Complexation of Triorganotin Derivatives of [18]Crown-6- and [15]Crown-5-(benzo-4-carboxylate) with Alkali Thiocyanates

Martine Kemmer,[a, c] Monique Biesemans,[a, b] Marcel Gielen,[a, c] José C. Martins,[b] Volker Gramlich,[d] and Rudolph Willem*[a, b]

Abstract: Investigations of the simultaneous complexation of tri-*n*-butyltin and triphenyltin derivatives of [18]crown-6- or [15]crown-5-(benzo-4-carboxylate) by the anion and cation from NaSCN or KSCN are reported. The crystal structure of $[Na^+ \subset$ [15]crown-5-{C_6H_3-4-$COOSn(C_6H_5)_3NCS\}^-$], **4**·NaSCN, displays an unusual zwitterionic nature with one intramolecular charge separation characterized by an Na–Sn distance of 9.29(1) Å, and several intermolecular charge separations, the shortest being 5.48(1) Å. Similar distances (9.70(2), 9.28(2), intramolecular; 5.40(2) and 5.41(2) Å, shortest intermolecular) are observed in the more complicated structure of the corresponding [18]crown-6-(benzo-4-carboxylate) derivative, **3**·NaSCN, with two independent molecules in the asymmetric unit. For the tri-*n*-butyltin analogues **1** and **2**, complex equilibria were observed in acetone and unraveled by variable temperature ^{13}C, ^{117}Sn, and ^{23}Na NMR studies. Their complexes with KSCN and NaSCN undergo decomposition in acetone solution, as evidenced by the transformation of $[K^+ \subset$ [18]crown-6-{C_6H_3-4-$COOSn(nBu)_3NCS\}^-$], into tri-*n*-butyltin isothiocyanate and a novel dimeric potassium [18]crown-6-(benzo-4-carboxylate), the structure of which was elucidated by X-ray diffraction analysis.

Keywords: crown compounds · host–guest systems · NMR spectroscopy · organotin chemistry · structure elucidation

Introduction

The complexation chemistry of host molecules designed for simultaneous anion and cation binding represents a so far rather unexplored topic.[1] Until now, attention has been mainly devoted to the complexation of cations by preorganized host molecules.[2] Studies on the interactions between crown ethers and various inorganic and organic cations have initiated wide applications in chemistry, biology, medicine, and technology.[3] The binding properties of Lewis acidic metal centers towards anions or neutral molecules are likewise well documented.[4] One such center is the Sn atom, the Lewis acidity of which has been the subject of many studies, especially on organotin halides.[5] Fewer studies have been reported on interactions of Lewis bases with organotin carboxylates,[6] despite widespread interest for their in vitro antitumor activity[7] and their rich structural diversity in the solid state.[8] Recently, we reported on the synthesis and characterization of several organotin derivatives of [18]crown-6- and [15]crown-5-(benzo-4-carboxylate), as well as on their in vitro antitumor activities against human tumor cell lines.[9] To the best of our knowledge, only one other example of a crown ether bound to tin through covalent bonds has been described so far.[10]

This paper reports on a novel type of MSCN (M = Na, K) salt complexation by a new class of host molecules that contain both a crown ether susceptible to interaction with the cation and a Lewis acidic tin center that potentially acts as an anion carrier. The question addressed is whether only the cation or the anion is involved in a monotopic interaction, or whether both ions are involved in a heterotopic interaction.[1k]

[a] Prof. Dr. R. Willem, M. Kemmer, Prof. Dr. M. Biesemans, Prof. Dr. M. Gielen
AOSC Unit, Faculty of Applied Sciences
Free University of Brussels (VUB)
Pleinlaan 2, 1050 Brussels (Belgium)
Fax: (+32) 2-6293281
E-mail: rwillem@vub.ac.be

[b] Prof. Dr. R. Willem, Prof. Dr. M. Biesemans, Dr. J. C. Martins
High-Resolution NMR Centre (HNMR)
Free University of Brussels (VUB)
Pleinlaan 2, 1050 Brussels (Belgium)

[c] M. Kemmer, Prof. Dr. M. Gielen
Free University of Brussels (ULB)
Service de Chimie Organique
Av. F. D. Roosevelt 50, 1050 Brussels (Belgium)

[d] Prof. Dr. V. Gramlich
Laboratorium für Kristallographie
Eidgenössiche Technische Hochschule (ETH) Zürich
8092 Zürich (Switzerland)

Supporting information for this article is available on the WWW under http://www.wiley-vch.de/home/chemistry/ or from the author. Packing diagram of potassium [18]crown-6-(benzo-4-carboxylate) (Figure S1) is available.

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If the latter case holds, the additional question is whether anions and cations remain electrostatically paired or undergo a charge separation from their initial ion pair.

The complexes [18]crown-6-{C_6H_3-4-$COOSn(C_6H_5)_3$}·NaSCN (**3**·NaSCN) and [15]crown-5-{C_6H_3-4-$COOSn(C_6H_5)_3$}·NaSCN (**4**·NaSCN) have been characterized by X-ray diffraction. The elucidation of complex equilibria between several solution species in the tri-*n*-butyltin analogues **1** and **2** was achieved by ^{1}H, ^{13}C, ^{23}Na, and ^{117}Sn NMR spectroscopy at variable temperature. ^{23}Na NMR data provide information as to whether the cation is trapped in the cavity of the crown ether moiety, while ^{117}Sn NMR data provide information on tin–anion interactions. The X-ray crystal structure of a novel dimeric salt, potassium [18]crown-6-(benzo-4-carboxylate), isolated from mixtures of [18]crown-6-{C_6H_3-4-$COOSn(nBu)_3$} and KSCN, sheds light on the ion-separation chemistry of such systems.

Results and Discussion

Synthetic aspects: An overview of the MSCN (M = Na, K) adducts investigated is given in Figure 1. The thiocyanate anion is known as an ambidentate ligand[11] that can either

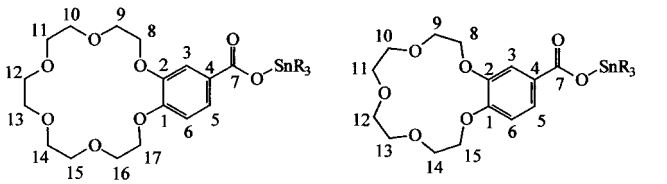

Figure 1. Organotin carboxylates and their alkali salt complexes.

bind in the monodentate mode, giving rise to M–SCN or M–NCS bonds, or can act as a bridging bidentate ligand in M–SCN–M′-like moieties. In the solid state, trimethyltin and triphenyltin thiocyanates exist as polymeric zigzag S→Sn–N=C=S→Sn chains.[12] When the crown ether **1** was mixed with KSCN in a 1:1 molar ratio, crude **1**·KSCN, unsuitable for X-ray diffraction, was obtained (see Experimental Section). The Mössbauer data (isomer shift = 1.39 mm s^{-1}, quadrupole splitting = 3.51 mm s^{-1}) of this crude **1**·KSCN are in agreement with the presence of a five-coordinate trigonal bipyramidal tin atom with two electronegative carboxylate and thiocyanate groups in apical positions.[13] Its IR spectrum reveals a stretch frequency at 2060 cm^{-1}, characteristic of N-bonded metal thiocyanates,[14] as well as a set of three overlapping lines between 1578 and 1615 cm^{-1}, both showing not only that the solid is amorphous or polymorphic, but contains a five-coordinate tin to which thiocyanate is bound. Crude **1**·KSCN is further evidenced to contain the proposed five-coordinate [$(nBu)_3Sn(OOCR')(NCS)$]$^-$ moiety by the fact that, besides the above-mentioned single narrow IR SCN stretching band at 2060 cm^{-1}, no band characteristic for pure $(nBu)_3SnNCS$ (2080 cm^{-1}) or for KSCN (2048 cm^{-1}) is observed. While crude **1**·KSCN undoubtedly contains the desired complex, attempts to recrystallize it from acetone lead to its decomposition into potassium [18]crown-6-(benzo-4-carboxylate) and tri-*n*-butyltin isothiocyanate. The former product was identified in the crystalline state by X-ray diffraction analysis, the results of which are presented below; moreover its ^{119}Sn NMR spectrum confirmed the total absence of tin. The other decomposition product, tri-*n*-butyltin isothiocyanate, was identified by evaporation of the filtrate of this crystallization to dryness and extraction of the residue with hexane; the ^{119}Sn NMR spectrum of this hexane extract redissolved in $CDCl_3$ revealed essentially only the resonance of $(nBu)_3SnNCS$ ($\delta = +85.1$, ca. 10 mg in 0.5 mL), as assessed by comparison with the ^{119}Sn spectrum of a sample of $(nBu)_3SnNCS$ synthesized independently (see Experimental Section). No evidence was found in crude **1**·KSCN for the presence of significant amounts of uncomplexed **1**, although neither this, nor the possibility that **1**·KSCN also exists in part as an undefined mixture of benzocrown carboxylate, tri-*n*-butyltin functionality, potassium cations, and thiocyanate anions can be formally excluded. Similar results were obtained for the NaSCN adduct of **1**, as well as the NaSCN and KSCN adducts of **2**.

