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New stable germylenes, stannylenes, and related compounds. 8. Amidogermanium(II) and -tin(II) chlorides R_2N-E^{14}-Cl (E^{14} = Ge, R = Et; E^{14} = Sn, R = Me) revealing new structural motifs†

Victor N. Khrustalev[1]*, Ivan V. Glukhov[1], Irina V. Borisova[2] and Nikolay N. Zemlyansky[2]

[1]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991, Moscow, Russian Federation
[2]A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, 29 Leninsky prosp., 119991, Moscow, Russian Federation

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New stable amidogermanium(II) and -tin(II) chlorides $R_2N{-}E^{14}{-}Cl$ [E^{14} = Ge, R = Et (1), E^{14} = Sn, R = Me (2)] have been synthesized and their crystal structures have been determined by X-ray diffraction analysis. Both 1 and 2 are dimers formed via the two intermolecular $E^{14} \leftarrow N$ dative interactions, with the bridged amido ligands and the terminal chloro ligands. The central $E^{14}{}_2N_2$ four-membered ring has a butterfly conformation in the germanium derivative 1 and a planar conformation in the tin derivative 2. The chloride atoms are disposed in the *trans*-configuration relative to the four-membered ring. Both structures 1 and 2 reveal new previously unobserved structural motifs for amidogermanium(II) and -tin(II) chlorides, respectively. The electronic structures of 1 and 2 were studied by quantum chemistry within the DFT approach. Copyright © 2007 John Wiley & Sons, Ltd.

KEYWORDS: germanium(II) and tin(II); chlorides; amides; alkylamino ligands; crystal structure

INTRODUCTION

Chloroamides of low-valence Group 14 elements are attractive owing to the variety of their structures as well as thier very interesting reactivity. Depending on substituents at the nitrogen atom, they can exist both as monomers and oligomers formed via bridged chloro and/or amido ligands as well as possible forming cyclic and acyclic complexes in different conformations. Some of these species (e.g. **3**[1], **4**[2], **5**[3], **6**–**7**[4], **8**[5], **9**[2], **10**[6], **11**[7], Scheme 1) were synthesized and investigated using different physical and chemical methods. Furthermore, complexes with different structures possess distinct reactivity. As found very recently, the reaction of **6** with AgOCN afforded unusual 1,3-diaza-2,4-distannacyclobutanediide.[8] Moreover, the use of **8** as a precursor for the reductive elimination yielded the first body-centered 15-membered Group 14 metal cluster-bearing amido ligands, whereas the analogous reactions of **6** and **7** gave rise to elemental tin and a tar of unidentified content, respectively.[5]

The present paper is a contribution to the chemistry of thermally stable amidogermanium(II) and -tin(II) chlorides $Et_2N{-}Ge{-}Cl$ (**1**) and $Me_2N{-}Sn{-}Cl$ (**2**), in which the E^{14} (E^{14} = Group 14 element) centers bear small diethylamino or dimethylamino ligands. No X-ray crystal structures of divalent Group 14 chlorides with smaller alkylamino substituents have been published so far. Complex **1** is just the second compound of this class in the case of germanium(II), the structure of which was studied by X-ray diffraction analysis. The only known monomeric amidogermanium(II) chloride $Cl{-}Ge{-}N(Bu^t)(SiMe_2{-}NHBu^t)$ (**3**) (Scheme 1), stabilized both by the intramolecular Ge ← N coordination bond

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*Correspondence to: Victor N. Khrustalev, A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, 28 ul. Vavilova, 119991, Moscow, Russian Federation.
E-mail: vkh@xray.ineos.ac.ru

