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Solubilizing Sodium Fluoride in Acetonitrile: Synthesis, Molecular Structure, and Complexation Behavior of Bis(organostannyl)methyl-Substituted Crown Ethers**

Gregor Reeske, Gerrit Bradtmöller, Markus Schürmann, and Klaus Jurkschat*[a]

Abstract: The synthesis of the crown-ether-substituted bis(organostannyl)-methanes $Ph_3SnCH_2Sn(Ph_2)$-CH_2-[16]crown-5 (**1**) and $Ph_2ISnCH_2Sn(I)(Ph)$-CH_2-[16]crown-5 (**2**) is reported. Both compounds have been characterized by elemental analyses, ^1H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectroscopy, and in the case of compound **2** also by electrospray ionization mass spectrometry. Single-crystal X-ray diffraction analysis revealed for the aqua complex **2**·H_2O trigonal–bipyramidal-configured tin atoms with intramolecular Sn(1)···O(1) and Sn(2)···O(1W) distances of 2.555(2) and 2.440(3) Å, respectively. The water molecule is trapped in a sandwich-like fashion between the crown ether oxygen atoms O(2) and O(4) and the Sn(2) atom. NMR spectroscopy unambiguously proved the ability of compound **2** in acetonitrile to overcome the high lattice energy of sodium fluoride and to complex the latter under charge separation.

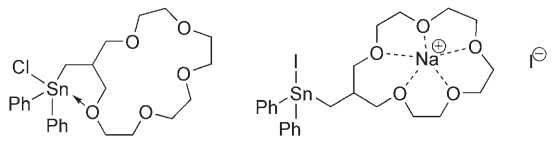
Keywords: crown compounds · heteroditopic complexation · host–guest systems · Lewis acids · sodium fluoride · structure elucidation · tin

Introduction

The simultaneous and selective complexation of anions and cations by so-called ditopic hosts is a rather popular topic in contemporary host–guest chemistry and a variety of appropriate molecules that are capable of binding selected salts have been reported.[1–9] Recent developments have focused on the recognition of heavy-metal salts such as nickel or copper sulfate for hydrometallurgical applications.[10–12] Well-designed binding sites that combine electrostatic or hydrogen-bonding interactions enable ditopic host molecules to do this.

An alternative but still much less developed strategy for simultaneous cation and anion binding involves linking crown ether type entities to Lewis acidic organometal/-element fragments. This concept has been shown to be successful for an organoboron-substituted crown ether[13,14] which binds the ion pair potassium fluoride, KF, and for organotin-substituted crown ethers which complex sodium thiocyanate, NaSCN,[15] and are able to transport it from aqueous solution through an organic phase.[16]

Recently we reported the organotin-substituted crown ethers $Ph_{(3-n)}X_nSnCH_2$-[16]crown-5 (X = F, Cl, Br, I, SCN; $n = 1$, 2) and studied the complexation behavior of the chloro-substituted derivative **A** ($n = 1$, X = Cl) towards several salts.[17]



A B

Reaction of compound **A** with two molar equivalents of sodium iodide, NaI, quantitatively gave sodium chloride, NaCl, and the sodium iodide complex **B** of the corresponding iododiphenylstannyl-substituted crown ether. In compound **B**, the latter complexes sodium iodide through the crown ether moiety, but without charge separation. That is,

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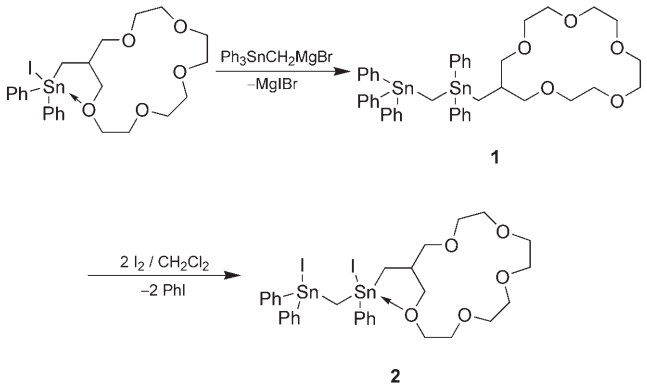
the Lewis acidity of the tin atom in compound **B** is not high enough to overcome the coulombic forces and to complex the iodide anion. Addition of tetrabutylammonium fluoride trihydrate, *n*-$Bu_4NF{\cdot}3H_2O$, to a solution of **B** caused precipitation of sodium fluoride, NaF, and the quantitative formation of the triorganotin iodide Ph_2ISnCH_2-[16]crown-5. Apparently, the driving force for this reaction is the rather high lattice energy of sodium fluoride which cannot be compensated for by the complexing ligand.

From our previous studies we know that as a result of cooperative binding bis(organostannyl)methanes such as $Ph_2XSnCH_2SnXPh_2$ (X = halogen) are excellent fluoride ion acceptors.[18] Linking such a bis(organostannyl)methane moiety to an appropriate sodium-cation-specific crown ether should enhance the chance of charge separation by ditopic complexation of sodium fluoride.

Herein we report the first example of such a compound, namely $Ph_2ISnCH_2Sn(I)(Ph)$-CH_2-[16]crown-5, and study by means of NMR spectroscopy its complexation behavior towards sodium fluoride.



Scheme 1. Synthesis of the bis(organostannyl)methane derivatives **1** and **2**.

Results and Discussion

Synthetic aspects and molecular structures in the solid state: Reaction in THF of the triorganotin iodide with triphenylstannylmethylmagnesium bromide[19] provided, after column chromatography, analytically pure **1** as a colorless oil (Scheme 1). Two of its phenyl groups were removed by reaction in CH_2Cl_2 of compound **1** with two molar equivalents of iodine to give the corresponding bis(iododiorganostannyl)methane **2**.

