

New stable germylenes, stannylenes, and related compounds.

5. Germanium(II) and tin(II) azides

$[\text{N}_3\text{-E}^{14}\text{-OCH}_2\text{CH}_2\text{NMe}_2]_2$ ($\text{E}^{14} = \text{Ge}, \text{Sn}$): synthesis and structure

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Abstract

New stable azido derivatives of divalent germanium and tin $[\text{N}_3\text{-E}^{14}\text{-OCH}_2\text{CH}_2\text{NMe}_2]_2$ ($\text{E}^{14} = \text{Ge}$ (**1**), Sn (**2**)) have been synthesized by use of the β -dimethylaminoethoxy ligand that forms the intramolecular $\text{E}^{14} \leftarrow \text{N}$ coordination bond. Their crystal structures have been determined by X-ray diffraction analysis. Compounds **1** and **2** are centrosymmetric dimers via two intermolecular dative $\text{E}^{14} \leftarrow \text{O}$ interactions with essentially linear monodentate azide ligands. The dominant canonical form of the E^{14} -azide moieties is $\text{E}^{14}\text{-N-N}\equiv\text{N}$.

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1. Introduction

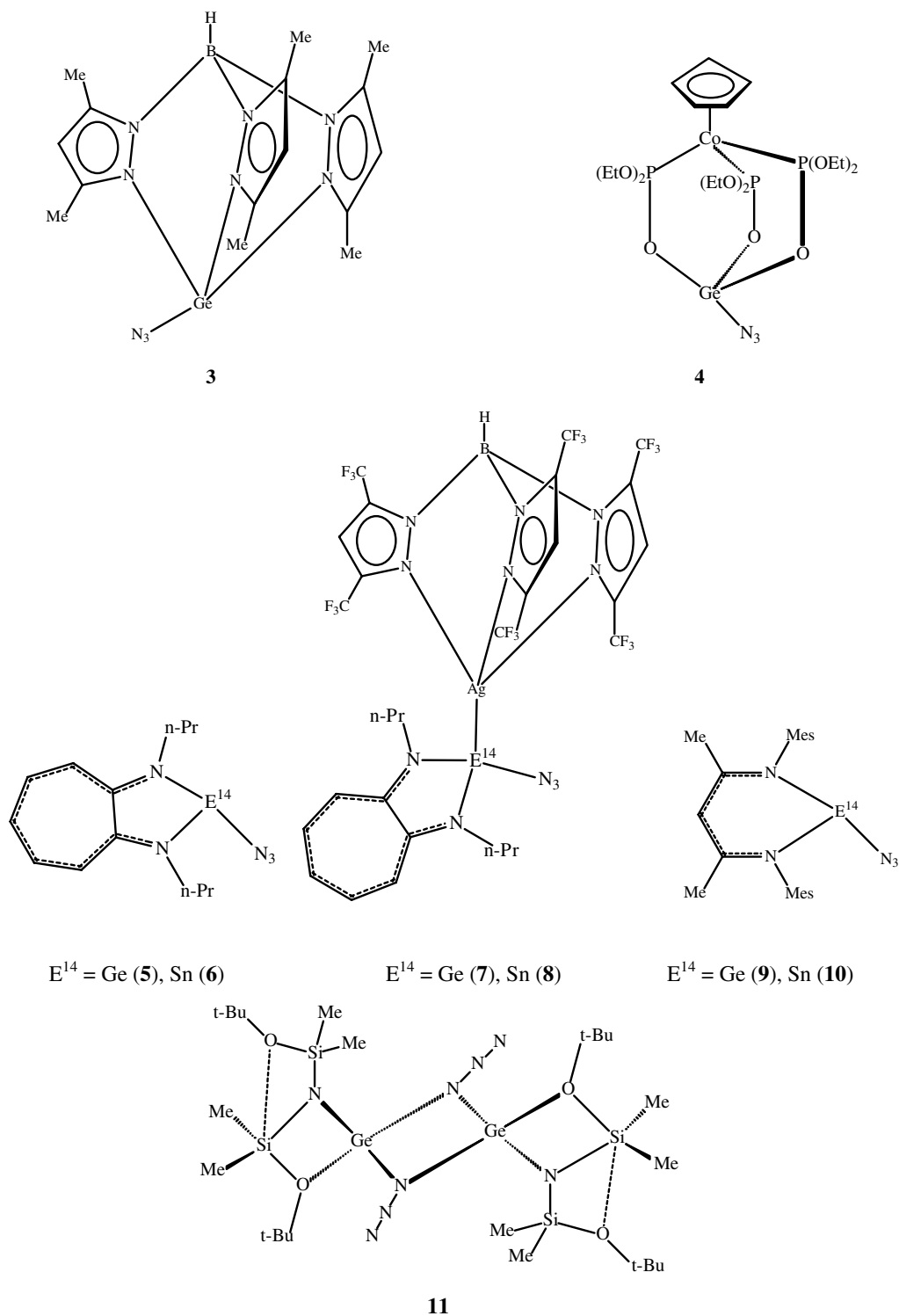
There is considerable current interest in both theoretical and practical aspects of covalent azides. Azido derivatives of carbon represent the most widely studied group of compounds among this family [1–3]. They are excellent starting materials for the preparation of a variety of organic and inorganic compounds [1,2,4–7]. Related azides of heavier group 14 members such as those of silicon(IV) and tin(IV) are also fairly well known [3,8]. Some of these are commercially available as well. In contrast, very little is known about the azide derivatives of low-valent group 14 elements [9–15]. One of the difficulties in isolating such species is their tendency to decompose with the elimination of molecular

