# Syntheses of new hexacoordinate germanium(IV) complexes. Crystal structures and properties of [GeCl$_4$(TMEDA)] and [GeCl$_2$(N$_3$)$_2$(TMEDA)]

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The simple high-yield syntheses and some characterization of new hexacoordinate [GeCl$_4$(TMEDA)] (**1**) and [GeCl$_2$(N$_3$)$_2$(TMEDA)] (**2**) are reported. The crystal structures of neutral **1** and **2** are described. Some electronic, geometrical, and thermodynamic features of **1** and **2** were computationally investigated at the B3LYP density functional level of theory.

Within the last decade we have witnessed an increasing and rapid development of materials chemistry, in areas such as semiconductors, high temperature superconductivities, electronic composites, and ceramics. The latter are of major importance and the best known representative is silicon nitride, which combines great hardness, wear resistance, chemical stability and high mechanical strength. Titanium nitride with similar properties is used in microelectronics.[1] Germanium nitride is an attractive candidate in this respect and particularly promising are precursors that contain azide (–N$_3$) groups as the nitrogen source.[1d,e] Studies of such systems are rare and include some synthetic and spectroscopic work on tetrahedral [Ge(Me)$_n$(N$_3$)$_{4-n}$] ($n = 0$–3)[1b] and [GeTp'(N$_3$)] [Tp' = HB(3,5-Me$_2$pz)$_3$][2] as well as on the mixed azido-(chloro)germyl complexes *trans*-[(η$^5$-C$_5$Me$_5$)W(CO)(PMe$_3$)$_2$ {GeCl$_{3-m}$(N$_3$)$_m$}].[3] Surprisingly, there is very little structural data available for such germanium species and especially for six coordinated systems.[1f,g,h] Besides the importance of such molecules from a materials science perspective, hypercoordinate complexes have been extensively investigated for their role in the mechanism of both organic and organometallic reactions.[4–6] We report herein the syntheses and reactivity of new hexacoordinate germanium(IV) species and present the first structure of a neutral octahedral bisazide germanium(IV) complex stabilized by a tertiary bisamine.

## Results and discussion

As shown in Scheme 1, GeCl$_4$ and 1 equiv of TMEDA were combined in THF at room temperature (RT). After 12 h workup gave colorless, air sensitive powders in 87–55% yields. Microanalyses confirmed formation of the target neutral [GeCl$_4$(TMEDA)] (**1**).
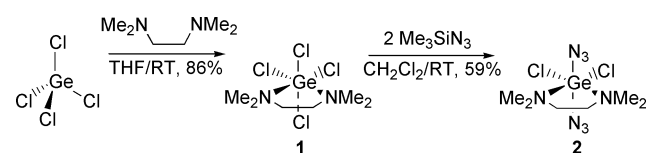


**Scheme 1**  Syntheses of hexacoordinate germanium(IV) complexes.

Colorless needles of **1** were grown by slow diffusion of hexanes into the THF solution of **1**. The monomeric **1** reveals a distorted octahedral germanium with four chlorine atoms and two nitrogen atoms from the chelating TMEDA (Fig. 1). The Ge–N1 and Ge–N2 bond distances of 2.148(12) Å and 2.156(10) Å are close to that of the related [GeCl$_4$(NMe$_3$)$_2$] compound [2.19(3) Å],[7] but longer than those in [GeF$_4$(bipy)] [2.023(4) Å and 2.029(4) Å].[8]

We next sought to exchange chlorine atoms in **1** for azido groups. Complex **1** was treated with 2 equiv of [Me$_3$SiN$_3$] in CH$_2$Cl$_2$ at RT to give [GeCl$_2$(N$_3$)$_2$(TMEDA)] (**2**) in 59% yield. Complex **2** was isolated as a colorless, air-sensitive and volatile solid that is insoluble in hydrocarbons. It violently decomposes slightly above 120 °C. Colorless needles of **2** were grown from CH$_2$Cl$_2$. The X-ray analysis of **2** reveals a neutral monomeric [GeCl$_2$(N$_3$)$_2$(TMEDA)] with hexacoordinate germanium surrounded by two mutually *trans* azide groups, two chlorine atoms, and two nitrogen atoms of the chelating TMEDA ligand. The octahedral environment of the germanium atom (Fig. 1) is distorted, as shown by the N1–Ge–N1' and N2–Ge–N2' bond angles of 83.69(17)° and 173.20(17)°. The Ge–N2 bond is 1.945(3) Å and is similar to the related values of 1.948(4) Å found for [{Fe(CO)$_2$(Cp)}$_2$-Ge(N$_3$)$_2$][1f] and 1.963(4) Å for [Ge(tptp)(N$_3$)$_2$].[1g] As observed for other azides of main group elements,[9,10] the azide groups in **2** are slightly bent with a mean N2–N3–N4 bond angle 177.0(4)° and two significantly different nitrogen-nitrogen bond lengths of 1.215(4) and 1.132(5) Å for N2–N3 and N3–N4, which are comparable to the experimental values of N=N (1.20[11a] or 1.24[11b] Å) and N≡N (1.10[11a] and 1.098[11b] Å) bond distances. The Ge–N1 [2.138(3) Å] and the Ge–Cl1 [2.2700(11) Å] distances are also near the values observed in **1**.