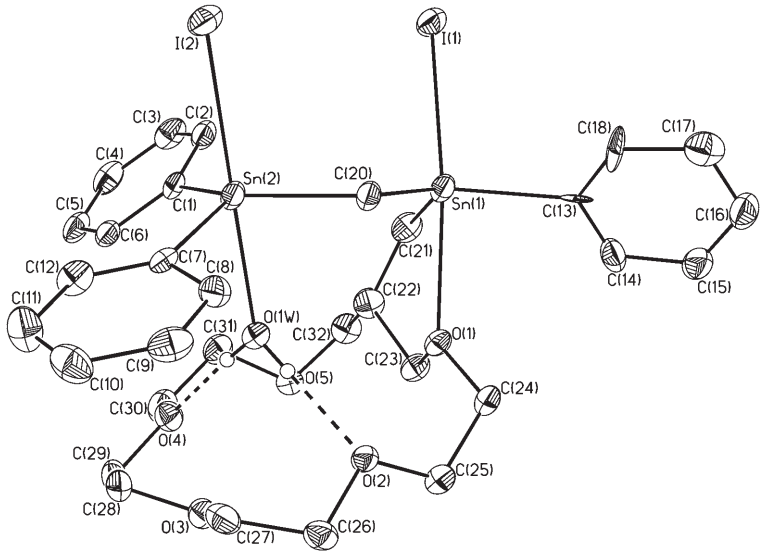


Figure 1. Molecular structure of **2**·H_2O showing 30% probability displacement ellipsoids and the crystallographic numbering scheme.

Crystallization of compound **2** from diethyl ether at −5 °C in the presence of air moisture afforded single crystals of the aqua complex **2**·H_2O as its diethyl ether solvate. The molecular structure of compound **2**·H_2O is shown in Figure 1; selected geometrical parameters and crystallographic data are collected in Tables 1 and 2, respectively.

Both of the tin atoms in **2**·H_2O are pentacoordinated and show a distorted trigonal bipyramidal configuration [geometrical goodness[20] $\Delta\Sigma(\vartheta) = 54.5°$ (Sn(1)) and 63.5° (Sn(2))] with the carbon atoms C(13), C(20), C(21) (at Sn(1)) and C(1), C(7), C(20) (at Sn(2)) occupying the equatorial positions and O(1), I(1) (at Sn(1)) and O(1W), I(2) (at Sn(2)) occupying the axial positions. The Sn(1) atom is displaced by 0.34 in the direction of I(1) and the Sn(2) atom is displaced by 0.27 Å in the direction of I(2) from the planes defined by the corresponding carbon atoms. The intramolecular Sn(1)–O(1) distance of 2.555(2) Å is rather similar to that of the organostannyl-substituted crown ether Ph_2ISn-CH_2-[16]crown-5 (2.554(2) Å).[17] Compared with this, the Sn(2)–O(1W) distance of 2.440(3) Å, with the water molecule being trapped in a sandwich-like manner between Sn(2) and the crown ether oxygen atoms O(2) and O(4), is shorter. The distance is comparable to that of 2.469(4) Å found in the aqua complex $Ph_2ClSn(CH_2)_2$-[15]benzocrown-5·H_2O.[16] As in the latter compound, the complexation of the water molecule in the aqua complex **2**·H_2O is supported by two hydrogen bridges with O(1W)···O(2) and O(1W)···O(4) distances of 2.813(4) and 2.842(4) Å, respectively.

Structure of 2·H_2O in solution: At ambient temperature, the ^{119}Sn NMR spectrum of **2**·H_2O ($CDCl_3$) shows two equally intense resonances at $\delta = -56$ ppm ($^2J(^{117/119}Sn{-}^{119}Sn) = 278$ Hz, signal a, $Ph_2(I)SnCH_2$-) and $\delta = -82$ ppm ($^2J(^{117/}$

Table 1. Selected bond lengths [Å] and angles [°] for compound **2**·H_2O.

Sn(1)–C(13)	2.224(4)	O(1)–C(23)	1.435(4)
Sn(1)–C(20)	2.116(3)	O(2)–C(25)	1.416(4)
Sn(1)–C(21)	2.118(3)	O(2)–C(26)	1.425(4)
Sn(1)–I(1)	2.8105(4)	O(4)–C(30)	1.427(4)
Sn(1)–O(1)	2.555(2)	O(4)–C(29)	1.431(4)
Sn(2)–C(1)	2.137(4)	O(2)–H(2W)	2.01(5)
Sn(2)–C(7)	2.148(4)	O(4)–H(1W)	2.01(4)
Sn(2)–C(20)	2.126(3)	O(1W)–H(1W)	0.84 (4)
Sn(2)–I(2)	2.8345(4)	O(1W)–H(2W)	0.82(5)
Sn(2)–O(1W)	2.440(3)	O(1W)–O(2)	2.831(4)
C(21)–C(22)	1.482(4)	O(1W)–O(4)	2.842(4)
O(1)–C(24)	1.434(3)		
C(1)-Sn(2)-C(7)	119.25(15)	C(20)-Sn(1)-I(1)	98.65(9)
C(1)-Sn(2)-C(20)	122.31(14)	C(20)-Sn(2)-I(2)	96.74(9)
C(1)-Sn(2)-I(2)	98.51(9)	C(20)-Sn(1)-O(1)	83.57(11)
C(1)-Sn(2)-O(1W)	80.48(13)	C(20)-Sn(2)-O(1W)	83.10(12)
C(7)-Sn(2)-O(1W)	85.05(11)	C(21)-Sn(1)-C(13)	115.39(14)
C(7)-Sn(2)-I(2)	96.23(9)	C(21)-Sn(1)-I(1)	99.05(10)
C(7)-Sn(2)-C(20)	113.79(14)	C(21)-Sn(1)-O(1)	73.17(11)
C(13)-Sn(1)-I(1)	99.82(9)	C(22)-C(21)-Sn(1)	113.50(3)
C(13)-Sn(1)-O(1)	86.77(10)	O(1)-Sn(1)-I(1)	171.53(5)
C(20)-Sn(1)-C(13)	112.27(13)	O(1W)-Sn(2)-I(2)	178.66(8)
C(20)-Sn(1)-C(21)	124.83(14)	Sn(1)-C(20)-Sn(2)	123.78(15)

Table 2. Crystallographic data for **2**·H_2O.

