Organotin Fluorides

Water-Soluble Organotin Compounds – Syntheses, Structures and Reactivity towards Fluoride Anions in Water


Abstract: Herein, we report the syntheses of the water-soluble organotin compounds \([\text{Me}_2\text{H}N(CH_2)_3]_2\text{SnF}_2\text{Cl}_2\) (1, X = Cl, Y = ClO_4") and \([\text{Me}_2\text{H}N(CH_2)_3]_2\text{SnF}_2\text{Cl}\) (2, X = Cl, Y = ClO_4") and \([\text{Me}_2\text{H}N(CH_2)_3]_2\text{SnF}_2\text{Cl}\) (3, X = Cl, Y = ClO_4") and \([\text{Me}_2\text{H}N(CH_2)_3]_2\text{SnF}_2\text{Cl}\) (4, X = Cl, Y = ClO_4"). The compounds were characterized by elemental analysis, electro spray mass spectrometry, \(^1H, ^{13}C, ^{19}F, \text{and} ^{119}Sn\) NMR spectroscopy, and in the case of compounds 1, 3 and 4, by single-crystal X-ray diffraction analysis. The reaction of compound 2 with fluoride anions in water was investigated by NMR spectroscopy. DFT calculations accompany the experimental work.

Introduction

For many years, research on selective anion recognition is a hot topic in host-guest and supramolecular chemistry, the achievements of which have been regularly reviewed.[1] Considerable efforts have been devoted to the study of the complexation of fluoride anions, both by purely organic hosts and organometallic Lewis acids.[2,3] Among halide anions, fluoride emerges due to its high charge density, Brønsted basicity, and high hydration enthalpy (more than 500 kJ/mol). The latter makes it a structure-directing agent, the former is toxic at high concentrations.[4] Organotin-based receptors show a high capacity for binding fluoride anions in organic solvents.[5–7] This is attributed to the Lewis acidity of the tin centre which in turn is enhanced by electron-withdrawing substituents.[8] Some organotin compounds were studied as ionophores for fluoride anion selective electrodes.[9] Representative examples are bis[fluoro-di-n-octylstannyl]methane, \((n\text{-octyl}_2\text{Sn})_2\text{CH}_2\) that is commercially available for this purpose,[10] and \(\text{o-SnPhF}_2\text{C}_6\text{H}_4\text{CH}_2\text{NMe}_2\).[9b] The former shows a de

Results and Discussion

Syntheses of Compounds 1 – 4 and Molecular Structures in the Solid State

The reaction in water of the diorganotin dichloride \([\text{Me}_2\text{N}(\text{CH}_2)_3]_2\text{SnCl}_2\) with two molar equivs. of perchloric acid, HClO_4", gave the corresponding ammonium perchlorate \([\text{Me}_2\text{H}N(CH_2)_3]_2\text{SnCl}_2\text{Cl}\text{O}_4\) (1), in quantitative yield. Furthermore, the reaction of compound 1 with two molar equivs. of tetraethylammonium fluoride, \(\text{NEt}_4\text{F}\), in \(\text{CH}_3\text{CN}\) gave, via halide exchange, the corresponding fluoride-substituted derivative \([\text{Me}_2\text{H}N(CH_2)_3]_2\text{SnF}_2\text{Cl}\text{O}_4\) (2), in quantitative yield (Scheme 1).

Compound 2 was also synthesized, in quantitative yield, by the reaction of \([\text{Me}_2\text{N}(\text{CH}_2)_3]_2\text{SnF}_2\text{Cl}\text{O}_4\) with two molar equivs. of HClO_4 (Scheme 2).

Similarly, the reaction of \([\text{Me}_2\text{N}(\text{CH}_2)_3]_2\text{SnCl}_2\) with two molar equivs. of HCl in water gave the zwitterionic diorganotetrafluorotellurodichloride stannate \([\text{Me}_2\text{H}N(CH_2)_3]_2\text{SnCl}_2\) (3, in quantitative yield (Scheme 1).

The reaction of compound 3 with four molar equivs. of \(\text{NET}_4\text{F}\) in \(\text{CH}_3\text{CN}\) gave, again via halide anion exchange,
Scheme 1. Syntheses of the diorganotin chlorides 1 and 3 and the diorganotin fluorides 2 and 4.

Scheme 2. Alternative synthesis of compound [(Me₂(H)N(CH₂)₃)₂SnF₂](ClO₄)₂, 2.

The colorless compounds 1–4 show good solubility in water but poor solubility in organic solvents. Compound 1 shows moderate solubility in acetonitrile, and compound 2 is moderately soluble in acetone and acetonitrile. Single crystals of compounds 1 and 3 suitable for X-ray diffraction analyses were each obtained by slow evaporation of the corresponding solution in water at room temperature. Single crystals of compound 4 were obtained as its water solvate 4·4H₂O by recrystallization from acetonitrile under non-inert conditions.

Both compounds 1 and 4·4H₂O crystallized in the triclinic space group P1̅, whereas compound 3 crystallized in the monoclinic space group P2₁/c [see Experimental Section and Supporting Information (SI) for further crystallographic and structural data (Tables S1–S12)]. Figures 1–6 show the molecular structures of compounds 1, 3 and 4·4H₂O, including some features in the crystal packing of compounds 1 and 4·4H₂O. The corresponding figure captions contain selected interatomic distances and angles.