nitrogen, leading to high-valent group 14 compounds. The lead(II) azide $\text{Pb}(\text{N}_3)_2$, for example, is widely used as a primary explosive [3,15–17]. There are only a very few structurally characterized compounds of this type in the literature to our knowledge. Those include $[\text{HB}(3,5\text{-Me}_2\text{Pz})_3]\text{GeN}_3$ (**3**) [9], $[\text{CpCo}\{\text{P}(\text{O})(\text{OEt})_2\}_3]\text{GeN}_3$ (**4**) [10], $[(n\text{-Pr})_2\text{ATI}]\text{E}^{14}\text{N}_3$ ($\text{E}^{14} = \text{Ge}$ (**5**) or Sn (**6**); ATI = aminotroponimate ligand) [11], $[\text{HB}(3,5\text{-CF}_3)_2\text{Pz})_3]\text{AgE}^{14}(\text{N}_3)[(n\text{-Pr})_2\text{ATI}]$ ($\text{E}^{14} = \text{Ge}$ (**7**) or Sn (**8**)) [12], $[(\text{Mes})_2\text{DAP}]\text{E}^{14}\text{N}_3$ ($\text{E}^{14} = \text{Ge}$ (**9**) or Sn (**10**); DAP = diazapentadienyl ligand) [13], $\{[t\text{-BuO}(\text{Me}_2)\text{-Si}]_2\text{NGe-}\mu\text{-N}_3\text{-}\}_2$ (**11**) [14] and $\text{Pb}(\text{N}_3)_2$ (**12**) [15] (Scheme 1).

The scarcity of information on azides of low-valent group 14 elements prompted us to explore this area in more detail. Recently, we have demonstrated the successful utility of the β -dimethylaminoethoxy ligand [18–20] which stabilizes monomeric germanium(II) and

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Scheme 1.

tin(II) derivatives by forming an intramolecular $E^{14} \leftarrow N$ coordination bond. These compounds come into the redistribution reactions rather than the oxidative ones. In this paper, we describe the use of the β -dimethylaminoethoxy ligand to obtain thermally stable covalent azides of Ge(II) and Sn(II).

2. Experimental section

2.1. General procedures

All manipulations were carried out under purified argon atmosphere by use standard Schlenk and

high-vacuum-line techniques. The solvents commercially available were purified by conventional methods, and distilled immediately prior to use. The compounds $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ and $\text{ClGe}(\text{OCH}_2\text{CH}_2\text{NMe}_2)$ were prepared according to the procedures described by us previously [19,20]. NMR spectra were recorded on Bruker AM-360 NMR spectrometer at 360.134 MHz (^1H), 90.555 MHz (^{13}C), and 111.92 MHz (^{119}Sn) for the samples in THF- d_8 . Chemical shifts are relative to SiMe_4 for H, C or indirectly referenced to TMS via the solvent signals and relative to SnMe_4 for ^{119}Sn . Accuracy of coupling constant determination is ± 0.1 Hz, accuracy of chemical shift measurements is ± 0.01 ppm (^1H), ± 0.05 ppm (^{13}C), and ± 0.2 ppm (^{119}Sn).

