

New stable germylenes, stannylenes, and related compounds

6. Heteroleptic germanium(II) and tin(II) compounds

$[(\text{SiMe}_3)_2\text{N-E}^{14}\text{-OCH}_2\text{CH}_2\text{NMe}_2]_n$ ($\text{E}^{14} = \text{Ge}, n = 1; \text{Sn}, n = 2$): synthesis and structure

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Abstract

New stable heteroleptic germanium(II) and tin(II) compounds $[(\text{SiMe}_3)_2\text{N-E}^{14}\text{-OCH}_2\text{CH}_2\text{NMe}_2]_n$ ($\text{E}^{14} = \text{Ge}, n = 1$ (**1**), $\text{Sn}, n = 2$ (**2**)) have been synthesized and their crystal structures have been determined by X-ray diffraction analysis. While compound **1** is monomer stabilized by intramolecular $\text{Ge} \leftarrow \text{N}$ coordination, compound **2** is associated to dimer via intermolecular dative $\text{Sn} \leftarrow \text{O}$ interactions.

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1. Introduction

In the past decade, considerable progress has been made in the chemistry of stable organic derivatives of divalent germanium and tin. Steric protection of the E^{14} atom by bulky substituents, σ -acceptor ability of the electronegative heteroatoms X ($\text{X} = \text{O}, \text{S}, \text{Hal}$) and intramolecular coordination $\text{E}^{14} \leftarrow \text{Y}$ ($\text{Y} = \text{N}, \text{O}$) with donor groups of suitable geometry in side chains are the main factors responsible for their kinetic and thermodynamic stabilization. In continuation of our investigation on the relative contributions of different factors to the stabilization of germanium(II) and tin(II) com-

pounds [1–4], we report here the synthesis and the results of experimental (X-ray, NMR) studies of two stable heteroleptic compounds $[(\text{SiMe}_3)_2\text{N-E}^{14}\text{-OCH}_2\text{CH}_2\text{NMe}_2]_n$ ($\text{E}^{14} = \text{Ge}, n = 1$ (**1**); $\text{Sn}, n = 2$ (**2**)). It should be noted that the structural chemistry of unsymmetrical derivatives of divalent Group 14 elements has not been extensively studied [5,6]. Moreover, within this class of compounds, only a few alkoxy and aryloxy derivatives of germanium(II) and tin(II) have been structurally characterized, including $[\text{ClE}^{14}\text{OBu}^t]_2$ ($\text{E}^{14} = \text{Ge}$ (**3**) [7], Sn (**4**) [7,8]), $[(\text{SiMe}_3)_2\text{NSnOBu}^t]_2$ (**5**) [9], $(\text{SiMe}_3)_2\text{NSnOAr}^*$ ($\text{Ar}^* = 2,6\text{-di-tert-butyl-4-methylphenyl}$) (**6**) [10], $[\text{Ph}_3\text{SiOE}^{14}\text{OBu}^t]_2$ ($\text{E}^{14} = \text{Ge}$ (**7**), Sn (**8**)) [11], Ar^iGeOR ($\text{Ar}^i = 2,4\text{-di-tert-butyl-6-((dimethylamino)methyl)phenyl}$; $\text{R} = \text{Pr}^i$ (**9**), Et (**10**)) [12], $\{\text{HC}[\text{C}(\text{Me})\text{NAr}^i]_2\}\text{SnOPr}^i$ ($\text{Ar}^i = 2,6\text{-Pr}^i\text{C}_6\text{H}_3$) (**11**)

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[13], $[\text{PhC}(\text{NSiMe}_2\text{R})_2]\text{SnOCPh}_3$ (R = Me (**12**), Ph (**13**)) [14], $\text{RGeOCH}_2\text{CH}_2\text{NMe}_2$ (R = Cl (**14**), OCOMe (**15**)) [3], and $[\text{N}_3\text{E}^{14}\text{OCH}_2\text{CH}_2\text{NMe}_2]_2$ (E^{14} = Ge (**16**), Sn (**17**)) [4].

