the solvate $Ph\text{-}Ge(OCH_2CH_2NMe_2)_2Cl\cdot 2CHCl_3$ have also been considered. All molecules studied contain two $Ge\leftarrow NMe_2$ coordination bonds. The isomers with broken coordination bonds have been excluded from consideration.



A **B** **C** **D**

The calculated structure of $[Ph\text{-}Ge(OCH_2CH_2NMe_2)_2][Cl]\cdot 2CHCl_3$ (**D**) and the X-ray data for $\mathbf{1b}\cdot 2CHCl_3$ in the crystal are in a good agreement. Calculated values of C−H, C−C, C−N, C−O, Ge−O, and Ge−C bonds differ from X-ray values by less than 0.05 Å, which is typical for density functional methods.[9] The calculated interatomic distances $Ge\cdots Cl^-$ and $Cl^-\cdots H$ are shorter than in the crystal by 0.69 and 0.12 Å, respectively. We suppose that this is due to crystal-packing effects not taken into consideration in the calculations of isolated molecules, which can strongly affect interatomic distances between the ionic species. We also suppose that shortening of the $Ge\cdots Cl^-$ distance leads to lengthening of $Ge\leftarrow NMe_2$ coordination bonds by about 0.09 Å with respect to the X-ray data.

The geometries of molecules **A** and **C** correspond to a distorted square bipyramid. Two oxygen, one carbon, and one chlorine atom occupy equatorial positions, and two nitrogen atoms reside in axial positions. The distortion is manifested in (i) the deviation of the N−Ge−N angles from the ideal 180° by about 14.5° and (ii) a slightly nonplanar disposition of the Ph, Cl, and alkoxy substituents around the germanium atom: Cl−C−O−O dihedral angles are about 7°. It is important to stress that the formation of two $H\cdots Cl^-$ contacts in molecule **C** leads to significant lengthening of the Ge−Cl covalent bond by 0.167 Å. Consequently, the Ge−C, Ge−O, and $Ge\leftarrow NMe_2$ distances shorten by 0.013, 0.02, and 0.01 Å, respectively.

The geometry of ionic complex **D** is discussed above. It should be stressed that the formation of the $H\cdots Cl^-$ coordination bonds in **D** leads to lengthening of the $Ge\cdots Cl^-$ contact by 0.219 Å in comparison to **B**. Shortening of the Ge−C, Ge−O, and $Ge\leftarrow NMe_2$ bonds is not as pronounced as for the **A**−**C** pair: it does not exceed 0.006 Å.

Structure **A** is energetically more favorable than the ionic form **B**, $\Delta G°(\mathbf{A}) - \Delta G°(\mathbf{B}) = -6.8$ kcal/mol.[10] The solvation of both covalent and ionic molecules **A** and **B** with two chloroform molecules is endothermic, $\Delta H° = -6.9$ and -14.6 kcal/mol, respectively. Contrary to the nonsolvated molecules, the solvated ionic form **D** lies lower in energy than the covalent form **C**, $\Delta G°(\mathbf{D}) - \Delta G°(\mathbf{C}) = -1.1$ kcal/mol. The solvated ionic form **D**, observed in the crystal, corresponds to the global minimum of the potential energy surface. Relative concentrations of two forms **D** and **C** in chloroform solutions can be estimated using equation 3. The value of 6.4:1 perfectly fits our NMR measurements, which gave a value of 6.5:1. Thus, calculations confirm the crucial role of solvation with chloroform for the formation of the ionic form **D**.

$$\frac{C(\mathbf{D})}{C(\mathbf{C})} = \exp\left(\frac{-\Delta G^0}{RT}\right) = \exp\left(\frac{1.1 \times 4.18 \times 1000}{8.31 \times 298.15}\right) = 6.4 \quad (3)$$

We have also performed an AIM analysis[11] of all molecules (for details, see the Supporting Information). It should be stressed that the Ph group takes part in the stabilization of the positive charge on the germanium atom in the ionic form **D**. Calculated ellipticity (ϵ) of the bond critical point corresponding to the Ge−C bond is 0.06, indicating some π-bonding between these two atoms. To compare, $\epsilon = 0$ in ethane, 0.23 in benzene, and 0.45 in ethylene.[11]

Conclusion

The data presented above show that the pentacoordinate germyl cation $[PhGe(OCH_2CH_2NMe_2)_2]^+$ can be stabilized by the electronic effects of the β-dimethylaminoethoxy ligands without any steric shielding of the germanium atom even in the presence of the highly nucleophilic chloride anion. The weak $p_z-\pi$ interaction between the germanium atom and the phenyl substituent as well as the solvation of the chloride anion by the chloroform molecules are the factors responsible for the additional stabilization of the ionic form **1b**.