2.2. [Triethyl][azido]tin, Et_3SnN_3

Me_3SiN_3 (2.70 ml, 20.42 mmol) was added at room temperature to white crystals of Et_3SnF (4.59 g, 20.42 mmol). The reaction mixture was heated for 10 min at 50–60 °C. The product was isolated by distillation at 63–65 °C/1 Torr. White crystals (4.10 g; 89.3%) of Et_3SnN_3 were obtained: m.p. 38–39 °C, which is in accordance with the literature data [21].

2.3. [(Dimethylamino)ethoxy][azido]germanium, $[\text{N}_3\text{-Ge-OCH}_2\text{CH}_2\text{NMe}_2]_2$ (**1**)

A solution of Et_3SnN_3 (1.1196 g, 4.52 mmol) in THF (10 ml) was added at room temperature to a solution of $\text{ClGe}(\text{OCH}_2\text{CH}_2\text{NMe}_2)$ (0.8800 g, 4.48 mmol) in THF (15 ml). The reaction mixture was heated up to boiling for 5 min. After that the mixture was filtered, the filtrate concentrated to the volume of ~ 6 ml, and cooled down to -12 °C to give white crystals. The resulting mixture was filtered and the resulting products were vacuum-dried. White crystals (0.91 g; 90%) of **1** were obtained: m.p. 77–78 °C (in sealed capillary, with decomposition). Anal. Calc. for $\text{C}_4\text{H}_{10}\text{N}_4\text{OGe}$: C, 23.70; H, 4.97; N, 27.63. Found: C, 23.5; H, 5.04; N, 27.47%. ^1H NMR (360 MHz, THF- d_8 , 25 °C): $\delta = 2.02$ (s, 6H, Me_2N), 2.96 (br, t, 2H, CH_2N), 4.31 (br, t, 2H, CH_2O); ^{13}C NMR (90.356 MHz, THF- d_8 , 25 °C): $\delta = 45.90$ (Me_2N), 61.74 (CH_2N), 67.07 (br, CH_2O).

2.4. [(Dimethylamino)ethoxy][azido]tin, $[\text{N}_3\text{-Sn-OCH}_2\text{CH}_2\text{NMe}_2]_2$ (**2**)

Solution of Me_3SiN_3 (1.3081 g, 11.4 mmol) in 30 ml THF was added slowly to a stirred solution of $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ (3.1882 g, 10.8 mmol) in 120 ml THF at -40 to -50 °C. A small amount of precipitate appeared without elimination of nitrogen. Under heating of the mixture to -20 to 0 °C a big amount of white precipitate appeared. When the temperature of the solution has risen to room value the precipitate solved. The

mixture was kept at room temperature during 3 days. The solvent was removed by distillation under vacuum 20 °C/1 Torr during 0.5 h. The residue (2.71 g, $\sim 100\%$) was crystallized from THF at -12 °C. White crystals (1.9 g; 70%) of **2** were obtained: m.p. 153 (in sealed capillary, with decomposition). Anal. Calc. for $\text{C}_4\text{H}_{10}\text{N}_4\text{OSn}$: C, 19.31; H, 4.05; N, 22.52. Found: C, 19.69; H, 3.94; N, 22.7%. ^1H NMR (360 MHz, THF- d_8 , 25 °C): $\delta = 2.36$ (s, 6H, Me_2N), 2.76 (t, br, 2H, NCH_2 , 3J (H,H) = 4.8 Hz), 3.99 (t, br, 2H, OCH_2 , 3J (H,H) = 4.8 Hz); ^{13}C NMR (90.356 MHz, THF- d_8 , 25 °C): $\delta = 43.53$ (Me_2N), 59.35 (NCH_2), 60.91 (OCH_2).

