Recognition of Organotin Compounds by Macrocyclic Polyethers: A Novel Pentacoordinate Tin–Coronand Complex

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Despite the extraordinary advances in the molecular recognition of charged species,[1,2] definite complexes between various uncharged molecules are still relatively unexplored.[1b] Since Pederson's first report of crystalline complexes between uncharged molecules such as thiourea and crown ethers,[3] molecular recognition studies in this area have generally been limited to polar, organic N–H or C–H containing molecules.[1b] Notable exceptions are molecular complexes of magnesium with polyethers described by Richey and Bickelhaupt[4a] and calixarene complexes of organoaluminums reported by Atwood.[4b] More recently, macrocyclic polyether complexes of inorganic tin(II) and –(IV) compounds have been described.[5] No definitive structural studies, however, are available for organotin complexes of macrocyclic polyethers.[6]

In this communication we report a new class of neutral, hypervalent organotin complexes of 1,3-xylyl-18-crown-5 and the structural characterization of the first representative example: the pentacoordinate organotin–coronand complex 1. *We believe this class of host–guest compounds is important for the following reasons*: Organotin halides are readily hydrolyzed to afford stannoxanes that exhibit a variety of structural types which are formal intermediates en route to the final products along the hydrolytic pathway.[7] In the presence of 1,3-xylyl-18-crown-5, however, organotin compounds of the type $Me_{3-x}SnCl_{x+1}$ form hypervalent organotin complexes with the coronand upon addition of water. Studies of the pentacoordinated tin compounds, in particular, are of special significance in structural tin chemistry because of the probable role of these compounds as intermediates in nucleophilic substitution reactions of organotin compounds.[8] Second, it has been shown recently that the molecular geometry of the pentacoordinated state is significantly influenced in solution and in the solid state by effects such as hydrogen-bonding[9] or cation–anion interactions.[10] An intimate knowledge of structural

details for these complexes, therefore, is crucial toward understanding the manner in which the organized system is constructed in the desired arrangement by various intermolecular forces and to determine whether the stereochemical principles developed for main group compounds are applicable.[11]

The essential role of water in the solvation of xylyl-substituted crown ethers in chlorinated hydrocarbons was demonstrated, and this complexation ability increases as the ring size becomes larger.[12] With these observations in mind, a series of organotin chlorides of the type $Me_{3-x}SnCl_{x+1}$ were combined with 1,3-xylyl-18-crown-5, followed by the addition of water, as summarized in Scheme I. Normally, triorganotin halides yield dimeric hydroxides upon hydrolysis, which later condense to corresponding bis(triorganotin) oxides.[7a] Hydrolysis of diorganotin dihalides results in stannoxanes which exhibit "ladder" structures composed of Sn_2O_2 units.[7b] Two further structural types, namely "extended ladders" and "drum" motifs, are observed in the hydrolysis of monoorganotin halides.[7c] Instead of undergoing hydrolysis, Me_2SnCl_2 and Me_3SnCl form crystalline 2:1 adducts (**1, 3**, respectively) with the coronand in high yields (>90%) regardless of the mole ratios used, whereas Me_3SnCl_3 affords a 1:1 adduct (**2**). The solution-state behavior of **1–3** was investigated by ^1H, $^{13}C\{^1H\}$, and $^{119}Sn\{^1H\}$ NMR spectroscopy, with selected data summarized in Table I.[13]

Relatively little information can be discerned from the chemical shifts of the trimethyltin protons and carbons; however, the magnitudes of $^2J|^1H^{119}Sn|$ and $^1J|^{13}C^{119}Sn|$ for **1–3** as compared to their respective organotin precursor indicate penta- or hexacoordinate structures.[14] The ^{119}Sn chemical shift data, however, offer poignant structural information regarding host–guest complexation for **1–3**, since changes in the coordination number at tin have a dramatic effect upon the shielding. Markedly upfield shifts of $\delta(^{119}Sn)$ for **1–3** as compared to their respective uncomplexed organotin compounds are observed. The increase in the shielding of the tin nucleus has been interpreted as a reduction of the Sn(5d)–Cl(3p) orbital overlap.[9,10] The difference in the ^{119}Sn chemical shifts $(\Delta\delta(^{119}Sn))$ reasonably reflects formation of the host–guest complex and serves to indicate the coordination geometry of the organotin complex. Moreover, $\delta(^{119}Sn)$ for **1–3** is temperature dependent and, at their respective low-temperature limits, the structures of the complexes can be described as either penta- or hexacoordinate, with structures ranging from distorted trigonal bipyramidal (**1, 3**) to distorted octahedral (**2**) geometries.