The IR, $^{15}$N NMR, and MS spectra agree well with the structural assignment of **2**. First, **2** displays the expected absorptions of symmetric and asymmetric modes of covalently bonded terminal azide groups at 1290 and 2130 cm$^{-1}$. The spectrum also shows bands at 672, 448 and 298 cm$^{-1}$ due to ν(Ge–N$_3$), ν(Ge–N) and ν(Ge–Cl) stretching modes, respectively. The asymmetric ν(N$_3$) absorption in **2** appears at a similar frequency to that of [Ge(Me)$_3$(N$_3$)] (2103 cm$^{-1}$)[1e] and higher than that of [GeTp'(N$_3$)] (2043 cm$^{-1}$).[3] Second, the $^{15}$N
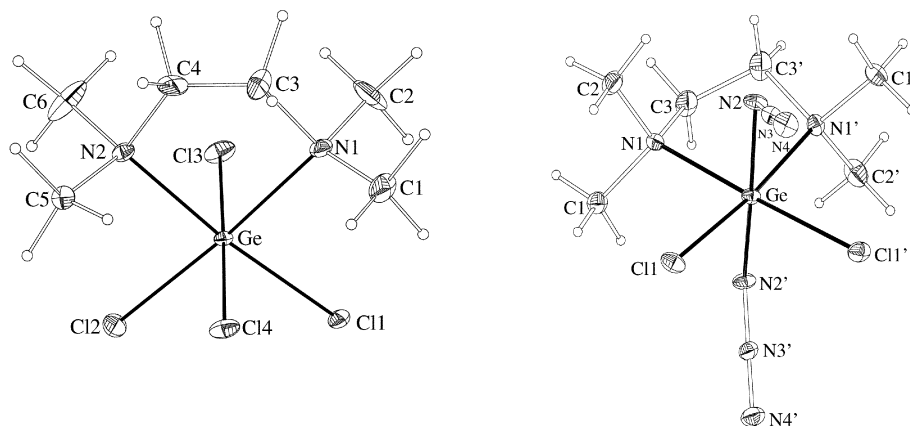
**Fig. 1** Molecular structure of **1** (left) and **2** (right). Key bond lengths (Å) for **1**: Ge–Cl1, 2.247(3); Ge–Cl2, 2.236(4); Ge–Cl3, 2.253(5); Ge–Cl4, 2.248(4); Ge–N1, 2.148(12); Ge–N2, 2.156(10); for **2**: Ge–N1, 2.138(3); Ge–N2, 1.945(3); Ge–Cl1, 2.2700(11); N2–N3, 1.215(4); N3–N4, 1.132(5). Key bond angles (deg) for **1**: Cl1–Ge–Cl2, 95.28(18); Cl1–Ge–Cl3, 90.0(2); Cl1–Ge–Cl4, 89.56(18); Cl1–Ge–N1, 89.1(4); Cl1–Ge–N2, 174.0(3); Cl2–Ge–Cl3, 88.8(2); Cl2–Ge–Cl4, 89.3(2); Cl2–Ge–N1, 175.6(4); Cl2–Ge–N2, 90.7(4); Cl3–Ge–Cl4, 178.0(2); Cl3–Ge–N1, 90.9(5); Cl3–Ge–N2, 90.6(3); Cl4–Ge–N1, 91.0(5); Cl4–Ge–N2, 90.1(3); N1–Ge–N2, 85.0(5); for **2**: Cl1–Ge–Cl1′, 93.94(6); Cl1–Ge–N1, 91.24(9); Cl1–Ge–N1′, 174.35(9); Cl1–Ge–N2, 91.27(10); Cl1–Ge–N2′, 93.37(11); N1–Ge–N1′, 83.69(17); N1–Ge–N2, 88.76(13); N1–Ge–N2′, 86.18(13); N2–Ge–N2′, 173.20(17); N2–N3–N4, 177.0(4); Ge–N2–N3, 116.3(2).