Experimental Section

General Procedures. All manipulations were carried out under a purified argon atmosphere using standard Schlenk and high-vacuum-line techniques. The commercially available solvents were purified by conventional methods and distilled immediately prior

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to use. The $PhGeCl_3$ was purchased from Aldrich. The $Et_3GeOCH_2CH_2NMe_2$ was synthesized as described earlier.[2a] NMR spectra were recorded on a Bruker AM-360 NMR spectrometer at 360.134 MHz (^1H) and 90.555 MHz (^{13}C) in $CDCl_3$. Chemical shifts are relative to $SiMe_4$ for H and C or indirectly referenced to TMS via the solvent signals. Accuracy of chemical shift measurements is ±0.01 ppm (^1H) and ±0.05 ppm (^{13}C). The melting point was measured in a sealed capillary using a SANYO Gallenkamp PLC melting point apparatus without any additional corrections. The elemental analysis was performed on a Carlo Erba EA1108 CHNS-O elemental analyzer.

Phenylbis[*N*-(dimethylamino)ethoxy]germanium Chloride (1). A solution of $Et_3GeOCH_2CH_2NMe_2$ (4.63 g, 18.70 mmol) in THF (30 mL) was added slowly to a stirred solution of $PhGeCl_3$ (2.39 g, 9.34 mmol) in THF (20 mL) at room temperature. A large amount of white precipitate immediately appeared. After stirring for 2.5 h the white precipitate was filtered, washed with THF, and dried in vacuo. The yield of white solid is 3.24 g (96%). Mp: 193 °C (with dec). Anal. Calcd for $C_{14}H_{25}N_2O_2ClGe$ ($M_r = 361.40$): C, 46.53; H, 6.97; N, 7.75. Found: C, 46.31; H, 7.23; N, 7.53. ^1H NMR ($CDCl_3$): for **1a** δ 2.47 (s, 12H, NMe_2), 2.95 (m, br, 4H, CH_2N), 3.80 (m, br, 4H, CH_2O); for **1b** δ 2.00, 2.57 (two s, 12H, NMe_2), 2.75, 3.02 (two m, br, 4H, CH_2N), 3.97 (m, br, 4H, CH_2O); 7.40–7.43 (m, Ph) (for both forms). ^{13}C NMR ($CDCl_3$): for **1a** δ 42.46 (Me_2N), 54.80 (CH_2N), 58.05 (CH_2O), 127.25 (*m*-Ph) (registration of the remaining Ph signals for **1a** is not possible due to their low intensity); for **1b** δ 43.37, 44.15 (Me_2N), 56.10 (CH_2N), 57.84 (CH_2O); 127.04 (*ipso*-Ph), 128.24 (*m*-Ph), 130.77 (*p*-Ph), 130.96 (*o*-Ph).

X-ray Crystal Structure Analysis. Data were collected at 120 K on a Bruker three-circle diffractometer equipped with a SMART 1000 CCD detector and corrected for Lorentz and polarization effects and for absorption.[12] For details, see Table 1. The structure was solved by direct methods and refined by a full-matrix least-squares technique on F^2 with anisotropic displacement parameters for all non-H atoms. The unit cell contains two solvate chloroform molecules, which are disordered over two sites by rotation around the C–H bond, with the occupancies of 0.7:0.3. The H atoms were placed in calculated positions and refined in the riding mode with fixed thermal parameters. All calculations were carried out using the SHELXTL PLUS program (PC Version 5.0).[13] Crystallographic data for **1b**·$2CHCl_3$ have been deposited with the Cambridge Crystallographic Data Center, CCDC 279030. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax +44 1223 336033; e-mail deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

Table 1. Crystallographic Data for 1b·$2CHCl_3$

empirical formula	$C_{16}H_{27}N_2O_2Cl_7Ge$
fw	600.14
cryst syst	monoclinic
space group	*C*2/*c*
a (Å)	17.6994(10)
b (Å)	13.0612(10)
c (Å)	11.8471(8)
β (deg)	103.055(2)
V (Å^3)	2668.0(3)
Z	4
d_c (g cm^{-3})	1.494
μ (mm^{-1})	1.864
θ range (deg)	1.96 to 30.05
no. of measd/indep reflns/R_{int}	15 232/3876/0.051
no. of reflns with $I > 2\sigma(I)$	3021
R1; wR2 ($I > 2\sigma(I)$)	0.070; 0.083
R1; wR2 (all data)	0.207; 0.225

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Supporting Information Available: Tables of atom coordinates, bond lengths, bond and torsion angles, anisotropic displacement parameters for **1b**·$2CHCl_3$, and quantum-chemical calculations. This material is available free of charge via the Internet at http://pubs.acs.org.

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