Nevertheless, crude **1**·KSCN, **1**·NaSCN, **2**·KSCN, and **2**·NaSCN—where necessary, after filtration of the precipitated alkali benzocrown carboxylate to give sufficiently stable and long-lived solutions suitable for multinuclear NMR analysis—revealed the existence of complex equilibria (see below). In contrast to **1** and **2**, the triphenyltin crown ethers **3** and **4** combined with NaSCN in a 1:1 molar ratio did provide tin-containing crystals of **3**·NaSCN and **4**·NaSCN, suitable for the X-ray diffraction analysis presented below. However, these complexes appear to be quite insoluble after solvent evaporation or crystal filtration. Accordingly, the presence of tin was only revealed by a proton-detected ^{119}Sn correlation spectrum that displays two ^{119}Sn resonances, at $\delta = -185$ and -232 for **4**·NaSCN and at $\delta = -190$ and -235 (with a minor one at -128, not analyzed) for **3**·NaSCN in [D_4]methanol at 273 K; these signals were ascribed to five-coordinate tin complexed by thiocyanate and methanol, respectively (see below). A ^{23}Na NMR spectrum confirms the presence of the sodium ion.

Crystal structures of 3·NaSCN [$Na^+ \subset$ [18]crown-6-{C_6H_3-4-$COOSnPh_3(NCS)$}$^-$] and 4·NaSCN [$Na^+ \subset$ [15]crown-5-{C_6H_3-4-$COOSnPh_3(NCS)$}$^-$]: To the best of our knowledge, the structures of **3**·NaSCN (Figure 2) and **4**·NaSCN (Figure 3) reveal novel organotin zwitterionic structures which result from a host molecule that simultaneously traps the Na^+ ion in the crown ether moiety and the NCS^- anion at the tin moiety. These complexes exhibit very unusual structures in which the countercation is located extremely far away from the anionic tin center. Thus, a zwitterion with an unusually large intramolecular charge separation results, with intramolecular Sn–Na distances of 9.70(2) and 9.28(2) Å for the two independent molecules of **3**·NaSCN and 9.29(1) Å for **4**·NaSCN (additional information is given in Tables 1 and 2).

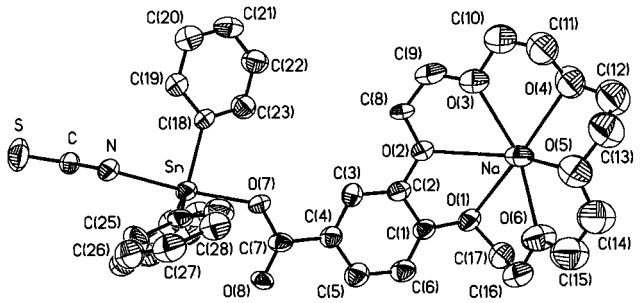

Figure 2. Molecular structure of **3**·NaSCN. Atomic displacement parameters are drawn at the 30% probability level.

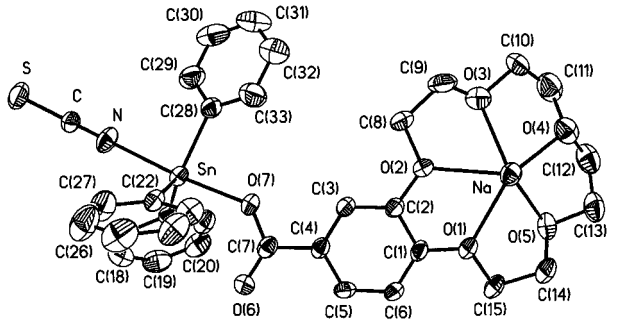

Figure 3. Molecular structure of **4**·NaSCN. Atomic displacement parameters are drawn at the 30% probability level.

Table 1. Selected bond lengths [Å] and angles [°] for **3**·NaSCN.[a]

Molecule 1		Molecule 2	
N–C	1.16(2)	N′–C′	1.10(2)
S–C	1.57(2)	S–C′	1.54(2)
Sn–N	2.34(2)	Sn′–N′	2.43(2)
Sn–C(30)	2.12(1)	Sn′–C(24′)	2.12(1)
Sn–C(24)	2.11(1)	Sn′–C(30′)	2.12(1)
Sn–C(18)	2.17(1)	Sn′–C(18′)	2.12(1)
Sn–O(7)	2.17(1)	Sn′–O(7′)	2.17(1)
Na–O(8)^{I}	2.31(1)	Na′–O(8′)^{II}	2.27(1)
Na–O(6)	2.43(2)	Na′–O(2′)	2.44(2)
Na–O(3)	2.53(2)	Na′–O(3′)	2.50(2)
Na–O(4)	2.64(2)	Na′–O(4′)	2.54(2)
Na–O(1)	2.71(2)	Na′–O(6′)	2.55(2)
Na–O(5)	2.70(2)	Na′–O(5′)	2.60(2)
Na–O(2)	2.87(2)	Na′–O(1′)	2.60(2)
C-N-Sn	170(2)	C′-N′-Sn′	171(2)
N-C-S	175(2)	N′-C′-S′	178(2)
C(30)-Sn-C(24)	129.3(4)	C(24′)-Sn′-C(30′)	122.5(4)
C(30)-Sn-C(18)	113.5(4)	C(24′)-Sn′-C(18′)	117.1(4)
C(24)-Sn-C(18)	116.9(4)	C(30′)-Sn′-C(18′)	119.1(4)
C(30)-Sn-O(7)	96.4(4)	C(24′)-Sn′-O(7′)	95.2(4)
C(24)-Sn-O(7)	92.7(4)	C(30′)-Sn′-O(7′)	98.3(4)
C(18)-Sn-O(7)	85.7(4)	C(18′)-Sn′-O(7′)	87.3(4)
C(30)-Sn-N	85.9(4)	C(24′)-Sn′-N′	87.1(5)
C(24)-Sn-N	89.4(4)	C(30′)-Sn′-N′	82.7(5)
C(18)-Sn-N	89.1(4)	C(18′)-Sn′-N′	89.3(4)
O(7)-Sn-N	174.8(4)	O(7′)-Sn′-N′	176.1(5)

[a] Symmetry transformations used to generate equivalent atoms: I: $2-x$, $2-y$, $z-1/2$; II: $2-x+3/2$, $y-1/2$, $z+1/2$.

The molecular structures of these two independent molecules in the asymmetric unit of **3**·NaSCN are similar. Only one representative is shown in Figure 2. Furthermore, as can be seen from Figure 3, the structure of **4**·NaSCN is also not very different from the one observed for **3**·NaSCN. The five-coordinate triphenylcarboxylatoisothiocyanato stannate moiety has a trigonal bipyramidal structure in both compounds; this is very similar to that of isothiocyanatotriphenyl(pyridinium-2-carboxylato) stannate (**5**), described previously by Gabe et al.[15] The geometry around the tin atom is that of a distorted trigonal bipyramid, with the three phenyl groups occupying the equatorial positions and the apical sites occupied by the nitrogen of the isothiocyanate group and one carboxyl oxygen of the carboxycrown ethers. The average Sn–C(Ph) distance of 2.125(4) Å in **4**·NaSCN compares well with the value of 2.114 Å for **5**,[15] while the average values for the two independent molecules of **3**·NaSCN, 2.13(3) and 2.12(3) Å are more dispersed. Nevertheless, they all lie well within the range 2.105–2.16 Å of Sn–C(Ph) distances reported in the literature.[16] There is no significant information concerning any deviation from coplanarity. The Sn–O distances observed are identical within experimental error, 2.17(2) and 2.17(2) Å for the two independent units of **3**·NaSCN and 2.172(4) Å for **4**·NaSCN. These values are somewhat shorter than the distances for **5**,[15] whereas the Sn–N distances, especially in **3**·NaSCN, are larger than the value of 2.28 Å reported.[15] The NCS moiety is almost linear with NCS angles of 175(2) and 178(2)° for **3**·NaSCN and 179.6(6)° for **4**·NaSCN. The CNSn angles of 170(2) and 171(2)° in **3**·NaSCN are smaller than that in **4**·NaSCN (161.9(5)°). Similar values are found in other tin isothiocyanates.[11, 15]

