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Organotin Fluorides

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

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Abstract: Herein, we report the syntheses of the water-soluble organotin compounds $[\{Me_2(H)N(CH_2)_3\}_2SnX_2]Y_2$ (**1**, X = Cl, Y = ClO_4; **2**, X = F, Y = ClO_4) and $\{Me_2(H)N(CH_2)_3\}_2SnX_4$ (**3**, X = Cl; **4**, X = F). The compounds were characterized by elemental analysis, electrospray mass spectrometry, ^1H, ^{13}C, ^{19}F, 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/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 anion in water. Among other reasons,[2d] the special interest towards fluoride sensing/recognition stems from the need of careful monitoring its concentration in drinking water, since fluoride 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 center 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, $(n\text{-octyl}_2FSn)_2CH_2$ that is commercially available for this purpose,[9a] and o-SnPhF$_2$C$_6$H$_4$CH$_2$NMe$_2$.[9b] The former shows a de-

creased stability as result of partial hydrolysis under the experimental (environmental) conditions. To the best of our knowledge, the latter is the only tin-based receptor for fluoride anions that works in aqueous media. Intramolecular N→Sn coordination protects this compound against hydrolysis.

Herein, we report the syntheses of water-soluble dimethyl-ammoniumpropyl-substituted organotin compounds **1–4**. The ability of the organotin-substituted ammonium perchlorate $[\{Me_2(H)N(CH_2)_3\}_2SnF_2](ClO_4)_2$, **2**, to bind fluoride anions in water is also investigated. In particular, the selectivity of compound **2** towards fluoride anions over other halides and the effect of the pH of the solution on the fluoride binding of this receptor are also discussed.

Results and Discussion

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

The reaction in water of the diorganotin dichloride $[Me_2N(CH_2)_3]_2SnCl_2$[10] with two molar equivs. of perchloric acid, $HClO_4$, gave the corresponding ammonium perchlorate $[\{Me_2(H)N(CH_2)_3\}_2SnCl_2](ClO_4)_2$, **1**, in quantitative yield. Furthermore, the reaction of compound **1** with two molar equivs. of tetraethylammonium fluoride, $NEt_4F\cdot2H_2O$, in CH_3CN gave, via halide exchange, the corresponding fluorine-substituted derivative $[\{Me_2(H)N(CH_2)_3\}_2SnF_2](ClO_4)_2$, **2**, in quantitative yield (Scheme 1).

Compound **2** was also synthesized, in quantitative yield, by the reaction of $[Me_2N(CH_2)_3]_2SnF_2\cdot2H_2O$[10] with two molar equivs. of $HClO_4$ (Scheme 2).

Similarly, the reaction of $[Me_2N(CH_2)_3]_2SnCl_2$[10] with two molar equivs. of HCl in water gave the zwitterionic diorganotetrachlorido stannate $\{Me_2(H)N(CH_2)_3\}_2SnCl_4$, **3**, in quantitative yield (Scheme 1).
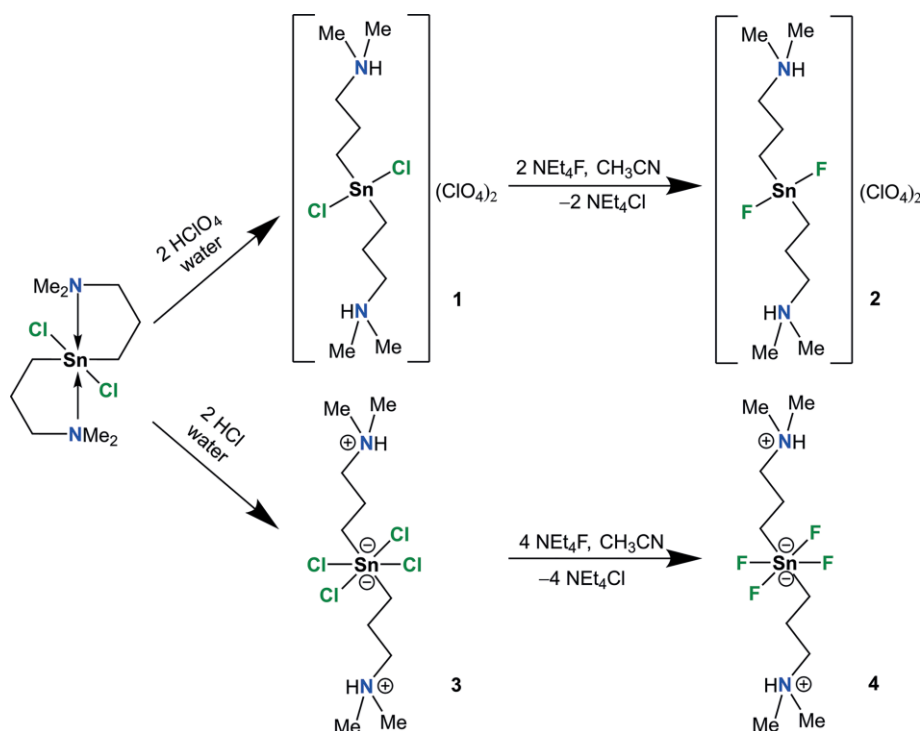
The reaction of compound **3** with four molar equivs. of $NEt_4F\cdot2H_2O$ in CH_3CN gave, again via halide anion exchange,

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Scheme 1. Syntheses of the diorganotin chlorides **1** and **3** and the diorganotin fluorides **2** and **4**.
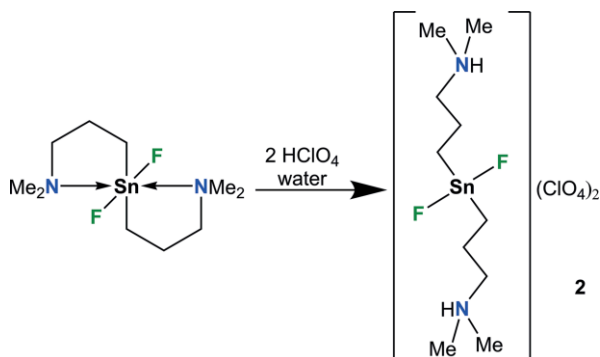
Scheme 2. Alternative synthesis of compound [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$](ClO$_4$)$_2$, **2**.

the corresponding zwitterionic fluorine-substituted compound {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_4$, **4**, in quantitative yield (Scheme 1).

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**·4H$_2$O by recrystallization from acetonitrile under non-inert conditions.

Both compounds **1** and **4**·4H$_2$O crystallized in the triclinic space group P1̄, whereas compound **3** crystallized in the monoclinic space group P2$_1$/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**·4H$_2$O, including some features in the crystal packing of compounds **1** and **4**·4H$_2$O. 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-tBu-2,6-{P(O)(OiPr)$_2$}$_2$C$_6$H$_2$(ClO$_4$)SnCr(CO)$_5$] [Sn–O 2.170(3) Å],[11] FcP(O)(O-iPr)$_2$SnPh$_2$(ClO$_4$) [Sn–O 2.283(4) Å],[12] and FcP(O)(O-iPr)$_2$SnPhI(ClO$_4$) [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 iPr$_2$SnCl$_2$ [2.357(1), 2.369(1) Å],[14a] tBu$_2$SnCl$_2$ [2.334(1), 2.335(1) Å][14a] and Ar$_2$SnCl$_2$ [Ar = 2,6-Et$_2$C$_6$H$_3$, 2,6-iPr$_2$C$_6$H$_3$, 2,4,6-iPr$_3$C$_6$H$_2$: 2.353(2)-2.361(7) Å];[14b] they are in the same range as reported for the Sn–Cl distances in [{SnPh$_2$Cl$_2$}(1κO^{2}N^2,2κO^2-μ-L)M] [2.4438(6), 2.4608(6) Å, M =

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Ni; 2.4339(7), 2.4580(7) Å, M = Cu],[14c] SnEt$_2$Cl$_2$·H$_2$O [Sn–Cl$_{equ}$ 2.3951(4) Å],[14d] {2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$SnCl$_2$ [2.4394(5) Å],[14e] {2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$SnCl$_2$ [2.4390(3) Å],[14f] {2-(Me$_2$NCH$_2$)C$_6$H$_4$}PhSnCl$_2$ [2.3547(11), 2.4481(11) Å],[14f] and {2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_2$SnCl$_2$ [2.4206(12), 2.4529(12) Å],[14g] but shorter than those found in the diorganotetrachloridostannate derivative **3** [2.6074(8), 2.6260(7) Å, see below].
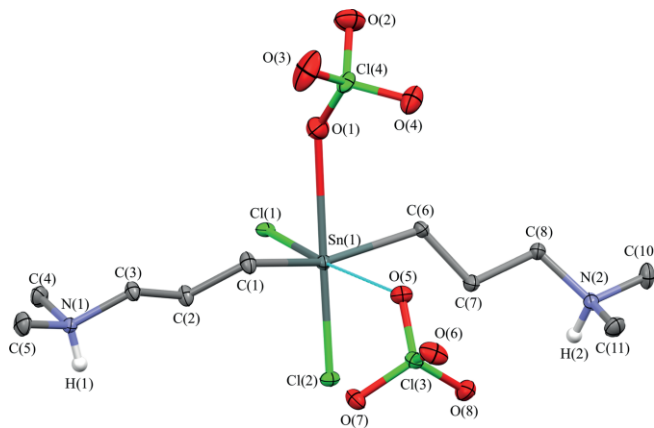

