ORGANOMETALLICS

Structural and spectroscopic studies of cation-anion interactions in pentacoordinate organotin compounds

Stephen E. Johnson, and Carolyn B. Knobler

Organometallics, **1992**, 11 (11), 3684-3690• DOI: 10.1021/om00059a035 • Publication Date (Web): 01 May 2002

Organometallics is published by the American Chemical Society. 1155 Sixteenth Street
N.W., Washington, DC 20036

3684 *Organometallics* 1992, *11*, 3684-3690

Structural and Spectroscopic Studies of Cation–Anion Interactions in Pentacoordinate Organotin Compounds[1]

Stephen E. Johnson* and Carolyn B. Knobler

Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California 90024-1569

Received May 29, 1992

A series of anionic organotin compounds of the type $[Me_3SnCl_2][M]$ (M^+ = n-Bu_4N (**3**), K(18-crown-6) (**4**)) and the type $[Me_3SnCl(X)][M]$ (M^+ = Et_4N, X = CN (**5**); M^+ = K(18-crown-6), X = CN (**6**); M^+ = K(18-crown-6), X = F (**7**)) is described. The ability of a particular cation to interact with its corresponding organotin anion was investigated in the solid state and compared with its behavior in solution. The molecular structures of organotin anions **4** and **6** have been studied by X-ray crystallography. Both compounds exhibit infinite-chain structures of cations and anions in the solid state, in contrast to related organotin anions. Compound **4** crystallized in the monoclinic space group $C2/c$ with a = 12.546 (1) Å, b = 17.988 (1) Å, c = 17.996 (2) Å, β = 90.266 (2)°, V = 1259 Å^3, Z = 4, and R = 0.064. Compound **6** crystallized in the monoclinic space group $P2_1$ with a = 7.920 (1) Å, b = 21.026 (2) Å, c = 7.649 (6) Å, β = 98.762 (2)°, V = 1259 Å^3, Z = 2, and R = 0.057. The nature of the cation–anion interactions in solution for salts **2**–**7** was investigated by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. Solid-state CP/MAS ^{13}C and ^{119}Sn NMR spectra were obtained for compounds **5** and **6**. The solution-to-solid chemical shift differences are discussed in terms of the solid-state structures.

Introduction

Studies of pentacoordinated tin compounds 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.[2] An intimate knowledge of structural details, therefore, is of importance in understanding the nature of bonding in these compounds and to determine whether the stereochemical principles established for main-group compounds are applicable.[3] Structures of pentacoordinated organotin compounds have been known[2b] since the 1960s, and these compounds currently have been utilized as an important structural moiety in anion complexation hosts.[4,5] The binding of halides (F^-, Cl^-, Br^-) in these macrocyclic hosts incorporating tin has been investigated by ^{119}Sn NMR studies, and $\delta(^{119}Sn)$ reflects the change in coordination number at tin with increasing halide concentration. Available crystallographic data for a free host and its corresponding anion complex suggests the pentacoordinated tin fragment, rather than the carbon skeleton, plays the major role in determining the conformation of the heterocycle.[4d] Despite this fact, very little is known regarding the manner in which the pentacoordinated state is influenced by effects such as hydrogen-bonding or cation–anion interactions. We have recently described some interesting structural distortions from idealized trigonal-bipyramidal (TBP) geometry for a salt with a triorganotin anion and a cation capable of extensive hydrogen-bonding interactions.[6]

With these observations in mind, a series of salts containing triorganotin anions with a variety of cations was prepared. Herein the isolation, solid-state studies, and solution-state studies are reported for compounds **2**–**7**. The molecular structures of stannates **4** and **6** represent new examples of pentacoordinated tin anions that are observed to interact with their gegenion (potassium 18-crown-6) in the solid state. The nature of these cation–anion interactions in solution was investigated by ^1H, ^{13}C, and ^{119}Sn NMR spectroscopy. Solid-state CP/MAS ^{13}C and ^{119}Sn NMR spectra were obtained for compounds **5** and **6** in order to evaluate differences in the solid-state and solution-state structures.

Results and Discussion

Synthesis. All pentacoordinated organotin anions **2**–**7** were prepared by nucleophilic addition of halides (Cl, F) or cyanide to Me_3SnCl (**1**), as summarized in Scheme I. The derivatives **2**, **3**, and **5** were prepared by reaction of the appropriate tetraalkylammonium halide with **1** in methylene chloride solution in yields ranging from 62 to 71%. The compounds were susceptible to hydrolysis over time. This was particularly true in the case of **5**, making its analysis and subsequent NMR study difficult. Protic impurities as well as hydrolysis product contamination affected this work. Nevertheless, **5** could be handled and analyzed in the absence of moisture. Quantitative yields of compounds **4**, **6**, and **7** were obtained using potassium halides (KCl, KF) and 18-crown-6 in toluene solution. These salts are very stable to hydrolysis and may be handled for prolonged periods in air.

Scheme I

(1) tetraalkylammonium stannates

$$Me_3SnCl + R_4NX \xrightarrow[CH_3CN]{CH_2Cl_2\ \text{or}} [R_4N][Me_3SnCl(X)]$$

2: R = Et, X = Cl
3: R = Bu, X = Cl
5: R = Et, X = CN

(2) potassium 18-crown-6 stannates

$$Me_3SnCl + KX + 18\text{-crown-6} \xrightarrow{C_6H_5CH_3} [K(18\text{-crown-6})][Me_3SnCl(X)]$$

4: X = Cl
6: X = CN
7: X = F

---

[1] Presented in part at the 200th National Meeting of the American Chemical Society, Washington, DC Aug 1990; Abstract INOR 31. This work was performed at the Institute for Inorganic Chemistry, University of Munich, and at UCLA.

[2] (a) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251. (b) Holmes, R. R. *Prog. Inorg. Chem.* **1984**, *32*, 119. (c) Harrison, P. G. In *The Chemistry of Tin*; Harrison, P. G., Ed.; Blackie: London, 1989.

[3] Holmes, R. R. *Acc. Chem. Res.* **1979**, *12*, 257 and references cited therein.

[4] (a) Newcomb, M.; Horner, J. H.; Blanda, M. T. *J. Am. Chem. Soc.* **1987**, *109*, 7878. (b) Newcomb, M.; Madonik, A. M.; Blanda, M. T.; Judice, J. K. *Organometallics* **1987**, *6*, 145. (c) Newcomb, M.; Blanda, M. T. *Tetrahedron Lett.* **1988**, *29*, 4261. (d) Newcomb, M.; Horner, J. H.; Blanda, M. T.; Squattrito, P. J. *J. Am. Chem. Soc.* **1989**, *111*, 6294.

[5] (a) Jurkschat, K.; Kuivila, H. G.; Liu, S.; Zubieta, J. *Organometallics* **1989**, *8*, 2755. (b) Jurkschat, K.; Rühlmann, A.; Tzschach, A. *J. Organomet. Chem.* **1990**, *381*, C53.

[6] Johnson, S. E.; Polborn, K.; Nöth, H. *Inorg. Chem.* **1991**, *30*, 1410.