Table 2. Selected bond lengths [Å] and angles [°] for **4**·NaSCN.[a]

N–C	1.139(7)	Na–O(6)^{I}	2.229(5)
S–C	1.597(7)	Na–O(1)	2.355(5)
Sn–N	2.294(6)	Na–O(4)	2.372(5)
Sn–C(28)	2.128(4)	Na–O(3)	2.375(5)
Sn–C(16)	2.126(4)	Na–O(5)	2.416(5)
Sn–C(22)	2.120(4)	Na–O(2)	2.423(5)
Sn–O(7)	2.172(4)		
C-N-Sn	161.9(5)	C(16)-Sn-O(7)	94.0(2)
N-C-S	179.6(6)	C(22)-Sn-O(7)	92.0(2)
C(28)-Sn-C(16)	117.9(2)	C(28)-Sn-N	88.3(2)
C(28)-Sn-C(22)	119.1(2)	C(16)-Sn-N	89.4(2)
C(16)-Sn-O(22)	122.8(2)	C(22)-Sn-N	89.2(2)
C(28)-Sn-O(7)	87.0(2)	O(7)-Sn-N	175.1(2)

[a] Symmetry transformations used to generate equivalent atoms: I: $-x-1/2$, $y-1/2$, $-z+1/2$.

Although the space groups and unit cells of **3**·NaSCN and **4**·NaSCN (see Table 6 in the Experimental Section) are very different, the supramolecular arrangements are comparable. The coordination of Na^+ by the crown oxygen atoms is completed by the second carboxylate oxygen, which results in polymeric chains (Figure 4). In the packing diagram of **4**·NaSCN, these zig-zag chains are generated by the 2_1 screw axes of the corresponding space group $P2_1/n$. The shortest intermolecular $Na^+ \cdots Sn^-$ distances of 5.40(5) and 5.41(4) Å for **3**·NaSCN and 5.48(1) Å for **4**·NaSCN occur along these chains. They are notably shorter than the intramolecular $Na^+ \cdots Sn^-$ distances. Nevertheless, as can be deduced from Figure 4, Na^+ and SCN^- are evidently no longer electrostatically bound. The NCS groups point towards the cavities separating the zigzag chains and the packing of the chains in

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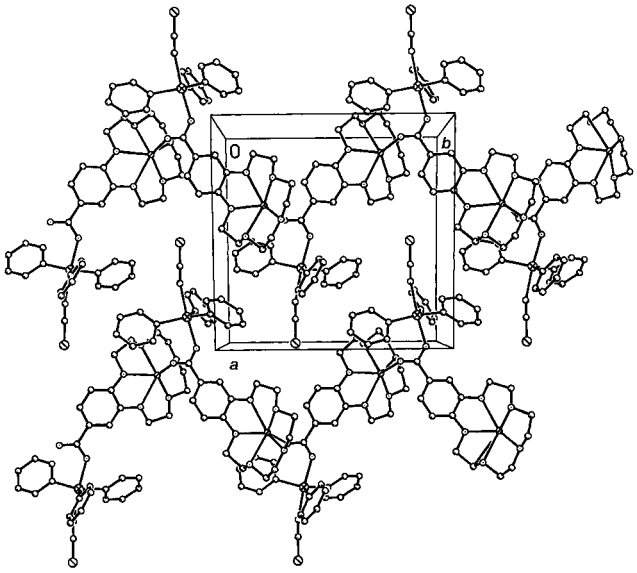

Figure 4. Packing of the **4**·NaSCN-chains.

the third dimension is generated by the *n*-glide plane perpendicular to the chains, thus generating a dense packing resembling a hexagonal close packing of tubes. In a similar way, chains are formed by the two independent molecules of **3**·NaSCN with $Na^+\cdots Sn^-$ distances 5.40(5) and 5.41(4) Å. Further interchain Na^+Sn^- distances above 6.9 Å occur in both **3**·NaSCN and **4**·NaSCN.

The long unit cell of **3**·NaSCN is the result of a four-layer packing: in a (first) layer, similar chains to those observed in **4**·NaSCN run parallel to, and are generated by, the 2_1 axis along the crystallographic *c* axis of the corresponding space group $Pna2_1$. In an adjacent (second) layer, similar but crystallographically independent chains run parallel to the crystallographic $b-c$ diagonal; these chains are generated by the crystallographic *n*-glide plane of $Pna2_1$. The next two layers can be considered to be generated by the *a*-glide plane from the first layer and the second: the third one again contains chains that running parallel to the *c* axis, and the last (fourth) layer contains chains again running diagonal, equivalent to the second layer, but this time along the $b+c$ diagonal (roughly perpendicular to the chain direction in the second layer). The next (fifth) layer is finally given by the rather long orthorhombic *b*-stacking period of 48.24(4) Å. There is no evidence for any channel formation. Further selected bond lengths and angles are given in Tables 1 and 2.

Crystal structure of potassium [18]crown-6-(benzo-4-carboxylate): The dimeric complex of potassium [18]crown-6-(benzo-4-carboxylate) is generated by the crystallographic inversion center of the space group $P2_1/c$ (Figure 5). The coordination of K^+ is a distorted hexagonal bipyramid with the crown oxygen atoms in the equatorial plane and a carboxylate oxygen of a neighboring molecule and a water molecule at the apical sites; this results in a dimer with a head-to-tail arrangement. Although the shortest distance to K^+ involves the water oxygen, the $O(H_2O)$-K^+-O(crown) angles are smaller than the O(COO)-K^+-O(crown) angles from the carboxylate oxygen at the opposite apex of the bipyramid.

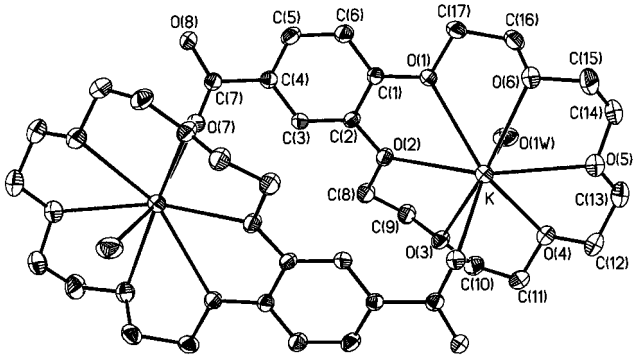

Figure 5. Molecular structure of dimeric potassium [18]crown-6-(benzo-4-carboxylate). Atomic displacement parameters are drawn at the 30% probability level.

Selected bond lengths and angles are given in Table 3. The molecules are packed as sheets perpendicular to their long axes. These layers are held together by a hydrogen-bonded network involving three additional water molecules. They occur between the terminal oxygens O(7) and O(8) and with distances between 2.8 and 2.9 Å.

Table 3. Selected bond lengths [Å] and angles [°] for [{[18]crown-6-(C_6H_3-COOK)}$_2$].[a]

O(2)–K	2.822(3)	O(5)–K	2.812(3)
O(1)–K	2.869(3)	O(4)–K	2.817(3)
O(6)–K	2.909(3)	K–O(1W)	2.704(3)
O(3)–K	2.831(3)	K–O(7)^I	2.745(4)
O(1W)-K-O(7)^I	150.53(7)	O(7)^I-K-O(1)	121.04(9)
O(1W)-K-O(1)	79.76(11)	O(7)^I-K-O(2)	94.68(10)
O(1W)-K-O(2)	80.93(9)	O(7)^I-K-O(3)	77.75(7)
O(1W)-K-O(3)	74.86(10)	O(7)^I-K-O(4)	91.57(8)
O(1W)-K-O(4)	65.42(9)	O(7)^I-K-O(5)	105.31(10)
O(1W)-K-O(5)	80.33(9)	O(7)^I-K-O(6)	119.66(8)
O(1W)-K-O(6)	88.62(10)		

[a] Symmetry transformations used to generate equivalent atoms: I: $-x+1, -y, -z$.

Solution-state chemistry: In the course of investigations on **1**·MSCN and **2**·MSCN in solution, presented below, it clearly appeared that, as a consequence of their instability, $(n\text{Bu})_3\text{SnNCS}$ is involved in the complicated solution chemistry of the complexes. It was therefore necessary to perform a detailed study on the solution chemistry of $(n\text{Bu})_3\text{SnNCS}$, which, on its own, appears quite complex in [D_6]acetone. In a similar fashion, the [18]crown-6 and [15]crown-5 ethers, as well as the free tri-*n*-butyltin carboxylates **1** and **2**, were also investigated.