2. Experimental

2.1. General procedures

All manipulations were carried out under purified argon atmosphere using standard Schlenk and high-vacuum-line techniques. The commercially available solvents were purified by conventional methods and distilled immediately prior to use. $\text{Ge}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ [2], $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ [2], $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ [15], $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ [16] were synthesized as described earlier. NMR spectra were recorded on Bruker AM-360 NMR spectrometer at 360.134 MHz (^1H) and 90.555 MHz (^{13}C) for the samples in C_6D_6 and $\text{CD}_3\text{C}_6\text{H}_5$. Chemical shifts are relative to SiMe_4 . The accuracy of coupling constant determination is ± 0.1 Hz, the accuracy of chemical shift measurements is ± 0.01 ppm (^1H) and ± 0.05 ppm (^{13}C).

2.2. $[(\text{Dimethylamino})\text{ethoxy}][(\text{trimethylsilyl})\text{amido}]$ germanium, $(\text{Me}_3\text{Si})_2\text{N-Ge-OCH}_2\text{CH}_2\text{NMe}_2$ (**1**)

A solution of $\text{Ge}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ (1.90 g, 7.7 mmol) in THF (10 ml) was added at room temperature to a stirred solution of $\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$ (3.02 g, 7.7 mmol) in THF (10 ml). The reaction mixture was heated to boiling for 5 min. After that, the mixture was filtered and volatiles were evaporated in vacuo. The yield of white solid is 4.6 g (94%). The resulting product was crystallized from hexane at -12 °C, giving **1** as white crystals; M.p. 33–34 °C (in sealed capillary). ^1H NMR ($\text{CD}_3\text{C}_6\text{D}_5$): δ 0.39 (s, 9H, Me_3Si , $^2J_{\text{SiH}} = 6.4$, $^1J_{\text{CH}} = 117.7$); 2.11 (s, 6H, Me_2N , $^1J_{\text{CH}} = 136.8$), 2.12 (br, t, 2H, CH_2N , $^3J_{\text{HH}} = 5.4$), 3.90 (br, t, 2H, CH_2O , $^3J = 5.4$). ^{13}C NMR ($\text{CD}_3\text{C}_6\text{D}_5$): δ 6.52 (Me_3Si , $^1J_{\text{SiC}} = 55.4$), 45.21 (Me_2N), 60.94 (CH_2N), 62.64 (CH_2O). Anal. Calc. for $\text{C}_{10}\text{H}_{28}\text{GeN}_2\text{OSi}_2$: C, 37.41; H, 8.79. Found: C, 37.75; H, 8.92%.

2.3. $\text{Bis}\{[(\text{dimethylamino})\text{ethoxy}][(\text{trimethylsilyl})\text{amido}]\text{tin}\}$, $[(\text{Me}_3\text{Si})_2\text{N-Sn-OCH}_2\text{CH}_2\text{NMe}_2]_2$ (**2**)

A solution of $\text{Sn}(\text{OCH}_2\text{CH}_2\text{NMe}_2)_2$ (1.23 g, 4.2 mmol) in THF (10 ml) was added at room temperature to a stirred solution of $\text{Sn}[\text{N}(\text{SiMe}_3)_2]_2$ (1.83 g, 4.2 mmol) in THF (10 ml). The reaction mixture was heated to boiling for 5 min. After that, the mixture was filtered and volatiles were evaporated in vacuo. The yield of white solid is 3.43 g (95%). The resulting product was

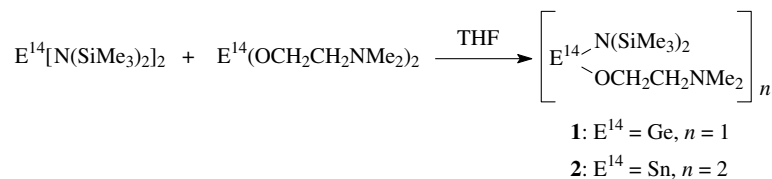
crystallized from hexane at -12 °C, giving **2** as white crystals; M.p. 142–143 °C (in sealed capillary). ^1H NMR (C_6D_6): δ 0.43 (s, 9H, Me_3Si , $^2J_{\text{SiH}} = 5.8$), 1.98 (s, 6H, Me_2N), 2.23 (br, s, 2H, CH_2N), 3.71 (t, 2H, CH_2O , $^3J_{\text{HH}} = 5.3$). ^{13}C NMR (C_6D_6): δ 7.41 (Me_3Si , $^1J_{\text{SiC}} = 54.6$, $^3J_{\text{SnNSiC}} = 37.3$), 44.31 (Me_2N), 57.88 (CH_2N), 61.14 (CH_2O). Anal. Calc. for $\text{C}_{10}\text{H}_{28}\text{N}_2\text{O-Si}_2\text{Sn}$: C, 32.71; H, 7.69. Found: C, 32.94; H, 7.87%.