The molecular structure of **1** was determined from an X-ray

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(13) Data for **1**: 96% yield; mp 87–90 °C; ^1H NMR (360 MHz, CDCl₃, 25 °C) δ = 1.14 (s, 12 H, Me₂Sn–), 3.24 (br s, 4 H, H₂O), 3.68 (s, 16 H, OCH₂CH₂O), 4.60 (s, 4 H, Ar–CH₂O–), 7.11–7.74 (m, 4 H, Ar H); $^{13}C\{^1H\}$ NMR (50.3 MHz, CDCl₃, 25 °C) δ = 8.27 (s, Me₂Sn–), 69.4 (s, –OCH₂CH₂O–), 70.3 (s, –OCH₂CH₂O–), 72.9 (s, Ar–CH₂O–), 126.7 (s, *m*-Ar, C), 127.2 (s, Ar C), 127.9 (s, *p*-Ar C), 138.4 (s, *o*-Ar C); ^{119}Sn NMR (186.5 MHz, CDCl₃, 25 °C) δ = 82.5; IR (KBr) 3480, 3340 cm⁻¹ br, s ν(O–H), 1115 cm⁻¹ s ν(C–O) Anal. Calcd for C₂₀H₄₀O₇Cl₄Sn₂: C, 31.12; H, 5.23. Found: C, 30.88; H, 5.07. FAB MS: *m/e* 297 (C₂₆H₂₄O₅)⁺, *m/e* 238 (C₂H₈OCl₂Sn)⁺.

(14) **1**: $^2J|^1H^{119}Sn|$ = 72 Hz; $^1J|^{13}C^{119}Sn|$ = 539 Hz. **2**: $^2J|^1H^{119}Sn|$ = 109 Hz; $^1J|^{13}C^{119}Sn|$ = 891 Hz. **3**: $^2J|^1H^{119}Sn|$ = 60 Hz; $^1J|^{13}C^{119}Sn|$ = 414 Hz.
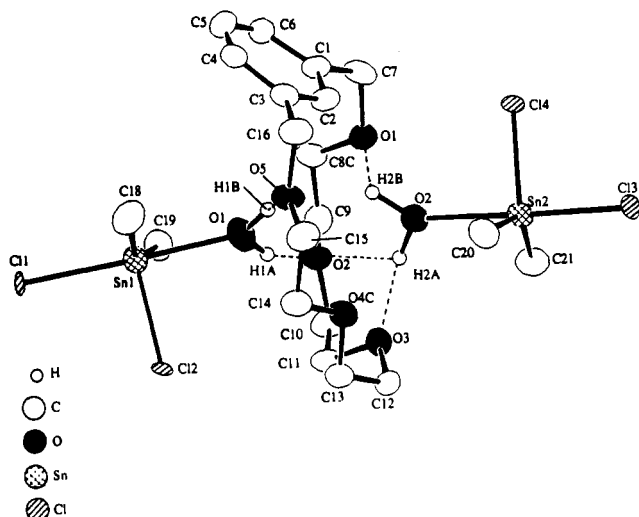
Scheme I
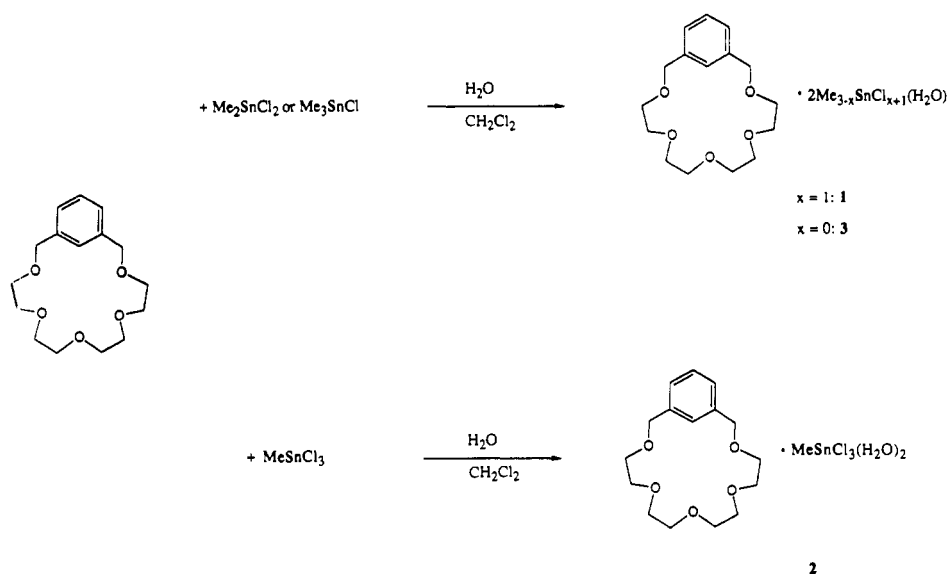
Table I. Selected ^{119}Sn NMR Data for Organotin–Coronand Complexes

compd	$\delta(^{119}Sn)$ (ppm)	complex	$\delta(^{119}Sn)$ (ppm)	$\Delta\delta(^{119}Sn)^a$
Me$_2$SnCl$_2$	127.5	1	82.5	45.0
MeSnCl$_3$	6.30	2	−169.2	176
Me$_3$SnCl	153.5	3	120.0	33.6