The Sn(1) atom in the ammonium perchlorate derivative 1 is in a distorted octahedral [4+2]-coordination environment (Figure 1). The distortion from the ideal octahedral geometry is demonstrated by the observed values for the C(1)–Sn(1)–C(6), O(1)–Sn(1)–Cl(2), and O(5)–Sn(1)–Cl(2) angles of 141.60(13), 177.65(8), and 176.38(5), respectively. The O(1) and O(6) atoms approach the tin atom via the tetrahedral faces defined by C(1), C(6), Cl(1), and C(1), C(6), Cl(2), respectively. The Sn(1)–O(1) [2.757(3) Å] and Sn(1)–O(5) [3.051(3) Å] distances differ considerably from each other, thus suggesting an ion-pair character for the compound. The Sn–O distances within the molecular unit of compound 1 are larger than the Sn–O (perchlorate) distances reported for the organostannylene complex [4-tBu₂,6-{P(O)(O)₂iPr₂}₂C₆H₄(ClO₄)SnCr(CO)₅] [Sn–O 2.170(3) Å][11] FcP(O)(O)iPr₂SnPh₂(ClO₄) [Sn–O 2.283(4) Å][12] and FcP(O)(O)iPr₂SnPh₂(ClO₄) [Sn–O 2.273(2) Å; Fc = ferrocene].[12] These notwithstanding, Sn–O distances in compound 1 are shorter than the sum of the van der Waals radii of oxygen and tin atoms (3.80 Å).[13a] The Sn(1)–Cl(1) and Sn(1)–Cl(2) distances of 2.4119(8) and 2.4234(8) Å, respectively, are close to the sum of the covalent radii (2.41 Å)[13b] of the atoms involved. These distances are longer than the Sn–Cl distances in the tetracoordinated diorganotin compounds iPr₂SnCl₂ [2.357(1), 2.369(1) Å][14a] 8Bu₃SnCl₂ [2.334(1), 2.335(1) Å][14a] and Ar₅SnCl₂ [Ar = 2,6-Et₂C₆H₃, 2,6-iPr₂C₆H₃, 2,4,6-iPr₃C₆H₂; 2.353(2)-2.361(7) Å][14b] they are in the same range as reported for the Sn–Cl distances in (SnPh₂Cl₂)(1κO²N₂,2κO²-µ-L)M [2.4438(6), 2.4608(6) Å; M =
Ni; 2.4339(7), 2.4580(7) Å, M = Cu[14c] SnEt2Cl2·H2O [Sn–Cl 2.3951(4) Å][14d] {2-(Me2NCH2)C6H4}2SnCl2 [2.4394(5) Å], {2-(Me2NCH2)C6H4}2SnCl2 [2.4390(3) Å][14e] but shorter than those found in the diorganotetrachlorostannate derivative 3 [2.6074(8), 2.6260(7) Å, see below].

Figure 1. Molecular structure of compound 1 with the labelling scheme adopted for the atom positions. Thermal ellipsoids are drawn at 30 % probability level. Hydrogen atoms are omitted for clarity except those on the nitrogen atoms. Selected interatomic distances [Å]: Sn(1)–Cl(1) 2.4119(8), Sn(1)–Cl(2) 2.4234(8), Sn(1)–O(1) 2.757(3), Sn(1)–O(5) 3.051(3), Sn(1)–C(1) 2.122(3), Sn(1)–C(6) 2.122(3), N(1)–H(1) 0.83(4), N(2)–H(2) 0.90(5). Selected interatomic angles [°]: C(1)–Sn(1)–C(6) 141.60(13), O(1)–Sn(1)–Cl(2) 177.65(8), O(5)–Sn(1)–Cl(2) 176.38(5).

The crystal packing of compound 1 is mainly determined by a set of N–H···O (perchlorate) and N–H···Cl hydrogen bonds. In particular, two perchlorate anions weakly interacting with the tin center (see above) bridge two [(Me2(H)N(CH2)3)2SnCl2]+ moieties via N–H···O hydrogen bonds, thus forming a cyclic supramolecular assembly (see Figure 2).

N(1)–H(1)···Cl(2) hydrogen bonds with a H(1)···Cl(2) distance of 2.79(5) Å (N(1)···Cl(2) 3.357(4) Å) primarily determine the interaction between these cyclic supramolecular structures, which pile up along the a-direction in the crystal packing of compound 1.

The molecular structure of compound 3 is centrosymmetric, as a half of the molecule comprises the crystallographic asymmetric unit and the other half is generated by a center of inversion (Figure 3). The tin atom shows an octahedral environment with the C(1)–Sn(1)–C(1)i, Cl(1)–Sn(1)–Cl(1)i and Cl(2)–Sn(1)–Cl(2)i angles being 180.0° (i = 1 – x, 1 – y, 1 – z). The Sn(1)–Cl(1) and Sn(1)–Cl(2) interatomic distances of 2.6074(8) Å and 2.6260(7) Å, respectively, are larger than the corresponding distances in compound 1. However, they fit well into Sn–Cl distances reported for related diorganotetrachlorostannates[15] ranging between 2.571(2) Å for (Hthiamine)SnPh2Cl4[15j] and 2.67(1) Å for (tetrathiafulvalene)3SnEt2Cl4.[15d] The different organic substituents (Me, Et, vinyl, Ph) and participation in hydrogen bonding account for the variation of these distances. A representative example for a diorganotetrachlorostannate(IV) is (C6H14N)2[Sn(C6H5)2Cl4].[15m] In this compound, the cyclo-hexyl-ammonium cations located in general positions and the stannate(IV) anion that is located on a two-fold rotation axis...
are connected through N–H···Cl hydrogen bonds determining a layered structure in the crystal lattice. Also in the case of compound 3, the crystal packing is determined by N(1)–H(1)···Cl(2)/Cl(1) hydrogen bonds with a H(1)···Cl(2) and H(1)···Cl(1) distances of 2.524(2) and 2.853(5) Å, respectively [N(1)–H(1) 0.91(3), N(1)–Cl(1) 3.312(2); N(1)–Cl(2) 3.400(3) Å; i = 1/2 − x, 1/2 + y, 1/2 − z; ii = −1/2 + x, 3/2 − y, −1/2 + z].

The Sn(1) atom in the centrosymmetric zwitterionic diaminodiantimony diorganotetrafluorido stannate water solvate 4·H2O is hexacoordinated by C(1), C(1A), F(1), F(1i), F(2), and F(2i) (i = 1 – x, 1 – y, 1 – z), and shows an almost ideal octahedral environment with C(1)–Sn(1)–C(1)i 180, H(2L) 0.806(18), F(2)–O(2L) 2.735(2) Å [O(2L)–H(3L) 0.799(18), F(2)–H(3L) 1.943(18), O(2L)–H(4L) 0.842(18)]. Selected interatomic angles (°): C(1)–Sn(1)–C(1)i 180, F(2)–Sn(1)–F(2)i 180.0, F(2)–Sn(1)–F(2)i 180.0. Symmetry operations: i = 1–x, 1/2 + y, 1/2 − z; ii = −1/2 + x, 3/2 − y, −1/2 + z.

For the dinuclear diorganotin difluoride triflic acid solvate SnF distances ranging between 2.128(8) and 2.352(12) Å were reported.[16g] The longer distances belong to μ2-bridging fluorine atoms.