Figure 1. Molecular structure of compound **1** with the labelling scheme adopted for the atom positions. Thermal ellipsoids are drawn at 30 % probability level. Hydrogen atoms are omitted for clarity except those on the nitrogen atoms. Selected interatomic distances [Å]: Sn(1)–Cl(1) 2.4119(8), Sn(1)–Cl(2) 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 [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnCl$_2$]$^{2+}$ moieties via N–H•••O hydrogen bonds, thus forming a cyclic supramolecular assembly (see Figure 2).
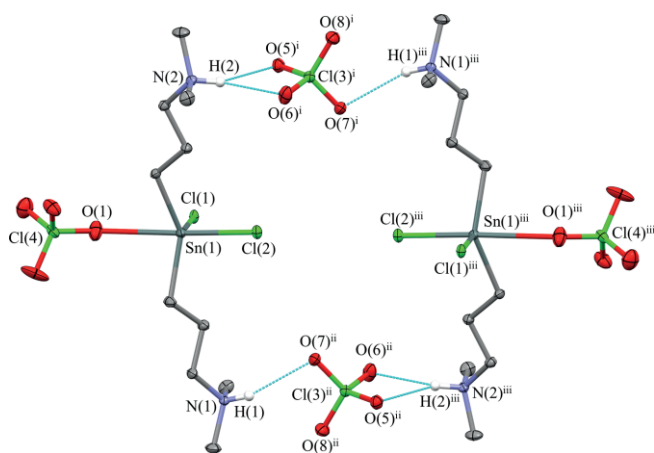

Figure 2. Selected portion of the crystal packing of compound **1** showing the interaction between the bis(3-dimethylammoniumpropyl)dichloridotin dication and the perchlorate anions. Only the hydrogen atoms interacting with the perchlorate anions are labelled. Selected interatomic distances [Å]: N(1)–O(7)^{ii} 3.036(4) [N(1)–H(1) 0.83(4), H(1)–O(7)^{ii} 2.31(4)], N(2)–O(5)^i 3.042(4) [N(2)–H(2) 0.90(5), H(2)–O(5)^i 2.19(5)], N(2)–O(6)^i 2.988(4) [H(2)–O(6)^i 2.26(4)]. Symmetry codes: ^{i} = 1 + x, y, z; ^{ii} = −x, 2 − y, 1 − z; ^{iii} = 1 − x, 2 − y, 1 − z. The Cl(3)-perchlorate anion coordinating Sn(1) is not shown.

N(1)–H(1)•••Cl(2) hydrogen bonds with a H(1)•••Cl(2) distance of 2.79(5) [N(1)–Cl(2)^{ii} 3.357(4), ^{ii} = −x, 2 − y, 1 − z] mainly determine the interaction between these cyclic supramolecular structures, which pile up along the a-direction in the crystal packing in 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 diorganotetrachlorido stannates[15] ranging between 2.571(2) Å for (Hthiamine)SnPh$_2$Cl$_4$[15j] and 2.67(1) Å for (tetrathiafulvalene)$_3$SnEt$_2$Cl$_4$.[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 diorganotetrachlorido stannate(IV) is (C$_6$H$_{14}$N)$_2$[Sn(C$_6$H$_5$)$_2$Cl$_4$].[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
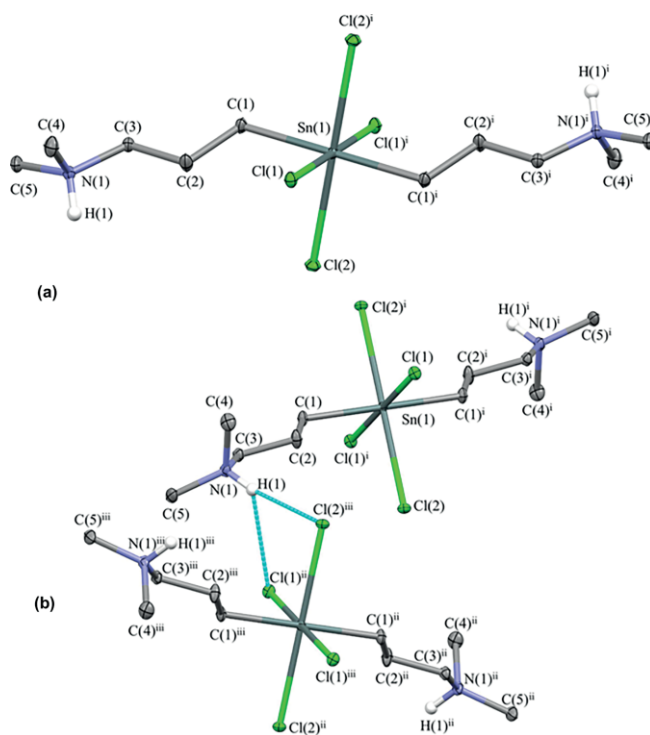

Figure 3. (a) Molecular structure of compound **3** with the labelling scheme adopted for the atom positions. Thermal ellipsoids are drawn at 30 % probability level. Hydrogen atoms are omitted for clarity except those on the tertiary nitrogen atoms. Selected interatomic distances [Å]: Sn(1)–Cl(1) 2.6074(8), Sn(1)–Cl(2) 2.6260(7), Sn(1)–C(1) 2.138(3). Selected interatomic angles (°): C(1)–Sn(1)–C(1)^i 180, Cl(1)–Sn(1)–Cl(1)^i 180, Cl(2)–Sn(1)–Cl(2)^i 180.0. Symmetry operations: ^{i} = 1 − x, 1 − y, 1 − z. (b) Selected portion of the crystal packing of compound **3** showing the N(1)–H(1)•••Cl(1)^{ii} and N(1)–H(1)•••Cl(1)^{iii} hydrogen bonds connecting symmetry related molecules. N(1)–Cl(1)^{ii} 3.312(2), N(1)–Cl(2)^{iii} 3.400(3) Å. Symmetry operations: ^{i} = 1 − x, 1 − y, 1 − z; ^{ii} = 1/2 − x, 1/2 + y, 1/2 − z; ^{iii} = −1/2 + x, 3/2 − y, −1/2 + z.

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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 2.52(4) and 2.85(3) Å, respectively [N(1)–H(1) 0.91(3), N(1)–Cl(1)^{ii} 3.312(2); N(1)–Cl(2)^{iii} 3.400(3) Å; ^{ii} = 1/2 − x, 1/2 + y, 1/2 − z; ^{iii} = −1/2 + x, 3/2 − y, −1/2 + z].

The Sn(1) atom in the centrosymmetric zwitterionic diammonium diorganotetrafluorido stannate water solvate **4**·4H$_2$O is hexacoordinated by C(1), C(1A), F(1), F(1)^{i}, F(2), and F(2)^{i} (i = 1 − x, 1 − y, 1 − z), and shows an almost ideal octahedral environment with C(1)–Sn(1)–C(1)^{i}, F(1)–Sn(1)–F(1)^{i} and F(2)–Sn(1)–F(2)^{i} angles of 180.0° (Figure 4). The Sn(1)–F(1) [2.0827(13) Å] and Sn(1)–F(2) [2.1172(13) Å] distances are in the range of the corresponding distances reported for the compounds (NH$_4$)$_2$[SnMe$_2$F$_4$] [2.121(5), 2.135(4) Å],[16a] K$_2$[SnMe$_2$F$_4$]·2H$_2$O [2.064(14) – 2.135(2) Å],[16b] {Me$_2$N(CH$_2$Cl)(CH$_2$)$_3$}$_2$SnF$_4$·2H$_2$O (2.059(4) – 2.108(4) Å),[16c] [2-{Ph$_2$P(O)CH$_2$}C$_6$H$_4$]$_2$SnF$_2$ [2.008(3), 2012(3) Å],[16c] and [2,6-{P(O)(OEt)$_2$}$_2$-4-tBu-C$_6$H$_2$]SnF$_2$Ph·0.5 H$_2$O [2.017(2), 2.012(2) Å].[16d] They are, however, longer than the Sn–F distances in the intramolecularly N→Sn coordinated organotin fluoride derivatives {2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$SnF$_2$ [1.9726(14),[14e] 1.9774(13),[14e] 1.981(1),[14h] 1.991(1),[14h] Å], {2-(Et$_2$NCH$_2$)C$_6$H$_4$}$_2$SnF$_2$ [1.994(2), 1.976(3) Å],[14g] {2,6-(Me$_2$NCH$_2$)$_2$C$_6$H$_3$}$_2$SnF$_2$ [1.988(2), 1.984(2) Å],[16e] and [Sn{CH(SiMe$_3$)-C$_9$H$_6$N-8}$_2$F$_2$] [1.981(3), 1.980(5) Å],[16f] as well as for the 1,8-bis(dimethylamino)naphthalenium diorganotrifluorido stannate [C$_{14}$H$_{19}$N$_2$][(C$_2$F$_5$)$_2$SnF$_3$(thf)] [196.73(9), 198.65(9), 197.17(9) Å][8] and the 1,10-phenanthroline complex [(C$_2$F$_5$)$_2$SnF$_2$(phen)] [1.962(2), 1.970(2) Å].[8]
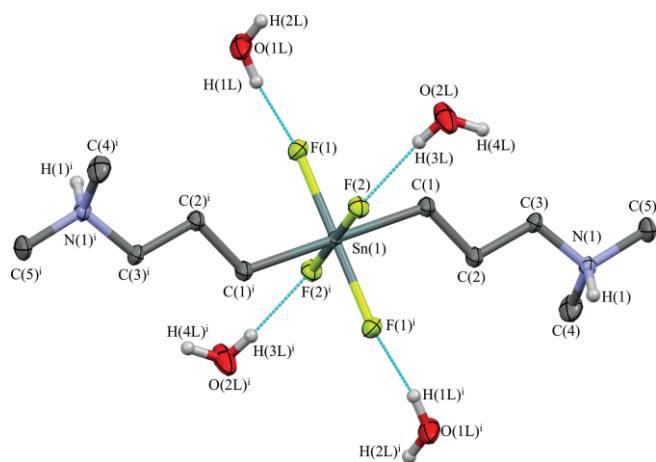