2.5. X-ray structure determination

Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1000 CCD detector (for **1**) and automated four-circle diffractometer Syntex P2₁ (for **2**); in the case of **1** data were corrected for absorption [22]. For details see Table 1. The structures were solved by direct methods and by full-matrix least-squares refinement with anisotropic thermal parameters for non-hydrogen atoms. The hydrogen atoms in the structure **1** were located in difference Fourier syntheses and refined isotropically. The hydrogen atoms in the structure **2** were placed in calculated positions and refined in the riding model with fixed thermal parameters. All calculations were carried out by use of the SHELXTL PLUS (PC Version 5.10) program [23].

3. Results and discussion

3.1. Synthesis

The compounds $\text{N}_3\text{-E}^{14}\text{-OCH}_2\text{CH}_2\text{NMe}_2$ ($\text{E}^{14} = \text{Ge}$ (**1**), Sn (**2**)) were prepared in good yield by the X-exchange reactions of $\text{XM}(\text{OCH}_2\text{CH}_2\text{NMe}_2)$ ($\text{X} = \text{Cl}$ for Ge, $\text{X} = \text{OCH}_2\text{CH}_2\text{NMe}_2$ for Sn) with Et_3SnN_3 or Me_3SiN_3 , in a 1:1 ratio of the reagents in THF (Scheme 2).

Both $\text{N}_3\text{-E}^{14}\text{-OCH}_2\text{CH}_2\text{NMe}_2$ are white crystalline substances which are very sensitive to traces of oxygen and moisture. They are soluble in THF and insoluble in nonpolar organic solvents.

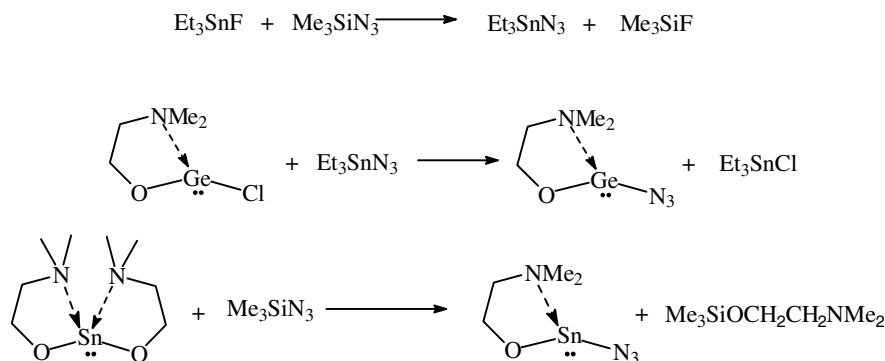
3.2. Solid-state structures of $[\text{N}_3\text{-E}^{14}\text{-OCH}_2\text{CH}_2\text{NMe}_2]_2$ ($\text{E}^{14} = \text{Ge}$ (**1**), Sn (**2**))

Crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained from THF solution. The molecular structures of **1** and **2** are shown in Figs. 1 and 2. Selected bond lengths and angles are presented in Table 2.

Compounds **1** and **2** were found to be centrosymmetric dimers via two intermolecular dative $\text{E}^{14} \leftarrow \text{O}$ bonds. They consist of two $\text{N}_3\text{E}^{14}\text{OCH}_2\text{CH}_2\text{NMe}_2$ units, sharing an $\text{E}_2^{14}\text{O}_2$ four-membered ring. A molecular