Each fluorine substituent of 4·H2O is involved in a hydrogen bridge with a water molecule at F(1)–O(1L) and F(2)–O(2L) distances of 2.625(2) and 2.735(2) Å, respectively.

Analogously to compound 1, the crystal structure of compound 4·H2O also contains different hydrogen bond bridges (Figure 5).

In particular, discrete tetrameric (H2O)4 water clusters assemble the diorganotetrafluorido stannate units via F···H–O hydrogen bonds in layers (Figure 5). The (H2O)4 water clusters can be described as square-like cyclic assemblies of hydrogen-bonded water molecules that interact at their corners with the F atoms of the diorganotetrafluorido stannate moieties. The stitching pattern determined by the (H2O)4 water clusters features sequences of fused 8-membered and 16-membered cyclic motifs (Figure 5). N–H···F interactions [H···F = 1.89(3), N···F = 2.705(3) Å] pack symmetry-related units of compound 4 along the a-direction (Figure 6).
We wish to underline the major role played by the halide ligands in 3 (chloride) and 4 (fluoride) disposed in the equatorial plane of the pseudo-octahedral coordination sphere at the tin(IV) center, in determining the crystal packing via H-bonds involving either the protonated ammine groups or solvate water molecules. The same features can be recognized in compound 1, in which also the perchlorate counter-ion contributes to the packing in the lattice.

**Characterization of Compounds 1–4 in Solution by NMR Spectroscopy and Electrospray Mass Spectrometry**

The compounds \([\text{Me}_2N(CH_2)_3]_2\text{SnF}_2\cdot2\text{H}_2\text{O}, [\text{Me}_2N(CH_2)_3]_2\text{SnCl}_2\cdot2\text{H}_2\text{O}, [\text{Me}_2N(CH_2)_3]_2\text{SnCl}_2\cdot2\text{H}_2\text{O}, [\text{Me}_2N(CH_2)_3]_2\text{SnF}_2\cdot2\text{H}_2\text{O}\) were observed. The addition of a broad resonance at \(\delta = 2.82\) ppm. This resonance is shifted by 0.34 ppm to lower field in comparison with that measured for \([\text{Me}_2N(CH_2)_3]_2\text{SnF}_2\cdot2\text{H}_2\text{O}\) (2.48 ppm in D$_2$O). In CD$_2$CN and [D$_6$]acetone solutions, the NCH$_3$ protons appear as doublet resonances at 2.86 ppm \([J(\text{H}^{-1-\text{H}}) = 4.76\text{ Hz}]\) and 3.00 ppm \([J(\text{H}^{-1-\text{H}}) = 4.39\text{ Hz}]\), respectively.

Noteworthy, the coupling constants \(2J(\text{H}^{-1-\text{Sn}})\) of the SnCH$_2$ protons in compound 2 are about 95 Hz (in CD$_2$CN) and 105 Hz (in [D$_6$]acetone and D$_2$O). These values are characteristic for hexacoordinated diorganotin(IV) compounds with the organic substituents being trans-disposed, and are a little larger than the corresponding coupling constants measured for the hexacoordinated organotin compound \([\text{Me}_2N(CH_2)_3]_2\text{SnF}_2\cdot2\text{H}_2\text{O}\) (90 Hz in D$_2$O, 94 Hz in CD$_2$Cl$_2$ at –60 °C).[10]

A $^{119}$Sn NMR spectrum of compound 3 in D$_2$O showed one resonance at \(\delta = –264\). In a $^{13}$C NMR spectrum a resonance at \(\delta = 31.0\) \([J(13\text{C}^{-1-\text{Sn}}) = 938/976\text{ Hz}]\) assigned to the SnCH$_2$ carbon atom was observed. This chemical shift is similar to those for the corresponding carbon atoms in compound 1 at \(\delta = 29.9\) \([J(13\text{C}^{-1-\text{Sn}}) = 95/1003\text{ Hz}]\) and in the hexacoordinated organotin compound \([\text{Me}_2N(CH_2)_3]_2\text{SnCl}_2\) at \(\delta = 31\) \([J(13\text{C}^{-1-\text{Sn}}) = 922\text{ Hz}]\).[14] Measured in CDCl$_3$. In a $^1$H NMR spectrum of the same sample a chemical shift of the SnCH$_2$ protons at \(\delta = 1.55\) \([J(\text{H}^{-1-\text{Sn}}) = 1135.6\text{ Hz}]\) hints with caution to a trinuclear cluster of composition C$_{30}$H$_{81}$N$_6$O$_7$Cl$_4$Sn$_3$ (calcd. $m$/z = 311.0) was found. This is assigned to a tinoxo cluster of composition C$_{30}$H$_{81}$N$_6$O$_7$Cl$_4$Sn$_3$ (calcd. $m$/z = 311.0). In the negative mode, a mass cluster centered at \(m/z = 311.0\) was found. This is assigned to \([\text{Me}_2N(CH_2)_3]_2\text{SnF}_2\cdot2\text{H}_2\text{O}\).

The electrospray ionization mass spectra (positive mode, see Supporting Information) of compounds 1, 2, and 3 in water/acetonitrile solution showed each a mass cluster centered at \(m/z = 309.1\) that is assigned to \([\text{Me}_2N(CH_2)_3]_2\text{SnOH}\). In addition, the spectra of compounds 1 and 3 show a mass cluster centered at \(m/z = 327.1\) which belongs to \([\text{Me}_2N(CH_2)_3]_2\text{SnCl}\). Notably, the spectrum of compound 3 showed also a mass cluster centered at \(m/z = 1135.6\) that hints with caution to a trinuclear tinoxo cluster of composition C$_{30}$H$_{81}$N$_6$O$_7$Cl$_4$Sn$_3$ (calcd. $m$/z = 313.5). In the case of compound 4, a mass cluster centered at \(m/z = 311.0\) was found. This is assigned to \([\text{Me}_2N(CH_2)_3]_2\text{SnF}_2\cdot2\text{H}_2\text{O}\).