Figure 4. Molecular structure of compound **4**·4H$_2$O with the labelling scheme adopted for the atom positions. Thermal ellipsoids are drawn at 30 % probability level. Hydrogen atoms are omitted for clarity except those on the tertiary nitrogen atoms and those involved in H···F interactions. Selected interatomic distances [Å]: Sn(1)–F(1) 2.0827(13), Sn(1)–F(2) 2.1172(13), Sn(1)–C(1) 2.138(2), F(1)–O(1L) 2.625(2) [O(1L)–H(1L) 0.804(18), F(1)–H(1L) 1.853], O(1L)–H(2L) 0.806(18), F(2)–O(2L) 2.735(2) [O(2L)–H(3L) 0.799(18), F(2)–H(3L) 1.943], O(2L)–H(4L) 0.842(18). Selected interatomic angles (°): C(1)–Sn(1)–C(1)^{i} 180, F(1)–Sn(1)–F(1)^{i} 180.0, F(2)–Sn(1)–F(2)^{i} 180.0. Symmetry operations: ^{i} = 1 − x, 1 − y, 1 − z.

For the dinuclear diorganotin difluoride triflic acid solvate [{2-(Me$_2$NCH$_2$)C$_6$H$_4$}$_2$SnF$_2$]$_2$·2HOTf, Sn–F distances ranging between 2.128(8) and 2.352(12) Å were reported.[16g] The longer distances belong to μ$_2$-bridging fluorine atoms.

Each fluorine substituent **4**·4H$_2$O 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**·4H$_2$O also contains different hydrogen bond bridges (Figure 5).
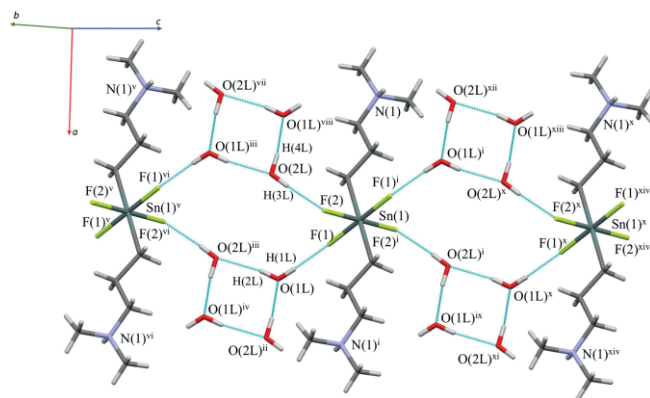

Figure 5. Selected portion of the crystal packing of compound **4**·4H$_2$O showing the Sn–F···H–O–H···O–H···F–Sn hydrogen bonds connecting the molecules via formation of a 16-membered ring, and square-like clusters of hydrogen bound water molecules. Selected contacts: O(1L)···H(4L)^{ii} 1.86(2), O(2L)···H(2L)^{iii} 2.00(2) Å. Symmetry operations: ^{i} = 1 − x, 1 − y, 1 − z; ^{ii} = 1 + x, y, z; ^{iii} = 1 − x, 2 − y, −z; ^{iv} = 2 − x, 2 − y, −z; ^{v} = x, 1 + y, −1 + z; ^{vi} = 1 − x, 2 − y, −z; ^{vii} = −x, 2 − y, −z; ^{viii} = −1 + x, y, z; ^{ix} = 2 − x, 1 − y, 1 − z; ^{x} = x, −1 + y, 1 + z; ^{xi} = 1 + x, −1 + y, 1 + z; ^{xii} = −x, 1 − y, 1 − z; ^{xiii} = −1 + x, −1 + y, 1 + z; ^{xiv} = 1 − x, −y, 2 − z.

In particular, discrete tetrameric (H$_2$O)$_4$ water clusters assemble the diorganotetrafluorido stannate units via F···H–O hydrogen bonds in layers (Figure 5). The (H$_2$O)$_4$ 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 (H$_2$O)$_4$ 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).
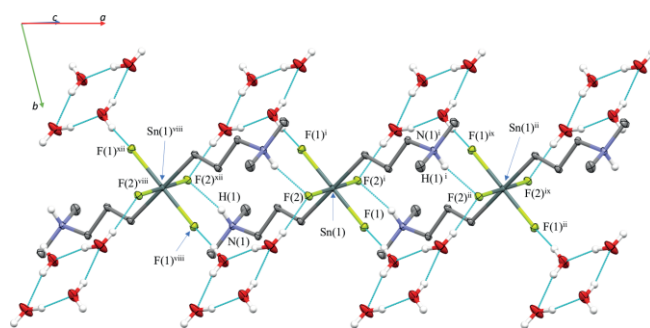

Figure 6. Selected portion of the crystal packing of compound **4**·4H$_2$O showing the N–H···F–Sn hydrogen bonds connecting symmetry-related units of compound **4** along the a-direction. For symmetry operation see Figure 5.

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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-anion contributes to the packing in the crystal lattice.

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

The compounds $\{Me_2N(CH_2)_3\}_2SnF_2 \cdot 2H_2O$, $[\{Me_2(H)N(CH_2)_3\}_2SnCl_2](ClO_4)_2$ (**1**), $[\{Me_2(H)N(CH_2)_3\}_2SnF_2](ClO_4)_2$ (**2**), $\{Me_2(H)N(CH_2)_3\}_2SnCl_4$ (**3**), $\{Me_2(H)N(CH_2)_3\}_2SnF_4$ (**4**) were completely characterized by NMR spectroscopy (see Supporting Information). A ^1H NMR spectrum of the bis(3-dimethylammoniumpropyl)dichloridotin perchlorate **1** in D_2O showed one signal for the $SnCH_2$ protons at $\delta = 1.58$ ppm with $[^2J(^1H-^{119}Sn) = 104$ Hz]. A ^{13}C NMR spectrum of the same sample reveals one signal for the $SnCH_2$ carbon atoms at $\delta = 29.9$ ppm $[^1J(^{13}C-^{117/119}Sn) = 959/1003$ Hz]. These NMR data are typical for hexacoordinated diorganotin compounds with the *trans*-disposed organic substituents.[10] A ^{119}Sn NMR spectrum of compound **1** in D_2O shows a single resonance at $\delta = -310$ ppm. This signal is more high field-shifted than the resonances for comparable intramolecularly hexacoordinated diorganotin dichlorides $\{Me_2N(CH_2)_2CMe_2\}_2SnCl_2$ ($\delta = -257.5$ ppm),[17] $\{Me_2N(CH_2)_3\}_2SnCl_2$ ($\delta = -185$ ppm),[10] and $\{CH_2N(Me)CH_2CH_2CH_2\}_2SnCl_2$ ($\delta = -176.5$ ppm).[18] The differences are likely the result of compound **1** having no intramolecular N→Sn coordination involving five-membered chelate rings but intermolecular H_2O→Sn coordination instead.