Table 1
Crystallographic Data for **1** and **2**

Compound	1	2
Empirical formula	C ₈ H ₂₀ N ₈ O ₂ Ge ₂	C ₈ H ₂₀ N ₈ O ₂ Sn ₂
Formula weight	405.50	497.70
Temperature (K)	120(2)	158(2)
Crystal size (mm)	0.30 × 0.24 × 0.12	0.24 × 0.18 × 0.12
Cryst system	Monoclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> $\bar{1}$
Unit cell dimensions		
<i>a</i> (Å)	9.001(3)	5.9279(8)
<i>b</i> (Å)	7.849(3)	7.6975(10)
<i>c</i> (Å)	12.041(4)	9.3233(13)
α (°)	90	87.545(11)
β (°)	109.475(5)	73.088(11)
γ (°)	90	87.602(11)
<i>V</i> (Å ³)	802.0(5)	406.46(9)
<i>Z</i>	2	1
<i>D</i> _c (g cm ⁻³)	1.679	2.033
<i>F</i> (0 0 0)	408	240
μ (mm ⁻¹)	3.762	3.087
θ Range (deg)	3.16 to 26.93	3.55 to 28.00
Index range	-11 ≤ <i>h</i> ≤ 10, -9 ≤ <i>k</i> ≤ 10, -15 ≤ <i>l</i> ≤ 12	0 ≤ <i>h</i> ≤ 7, -10 ≤ <i>k</i> ≤ 10, -11 ≤ <i>l</i> ≤ 12
Number of reflections collected	4542	2035
Number of unique reflections	1693	1864
Number of reflections with <i>I</i> > 2σ(<i>I</i>)	1080	1748
<i>R</i> ₁ ; <i>wR</i> ₂ (<i>I</i> > 2σ(<i>I</i>))	0.0425; 0.0856	0.0411; 0.0999
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.0797; 0.0944	0.0445; 0.1036
Data/restraints/parameters	1693/0/131	1864/0/91
GOF on <i>F</i> ²	1.006	1.041
Max shift/error	0.001	0.001
Largest difference peak/hole (e Å ⁻³)	1.422/-0.553	2.261/-2.537
Absorption cor <i>T</i> _{max} ; <i>T</i> _{min}	0.647; 0.451	None



Scheme 2.

inversion center lies at the center of this ring relating the unprimed to primed atoms.

The E¹⁴ atoms have a distorted trigonal bipyramidal configuration with a lone electron pair in the equatorial position. The stereochemically active lone pairs at E¹⁴ atoms push back the atoms at the axial positions towards the equatorial bonded atoms. The resulting distortions towards a tetragonal pyramid are evident in the N(1)–E¹⁴–O(1A) bond angles of 146.8(1)° for **1** and 139.3(1)° for **2** (Table 2).

The E¹⁴–O bond lengths in both **1** and **2** (1.886(3) and 2.338(3) Å for **1** and 2.126(3) and 2.224(3) Å for **2**, Table 2) are significantly different. In the case of Sn(II), however, they are more equalized than in the case of Ge(II). Furthermore, the Ge(1)–N(1) coordination bond lengths in **1** (2.220(4) Å) are considerably smaller than those in Ge(OCH₂CH₂NMe₂)₂ (2.324(2)–2.346(2) Å) [18,19]. In contrast to **1**, the Sn(1)–N(1) coordination bond lengths in **2** (2.505(5) Å) are considerably larger than those in Sn(OCH₂CH₂NMe₂)₂ (2.458(2) Å) [19]. These findings

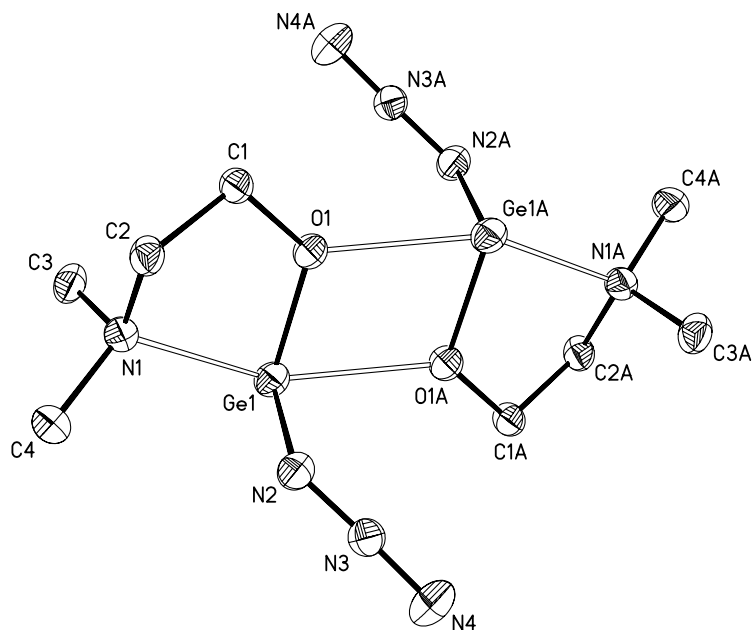


Fig. 1. The structure of compound **1** (50% probability ellipsoids). The labeling A denotes symmetrically equivalent atom relative to the inversion center.