Coordination behavior of $(nBu)_3SnNCS$: At 303 K, concentrated $(n\text{Bu})_3\text{SnNCS}$ (130 mg per 550 µL) in [D_6]acetone reveals a rather broad ^{117}Sn resonance at $\delta = 19.1$, while, upon dilution (20 mg per 550 µL), it shows a sharper one at $\delta = 16.5$ (Figure 6). Upon lowering the temperature to 183 K, both concentrated and diluted solutions give rise to decoalescence into three resonances (A, B, and C), with relative intensities depending on the concentration. At high concentration, resonances A ($\delta = 76.1$, 11%) and B ($\delta = -12.6$, 85%) are moderately sharp, while resonance C is hardly visible as a

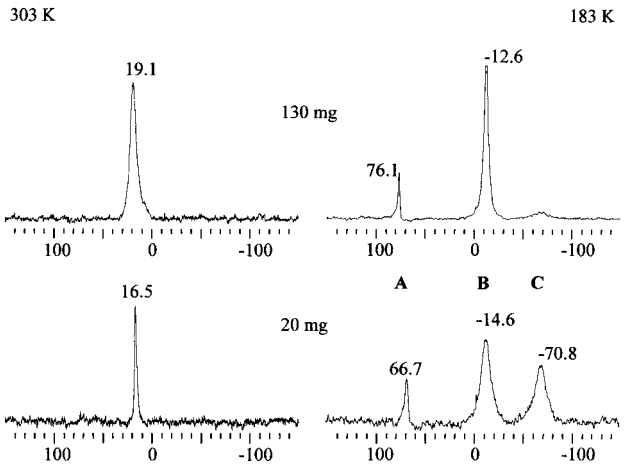

Figure 6. Temperature and concentration dependence of the ^{117}Sn NMR spectrum of $(n\mathrm{Bu})_3$SnNCS in [D$_6$]acetone. Sample volume 550 µl.

broad hump ($\delta \sim -70$, 4%). By contrast, at low concentration, the same resonances appear with different intensities and are unexpectedly broader. Resonance A is slightly shifted to low frequency ($\delta = 66.7$) and hardly increases in intensity (15%) upon dilution. Resonance B (50%) keeps roughly the same chemical shift, whereas resonance C shows a dramatic increase in intensity (35%). These observations, which are fully temperature reversible, are interpreted as follows. Resonance A basically corresponds to four-coordinate $(n\mathrm{Bu})_3$SnNCS (^{119}Sn NMR, $\delta = 72.6$ in [D$_8$]toluene, 120 mg per 550 µL; $\delta = 19.1$ in [D$_6$]acetone, 130 mg per 550 µL), as supported by the ^{119}Sn chemical shift of Me_3SnNCS in a non-coordinating solvent (Ref. [17]: $\delta = 58.7$ in [D$_6$]benzene, 20%; $\delta = 67.9$, 1.25%). The concentration dependence of resonance A necessarily results from fast association – dissociation exchanges between unbound $(n\mathrm{Bu})_3$SnNCS and terminal $(n\mathrm{Bu})_3$SnNCS in oligomeric species of the $(n\mathrm{Bu})_3\mathit{Sn}\mathrm{NCS} \rightarrow \mathrm{Sn}(n\mathrm{Bu})_3\mathrm{NCS} \rightarrow \ldots$ type. The chemical shift value of resonance A is in agreement with four-coordinate tin in these mutually exchanging species. Resonance B is, accordingly, assigned to the average of internal and terminal five-coordinate $n\mathrm{Bu}_3$SnNCS in the same oligomeric species, $(n\mathrm{Bu})_3\mathrm{SnNCS} \rightarrow \mathit{Sn}(n\mathrm{Bu})_3\mathrm{NCS} \rightarrow \mathit{Sn}(n\mathrm{Bu})_3\mathrm{NCS}$. The strong increase in the intensity of resonance C at the expense of B upon dilution is ascribed to the [D$_6$]acetone solvent-determined $(\mathrm{CD}_3)_2\mathrm{C{=}O} \rightarrow \mathrm{Sn}$ associations, which gain in importance at a lower $(n\mathrm{Bu})_3$SnNCS concentration. Globally, these observations indicate a complex equilibrium involving three types of tin environment modulated both by concentration and temperature effects. Thus, dilution favors dissociation of $(n\mathrm{Bu})_3\mathrm{SnNCS} \rightarrow \mathrm{Sn}(n\mathrm{Bu})_3\mathrm{NCS}$ oligomers towards $(\mathrm{CD}_3)_2\mathrm{C{=}O} \rightarrow \mathrm{Sn}$ interactions that, reasonably, appear more shielded at tin. A decrease in temperature favors five-coordination at the expense of four-coordination, as supported by the global low frequency shift of the average ^{117}Sn signal that results. In parallel, the $^1J(^{13}\mathrm{C},^{117/119}\mathrm{Sn})$ coupling constants increasing when the temperature decreases [in Hz: 412/420 (303 K), 451/471 (183 K), 20 mg; 400/418 (303 K), 435/456 (183 K), 130 mg] is in line with this proposal, as are Mössbauer data. The QS (quadrupolar splitting) of 3.75 mm s^{-1} for solid $(n\mathrm{Bu})_3$SnNCS at liquid nitrogen temperature (isomer shift (IS) = 1.54 mm s^{-1}) is in agreement with a five-coordinate, trigonal bipyramidal diapical $\mathrm{NCS} \rightarrow \mathrm{Sn}(n\mathrm{Bu})_3\mathrm{NCS}$ configuration. Interestingly, a frozen solution of $(n\mathrm{Bu})_3$SnNCS in acetone provides a similar QS of 3.71 mm s^{-1} (IS = 1.47 mm s^{-1}) in agreement with the same geometry at tin, either from $\mathrm{NCS} \rightarrow \mathrm{Sn}(n\mathrm{Bu})_3\mathrm{NCS}$, $(\mathrm{CH}_3)_2\mathrm{C{=}O} \rightarrow \mathrm{Sn}(n\mathrm{Bu})_3\mathrm{NCS}$, or both. Hence the coordination behavior at tin, whatever the complexing ligand, is comparable in acetone and in the solid state.

*Coordination behavior of the free tri-n-butyltin carboxylates **1** and **2** derived from the benzo-4-carboxylate-substituted crown ethers in [D$_6$]acetone*: The $^1J(^{13}\mathrm{C},^{117/119}\mathrm{Sn})$ coupling constants of free **1** and **2** are characteristic, albeit only to a limited extent, for higher coordination at the tin atom in the presence of acetone rather than in chloroform (**1**: 378/396 Hz in [D$_6$]acetone 20 mg per 550 µL; 341/358 Hz in $CDCl_3$[9a]). The small concentration dependence of the ^{117}Sn chemical shifts of **1** in [D$_6$]acetone at 303 K (130 mg per 550 µL, $\delta = 71.5$; 20 mg per 550 µL, $\delta = 76.1$) increases at 223 K, displaying values of $\delta = -11.4$ and $+23.2$, respectively, that is, a shift of the ^{117}Sn resonances to lower frequency. These data indicate that 1) a tin carboxylate aggregation is only very slightly favored upon an increase in concentration at room temperature and 2) the formation of intermolecular aggregates favored at high concentration and the competitive complexation by [D$_6$]acetone both occur to a greater extent at low temperature. The absence of any ^{117}Sn signal decoalescence down to 223 K indicates that carboxylate aggregation and complexation by [D$_6$]acetone are two processes in fast exchange on the ^{117}Sn NMR timescale, even at the lowest temperature investigated.

Complexation of [18]crown-6 (18C6) and [15]crown-5 (15C5): To get an insight into the complexation of the Na^+ into a crown ether moiety in the absence of any further group interferences, ^{23}Na NMR spectra of NaSCN, 18C6 · NaSCN, 18C6 · 2 NaSCN, 15C5 · NaSCN and 15C5 · 2 NaSCN were recorded in [D$_6$]acetone (Table 4). At 303 K, a single ^{23}Na resonance appears at $\delta = -4.9$ for NaSCN, at $\delta = -13.7$ for 18C6 · NaSCN, and at $\delta = -8.3$ for 18C6 · 2 NaSCN.

The low-temperature ^{23}Na spectrum of 18C6 · 2 NaSCN shows a decoalescence of the single resonance into two resonances, enabling two species to be discriminated. The ^{23}Na chemical shift of 18C6 · 2 NaSCN at room temperature corresponds roughly to the average of the signals of 18C6 · NaSCN and free NaSCN. Thus, lowering the temperature to

Table 4. ^{23}Na NMR chemical shifts[a] in [D$_6$]acetone for pure NaSCN, mixtures of crown ethers 18C6 and 15C5 and NaSCN, and mixtures of **1** and **2** and NaSCN.