0276-7333/92/2311-3684$03.00/0

Table I. ^{1}H NMR Data for Triorganotin(IV) Compounds

compd	solvent	δ(Me$_3$Sn), ppm	$^{2}J|^{1}$H^{119}Sn$|$, Hz	δ(cation), ppm
Me$_3$SnCl (1)	CDCl$_3$	0.65[a,b]	59	
[Et$_4$N][Me$_3$SnCl$_2$] (2)	CDCl$_3$	0.75[a,b]	71	1.40 (Me), 3.42 (CH$_2$–N)
[Bu$_4$N][Me$_3$SnCl$_2$] (3)	CDCl$_3$	0.70[b]	71	0.910 (Me), 1.10–1.50 (–CH$_2$CH$_2$–), 3.18 (–CH$_2$N)
[K(18-crown-6)][Me$_3$SnCl$_2$] (4)	CDCl$_3$	0.84[b]	70	3.65 (–CH$_2$CH$_2$–)
[Et$_4$N][Me$_3$SnCl(CN)] (5)	CD$_3$CN	0.41[b]	69	1.38 (Me), 3.39 (CH$_2$N)
[K(18-crown-6)][Me$_3$SnCl(NC)] (6)	CDCl$_3$	0.45[b]	71	3.48 (–CH$_2$CH$_2$–)
[K(18-crown-6)][Me$_3$SnCl(F)] (7)	CDCl$_3$	0.74[b]	70	3.65 (–CH$_2$CH$_2$–)
[tmpH$_2$][Me$_3$SnCl$_2$] (8)	CDCl$_3$	0.68[c]	60	1.58 (Me), 1.72 (–CH$_2$– ring), 8.42 (NH)

[a] Reference 33. [b] This work. [c] Reference 6.

Table II. ^{13}C NMR Data for Triorganotin(IV) Compounds

compd	solvent	δ(Me$_3$Sn), ppm	$^{1}J|^{13}$C^{119}Sn$|$, Hz	other δ(^{13}C) data, ppm
Me$_3$SnCl (1)	CDCl$_3$	–0.87	379	
[Et$_4$N][Me$_3$SnCl$_2$] (2)	CDCl$_3$	6.41	525	7.28 (Me), 52.1 (CH$_2$N)
[Bu$_4$N][Me$_3$SnCl$_2$] (3)	CDCl$_3$	6.19	522	13.4 (Me), 19.5 (–CH$_2$–), 23.8 (–CH$_2$–), 58.8 (CH$_2$N)
[K(18-crown-6)][Me$_3$SnCl$_2$] (4)	CDCl$_3$	5.81	507	69.9 (–CH$_2$CH$_2$–)
[Et$_4$N][Me$_3$SnCl(CN)] (5)	CD$_3$CN	–1.54	509	7.35 (Me), 52.2 (CH$_2$N), 135 (–CN)
[K(18-crown-6)][Me$_3$SnCl(NC)] (6)	CDCl$_3$	–0.11	538	69.9 (–CH$_2$CH$_2$–), 138 (–CN)
[K(18-crown-6)][Me$_3$SnF(Cl)] (7)	CDCl$_3$	4.76	508	70.2 (–CH$_2$CH$_2$–)
[tmpH$_2$][Me$_3$SnCl$_2$][a] (8)	CDCl$_3$	0.05	400	16.3 (–CH$_2$–), 27.6 (Me), 35.2 (–CH$_2$–), 56.9 (q C)

[a] Reference 6.

Table III. ^{119}Sn NMR Data for Triorganotin(IV) Compounds

compd	solvent	concn, mol %	temp, °C	δ(^{119}Sn), ppm
Me$_3$SnCl[a] (1)	CDCl$_3$	33	20	165.7
	CDCl$_3$	15	20	171.2
	acetone	30.5	20	119.8
[Et$_4$N][Me$_3$SnCl$_2$][c] (2)	acetone	33	20	–53
[Bu$_4$N][Me$_3$SnCl$_2$][b] (3)	CDCl$_3$	33	21	–22.1
[K(18-crown-6)][Me$_3$SnCl$_2$][b] (4)	CDCl$_3$	33	20	–6.7
[Et$_4$N][Me$_3$SnCl(CN)][b] (5)	CD$_3$CN	33	21	–149.0
[K(18-crown-6)][Me$_3$SnCl(NC)][b] (6)	CDCl$_3$	33	20	–166.9
[K(18-crown-6)][Me$_3$SnCl(F)][b] (7)	CDCl$_3$	33	21	6.09
[tmpH$_2$][Me$_3$SnCl$_2$][d] (8)	CDCl$_3$	33	20	153.7
			–30	134.5
			–60	101.3
			–69	93.1

[a] Reference 11a. [b] This work. [c] Reference 11b. [d] Reference 6.

NMR Behavior. All triorganotin anions were characterized in solution by a combination of ^{1}H, ^{13}C{^{1}H}, and ^{119}Sn{^{1}H}NMR spectroscopy. The ^{1}H NMR data for compounds 1–8 and some related triorganotin halides are summarized in Table I. Relatively little information can be discerned from the chemical shifts of the trimethyltin protons. The important information lies in the magnitude of the two-bond proton–tin coupling constants, $^{2}J|^{1}$H^{119}Sn$|$. Since the coupling constant is related via the Fermi contact term to the s-electron density in the bond, magnitudes of J are used to infer valence electron distribution in tin–carbon bonds and, indeed, have been shown to be directly related to minimal changes occurring in the C–H bonds.[7,8] The increase of $^{2}J|^{1}$H^{119}Sn$|$ from 1 to the pentacoordinate anions 2–8 can be interpreted as a redistribution of the s-electron density in the Sn–C bonds, with a concomitant increase in the p character of the Sn–X bonds in accordance with Bent's principle.[9] The decreased magnitude of $^{2}J|^{1}$H^{119}Sn$|$ for 8 was attributed to the effects of hydrogen-bonding interactions as compared to other organotin anions.[6] The magnitude of the two-bond coupling for the other stannates was on the order of 70 Hz, irrespective of differences in cation (e.g. 3 vs 4) or anion (e.g. 4 vs 6).

The ^{13}C NMR data for compounds 1–8 are summarized in Table II. The one-bond carbon–tin coupling constant, $^{1}J|^{13}$C^{119}Sn$|$, is a somewhat more sensitive indicator of the electron distribution changes in tin–carbon bonds. A similar increase in the magnitude of $^{1}J|^{13}$C^{119}Sn$|$ is observed for compounds 2–8 as compared to the value for 1. Again, the decreased magnitude of $^{1}J|^{13}$C^{119}Sn$|$ for 8 reflects the effects of hydrogen-bonding interactions in solution as compared to other pentacoordinate tin anions.[6] The one-bond Sn–C couplings are difficult to interpret as indicative of cation–anion interactions in related stannates, since the effects are more subtle than those of hydrogen-bonding interactions in solution. For example, the magnitude of the one-bond coupling is somewhat larger for 3 as compared to that in 4, as opposed to the case of the cyanide-substituted tin anions, where the coupling constant of 5 is somewhat smaller than that observed for 6. In the latter case, such effects could be attributed to different polarities of the solvent systems (CD$_3$CN vs CDCl$_3$). The relative magnitude of the chemical shift of the cyanide group for 5 (δ 135) as compared to that for 6 (δ 138) is difficult to interpret as well, being more consistent with cyano coordination.[10]

The ^{119}Sn chemical shift data for compounds 1–8 are summarized in Table III. Several points are worth noting. Changes in the coordination number at tin can have a dramatic effect upon the shielding, and a wide range of δ(^{119}Sn) values are observed from the relatively deshielded Me$_3$SnCl (1) to the more shielded anionic derivatives 2–8. The influence of hydrogen bonding in solution is reflected in a markedly downfield shift for 8 as compared to the other pentacoordinate tin anions. The decrease in the shielding of the tin nucleus has been interpreted as a reduction of the Sn(5d)–Cl(3p) orbital overlap.[6,11] Moreover, δ(^{119}Sn) for 8 is strongly temperature dependent and, at the low-temperature limit, the structure of the tin anion is described as distorted halfway between idealized four-

---

[7] Kuivila, H. G.; Considine, J. L.; Sarma, R. H.; Mynott, R. J. *J. Organomet. Chem.* **1976**, *111*, 179.

