Unexpected formation of a dimeric cation-anionic complex of hypercoordinated tin in the reaction of bis[(2-oxopyrrolidino)methyl]tin dichloride with $AgBF_4$

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A new cation-anionic complex of hypercoordinated tin, $\{[L_2Sn(OH)]^+BF_4^-\}_2$ (L is a bidentate (2-oxopyrrolidino)methyl C,O-chelating ligand), was obtained by the reaction of L_2SnCl_2 with $AgBF_4$ and structurally characterized by X-ray diffraction analysis. In crystalline form, the BF_4^- anions are bound to the dications through O—H...F hydrogen bonds (the H—F distance is 1.78 Å). The octahedral coordination of the Sn atoms is strongly distorted because of a weak additional interaction with solvate molecules of dioxane (the Sn—O distance is 3.16 Å).

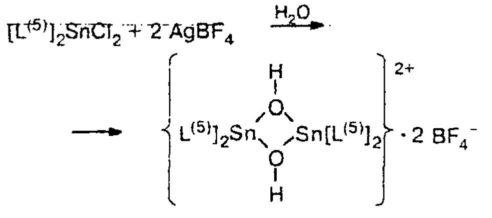
Key words: hypercoordinated tin compounds, intramolecular coordination, X-ray diffraction analysis.

Depending on the nature of the nucleophile in a reagent, the reaction of bis(lactamomethyl)germanium dichlorides $[L^{(n)}]_2GeCl_2$ (L is a bidentate lactamomethyl C,O-chelating ligand, n = 5—7 is the lactam ring size) with lithium (LiX) and silver salts (AgX) and trimethylsilyl derivatives Me_3SiX (X = F, Br, I, OTf, and ClO_4) results in different types of final products.[1] If the nucleophugality of an entering (F or Br) group is close to that of the leaving group (Cl), both chlorine atoms are replaced by a nucleophile to give compounds with the same stereochemical configuration of the central atom as that of the starting dichlorides (according to X-ray data). The C atoms are *trans* and the coordinating O and Hal atoms are *cis* to each other (*cis*-$[L^{(n)}]_2GeX_2$). If the nucleophugalities of an entering (I, OTf, or ClO_4) and a leaving (Cl) group differ significantly, only one halogen atom is replaced by the nucleophile, and the reaction product has *trans*-arranged C and O atoms and monodentate ligands (*trans*-$[L^{(n)}]_2Ge(Cl)X$). In the solid state, these monochlorides are molecular complexes of six-coordinate germanium with a covalent Ge—Cl bond and a predominantly ionic X→Ge bond. They possess higher conductivities (in CH_2Cl_2) than covalent $[L^{(n)}]_2GeX_2$ dihalides, thus suggesting that solutions of $[L^{(n)}]_2Ge(Cl)X$ monochlorides contain $\{[L^{(n)}]_2Ge(Cl)\}^+$ germacenium ions stabilized by two intraionic O→Ge coordination bonds.[1]

In contrast, the reaction of dichlorides *cis*-$[L^{(n)}]_2SnCl_2$ with lithium halides yields covalent dihalides $[L^{(n)}]_2SnX_2$ (X = Br and I) with retention of *cis*-configuration of the starting dichloride.[2]

The goal of the present work was to obtain tin compounds definitely possessing *trans*-configuration of the coordination center (*i.e.*, halides $[L^{(n)}]_2Sn(Cl)X$ of the *trans*-type) as precursors of the Sn analogs of the above-mentioned germacenium ions. For this purpose, we studied the reaction of a five-membered lactam derivative, $[L^{(5)}]_2SnCl_2$, with $AgBF_4$. Note that $AgBF_4$ reacts with a similar dichloride, $[L^{(7)}]_2GeCl_2$, to give a product in which one Cl atom is replaced by F, while the other by a BF_4 group, *i.e.*, a cation-anionic complex $[L^{(7)}]_2Ge(F)BF_4$.[1—3]

It turned out that, as with $[L^{(7)}]_2GeCl_2$, the reaction of its Sn analog, $[L^{(5)}]_2SnCl_2$, with $AgBF_4$ in acetonitrile (under conditions without special precautions against atmospheric moisture) also occurs with replacement of both Cl atoms. However, unexpectedly, the reaction product was a dimeric cation-anionic complex **1**, which is similar to some extent to disiloxane cation-anionic complexes, $\{[L^{(n)}]_2SiOSi[L^{(n)}]_2\}^{2+} \cdot X^{2-}$ (X = $HgCl_4^{2-}$ and $Hg_2Cl_6^{2-}$),[4] containing disilicenium dications stabilized by an intraionic O→Si coordination bond.