NMR spectrum of **2** show three characteristic well-resolved resonances at −137.0, −181.7 and −321.7 ppm, which have been assigned to the chemically inequivalent nitrogen atoms of the coordinated azide groups[9,10] (the nitrogen signal of TMEDA was assigned to be at −275.0 ppm). Third, the mass spectrum showed ions with masses corresponding to $2^+ - Cl$ and $2^+ - N_3$ as the most intense peaks.

We sought to further clarify the electronic and geometrical features of **1** and **2** computationally.[12] Frequency calculations at the B3LYP/6-31(d) density functional level of theory reveal **1** and **2** in $C_2$ symmetry to be energy minima. The computed bond lengths and angles of **1** and **2** at B3LYP/6-311+G(d,p) agree well with those found by X-ray analysis.[13] Calculation of vibrational modes for terminal azide predicted bands at 1296/1297 cm$^{-1}$ for the $v(-N-N_2)$, and 2175/2180 cm$^{-1}$ for $v(-N_2-N)$.[14] The symmetrical mode is close to the experimental finding (1290 cm$^{-1}$) while we observed only one broad band for the asymmetric mode at 2130 cm$^{-1}$, which might be a superposition of two bands. In addition, the fingerprint region due to $v(-N_3)$ bending, $v(Ge-N_3)$ and $v(Ge-Cl)$ stretching modes was also reproduced well. We have also computed the enthalpy of reactions ($\Delta H$) for **1** and **2** on the basis of the reactions (**1**) and (**2**).

$$GeCl_4 + TMEDA \rightarrow \mathbf{1} \qquad (1)$$

$$[GeCl_2(N_3)_2] + TMEDA \rightarrow \mathbf{2} \qquad (2)$$
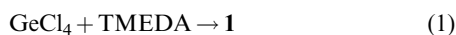
At the MP2(fu) level with the SHATZ + 2p basis set and the B3LYP/6-311 + G(d,p) geometries [MP2(fu)/SHATZ + 2p// B3LYP/6-311 + G(d,p) + ZPE {B3LYP/6-31G(d)}],[15] the calculated $\Delta H$ values of −11.5 and −40.5 kcal mol$^{-1}$ for reactions (1) and (2), respectively, reveal the driving force for the formation of the hexacoordinate **1** and **2**.

As stated above, we were interested in determining a synthetic route to germanium(IV) azide as potential inorganic precursors to metal nitride. This study has shown that the germanium adduct with a tertiary amine [GeCl$_4$(TMEDA)] can be a valuable starting material and a range of new germanium derivatives can be obtained. The stabilizing effect of the chelating ligand allows the use of this compound with a high azide nitrogen to germanium ratio. Finally, as group 14 is descended, the polarity of the M–N$_3$ bond increases, and the resemblance to ionic azide ligands is likely to became stronger, ionic azides (*e.g.*, N$_3^-$) are linear and symmetric with N–N band distances of 1.16 Å.[11a] Clearly, further structural studies

of group 14 azides are required to probe the valence-bond contribution. Reactivity studies of compounds **1** and **2** are currently underway.

## Experimental

### Syntheses

**[GeCl$_4$(TMEDA)] (1).** A Schlenk flask was charged with GeCl$_4$ (1.00 mL, 1.88 g, 8.77 mmol) and THF (50 mL). The solution was placed in an ice bath and TMEDA (1.34 mL, 1.03 g, 8.79 mmol) was added by syringe. The solution was allowed to reach ambient temperature and was stirred for 12 h. The resulting suspension was allowed to settle and was filtered. The remaining solid was extracted with dry THF (3 × 5 mL), the filtrates were combined and cooled overnight at −5 °C to give a colorless crystalline solid (2.50 g, 7.56 mmol, 86%). Anal calcd for C$_6$H$_{16}$Cl$_4$GeN$_2$: C, 21.8; H, 4.9; Cl, 42.9; Ge, 22.0; N, 8.5. Found: C, 21.6; H, 4.5; Cl, 42.8; Ge, 21.0; N, 8.4. IR (Nujol, cm$^{-1}$): 334 (vs), 403 (w), 452 (m), 760 (m), 791 (s), 947 (s), 998 (vs), 1042 (m), 1170 (w), 1234 (m), 1282 (s).