	303 K	183 K
NaSCN	−4.9	
18C6 · NaSCN	−13.7	−16.4
18C6 · 2 NaSCN	−8.3	−4.8, −16.4
15C5 · NaSCN	−3.6	−5.7
15C5 · 2 NaSCN	−3.7	−6.6
1 · NaSCN	−14.2	−17.6
2 · NaSCN	−4.9	−5.4

[a] Chemical shifts reported in ppm with respect to NaCl (D_2O).

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183 K freezes out the Na^+ exchange equilibrium and reveals both the complexed and free ion in comparable amounts; the ^{23}Na chemical shift at $\delta = -4.8$ and -16.4 corresponds to the uncomplexed and complexed cations, respectively. Since 18C6 · NaSCN exhibits one single resonance at $\delta = -16.4$ it can be concluded that Na^+ complexation by 18C6 is complete. By contrast, the single ^{23}Na resonance around $\delta = -5$ for 15C5 · NaSCN and for 15C5 · 2 NaSCN, at 303 K as well as 183 K, indicates essentially little complexation of the cation even though the slight shift to lower frequency upon temperature decrease leaves hardly any doubt about the existence of a fast equilibrium between free and bound Na^+, with the free state remaining most abundant.

Complexation of tri-n-butyltin carboxylates derived from the reaction of benzo-4-carboxylate-substituted crown ethers with alkali thiocyanates: As for **1** · KSCN, the crude precipitates **1** · NaSCN, **2** · NaSCN, and **2** · KSCN, which are tin-free and almost insoluble in acetone, are identified, from ^1H NMR data in [D_4]methanol, to be the corresponding alkali [18]crown-6 or [15]crown-5-(benzo-4-carboxylate). Two kinds of interactions govern their formation: on one hand, the complexation of the crown ether moiety by the alkali cation modulated by the ring size of the crown ether and the diameter of the cation, (see ^{23}Na NMR results above) and, on the other hand, the salt formation leading to $-COO^-Na^+$ or $-COO^-K^+$ ionic bonds, which can be understood on the basis of the hard/soft acid/base (HSAB) principle.[18] The [(crown-C_6H_3-COOM)$_2$] formation is accounted for by the reaction given in Equation (1):

$$2[M^+ \subset \{\text{crown-}C_6H_3\text{-COOSn}(n\text{Bu})_3\text{NCS}\}^-] \rightleftharpoons [\{\text{crown-}C_6H_3\text{-COO}^-M^+\}_2] + 2(n\text{Bu})_3\text{SnNCS} \quad (1)$$

It dominates over the generation of [$M^+ \subset$ {crown-C_6H_3-4-COOSn(nBu)$_3$NCS}$^-$], even though the [(crown-C_6H_3-4-COOM)$_2$] precipitates are generated to variable extents: **1** · KSCN, 0 %; **2** · KSCN, 8 %; **1** · NaSCN, 30 %; **2** · NaSCN, 33 %. Additional evidence for this proposed heterogeneous equilibrium is that while no [(crown-C_6H_3-COOM)$_2$] precipitate was obtained from **1** · KSCN, it was nevertheless eventually generated by adding an excess of KSCN.

However, after complete evaporation of a solution of **1** · KSCN, and partial redissolution of the residue in a small portion of acetone, the ^1H spectrum of the supernatant also reveals the release of free [18]crown-6-{C_6H_3-4-COOSn(nBu)$_3$} (**1**), which evidences the reversibility of the formation of [$M^+ \subset$ {crown-C_6H_3-4-COOSn(nBu)$_3$NCS}$^-$]. Actually, it is only after removal of this supernatant and complete redissolution of the residue in acetone that crystals of [{[18]crown-6-(C_6H_3-4-COOK)}$_2$] suitable for X-ray analysis were produced upon slow evaporation of the solvent.

The ^{117}Sn NMR spectra of the filtrates at room temperature (Table 5) reveal a single broad resonance at variable ^{117}Sn chemical shifts. Noticeable differences between free and complexed tri-*n*-butyltin carboxylates appear for the ^{117}Sn chemical shifts and the $^1J(^{13}C,^{117/119}Sn)$ coupling constants (Table 5). For example, at 303 K, the **1** · NaSCN has ^{117}Sn $\delta = -27.4$ and $^1J(^{13}C,^{117/119}Sn) = 453/474$ Hz, while free **1** exhibits $\delta = 76.1$ and $^1J(^{13}C,^{117/119}Sn) = 378/396$ Hz. Overall, this observation reveals a higher coordination at tin for **1** · NaSCN than for free **1**, with fast ligand exchange kinetics indicated by the single ^{117}Sn resonance. Low-temperature data confirm this interpretation, since at 223 K at least two species are observed, as a result of ^{117}Sn resonance decoalescence upon decreasing the temperature from 303 K to 223 K. At 223 K, a minor ^{117}Sn resonance around $\delta = -135$ is observed in all cases. The major resonances of **1** · NaSCN ($\delta = -49.3$) and **2** · NaSCN ($\delta = -52.6$) appear at significantly higher frequencies in comparison with **1** · KSCN ($\delta = -95.9$) and **2** · KSCN (two signals: $\delta = -86.4$ and -92.2), but they all shift to lower frequencies upon a decrease in temperature. Globally, these results reveal the existence of at least two equilibria: one that is slow on the ^{117}Sn NMR timescale, leading to complete decoalescence of the minor resonance around $\delta = -135$, and another still fast between two (or more in the case of **2** · KSCN) less-coordinated species. The minor resonance (18 % for **1** · NaSCN and 46 % for **2** · NaSCN) is assigned to the species in which thiocyanate anion complexation of tin is strongest, that is, species a and/or d (Figure 7). The ^{23}Na NMR data (Table 4) of **1** · NaSCN is clearly in agreement with species a and/or e being dominant; only a single ^{23}Na resonance characteristic of bound sodium ($\delta = -17.6$) being observed without any decoalescence even at low temperature (183 K). By contrast, the single ^{23}Na resonance at 183 K, characteristic of unbound sodium ($\delta = -5.4$) for **2** · NaSCN clearly supports species d being dominant, emphasizing the influence of the ring size of the crown ether on sodium ion complexation.

The major ^{117}Sn resonance is assigned to exchange-averaging species b, c, and e (Figure 7). In species c, the ^{117}Sn chemical shift should be intermediate between those of species b and e (four-coordinate tin) solvated by acetone and species a and d (five-coordinate tin) bound to thiocyanate. In species c, the interaction of NCS^- with Sn should be weaker than in a and d, explaining the faster exchange averaging of c with b and e than with a and d. The strong influence of the alkali cation on the ^{117}Sn chemical shift arises from species c, which is the only one in which the alkali cation is close enough to tin to modulate significantly the ^{117}Sn resonance of averaging b, c, and e. In this model, KSCN is

Table 5. ^{117}Sn chemical shifts [ppm] and $^1J(^{13}C,^{117/119}Sn)$ coupling constants [Hz] obtained for **1**, **2**, **1** · NaSCN, **1** · KSCN, **2** · NaSCN, and **2** · KSCN in [D_6]acetone at two different temperatures.

	^{117}Sn		$^1J(^{13}C,^{117/119}Sn)$	
	303 K	223 K	303 K	223 K
1 (20 mg)	76.1	23.2	378/396	
1 (130 mg)	71.5	−11.4	389/407	~467
2 (20 mg)	79.1	23.2		
1 · NaSCN	−27.4	−49.3	453/474	479/504
		−134.6		
1 · KSCN	−65.7	−95.9	490/513	516/536
		−136.8		
2 · NaSCN	[a]	−52.6	460/481	481/506
		−136.3		
2 · KSCN	−63.9	−86.4	481/503	515/538
		−92.2		
		−137.4		

[a] No signal, broad exchange averaging.