[8] Al-Allaf, T. A. K. *J. Organomet. Chem.* **1986**, *306*, 337.

[9] Das, M. K.; Harrison, P. G. *Inorg. Chim. Acta* **1972**, *6*, 17.

[10] Breitmaier, E.; Voelter, W. *Carbon-13 NMR Spectroscopy*; VCH: New York, 1987.

[11] (a) Smith, P. J.; Tupicauskas, A. P. *Annu. Rep. NMR Spectrosc.* **1978**, *25*, 892. (b) Harrison, P. G.; Ulrich, S. E.; Zuckerman, J. J. *J. Am. Chem. Soc.* **1971**, *93*, 5398.

Table IV. Solid-State ^{13}C and ^{119}Sn NMR Data for Triorganotin(IV) Compounds

compd	$\delta(Me_3Sn)$, ppm	δ(Sn), ppm^a	$^1J|^{13}C^{119}Sn|$, Hz^b	$\Delta\delta(^{119}Sn)$,^{c} ppm
5	2.9	−204.4	590	53.4
6	3.3	−220.3	700	53.4

^{a} Center band. ^{b} $|^1J|$ values have been rounded to nearest decade and are ±10 Hz. ^{c} $\Delta\delta(^{119}Sn) = \delta(\text{solid}) - \delta(\text{solution})$.

and five-coordinate geometries. A relatively deshielded tin signal is also observed for **4** as compared to the respective tetraalkylammonium analogues **2** and **3**, although the signal for **4** is smaller in magnitude than that observed for **8**. While there are undoubtedly some effects attributed to solvent system (CD_3CN vs $CDCl_3$), the difference in $\delta(^{119}Sn)$ for **5** versus **6** appears to reflect yet another consequence of such interactions, namely, the manner in which the cyanide group is bonded to tin. The $\delta(^{119}Sn)$ values for compounds **1**–**7** suggest exchange phenomena occur in solution. The compounds undergo an equilibrium according to eq 1. The position of $\delta(^{119}Sn)$ and the rate

$$Me_3SnCl + M^+X^- \rightleftarrows [Me_3SnCl(X)]^- + M^+ \qquad (1)$$

(indicated by the line width) of this equilibrium depend on X^-, the cation M^+, and temperature. In particular, compounds **5** and **6** exhibited significantly broadened spectra, presumably indicating exchange of cyanide. It was not possible, however, to slow the exchange process to determine experimentally the limiting values for the tin anions in solution.

Solid-State NMR Behavior. ^{13}C and ^{119}Sn CP/MAS NMR was employed to further probe the nature of the solid-state structures of **5** and **6**. The data for these compounds are summarized in Table IV. The ^{13}C chemical shifts of the methyl carbons and $^1J|^{13}C^{119}Sn|$ values for **5** and **6** were consistent with a pentacoordinated environment at tin.[12] The only difficulty encountered was the presence of high-abundance, spin-active chlorine and nitrogen nuclei, which resulted in substantial line broadening.[13,14] A similar trend emerged for the coordination geometry at tin in the values of $\delta(^{119}Sn)$ for **5** and **6**.[15] The difference in the ^{119}Sn chemical shift in the solid state versus that in solution ($\Delta\delta(^{119}Sn) = \delta(\text{solid}) - \delta(\text{solution})$) was the same (53.4) for both compounds. The increased ^{119}Sn shielding for **6** as compared to **5** reflects a change in the manner in which cyanide coordinates to tin in the former compound, due to interaction of the tin anion with the potassium 18-crown-6 cation. The results are fully in accord with the vibrational analysis and molecular structure of **6**.

Vibrational Spectra. IR data were measured for compounds **3**–**8**, and selected vibrations are summarized in Table V. The effects of hydrogen-bonding interactions are seen from the IR data for **8**, with fundamental N–H stretching vibrations and characteristic N–H deformations observed.[6] The shift in frequency of the antisymmetric N–H stretching mode correlates relatively well with the N–H···Cl bond lengths observed for other compounds exhibiting this type of hydrogen-bonding interaction.[16,17]

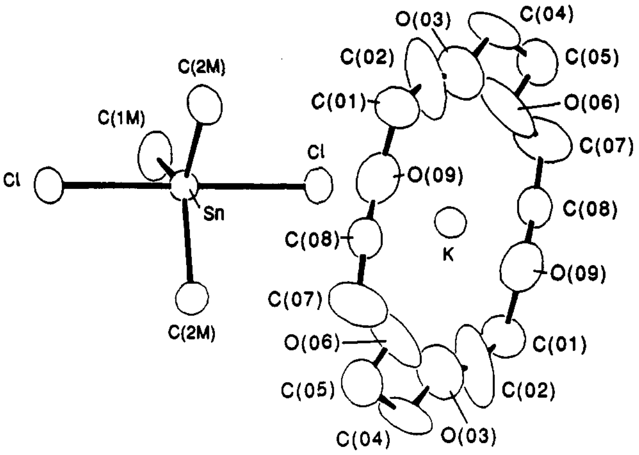


Figure 1. ORTEP representation of **4** showing the numbering scheme. All hydrogen atoms were removed for clarity. Ellipsoids were drawn at the 0.2 probability level.

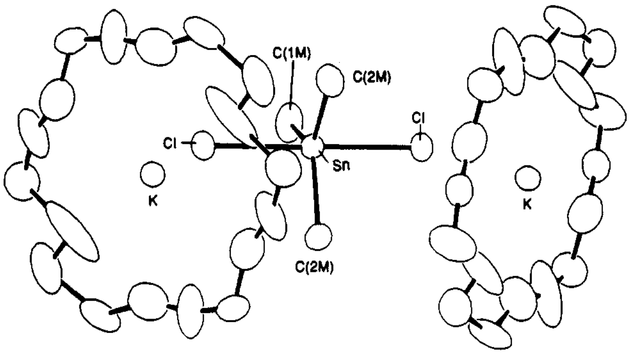


Figure 2. Two units of the infinite polymeric chain for **4** indicating cation–anion interactions.

The change in the Sn–C fundamental is, as expected, not significant for compounds **2**–**8**, while the interesting fundamental stretching mode, ν(Sn–Cl), is IR-inactive.[18] The IR data for compounds **5** and **6** are quite informative with regard to the nature of the binding of the cyanide ligand in these anions. Compound **5** exhibits a ν(C–N) fundamental at 2350.2 cm^{-1}, characteristic of C-bonded cyanide. This is in marked contrast to **6**, which exhibits a fundamental centered at 1974.8 cm^{-1}, consistent with N-bonded isocyanide.[19] The ambidentate nature of cyanide is well established for transition-metal compounds.[20] Relatively little data, however, are available for main-group derivatives with the exception of some organosilicon derivatives.[21] To our knowledge, this is a new feature for pentacoordinate compounds of tin.