2.4. X-ray structure determinations

Data were collected on a Bruker three-circle diffractometer equipped with a SMART 1000 CCD detector and corrected for absorption [17]. 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 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 program (PC Version 5.10) [18].

Table 1
Crystallographic data for **1** and **2**

Compound	1	2
Empirical formula	$\text{C}_{10}\text{H}_{28}\text{N}_2\text{OSi}_2\text{Ge}$	$\text{C}_{20}\text{H}_{56}\text{N}_4\text{O}_2\text{Si}_4\text{Sn}_2$
Fw	321.11	734.43
Temperature (K)	120(2)	120(2)
Cryst size (mm)	$0.40 \times 0.30 \times 0.20$	$0.36 \times 0.30 \times 0.24$
Cryst syst	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> (Å)	6.4589(5)	8.7474(6)
<i>b</i> (Å)	9.5492(7)	8.9194(6)
<i>c</i> (Å)	14.1005(10)	23.9118(17)
α (°)	91.6190(10)	80.4830(10)
β (°)	91.6970(10)	86.6410(10)
γ (°)	105.1140(10)	68.4080(10)
<i>V</i> (Å ³)	838.65(11)	1710.8(2)
<i>Z</i>	2	2
<i>d</i> _c (g cm ⁻³)	1.272	1.426
<i>F</i> (0 0 0)	340	752
μ (mm ⁻¹)	1.957	1.621
θ range (°)	2.21 to 28.03	0.86 to 30.01
Index range	$-8 \leq h \leq 8$ $-12 \leq k \leq 12$ $-18 \leq l \leq 18$	$-11 \leq h \leq 12$ $-12 \leq k \leq 12$ $-33 \leq l \leq 33$
Number of reflections collected	7202	20462
Number of unique reflections	3935	9868
Number of reflections with $I > 2\sigma(I)$	3575	7985
<i>R</i> ; <i>wR</i> ₂ ($I > 2\sigma(I)$)	0.0254; 0.0661	0.0405; 0.0929
<i>R</i> ₁ ; <i>wR</i> ₂ (all data)	0.0286; 0.0676	0.0522; 0.0979
Data/restraints/parameters	3935/0/145	9868/0/289
Goodness-of-fit on <i>F</i> ²	1.052	1.035
Max shift/error	0.001	0.001
Largest different peak/hole (e Å ⁻³)	0.407/−0.387	1.771/−1.272
Absorption correction	0.696; 0.508	0.697; 0.593
<i>T</i> _{max} ; <i>T</i> _{min}		

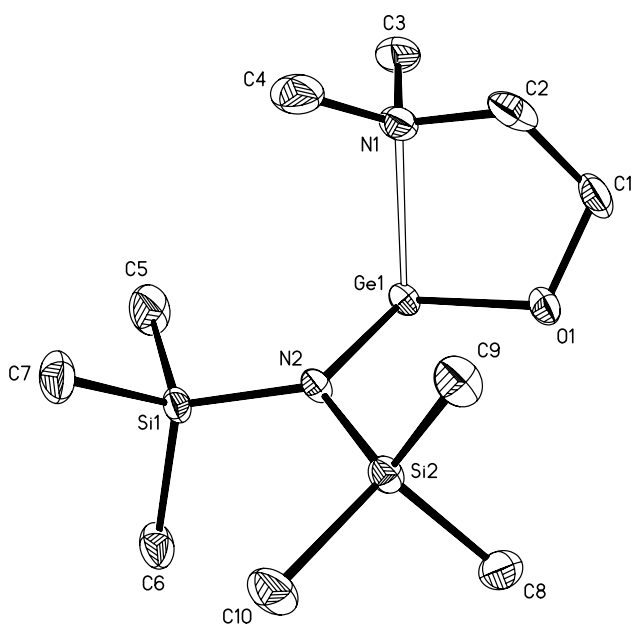
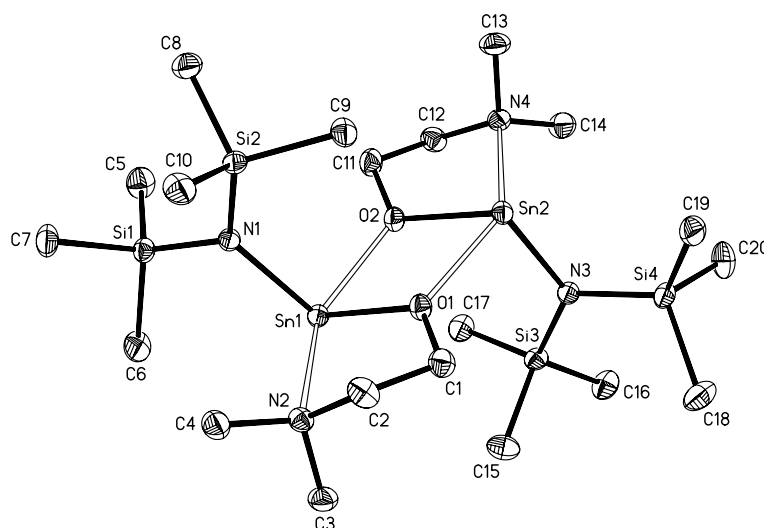