Reactivity of Compound 2 towards Fluoride Anions in Water

The diorganotin compound \([\text{Me}_2N(CH_2)_3]_2\text{SnF}_2\cdot2\text{H}_2\text{O}, 2\) reacts with both sodium and potassium fluoride giving compound \([\text{Me}_2N(CH_2)_3]_2\text{SnF}_4\) (Scheme 3a). The formation of compound 4 was established by $^1$H, $^{13}$C, $^{19}$F, and $^{119}$Sn NMR spectroscopy (see Supporting Information). When KF was made to react with compound 2, the precipitation of poorly soluble KClO$_4$ was observed, further favoring the formation of compound 4.
Scheme 3. (a) Synthesis of the organotin compound 4 by the reaction in water of compound 2 with two molar equivs. of sodium or potassium fluoride. (b) Schematic representation of the ionization equilibrium responsible for the absence of $^{1}J_{(19F-^{117}/^{119}Sn)}$ and $^{1}J_{(^{119}Sn-19F)}$ couplings in the NMR spectra of compound 4.

The $^1H$ NMR spectra of the reaction mixtures in D$_2$O containing compound 2 and two molar equivs. of NaF or KF, shows that the unresolved coupling constant $^{1}J(^{1}H-^{117}/^{119}Sn)$ of the SnCH$_2$ protons in compound 4 is about 110 Hz (when KF is used) and 120 Hz (when a higher concentration of compound 2 is used for the reaction with NaF). In the $^{13}C$ NMR spectra, the unresolved coupling constants $^{1}J(^{13}C-^{117}/^{119}Sn)$ of 145 Hz (KF) and 159 Hz (NaF) are close to the value of 164 Hz found for 2 (in D$_2$O). The $^{19}F$ NMR spectra of the same samples show a single resonance at $\delta = -125$ without coupling satellites $^{1}J(^{19}F-^{117}/^{119}Sn)$. This resonance is close to −123 ppm measured for 1 in D$_2$O, and that reported for the complex salt K$_2$[Me$_2$SnF$_4$·2H$_2$O]. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm. A $^{119}$Sn NMR spectrum of a solution of compound 2 in D$_2$O to which two molar equivs. of NaF had been added shows one signal at $-122$ ppm.

Effect of Solution pH on the Behavior of (Me$_2$(H)N(CH$_2$)$_3$)$_2$SnF$_4$

In order to verify the effect of pH on the structure of (Me$_2$(H)N(CH$_2$)$_3$)$_2$SnF$_4$, a few drops of aqueous NaOH solution were added to the NMR tube containing compound 4 in D$_2$O. The experiment shows that exclusively the diorganotin compound (Me$_2$N(CH$_2$)$_3$)$_2$SnF$_2$ is formed. Under basic conditions, pH > 8, compound 4 undergoes deprotonation of the ammonium terminal group. This reaction is accompanied by loss of fluoride anions forming the neutral compound (Me$_2$N(CH$_2$)$_3$)$_2$SnF$_2$, (Scheme 4).

The reversibility of binding/releasing of fluoride anions in the reaction of compound 2 with NaF or KF depends on the pH of the solution, which is very important especially for most practical purposes. Thus, a reusable feature of compound 2 as fluoride receptor could be established as deprotonation of compound (Me$_2$(H)N(CH$_2$)$_3$)$_2$SnF$_4$, takes place in basic solutions coincide with the formation of the compound (Me$_2$N(CH$_2$)$_3$)$_2$SnF$_2$ that is in turn easily to be further separated from other fluoride salts, NaF or KF, using extraction by dichloromethane as a solvent (Scheme 5).

Binding Selectivity of Compound [(Me$_2$(H)N(CH$_2$)$_3$)$_2$SnF$_2$]ClO$_4$, 2, towards Fluoride Anions

NMR measurements were used for studying the selectivity of compound 2 towards different anions. For this purpose, fluoride, chloride, bromide, and iodide anions were chosen. The reaction in D$_2$O of compound 2 with a mixture consisting of two molar equivs. of NaF, NaCl, NaBr, and NaI, monitored by means of $^1H$, $^{13}C$ and $^{19}F$ NMR spectroscopy (see Supporting Information, Figures S34–S36b), gave exclusively compound 4 with the binding of fluoride anion in 4 being favored over chloride, bromide and iodide (see Theoretical calculations below).
The selectivity in water of 2 towards fluoride is a prerequisite for a real application as any selective fluoride receptor should be able to bind fluoride anions in real samples in the presence of other anions.

**Theoretical Calculations**

In order to get a deeper insight into the nature of the bonding and the reactivity of the compounds discussed above, theoretical calculations were carried out at density functional theory (DFT) level,[20] by adopting the hybrid mPW1PW functional[21] along with Ahlrichs and Schäfer double-ζ basis sets[22] in the Def2SVP Weigend formulation.[23] As a validation of the computational setup, the metric parameters optimized at the DFT level were compared with the relevant structural ones for compound 3. In the optimized structure, average Sn–Cl (d_{Sn–Cl} = 2.727 Å) and Sn–C distances (d_{Sn–C} = 2.177 Å) are only very slightly overestimated as compared to the corresponding structural ones (2.616 and 2.138 Å, respectively). As expected, the natural charge on the central tin ion (Q_{Sn} = 1.643 [e]) on the chloride anions (Q_{Cl} = –0.574 [e]) and on the C(1)/C(1A) atoms (Q_{C} = –0.924 [e]), along with the average Wiberg bond indices[24] (WBI Sn–Cl = 0.433) clearly testify for strongly polarized interactions between the central cation and the C(1), C(1A), Cl(2) and Cl(2A) coordinating atoms. A second order perturbation theory (SOPT) analysis of Fock Matrix in NBO basis shows that in the gas phase the N–H groups are involved in a hydrogen bonding interaction with two of the chloride anions (LP(Cl) → BD*(N–H), 29.28 kcal/mol), responsible for the slight elongation of the average Sn–Cl distances with respect to the structural ones. By neglecting the interactions with crystallization water molecules, similar considerations can be done for compound 4, where fluoride anions in place of chlorides result in an increase in the ionic character of the Sn–halide bond (Q_{Sn} = 2.264 and 1.838 [e], respectively), as testified by the elongation of the optimized Sn–N distances (d_{Sn–N} = 2.410 and 2.468 Å, for X = F and Cl, respectively).