	2·H_2O
formula	$C_{33}H_{47}I_2O_{6.5}Sn_2$
M_r	1038.89
crystal system	monoclinic
cryst size [mm]	$0.20\times0.12\times0.04$
space group	$P2(1)/c$
a [Å]	10.0507(7)
b [Å]	13.8714(9)
c [Å]	27.9624(18)
α [°]	90
β [°]	90.807(3)
γ [°]	90
V [Å^3]	3898.1(4)
Z	4
ρ_{calcd} [Mg m^3]	1.770
μ [mm^{-1}]	2.904
$F(000)$	2012
θ range [°]	2.91–27.50
index ranges	$-13\le h\le13$
	$-17\le k\le17$
	$-36\le l\le36$
no. of reflns collcd	45325
completeness to θ_{max} [%]	99.2
no. of indep reflns/R_{int}	8869/0.046
no. of reflns obsd with ($I>2\sigma(I)$)	4427
no. of refined parameters	392
GoF (F^2)	0.714
$R_1(F)$ ($I>2\sigma(I)$)	0.0292
$wR_2(F^2)$ (all data)	0.0454

^{119}Sn–^{119}Sn) = 278 Hz, signal b, -CH_2(Ph)(I)*Sn*CH_2-). At −60 °C the two signals shift to a lower frequency by 14 and 6 ppm, respectively, and exhibit considerable line-broadening (a: $\delta=-70$ ppm, $\nu(^1/_2)=1800$ Hz; b: $\delta=-88$ ppm, $\nu(^1/_2)=450$ Hz). The monophenyl-substituted tin atom (Sn1 according to the numbering scheme shown in Scheme 3, see the Experimental Section) is five-coordinate, as evidenced by its low-frequency shift relative to the value of $\delta=-15$ ppm for $PhMe_2SnI$[21] which contains a tetracoordinated tin atom. The diphenyl-substituted tin atom (Sn2, Scheme 3) is unambiguously four-coordinate as evidenced by its chemical shift which is rather close to that of Ph_2MeSnI ($\delta=-68$ ppm).[22] As a result of the intramolecular O→Sn1 interaction the configurational stability of the corresponding tin atom is enhanced and consequently the Sn*C*H_2Sn and Sn*C*H_2CH protons are diastereotopic and show AB- and ABX-type resonances (Figure 2), respectively, at $\delta=1.72/1.92$ ppm ($^2J(^1H–^1H)=12$, $^2J(^1H–^{117/119}Sn)=72$ Hz) and 1.10/1.45 ppm ($^2J(^1H–^1H)=12$, $^3J(^1H–^1H)=6$, $^2J(^1H–^{117/119}Sn)=72$ Hz). The water protons appear as a singlet at $\delta=1.61$ ppm. There is no NOE between these protons and the protons of the crown ether indicating the aqua complex **2**·H_2O is kinetically labile on the ^{1}H NMR timescale.

The electrospray ionization mass spectrum of compound **2** (positive mode) showed a major-intense mass cluster centered at *m*/*z* 747.1 which has been assigned to $[Ph_2(OH)SnCH_2Sn(Ph)\text{-}CH_2\text{-}[16]crown\text{-}5]^+$. Also present

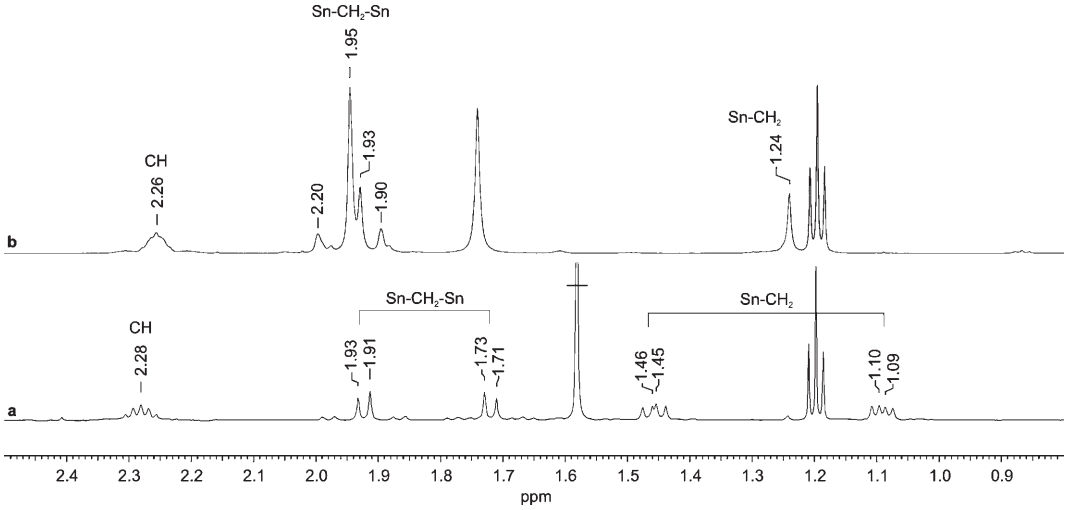
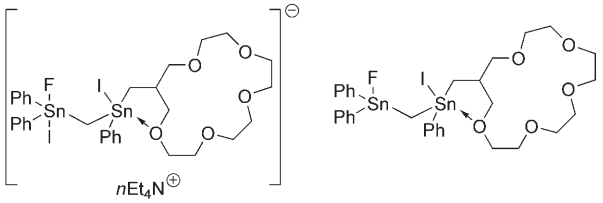