Scheme 1.

3. Results and discussion

3.1. Synthesis of $[(Me_3Si)_2N-E^{14}-OCH_2CH_2NMe_2]_n$ ($E^{14} = Ge, n = 1$ (1); $Sn, n = 2$ (2))

Compounds **1** and **2** are formed easily in good yields by the exchange reactions of $E^{14}(OCH_2CH_2NMe_2)_2$

Fig. 1. The structure of compound **1** (50% probability ellipsoids).Fig. 2. The structure of compound **2** (40% probability ellipsoids).

with $E^{14}[N(SiMe_3)_2]_2$ at 1:1 reagents ratio in THF upon heating for few minutes (Scheme 1).

Both **1** and **2** are white crystalline substances, which are very sensitive to traces of oxygen and moisture. They are soluble in THF and benzene, slightly soluble in hexane.

3.2. Solid-state structures of $[(Me_3Si)_2N-E^{14}-OCH_2CH_2NMe_2]_n$ ($E^{14} = Ge, n = 1$ (1); $Sn, n = 2$ (2))

Crystals of **1** and **2** suitable for X-ray diffraction analysis were obtained from hexane solution. The molecular structures of **1** and **2** are shown in Figs. 1 and 2. Selected bond lengths and angles are presented in Tables 2 and 3.

Compound **1** is monomer with three-coordinated germanium atom forming one σ -bond to each substituent and an additional $Ge \leftarrow N$ coordination bond. As expected, the coordination $Ge \leftarrow N$ interaction appears to be greater than that in a tetra-coordinated germanium(II) atom: the distance $Ge(1) \leftarrow N(1)$ (2.253(1) Å) in **1** is significantly shorter than in compound $Ge(OCH_2CH_2NMe_2)_2$ (2.324(2)–2.346(2) Å) [1,2], Table 2. However, it is much longer than those observed in previously studied amino-functionalized $Ge(II)$ compounds of this type (2.092(3)–2.165(5) Å) [3,12,19,20]. This value of the $Ge \leftarrow N$ bond length in **1** may be due to some degree of π -bonding between germanium and nitrogen N(2) of the $N(SiMe_3)_2$ group. The planar

Table 2
Comparison of selected structural data (Å and deg.) for several crystalline germanium(II) amides and alkoxides (R = SiMe₃, R' = CH₂CH₂NMe₂)

	Ge(NR ₂) ₂ [*]	Ge(OR') ₂ [*]	(R ₂ N)Ge(OR')
Ge(1)–O(1)	–	1.861(1)–1.870(1)	1.8501(12)
Ge(1)–N(2)	1.873(5), 1.878(5)	–	1.9085(14)
Ge(1) ← N(1)	–	2.324(2)–2.346(2)	2.2525(14)
O(1)–Ge(1)–N(2)	107.1(2)	98.79(6), 98.91(7)	97.73(5)
O(1)–Ge(1) ← N(1)	–	80.78(6), 80.48(6)	82.81(6)
N(2)–Ge(1) ← N(1)	–	83.89(6), 84.21(6)	100.68(6)
Si(1)–N(2)–Ge(1)	113.0(3)	–	114.53(7)
Si(2)–N(2)–Ge(1)	125.3(3)	–	120.18(7)
References	[15]	[1,2]	This work

^{*} The numbering corresponds to compound (R₂N)Ge(OR'); for the other compounds geometric parameters involving topologically equivalent atoms are given.

geometry at the nitrogen N(2) atom (sum of angles at N(2) = 358.0°) also implies such an interaction.