In a ^1H NMR spectrum of compound **1** in CD_3CN, the resonance of the NCH_3 protons, found at $\delta = 2.87$ in D_2O, appears as a doublet resonance at $\delta = 2.84$ $[^3J(^1H-^1H) = 5.4$ Hz]. In addition, a broad resonance at $\delta = 7.26$ relating to the NH proton was observed. The $^2J(^1H-^{119}Sn)$ and $^1J(^{13}C-^{119}Sn)$ coupling constants of 78 and 682 Hz, respectively, belonging to the corresponding nuclei of the $SnCH_2$ moiety are distinctly smaller than those found in D_2O. With caution, we trace this to the organic substituents being *cis*-disposed in solution.

A ^{119}Sn NMR spectrum of compound **2** in $[D_6]$acetone at ambient temperature showed a broad signal at $\delta = -340$ ($\nu_{1/2} = 206$ Hz) without $^1J(^{119}Sn-^{19}F)$ couplings satellites. A ^{19}F NMR spectrum of compound **2** in D_2O and $[D_6]$acetone showed signals at $\delta = -141$ and -145, respectively. The chemical shift in D_2O is 18 ppm at higher field shifted in comparison with that measured for $\{Me_2N(CH_2)_3\}_2SnF_2 \cdot 2H_2O$ in D_2O at -123 ppm.

^1H NMR spectra of compound **2** were recorded in different solvents. They showed that the chemical shift of the N*H* proton depends on the solvent used and it varies from 7.57 ppm (in CD_3CN) to 8.58 ppm (in $[D_6]$acetone). No signal for the N*H* proton was found in D_2O indicating D–H exchange being fast on the ^1H NMR time scale.

In D_2O, the NCH_3 protons of compound **2** showed a single resonance at 2.82 ppm. This resonance is shifted by 0.34 ppm

to lower field in comparison with that measured for $\{Me_2N(CH_2)_3\}_2SnF_2 \cdot 2H_2O$ (2.48 ppm in D_2O). In CD_3CN and $[D_6]$acetone solutions, the NCH_3 protons appear as doublet resonances at 2.86 ppm $[^3J(^1H-^1H) = 4.76$ Hz] and 3.00 ppm $[^3J(^1H-^1H) = 4.39$ Hz], respectively.

Noteworthy, the coupling constants $^2J(^1H-^{119}Sn)$ of the $SnCH_2$ protons in compound **2** are about 95 Hz (in CD_3CN) and 105 Hz (in $[D_6]$acetone and D_2O). 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 $\{Me_2N(CH_2)_3\}_2SnF_2 \cdot 2H_2O$ (90 Hz in D_2O, 94 Hz in CD_2Cl_2 at -60 °C).[10]

A ^{119}Sn NMR spectrum of compound **3** in D_2O showed one resonance at $\delta = -264$. In a ^{13}C NMR spectrum a resonance at $\delta = 31.0$ $[^1J(^{13}C-^{117/119}Sn) = 938/976$ Hz] assigned to the $SnCH_2$ carbon atom was observed. This chemical shift is similar to those found for the corresponding carbon atoms in compound **1** at $\delta = 29.9$ $[^1J(^{13}C-^{117/119}Sn) = 959/1003]$ and in the hexacoordinated organotin compound $\{Me_2N(CH_2)_3\}_2SnCl_2$ at $\delta = 31$ $[^1J(^{13}C-^{119}Sn) = 922$ Hz],[14] measured in $CDCl_3$. In a ^1H NMR spectrum of the same sample a chemical shift of the $SnCH_2$ protons at $\delta = 1.55$ $[^2J(^1H-^{119}Sn) = 102$ Hz] was observed. The data indicate unambiguously a hexacoordinated tin center with the organic substituents being *trans*-disposed.

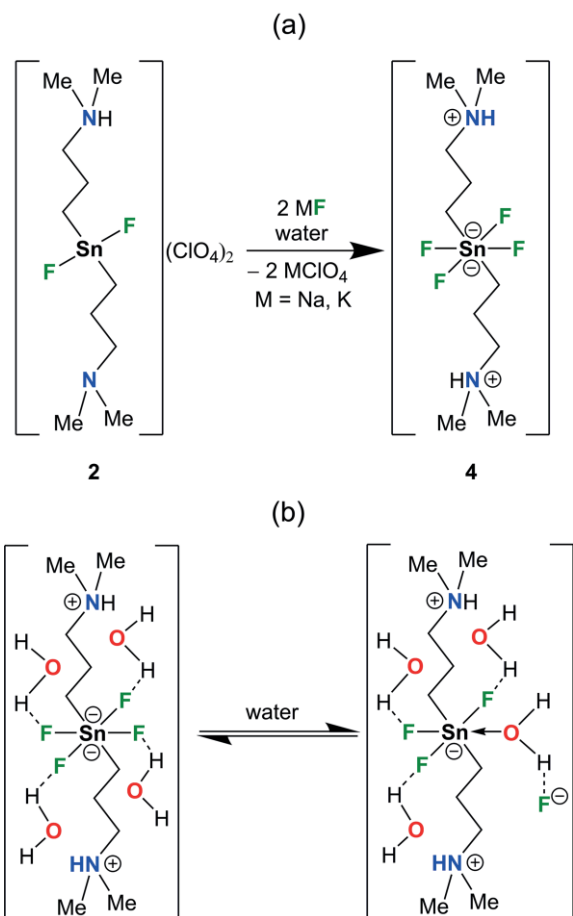A ^{19}F NMR spectrum of compound **4** (60 mg) in D_2O showed one resonance at -126 ppm. In a ^{119}Sn NMR spectrum in D_2O a chemical shift at -405 ppm was observed. However, no $^1J(^{119}Sn-^{19}F)$ coupling satellites were found, indicative for high ionic character and kinetic lability of the Sn–F bond.

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 $[\{Me_2N(CH_2)_3\}_2SnOH]^+$. In addition, the spectra of compounds **1** and **3** show a mass cluster centered at $m/z = 327.1$ which belongs to $[\{Me_2N(CH_2)_3\}_2SnCl]^+$. 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 $C_{30}H_{81}N_6O_7Cl_4Sn_3$ (calcd. $m/z = 1135.1969$). In the case of compound **4**, a mass cluster centered at $m/z = 311.0$ was found. This is assigned to $[\{Me_2N(CH_2)_3\}_2SnF]^+$.

In the negative mode, a mass cluster centered at $m/z = 507.0$ was found for compound **2**, corresponding to the anion $[\{Me_2N(CH_2)_3\}_2SnOH(ClO_4)_2]^-$.

Reactivity of Compound 2 towards Fluoride Anions in Water

The diorganotin compound $[\{Me_2(H)N(CH_2)_3\}_2SnF_2](ClO_4)_2$, **2**, reacts with both sodium and potassium fluoride giving compound $\{Me_2(H)N(CH_2)_3\}_2SnF_4$, **4** (Scheme 3a). The formation of compound **4** was established by ^1H, ^{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**.

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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 $^1J(^{19}F-^{117/119}Sn)$ and $^1J(^{119}Sn-^{19}F)$ couplings in the NMR spectra of compound **4**.

The ^1H NMR spectra of the reaction mixtures in D_2O containing compound **2** and two molar equivs. of NaF or KF, shows that the unresolved coupling constant $^2J(^1H-^{117/119}Sn)$ 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 $^3J(^{13}C-^{117/119}Sn)$ of 145 Hz (KF) and 159 Hz (NaF) are close to the value of 164 Hz found for **2** (in D_2O). The ^{19}F NMR spectra of the same samples show a single resonance at $\delta = -125$ without coupling satellites $^1J(^{19}F-^{117/119}Sn)$. This resonance is close to −123 ppm measured for **1** in D_2O, and that reported for the complex salt $K_2[Me_2SnF_4]\cdot2H_2O$ in D_2O at −122 ppm.[16b] A ^{119}Sn NMR spectrum of a solution of compound **2** in D_2O to which two molar equivs. of NaF had been added shows one signal at −412 ppm with no coupling involving ^{19}F observed. Similar chemical shifts have been observed for the hexacoordinated organotin compound $\{Me_2N(CH_2Cl)(CH_2)_3\}_2SnF_4$ ($\delta^{119}Sn$ −455) and ($\delta^{19}F$ −128) measured in CD_3OD.[19a]

NMR data suggest a fast equilibrium (Scheme 3b) on both the ^{19}F and ^{119}Sn NMR time scale. No $^1J(^{19}F-^{117/119}Sn)$ and $^1J(^{119}Sn-^{19}F)$ couplings were observed in the corresponding NMR spectra. Kinetic lability of the Sn–F bond was also reported for organofluorido stannate complexes such as $K_2[Me_2SnF_4]\cdot2H_2O$,[16b] $N(nBu)_4[Ph_2SnF_3]$,[19b] $N(nBu)_4[Ph_2-(Me_3SiCH_2)SnF_2]$,[19c] and $NEt_4[(Ph_2FSn)_2CH_2F]$.[19c]