Description of the Molecular Structure of 4. The molecular structure of **4** is presented in Figure 1. Table VI lists selected interatomic distances and angles, and the atomic coordinates are summarized in Table VII. The Sn–C bond lengths are all within 0.004 Å of the average value of 2.110 (12) Å. The C–Sn–C angles are all within 0.9° of the average value of 119.6 (4)°, and the C–Sn–Cl bond angles are all within 0.3° of the average value of 90.2 (2)°. A crystallographic 2-fold axis passes through Sn and C(1M). The Cl–Sn–Cl fragment is essentially linear

---

(12) Lockhart, T. P.; Manders, W. F. *J. Am. Chem. Soc.* **1987**, *109*, 7015.

(13) Fleming, W. W.; Fyfe, C. A.; Hyerla, J. R.; Vanni, H.; Yannoni, C. S. *Macromolecules* **1980**, *13*, 460.

(14) Wasylishen, R. E.; Fyfe, C. A. *Annu. Rep. NMR Spectrosc.* **1982**, *12*, 1.

(15) Harris, R. K.; Sebald, A.; Furlani, D.; Tagliavini, G. *Organometallics* **1988**, *7*, 388 and references cited therein.

(16) Hamilton, W. C.; Ibers, J. A. *Hydrogen Bonding in Solids*; W. A. Benjamin: New York, 1968; pp 16, 86–87.

(17) Nakamoto, K.; Margoshes, M.; Rundle, R. E. *J. Am. Chem. Soc.* **1955**, *77*, 6480.

(18) Beattie, I. R.; Stokes, F. C.; Alexander, L. E. *J. Chem. Soc., Dalton Trans.* **1973**, 465.

(19) Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*; Wiley: New York, 1978.

(20) Shriver, D. F. *Struct. Bonding* **1966**, *1*, 32.

(21) (a) Eaborn, C. *J. Chem. Soc.* **1949**, 2755. (b) Linton, H. R.; Nixon, E. R. *Spectrochim. Acta* **1958**, *10*, 299. (c) Linton, H. R.; Nixon, E. R. *J. Chem. Phys.* **1958**, *28*, 990.

Table V. Selected Vibrational Data for Triorganotin(IV) Compounds

compd	freq, cm^{-1} (assignt)	ref
$[Bu_4N][Me_3SnCl_2]$ (3)	547.1 (ν(Sn–C))	this work
$[K(18\text{-crown-}6)][Me_3SnCl_2]$ (4)	543.9 (ν(Sn–C))	this work
$[Et_4N][Me_3SnCl(CN)]$ (5)	541.3 (ν(Sn–C)), 2350 (ν(CN))	this work
$[K(18\text{-crown-}6)][Me_3SnCl(NC)]$ (6)	537.8 (ν(Sn–C)), 1974.8 (ν(NC))	this work
$[K(18\text{-crown-}6)][Me_3SnCl(F')]$ (7)	544.0 (ν(Sn–C))	this work
$[tmpH_2][Me_3SnCl_2]$ (8)	539.9 (ν(Sn–C)), 883.2 (NH_2 rock), 1421 (NH_2 wag), 1587 ($\nu(NH_2)$ scissor), 2772 ($\nu(NH_2)_{sym}$), 2946 ($\nu(NH_2)_{asym}$)	6

Table VI. Selected Interatomic Distances and Angles for 4[a]

	Distances (Å)		
Sn–Cl	2.618 (2)	K–O(03)	2.90 (1)
Sn–C(1M)	2.106 (14)	K–O(06)	2.72 (2)
Sn–C(2M)	2.113 (10)	K–O(09)	2.875 (13)
K–Cl	3.188 (2)		
	Angles (deg)		
Cl–Sn–Cl	179.42 (9)	Cl–Sn–C(1M)	89.7 (1)
C(2M)–Sn–C(2M),2	118.8 (5)	Cl–Sn–C(2M)	90.3 (3)
C(1M)–Sn–C(2M)	120.6 (3)		

[a] C(2M),2 is related by a 2-fold axis to C(2M).

Table VII. Positional and Equivalent Isotropic Thermal Parameters for 4[a]

atom	x	y	z	$\langle U^2\rangle$, Å^2
Sn	0.5000	0.2331 (1)	0.2500	0.070 (1)
Cl	0.4995 (2)	0.2343 (2)	0.3955 (1)	0.098 (2)
C(1M)	0.5000	0.4247 (12)	0.2500	0.125 (16)
C(2M)	0.3550 (8)	0.1352 (11)	0.2490 (5)	0.111 (6)
K	0.5000	0.0000	0.5000	0.079 (1)
C(01)	0.7091 (9)	0.1612 (16)	0.5947 (8)	0.149 (7)
C(02)	0.7344 (22)	0.0807 (18)	0.5521 (9)	0.261 (36)
C(04)	0.7762 (10)	−0.0598 (20)	0.4570 (11)	0.208 (8)
C(05)	0.7085 (16)	−0.1430 (19)	0.3937 (9)	0.168 (17)
C(07)	0.5691 (16)	−0.2345 (17)	0.3668 (12)	0.199 (15)
C(08)	0.4746 (14)	−0.2102 (21)	0.3736 (8)	0.320 (18)
O(03)	0.7780 (12)	0.0236 (18)	0.5049 (8)	0.196 (11)
O(06)	0.6400 (15)	−0.1408 (13)	0.4238 (10)	0.214 (25)
O(09)	0.3987 (11)	−0.1548 (14)	0.3919 (6)	0.188 (11)

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Table VIII. Selected Interatomic Distances and Angles for 6

	Distances (Å)		
Sn–Cl	2.73 (2)	K–O(1C)	2.84 (2)
Sn–N(1A)	2.654 (17)	K–O(4C)	2.87 (2)
Sn–C(1M)	2.128 (12)	K–O(7C)	2.78 (2)
Sn–C(2M)	2.128 (14)	K–O(10C)	2.75 (3)
Sn–C(3M)	2.129 (15)	K–O(13C)	2.77 (3)
K–Cl	3.33 (2)	K–O(16C)	2.82 (2)
K–C(1A)	2.75 (3)	C(1A)–N(1A)	0.88 (4)
	Angles (deg)		
C(1A)–Sn–Cl	177.3 (4)	Cl–Sn–C(2M)	84.8 (7)
C(1M)–Sn–C(2M)	119.9 (9)	Cl–Sn–C(3M)	92.8 (6)
C(1M)–Sn–C(3M)	117.5 (8)	Sn–N(1A)–C(1A)	178 (2)
C(2M)–Sn–C(3M)	122.3 (9)	Cl–K–N(1A)	178.4 (5)
Cl–Sn–C(1M)	87.0 (6)		

(179.42 (9)°). The K–Cl contact (3.188 Å) is comparable to the contact in KCl (3.139 Å).[22a,23] The cation–anion interaction is further evidenced by the infinite-chain structure adopted by the cation–anion pair (Figure 2). Potassium is coordinated to the oxygen atoms of 18-crown-6 at distances ranging from 2.72 to 2.90 Å and is located on a center of symmetry. These values are somewhat larger than the sum of the van der Waals radius for O and the ionic radius of K^+ (2.73 Å).[22b] The oxygen atoms of the 18-crown-6 ligand are planar to within 0.17 Å.