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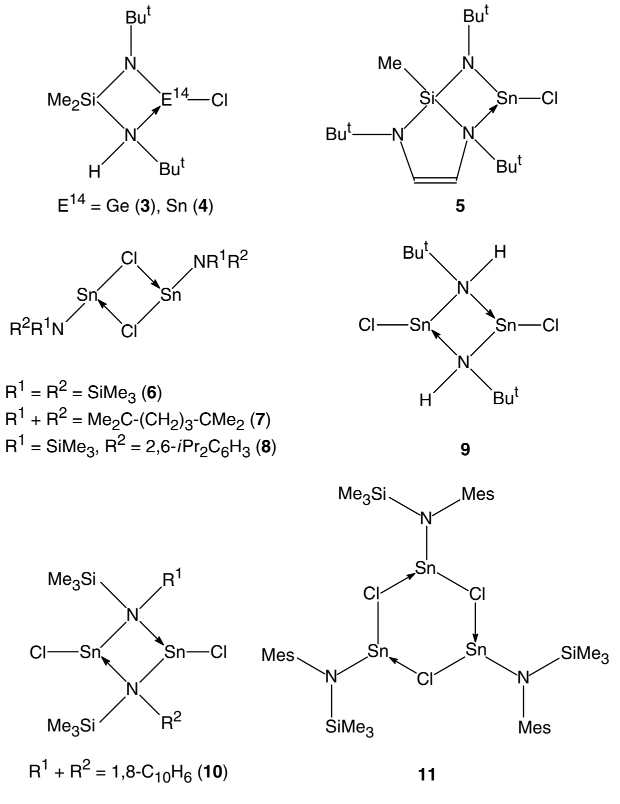


Scheme 1. .

and the bulk *tert*-butyl substituents, has been structurally characterized by Veith and co-authors.[1]

Two structural aspects of the compounds **1** and **2** are of interest: (1) the association type they form; and (2) the metal–ligand bonding, i.e. which of the two ligands, NR_2 or Cl, is bridging.

EXPERIMENTAL

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 to use. Et_3GeNEt_2[9] and $GeCl_2{\cdot}$dioxane[10] were prepared according to the procedures described in the literature. NMR spectra were recorded on a Bruker AM-360 NMR spectrometer at 360.134 MHz (^{1}H), 90.555 MHz (^{13}C) and 111.92 MHz (^{119}Sn) for the sample in C_6D_6. Chemical shifts are relative to $SiMe_4$ for H and C or indirectly referenced to TMS via the solvent signals and relative to $SnMe_4$ for ^{119}Sn. The accuracy of the coupling constant determination is ±0.1 Hz, and the accuracy of chemical shift measurements is ±0.01 ppm (^{1}H), ±0.05 ppm (^{13}C) and ±0.2 ppm (^{119}Sn). Melting point was measured (in a sealed vacuum capillary) with a Sanyo Gallekamp MeltingPoint apparatus. Elemental analyses were performed on a Carlo Erba EA1108 CHNS-O elemental analyzer at the A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, Moscow, Russian Federation.

Synthesis of diethylaminogermanium(II) chloride, $[Et_2NGeCl]_2$ (1)

A mixture of Et_3GeNEt_2 (1.61 g, 6.95 mmol) and $GeCl_2{\cdot}$dioxane (1.35 g, 5.83 mmol) in 20 ml THF was kept at ambient temperature for 1 h. All volatile components were removed *in vacuo* at 20–70 °C/1 Torr. The residue was re-crystallized from hexane at −12 °C to give **1** as white crystals. The yield was 0.63 g (59%); $T_{m.p.} = 93–103\,°C$ (with decomposition). ^{1}H NMR (C_6D_6), δ_H: 0.80 (t, 12H, Me, $^3J_{HH} = 7.1$ Hz), 3.05–3.22 (m, 8H, CH_2N, m, 10 signals, AB-part of ABX_3-spectra). ^{13}C NMR (C_6D_6), δ_C: 10.34 (Me), 42.79 (CH_2N). Anal. calcd for $C_4H_{10}NClGe$: C 26.67; H 5.59; N 7.77. Found: C, 26.53; H, 5.51; N 7.63.