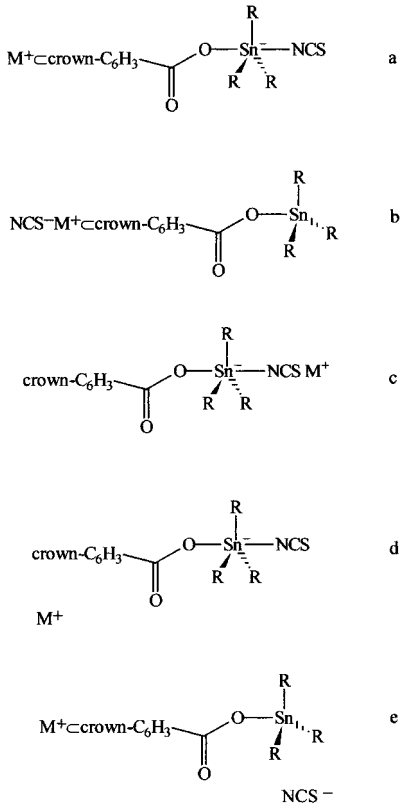

Figure 7. Possible zwitterionic ion pairings.

expected to shield the ^{117}Sn nucleus more than NaSCN, as observed (ca. $\delta = -90$, -50, respectively), because of the larger size and stronger HSAB[18] interaction of sulfur with the K^+ than the Na^+ ion. The higher average $^1J(^{13}C,^{117/119}Sn)$ coupling constants of the major resonance of **1** · KSCN and **2** · KSCN relative to **1** · NaSCN and **2** · NaSCN also reflects a more preponderant role of species c with potassium than sodium in the averaging equilibrium, which remains fast down to 223 K. The structure of species a is the one found in the crystalline state for **3** · NaSCN and **4** · NaSCN.

Involvement of $(n\text{Bu})_3$SnNCS in these equilibria is supported by the fact that external addition of an aliquot of the latter to **1** · KSCN reveals only a major and minor resonance; the latter, around $\delta = -130$, reflecting the fact that the equilibrating species a and d still remain, without appearance of any additional ^{117}Sn resonance from $(n\text{Bu})_3$SnNCS alone (around $\delta = 15-20$, see Figure 6). Indeed, the addition of $(n\text{Bu})_3$SnNCS shifts the average major resonance from $\delta = -92$ to -20. Remarkably, the equilibrium between $(n\text{Bu})_3$SnNCS, and species b, c, and e is sufficiently fast on the NMR timescale for only a single ^{117}Sn resonance to be observed for all of them, even down to 223 K.

Conclusion

The tri-*n*-butyltin and triphenyltin derivatives of [18]crown-6- or [15]crown-5-(benzo-4-carboxylate) are receptors capable of heterotopically binding MSCN (M = Na, K) ion pairs. The Lewis acidic complexation by the thiocyanate anion cooperates with the crown ether complexation by the alkali cation and leads to a significant charge separation evidenced by X-ray data in the crystalline state and by NMR spectroscopic data in solution. The fact that only the tri-*n*-butyltin, and not the triphenyltin compounds, undergo elimination of the carboxylate ligand can be rationalized on the basis of the higher Lewis acidity of triphenyltin compounds. More specifically, an addition $(NCS)^-$/elimination ($RCOO^-$ or NCS^-) process is more probable for tri-*n*-butyltin compounds. These results are complementary to those of a recent study on selective anion recognition in which tri-*n*-butyltin carboxylates exhibited better electrochemical responses towards chloride anions, due to their more reversible donor–acceptor interactions, relative to their triphenyltin analogues.[6d] Furthermore, it is evidenced that the presence of the species involved in the complexation of crown ethers **1** and **2** modifies considerably the coordination behavior of $(n\text{Bu})_3$SnNCS in acetone.

Experimental Section

Synthetic procedures: Complexation of the triorganotin crown benzo-4-carboxylates **1**, **2**, and **4**[9a] (Figure 1) by sodium or potassium thiocyanate in a molar ratio 1:1 was achieved in acetone (10 mL) by simply mixing typically 0.15 mmol (100 mg of **1**, 93 mg of **2**, 14.8 mg of KSCN, 12.3 mg of NaSCN) of the reactants at room temperature. This solvent was chosen so as to satisfy the requirement to solubilize both starting materials simultaneously.[19] After evaporation of the solvent, a crude solid of **1** · KSCN was left, while for **2** · NaSCN, **2** · KSCN, and **1** · NaSCN a mixture of an oil and a solid was obtained. In all cases, the crude compounds were rapidly washed with acetone (ca. 5 mL) to remove the oily component. The residues were redissolved in acetone (10 mL) in an attempt to isolate crystalline adducts, which failed for **1** · NaSCN, **2** · NaSCN, and **2** · KSCN, since precipitation to amorphous insoluble solids occurred. Accordingly, all NMR studies on the latter compounds were performed on the corresponding filtrates, since ^{1}H NMR spectroscopy of the precipitates redissolved in [D_4]methanol revealed the absence of tri-*n*-butyltin moieties.

In the case of **1** · KSCN, the residue was likewise redissolved in acetone (10 mL). The solution was slowly evaporated for 24 hours; the crystals grown were removed with a spatula and simply dried in air. The crystals were used for X-ray diffraction data acquisition and for NMR characterization in [D_4]methanol, which also revealed the absence of $(n\text{Bu})_3$Sn moieties. This crystalline product was identified as potassium [18]crown-6-(benzo-4-carboxylate): m.p. 115 °C; elemental analysis calcd (%) for $C_{17}H_{23}KO_8 \cdot 3H_2O$ (466.52): C 45.52, H 6.53, K 8.72; found C 45.4, H 6.6, K 8.0 (cf. analysis calcd for $C_{17}H_{23}KO_8 \cdot 4H_2O$ (442.26): C 43.77, H 6.70, K 8.38).

Crude **4** · NaSCN was obtained by mixing **4** (65 mg) with NaSCN (7.7 mg) in acetone (10 mL). After complete evaporation of the solvent, **4** · NaSCN appeared no longer soluble in acetone. Crude **4** · NaSCN was heated under reflux in methanol for 10 minutes. A residue was filtered off from the hot methanol solution.

Slow solvent evaporation of the residual filtrate yielded crystals suitable for structure determination by X-ray diffraction: m.p. 260–262 °C; elemental analysis calcd (%) for $C_{34}H_{34}NNaO_7SSn$ (742.36): C 54.98, H 4.87, N 1.78, Na 2.92, Sn 15.99; found C 55.1, H 4.6, N 2.0, Na 2.9, Sn 14.7.

3 · KSCN and **4** · KSCN yielded only unidentified mixtures from which a pure solid could not be isolated.

The complex **3** · NaSCN was generated by mixing **3** (106 mg) with NaSCN (12 mg) in acetonitrile (40 mL). The solution was allowed to evaporate slowly for 4 days. A few crystals (ca. 1 mg) identified as **3** · NaSCN, insoluble in methanol, were also observed (m.p. 248–250 °C) and removed with a spatula. They were unsuitable for X-ray diffraction. Crystals of **3** · $NaSCN \cdot 3H_2O$ grown from slow evaporation of the acetonitrile solution (m.p. 220–222 °C) were readily soluble in methanol or acetonitrile:

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elemental analysis calcd (%) for $C_{36}H_{38}NNaO_8SSn \cdot 3H_2O$ (840.51): C 51.44, H 5.29, N 1.67, Na 2.74, Sn 14.12; found C 51.6, H 5.2, N 1.7, Na 2.6, Sn 13.8. The presence of water was further confirmed by thermogravimetric analysis (TGA), for which a weight loss of 6.5% between 40–120 °C was attributed to H_2O (calcd 6.4%). DSC experiments reveal the evaporation of 5.2% H_2O. These crystals (80 mg) were unsuitable for X-ray analysis. However, a very small fragment was cut off from one of these crystals and its structure determined.

Tri-*n*-butyltin isothiocyanate, $(n\mathrm{Bu})_3\mathrm{SnNCS}$, was prepared from tri-*n*-butyltin chloride and potassium thiocyanate according to a known procedure.[20] Crown ether 18C6 was purified by recrystallization from acetonitrile.[21]

NMR experiments: The samples for ^{13}C, ^{23}Na, and ^{117}Sn NMR spectroscopy were prepared by dissolving **1** or **2** (ca. 100 mg) with the equivalent amount of alkali salt in [D$_6$]acetone (550 μL). ^1H, ^{13}C, and ^{117}Sn spectra were recorded at 303, and at 223 or 233 K, unless otherwise indicated. The ^{23}Na chemical shifts (spin $I = 3/2$) were measured at 303 and 183 K.