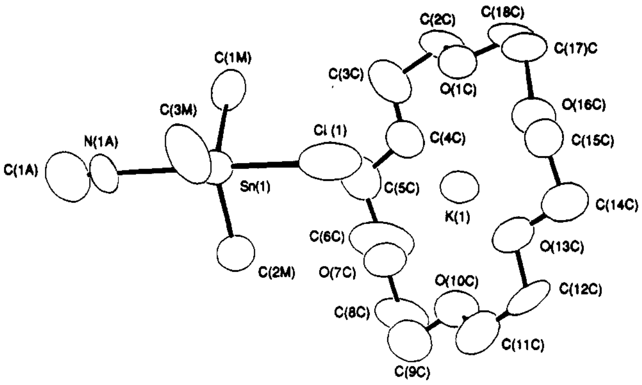


Figure 3. ORTEP representation of 6 showing the numbering scheme. All hydrogen atoms were removed for clarity. Ellipsoids were drawn at the 0.5 probability level.

Table IX. Positional and Equivalent Isotropic Thermal Parameters for 6[a]

atom	x	y	z	$\langle U^2\rangle$, Å^2
Sn	0.77378 (9)	0.5000	−0.21062 (9)	0.073 (5)
Cl	0.7772 (11)	0.3703 (8)	−0.2043 (13)	0.151 (6)
K	1.0018 (12)	0.2503 (6)	−0.0022 (15)	0.075 (1)
C(1M)	0.6851 (17)	0.4959 (18)	0.0380 (15)	0.072 (9)
C(2M)	1.0395 (17)	0.4915 (21)	−0.2226 (22)	0.072 (8)
C(3M)	0.5867 (22)	0.5031 (14)	−0.4420 (17)	0.090 (16)
C(1A)	0.7845 (33)	0.6679 (16)	−0.2039 (28)	0.074 (21)
N(1A)	0.7805 (21)	0.6262 (8)	−0.2025 (16)	0.096 (12)
O(1C)	0.7388 (22)	0.2514 (11)	0.2113 (24)	0.154 (10)
C(2C)	0.7789 (26)	0.2815 (12)	0.3699 (21)	0.092 (10)
C(3C)	0.8642 (34)	0.3442 (12)	0.3347 (31)	0.118 (19)
O(4C)	1.0243 (26)	0.3341 (10)	0.2969 (24)	0.106 (12)
C(5C)	1.1267 (43)	0.3887 (15)	0.2764 (44)	0.110 (22)
C(6C)	1.2882 (53)	0.3700 (23)	0.2110 (53)	0.120 (26)
O(7C)	1.2322 (26)	0.3505 (11)	0.0207 (35)	0.103 (11)
C(8C)	1.3829 (31)	0.3373 (16)	−0.0219 (38)	0.100 (12)
C(9C)	1.3388 (52)	0.3112 (23)	−0.2290 (45)	0.108 (20)
O(10C)	1.2600 (30)	0.2551 (14)	−0.2054 (32)	0.075 (22)
C(11C)	1.2349 (43)	0.2182 (16)	−0.3750 (44)	0.089 (23)
C(12C)	1.1511 (35)	0.1580 (15)	−0.3447 (40)	0.099 (25)
O(13C)	0.9851 (25)	0.1692 (12)	−0.2903 (31)	0.111 (11)
C(14C)	0.9062 (43)	0.1075 (17)	−0.2636 (53)	0.090 (13)
C(15C)	0.7340 (28)	0.1250 (13)	−0.2101 (29)	0.098 (10)
O(16C)	0.7646 (24)	0.1492 (11)	−0.0458 (27)	0.129 (11)
C(17C)	0.6150 (32)	0.1588 (15)	0.0681 (37)	0.110 (12)
C(18C)	0.6800 (43)	0.1868 (17)	0.2309 (47)	0.054 (14)

[a] Units of each esd, in parentheses, are those of the least significant digit of the corresponding parameter.

Description of the Molecular Structure of 6. The molecular structure of 6 is presented in Figure 3; Table VIII lists selected interatomic distances and angles, while the atomic coordinates are summarized in Table IX. The tin anion is a fairly regular trigonal bipyramid similar to 4; the chloride and isocyanide ligands occupy axial positions at distances of 2.73 (2) and 2.654 (17) Å, respectively. The Sn–C bond lengths are all within 0.001 Å of the average value of 2.128 (13) Å. The C–Sn–C angles are all within 2.4° of the average value of 119.9 (9)°; the C–Sn–Cl

---

(22) (a) Pauling, L. *The Nature of the Chemical Bond*; Cornell University Press: Ithaca, NY, 1960; p 520. (b) *Ibid.*, p 514.

(23) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, U.K., 1984.

Table X. X-ray Structural Data for Triorganotin(IV) Compounds

compd	Sn–Cl, Å	Sn–C, Å	∠C–Sn–C, deg	∠C–Sn–Cl, deg	∠Cl–Sn–X, deg
Me_3SnCl (1)	2.434 (5)	2.14 (3)	117.2 (8)	99.5 (5)	176.8
135 K X-ray[a]	3.259 (5)				
363 K ed[b]	2.351 (7)	2.106 (6)	114.9 (16)	103.2 (6)	
$[K(18\text{-crown-}6)][Me_3SnCl_2]$[e] (4)	2.618 (2)	2.106 (14)	120.6 (3)	90.3 (3)	179.42 (9)
	2.605 (4)	2.113 (10)	118.8 (5)	89.7 (1)	
$[K(18\text{-crown-}6)][Me_3SnCl(NC)]$[e] (6)	2.73 (2)	2.128 (14)	119.9 (9)	84.8 (7)	
		2.128 (12)	117.5 (8)	87.0 (6)	177.3 (4)
		2.129 (15)	122.3 (9)	92.8 (6)	
$[tmpH_2][Me_3SnCl_2]$[f] (8)	2.454 (2)	2.117 (8)	118.6 (3)	97.9 (2)	
	3.034 (3)	2.134 (9)	119.7 (3)	96.1 (2)	179.2 (2)
		2.113 (8)	117.1 (3)	97.5 (2)	
$[Mo_3(\eta^5\text{-}C_5H_5)_3S_4][Me_3SnCl_2]$[c] (9)	2.696 (3)	2.12 (1)			
	2.572 (4)				
$[Au\{S(AuPPh_3)_2\}_2][Me_3SnCl_2]$[d] (10)	2.622 (9)	2.25 (4)	111.8 (20)	92.1 (12)	
			124.1 (11)	89.4 (13)	178.7 (4)
				88.6 (12)	

[a] Reference 25a. [b] Reference 25b. [c] Reference 27. [d] Reference 28. [e] This work. [f] Reference 6.