Synthesis of dimethylaminotin(II) chloride, $[Me_2NSnCl]_2$ (2)

A mixture of $[Sn(NMe_2)_2]_2$[11] (1.768 g, 3.47 mmol) in 20 ml Et_2O and $SnCl_2$ (0.6578 g, 3.47 mmol) in 10 ml THF was stirred at ambient temperature for 12 h. All volatile components were removed *in vacuo* at 20–70 °C/1 Torr. The residue was re-crystallized from hexane–THF (1 : 1) at −12 °C to give **2** as white crystals. The yield was 0.60 g (43.6%); compound **2** decomposes without melting at 151.7–154.5 °C. Anal. calcd for C_2H_6NClSn: C 12.12; H 3.05; N 7.07. Found: C, 11.93; H, 3.17; N 7.23. ^{1}H NMR (THF-d_8), δ_H: 2.76 (Me_2N). ^{13}C NMR (THF-d_8), δ_C: 43.08 (Me_2N). ^{119}Sn NMR (THF-d_8), δ_{Sn}: −332.86.

Crystal structure determinations

Data were collected on a three-circle Bruker SMART 1000 CCD (for **1**) and four-circle Syntex $P2_1$ (for **2**) diffractometers and corrected for Lorentz and polarization effects and for absorption using SADABS[12] in the case of **1** or ψ-scan[13] in the case of **2**; see Table 1. The structures were solved by direct methods and refined by a full-matrix least-squares technique on F^2, with anisotropic thermal parameters for non-hydrogen atoms; hydrogen atoms were placed in calculated positions. There are high positive residual electron density peaks of 1.24 e/Å^3 (0.69 Å from Cl1) and 1.51 e/Å^3 (0.54 Å from Cl2) in the structure of **1** and 1.19 e/Å^3 (0.77 Å from Sn1) in the structure of **2** due to the specific arrangement of the chloride atoms on the mirror plane in **1** as well as the considerable absorption effects both in **1** and **2** which could not be completely corrected. All calculations were carried out using the SHELXTL PLUS (PC Version 5.10) program.[14] CCDC deposition numbers: 637973 (**1**) and 637974 (**2**).

Computatonal details

Density Functional Theory (DFT) calculations for **2** and its germanium analog **1a** were performed with the Gaussian 03 software package[15] at the B3LYP level of theory with the C_1 symmetry using DGDZVP basis set with DGA1 density fitting

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

Compound	**1**	**2**
Empirical formula	$C_8H_{20}Cl_2N_2Ge_2$	$C_4H_{12}Cl_2N_2Sn_2$
Fw	360.34	396.44
Temperature (K)	120(2)	173(2)
Crystal system	Orthorhombic	Triclinic
Space group	*Pnma*	$P-1$
a (Å)	11.9153(11)	6.365(2)
b (Å)	10.5148(9)	6.822(2)
c (Å)	11.0124(9)	7.370(2)
α (deg)	90	73.81(2)
β (deg)	90	68.14(2)
γ (deg)	90	64.57(2)
V (Å^3)	1379.7(2) Å^3	265.52(14)
Z	4 (dimers)	1 (dimer)
D_c (g cm^{-3})	1.735	2.480
µ (mm^{-1})	4.714	5.149
θ range (deg)	2.5–28.0	3.3–30.0
No. of reflections collected	12 995	1620
No. of unique reflections	1704 [$R_{int} = 0.029$]	1503 [$R_{int} = 0.047$]
No. of reflections with $I > 2\sigma(I)$	1532	1494
$R1$; $wR2$ [$I > 2\sigma(I)$]	0.037; 0.092	0.048; 0.120
$R1$; $wR2$ (all data)	0.041; 0.095	0.048; 0.120
Data/restraints/ parameters	1704/0/84	1503/0/46
Largest difference peak/hole (eÅ^{-3})	1.51/−0.83	1.19/−1.12

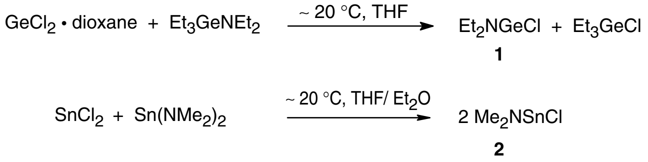
procedure for all atoms, starting from the X-ray structural data for **2**. Geometry optimization in both cases converged to the non-planar geometry of the central ring (see text). To calculate the planar conformation of these molecules we constrained the values of N(1)–E^{14}(1)–N(2)–E^{14}(2) dihedral angles at 0° (see Supplementary materials). As convergence criteria, the tight threshold limits of 1.5×10^{-5} and 1.0×10^{-5} a.u. in all cases were applied, for the maximum force and displacement, respectively. To improve on the accuracy of the B3LYP calculations, the pruned (99,590) grid (keyword Grid = Ultrafine) was used for all molecules.