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$L^{(5)}$ is (2-oxo-1-pyrrolidinyl)methyl

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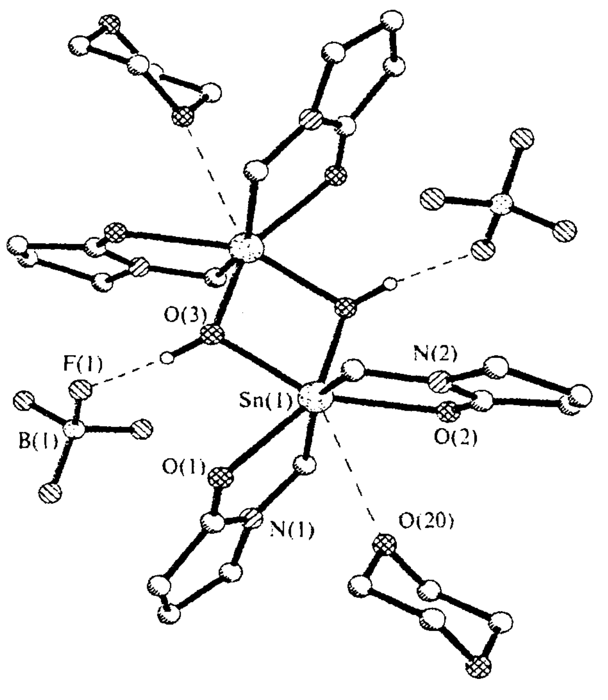

Fig. 1. Structure of the cation-anionic complex **1** in the crystal (a stoichiometric unit is depicted; only hydrogen atoms involved in H-bonding are shown).

The composition of complex **1** was confirmed by IR and ^{1}H NMR spectroscopy and its structure was proved by X-ray diffraction analysis.

According to X-ray data,* the cation-anionic complex **1** in the crystal is centrosymmetric (Fig. 1), *i.e.*, the dications with attached dioxane molecules are located in crystallographic inversion centers. The electrostatic interaction of the dication with BF_4^- anions is complemented by rather strong O—H...F hydrogen bonds (the H—F distance is equal to 1.78 Å, and the O—H—F angle is 172°). The octahedral coordination of the Sn atoms is appreciably distorted because of an additional Sn...O (dioxane) interaction. The Sn...O (dioxane) distance amounts to 3.16 Å, *i.e.*, it is shorter by ~0.5 Å than the sum of van der Waals radii of these atoms. As a result, the C—Sn—C, C—Sn—O, and O—Sn—O angles between Sn—*trans*-C(O) bonds in the dication are 151—153°. Insofar as each dioxane molecule is bound to two dications, the latter form polymeric chains in the crystal, which is generally characteristic of tin compounds.

Recently, X-ray data on dimeric complexes $[Bu^n_2Sn(H_2O)OH]_2^{2+}(OTf^-)_2$ (**2**)[6] and $(RL'SnOMe)_2$ (**3**)[7] (R = —C(Et)=CHMe and L' is a bidentate C,O-chelating ligand, —C(Me)=C(Et)BEt$_2$O(Me)—) have been published. In the structure of the cation-anionic complex **2**, the bond between the six-coordinate Sn atom and the O atom of the triflate ligand is relatively weak (2.622 Å), whereas the Sn atom in "neutral" complex **3** is five-coordinate. Both compounds have hydroxy (methoxy) bridges whose O atoms are included in a four-membered $\overline{\text{Sn—O(X)—Sn—O(X)}}$ ring (X = H and Me, respectively). Unlike complex **1**, complex **2** does not form H-bonds between the anions and the dication.

Experimental

The IR spectrum of a ~5% solution of compound **1** in $CHCl_3$ was recorded on a Specord IR-75 instrument (KBr).

The ^{1}H NMR spectrum of a solution of **1** in $CDCl_3$ (C = 0.5 mol L^{-1}) was obtained with a Varian XL-400 spectrometer (400.1 MHz) in the pulse regime followed by Fourier transform and ^{2}H-stabilization of resonance conditions. ^{1}H chemical shifts are referred to Me_4Si as the internal standard.