NMR spectra for basic compound characterization were acquired on a Bruker Avance DRX250 instrument equipped with a Quattro probe tuned to 250.13, 62.93, and 89.15 MHz for ^1H, ^{13}C and ^{117}Sn nuclei, respectively. Other NMR data were acquired on a Bruker AMX500 spectrometer at 125.77, 186.50, and 132.29 MHz for ^{13}C, ^{119}Sn, and ^{23}Na nuclei, respectively. ^1H and ^{13}C chemical shifts were referenced to the appropriate residual solvent peak with the usual values calibrated against TMS. The ^{117}Sn and ^{119}Sn reference frequencies were calculated from the absolute references $\Xi(^{117}Sn) = 35.632295$ MHz and $\Xi(^{119}Sn) = 37.290655$ MHz.[22a] The ^{23}Na chemical shifts were measured by using an external reference of sodium chloride (30 mg) in D_2O (0.5 mL). The ^1H,^{119}Sn HMQC correlation spectra of **3**·NaSCN and **4**·NaSCN were acquired as previously described.[22b]

Abbreviations: s = singlet; brs = broad singlet, d = doublet; t = triplet, dd = doublet of doublets; m = complex multiplet; tq = triplet of quartets; Ψs = pseudo singlet. Assignments as in ref. [9a] (the order of the assignments is presented in increasing order of labeled proton or carbon atoms):

Complex 1·NaSCN: ^1H NMR ([D$_6$]acetone): $\delta = 7.54$ (d, $^4J(H,H) = 2$ Hz, 1H; H(3)), 7.61 (dd, $^3J(H,H) = 8$ Hz, $^4J(H,H) = 2$ Hz, 1H; H(5)), 6.96 (d, $^3J(H,H) = 8$ Hz, 1H; H(6)), 4.18–4.22 (m, 4H; H(8), H(17)), 3.87–3.95 (m, 4H; H(9), (16)), 3.60–3.75 (m, 12H; H(10)–H(15)), 1.23 (t $^3J(H,H) = 8$ Hz, $^2J(H,Sn) = 61/64$ Hz, 6H; H(α)), 1.62–1.77 (m, $^3J(H,Sn) \approx 63$ Hz, 6H; H(β)), 1.35 (tq, $^3J(H,H) = 7$, 7 Hz, 6H; H(γ)), 0.88 (t, $^3J(H,H) = 7$ Hz, 9H; H(δ)); ^{13}C NMR ([D$_6$]acetone): $\delta = 135.5$ (NCS), 151.0 (C(1)), 147.7 (C(2)), 113.6 (C(3)), 128.9 (C(4)), 124.1 (C(5)), 111.4 (C(6)), 170.4 (C(7)), 67.7, 68.0 (C(8), C(17)), 69.57, 69.64 (C(9), C(16)), 70.29, 70.34, 70.4, 70.7 (1C, 1C, 2C, 2C; C(10)–C(15)), 19.2 ($^1J(C,Sn) = 453/474$ Hz; C(α)), 28.9 ($^2J(C,Sn) \approx 27$ Hz; C(β)), 27.6 ($^3J(C,Sn) \approx 73$ Hz; C(γ)), 14.1 (C(δ)).

Complex 1·KSCN: ^1H NMR([D$_6$]acetone): $\delta = 7.59$ (brs; H(3)), 7.60 (dd, $^3J(H,H) = 8$ Hz, $^4J(H,H) = 2$ Hz, 1H; H(5)), 6.99 (d, $^3J(H,H) = 8$ Hz, 1H; H(6)), 4.22–4.37 (m, 4H; H(8), H(17)), 3.90–4.03 (m, 4H; H(9), H(16)), 3.65–3.83 (m, 12H; H(10)–H(15)), 1.22 (t, $^3J(H,H) = 8$ Hz, $^2J(H,Sn) \approx 64$ Hz, 6H; H(α)), 1.63–1.81 (m, $^3J(H,Sn) \approx 62$ Hz, 6H; H(β)), 1.35 (tq, $^3J(H,H) = 7$ Hz, $^3J(H,H) = 7$ Hz, 6H; H(γ)), 0.88 (t, $^3J(H,H) = 7$ Hz, 9H; H(δ)); ^{13}C NMR ([D$_6$]acetone): $\delta = 134.3$ (NCS), 149.7 (C(1)), 146.9 (C(2)), 113.2 (C(3)), 130.8 (C(4)), 123.8 (C(5)), 111.1 (C(6)), 169.7 (C(7)), 67.8, 68.2 (C(8), C(17)), 69.5, 69.6 (C(9), C(16)), 70.5, 70.6, 70.7 (1C, 3C, 2C; C(10)–C(15)), 19.8 ($^1J(C,Sn) = 491/513$ Hz; C(α)), 29.0 ($^2J(C,Sn) \approx 28$ Hz; C(β)), 27.6 ($^3J(C,Sn) = 75/78$ Hz; C(γ)), 14.1 (C(δ)).

Complex 2·NaSCN: ^1H NMR ([D$_6$]acetone): $\delta = 7.59$ (brs, 1H; H(3)), 7.63 (dd, $^3J(H,H) = 8$ Hz, $^4J(H,H) = 2$ Hz, 1H; H(5)), 7.03 (d, $^3J(H,H) = 8$ Hz, 1H; H(6)), 4.22–4.32 (m, 4H; H(8), H(15)), 3.91–4.00 (m; H(9), H(14)), 3.72–3.84 (m, 4H; H(10)–H(13)), 1.19 (t, $^3J(H,H) = 8$ Hz, $^2J(H,Sn) = 62/64$ Hz, 6H; H(α)), 1.59–1.72 (m, $^3J(H,Sn) \approx 64$ Hz, 6H; H(β)), 1.32 (tq, $^3J(H,H) = 7$, 7 Hz, 6H; H(γ)), 0.86, (t, $^3J(H,H) = 7$ Hz, 9H; H(δ)); ^{13}C NMR ([D$_6$]acetone): $\delta = 135.8$ (NCS), 151.0 (C(1)), 147.6 (C(2)), 115.7 (C(3)), 129.6 (C(4)), 125.1 (C(5)), 113.1 (C(6)), 170.3 (C(7)), 68.3, 68.4 (C(8), C(15)), 68.7, 68.9 (C(9), C(14)), 69.2, 69.3, 69.80, 69.81 (C(10)–C(13)), 19.3 ($^1J(C,Sn) = 460/481$ Hz; C(α)), 28.9 ($^2J(C,Sn) \approx 27$ Hz; C(β)), 27.6 ($^3J(C,Sn) = 71/74$ Hz; C(γ)), 14.1 (C(δ)).

Complex 2·KSCN: ^1H NMR ([D$_6$]acetone): $\delta = 7.41$ (brs, 1H; H(3)), 7.64 (d, $^3J(H,H) = 8$ Hz, 1H; H(5)), 6.76 (d, $^3J(H,H) = 8$ Hz, 1H; H(6)), 3.92–4.05 (m, 4H; H(8), H(15)), 3.65–3.85 (m, 12H; H(9)–H(14)), 1.23 (t, $^3J(H,H) = 8$ Hz, $^2J(H,Sn) = 64/66$ Hz, 6H; H(α)), 1.64–1.79 (m, $^3J(H,Sn) \approx 63$ Hz, 6H; H(β)), 1.36 (tq, $^3J(H,H) = 7$, 7 Hz, 6H; H(γ)), 0.89 (t, $^3J(H,H) = 7$ Hz, 9H; H(δ)); ^{13}C NMR ([D$_6$]acetone): $\delta = 134.9$ (NCS), 150.6 (C(1)), 147.4 (C(2)), 115.0 (C(3)), 129.8 (C(4)), 124.4 (C(5)), 112.5 (C(6)), 170.5 (C(7)), 67.6 (2C; C(8), C(15)), 67.8, 67.9 (C(9), C(14)), 68.5, 69.3 (2C, 2C; C(10)–C(13)), 19.7 ($^1J(C,Sn) = 481/503$ Hz; C(α)), 29.0 ($^2J(C,Sn) \approx 28$ Hz; C(β)), 27.6 ($^3J(C,Sn) = 73/76$ Hz; C(γ)), 14.1 (C(δ)).

Complex 3·NaSCN: ^1H NMR ([D$_4$]methanol): $\delta = 7.74–7.84$ (m, $^3J(H,Sn) \approx 60$ Hz, 6H; H_{ortho}), 7.36–7.57 (m, 9H; $H_{meta,para}$), 7.55 (d, $^4J(H,H) = 2$ Hz, 1H; H(3)), 7.62 (dd, $^3J(H,H) = 9$, $^4J(H,H) = 2$ Hz, 1H; H(5)), 6.99 (d, $^3J(H,H) = 9$ Hz, 1H; H(6)), 4.18–4.26 (m, 4H; H(8), H(17)), 3.85–3.92 (m, 4H; H(9), H(16)), 3.60–3.73 (m, 12H; H(10)–H(15)); ^{23}Na NMR ([D$_4$]methanol): $\delta = -9.1$.