RESULTS AND DISCUSSION

Synthesis of 1 and 2

The syntheses of **1** and **2** were performed by mixing of two corresponding reagents in equimolar ratio in THF or THF/Et$_2$O solution, respectively, at ambient temperature in good yields (Scheme 2).

Compounds **1** and **2** are soluble in standard organic solvents and stable under anaerobic conditions.



$$GeCl_2 \cdot dioxane + Et_3GeNEt_2 \xrightarrow{\sim 20\ °C,\ THF} \underset{\mathbf{1}}{Et_2NGeCl} + Et_3GeCl$$

$$SnCl_2 + Sn(NMe_2)_2 \xrightarrow{\sim 20\ °C,\ THF/\ Et_2O} \underset{\mathbf{2}}{2\ Me_2NSnCl}$$

Scheme 2. Preparation of germanium (II) and tin (II) derivatives 1 and 2.

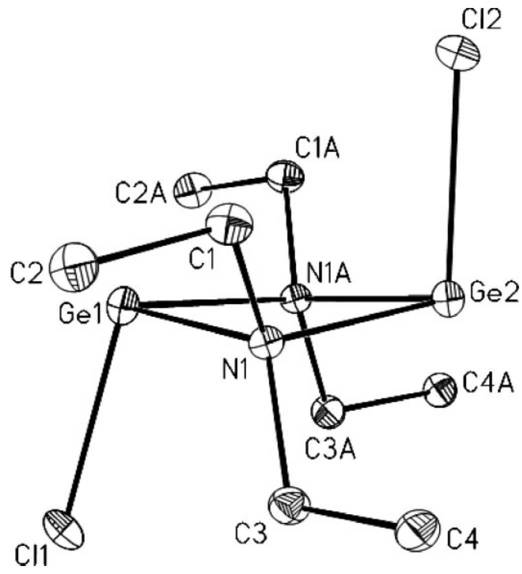


Figure 1. The structure of compound **1** (50% probability ellipsoids). The H atoms are omitted for clarity. The label A denotes symmetry operation: $x, 1/2 - y, z$.

Solid-state structures of 1 and 2

Unambiguous identification of **1** and **2** was accomplished by means of single-crystal structure determination. The molecular structures of **1** and **2** along with the atom numbering schemes are shown in Figs 1 and 2, and bond lengths and angles are listed in Tables 2 and 3, respectively.

The X-ray diffraction study revealed that both compounds are dimers formed via the two intermolecular E^{14} ← N dative interactions and consist of the central $E^{14}{}_2N_2$ four-membered ring with the bridging dialkylamino ligands and the terminal chloro ligands. The molecular structure of **1** has crystallographic mirror symmetry with the Ge$_2$Cl$_2$ core lying on the plane. The dimeric molecule in **2** is situated about a center of inversion. The dialkylamino bridges both in **1** and **2** are slightly bent from the symmetric arrangement between the E^{14} atoms. The E^{14}–N bond lengths [2.034(2) and 2.073(2) Å for **1** and 2.229(4) and 2.267(4) Å for **2**] are considerably longer than those in nucleophilic diaminogermylenes [1.855(2)–1.897(4) Å[16–18]] and -stannylenes [2.057(3)–2.133(2) Å[7,19–21]], but shorter than the corresponding E^{14} ← N$_{alk}$ coordination bond distances [2.093(6)–2.165(5) Å for the Ge ← N$_{alk}$ bond distances[1,22–25] and 2.347(6) Å[2] and 2.368(6) Å[3]