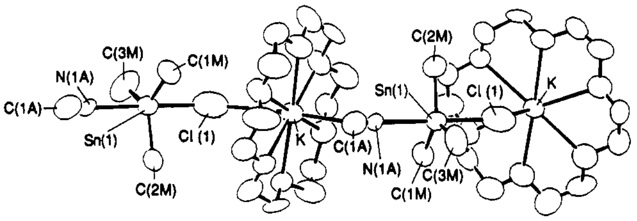
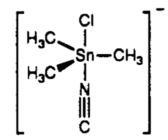
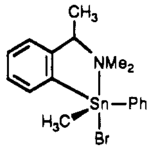
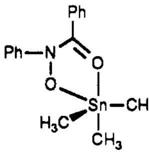


Figure 4. Two units of the infinite polymeric chain for **6** indicating cation–anion interactions.

bond angles are all within 1.7° of the average value of 88.2 (6)°, and the C–Sn–N bond angles are all within 1.4° of the average value of 91.8 (7)°. The N–Sn–Cl fragment is essentially linear (177.3 (4)°). The K–C contact (2.75 Å) and the K–Cl contact (3.33 Å) are comparable to that observed for KCN (2.8 Å)[24] and for KCl (3.139 Å),[22a,23] respectively. The CN group in an isocyanide orientation serves to link the cation and anion in the infinite-chain structure adopted by the cation–anion pair (Figure 4). The coordination sphere of the potassium is completed by the six oxygen atoms of the crown ether at distances ranging from 2.75 to 2.87 Å. These values are somewhat larger than the sum of the van der Waals radius for O and the ionic radius of K^+ (2.73 Å).[22b]

Structural Comparisons. It is of interest to compare the structural parameters for 4 and 6 with the X-ray data reported for 1 and related pentacoordinate tin anions 8–10, as summarized in Table X. The Sn–Cl bond parameter is informative, since all compounds share this structural feature. The Sn–Cl distances range from 2.35 to 3.26 Å. The dissimilar Sn–Cl distance in the solid-state structure of 1 has been interpreted in terms of an intramolecular and an intermolecular Sn–Cl bond contact,[25] since the association is disrupted upon melting or dissolution.[26] The dissimilar bond distance in 8 reflects the influence of hydrogen-bonding interactions in the solid state, as the anion is distorted halfway between idealized four- and five-coordinate geometries.[6] The Sn–Cl contacts for the derivatives of $[Me_3SnCl_2]^-$ 4, 9, and 10 do not exhibit much variation, ranging from 2.57 to 2.69 Å. The compounds 9[27] and 10[28] are composed of discrete cations and anions, whereas the crown ether compound 4 consists of an infinite chain of cations and anions. There appears to be little variation in the Sn–C bond parameters for the five-coordinate anions, and the geometry of the Cl–Sn–X fragment is essentially linear.

Table XI. Structural Data for Organotin(IV) Compounds

compd	Sn–X, Å	ref
 **6**	Sn–N: 2.654 (17) Sn–Cl: 2.73 (2) Sn–C: 2.128 (12), 2.129 (15)	this work
 **11**	Sn–N: 2.476 (6) $Sn–C_{eq}$: 2.160 (10)	31
 **12**[a]	$Sn–C_{ax}$: 2.180 (10), 2.220 (20) $Sn–C_{eq}$: 2.060 (20), 2.155 (9)	32

[a] Two independent molecules per unit cell.

The nature of the bonding of cyanide for compound 6 is further clarified when compared with compounds 11 and 12, summarized in Table XI.[29] The Sn–N contact for 6 (2.65 Å) is more consistent with the Sn–N bond distance observed for 11 (2.47 Å)[31] than the axial Sn–C bond distance measured for 12 (2.22 Å).[32]

The structural data obtained by X-ray crystallography for 6 can be directly correlated with the solid-state NMR

---

(24) Bozorth, R. M. *J. Am. Chem. Soc.* **1922**, *44*, 317.

(25) (a) Hossain, M. B.; Lefferts, J. L.; Molloy, K. C.; Van der Helm, D.; Zuckerman, J. J. *Inorg. Chim. Acta* **1979**, *36*, L409. (b) Beagly, B.; McAloon, K.; Freeman, J. M. *Acta Crystallogr.* **1974**, *B30*, 444.

(26) (a) Kriegsmann, H.; Pitschtchan, S. Z. *Anorg. Allg. Chem.* **1961**, *308*, 212. (b) Alcock, N. W.; Sawyer, J. F. *J. Chem. Soc., Dalton Trans.* 1977, 1090. (c) Parish, R. V.; Platt, R. H. *Inorg. Chim. Acta* **1970**, *4*, 65.

(27) Vergamini, P. J.; Vahrenkamp, H.; Dahl, L. *J. Am. Chem. Soc.* **1971**, *93*, 6327.

(28) Jones, P. G.; Lensch, C.; Sheldrick, G. M. *Z. Naturforsch.* **1982**, *37B*, 141.

(29) Compounds 11 and 12 are the only comparable examples of five-coordinate tin, since there are no available crystallographic data for anionic compounds to compare with 6. The Sn–CN bond in Me_3SnCN was reported as an average value, since the apparent amplitude of vibration reflected an average of two different kinds of atoms, which must be at different positions.[30] This length, therefore, is not comparable to that in 6.

(30) Schlemper, E. O.; Britton, D. *Inorg. Chem.* **1966**, *5*, 507.

(31) Van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G.; Pontanagel, W. M. G. F.; Kroon, J.; Spek, A. *J. Am. Chem. Soc.* **1978**, *100*, 5021.

(32) Harrison, P. G.; King, T. J.; Molloy, K. C. *J. Organomet. Chem.* **1980**, *185*, 199.

data and provide an illuminating comparison between solid- and solution-phase structures of **5** and **6**. The isocyanide orientation of the CN group in **6** allows for interaction of the potassium 18-crown-6 cation with the tin anion; this interaction is reflected by a more shielded tin signal. Since there is no possibility for the tetraethylammonium cation of **5** to exhibit such an interaction, the decreased ^{119}Sn shielding reasonably reflects C-bonded coordination of the cyano group. The "tight-ion" pair formed by **6** in the solid state is somewhat disrupted in solution, as evidenced by an exchange-broadened ^{119}Sn signal. The fact that $\Delta\delta(^{119}\mathrm{Sn})$ is the same for both **5** and **6** indicates that the magnitude of the ^{119}Sn chemical shift also appears to be a reliable measure of cation–anion interactions for **6** in solution.

Conclusions

The structural analyses of **4** and **6** confirm the conclusions drawn from the spectroscopic data, namely that cation–anion interactions influence the solution-state behavior and the solid-state structures for these anionic tin compounds. The nature of these interactions, while not as large in magnitude as the effects of hydrogen bonding, nevertheless impart changes in the geometry of the pentacoordinate state as compared to examples where such an interaction is absent. To our knowledge, this is a new feature for pentacoordinate derivatives of tin. The infinite-chain structures of **4** and **6** are unique as compared to other cationic derivatives of these tin anions. The crystal structure of **6** is unusual in that the strongly nucleophilic cyanide would exhibit N-bonded coordination on Sn rather than a C-bonded orientation. The results suggest that novel macropolycyclic hosts could be developed incorporating a Lewis acidic site along with a crown ether moiety. One could envision that these novel inorganic hosts would exhibit interesting cooperative binding of both cations and anions. Research efforts in this direction are currently in progress.