Figure 2. ^{1}H NMR (599.83 MHz, $CDCl_3$,) spectra of a) **2**·H_2O and b) **2**·H_2O in the presence of NaI.

are minor-intense mass clusters centered at *m/z* 857.1, assigned to $[Ph_2ISnCH_2Sn(Ph)\text{-}CH_2\text{-}[16]crown\text{-}5]^+$, *m/z* 897.0 (not assigned), and *m/z* 1007.0, assigned to $[Ph_2ISnCH_2SnI(Ph)\text{-}CH_2\text{-}[16]crown\text{-}5{\cdot}Na]^+$. The addition of sodium iodide to the solution of **2** resulted in an increase in the intensity of the final mass cluster (becoming major-intense) which indicates the high affinity of the crown ether moiety for the sodium cation (see the Complexation studies below).

Complexation studies: The ^{119}Sn NMR (149.21 MHz) spectrum at room temperature of a solution of compound **2** in CD_2Cl_2 to which had been added one molar equivalent of tetraethylammonium fluoride dihydrate, $Et_4NF{\cdot}2H_2O$, displayed only one resonance at $\delta = -90$ ppm which was assigned to Sn1 (see Scheme 3). At $-60\,^\circ C$ a second signal of equal integral ratio appeared as a doublet at $\delta = -29$ ppm [$^1J(^{119}Sn{-}^{19}F) = 1688$ Hz] whereas the first signal remained virtually unchanged ($\delta = -91$ ppm). The spectra are consistent with the organofluorostannate complex **2a** although the high-frequency shift of the doublet with respect to the corresponding signal for compound **2** at $\delta = -70$ ppm is unexpected.



2a

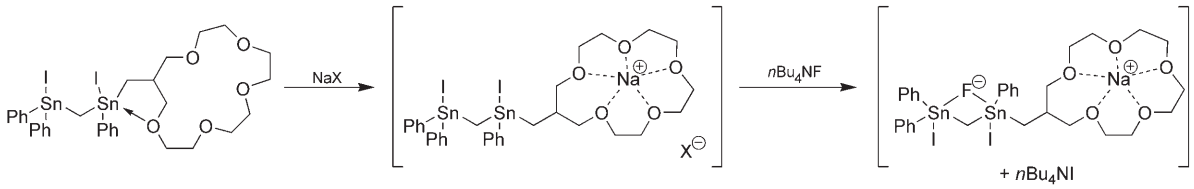
2b

The major argument ruling out simple iodide–fluoride exchange to give the organotin fluoride **2b** is the magnitude of the $^1J(^{119}Sn{-}^{19}F)$ coupling (1688 Hz) which is smaller than the coupling of 2380 Hz measured for $Ph_2(Me_3SiCH_2)SnF$[23] and is indicative of a fluorine atom in the axial position of a trigonal-bipyramidal-configured triorganostannate ion.[24] The ^{19}F NMR spectrum showed a broad resonance at $\delta = -133.6$ ppm ($\nu(^1/_2) = 466$ Hz) and indicates for **2a** a terminal rather than a bridging fluorine atom, that is, preference for the five-membered chelate involving intramolecular O→Sn coordination over a four-membered $CH_2(Sn)_2F$ ring.

The ^{119}Sn NMR spectra of solutions of compound **2** at ambient temperature to which had been added one molar equivalent of sodium tetraphenylborate, $NaBPh_4$, and sodium iodide, NaI, displayed equally intense resonances at $\delta = 15$ and -60 ppm and at $\delta = -22$ and -80 ppm, respectively. These data are consistent with the formation of complexes **2c** and **2d** (Scheme 2). Somewhat unexpected is the difference between the chemical shifts of the tetraphenylborate **2c** and the iodide **2d**. This difference might be a hint that for the latter compound there is, on the ^{119}Sn NMR timescale, a fast equilibrium between species in which the iodide anion coordinates to the tin atoms and, by electrostatic attraction, to the sodium cation, but with the population of the latter species dominating. Interestingly, the ^1H NMR spectra of both **2c** and **2d** in $CDCl_3$ show singlet and doublet resonances for the $SnCH_2Sn$ and $SnCH_2CH$ protons, respectively, instead of the AB- and ABX-type resonances observed for **2**·H_2O (see Figure 2). This observation is in line with the rupture of the intramolecular O→Sn1 interaction which is in turn associated with a decrease in the configurational stability of the tin atom, the loss of diastereotopism of the methylene protons, and with the sodium cation being coordinated by the crown ether oxygen atoms.

Most remarkably and in contrast to the results reported for $Ph_2ISn\text{-}CH_2\text{-}[16]crown\text{-}5{\cdot}NaI$,[17] no precipitation of sodium fluoride (lattice energy 930 kJ mol^{-1})[25] occurred upon addition of one molar equivalent of tetrabutylammonium fluoride trihydrate, $n\text{-}Bu_4NF{\cdot}3H_2O$, to the solution of complex **2d**. The ^{119}Sn NMR spectrum at $-40\,^\circ C$ of the clear solution showed two equally intense doublet resonances at $\delta = -83$ ppm ($^1J(^{119}Sn{-}^{19}F) = 672$ Hz) and $\delta = -159$ ppm ($^1J(^{119}Sn{-}^{19}F) = 632$ Hz). The ^{19}F NMR spectrum revealed a broad single resonance at $\delta = -99$ ppm ($^1J(^{19}F{-}^{117/119}Sn) = 610$ Hz, $\nu(^1/_2) = 205$ Hz). The chemical shift as well as the coupling constant are comparable to those of the organostannate complex $[(Ph_2ISn)_2CH_2F]^-[n\text{-}Bu_4N]^+$ ($\delta = -100$ ppm, $^1J(^{119}Sn{-}^{19}F) = 780$ Hz)[26] and indicate in situ formation of the complex **2e**. That the sodium cation in **2e** is indeed coordinated by the crown ether oxygen atoms receives support from the ^{13}C NMR spectrum which shows the typical low-frequency shift of the C14/C16 resonance to $\delta = 77.4$ ppm.[15,17]

