New stable germylenes, stannylenes, and related compounds
7.* Synthesis and structures of compounds $Hal—Sn—OCH_2CH_2NMe_2$ (Hal = Cl or F)

V. N. Khrustalev,[a*] *N. N. Zemlyansky,*[b] *I. V. Borisova,*[b]
M. G. Kuznetsova,[b] *E. B. Krut´ko,*[b] *and M. Yu. Antipin*[a]

[a]*A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences,*
28 ul. Vavilova, 119991 Moscow, Russian Federation.
Fax: +7 (495) 135 5085. E-mail: vkh@xray.ineos.ac.ru
[b]*A. V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences,*
29 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (495) 230 2224

New stable divalent tin derivatives containing no bulky substituents at the metal atom, $Hal—Sn—OCH_2CH_2NMe_2$ (Hal = Cl or F), were synthesized, and their crystal structures were studied by X-ray diffraction. Unlike the analogous monomeric divalent germanium derivative $Cl—Ge—OCH_2CH_2NMe_2$, the new compounds are centrosymmetric dimers formed *via* two intermolecular Sn←O coordination bonds.

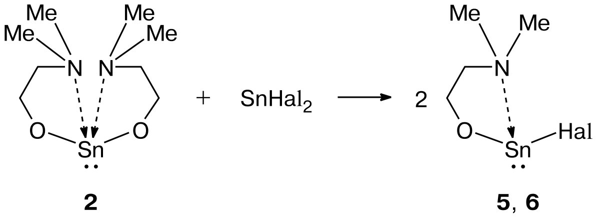
Key words: tin(II), halides, β-dimethylaminoethoxy ligand, synthesis, X-ray diffraction study.

Earlier,[2] we have demonstrated that bidentate β-dimethylaminoethoxy ligands stabilize the divalent germanium and tin compounds $M(OCH_2CH_2NMe_2)_2$ (M = Ge (**1**) or Sn (**2**)) in the monomeric form without steric shielding of the reactive center M by the bulky substituents. In the case of the germanium(II) derivatives, the presence of only one $Me_2NCH_2CH_2O$ ligand is sufficient for stabilization of the monomeric unsymmetrical compounds $XGeOCH_2CH_2NMe_2$ (X = Cl (**3**) or OAc (**4**)).[3] In the present study, we synthesized new stable divalent tin derivatives $Hal—Sn—OCH_2CH_2NMe_2$ (Hal = Cl (**5**) or F (**6**)) analogous to the previously studied germanium(II) derivative **3** and established their structures by X-ray diffraction.

Results and Discussion

Divalent tin chloro- and fluoroalkoxides $ClSnOCH_2CH_2NMe_2$ (**5**) and $FSnOCH_2CH_2NMe_2$ (**6**) were prepared according to a known procedure for the synthesis of tin(II) alkoxyhalides containing no intramolecular coordination bonds,[4—7] *i.e.*, by the reactions of equimolar amounts of $Sn(OCH_2CH_2NMe_2)_2$ (**2**) and tin dihalides in THF at ~20 °C (Scheme 1).

Scheme 1



Hal = Cl (**5**), F (**6**)

Compounds **5** and **6** are colorless crystalline substances unstable in the presence of even trace amounts of atmospheric oxygen and moisture and soluble in polar aprotic organic solvents. The compositions of these compounds were determined by elemental analysis and confirmed by NMR spectroscopy.

The structures of compounds **5** and **6** were studied by X-ray diffraction. Unfortunately, crystals of fluoro derivative **6** were of poor quality and, consequently, the experimental data did not allow us to discuss its structure in detail. However, the principal structure of this compound was unambiguously established, and it is similar to that of chloroalkoxide **5**. Hence, we comprehensively discuss only the structure of compound **5**.

We found that, unlike monomeric germanium(II) alkoxychloride **3**, tin(II) derivatives **5** and **6**, like $[N_3SnOCH_2CH_2NMe_2]_2$ (**7**)[8] and $[(Me_3Si)_2NSnOCH_2CH_2NMe_2]_2$ (**8**),[1] are centrosymmet-

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* For Part 6, see Ref. 1.