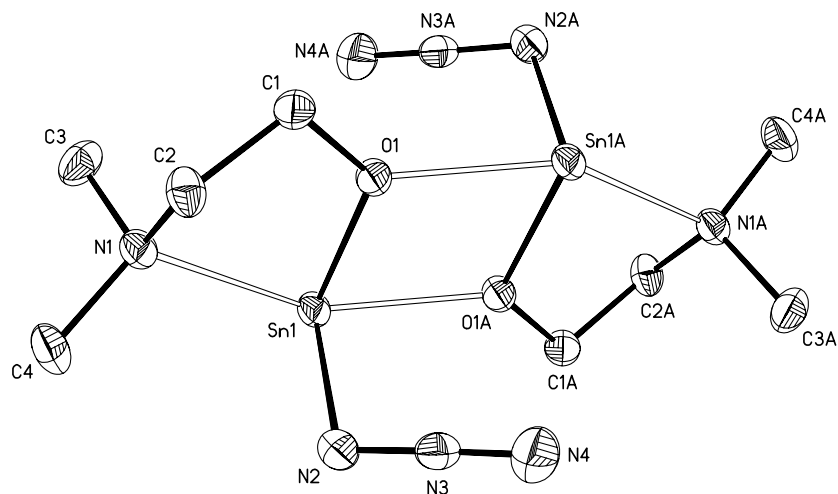


Fig. 2. The structure of compound **2** (50% probability ellipsoids). The labeling A denotes symmetrically equivalent atom relative to the inversion center.

indicate that in the Sn(II) dimer **2** molecules are more strongly bonded than in the Ge(II) dimer **1** due to the larger size of the Sn atom in comparison with the Ge atom. Apparently, the σ -acceptor ability of the azido-group is not large enough to stabilize the monomeric species **1** and **2**.

It is important to point out that the molecules of **1** and **2** could form the dimers via μ -bridging N_α atoms of the azido groups, as observed in the intramolecularly stabilized germanium(II) azide **11** [14]. However, the formation of dimers by μ -bridging oxygen atoms is decidedly more favorable. The structure of the dimeric germanium(II) azide **11** is obviously determined by the steric reasons which are absent in compounds **1** and **2**.

The azide moieties in both **1** and **2** are almost linear as evident from the N–N–N bond angles of $176.5(5)^\circ$ for **1** and $178.5(6)^\circ$ for **2**. The bonding in the $E^{14}N_3$ species may be described by two main canonical forms: $E^{14}-N=N=N$ and $E^{14}-N-N\equiv N$. In addition, an ionic resonance form $[E^{14}]^{(+)}[N_3]^{(-)}$ may also contribute to a certain degree to the overall bonding pattern. It was found previously that the dominant canonical form of the E^{14} -azide moieties in **3**, **4**, **6** and **8** is $E^{14}-N=N=N$ [9–12], whereas that in **5**, **7**, **9** and **10** is $E^{14}-N-N\equiv N$ [11–13]. In compounds **1** and **2** the $N_\alpha-N_\beta$ bonds of the azide groups ($1.226(5)$ Å for **1** and $1.214(7)$ Å for **2**) are longer than the $N_\beta-N_\gamma$ bonds ($1.153(5)$ Å for **1** and $1.149(8)$ Å for **2**), the difference ΔNN 0.073 Å for

Table 2
Selected bond lengths [Å] and angles [°] for **1** and **2**

	1 (E ¹⁴ = Ge)	2 (E ¹⁴ = Sn)
E ¹⁴ (1)–O(1)	1.886(3)	2.125(4)
E ¹⁴ (1)–O(1A)*	2.338(3)	2.225(4)
E ¹⁴ (1)–N(1)	2.220(4)	2.505(5)
E ¹⁴ (1)–N(2)	2.016(4)	2.220(5)
O(1)–C(1)	1.442(5)	1.424(6)
N(2)–N(3)	1.226(5)	1.214(7)
N(3)–N(4)	1.153(5)	1.149(8)
O(1)–E ¹⁴ (1)–N(2)	97.30(15)	90.30(17)
O(1)–E ¹⁴ (1)–N(1)	80.30(14)	72.36(14)
N(2)–E ¹⁴ (1)–N(1)	85.48(15)	83.44(17)
O(1)–E ¹⁴ (1)–O(1A)	69.65(14)	68.34(16)
N(2)–E ¹⁴ (1)–O(1A)	84.74(14)	86.52(17)
N(1)–E ¹⁴ (1)–O(1A)	146.83(13)	139.29(14)
E ¹⁴ (1)–O(1)–E ¹⁴ (1A)	110.35(14)	111.66(16)
C(1)–O(1)–E ¹⁴ (1)	120.6(3)	122.3(3)
N(3)–N(2)–E ¹⁴ (1)	117.5(3)	115.4(4)
N(4)–N(3)–N(2)	176.5(5)	178.5(6)