^{a} $\Delta\delta(^{119}Sn) = |\delta(^{119}Sn(precursor)) - \delta(^{119}Sn(complex))|$; $T = 21$ °C.

Figure 1. ORTEP representation of 1 showing the numbering scheme. All hydrogen atoms except those of the water ligands were removed for clarity. Ellipsoids were drawn at the 0.5 probability level.

diffraction study[15] and is presented in Figure 1. The coronand contains two crystallographically independent Me$_2$SnCl$_2$(H$_2$O) guests. They can be considered as axially distorted trigonal bipyramidal structures of C_s-*m* symmetry. In each one the chlorine ligand is oriented trans to the water ligand and the Sn-(1)–Cl(1) and Sn(2)–Cl(3) bond distances of 2.583(2) and 2.535-(2) Å are nearly equal and are significantly longer than their respective Sn(1)–Cl(2) and Sn(2)–Cl(4) bond contacts, 2.472-(2) and 2.459(2) Å. The two Sn–O distances of 2.409(9) and 2.405(9) Å are equal, and the O–Sn–Cl bond angles of 176.9(2)

and 177.8(2)° indicate an essentially linear geometry at tin. The four Sn–C bond lengths are all within 0.015 Å of the average value of 2.107(14) Å, and the two C–Sn–C bond angles are 145.0-(5) and 137.7(5)°, respectively. The hydrogen-bonding interactions of water molecules with oxygen atoms of the coronand are evidenced by O(crown)–O(water) contacts on the order of or smaller than the sum of the van der Waals radius for the respective atoms (2.8 Å).[16] The IR data for complexes 1–3 reflect hydrogen-bonding interactions in the solid state as well, with broad ν(O–H) stretches from 3200 to 3500 cm^{-1} and a shift of the asymmetric stretching fundamental, ν(C–O), to lower frequencies.[16]

The structural analysis of 1 confirms the conclusions drawn from the spectroscopic data, namely, that complexation of tri- or diorganotin compounds by the coronand occurs with the molecules of hydration acting as ligands to afford pentacoordinate tin derivatives. Although it can be argued the interaction is indirect and mediated by the molecules of hydration, to our knowledge, complexation of this type is a new feature in structural organotin chemistry. This is in contrast to structural data for 2 or inorganic tin(IV) compounds of crown ethers, where hexacoordinated geometries for tin and coordination polymers are observed.[5a–c] Moreover, the intrinsic duality of hydrogen-bonding interactions in the complexes is highlighted: stabilization of the Lewis acid anchoring ligand while changes are imparted in the geometry of the pentacoordinate state, as compared to examples where such an interaction is absent. It is conceivable that such interactions play an important role in the biological activity of organotin compounds.[17] Determination of thermodynamic parameters for complexes 1–3 (i.e. equilibrium constants) and a study of their hydrolysis pathways are under active investigation.

Supplementary Material Available: Tables of crystallographic parameters, positional and thermal parameters, and complete interatomic distances and angles for 1 and crystallographic parameters, for 2, text describing additional characterization data for complexes 1–3 and details of crystallographic procedures for 1, and an ORTEP figure (10 pages). Ordering information is given on any current masthead page.

(15) Crystallographic data for 1: triclinic, space group $P\bar{1}$, with $a = 9.7036$-(6) Å, $b = 10.4796(6)$ Å, $c = 16.3363(9)$ Å, $\alpha = 81.842(2)°$, $\beta = 80.126$-(2)°, $\gamma = 73.746(2)°$, $V = 1563$ Å^3, $Z = 2$, $\rho_{calcd} = 1.64$ g·cm^{-3}. Data were collected on a Picker FACS-1 diffractometer, using Mo Kα radiation, to a maximum $2\theta = 60°$, giving 9118 unique reflections, and the structure was solved by heavy-atom methods. The final discrepancy index was $R = 0.081$ and $R_w = 0.103$, for 6120 independent reflections with $I > 3\sigma(I)$.

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