By protonation of both N donor sites in {Me₂N(CH₂)₃}SnX₂, the [{Me₂(H)N(CH₂)₃}SnX₂]²⁺ (X = F, Cl) dication is formed. In the absence of further coordinating species, such as the perchlorate anion in the solid-state structure of compound 1 (Figure 2), these species are calculated to show a pseudo-tetrahedral geometry at the central Sn cation (X = F: F–Sn–F 101.32, C–Sn–C 127.01, C–Sn–Cl 105.52°). Worthy of note, both [{Me₂(H)N(CH₂)₃}SnX₂]²⁺ dication can be stabilized by two intramolecular hydrogen bonds N–H···X analogous to those discussed above for compound 3, but remarkably stronger for X = F (31.21 and 6.67 kcal/mol for X = F and Cl, respectively), as a consequence both of the different charge on the halide (Q_X = –0.669 and –0.484 [e], for X = F and Cl, respectively) and the deviation from the linearity of the N–H···X moiety due to the increase in the Sn–X distance on passing from X = F to X = Cl (X = F: d_{Sn–F} = 1.986 Å, N–H···F = 170.38°; X = Cl: d_{Sn–Cl} = 2.395 Å, N–H···Cl = 141.58°). Therefore, among [{Me₂(H)N(CH₂)₃}₂SnX₃]²⁺ dications, the one with X = F, due to the short Sn–F distance, is the most significantly stabilized (by 9.728 kcal/mol in terms of total electronic energy) by the formation of intramolecular hydrogen bonds. In order to verify the effect of solvation on the hydrogen bonding formation, the calculations on [{Me₂(H)N(CH₂)₃}₂SnF₃]²⁺ were repeated by implicitly keeping into account the presence of water by using the integral DFT calculations were extended to the precursors {Me₂N(CH₂)₃}SnX₂ (X = F, Cl), for which no structural determinations are available. In both compounds, the central Sn ion displays an octahedral coordination geometry achieved by two halides and two CₙN-coordinating dimethylaminopropyl ligands. The pattern of Sn–C and Sn–X bond lengths for {Me₂N(CH₂)₃}SnCl₂ and {Me₂N(CH₂)₃}SnF₂ is similar to that calculated for compounds 3 and 4, respectively (X = F: d_{Sn–F} = 2.050, d_{Sn–C} = 2.161; X = Cl: d_{Sn–Cl} = 2.554, d_{Sn–C} = 2.162 Å). Notably, on passing from X = F to X = Cl, the positive charge on the Sn center decreases (Q_{Sn} = 2.264 and 1.838 [e], respectively), parallely reducing the N–Sn Charge-Transfer (CT) interaction, as testified by the elongation of the optimized Sn–N distances (d_{Sn–N} = 2.410 and 2.468 Å, for X = F and Cl, respectively).

![Scheme 5. {Me₂(H)N(CH₂)₃}SnF₂(ClO₄)₂ (2) as a fluoride receptor in water.](image-url)
The reaction enthalpies counting for the selectivity of compound 8.249 kcal/mol. Therefore, we turned to examine the possible reactions accounting for the selectivity of compound 2 towards the fluoride anion. In order to find a quantitative explanation, the thermochemistry of the following chemical reactions was investigated:

1) \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^2+ + 2 \text{F}^- \rightarrow \{\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3\}_2\text{SnF}_4\)

2) \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^2+ + 2 \text{Cl}^- \rightarrow \{\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3\}_2\text{SnCl}_2\)

3) \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^{2+} \rightarrow \{\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3\}_2\text{SnF}_2\)

4) \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^{2+} + 2 \text{Br}^- \rightarrow \{\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3\}_2\text{SnBr}_2\)

5) \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^{2+} + 4 \text{Cl}^– \rightarrow \{\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3\}_2\text{SnCl}_4\)

6) \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^{2+} + 4 \text{Br}^- \rightarrow \{\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3\}_2\text{SnBr}_4\)

7) \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^{2+} + 4 \text{I}^- \rightarrow \{\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3\}_2\text{SnI}_4\)

All reactions start from the cation \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^{2+}\) of the salt 2, under the hypothesis that the added halide can lead to neutral hexacoordinated Sn products, analogous to compound 4 (reaction 1). Under these conditions, the possibility of the addition of two molar equivs. of Cl, Br, and I was kept into account to give \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnX}_2\) neutral species in a cis or trans arrangement (X = Cl, Br, I; reactions 2–4). Moreover, the complete replacement of the fluoride anions in \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^{2+}\) to give \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnX}_4\) was also considered (reactions 5–7). Zero-point energies (ZPE), thermal corrections to enthalpies, Gibbs free energies and entropies were calculated at 298.15 K both in the gas phase and in water for all the species participating as reactants and products to the reactions 1–7, for which the reaction enthalpies \(\Delta H\), entropies \(\Delta S\), and free energies \(\Delta G\) were obtained (Table 1 and Table 2).

Table 1. Thermochemistry DFT-calculations (a.u.) for the reactions 1–7 (see text) in water at 298.15 K. For all reactions, the H–bonding stabilized form of the \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnF}_2^{2+}\) was considered as the starting reagent.

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta H)</th>
<th>(\Delta S)</th>
<th>(\Delta G)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–1.1073</td>
<td>1.422 × 10(^{-3})</td>
<td>0.2420</td>
</tr>
<tr>
<td>2 (cis product)</td>
<td>–0.5497</td>
<td>1.025 × 10(^{-4})</td>
<td>0.0306</td>
</tr>
<tr>
<td>2 (trans product)</td>
<td>–0.5949</td>
<td>1.041 × 10(^{-4})</td>
<td>0.0310</td>
</tr>
<tr>
<td>3 (cis product)</td>
<td>–0.4892</td>
<td>1.001 × 10(^{-4})</td>
<td>0.0298</td>
</tr>
<tr>
<td>3 (trans product)</td>
<td>–0.4965</td>
<td>1.007 × 10(^{-4})</td>
<td>0.0300</td>
</tr>
<tr>
<td>4 (cis product)</td>
<td>–0.4360</td>
<td>9.620 × 10(^{-5})</td>
<td>0.0287</td>
</tr>
<tr>
<td>4 (trans product)</td>
<td>–0.4383</td>
<td>9.619 × 10(^{-5})</td>
<td>0.0287</td>
</tr>
<tr>
<td>5</td>
<td>–0.3622</td>
<td>9.347 × 10(^{-5})</td>
<td>0.0279</td>
</tr>
<tr>
<td>6</td>
<td>–0.2397</td>
<td>9.122 × 10(^{-5})</td>
<td>0.0272</td>
</tr>
<tr>
<td>7</td>
<td>–0.1309</td>
<td>8.627 × 10(^{-5})</td>
<td>0.0257</td>
</tr>
</tbody>
</table>