* The labeling A denotes symmetrically equivalent atom relative to the inversion center.

1 and 0.065 Å for **2** is comparable to that observed for **5** ($\Delta_{\text{NN}} = 0.053$ Å), **7** ($\Delta_{\text{NN}} = 0.083$ Å), **9** ($\Delta_{\text{NN}} = 0.047$ Å), and **10** ($\Delta_{\text{NN}} = 0.099$ Å). The E¹⁴–N_{azide} bond lengths in **1** (2.016(4) Å) and **2** (2.220(5) Å) are also close

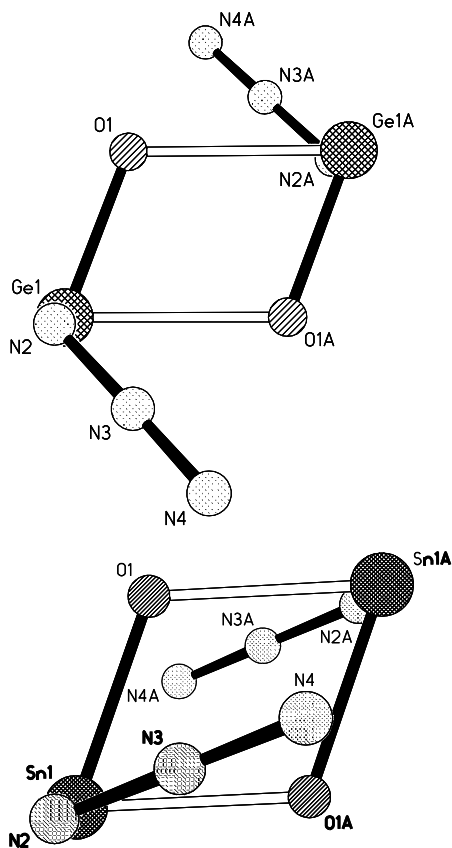


Fig. 3. Fragments of crystal structures **1** and **2** indicating disposition of azide groups relative to E₂O₂ ring plane.

to those found in **5** (2.047(2) Å), **9** (1.979(5) Å), and **10** (2.198(5) Å), respectively. Thus, the N–N bond lengths in both **1** and **2** strongly suggest that the dominant canonical form of the E¹⁴-azide moieties is E¹⁴–N–N≡N.

Interestingly, regardless of the μ-bridging N_α atoms the dominant canonical form of the Ge-azide moieties in the dimer **11** are also Ge–N–N≡N (N_α–N_β 1.215(1), N_β–N_γ 1.150(1), $\Delta_{\text{NN}} = 0.065$ Å) [14].

It is interesting to note that the X-ray crystal structure of **1** reveals azide moieties turned away from the Ge₂O₂ ring plane (the torsion angle O(1)–Ge(1)–N(2)–N(3) is 114.6(3)°, Fig. 3) while structural data for **2** show azide groups occupying sites above the Sn₂O₂ ring plane (the torsion angle O(1)–Sn(1)–N(2)–N(3) is 49.0(5)°, Fig. 3). The E¹⁴–N–N bond angles in **1** and **2** (117.5(3)° for **1** and 115.4(4)° for **2**) are very similar.

4. Conclusion

Data presented above show that, even though in the dimeric form, germanium(II) and tin(II) azides can be isolated as thermally stable solids owing to electronic effects of the β-dimethylaminoethoxy ligand. Our studies imply that this concept can be extended also to other interesting classes of divalent group 14 compounds.

5. Supplementary material

Crystallographic Data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos. 242734 and 242735. 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).

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