Complex 4·NaSCN: ^1H NMR ([D$_4$]methanol): $\delta = 7.85–7.92$ (m, $^3J(H,Sn) \approx 61$ Hz, 6H; H_{ortho}), 7.47–7.59 (m, 9H; $H_{meta,para}$), 7.64 (d, $^3J(H,H) = 2$ Hz, 1H; H(3)), 7.71 (dd, $^3J(H,H) = 8$, $^4J(H,H) = 2$ Hz, 1H; H(5)), 7.08 (d, $^3J(H,H) = 8$ Hz, 1H; H(6)), 4.21–4.30 (m, 4H; H(8), H(15)), 3.91–3.99 (m, 4H; H(9), H(14)), 3.80 (Ψs, 8H; H(10)–H(13)); ^{23}Na NMR ([D$_4$]methanol, 273 K): $\delta = -2.7$.

Sodium [18]crown-6-(benzo-4-carboxylate): ^1H NMR ([D$_4$]methanol): $\delta = 7.58$ (d, $^4J(H,H) = 2$ Hz, 1H; H(3)), 7.59 (d, $^3J(H,H) = 8$ Hz, $^4J(H,H) = 2$ Hz, 1H; H(5)), 6.95 (d, $^3J(H,H) = 8$ Hz, 1H; H(6)), 4.19–4.27 (m, 4H; H(8), H(17)), 3.86–3.94 (m, 4H; H(9), H(16)), 3.61–3.74 (m, 12H; H(10)–H(15)); ^{23}Na NMR ([D$_4$]methanol): $\delta = -8.6$.

Potassium [18]crown-6-(benzo-4-carboxylate): ^1H NMR ([D$_4$]methanol): $\delta = 7.62$ (d, $^4J(H,H) = 2$ Hz, 1H; H(3)), 7.59 (dd, $^3J(H,H) = 8$ Hz, $^4J(H,H) = 2$ Hz, 1H; H(5)), 6.98 (d, $^3J(H,H) = 8$ Hz, 1H; H(6)), 4.22–4.30 (m, 4H; H(8), H(17)), 3.85–3.92 (m, 4H; H(9), H(16)), 3.63–3.76 (m, 12H; H(10)–H(15)).

Sodium [15]crown-5-(benzo-4-carboxylate): ^1H NMR ([D$_4$]methanol): $\delta = 7.55$ (d, $^3J(H,H) = 2$ Hz, 1H; H(3)), 7.62 (dd, $^3J(H,H) = 8$, $^4J(H,H) = 2$ Hz, 1H; H(5)), 6.96 (d, $^3J(H,H) = 8$ Hz, 1H; H(6)), 4.11–4.20 (m, 4H; H(8), H(15)), 3.84–3.91 (m, 4H; H(9), H(14)), 3.68–3.76 (m, 8H; H(10)–H(13)); ^{23}Na NMR ([D$_4$]methanol): $\delta = -3.5$.

Potassium [15]crown-5-(benzo-4-carboxylate): ^1H NMR ([D$_4$]methanol): $\delta = 7.59$ (d, $^4J(H,H) = 2$ Hz, 1H; H(3)), 7.60 (dd, $^3J(H,H) = 9$ Hz, $^4J(H,H) = 2$ Hz, 1H; H(5)), 6.91 (d, $^3J(H,H) = 9$ Hz, 1H; H(6)), 4.09–4.15, 4.18–4.22 (m, 4H; H(8), H(15)), 3.78–3.86 (m, 4H; H(9), H(14)), 3.63–3.75 (m, 8H; H(10)–H(13)).

Crystal structure determinations: It was rather difficult to obtain crystals of **3**·NaSCN, **4**·NaSCN, and potassium [18]crown-6-benzo-4-carboxylate) suitable for single-crystal structure analysis. Damage of the soft crystals during manipulation, transport, and mounting was unavoidable. Experimental data are given in Table 6. A PICKER-STOE diffractometer ($\lambda(Cu_{K\alpha}) = 1.5418$ Å), was used for **3**·NaSCN and potassium [18]crown-6-(benzo-4-carboxylate), and a SYNTEX P21 diffractometer ($\lambda(Mo_{K\alpha}) = 0.7107$ Å) for **4**·NaSCN; all measurements were performed at room temperature and with the use of graphite monochromators. Although the crystal structures could be solved and refined by standard methods of the SHELXTL package of crystallographic programs,[23] an additional final restrained refinement was used in order to account for the limited resolution and data-to-parameter ratio of the structures. In the latter approach, all C–C and C–O single bond lengths of the crown ethers were constrained to be equal as well as the bond angles and the benzene rings idealized, so that finally the conformation, metal environment, and packing were further refined. The non-centrosymmetric space group $Pna2_1$ of **3**·NaSCN with two independent molecules per asymmetric unit required a careful check: only by the definite absence of mirror planes in the refined structure could the alternative centrosymmetric space group *Pnam* (standard setting *Pnma*) be ruled out. The structure was finally refined as an inversion twin.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 162452 (**3**·NaSCN), CCDC 162453 (**4**·NaSCN), and CCDC 162454 (potassium [18]crown-6-(benzo-4-carboxylate)). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

IR and Mössbauer spectroscopy: IR data were recorded in the Fourier transform mode from a Perkin–Elmer System 2000 FT-IR spectrometer, by using an MIR beam. Samples of **1**·KSCN, **3**·NaSCN, and **4**·NaSCN

Table 6. Experimental data for the X-ray diffraction study.

	3·NaSCN	**4**·NaSCN	[{[18]crown-6-(C_6H_3-4-COOK)}$_2$]
formula	$C_{36}H_{38}NNaO_8SSn$	$C_{34}H_{34}NNaO_7SSn$	$C_{34}H_{62}K_2O_{24}$
M_r	768.41	742.36	933.04
crystal system	orthorhombic	monoclinic	monoclinic
space group	$Pna2_1$	$P2_1/n$	$P2_1/c$
a [Å]	48.24(4)	15.018(7)	17.11(2)
b [Å]	10.032(7)	15.138(6)	7.156(6)
c [Å]	14.998(9)	15.156(7)	18.21(2)
β [°]	90	100.06(3)	96.88(9)
V [Å^3]	7253(9)	3393(3)	2214(4)
Z	8	4	2
ρ_{calcd} [g cm^{-3}]	1.440	1.453	1.399
μ [mm^{-1}]	6.681	0.875	2.637
$F(000)$	3216	1512	992
crystal size [mm]	0.1 × 0.05 × 0.05	0.4 × 0.3 × 0.1	0.4 × 0.2 × 0.1
θ range [°]	1.83 to 50	1.76 to 20.04	2.60 to 50
data/restraints/parameters	2921/1213/778	3204/562/377	2271/382/300
GOF on F^2	1.085	1.092	1.042
R_1 [$I > 2\sigma(I)$][a]	0.073	0.038	0.031
wR_2 (all data)[b]	0.201	0.102	0.086
$\Delta\rho_{max/min}$ [e Å^{-3}]	1.04/ − 1.37	0.73/ − 0.42	0.25/ − 0.16

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma wF_o^2]^{1/2}$.

were prepared as KBr pellets with about 3 mg of product and 200 mg of dry KBr. The IR spectrum of $(n\text{Bu})_3$SnNCS was recorded between two KBr pellets.

1·KSCN: $\tilde{\nu}_{SCN} = 2060$ cm^{-1} (SCN); **3**·NaSCN: $\tilde{\nu}_{SCN} = 2066$ cm^{-1}; **4**·NaSCN: $\tilde{\nu}_{SCN} = 2065$ cm^{-1}; $(n\text{Bu})_3$SnNCS: $\tilde{\nu}_{SCN} = 2080$ cm^{-1}.

The Mössbauer spectra were recorded as previously described.[14]

Mass spectrometry: The electrospray mass spectra[25] were recorded in the cationic mode on a Micromass Quattro II instrument coupled to a Masslynx system (ionization in an electric field of 3.5 kV; source temperature: 80 °C; source pressure 1 atm; analyzer pressure 10^{-5} mbar). The following monoisotopic fragment ions (^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{23}Na, ^{39}K, ^{120}Sn) were observed in the cationic mode in methanol: **1**·NaSCN: m/z: 669 $[M+Na]^+$; **1**·KSCN: m/z: 685 $[M+K]^+$; **2**·NaSCN: m/z: 625 $[M+Na]^+$; **2**·KSCN: m/z: 641 $[M+K]^+$; **3**·NaSCN: m/z: 739 $[M+Na]^+$; **4**·NaSCN: m/z: 685 $[M+Na]^+$; $(n\text{Bu})_3$SnNCS: m/z: 640 $[M+(n\text{Bu})_3\text{Sn}]^+$.

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