For all the reactions considered, the entropy terms \(\Delta S\) are largely smaller than the corresponding enthalpy variations \(\Delta H\). The reaction enthalpies \(\Delta H\) decrease systematically on passing from reaction 1 to reaction 7. A SOPT analysis clearly shows that the replacement of two fluoride anions in compound 4 with two halide anions X to give \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnX}_2\) species (reactions 2–4; X = Cl, Br, I) induces a weakening in the N–H–F hydrogen bonding interactions systematically depending on the electronegativity of the X species (LPF → BPD(N–H), 133.7, 123.2, 118.1, and 109.1 kcal/mol for compounds 4, \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnCl}_2\), \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnBr}_2\), and \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnI}_2\), respectively, in the gas phase; 74.7, 64.3, 61.0, and 56.8 kcal/mol for compound 4, \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnCl}_2\), \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnBr}_2\), and \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnI}_2\), respectively, in water). As a result of the natural charge variation on the tin central ion \(Q_{\text{Sn}}\), the reaction 1 is calculated to be more than twice exothermic than reactions 2–7, thus accounting for the selectivity of the identity of the halides bound to the Sn center, while reactions 5–7 are endergonic and therefore thermodynamically not favored.

Summarily, thermochemistry, mostly as a result to the different role played by hydrogen bonding interactions in dependend of the identity of the halides bound to the Sn center, clearly indicates that reaction 1 is largely more thermodynamically favored than reactions 2–7, thus accounting for the selectivity of compound 2 toward fluoride anion as compared to chloride, bromide, and iodide anions. Interestingly, it is conceivable that the small 19F NMR signal at –150 ppm (accounting for about 2% of the fluoride anion) observed when a water solution of compound 2 is added with 2 molar equivs. of NaF, NaCl, NaBr, and NaI (see above), can be representative of the formation of a small but NMR-detectable amount of the neutral species \([\text{Me}_2(\text{H})\text{N}(\text{CH}_2)_3]_2\text{SnCl}_2\).
Conclusion and Outlook

A set of water-soluble diorganotin compounds was synthesized and characterized by microanalysis and spectroscopic, structural and theoretical means. The easy-to-prepare diorganotin dichloride \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnCl}_2\) can, via subsequent reactions in water with perchloric acid and tetraethylammonium fluoride, be quantitatively transformed into the organotin perchlorate salt \([(\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_2]_2\text{ClO}_4\text{·}2\text{H}_2\text{O}\), which in turn shows to be an ideal selective fluoride receptor affording the zwitterionic diammonium diorganotetrafluorido stannate \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_4\text{·}4\text{H}_2\text{O}\). Notably, the selectivity of compound 2 towards the \(\text{F}^-\) anion as compared to \(\text{Cl}^-\), \(\text{Br}^-\), and \(\Gamma^-\), is nicely accounted for by thermochemistry calculations carried out at DFT level, that also evidence the fundamental role played by solvation. In fact, 2, thanks to an increased electrophilicity of the tin center as compared to compound 1, reacts with fluoride anions in water outperforming the competitive nature of other halide anions. In addition, compound 2 can be regenerated by treating 4 with a water solution at pH > 9 via the neutral intermediate \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_2\text{·}2\text{H}_2\text{O}\), which is soluble in organic solvents. The easy regeneration of compound 2 as selective fluoride receptor in water solution, is an added value for potential applications in separation processes and recovery of fluoride anions under environmental conditions.

Futhermore on this matter, we recall that bincentric Lewis acids such as \(\text{R}_2\text{FSn(CH}_2\text{)}_n\text{SnF}_2\text{·}2\text{H}_2\text{O}\) bind effectively fluoride anion in dichloromethane. Functionalization with 3-dimethylaminiumpropyl substituents, \(\text{Me}_2\text{H(CH}_2\text{)}_3\text{CH}_2\text{Br}\), would increase the solubility of these systems in water, thus affording new alternatives for fluoride receptors in aqueous media based on the \(-\text{Sn(CH}_2\text{)}_n\text{Sn}-(n = 1, 2, 2)\) system.

Experimental Section

General Methods: Bis[3-(dimethylamino)propyl]tin dichloride, \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnCl}_2\) was synthesized as reported in the literature. Perchloric acid, potassium fluoride, sodium fluoride, sodium chloride, sodium bromide, sodium iodide, tetraethylammonium fluoride and tetramethylammonium chloride were commercially available, and they were used without further purification. Bruker DPX–300, DRX–400 and AVIII–500 spectrometers were used to obtain \(^1\text{H}, ^{13}\text{C}, ^{19}\text{F}\), and \(^{119}\text{Sn}\) NMR spectra. Solution \(^1\text{H}, ^{13}\text{C}, ^{19}\text{F}\), and \(^{119}\text{Sn}\) NMR chemical shifts \(\delta\) are given in ppm and were referenced to \(\text{Me}_2\text{Si}(\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnCl}_2\) (1.00 ppm) and to TMS \((^1\text{H})\), to \(\text{CF}_3\text{CF}_2\text{Cl}\) \((^{13}\text{C})\), and to \(\text{Me}_2\text{Sn}\) \((^{119}\text{Sn})\). Elemental analyses were performed on a LECO–CHNS–932 analyzer. The electrospray mass spectra were recorded with a Thermoquest–Finnigan instrument. The mixture \(\text{CH}_2\text{CN/H}_2\text{O}(1/4 v/v)\) was used as the mobile phase.

X-ray Crystallography: A summary of the crystal data and refinement parameters for \(1, 3\) and \(4\cdot\text{H}_2\text{O}\) is given in the Supporting Information (Table S1). Single-crystal X-ray diffraction data for compounds \(1, 3\) and \(4\cdot\text{H}_2\text{O}\) were collected at 173 K on an Oxford Xcalibur Sapphire 3 diffractometer. The absorptions were corrected by SCALES53 ABSPACK multi-scan method.[27] The structures were solved by direct methods with SHELXT-2001[28] and refined on \(F^2\) by using SHELXL-2014.[29] The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using the riding model, except for the N–H atoms, and hydrogen atoms of water molecule in compound 4, which were located by a difference Fourier map and refined isotropically.