Experimental Section

General Considerations. Standard glovebox, Schlenk, and vacuum line techniques were employed for all manipulation of air- and moisture-sensitive compounds. Reaction solvents were reagent grade and were distilled from appropriate drying agents under argon before use. Toluene was distilled from sodium benzophenone ketyl. Methylene chloride and hexane were dried over CaH_2. Deuteriated solvents were obtained from Cambridge Isotope Laboratories. Compound **2** was prepared by a literature method.[33] Tetra-*n*-butylammonium chloride (Fluka) and trimethyltin chloride (**1**), potassium chloride, potassium fluoride, and 18-crown-6 (Aldrich) were used as received.

Physical Measurements. NMR spectra were obtained on JEOL FX 90- and 270-MHz and Bruker AF 200-MHz and AM 360- and 500-MHz spectrometers. ^{1}H and ^{13}C chemical shifts for ^{1}H and ^{13}C NMR spectra were referenced to deuteriated solvents as internal standards. Chemical shift values for ^{119}Sn spectra were referenced relative to external Me_4Sn (0.00 ppm). Resonances observed upfield of the references were assigned negative chemical shift values in all cases. Infrared spectra were obtained as Nujol mulls and were recorded on Nicolet and Perkin-Elmer FT IR instruments. Xenon FAB mass spectra were obtained on an AEI Ltd. Model MS-9 spectrometer. Elemental analyses were performed at the University of Munich microanalysis laboratory.

Preparation of Tetra-*n*-butylammonium Trimethyldichlorostannate (3). Equivalent amounts of **1** (3.58 g, 18.0 mmol) and tetra-*n*-butylammonium chloride (5.00 g, 18.0 mmol) were combined in CH_2Cl_2 (100 mL) at ambient temperature with stirring. The mixture was stirred overnight. The solution was concentrated in vacuo to produce a white crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 6.09 g of **3** in 71% yield: mp 186 °C dec. This compound is somewhat hygroscopic and should be stored in a moisture-free environment. ^{1}H NMR ($CDCl_3$): δ 0.68 (s, 9 H, Me_3Sn–, $^{2}J_{^{1}\mathrm{H}^{119}\mathrm{Sn}}$ = 70.8 Hz), 0.91 (t, 12 H, –CH_3, J_{HH} = 6.1 Hz), 1.10–1.50 (m, 8 H, –CH_2CH_2–), 3.18 (t, 8 H, NCH_2–, J_{HH} = 9.8 Hz). ^{13}C NMR ($CDCl_3$): δ 6.19 (s, Me_3Sn–, $^{1}J_{^{13}\mathrm{C}^{119}\mathrm{Sn}}$ = 522 Hz), 13.4 (s, –CH_3), 19.8 (s, –$C\mathit{H}_2CH_3$), 23.8 (s, –CH_2CH_2N), 58.8 (s, –CH_2N). ^{119}Sn NMR ($CDCl_3$): δ –22.1. Anal. Calcd for $C_{19}H_{45}NSnCl_2$: C, 47.81; H, 9.52; N, 2.94. Found: C, 47.15; H, 9.67; N, 2.94.

Preparation of Potassium 18-Crown-6 Trimethyldichlorostannate (4). Equivalent amounts of **1** (3.77 g, 18.9 mmol), 18-crown-6 (5.00 g, 18.9 mmol), and potassium chloride (1.41 g, 18.9 mmol) were combined in toluene (75 mL) at ambient temperature with stirring. Precipitate formation was observed after stirring the reactants for 48 h. The precipitate was collected by vacuum filtration to yield a white crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 9.36 g of **4** in 92% yield: mp 176–179 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.84 (s, 9 H, Me_3Sn–, $^{2}J_{^{1}\mathrm{H}^{119}\mathrm{Sn}}$ = 70.3 Hz), 3.65 (s, 24 H, 18-crown-6). ^{13}C NMR ($CDCl_3$): δ 5.81 (s, Me_3Sn–, $^{1}J_{^{13}\mathrm{C}^{119}\mathrm{Sn}}$ = 507 Hz), 69.9 (s, 18-crown-6). ^{119}Sn NMR ($CDCl_3$): –6.74. Anal. Calcd for $C_{15}H_{33}O_6KSnCl_2$: C, 33.47; H, 5.73. Found: C, 33.48; H, 5.73.

Preparation of Tetraethylammonium Trimethylchlorocyanostannate (5). Equivalent amounts of **1** (6.37 g, 32.0 mmol) and tetra-*n*-butylammonium cyanide (5.00 g, 32.0 mmol) were combined in CH_3CN (100 mL) at ambient temperature with stirring. The mixture was stirred overnight. The solution was concentrated in vacuo to produce a white crystalline material. Recrystallization from a mixture of CH_3CN and hexane afforded 7.05 g of **5** in 62% yield: mp 196 °C dec. The compound is very sensitive toward moisture and/or air and should be handled under an inert atmosphere. ^{1}H NMR (CD_3CN): δ 0.41 (s, 9 H, Me_3Sn–, $^{2}J_{^{1}\mathrm{H}^{119}\mathrm{Sn}}$ = 69.1 Hz), 1.18 (t, 12 H, –CH_3, J_{HH} = 8.8 Hz), 3.21 (q, 8 H, NCH_2–, J_{HH} = 7.2 Hz). ^{13}C NMR (CD_3CN): δ –1.54 (s, Me_3Sn–, $^{1}J_{^{13}\mathrm{C}^{119}\mathrm{Sn}}$ = 509 Hz), 7.35 (s, –CH_3), 52.2 (s, –CH_2N), 135 (s, –CN). ^{119}Sn NMR (CD_3CN): δ –149.0. Negative-ion FAB MS: theoretical ion distribution for C_4H_9SnNCl centered around *m/z* 225.28, observed ion distribution centered at *m/z* 225. Anal. Calcd for $C_{12}H_{29}N_2SnCl$: C, 40.53; H, 8.24; N, 7.88. Found: C, 40.15; H, 7.87; N, 7.94.

Preparation of Potassium 18-Crown-6 Trimethylchlorocyanostannate (6). Equivalent amounts of **1** (5.00 g, 25.1 mmol), 18-crown-6 (6.63 g, 25.1 mmol), and potassium chloride (1.63 g, 25.1 mmol) were combined in toluene (75 mL) at ambient temperature with stirring. Precipitate formation was observed shortly after stirring the reactants, and the mixture was stirred for 24 h. The precipitate was collected by vacuum filtration to yield a white crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 11.7 g of **6** in 88% yield: mp 172–176 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.45 (s, 9 H, Me_3Sn–, $^{2}J_{^{1}\mathrm{H}^{119}\mathrm{Sn}}$ = 71.1 Hz), 3.48 (s, 24 H, 18-crown-6). ^{13}C NMR ($CDCl_3$): δ –0.11 (s, Me_3Sn–, $^{1}J_{^{13}\mathrm{C}^{119}\mathrm{Sn}}$ = 537 Hz), 69.9 (s, 18-crown-6), 138 (s, –CN). ^{119}Sn NMR ($CDCl_3$): δ –166.9. Anal. Calcd for $C_{16}H_{33}O_6KNSnCl$: C, 36.34; H, 6.30. Found: C, 35.88; H, 6.07. Negative-ion FAB MS: theoretical ion distribution for C_4H_9SnNCl centered around *m/z* 225.28, observed ion distribution centered at *m/z* 225.