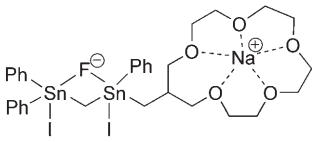
Notably, attempts to generate complex **2e** in the absence of $n\text{-}Bu_4NI$ by adding sodium fluoride to a solution of **2**·H_2O in dichloromethane failed. This is either a kinetic problem or the tetrabutylammonium iodide plays a vital role in the stabilization of complex **2e** by forming a sort of double salt, that is, a tetrabutylammonium triorganofluoroiodostannate·sodium iodide salt stabilized by a crown ether.



2 | **2c**, X = BPh_4; **2d**, X = I | **2e**

Scheme 2. Reaction of **2** with $NaBPh_4$ and NaI and of **2d** with $n\text{-}Bu_4NF$.

By changing the solvent to the more polar acetonitrile, we observed kinetically controlled complexation and formation of the heteroditopic complex **2**·NaF.



2·NaF

Thus, the ^{119}Sn NMR spectrum at room temperature of a solution of compound **2**·H_2O in CD_3CN to which had been added NaF and which had been stored for five days showed two broad resonances at $\delta = -92$ ppm ($\nu(^1/_2) = 3674$ Hz) and $\delta = -159$ ppm ($\nu(^1/_2) = 1715$ Hz). The ^{19}F NMR spectrum of the same solution displayed a single broad signal at $\delta = -102$ ppm ($\nu(^1/_2) = 782$ Hz). At $-20\,^\circ$C the ^{119}Sn NMR spectrum revealed two doublet resonances at $\delta = -101$ ppm ($^1J(^{119}\text{Sn}-^{19}\text{F}) = 717$ Hz) and $\delta = -167$ ppm ($^1J(^{119}\text{Sn}-^{19}\text{F}) = 743$ Hz), respectively, whereas the ^{19}F NMR spectrum displayed a singlet resonance at $\delta = -100$ ppm ($\nu(^1/_2) = 145$ Hz) which is flanked by unresolved satellites of $^1J(^{19}\text{F}-^{117/119}\text{Sn}) = 712$ Hz. Most importantly, the satellite-to-signal-to-satellite-integral ratio of 15.9:67.7:16.4 almost perfectly fits the calculated ratio of 17.16:65.68:17.16 and, together with the magnitude of the coupling constant, unambiguously indicates a Sn–F–Sn bridge in **2**·NaF. Because of the different substituent patterns the two tin atoms in **2**·NaF are chemically and magnetically nonequivalent. Consequently, the ^{19}F NMR spectrum is of an AXX′YY′ type with A = ^{19}F, X,X′ = ^{117,119}Sn1, and Y,Y′ = ^{117,119}Sn2 (see Scheme 3 for numbering).

Complexation of the sodium cation in **2**·NaF by the crown ether moiety is unambiguously confirmed 1) by the characteristic high-field shifts of the crown ether proton and carbon resonances in the ^{1}H and ^{13}C NMR spectra, respectively, and 2) by the broad ^{23}Na NMR resonance at $\delta = 2.51$ ppm ($\nu(^1/_2) = 496$ Hz). Both the chemical shift and the half-width are characteristic of a sodium cation coordinated to a crown moiety.[27–29] Notably, pure sodium fluoride is insoluble in acetonitrile and gives no ^{23}Na signal at all.

Recently there has been growing interest in designing hosts that are able to complex the fluoride ion in aqueous solution.[30,31] Attempts to study the ability of compound **2**·H_2O to capture sodium fluoride in water failed because of its rather limited solubility in this solvent. However, the fact that **2**·H_2O already contains water and that the acetonitrile was not specifically dried prior to use makes it likely that water will not preclude fluoride complexation by the organotin moiety.

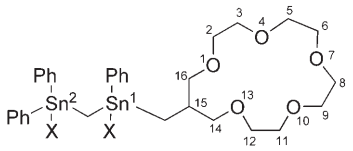
Conclusion

In this work we have demonstrated that linking a bicentric organotin-based Lewis acid with a crown ether moiety provides the robust ditopic host $Ph_2ISnCH_2Sn(I)(Ph)$-CH_2-[16]crown-5 (**2**) which is, in contrast to its monotin-substituted analogue $Ph_2ClSnCH_2$-[16]crown-5, capable of overcoming even the high lattice energy of sodium fluoride and solubilizing the latter in organic solvents such as acetonitrile. Given the fact that crown ethers and related compounds have been known for a long time and have been optimized for selective complexation of a variety of cations it is evident that for improving the complexation ability of ditopic hosts the anion binding site plays a vital role. Consequently, combining crown ethers and related compounds with cyclic bi- and multicentric Lewis acids containing tin or other metals/metalloids such as boron, germanium, or mercury might lead to even better hosts.

Another challenge is to increase the hydrophilicity of the host by appropriate structural modifications to allow complexation studies in water.