Effect of Solution pH on the Behavior of $\{Me_2(H)N(CH_2)_3\}_2SnF_4$

In order to verify the effect of pH on the structure of $\{Me_2(H)N(CH_2)_3\}_2SnF_4$, **4**, a few drops of aqueous NaOH solution were added to the NMR tube containing compound **4** in D_2O. The experiment shows that exclusively the diorganotin compound $\{Me_2N(CH_2)_3\}_2SnF_2$ 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 $\{Me_2N(CH_2)_3\}_2SnF_2$, (Scheme 4).
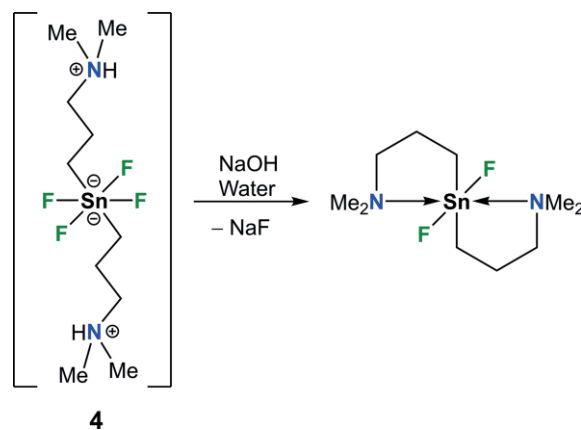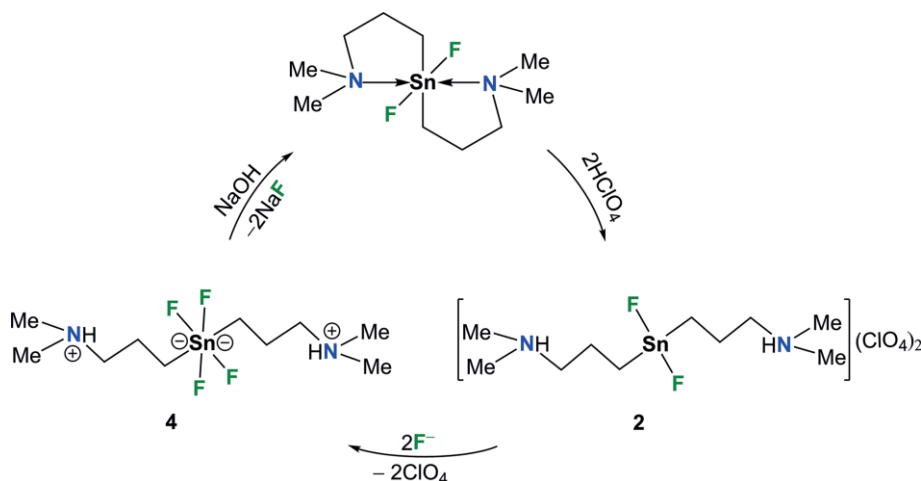

Scheme 4. The reaction of organotin compound **4** with NaOH.

Therefore, the reversibility of binding/releasing of fluoride anions in the reaction of compound **2** with KF or NaF 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 $\{Me_2(H)N(CH_2)_3\}_2SnF_4$, **4**, takes place in basic solutions coincide with the formation of the compound $\{Me_2N(CH_2)_3\}_2SnF_2$ 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 $[\{Me_2(H)N(CH_2)_3\}_2SnF_2](ClO_4)_2$, 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_2O 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).

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Scheme 5. [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$](ClO$_4$)$_2$ (**2**) as a fluoride receptor in water.

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–C = 0.621; 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} = 2.276 |e|, average Q_F = –0.700 |e|), affecting only marginally the Sn–C bonds (d_{Sn-C} = 2.153 Å; WBI Sn–C = 0.619), while H–bonds are remarkably strengthened [LP(F) → BD*(N–H), 133.7 kcal/mol] as compared to compound **3**.

DFT calculations were extended to the precursors {Me$_2$N(CH$_2$)$_3$}$_2$SnX$_2$ (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 C,N-coordinating dimethylaminopropyl ligands. The pattern of Sn–C and Sn–X bond lengths for {Me$_2$N(CH$_2$)$_3$}$_2$SnCl$_2$ and {Me$_2$N(CH$_2$)$_3$}$_2$SnF$_2$ 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).

By protonation of both N donor sites in {Me$_2$N(CH$_2$)$_3$}$_2$SnX$_2$, the [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnX$_2$]$^{2+}$ (X = F, Cl) dications are 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 136.38, C–Sn–F 102.52°; X = Cl: Cl–Sn–Cl 106.11, C–Sn–C 127.01, C–Sn–Cl 105.52°). Worthy of note, both [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnX$_2$]$^{2+}$ dications 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 Cl (X = F: d_{Sn-F} = 1.986 Å, N–H•••F = 170.38°; X = F: d_{Sn-Cl} = 2.395 Å, N–H•••Cl = 141.58°). Therefore, among [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnX$_2$]$^{2+}$ 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 [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$]$^{2+}$ were repeated by implicitly keeping into account the presence of water by using the integral

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equation formalism of the polarizable continuous model (IEF-PCM)[25] within the self-consistent reaction field (SCRF) approach. Under these conditions, calculations confirm the formation of the two hydrogen bonds, stabilizing the dication by 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) $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+} + 2\,F^- \rightarrow \{Me_2(H)N(CH_2)_3\}_2SnF_4$ (**4**)

2) $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+} + 2\,Cl^- \rightarrow \{Me_2(H)N(CH_2)_3\}_2SnCl_2F_2$

3) $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+} + 2\,Br^- \rightarrow \{Me_2(H)N(CH_2)_3\}_2SnBr_2F_2$

4) $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+} + 2\,I^- \rightarrow \{Me_2(H)N(CH_2)_3\}_2SnF_2I_2$

5) $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+} + 4\,Cl^- \rightarrow \{Me_2(H)N(CH_2)_3\}_2SnCl_4 + 2\,F^-$

6) $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+} + 4\,Br^- \rightarrow \{Me_2(H)N(CH_2)_3\}_2SnBr_4 + 2\,F^-$

7) $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+} + 4\,I^- \rightarrow \{Me_2(H)N(CH_2)_3\}_2SnI_4 + 2\,F^-$

All reactions start from the cation $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+}$ 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 $\{Me_2(H)N(CH_2)_3\}_2SnF_2X_2$ neutral species in a *cis* or *trans* arrangement (X = Cl, Br, I; reactions 2–4). Moreover, the complete replacement of the fluoride anions in $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+}$ to give $\{Me_2(H)N(CH_2)_3\}_2SnX_4$ 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 ΔH_r, entropies ΔS_r, and free energies ΔG_r were obtained (Table 1 and Table 2).

Table 1. Thermochemistry DFT-calculations (a.u.) for the reactions 1–7 (see text) in the gas phase at 298.15 K. For all reactions, the H–bonding stabilized form of the $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+}$ was considered as the starting reagent.

Reaction	ΔH_r	ΔS_r	$T \cdot \Delta S_r$	ΔG_r
1	−1.1073	1.422×10^{-3}	0.4240	−0.6833
2 (*cis* product)	−0.5497	1.025×10^{-4}	0.0306	−0.5191
2 (*trans* product)	−0.5494	1.041×10^{-4}	0.0310	−0.5183
3 (*cis* product)	−0.4892	1.001×10^{-4}	0.0298	−0.4594
3 (*trans* product)	−0.4905	1.007×10^{-4}	0.0300	−0.4605
4 (*cis* product)	−0.4360	9.620×10^{-5}	0.0287	−0.4073
4 (*trans* product)	−0.4383	9.619×10^{-5}	0.0287	−0.4096
5	−0.3622	9.347×10^{-5}	0.0279	−0.3344
6	−0.2397	9.122×10^{-5}	0.0272	−0.2125
7	−0.1309	8.627×10^{-5}	0.0257	−0.1052

For all the reactions considered, the entropy terms ΔS_r are largely smaller than the corresponding enthalpy variations ΔH_r. The reaction enthalpies ΔH_r 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**

Table 2. Thermochemistry DFT-calculations (a.u.) for the reactions 1–7 (see text) in water[a] at 298.15 K. For all reactions, the H–bonding stabilized form of the $[\{Me_2(H)N(CH_2)_3\}_2SnF_2]^{2+}$ was considered as the starting reagent.