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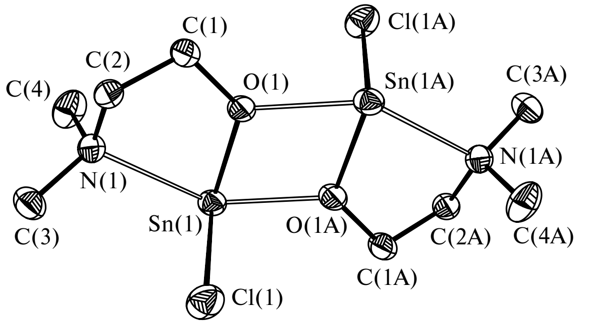

Fig. 1. Molecular structure of dimeric tin(II) chloroalkoxide **5** represented by anisotropic displacement ellipsoids drawn at the 50% probability level. Here and in Fig. 2, the coordination bonds are shown by empty lines; the suffix A refers to atoms related by an inversion center.

ric dimers formed *via* intermolecular Sn←O coordination bonds (Figs 1 and 2).

The four-membered Sn_2O_2 ring in the structure of **5**, like that in dimers **7** and **8**, is unsymmetrical. The lengths of the covalent bonds (Sn—O) are substantially different from those of the coordination bonds (Sn←O) (Table 1). It should be emphasized that the difference in the bond lengths in compound **5** (0.136 Å) is substantially larger than that in dimer **7** (0.100 Å) and is similar to this difference in dimer **8** (0.134 and 0.162 Å), which indicates that the bond between two monomeric fragments in **5** and **8** is weaker than that in dimer **7**. Apparently, this is due to the stronger σ-acceptor effect of the chlorine atom in **7** compared to that of the azido group in compound **5** and the steric effect of the bulky $(Me_3Si)_2N$ substituent in compound **8**.

It should be noted that the previously studied dimeric tin(II) complexes containing no intramolecular coordination bonds consist of virtually symmetrical bridging alkoxy groups. The Sn—O distances in the four-membered Sn_2O_2 rings in these compounds are 2.139(4), 2.141(4) and 2.153(2), 2.156(2) Å ($[ClSnOBu^t]_2$ (**9**)),[6,7] 2.168(4) and 2.173(4) Å ($[(Me_3Si)_2NSnOBu^t]_2$),[9] 2.079(4) and 2.099(4) Å ($[Ph_3SiOSnOBu^t]_2$),[10] 2.128(4) and 2.165(4) Å ($[Sn(OBu^t)_2]_2$),[6] and 2.141(2), 2.167(2), and 2.169(2), 2.193(2) Å (dinuclear calixarene $[Bu^t\text{-calix}]Sn_2$).[11] Moreover, the tin atoms in chloroalkoxide **9** are involved in short intermolecular nonbonded contacts with the chlorine atoms (3.619 or 3.722 Å; the sum of the van der Waals radii of the Sn and Cl atoms is ~4.00 Å).[12] In compound **5**, these contacts are absent (the shortest Sn...Cl distance in **5** is 5.235 Å).

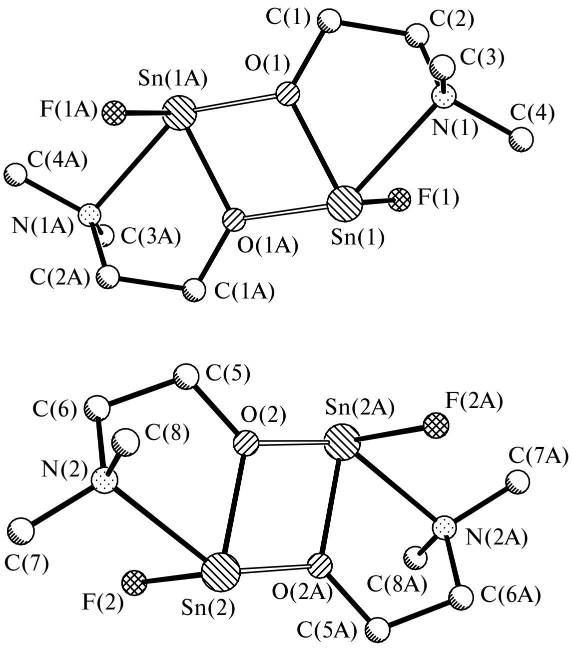

Fig. 2. Molecular structure of dimeric tin(II) fluoroalkoxide **6** (two crystallographically independent dimeric molecules are shown).