Experimental Section

General methods: All solvents were purified by distillation under nitrogen from the appropriate drying agents. Hydrostannylation was carried out under nitrogen. 15-Methylene-1,4,7,10,13-pentaoxacyclohexadecane,[32] triphenyltin hydride, Ph_3SnH,[33] and bromomethyltriphenylstannane, Ph_3SnCH_2Br,[19] were synthesized as described in the literature. The NMR experiments were carried out on a Bruker DRX 400, DPX 300, Varian Mercury 200, or Varian Inova 600 spectrometer. NMR experiments were carried out at ambient temperature unless a different temperature is specified. Chemical shifts (δ) are given in ppm and are referenced to the solvent peaks with the usual values calibrated against tetramethylsilane (^{1}H, ^{13}C) and tetramethylstannane (^{119}Sn). The numbering scheme for the crown ether moiety is pictured in Scheme 3. Electrospray mass spectra were recorded in the positive mode on a Thermoquest-Finnigan instrument using CH_3CN as the mobile phase. The samples were introduced as solutions in a mixture of CH_3CN and 1% formic acid (9:1 ratio) ($c = 10^{-4}$ mol L^{-1}) by using a syringe pump operating at 0.5 μL min^{-1}. The capillary voltage was 4.5 kV while the cone skimmer voltage was varied between 50 and 250 kV. Identification of the inspected ions was enabled by comparison of experimental and calculated isotope distribution patterns. The *m*/*z* values reported correspond to those of the most intense peak in the corresponding isotope pattern.



1, X = Ph
2, X = I

Scheme 3. Numbering scheme for the crown ether and tin atoms.

Crystallography: A single crystal suitable for X-ray analysis was taken directly from the reaction mixture and sealed with some dry paraffin oil. The data collection covered almost the whole sphere of reciprocal space with four sets at different *k* angles with 509 frames by ω rotation ($\Delta/\omega = 1^\circ$) at 2×60 s per frame. The crystal-to-detector distances were 4.4 cm. Crystal decay was monitored by repeating the initial frame at the end of the data collection. The data was not corrected for absorption effects. Analysis of the duplicate reflections showed there was no indication of any decay. The structures were solved by direct methods by using

SHELXS97[34] and successive difference Fourier syntheses. Refinements were made by full-matrix least-squares methods by using SHELXL97.[35]

The hydrogen atoms of the water molecule were located in the difference Fourier map and refined isotropically. The other hydrogen atoms were placed in geometrically calculated positions by using a riding model with isotropic temperature factors constrained at 1.2 for non-methyl and at 1.5 for methyl groups multiplied by the value of U_{eq} for the carrier carbon atom. The solvent molecule diethyl ether was isotropically refined with occupancies of 0.5.

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from the *International Tables for X-ray Crystallography*.[36] The figures were created by using SHELXTL.[37] Selected bond lengths and angles are given in Table 1 and the crystallographic data in Table 2.

CCDC-654666 (**2**·H_2O) contains the supplementary crystallographic data for this publication. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of 15-({diphenyl[(triphenylstannyl)methyl]stannyl}methyl)-1,4,7,10,13-pentaoxacyclohexadecane (1): A solution of (bromomagnesiomethyl)triphenylstannane, which had been prepared from (bromomethyltriphenyl)stannane (5.74 g, 12.9 mmol) and magnesium turnings (0.31 g, 12.9 mmol) in THF (100 mL), was added to a solution of iodo(1,4,7,10,13-pentaoxacyclohexadecan-15-ylmethyl)diphenylstannane (7.6 g, 11.7 mmol) in THF (150 mL). After the reaction mixture had been heated at reflux (12 h) and cooled to room temperature, it was hydrolyzed with water (50 mL). The organic layer was separated, dried with Na_2SO_4, and filtered. Evaporation of the solvent gave the crude product as a colorless oil which was purified by column chromatography on aluminium oxide. After the column had been washed with CH_2Cl_2 in order to remove impurities, elution with ethyl acetate gave 4.43 g (42%) of **1**. ^{1}H NMR ($CDCl_3$): $\delta = 0.82$ (s, $^2J(^1H–^{117/119}Sn) = 61.5$ Hz, 2H; Sn-CH_2-Sn), 1.00 (d, $^3J(^1H–^1H) = 7$, $^2J(^1H–^{117/119}Sn) = 58$ Hz, 2H), 2.17 (m, 1H; C*H*), 3.22–3.71 (m, 20H; OCH_2), 7.15–7.49 ppm (m, 25H; Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = -15.6$ ($^1J(^{13}C–^{117/119}Sn = 287$ Hz; Sn-*C*H_2-Sn), 12.0 ($^1J(^{13}C–^{117}Sn) = 393$, $^1J(^{13}C–^{119}Sn) = 410$ Hz; Sn*C*H_2), 37.0 ($^2J(^{13}C–^{117/119}Sn) = 20$ Hz; C-15), 69.6–70.8 (C-2–C-12), 74.4 ($^3J(^{13}C–^{117/119}Sn) = 51$ Hz; C-14/C-15), 128.0 ($^3J(^{13}C–^{117/119}Sn) = 47$ Hz; $SnPh_2$ C_m), 128.3 ($SnPh_2$ C_p), 128.3 ($^3J(^{13}C–^{117/119}Sn) = 47$ Hz; $SnPh_3$ C_m), 128.7 ($^4J(^{13}C–^{117/119}Sn) = 19$ Hz; $SnPh_3$ C_p), 136.5 ($^2J(^{13}C–^{117/119}Sn) = 37$ Hz; $SnPh_2$ C_o), 136.9 ($^2J(^{13}C–^{117/119}Sn) = 37$ Hz; $SnPh_3$ C_o), 139.8 ($^1J(^{13}C–^{117}Sn) = 482$, $^1J(^{13}C–^{119}Sn) = 505$, $^3J(^{13}C–^{117/119}Sn) = 9.7$ Hz; $SnPh_3$ C_i), 142.0 ppm ($^3J(^{13}C–^{117/119}Sn) = 13$ Hz; $SnPh_2$ C_i); ^{119}Sn{^{1}H} NMR ($CDCl_3$): $\delta = -56$ ($^2J(^{119}Sn–^{117}Sn) = 237$, $^2J(^{119}Sn–^{119}Sn) = 255$ Hz; $SnPh_2$), -77 ppm ($^2J(^{119}Sn–^{117}Sn) = 232$, $^2J(^{119}Sn–^{119}Sn) = 255$ Hz; Ph_3Sn); elemental analysis calcd (%) for $C_{43}H_{50}O_5Sn_2$ (884.27): C 58.4, H 5.7; found: C 58.2, H 5.7.