Reaction	ΔH_r	ΔS_r	$T \cdot \Delta S_r$	ΔG_r
1	−0.2330	9.805×10^{-5}	0.0292	−0.2038
2 (*cis* product)	−0.1140	9.260×10^{-5}	0.0276	−0.0864
2 (*trans* product)	−0.1138	9.234×10^{-5}	0.0275	−0.0863
3 (*cis* product)	−0.0728	8.584×10^{-5}	0.0256	−0.0471
3 (*trans* product)	−0.0724	8.561×10^{-5}	0.0255	−0.0468
4 (*cis* product)	−0.0430	7.748×10^{-5}	0.0231	−0.0198
4 (*trans* product)	−0.0409	7.905×10^{-5}	0.0236	−0.0174
5	0.0220	8.305×10^{-5}	0.0248	0.0468
6	0.1100	7.962×10^{-5}	0.0237	0.1337
7	0.1765	6.955×10^{-5}	0.0207	0.1972

[a] IEF-PCM SCRF model.

with two halide anions X^- to give $\{Me_2(H)N(CH_2)_3\}_2SnF_2X_2$ 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 (LP(F) → BD*(N–H), 133.7, 123.2, 118.1, and 109.1 kcal/mol for compound **4**, $\{Me_2(H)N(CH_2)_3\}_2SnCl_2F_2$, $\{Me_2(H)N(CH_2)_3\}_2SnBr_2F_2$, and $\{Me_2(H)N(CH_2)_3\}_2SnF_2I_2$, respectively, in the gas phase; 74.7, 64.3, 61.0, and 56.8 kcal/mol for compound **4**, $\{Me_2(H)N(CH_2)_3\}_2SnCl_2F_2$, $\{Me_2(H)N(CH_2)_3\}_2SnBr_2F_2$, and $\{Me_2(H)N(CH_2)_3\}_2SnF_2I_2$, respectively, in water), as a result of the natural charge variation on the tin central ion (Q_{Sn} = 2.276, 1.911, 1.835, and 1.711 |e| for compounds **4**, $\{Me_2(H)N(CH_2)_3\}_2SnCl_2F_2$, $\{Me_2(H)N(CH_2)_3\}_2SnBr_2F_2$, and $\{Me_2(H)N(CH_2)_3\}_2SnF_2I_2$, respectively, in the gas phase; 2.261, 1.949, 1.908, and 1.864 |e| for compounds **4**, $\{Me_2(H)N(CH_2)_3\}_2SnCl_2F_2$, $\{Me_2(H)N(CH_2)_3\}_2SnBr_2F_2$, and $\{Me_2(H)N(CH_2)_3\}_2SnF_2I_2$, respectively, in water). The same trend is further confirmed in reactions 5–7, where, as discussed above for $[\{Me_2(H)N(CH_2)_3\}_2SnX_2]^{2+}$ dications, interactions N–H•••X become progressively less important.

While in the gas phase all reactions are exothermic and exergonic (Table 1), solvation results in an increase in ΔH_r values paralleled by a dramatic decrease in entropic variations ΔS_r (and hence of the $T \cdot \Delta S_r$ terms, Table 2). Consequently, in water solution the reaction 1 is calculated to be more than twice exergonic than reactions 2–4, that show ΔG_r values close to zero, 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 dependence 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 ^{19}F 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 $\{Me_2(H)N(CH_2)_3\}_2SnCl_2F_2$.

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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 {Me$_2$N(CH$_2$)$_3$}$_2$SnCl$_2$ can, via subsequent reactions in water with perchloric acid and tetraethylammonium fluoride, be quantitatively transformed into the organotin perchlorate salt [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$](ClO$_4$)$_2$, **2**, which in turn shows to be an ideal selective fluoride receptor affording the zwitterionic diammonium diorganotetrafluorido stannate {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_4$, **4**. Notably, the selectivity of compound **2** towards the F$^-$ anion as compared to Cl$^-$, Br$^-$, and I$^-$, 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 {Me$_2$N(CH$_2$)$_3$}$_2$SnF$_2$, 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.

Furthermore on this matter, we recall that bicentric Lewis acids such as R$_2$FSn(CH$_2$)$_n$SnFR$_2$ (R = Ph, *n*-octyl; *n* = 1, 2) [5,9a,19c] bind effectively fluoride anion in dichloromethane. Functionalization with 3-dimethylammoniumpropyl substituents, Me$_2$(H)NCH$_2$CH$_2$CH$_2$, would increase the solubility of these systems in water, thus affording new alternatives for fluoride receptors in aqueous media based on the –Sn(CH$_2$)$_n$Sn– (*n* = 1, 2) core. Indeed, following previous work on {Me$_2$N(CH$_2$)$_3$}Ph(F)SnCH$_2$SnFPh$_2$,[26] preliminary studies reveal a convenient access to {Me$_2$(H)N(CH$_2$)$_3$}Cl$_2$Sn(CH$_2$)$_2$SnCl$_2$Ph·Cl which is soluble in water as expected, and reacts in this solvent with fluoride anion to afford {Me$_2$(H)N(CH$_2$)$_3$}Cl$_2$Sn-(CH$_2$)$_2$SnCl$_2$Ph·F (for details see Supporting Information). We encourage interested readers to make use of these preliminary findings.

Experimental Section

General Methods: Bis[3-(dimethylamino)propyl]tin dichloride, {Me$_2$N(CH$_2$)$_3$}$_2$SnCl$_2$,[10] was synthesized as reported in the literature. Perchloric acid, potassium fluoride, sodium fluoride, sodium chloride, sodium bromide, sodium iodide, tetraethyl ammonium 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}H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra. Solution ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR chemical shifts δ are given in ppm and were referenced to Me$_4$Si (^{1}H, ^{13}C), CFCl$_3$ (^{19}F), and Me$_4$Sn (^{119}Sn). Elemental analyses were performed on a LECO–CHNS–932 analyzer. The electrospray mass spectra were recorded with a Thermoquest–Finnigan instrument. The mixture CH$_3$CN/H$_2$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**·4H$_2$O is given in the Supporting Information (Table S1). Single-crystal X-ray diffraction data for com-

pounds **1**, **3** and **4**·4H$_2$O were collected at 173 K on an Oxford Xcalibur Sapphire 3 diffractometer. The absorptions were corrected by SCALES3 ABSPACK multi-scan method.[27] The structures were solved by direct methods with SHELXT-20014[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**·4H$_2$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//Def2SVP)[21–23] was benchmarked by comparing optimized and structural data for compound **3**. Calculations were extended to {Me$_2$N(CH$_2$)$_3$}$_2$SnX$_2$ and [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnX$_2$]$^{2+}$ (X = F, Cl), **4**, {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$X$_2$ (X = Cl, Br, I; *cis* and *trans* isomers), and {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnX$_4$ (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 atomic 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 (SOPT) 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 {Me$_2$N(CH$_2$)$_3$}$_2$SnF$_2$·2H$_2$O: To a suspension of bis[3-(dimethylamino)propyl]tin dichloride [Me$_2$N(CH$_2$)$_3$]$_2$SnCl$_2$ (3.00 g, 8.29 mmol) in CH$_2$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 CH$_2$Cl$_2$ was evaporated in vacuo giving 2.18 g (72 %) of {Me$_2$N(CH$_2$)$_3$}$_2$SnF$_2$·2H$_2$O as a white solid. ^{1}H NMR (300.13 MHz, D$_2$O): δ = 1.17 (t, ^2J(^{1}H–$^{117/119}$Sn) = 90.0 Hz, 4H, Sn–CH$_2$), 1.89 (m, ^3J(^{1}H–$^{117/119}$Sn) = 128.8 Hz, 4H, Sn–CH$_2$–CH$_2$), 2.48 (s, 12H, N(CH$_3$)$_2$), 2.69 (t, 4H, CH$_2$–N). ^{13}C{^{1}H} NMR (75.47 MHz, D$_2$O): δ = 17.3 (^1J(^{13}C–$^{117/119}$Sn) = 907 Hz, Sn–CH$_2$), 20.0 (Sn–CH$_2$–CH$_2$, ^2J(^{13}C–$^{117/119}$Sn) = 42 Hz), 43.7 N(CH$_3$)$_2$, 59.7 (^3J(^{13}C–$^{117/119}$Sn) = 102 Hz, CH$_2$–N). ^{19}F{^{1}H} NMR (282.40 MHz, D$_2$O): δ = –123. ^{119}Sn{^{1}H} NMR (111.92 MHz, D$_2$O): no signal observed. Anal. Calcd. (%) for C$_{10}$H$_{28}$F$_2$N$_2$O$_2$Sn (365.1): C 32.90, H 7.73, N 7.67; found C 32.9, H 7.6, N 7.7.