The Ge(1)–O(1) bond length in **1** (1.850(1) Å, Table 2) is similar to those in compounds **9** (1.856(2) Å) and **10** (1.844(3) Å), but is slightly longer than those in **14** (1.820(4) Å) and **15** (1.832(1) Å), in which steric hindrance is absent. The Ge(1)–N(2) bond length in **1** (1.909(1) Å) is comparable with Ge–N(SiMe₃)₂ bond lengths in Ge[N(SiMe₃)₂]₂ (1.873(5) and 1.878(5) Å, Table 2) [15], 1,4-[(SiMe₃)₂NGeN(SiMe₃)₂]₂C₆H₄ (1.885(5) Å) [21] and [Bu^tC(NSiMe₃)₂]₂GeN(SiMe₃)₂ (1.910(2) Å) [22], but markedly shorter than that in the sterically strained ArGeN(SiMe₃)₂ (Ar = 2,6-bis((diethylamino)-methyl)phenyl) (1.956(1) Å) [23].

The greater steric demands of the N(SiMe₃)₂ in relation to the OCH₂CH₂NMe₂ ligand is reflected in the smaller O(1)–Ge(1)–N(2) bond angle in **1** compared to corresponding angle between covalent bonds in Ge[N(SiMe₃)₂]₂ [15], in the larger N(1)–Ge(1)–N(2) bond angle in **1** in comparison with the relevant exocyclic bond angle in Ge(OCH₂CH₂NMe₂)₂, and in the smaller difference between the two Ge–N–Si angles in **1** compared with that in Ge[N(SiMe₃)₂]₂ (for the latter case, the wider angle is on the side of the molecule, which is *trans* to the lone pair), Table 2. The N(SiMe₃)₂ group is essentially coplanar to O(1)Ge(1)N(2)-plane (torsion angles Si(1)–N(2)–Ge(1)–O(1) and Si(2)–N(2)–Ge(1)–O(1) are equal to 177.73(7) and 13.27(9)°, respectively), one Si–C bond approximately eclipses the Ge(1)–N(2) bond, and the methyl groups are staggered to each other.

In contrast to **1**, compound **2** is dimer with two bridging OCH₂CH₂NMe₂ groups bonded to Sn in chelating fashion, two terminal, mutually *trans* N(SiMe₃)₂ groups, and trigonal-bipyramidally configured Sn(II) cores. The Sn(1) ← N(2) and Sn(2) ← N(4) distances (2.617(3) and 2.615(3) Å, respectively) show that coordination interactions between these atoms are significantly weakened; compare with Sn ← N bond lengths in Sn(OCH₂CH₂NMe₂)₂ (2.458(2) Å [2], Table 3) and **17** (2.505(5) Å [4]). However, they are clearly present, since the Sn₂O₂ ring has considerably different Sn–O bond lengths (2.133(2), 2.137(2) and 2.267(2), 2.299(2) Å), as

Table 3
Comparison of selected structural data (Å and deg.) for several crystalline tin(II) amides and alkoxides (R = SiMe₃, R' = CH₂CH₂NMe₂)