Deposition Numbers 1999722 (for 1), 1999723 (for 3), and 1999724 (for \(4\cdot\text{H}_2\text{O}\)) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

DFT Calculations: Quantum-mechanical calculations were carried out at density functional theory (DFT)[15] level with the Gaussian09 (rev. D.01)[30] commercial suite of computational software. The computational setup (mpW1PW/D62SVP)[21–23] was benchmarked by comparing optimized and structural data for compound 3. Calculations were extended to \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_2\) and \([(\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnX}_2]_2\) (X = F, Cl), 4, \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_2\text{·}2\text{H}_2\text{O}\) (X = Cl, Br, I; cis and trans isomers), and \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnX}_2\) (X = Cl, Br, I). For all the investigated compounds the geometries were optimized, starting from structural data when available. To determine the influence of the solvent on the properties of investigated compounds, calculations were also carried out in the presence of water, implicitly taken into account by means of the polarizable continuum model (PCM)[25] approach in its integral equation formalism variant (IEF-PCM), which describes the cavity of the solute within the reaction field (SCRF) through a set of overlapping spheres. The nature of the energy minima at the optimized geometries were verified by a vibrational analysis, computed by determining the second derivatives of the energy with respect to the orthogonal Cartesian atom coordinates and subsequently transforming to mass-weighted coordinates. The vibrational analysis also provided thermochemical data used to investigate the enthalpy, entropy, and free energy for reactions 1–7 (see main text) both in the gas phase and in water. Natural Bonding Orbitals, natural charges, and Wiberg bond indices[24] were calculated at the optimized geometries. A Second Order Perturbation Theory (SOP) Analysis of Fock Matrix in NBO Basis was also carried out to investigate intramolecular donor–acceptor and hydrogen bonding interactions. The programs Chemissian,[31] Molden 5.9.3,[32] and GaussView 5.0.9[33] were used to analyze optimized geometries and natural charge distributions.

Syntheses: Warning! Although we have encountered no issues during our studies, metal perchlorates are potentially explosive.

Synthesis of Bis[3-(dimethylamino)propyl]tin Difluoride \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_2\·\text{2H}_2\text{O}\): To a suspension of bis[3-(dimethylamino)propyl]tin dichloride \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnCl}_2\) (3.00 g, 8.29 mmol) in \(\text{CH}_2\text{Cl}_2\) (70 mL) was added potassium fluoride, KF (1.20 g, 20.72 mmol), and the mixture was stirred at room temperature for 10 days. The suspension was filtered and \(\text{CH}_2\text{Cl}_2\) was evaporated in vacuo giving 2.18 g (72 %) of \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_2\) or \(\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_2\·\text{2H}_2\text{O}\), which is soluble in water as expected, and reacts in this solvent with fluoride anion to afford \((\text{Me}_2\text{N(CH}_2\text{)}_3\text{)}_2\text{SnF}_2\text{·}2\text{H}_2\text{O}\) for details see Supporting Information. We encourage interested readers to make use of these preliminary findings.
Synthesis of [{Me₆(H)(N(CH₂)₃)₂SnCl₂}ClO₄]₂ (1): To a solution of [{Me₆(N(CH₂)₃)₂SnCl₂} (150 mg, 0.414 mmol) in water (5 mL) was added HClO₄ (139 mg, 60 % w/w solution). The solution was stirred for 5 hours followed by evaporation of water to yield 1 (229 mg, 98 %) as a white solid of m.p. 182–184 °C. ¹H NMR (400.25 MHz, D₂O): δ = 1.58 (t, 2J(¹H–¹H)/¹H/¹H/²Sn = 104.7 Hz, 4H, Sn–CH₂–CH₂), 2.11 (m, 4H, Sn–CH₂–CH₂), 2.87 (s, 12H, N(CH₂)₂), 3.16 (t, 4H, CH₂–N), 1.31(CH₃) NMR (100.64 MHz, D₂O): δ = 20.3 (Sn–CH₂–CH₂), 2.83 (s, 12H, N(CH₂)₂), 3.16 (t, 4H, CH₂–N), 7.26 (b, 2H, CH₂(N(CH₃)₂)). ¹²⁹Sn NMR (100.64 MHz, CD₃CN): δ = 13.8 (Sn–CH₂–CH₂), 2.84 (s, 12H, N(C≡CH₂)), 1.38 (t, 4H, N(C≡CH₂)), 4.18 (m, 4H, Sn–CH₂–CH₂). ¹³C{¹H} NMR (100.63 MHz, D₂O): δ = 64.4 (CH₃–CH₂–N), 120.1 (CH₂–N), 113.9 (CH₂–N), 19.9 (Sn–CH₂–CH₂), 25.7 (Sn–CH₂–CH₂), 42.7 (N(CH₂)₂), 51.9 (CH₃–N(CH₃)₂), 59.6 (CH₂–N). ¹⁹F{¹H} NMR (282.40 MHz, D₂O): δ = –23.8 (1H–1H) = 5.38 Hz), 12H, N(C≡CH₂), 507.0 (18, [{Me₆(N(CH₂)₃)₂SnOH}ClO₄]²⁻), negative mode, 99.1 (100, [ClO₄]²⁻).