**[GeCl$_2$(N$_3$)$_2$(TMEDA)] (2).** Dry trimethylsilyl azide (0.85 mL, 0.74 g, 6.08 mmol) was added to a suspension of **1** (1.00 g, 3.02 mmol) in CH$_2$Cl$_2$ (50 mL). The mixture was stirred at room temperature for 24 h at which time the solid had dissolved completely. The solution was concentrated to *ca.* 30 mL and cooled in a freezer at −18 °C to give **2** as colorless crystals (0.61 g, 1.77 mmol, 59%). Anal calcd for C$_6$H$_{16}$Cl$_2$GeN$_8$: C, 21.0; H, 4.7; Cl, 20.6; Ge, 21.1; N, 32.6. Found: C, 21.0; H, 4.3; Cl, 21.1; Ge, 20.9; N, 32.3. IR (Nujol, cm$^{-1}$): 298 (vs), 400 (s), 448 (s), 672 (s), 760 (m), 798 (m), 952 (s), 998 (m),

1074 (s), 1118 (m), 1200 (m), 1236 (s), 1290 (s), 2092 (vs). ESI-MS(THF): 310 ($M^+ - Cl + 2$, 100%); 301 ($M^+ - N_3$, 97%); a few other peaks between 120 and 400 of intensity <40% were observed.

## Computational method

All calculations were carried out using various methods as implemented in the Gaussian 98 program and methods.[12,16,17]

## Crystal data and refinement details

Colorless needles of **1** and **2**, suitable for X-ray crystallography, were grown by slow diffusion of hexanes into the THF solution of **1** or **2**. Data were collected using a KUMA-KM4 four-circle diffractometer with an Oxford Cryosystem Cryostream cooler. Cell parameters were obtained from 50 reflections with $18° < 2\theta < 22°$. The space group was determined from systematic absences and subsequent least-squares refinement. Three standard reflections (every 100 scans) showed no crystal decay. Lorentz, polarization, and absorption[18] corrections were applied. The structures were solved by standard heavy atom techniques with SHELXS and refined with SHELXL-97.[19] Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions were calculated and added to the structure factor calculations, but were not refined. Scattering factors, and $\Delta f'$ and $\Delta f''$ values, were taken from the literature.[20] The Flack parameter for **1** was 0.01(3).[21]

Crystal data for **1/2**: $C_6H_{16}Cl_4GeN_2/C_6H_{16}Cl_2GeN_8$, $M = 330.60/343.76$, orthorhombic/monoclinic, $a = 14.633(2)/8.570(2)$, $b = 7.328(3)/13.350(3)$, $c = 11.7250(10)/12.227(2)$ Å, $\beta = 90/108.63(3)°$, $u = 1257.3(6)/1325.6(5)$ Å$^3$, $T = 298(2)/110(2)$ K, space groups $Pna2_1/C2/c$, $Z = 4/4$, $\mu(K_\alpha) = 3.248/2.707$ mm$^{-1}$, 1858/5225 reflections measured, 1603/1174 unique ($R_{int} = 0.0419/0.0972$), which were used in calculations. Final $R$ values: $R_1$ $[I > 2\sigma(I)] = 0.0414/0.0485$; $wR_2$ (all data) $= 0.1418/0.1066$.

CCDC reference numbers 171326 and 171327. See http://www.rsc.org/suppdata/nj/b1/b110770b/ for crystallographic data in CIF or other electronic format.

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13  Some calculated bond lengths (Å) for **1** (Ge–Cl1 = 2.244, Ge–Cl3 = 2.305, Ge–N1 = 2.383) and **2** (Ge–Cl1 = 2.276, Ge–N1 = 2.310; Ge–N2 = 1.952; N2–N3 = 1.221; N3–N4 = 1.136) at the B3LYP/6-311 + G(d,p) level.

14  The calculated frequencies were scaled by an empirical factor of 0.9613 (see Ref. 12a, p. 64). The fingerprint region due to $\delta(-N_3)$ bending, $\nu$(Ge–N3) and $\nu$(Ge–Cl) stretching modes were computed to be 644/645, 376, 431/435, and 299/300 cm$^{-1}$, for **1** and **2**, respectively.

15  It is necessary to point out that the enthalpies of reaction at the hybrid B3LYP density functional level of theory depend very strongly on the size of the employed basis sets. Therefore we carried out CCSD(T) benchmark calculations with various basis sets on the model reaction of $GeF_4 + 2 NH_3 \rightarrow [Ge(F)_4(NH_3)_2]$. Based on the B3LYP/6-311 + G(3df,2p) geometries and the B3LYP/6-31G(d) calculated zero-point energies (ZPE), we found that the MP2(fu) method with the more flexible Shaefer, Horn and Alrichs[16] triple set basis including two set polarization functions and one set diffuse function (SHATZ+2p) provides nearly the same result as the highly correlated CCSD(T) method with the same basis set ($\Delta H = -30$ kcal mol$^{-1}$). We have also computed the isomer in which the two azide groups are *cis* to each other and the two chlorides are in *trans* positions. At the B3LYP/6-311+G(d,p) level and including the ZPE correction [B3LYP/6-31G(d)], the azide *trans* isomer is 2.7 kcal mol$^{-1}$ more stable than the *cis* one.

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