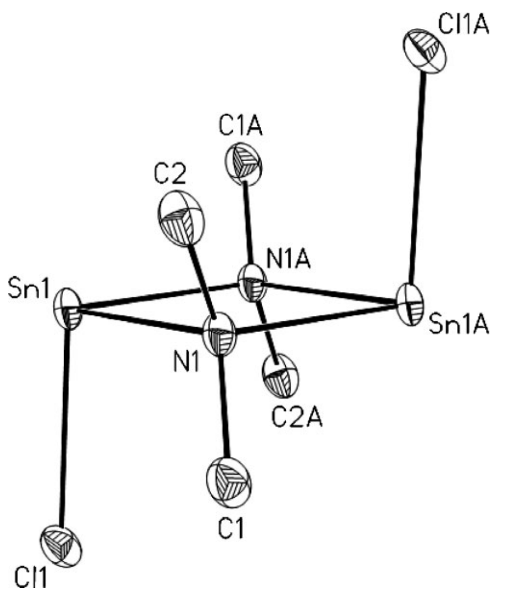


Figure 2. The structure of compound **2** (50% probability ellipsoids). The H atoms are omitted for clarity. The label A denotes symmetry operation: $-x$, $-y$, $-z$.

Table 2. Bond lengths (Å) and angles (deg) for **1**

Ge1–Cl1	2.2663(11)	Ge2–N1A	2.073(2)
Ge1–N1	2.034(2)	N1–C1	1.495(3)
Ge1–N1A[a]	2.034(2)	N1–C3	1.489(3)
Ge2–Cl2	2.2709(10)	C1–C2	1.514(4)
Ge2–N1	2.073(2)	C3–C4	1.513(4)
Cl1–Ge1–N1	98.44(6)	Ge1–N1–C3	119.76(16)
Cl1–Ge1–N1A	98.44(6)	Ge2–N1–C1	115.96(17)
N1–Ge1–N1A	84.35(12)	Ge2–N1–C3	105.41(16)
Cl2–Ge2–N1	97.22(6)	Ge1–N1–Ge2	95.92(9)
Cl2–Ge2–N1A	97.22(6)	C1–N1–C3	112.5(2)
N1–Ge2–N1A	82.42(12)	N1–C1–C2	113.4(2)
Ge1–N1–C1	106.64(16)	N1–C3–C4	114.5(2)

[a] The label A denotes symmetrically equivalent atom relative to the mirror plane. Symmetry operation: $x, 1/2 - y, z$.

for the Sn ← N_{alk} bond distances]. The E^{14}–Cl bond lengths [2.266(1) and 2.271(1) Å in **1** and 2.479(1) Å in **2**] are also significantly longer than those in the monomeric Cl–E^{14}–R [R = 2,6-bis(2,4,6-tri-isopropylphenyl)phenyl] [2.203(2) Å[26] and 2.409(2) Å[27]], respectively.

The germanium and tin atoms in **1** and **2** are coordinated in a distorted trigonal pyramidal fashion. The endocyclic angles at the E^{14} atoms are narrower than those at the nitrogen atoms (Tables 2 and 3). The exocyclic Cl–E^{14}–N angles are comparable to those in three-coordinate [$E^{14}X_3$] fragments of previously reported germanium(II) and tin(II) complexes. In agreement with the Bent's rule,[28] the bond angles at the tin atoms are smaller than those at the germanium atoms.

Table 3. Bond lengths (Å) and angles (deg) for **2**

Sn1–Cl1	2.4794(14)	N1–C1	1.476(6)
Sn1–N1	2.267(4)	N1–C2	1.472(6)
Sn1–N1A[a]	2.229(4)		
Cl1–Sn1–N1	92.98(11)	Sn1A–N1–C1	107.7(3)
Cl1–Sn1–N1A	93.95(11)	Sn1A–N1–C2	117.5(3)
N1–Sn1–N1A	80.62(16)	Sn1–N1–Sn1A	99.38(16)
Sn1–N1–C1	117.5(3)	C1–N1–C2	108.9(4)
Sn1–N1–C2	106.1(3)		

[a] The label A denotes symmetrically equivalent atom relative to the inversion center. Symmetry operation: $-x, -y, -z$.