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Synthesis of [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnCl$_2$](ClO$_4$)$_2$ (1): To a solution of {Me$_2$N(CH$_2$)$_3$}$_2$SnCl$_2$ (150 mg, 0.414 mmol) in water (5 mL) was added HClO$_4$ (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. ^{1}H NMR (400.25 MHz, D$_2$O): δ = 1.58 (t, ^2J(^{1}H–$^{117/119}$Sn) = 103.7 Hz, 4H, Sn–CH_2), 2.11 (m, 4H, Sn–CH$_2$–CH_2), 2.87 (s, 12H, N(CH_3)$_2$), 3.16 (t, 4H, CH_2–N). ^{13}C{^{1}H} NMR (100.64 MHz, D$_2$O): δ = 20.3 (Sn–CH$_2$–CH$_2$, ^2J(^{13}C–$^{117/119}$Sn) = 35 Hz), 29.9 (^1J(^{13}C–$^{117/119}$Sn) = 959/1003 Hz, Sn–CH$_2$), 42.7 N(CH$_3$)$_2$, 59.3 (^3J(^{13}C–$^{117/119}$Sn) = 189 Hz, CH$_2$–N). ^{119}Sn{^{1}H} NMR (149.26 MHz, D$_2$O): δ = –310. ^{1}H NMR (400.25 MHz, CD$_3$CN): δ = 1.75 (t, ^2J(^{1}H–$^{117/119}$Sn) = 78.3 Hz, 4H, Sn–CH_2), 2.14 (m, 4H, Sn–CH$_2$–CH_2), 2.84 (d, (^3J(^{1}H–^{1}H) = 5.38 Hz), 12H, N(CH_3)$_2$), 3.16 (t, 2H, CH_2–N), 7.26 (b, 2H, HN(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100.64 MHz, CD$_3$CN): δ = 21.7 (Sn–CH$_2$–CH$_2$), 29.1 (^1J(^{13}C–$^{117/119}$Sn) = 682 Hz, Sn–CH$_2$), 44.4 N(CH$_3$)$_2$, 60.9 (^3J(^{13}C–$^{117/119}$Sn) = 146 Hz, CH$_2$–N). ^{119}Sn{^{1}H} NMR (149.26 MHz, CD$_3$CN): δ = –56. Anal. Calcd. (%) for C$_{10}$H$_{26}$Cl$_4$N$_2$O$_8$Sn·H$_2$O (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, 206.1 (34, [Sn(OH)$_3$ + 2H$_2$O]$^+$), 309.1 (10, [{Me$_2$N(CH$_2$)$_3$}$_2$SnOH]$^+$), 327.1 (4, [{Me$_2$N(CH$_2$)$_3$}$_2$SnCl]$^+$), negative mode, 99.1 (100, [ClO$_4$]$^-$).

Synthesis of [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$](ClO$_4$)$_2$ (2): To a solution of {Me$_2$N(CH$_2$)$_3$}$_2$SnF$_2$·2H$_2$O (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. ^{1}H NMR (300.13 MHz, D$_2$O): δ = 1.28 (t, ^2J(^{1}H–$^{117/119}$Sn) = 104.7 Hz, 4H, Sn–CH_2), 1.99 (m, ^3J(^{1}H–$^{117/119}$Sn) = 95.1 Hz, 4H, Sn–CH$_2$–CH_2), 2.82 (s, 12H, N(CH_3)$_2$), 3.09 (t, 2H, CH_2–N). ^{1}H NMR (300.13 MHz, CD$_3$CN): δ = 1.49 (t, ^2J(^{1}H–$^{117/119}$Sn) = 95.1 Hz, 4H, Sn–CH_2), 2.06 (m, ^3J(^{1}H–$^{117/119}$Sn) = 79.0 Hz, 4H, Sn–CH$_2$–CH_2), 2.86 (d, ^3J(^{1}H–^{1}H) = 4.76 Hz, 12H, N(CH_3)$_2$), 3.15 (t, 4H, CH_2–N), 7.57 (b, 2H, HN(CH$_3$)$_2$). ^{1}H NMR (300.13 MHz, C$_3$D$_6$O): δ = 1.57 (t, ^2J(^{1}H–$^{117/119}$Sn) = 104.7 Hz, 4H, Sn–CH_2), 2.21 (m, ^3J(^{1}H–$^{117/119}$Sn) = 92.2 Hz, 4H, Sn–CH$_2$–CH_2), 3.00 (d, ^3J(^{1}H–^{1}H) = 4.39 Hz, 12H, N(CH_3)$_2$), 3.30 (t, 4H, CH_2–N), 8.6 (b, 2H, HN(CH$_3$)$_2$). ^{13}C{^{1}H} NMR (100.63 MHz, C$_3$D$_6$O): δ = 19.9 (Sn–CH$_2$–CH$_2$, ^2J(^{13}C–$^{117/119}$Sn) = 37 Hz), 24.6 (Sn–CH$_2$), 42.9 N(CH$_3$)$_2$, 59.8 (CH$_2$–N). ^{13}C{^{1}H} NMR (75.47 MHz, D$_2$O): δ = 19.7 (Sn–CH$_2$–CH$_2$, ^2J(^{13}C–$^{117/119}$Sn) = 33 Hz), 23.5 (^1J(^{13}C–$^{117/119}$Sn) = 977 Hz, Sn–CH$_2$), 42.5 N(CH$_3$)$_2$, 59.6 (CH$_2$–N, ^3J(^{13}C–$^{117/119}$Sn) = 165 Hz). ^{19}F{^{1}H} NMR (D$_2$O, 282.40 MHz): δ = –141. ^{19}F{^{1}H} NMR (282.40 MHz, C$_3$D$_6$O): δ = –145. ^{119}Sn{^{1}H} NMR (111.92 MHz, D$_2$O): no signal observed. ^{119}Sn{^{1}H} NMR (111.92 MHz, [D$_6$]acetone): δ = –340. ^{119}Sn{^{1}H} NMR (149.26 MHz, D$_2$O): δ = –359 ($\nu_{1/2}$ = 1215 Hz). Anal. Calcd. (%) for C$_{10}$H$_{26}$Cl$_2$F$_2$N$_2$O$_8$Sn (547.9): C 22.66, H 4.95, N 5.29; found C 22.2, H 5.1, N 5.2. Electrospray MS: m/z (%), positive mode, 309.1 (100, [{Me$_2$N(CH$_2$)$_3$}$_2$SnOH]$^+$), negative mode, 99.1 (100, [ClO$_4$]$^-$), 507.0 (18, [{Me$_2$N(CH$_2$)$_3$}$_2$SnOH(ClO$_4$)$_2$]$^-$).

Reaction of Compounds 1 with Two Molar Equivs. of NEt$_4$F·2H$_2$O: To a solution of [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnCl$_2$](ClO$_4$)$_2$, **1**, (40 mg, 0.07 mmol) in CH$_3$CN (10 mL) was added NEt$_4$F·2H$_2$O (26 mg, 0.14 mmol). A white precipitate was formed during stirring the solution for 5 hours. The precipitate was filtered, washed twice with CH$_3$CN and dried in vacuo to yield [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$](ClO$_4$)$_2$, **2**, (35 mg, 92 %) as a white solid. No melting point was determined. ^{1}H NMR (400.25 MHz, D$_2$O): δ = 1.23 (CH_3–CH$_2$N), 1.38 (t, 4H, Sn–CH_2), 2.05 (m, 4H, Sn–CH$_2$–CH_2), 2.86 (s, 12H, N(CH_3)$_2$), 3.14 (t, 4H, CH_2–N), 3.23 (CH$_3$–CH_2N). ^{13}C{^{1}H} NMR (100.64 MHz, D$_2$O): δ = 6.5 (CH_3–CH$_2$N), 19.9 (Sn–CH$_2$–CH$_2$), 25.7 (Sn–CH$_2$), 42.7 N(CH$_3$)$_2$, 51.9 (CH$_3$–CH$_2$N), 59.6 (CH$_2$–N). ^{19}F{^{1}H} NMR (D$_2$O, 376.61 MHz): δ = –144. ^{119}Sn{^{1}H} NMR (149.26 MHz, D$_2$O): δ = –359.

Synthesis of {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnCl$_4$ (3): To a solution of {Me$_2$N(CH$_2$)$_3$}$_2$SnCl$_2$ (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. ^{1}H NMR (500.08 MHz, D$_2$O): δ = 1.55 (t, ^2J(^{1}H–$^{117/119}$Sn) = 101.6 Hz, 4H, Sn–CH_2), 2.08 (m, 4H, Sn–CH$_2$–CH_2), 2.82 (s, 12H, N(CH_3)$_2$), 3.13 (t, 4H, CH_2–N). ^{13}C{^{1}H} NMR (125.75 MHz, D$_2$O): δ = 20.5 (Sn–CH$_2$–CH$_2$, ^2J(^{13}C–$^{117/119}$Sn) = 35 Hz), 31.0 (^1J(^{13}C–$^{117/119}$Sn) = 928/976 Hz, Sn–CH$_2$), 42.6 N(CH$_3$)$_2$, 59.2 (^3J(^{13}C–$^{117/119}$Sn) = 175/181 Hz, CH$_2$–N). ^{119}Sn{^{1}H} NMR (149.26 MHz, D$_2$O): δ = –264. Anal. Calcd. (%) for C$_{10}$H$_{26}$Cl$_4$N$_2$Sn (434.84): C 27.62, H 6.03, N 6.44; found C 27.5, H 5.8, N 6.5. Electrospray MS: m/z (%), positive mode, 327.1 (90, [{Me$_2$N(CH$_2$)$_3$}$_2$SnCl]$^+$), 309.1 (78, [{Me$_2$N(CH$_2$)$_3$}$_2$SnOH]$^+$), 206.0 (40, [Sn(OH)$_3$ + 2H$_2$O]$^+$), 1135.6 (1, [C$_{30}$H$_{81}$N$_6$O$_7$Cl$_4$Sn$_3$]$^+$).