The intramolecular Sn←N coordination bonds in the structures of **5** (2.499(4) Å) and **7** (2.505(5) Å) are substantially shorter than those in compound **8** (2.617(3) and 2.615(3) Å) due to the presence of sterically bulky substituents in the molecules of the two first compounds. However, these bonds are substantially longer than those

Table 1. Selected geometric parameters (bond lengths (*d*) and bond angles (ω)) in the dimers $[XSnOCH_2CH_2NMe_2]_2$ (X = Cl (**5**), N_3 (**7**), or $(Me_3Si)_2N$ (**8**))

Bond	*d*/Å			Angle	ω/deg			Angle	ω/deg		
	5	**7**	**8**		**5**	**7**	**8**		**5**	**7**	**8**
Sn—O	2.104(3)	2.125(4)	2.133(2), 2.137(2)	O—Sn—X	97.1(1)	90.3(2)	106.34(9), 103.3(1)	X—Sn←O	87.4(1)	86.5(2)	94.24(9), 95.10(9)
Sn←O	2.240(3)	2.225(4)	2.267(2), 2.299(2)	O—Sn←N	72.9(1)	72.4(1)	71.14(9), 71.19(9)	N→Sn←O	139.9(1)	139.3(1)	138.99(8), 138.97(9)
Sn←N	2.499(4)	2.505(5)	2.617(3), 2.615(3)	X—Sn←N	87.9(1)	83.4(2)	90.4(1), 93.0(1)	Sn—O→Sn	111.8(1)	111.7(2)	111.1(1), 112.2(1)
Sn—X	2.473(1)	2.220(5)	2.147(3), 2.143(3)	O—Sn←O	68.2(1)	68.3(2)	68.45(9), 67.79(9)				

in monomeric dialkoxide **2** (2.458(2) Å),[2] which is associated with their dimeric structures.

Because of the dimeric structure, the Sn atoms in compound **5** have a distorted trigonal-bipyramidal configuration with the lone electron pair in an equatorial position.[13] The distortions are manifested in deviations of the Cl—Sn—O bond angles from the ideal value (120°) for a trigonal bipyramid and deviations of the N→Sn←O bond angles from 180° (see Table 1). Such distortions are typical of dimeric Sn^{II} compounds containing the tin atom in a trigonal bipyramidal configuration and the lone electron pair in an equatorial position (see Table 1).

The oxygen atoms of the bridging $Me_2NCH_2CH_2O$ ligands have a planar geometry (the sum of the bond angles is 359.0°). The Sn...Sn distance in dimer **5** (3.597 Å) is indicative of the absence of interactions between these atoms.

Thus, we demonstrated that, as opposed to alkoxy derivatives of Ge^{II}, the presence of one intramolecular coordination bond and two sterically unhindered electron-withdrawing substituents is insufficient for stabilization of the corresponding Sn^{II} compounds in the monomeric form. As a result, unsymmetrical divalent tin compounds stabilized by one intramolecular coordination bond tend to form dimers (rather than coordination polymers) through bridging oxy ligands. The intramolecular Sn←O coordination bonds in these dimers are substantially longer than the Sn—O covalent bonds. Monodentate ligands (chlorine or fluorine) are not involved in intermolecular nonbonded interactions. Studies of the reactivity of haloalkoxides **5** and **6** are presently underway.

Experimental

All operations were carried out under dry argon purified from traces of oxygen using the standard Schlenk technique or *in vacuo*. Tetrahydrofuran was distilled over sodium, stored over benzophenone ketyl, and distilled into reaction vessels immediately before use. Compound **2** was synthesized according to a procedure described earlier.[10] Commercial SnF_2 (Aldrich) was used. The NMR spectra were recorded on a Bruker AM360 (360.13 MHz for ^1H, 90.55 MHz for ^{13}C, and 111.92 MHz for ^{119}Sn) instrument in ethanol-free dry $CDCl_3$. The chemical shifts in the ^1H and ^{13}C NMR spectra were measured in ppm relative to the signals of the solvent and converted to the δ scale according to standard formula. The chemical shifts in the ^{119}Sn NMR spectra were measured relative to $SnMe_4$ as the external standard. The accuracy of measurements of the chemical shifts is ±0.01 (^1H), ±0.05 (^{13}C), and ±0.2 ppm (^{119}Sn). The spin-spin coupling constants are given with an accuracy of ±0.1 Hz. The assignment of the signals in the ^{13}C NMR spectra was made using the APT technique. The melting points were measured in sealed tubes on a SANYO Gallenkamp PLC instrument. Elemental analysis was performed on an automated Carlo Erba EA1108 CHNS-O CHN microanalyzer.