The amido nitrogen atoms have a distorted tetrahedral environment. The angles at the nitrogen atoms from the more crowded side of the terminal chloride atoms are essentially (~10°) larger than those from the less crowded side.

The planes formed by two carbon and nitrogen atoms of the bridging amido groups are at the angles of 81.0(1) and 82.1(2)°, respectively, with respect to the $E^{14}{}_2N_2$ core and are tilted away from the terminal chloro groups. The chloride atoms are disposed in the *trans*-configuration relatively to the four-membered ring.

Obtuse E^{14}–N–E^{14} angles [95.9(1) and 99.4(2)°, respectively] together with the large $E^{14}\cdots E^{14}$ [3.051(1) and 3.429(1) Å, respectively] separation indicate no attractive interactions between the E^{14} atoms.

Although the structures of **1** and **2** are very similar, there are two striking distinctions between them. First, the conformations of the $E^{14}{}_2N_2$ four-membered rings are obviously different. The Ge_2N_2 four-membered ring in **1** has a butterfly conformation, with the folding angle along the N···N line of 13.3(1)°. In contrast to **1**, the dimers of **2** features an exactly planar Sn_2N_2 four-membered ring owing to the crystallographically imposed symmetry.

Second, the structure of **1** comprises isolated dimers and there are no unusually short intermolecular contacts between the germanium and chloride atoms. The shortest intermolecular Cl···Ge distance is Cl(2)···Ge(2) $[0.5 + x, y, 0.5 - z]$ 4.169(1) Å, which excludes any attractive interactions. Unlike **1**, the tin atoms in the structure of **2** form weak non-valence interactions with the chloride atoms of neighboring molecules [Sn(1)···Cl(1) $[-x, 1 - y, -z]$ 3.424(1) Å]. Therefore, the structure of **2** may be also described as a weak polymeric associate with the tetra-coordinate tin atoms.

It is very important to note that both structures of **1** and **2** represent new structural motifs for amidogermanium(II) and -tin(II) chlorides, respectively. As for tin, monomeric (**4, 5**) as well as dimeric (**6–10**) and trimeric (**11**) amidotin chlorides have been structurally characterized to date (see Scheme 1). By contrast, no crystal structures of associated oligomeric complexes have been published for germanium. Furthermore, in the sterically hindered dimeric amidotin chlorides **6–8**, only chloro ligands are bridging, whereas in the amidotin chloride **9**, both chloro and amido groups function as bridging ligands. Moreover, in contrast to that observed in **2**, the Sn_2N_2 four-membered rings in **9** and **10** have the butterfly conformations.

It is interesting to note that the phosphorus and arsenic tin-analogs of **2, 9** and **10**, i.e. $Bu^t_2E^{15}$-Sn–Cl [E^{15} = P (**12**), As (**13**)], represent isolated centrosymmetric dimers built up via μ-bridged $E^{15}Bu^t_2$-groups showing no unusually short intermolecular contacts.[29]

DFT calculations

Since **1** and **2** in the crystalline state display different conformations of the $E^{14}{}_2N_2$ four-membered rings, we have carried out quantum-chemical calculations of two model compounds in order to get a deeper insight into this problem. We have chosen **2** as one example and its germanium analog (**1a**) the second example so as to allow a direct comparison of identical germanium and tin derivatives. At the same time, the substitution of the ethyl group in **1** by the methyl group (**1a**) should not affect significantly the structure of the central ring. Thus, since **1a** and **2** exhibit similar properties in the molecular form, we attribute the differences observed to crystal packing forces and the emergence of aforementioned intermolecular interactions.