Synthesis of 15-({iodophenyl[(iododiphenylstannyl)methyl]stannyl}-methyl)-1,4,7,10,13-pentaoxacyclohexadecane (2): Iodine (1.95 g, 7.69 mmol) was added in small portions under ice-cooling to a stirred solution of **1** (3.40 g, 3.85 mmol) in CH_2Cl_2 (50 mL). The reaction mixture was stirred overnight. The solvent and the iodobenzene were removed in vacuo (1×10^{-3} Torr). Addition of CH_2Cl_2 (20 mL), filtration, and evaporation of the solvent afforded 3.66 g (96% yield) of **2** as a yellow oil. From this oil the elemental analysis was performed. Crystals were grown from a Et_2O solution of **2** at -5°C over several days to give the aqua complex **2**·H_2O as the ether solvate. M.p. 100°C; ^{1}H NMR ($CDCl_3$): $\delta =$ 1.10/1.45 (ABX-type resonance, $^2J(^1H–^1H) = 12$, $^3J(^1H–^1H) = 6$, $^2J(^1H–^{117/119}Sn) = 72$ Hz, 2H; SnCH_2), 1.72/1.92 (d, $^2J(^1H–^1H) = 12$, $^2J(^1H–^{117/119}Sn) =$ 72 Hz, 2H; SnCH_2Sn), 2.29 (m, 1H; 15-H), 3.25–3.77 (m, 20H; OCH_2), 7.28–7.91 ppm (m, 15H; Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 3.6$ ($^1J(^{13}C–^{117/119}Sn = 326$ Hz; Sn*C*H_2Sn), 20.2 ($^1J(^{13}C–^{117/119}Sn) = 488$, $^1J(^{13}C–^{119}Sn) =$ 507 Hz; Sn*C*H_2), 37.5 ($^2J(^{13}C–^{117/119}Sn) = 53$ Hz, C-15), 69.7–70.4 (C-2–C-12), 74.1 (C-14/C-15), 128.5 ($^3J(^{13}C–^{117/119}Sn) = 62$ Hz; SnPh C_m), 128.7 ($^3J(^{13}C–^{117/119}Sn) = 62$ Hz; $SnPh_2$ C_m), 129.38 ($^4J(^{13}C–^{117/119}Sn) = 14$ Hz; SnPh C_p), 129.7 ($^4J(^{13}C–^{117/119}Sn) = 13$ Hz; $SnPh_2$ C_p), 135.0 ($^2J(^{13}C–^{117/119}Sn) = 49$ Hz; SnPh C_o), 136.5 ($^2J(^{13}C–^{117/119}Sn) = 52$ Hz; $SnPh_2$ C_o), 137.9 ($SnPh_2$ C_i), 141.6 ppm ($^3J(^{13}C–^{117/119}Sn) = 28$ Hz; SnPh C_i); ^{119}Sn{^{1}H} NMR ($CDCl_3$): $\delta = -56$ ($^2J(^{119}Sn–^{117}Sn) = 260$, $^2J(^{119}Sn–^{119}Sn) = 278$ Hz, Sn(I)Ph_2), -82 ppm ($^2J(^{119}Sn–^{117}Sn) = 260$, $^2J(^{119}Sn–^{119}Sn) = 278$ Hz; SnPhI); ^{119}Sn{^{1}H} NMR (CD_2Cl_2, 213 K): $\delta = -70$ ($\nu(^1/_2) = 1800$ Hz; Sn(I)Ph_2), -88 ppm ($\nu(^1/_2) = 450$ Hz; SnPhI); elemental analysis calcd (%) for $C_{31}H_{40}I_2O_5Sn_2$ (983.88): C 37.8, H 4.1; found: C 37.7, H 4.1.

Complexation studies

In situ reaction of 2·H_2O: $Et_4NF·2H_2O$ (24.4 mg, 7.12×10^{-5} mol) was added to a solution of **2**·H_2O (70.0 mg, 7.12×10^{-5} mol) in CD_2Cl_2. ^{19}F NMR {^{1}H} δ: -133.6 ppm ($\nu(^1/_2) = 466$ Hz); ^{119}Sn{^{1}H} NMR (CD_2Cl_2): $\delta = -90$ ppm (Sn(I)Ph); ^{119}Sn{^{1}H} NMR (CD_2Cl_2, 213 K): $\delta = -29$ [d, $^1J(^{119}Sn–^{19}F) = 1688$ Hz; Sn(I)Ph_2F^-), -91 ppm (Sn(I)Ph).

In situ reaction of 2·H_2O with an excess of NaI: NaI (27.4 mg, 1.83×10^{-4} mol) was added to a solution of **2**·H_2O (60.0 mg, 6.10×10^{-5} mol) in $CDCl_3$. ^{1}H NMR ($CDCl_3$): $\delta = 1.91$ (d, $^3J(^1H–^1H) = 8$, $^2J(^1H–^{119/117}Sn) =$ 56 Hz, 2H; SnCH_2), 2.07 (s, $^2J(^1H–^{117/119}Sn) = 64$ Hz, 2H; SnCH_2Sn), 2.31 (m, 1H; 15-H), 3.05–3.09 (m, 2H; OCH_2), 3.35–3.80 (m, 18H; OCH_2), 7.26–7.38 (m, 10H; Ph), 7.63–7.90 ppm (m, 5H; Ph); ^{13}C{^{1}H} NMR ($CDCl_3$): $\delta = 23.1$ (Sn*C*H_2), 38.1 (C-15), 69.5–70.7 (O*C*H_2), 128.8 ($^3J(^{13}C–^{117/119}Sn) = 60$ Hz; SnPh C_m), 129.0 ($^3J(^{13}C–^{117/119}Sn) = 62$ Hz; $SnPh_2$ C_m), 129.9 (SnPh C_p), 130.1 ($^4J(^{13}C–^{117/119}Sn) = 13$ Hz; $SnPh_2$ C_p), 136.8 ($^2J(^{13}C–^{117/119}Sn) = 48$ Hz; $SnPh_2$ C_o), 137.0 ($^2J(^{13}C–^{117/119}Sn) = 50$ Hz; SnPh C_o), 139.1 ppm ($SnPh_2$ C_i); ^{19}F{^{1}H} NMR (CD_2Cl_2): $\delta = -133.6$ ppm ($\nu(^1/_2) = 466$ Hz); ^{119}Sn{^{1}H} NMR (CD_2Cl_2): $\delta = -80$ (Sn(I)Ph_2), -22 ppm (Sn(I)Ph).