Preparation of Potassium 18-Crown-6 Trimethylchlorofluorostannate (7). Equivalent amounts of **1** (5.00 g, 25.1 mmol), 18-crown-6 (6.63 g, 25.1 mmol), and potassium fluoride (1.46 g, 25.1 mmol) were combined in toluene (75 mL) at ambient temperature with stirring. Precipitate formation was observed shortly after stirring the reactants, and stirring was continued for 24 h. The precipitate was collected by vacuum filtration to yield a white crystalline material. Recrystallization from a mixture of CH_2Cl_2 and hexane afforded 11.8 g of **7** in 90% yield: mp 180–183 °C dec. ^{1}H NMR ($CDCl_3$): δ 0.74 (s, 9 H, Me_3Sn–, $^{2}J_{^{1}\mathrm{H}^{119}\mathrm{Sn}}$ = 70.3 Hz), 3.65 (s, 24 H, 18-crown-6). ^{13}C NMR ($CDCl_3$): δ 4.76 (s, Me_3Sn–, $^{1}J_{^{13}\mathrm{C}^{119}\mathrm{Sn}}$ = 508 Hz), 70.2 (s, 18-crown-6). ^{19}F NMR ($CDCl_3$): δ –135 (s, $^{1}J_{^{19}\mathrm{F}^{119}\mathrm{Sn}}$ = 1638 Hz). ^{119}Sn NMR ($CDCl_3$): δ 6.09. Anal. Calcd for $C_{15}H_{33}O_6KSnClF$: C, 34.53; H, 6.39. Found: C, 33.72; H, 6.07.

Collection and Reduction of X-ray Data for 4. A colorless crystal, obtained from a methylene chloride/hexane solution, was mounted on a fiber and placed on a Huber diffractometer con-

---

[33] Sau, A. C.; Carpino, L. C.; Holmes, R. R. *J. Organomet. Chem.* **1980**, *197*, 181.

Table XII. Details of the Crystallographic Data Collection for 4 and 6

	4	6
T, °C	25	25
cryst size, mm	0.28 × 0.35 × 0.25	0.30 × 0.25 × 0.35
appearance	colorless parallelepiped	colorless chunk
radiation (graphite monochromator)	Mo Kα	Mo Kα
wavelength, Å	0.7107	0.7107
space group	$C2/c$	$P2_1$
a, Å	12.546 (1)	7.920 (1)
b, Å	17.988 (1)	21.026 (2)
c, Å	17.996 (2)	7.650 (1)
β, deg	90.266 (4)	98.762 (2)
V, Å^3	2481	1259
Z	4	2
ρ(calcd), g cm^{-3}	1.44	1.39
μ, cm^{-1}	14.4	13.1
scan width		
below Kα_1	1.3	1.3
above Kα_2	1.6	1.6
scan rate, deg min^{-1}	3.0	3.0
no. of unique rflns	2243	2280
no. of obsd ($F^2 > 3\sigma(F^2)$) rflns	1960	1833
2θ(max), deg	50	50
data collected	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of params refined	122	244
R, R_w, GOF[a]	0.064, 0.104, 4.28	0.057, 0.066, 2.26

[a] GOF = $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where $w = 1/(\sigma^2|F_o|)$. $R = \sum||F_o| - |F_c||/|F_o|$. $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

structed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 44 accurately centered reflections ($7.7 < 2\theta < 20.4°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table XII. Data were collected at 25 °C in the θ–2θ scan mode. Three intense reflections (006, −2,2,1, 531) were monitored every 97 reflections to check stability. Intensities of these reflections did not decay during the course of the experiment (43.8 h). Of the 2243 unique reflections measured, 1960 were considered observed ($F^2 > 3\sigma(F^2)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects but not for absorption or for secondary extinction. Programs used in this work include locally modified versions of crystallographic programs listed in ref 34.

Solution and Refinement of the Structure of 4. Atoms were located by use of direct methods. All calculations were performed on a VAX 3100 computer. All non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were included in calculated positions as members of rigid groups: C–H = 1.0 Å, H–C–H = 109.5°. H atoms were assigned U values based approximately on the U value of the attached atom. Scattering factors for H were obtained from Stewart et al.[35] and for other atoms were taken from ref. 36. Anomalous dispersion terms were applied to the scattering of K, Cl, and Sn. The maximum and minimum peaks on a final difference electron density map were 0.5 e Å^{-3}, located in the region of the crown ether. Final positional and thermal parameters for non-hydrogen atoms are given in Table VII. The thermal parameters for the crown atoms were large compared to the atoms of the tin anion. Attempts at data collection at several lower temperatures failed because the crystals cracked.

Collection and Reduction of X-ray Data for 6. A colorless crystal, obtained from a methylene chloride/hexane solution, was mounted on a fiber and placed on a Huber diffractometer constructed by Professor C. E. Strouse of this department. Unit cell parameters were determined from a least-squares fit of 58 accurately centered reflections ($9.9 < 2\theta < 20.1°$). These dimensions and other parameters, including conditions of data collection, are summarized in Table XII. Data were collected at 25 °C in the θ–2θ scan mode. Three intense reflections (2,0,−2, 080, 3,1,−2) were monitored every 97 reflections to check stability. Intensities of these reflections decayed less than 7.0% during the course of the experiment (45.7 h). Of the 2280 unique reflections measured, 1833 were considered observed ($F^2 > 3\sigma(F^2)$) and were used in the subsequent structure analysis. Data were corrected for Lorentz and polarization effects and for secondary extinction but not for absorption. Other conditions for collection and reduction were the same as those that were applied to 4.

Solution and Refinement of the Structure of 6. Atoms were located by use of heavy-atom methods. All calculations were performed on a VAX 3100 computer. All non-hydrogen atoms were refined with anisotropic parameters. All hydrogen atoms were included in calculated positions as members of rigid groups: C–H = 1.0 Å, H–C–H = 109.5°. H atoms were assigned U values based approximately on the U value of the attached atom. Scattering factors for H were obtained from Stewart et al.[35] and for other atoms were taken from ref 36. Anomalous dispersion terms were applied to the scattering of K, Cl, and Sn. The maximum and minimum peaks on a final difference electron density map were 1.6 e Å^{-3}, located near Sn. Final positional and thermal parameters for non-hydrogen atoms are given in Table IX.

Acknowledgments. Generous support of this research by Professor M. Frederick Hawthorne (UCLA) and the Fonds der Chemische Industrie (University of Munich) is gratefully acknowledged. S.E.J. thanks the National Science Foundation for a Postdoctoral Fellowship (Grant NSF-CHE 90-01819). We wish to thank our reviewers for their helpful comments.

Supplementary Material Available: Tables of positional and thermal parameters and complete interatomic distances and angles for 4 and 6 (5 pages). Ordering information is given on any current masthead page.

OM920307+

---

(34) Computer programs: CARESS (Broach, Coppens, Becker, and Blessing), peak profile analysis, Lorentz and polarization corrections; ORFLS (Busing, Martin, and Levy), structure factor calculation and full-matrix least-squares refinement, ORTEP (Johnson), figure plotting; SHELX76 (Sheldrick), crystal structure package; SHELX86 (Sheldrick), crystal structure solution package.

(35) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(36) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.