Synthesis of {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_4$ (4):

(i) Reaction of Compound 3 with Four Molar Equivs. of NEt$_4$F·2H$_2$O: To a solution of {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnCl$_4$, **3**, (110 mg, 0.25 mmol) in CH$_3$CN (12 mL) was added NEt$_4$F·2H$_2$O (187 mg, 1.01 mmol). A white precipitate was formed during stirring the solution for 5 hours. The precipitate was filtered, washed twice with CH$_3$CN and dried in vacuo to yield **4** (88 mg, 94 %) as a white solid. Recrystallization from acetonitrile under non-inert conditions gave the water solvate **4**·4H$_2$O of m.p. 128–129 °C. NMR spectra of a solution of compound **4** (80 mg) in D$_2$O. ^{1}H NMR (400.25 MHz, D$_2$O): δ = 1.24 (t, ^2J(^{1}H–$^{117/119}$Sn) = 111.9 Hz, 4H, Sn–CH_2), 2.02 (m, ^3J(^{1}H–$^{117/119}$Sn) = 99.4 Hz, 4H, Sn–CH$_2$–CH_2), 2.84 (s, 12H, N(CH_3)$_2$), 3.12 (t, 4H, CH_2–N). ^{13}C{^{1}H} NMR (100.64 MHz, D$_2$O): δ = 20.0 (Sn–CH$_2$–CH$_2$), 23.6 (Sn–CH$_2$), 42.6 N(CH$_3$)$_2$, 59.9 (CH$_2$–N). ^{19}F{^{1}H} NMR (376.61 MHz, D$_2$O): δ = –126 (96 %), –130 (4 %, unresolved). ^{119}Sn{^{1}H} NMR (149.26 MHz, D$_2$O): –405 ($\nu_{1/2}$ = 1410 Hz). Anal. Calcd. (%) for C$_{10}$H$_{26}$F$_4$N$_2$Sn·3H$_2$O (423.08): C 28.39, H 7.62, N 6.62; found C 28.8, H 7.8, N 6.9. The sample used for the elemental analysis had been dried in vacuo. Apparently, one water molecule was removed. Electrospray MS: m/z (%), positive mode, 311.0 (100, [{Me$_2$N(CH$_2$)$_3$}$_2$SnF]$^+$), 331.1 (90, [**4** – 2F – H]$^+$).

(ii) Reaction of Compound 2 with Two Molar Equivs. of KF: To a solution of compound **2** (60 mg, 0.11 mmol) in D$_2$O was added KF (13 mg, 0.22 mmol) with stirring. A white precipitate of KClO$_4$ was formed immediately. Filtration and slow evaporation of the solvent afford compound **4** as a white solid. ^{1}H NMR (300.13 MHz, D$_2$O): δ = 1.27 (t, ^2J(^{1}H–$^{117/119}$Sn) = 109.8 Hz, 4H, Sn–CH_2), 2.11 (m, ^3J(^{1}H–$^{117/119}$Sn) = 101.7 Hz, 4H, Sn–CH$_2$–CH_2), 2.91 (s, 12H, N(CH_3)$_2$), 3.18 (t, 4H, CH_2–N). ^{13}C{^{1}H} NMR (100.63 MHz, D$_2$O): δ = 20.5 (^2J(^{13}C–$^{117/119}$Sn) = 36 Hz, Sn–CH$_2$–CH$_2$), 22.1 (Sn–CH$_2$), 43.1 N(CH$_3$)$_2$, 60.5 (^3J(^{13}C–$^{117/119}$Sn) = 145 Hz, CH$_2$–N). ^{19}F{^{1}H} NMR (282.40 MHz, D$_2$O): δ = –125. ^{119}Sn{^{1}H} NMR (111.92 MHz, D$_2$O): no signal was observed.

(iii) Reaction of Compound 2 with Two Molar Equivs. of NaF.

To a solution of compound **2** (101 mg, 0.19 mmol) in D$_2$O was added NaF (16 mg, 0.38 mmol). The solution was stirred for 10 min. From this solution, NMR data were recorded. ^{1}H NMR (200.13 MHz, D$_2$O): δ = 1.16 (t, ^2J(^{1}H–$^{117/119}$Sn) = 119.6 Hz, 4H, Sn–CH_2), 2.04 (m, ^3J(^{1}H–$^{117/119}$Sn) = 100.5/ 104.8 Hz, 4H, Sn–CH$_2$–CH_2), 2.88 (s, 12H, N(CH_3)$_2$), 3.15 (t, 4H, CH_2–N). ^{13}C{^{1}H} NMR (100.33 MHz, D$_2$O): δ = 20.7 (^2J(^{13}C–$^{117/119}$Sn) = 37 Hz, Sn–CH$_2$–CH$_2$), 23.6 (^1J(^{13}C–$^{117/119}$Sn) = 1102/1153 Hz, Sn–CH$_2$), 43.1 N(CH$_3$)$_2$, 60.6 (^3J(^{13}C–$^{117/119}$Sn) = 160 Hz, CH$_2$–N). ^{19}F{^{1}H} NMR (188.29 MHz, D$_2$O): δ = –125. ^{119}Sn{^{1}H} NMR (111.92 MHz, D$_2$O): δ = –412 ($\nu_{1/2}$ = 340 Hz).

Selectivity Study: To a solution containing NaF (10 mg, 0.24 mmol), NaCl (14 mg, 0.24 mmol), NaBr (24 mg, 0.24 mmol), and NaI (36 mg,

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0.24 mmol) in D_2O (0.6 mL) was added **2** (63 mg, 0.12 mmol.) The reaction mixture was stirred for 10 min. From this solution, NMR spectra were recorded. ^1H NMR (300.13 MHz, D_2O): δ = 1.26 (t, $^2J(^1H-^{117/119}Sn)$ = 106.9 Hz, 4H, Sn–CH_2), 2.08 (m, $^3J(^1H-^{117/119}Sn)$ = 96.6 Hz, 4H, Sn–CH$_2$–CH_2), 2.90 (s, 12H, N(CH_3)$_2$), 3.17 (t, 4H, CH_2–N). $^{13}C\{^1H\}$ NMR (75.47 MHz, D_2O): δ = 20.2 ($^2J(^{13}C-^{117/119}Sn)$ = 35 Hz, Sn–CH$_2$–CH_2), 21.8 (Sn–CH_2), 43.1 N(CH_3)$_2$, 60.2 ($^3J(^{13}C-^{117/119}Sn)$ = 154 Hz, CH_2–N). $^{19}F\{^1H\}$ NMR (282.40 MHz, D_2O): δ = −126 (97 %), −133 (1 %), −150 (2 %). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, D_2O): no signal was observed.

Studying the Effect of the Solution _p_H on the Behavior of {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_4$ (4): A solution of compound **4** (84 mg) in D_2O (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 _p_H = 9. The solution remained clear. ^1H NMR (300.13 MHz, D_2O): δ = 1.21 (t, $^2J(^1H-^{117/119}Sn)$ = 88.55 Hz, 4H, Sn–CH_2), 1.91 (m, $^3J(^1H-^{117/119}Sn)$ = 130.3 Hz, 4H, Sn–CH$_2$–CH_2), 2.47 (s, 12H, N(CH_3)$_2$), 2.66 (t, 4H, CH_2–N). $^{13}C\{^1H\}$ NMR (75.47 MHz, D_2O): δ = 17.0 (Sn–CH$_2$), 20.1 (Sn–CH$_2$–CH_2, $^2J(^{13}C-^{117/119}Sn)$ = 43 Hz), 43.9 N(CH_3)$_2$, 59.8 ($^3J(^{13}C-^{117/119}Sn)$ = 98 Hz, CH_2–N). $^{19}F\{^1H\}$ NMR (282.40 MHz, D_2O): δ = −120. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, D_2O): 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**·4H$_2$O (Tables S1–S12); ^1H, ^{13}C, ^{19}F and ^{119}Sn NMR spectra and Mass spectra for compounds **1**, **3**, and **4**. Preliminary results concerning water-soluble bicentric Lewis acids.

DFT-optimized geometries for compounds **3**, **4**, {Me$_2$N(CH$_2$)$_3$}$_2$SnX$_2$, and [{Me$_2$(H)N(CH$_2$)$_3$}$_2$SnX$_2$]$^{2+}$ (X = F, Cl), {Me$_2$(H)N(CH$_2$)$_3$}$_2$SnF$_2$X$_2$ (X = Cl, Br, I; _cis_ and _trans_ isomers), and {Me$_2$NH(CH$_2$)$_3$}$_2$SnX$_4$ (X = Cl, Br, I) are available in the orthogonal Cartesian format upon request to the authors.

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