Synthesis of [{Me₆(H)(N(CH₂)₃)₂SnF₂}ClO₄]₂ (2): To a solution of [{Me₆(N(CH₂)₃)₂SnF₂} (1.50 g, 4.11 mmol) in water (20 mL) was added perchloric acid (1.38 g, 8.22 mmol) (60 % w/w solution). The solution was stirred for 1 hour, and then water was evaporated giving 2.13 g (98 %) of compound 2 as a white solid of m.p. 250 °C. ¹H NMR (300.13 MHz, D₂O): δ = 1.28 (t, 2J(¹H–¹H)/¹H/¹H/²Sn = 104.7 Hz, 4H, Sn–CH₂–CH₂), 1.99 (m, 3J(¹H–¹H)/¹H/¹H/²Sn = 95.1 Hz, 4H, Sn–CH₂–CH₂), 2.82 (s, 12H, N(CH₂)₂), 3.09 (t, 2H, CH₂–N). ¹H NMR (300.13 MHz, CD₂CN): δ = 1.49 (t, 2J(¹H–¹H)/¹H/¹H/²Sn = 95.1 Hz, 4H, Sn–CH₂–CH₂), 2.06 (m, 3J(¹H–¹H)/¹H/¹H/²Sn = 79.0 Hz, 4H, Sn–CH₂–CH₂), 2.86 (d, 3J(¹H–¹H) = 4.76 Hz, 12H, N(CH₂)₂), 3.15 (t, 2H, CH₂–N), 7.57 (b, 2H, CH₂(N(CH₃)₂)). ¹¹⁹Sn NMR (100.31 MHz, CD₂Cl₂): δ = 1.57 (t, 2J(¹H–¹H)/¹H/¹H/²Sn = 104.7 Hz, 4H, Sn–CH₂–CH₂), 2.21 (m, 3J(¹H–¹H)/¹H/¹H/²Sn = 92.2 Hz, 4H, Sn–CH₂–CH₂), 3.00 (d, 3J(¹H–¹H)/¹H/¹H/²Sn = 4.39 Hz, 12H, N(CH₂)₂), 3.30 (t, 4H, CH₂–N), 8.6 (b, 2H, HN(CH₃)₂). ¹³C{¹H} NMR (100.63 MHz, CD₂Cl₂): δ = 19.9 (Sn–CH₂–CH₂), 2J(¹H–¹H)/¹H/¹H/²Sn = 37.1 Hz, 24.6 (Sn–CH₂–CH₂), 42.9 (N(CH₂)₂), 59.8 (CH₂–N), 1.3¹C(¹H) NMR (75.47 MHz, D₂O): δ = 19.7 (Sn–CH₂–CH₂), 2J(¹H–¹H)/¹H/¹H/²Sn = 33 Hz), 23.5 (1J(¹H–¹H)/¹H/¹H/²Sn = 977 Hz, Sn–CH₂–CH₂), 42.5 (N(CH₂)₂), 59.6 (CH₂–N), 3J(¹H–¹H)/¹H/¹H/²Sn = 165 Hz). ¹⁹F{¹H} NMR (D₂O, 282.40 MHz): δ = –141.1F{¹H} NMR (282.40 MHz, CD₂Cl₂): δ = –145.1 ¹¹⁹Sn{¹H} NMR (111.92 MHz, D₂O): δ = –114.0, ¹¹⁹Sn{¹H} NMR (119.92 MHz, D₂O [acetone]): δ = –340.1 ¹¹⁹Sn{¹H} NMR (149.26 MHz, D₂O): δ = –359 (νSn/2 = 1215 Hz). Anal. Calcld. (%) for C₁₄H₂₄F₂N₂O₇Sn = 562.8; C 20.68, H 4.86, N 4.82; found C 20.5, H 4.6, N 4.9. Electrospray MS: m/z (%), positive mode, 327.1 (90, [{Me₆(N(CH₂)₃)₂SnF}²⁻]), 206.0 (40, [SnOHO₂]²⁻), 113.5 (16, [{C₆H₇NO₃ClS}²⁻]).

Synthesis of [{Me₆(H)(N(CH₂)₃)₂SnCl₄}ClO₄]₂ (3): To a solution of [{Me₆(N(CH₂)₃)₂SnCl₂} (150 mg, 0.414 mmol) in water (5 mL) was added HCl (31 mg, 37 % w/w solution). The solution was stirred for 5 hours followed by evaporation of water to yield 3 (173 mg, 96 %) as a white solid. No melting point was determined. ¹H NMR (500.08 MHz, D₂O): δ = 1.55 (t, 2J(¹H–¹H)/¹H/¹H/²Sn = 101.6 Hz, 4H, Sn–CH₂–CH₂), 2.08 (m, 4H, Sn–CH₂–CH₂), 2.82 (s, 12H, N(CH₂)₂), 3.13 (t, 4H, CH₂–N), 1.3¹C(¹H) NMR (127.55 MHz, D₂O): δ = 20.5 (Sn–CH₂–CH₂), 2J(¹H–¹H)/¹H/¹H/²Sn = 35 Hz), 31.0 (1J(¹H–¹H)/¹H/¹H/²Sn = 928/976 Hz, Sn–CH₂–CH₂), 42.6 (N(CH₂)₂), 59.2 (1J(¹H–¹H)/¹H/¹H/²Sn = 175/181 Hz, NH–N). ¹¹⁹Sn{¹H} NMR (149.26 MHz, D₂O): δ = –264. Anal. Calcld. (%) for C₆H₁₂F₂N₆Sn₂ = 434.84; C 27.62, H 6.63, N 6.44; found C 27.5, H 5.8, N 6.5. Electrospray MS: m/z (%), positive mode, 327.1 (90, [{Me₆(N(CH₂)₃)₂SnCl}²⁻]), 309.1 (78, [{Me₆(N(CH₂)₃)₂SnOH}²⁻]), 206.0 (40, [SnOH₂]²⁻), 113.5 (16, [{C₆H₇NO₃ClS}²⁻]).
DFT-optimized geometries for compounds C2D2O (0.6 mL) was prepared, the NMR measurement was reported. To the same NMR sample few drops of NaOH solution in distilled water (10 % w/w) were added with stirring to get a solution of pH = 9. The solution remained clear. \( \delta \) (1H–117/119Sn) = 130.3 Hz, 4H, Sn–CH2–C2; 3.95 (s, 18H, N(CH2)3), 60.2 Hz (13C–117/119Sn) = 154 Hz, CH2–N; 19F{1H} NMR (282.40 MHz, D2O): \( \delta = -120 \) 119Sn{1H} NMR (111.92 MHz, D2O): no signal was observed.

Supporting Information (see footnote on the first page of this article): Crystallographic data, fractional atomic coordinates, atomic displacement parameters, geometric parameters, and hydrogen bond geometries for compounds 1, 3 and 4-4H2O (Tables S1–S12); 1H, 13C, 19F and 119Sn NMR spectra and Mass spectra for compounds 1, 3, and 4. Preliminary results concerning water-soluble bidentic Lewis acids.

DFT-optimized geometries for compounds 3, 4, (Me2N(CH2)3)2SnX2, and (Me2N(CH2)3)2SnF4 (X = F, Cl, Br, I; cis and trans isomers), and (Me2N(CH2)3)2SnF2X2 (X = Cl, Br, I; cis and trans isomers), and (Me2N(CH2)3)2SnF2X2 (X = Cl, Br, I; cis and trans isomers) are available in the orthogonal Cartesian format upon request to the authors.

Acknowledgments

M. A. and V. L. thank Università degli Studi di Cagliari (FIR 2016–2019) and Fondazione di Sardegna (FDS Progetti Biennali di Ateneo, annualità 2018) for financial support. Open access funding enabled and organized by Projekt DEAL.

Keywords: Tin · Fluorides · Cations · Lewis acids · Structure elucidation · Density functional calculations