(O—Sn)-Bischelate 2,2,4,4-tetrakis[(2-oxopyrrolidino)-methyl]cyclodistannoxane-1,3-dionium bis(boron tetrafluoride) (1) · 2 dioxane. A solution of $AgBF_4$ (0.97 g, 5 mmol) in 7 mL of MeCN was added to a boiling solution of bis[(2-oxopyrrolidino)methyl]tin dichloride (0.96 g, 2.5 mmol) in 30 mL of MeCN. The reaction mixture was refluxed for 30 min and then cooled; the precipitate of AgCl that formed was filtered off. The solvent was removed *in vacuo* to give compound **1** (0.8 g, 63%), m.p. 193—195 °C (dioxane). IR ($CHCl_3$), ν/cm^{-1}: 1505 m, 1610 s (NCO). ^{1}H NMR ($CDCl_3$), δ: 2.09 (m, 4 H, CCH_2C); 2.63 (m, 4 H, $COCH_2$); 2.85 (br.s, 4 H, $SnCH_2$); 3.74 (m, 4 H, NCH_2); 3.71 (m, 8 H, $C_4H_8O_2$). No signals from OH protons are observed, probably, because of deuterium exchange with the solvent.

A single crystal of compound **1** was obtained by recrystallization of a sample from dioxane. The X-ray diffraction analysis was performed on a Siemens P3/PC diffractometer (150 K, λ(Mo-Kα) radiation, θ/2θ scanning mode, $2\theta_{max}$ = 56°, 3833 measured reflection intensities). The colorless crystals of **1** are triclinic, a = 6.840(5) Å, b = 10.671(9) Å, c = 11.960(8) Å, α = 106.65(6)°, β = 93.29(6)°, γ = 91.67(6)°, V = 834(1) Å^3, d_{calc} = 1.843 g cm^{-3}, Z = 1 ($C_{24}H_{42}B_2N_4O_8F_8Sn_2$), space group $P\bar{1}$ (half of the molecule is in the independent area of the cell). The structure was solved by the Patterson method and refined for all F^2 by the least-squares method in the anisotropic approximation for nonhydrogen atoms. Hydrogen atoms were located using the "rider" model with fixed C—H distances and thermal parameters U = 0.05 Å^2. The H(31) atom bonded to an O atom was located from a difference map and refined with a fixed O—H distance. The final residuals are R_1 = 0.0436 and wR_2 = 0.1047, $GOOF$ = 1.061 from 2833 reflections with $I > 2\sigma(I)$. All computations were performed on an IBM PC with

Table 1. Main bond lengths (d) in the cation-anionic complex **1**

Bond	d/Å	Bond	d/Å
Sn(1)—O(3)	2.108(4)	O(3)—Sn(1a)	2.119(3)
Sn(1)—O(3a)	2.119(3)	O(3)—H(31)	0.963(30)
Sn(1)—C(1)	2.149(5)	N(1)—C(1)	1.437(6)
Sn(1)—O(1)	2.294(3)	N(1)—C(2)	1.321(6)
Sn(1)—O(2)	2.307(4)	B(1)—F(1)	1.401(7)
Sn(1)...O(20)	3.157(7)	B(1.)—F(2)	1.370(7)
O(1)—C(2)	1.251(6)	F(1)...H(31)	1.783(30)

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* For preliminary X-ray diffraction data see Ref. 5.

Table 2. Main bond angles (ω) in the cation-anionic complex **1**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
O(3)—Sn(1)—O(3a)	71.86(14)	O(3)—Sn(1)—O(2)	151.55(13)	Sn(1)—O(3)—Sn(1a)	108.14(14)
O(1)—C(2)—N(1)	123.6(4)	O(3a)—Sn(1)—O(2)	80.71(13)	Sn(1)—O(3)—H(31)	115.3(5)
O(1)—C(2)—C(3)	126.0(4)	C(1)—Sn(1)—O(2)	88.7(2)	Sn(1a)—O(3)—H(31)	115.7(5)
O(3)—Sn(1)—C(1)	102.4(2)	F(1)...H(31)—O(3)	172.1(5)	C(2)—N(1)—C(1)	122.2(4)
O(3a)—Sn(1)—C(1)	98.5(2)	B(1)—F(1)...H(31)	127.1(5)	O(20)—Sn(1)—O(1)	64.1
O(3)—Sn(1)—O(1)	81.72(13)	F(3)—B(1)—F(2)	108.8(5)	O(20)—Sn(1)—O(3)	75.3
O(3a)—Sn(1)—O(1)	151.88(12)	C(2)—O(1)—Sn(1)	108.8(3)	O(20)—Sn(1)—O(3)	75.3
C(1)—Sn(1)—O(1)	77.6(2)	N(1)—C(1)—Sn(1)	107.7(3)		

the SHELXTL PLUS program.[8] The main bond lengths and bond angles are presented in Tables 1 and 2, respectively. Other geometric parameters and atomic coordinates are available from the Cambridge Structural Database.

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