2-Dimethylaminoethoxychlorotin(II) (5). A solution of $Sn(OCH_2CH_2NMe_2)_2$ (**2**) (8.80 g, 29.9 mmol) in THF (30 mL) was added with stirring to a solution of $SnCl_2$ (5.97 g, 31.5 mmol) in THF (40 mL) at ~20 °C. After ~15 min, the slightly exothermic reaction produced a precipitate. Crystallization of the latter from the reaction mixture at −12 °C afforded colorless transparent prismatic crystals. The yield was 13.8 g (95%), m.p. ≥160 °C (with decomp.). Found (%): C, 19.67; H, 4.05; N, 5.60. $C_4H_{10}ClNOSn$. Calculated (%): C, 19.83; H, 4.16; N, 5.78. ^1H NMR, δ: 2.22 (s, 6 H, Me_2N); 2.59 (t, 2 H, CH_2N, ^3J = 5.5 Hz); 3.77 (t, 2 H, CH_2O, ^3J = 5.5 Hz). ^{13}C NMR, δ: 43.5 (Me_2N); 57.7 (CH_2N); 59.3 (CH_2O). ^{119}Sn NMR, δ: −332.8.

2-Dimethylaminoethoxyfluorotin(II) (6). A solution of $Sn(OCH_2CH_2NMe_2)_2$ (**2**) (3.3910 g, 11.5 mmol) in THF (40 mL) was added to SnF_2 (1.8048 g, 11.5 mmol) at ~20 °C. After completion of the slightly exothermic reaction, the mixture was heated to boiling over a short period of time, cooled, and filtered. The filtrate was concentrated *in vacuo*. A white solid substance was obtained in a yield of 4.81 g (93%). Crystallization of this substance from THF at −12 °C afforded compound **6**, m.p. 124—125 °C. Found (%): C, 21.57; H, 4.31; N, 6.48. $C_4H_{10}FNOSn$. Calculated (%): C, 21.28; H, 4.46; N, 6.20. ^1H NMR, δ: 2.28 (s, 6 H, Me_2N, $^1J_{C,H}$ = 136 Hz); 2.61 (br.s, 2 H, CH_2N); 3.86 (t, 2 H, CH_2O, $^3J_{H,H}$ = 5.2 Hz). ^{13}C NMR, δ: 43.1 (br, Me_2N); 58.14 (CH_2N); 59.9 (CH_2O).

X-ray diffraction study of compounds 5 and 6. Crystals of **5** ($C_8H_{20}Cl_2N_2O_2Sn_2$, M = 484.54) are monoclinic, space group $P2_1/c$, at T = 120 K a = 6.6006(12) Å, b = 11.171(2) Å, c = 10.9493(17) Å, β = 92.244(4)°, V = 806.7(2) Å^3, Z = 2, d_{calc} = 1.995 g cm^{-3}, $F(000)$ = 464, μ = 3.417 mm^{-1}. The unit cell parameters and intensities of 9212 reflections were measured on an automated Bruker SMART 1000 diffractometer equipped with a CCD area detector and a low-temperature Oxford CryoSystem device (Mo-Kα radiation, graphite monochromator, ω- and φ-scanning technique, θ ≤ 30.0°). The absorption correction was applied using the SADABS program.[14] The structure was solved by direct methods and refined by the full-matrix least-squares method with anisotropic displacement parameters for nonhydrogen atoms. Hydrogen atoms were positioned geometrically and refined isotropically with fixed positional (riding model) and thermal ($U_{iso}(H) = 1.5U_{eq}(C)$ for Me groups and $U_{iso}(H) = 1.2U_{eq}(C)$ for all other groups) parameters. The final R factors were R_1 = 0.0424 for 1670 independent reflections with $I > 2\sigma(I)$ and wR_2 = 0.1055 for all 2344 (R_{int} = 0.042) independent reflections.

Crystals of **6** ($C_8H_{20}F_2N_2O_2Sn_2$, M = 451.64) are monoclinic, space group $P2_1/n$, at T = 120 K a = 14.682(13) Å, b = 6.625(5) Å, c = 15.287(14) Å, β = 91.78(2)°, V = 1486(2) Å^3, Z = 4, d_{calc} = 2.019 g cm^{-3}, $F(000)$ = 864, μ = 3.373 mm^{-1}. The unit cell parameters and reflection intensities were measured on an automated Bruker SMART 1000 diffractometer equipped with a CCD area detector and a low-temperature Oxford CryoSystem device (Mo-Kα radiation, graphite monochromator, ω- and φ-scanning technique, θ ≤ 26.0°). All calculations were carried out with the use of the SHELXTL PLUS program package (version 5.10).[15] The tables of atomic coordinates and geometric parameters for compounds **5** and **6** were deposited with the Cambridge Structural Database.

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