In situ reaction of [2·NaI] with Bu_4NF: *n*Bu_4NF (71.0 mg, 1.94×10^{-4} mol) was added to a solution of **2**·NaI (220 mg, 1.94×10^{-4} mol) in CD_2Cl_2. ^{1}H NMR (CD_2Cl_2): $\delta = 0.97$ (t, $^3J(^1H–^1H) = 7$ Hz, 12H; -CH_3), 1.38 (complex pattern, 8H; CH_2CH$_3$), 1.59 (m, 8H; CH_2), 2.30 (m, 1H; 15-H), 2.58 (s, 2H), 3.17 (m, 8H; NCH_2), 3.25–3.60 (m, 20H; OCH_2), 7.15–7.38 (m, 9H; SnPh H_m and H_p), 7.75–7.95 ppm (m, 6H; SnPh H_o); ^{13}C{^{1}H} NMR (CD_2Cl_2): $\delta = 13.4$ (-*C*H$_3$), 19.6 (*C*H$_2$), 24 (*C*H$_2$), 58.9 (N*C*H$_2$), 69.1–69.9 (C-2–C-12), 77.4 (C-14/C-16), 127.7 ($^3J(^{13}C–^{117/119}Sn) = 64$ Hz; SnPh C_m), 127.9 ($^3J(^{13}C–^{117/119}Sn) = 66$ Hz; $SnPh_2$ C_m), 128.7 (SnPh and $SnPh_2$ C_p), 136.3 ($^2J(^{13}C–^{117/119}Sn) = 50$ Hz; $SnPh_2$ C_o), 136.6 (SnPh C_o), 142.0 and 143.3 ppm (SnPh and $SnPh_2$ C_i); ^{19}F{^{1}H} NMR (CD_2Cl_2): $\delta = -98.7$ ppm ($^1J(^{19}F–^{117/119}Sn = 610$ Hz); ^{119}Sn{^{1}H} NMR (CD_2Cl_2, 233 K): $\delta = -159$ (d, $^1J(^{119}Sn–^{19}F) = 632$ Hz; SnI(F)Ph_2), -83 ppm (d, $^1J(^{119}Sn–^{19}F) = 672$ Hz; -SnI(F)Ph).

In situ reaction of 2·H_2O with an excess of NaF: Sodium fluoride (13 mg, 3.05×10^{-4} mol) was added to a solution of **2**·H_2O (75 mg, 7.62×10^{-5} mol) in CD_3CN. NMR spectra were recorded after the solution had been kept for five days at room temperature. ^{1}H NMR (CD_3CN): $\delta = 1.52$ (d, $^2J(^1H–^1H) = 6$, $^2J(^1H–^{117/119}Sn) = 72$ Hz, 2H; SnCH_2), 2.15 (s, 2H; SnCH_2Sn), 2.31 (m, 1H; 15-H), 3.16 (m, 2H; OCH_2), 3.32 (m, 4H; OCH_2), 3.42–3.54 (complex pattern, 14H; OCH_2), 7.25–7.36 (complex pattern, 9H; H_m, H_p), 7.80–7.86 ppm (complex pattern, 6H; H_o); ^{13}C{^{1}H} NMR (CD_3CN): $\delta = 23.5$ (Sn*C*H_2), 38.1 ($^2J(^{13}C–^{117/119}Sn) = 21$ Hz, C-15), 69.8–70.9 (C-2–C-12), 78.42 ($^3J(^{13}C–^{117/119}Sn) = 60$ Hz; C-14/C-16), 128.6 ($^3J(^{13}C–^{117/119}Sn) = 62$ Hz; SnPh C_m), 128.9 ($^3J(^{13}C–^{117/119}Sn) = 68$ Hz; $SnPh_2$ C_m), 129.6 (SnPh C_p), 129.7 ($SnPh_2$, C_p), 137.1 ($^2J(^{13}C–^{117/119}Sn) =$ 50 Hz; $SnPh_2$ C_o), 137.3 (SnPh C_o), 144.1 and 144.2 ppm (SnPh and $SnPh_2$ C_i); ^{23}Na NMR (CD_3CN): $\delta = 2.5$ ppm ($\nu(^1/_2) = 496$ Hz); ^{19}F{^{1}H} NMR (CD_3CN): $\delta = -101.8$ ppm ($\nu(^1/_2) = 782$ Hz); ^{19}F{^{1}H} NMR (CD_3CN, 253 K): $\delta = -100.2$ ppm ($^1J(^{19}F–^{117/119}Sn) = 712$ Hz); ^{119}Sn{^{1}H} NMR (CD_3CN): $\delta = -92$ ($\nu(^1/_2) = 3674$ Hz), -159 ppm ($\nu(^1/_2) = 1715$ Hz); ^{119}Sn{^{1}H} NMR (CD_3CN, 253 K): $\delta = -100.5$ (d, $^1J(^{119}Sn–^{19}F) = 717$ Hz), -167.1 ppm (d, $^1J(^{119}Sn–^{19}F) = 743$ Hz).

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