According to our calculations, the minima of the potential energy surfaces both for **1a** and **2** correspond to the structures with the central $E^{14}{}_2N_2$ four-membered rings in the butterfly conformation similar to the one found for **1** in the crystal. The folding angles for **1a** and **2** are equal to 27.0 and 31.5°, respectively. At the same time, the planar conformations (see Supplementary materials for more details) represent transition states, which lie higher in energy by only 0.64 and 0.82 kcal/mol for **1a** and **2**, respectively. For both of these, one weak imaginary frequency was found (-26.4 and $-21.9\ cm^{-1}$, respectively), which corresponds to the conformational change from the planar structure to the butterfly one. This is in line with the known low puckering barrier for cyclobutane.[30–32]

The planar structures both for **1a** and **2** are very similar and correspond to the C_{2h} symmetry with the chloride atoms directed away from the centre of the molecule (the E^{14}–$E^{14'}$–Cl angles are equal to 100.7 and 95.9° for **1a** and **2**, respectively), while in the butterfly conformation, the two structures have the C_s symmetry (the mirror plane passes through both the E^{14} and chloride atoms) with the chloride atoms disposed in a different manner. One of them is directed outwards (like in the planar conformation) and the second one is oriented towards the second E^{14} atom (Fig. 3). The corresponding E^{14}–$E^{14'}$–Cl angles are equal to 86.2, 113.0 and 78.2, 109.9° for **1a** and **2**, respectively. This gives rise to the conclusion that the 'inwards'-oriented chloride atom comes closer to the second E^{14} atom (the $E^{14}\cdots$Cl separations are equal to 3.763 and 3.832 Å for **1a** and **2**, respectively). This might indicate additional stabilization of compound **2** by the formation of the Sn$\cdots$Cl intramolecular coordination, as it was found for compound **9**.[2] However, unlike **9**, no such an inward shift is observed in the crystal of **2** due to the absence of steric hindrances at the metal atom, which favors the formation of intermolecular interactions between the chloride atom and the metal atom of a neighboring molecule.

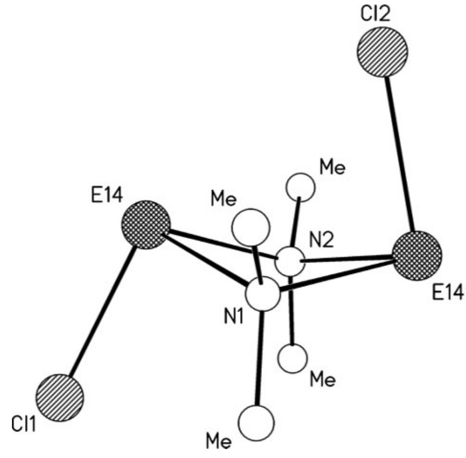


Figure 3. Calculated butterfly conformation for **1a** (E^{14} = Ge) and **2** (E^{14} = Sn) corresponding to the minimum of the potential energy surface.

CONCLUSIONS

In the present paper, two new stable amidogermanium(II) and -tin(II) chlorides R_2N–E^{14}–Cl [E^{14} = Ge, R = Et (**1**), E^{14} = Sn, R = Me (**2**)] bearing small diethylamino or dimethylamino ligands have been studied. Both **1** and **2** are dimers formed via the two intermolecular $E^{14} \leftarrow N$ dative interactions and comprise the central $E^{14}{}_2N_2$ four-membered rings. The finding that NR_2 rather than Cl acts as bridging ligands in **1** and **2** implies that NR_2 is superior to Cl as a bridging group for germanium(II) and tin(II) in sterically unhindered complexes.

DFT calculations indicate that the minima of the potential energy surfaces both for **1a** and **2** correspond to the structures with the central $E^{14}{}_2N_2$ four-membered rings in the butterfly conformation and the *trans* chloride atoms disposed in different manner. However, data described above show that the $E^{14}{}_2N_2$ ring can easily undergo conformational changes depending on different factors. Therefore, the intermolecular Sn$\cdots$Cl interactions in **2** lead to concomitant displacements of the chloride atoms and, apparently, are responsible for the planar conformation of the four-membered ring. In the case of Ge(II), due to the smaller van der Waals radius and strong preference for a three-coordinate fashion in comparison to higher coordination modes, such intermolecular interactions are absent and the energetically more stable butterfly conformation of the $E^{14}{}_2N_2$ ring is realized in **1**.

Further experiments concerning the reactivity of the new compounds **1** and **2** are currently underway.

Supplementary materials

Results of the DFT calculations. These data are available via the Internet at http://www.interscience.wiley.com./

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