	Sn(NR ₂) ₂ [*]	Sn(OR') ₂ [*]	[(R ₂ N)Sn(O ^t Bu)] ₂ [*]	[(R ₂ N)Sn(OR')] ₂
Sn(1)–O(1)	–	2.056(2)	2.168(4)	2.133(2)
Sn(1)–N(1)	2.088(6), 2.096(1)	–	2.128(5)	2.147(3)
Sn(1) ← O(2)	–	–	2.173(4)	2.267(2)
Sn(1) ← N(2)	–	2.458(2)	–	2.617(3)
Sn(2)–O(2)	–	–	–	2.137(2)
Sn(2)–N(3)	–	–	–	2.143(3)
Sn(2) ← O(1)	–	–	–	2.299(2)
Sn(2) ← N(4)	–	–	–	2.615(3)
O(1)–Sn(1)–N(1)	104.7(2)	96.52(11)	102.7(2)	106.34(9)
O(1)–Sn(1) ← O(2)	–	–	72.1(2)	68.45(9)
N(1)–Sn(1) ← O(2)	–	–	103.7(2)	94.24(9)
O(1)–Sn(1) ← N(2)	–	76.71(6)	–	71.14(9)
N(1)–Sn(1) ← N(2)	–	80.68(6)	–	90.42(10)
O(2) → Sn(1) ← N(2)	–	–	–	138.99(8)
O(2)–Sn(2)–N(3)	–	–	–	103.30(10)
O(2)–Sn(2) ← O(1)	–	–	–	67.79(9)
N(3)–Sn(2) ← O(1)	–	–	–	95.10(9)
O(2)–Sn(2) ← N(4)	–	–	–	71.19(9)
N(3)–Sn(2) ← N(4)	–	–	–	93.01(10)
O(1) → Sn(2) ← N(4)	–	–	–	138.97(9)
Si(1)–N(1)–Sn(1)	112.5(2)	–	107.8(3)	111.21(13)
Si(2)–N(1)–Sn(1)	123.9(2)	–	131.9(3)	129.70(14)
Si(3)–N(3)–Sn(2)	124.9(2)	–	–	128.40(15)
Si(4)–N(3)–Sn(2)	113.1(2)	–	–	112.11(14)
References	[16]	[2]	[9]	This work

^{*} The numbering corresponds to compound [(R₂N)Sn(OR')]₂; for the other compounds geometric parameters involving topologically equivalent atoms are given.

found in **17** (2.125(4) and 2.225(4) Å); compare with Sn–O bond lengths in the Sn₂O₂ rings of **4** (2.139(4) and 2.141(4) Å [7], 2.153(2) and 2.156(2) Å [8]), **5** (2.168(4) and 2.173(4) Å, Table 3, [9]), **8** (2.079(4) and 2.099(4) Å [11]), [Sn(OBu^t)₂]₂ (2.128(4) and 2.165(4) Å [7]), and binuclear tin(II) calix[4]arene [Bu^t-calix]Sn₂ (2.141(2) and 2.167(2) Å; 2.169(2) and 2.193(2) Å [24]).

The Sn–N(SiMe₃)₂ bond lengths in **2** (2.147(3) and 2.143(3) Å, Table 3) are close to those in the very sterically strained tin(II) compounds, such as [(SiMe₃)₂N]Sn[C(SiMe₃)₂C₅H₄N-2] (2.144(5) Å [25]) and [Bu^tC(NCy)₂]Sn[N(SiMe₃)₂] (2.134(4) Å [26]). However, they are substantially longer than those in other tin(II) compounds (range of values is 2.047(4)–2.121(2) Å [10,16,21,22,27–30]).

The oxygen centers are planar (angles at O sum to 359.4 and 358.8°), as are the nitrogen centers of the N(SiMe₃)₂ substituents (angles at N sum to 359.7 and 359.0°). Obtuse Sn–O–Sn angles together with the large Sn(1)⋯Sn(2) separation (3.657(1) Å) indicate there are no attractive interactions between the metal atoms.

The SiMe₃ groups have non-equivalent environments: two of them are located above and below the Sn₂O₂ ring and two others are directed towards tin lone pairs, those specify the differences between Si–N–Sn angles, Table 3. These differences (≈16°) are less than those in **5** (≈24°), but more than in Sn[N(SiMe₃)₂]₂ (≈11°) [16], Table 3. As for **1**, the methyl groups of the N(SiMe₃)₂ substituents are staggered to each other.

4. Conclusion

Data presented above show that substituent effects responsible for the stabilization of divalent Group 14 derivatives in the monomeric form are drastically different for homoleptic and heteroleptic compounds and thus do not follow the simple “building block” principle. So, in the case of tin(II), heteroleptic compound (SiMe₃)₂N–Sn–OCH₂CH₂NMe₂ is a dimer as opposed to homoleptic compounds Sn[N(SiMe₃)₂]₂ and Sn(OCH₂CH₂NMe₂)₂ which are monomers. This structural aspect of the chemistry of stable organic derivatives of divalent Group 14 elements is very intriguing. Investigations into other unsymmetrical compounds of germanium(II) and tin(II) are currently in progress.

5. Supplementary material

Crystallographic data for **1** and **2** have been deposited with the Cambridge Crystallographic Data Center, CCDC nos. 244748 and 244749. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK

(Fax +441223336033; e-mail: deposit@ccdc.cam.ac.uk or www.ccdc.cam.ac.uk).

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