Synthetic and Structural Studies of Tin(IV) Complexes of Crown Ethers †

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Fourteen inorganic tin(IV) and organotin(IV) complexes of crown ethers (L), of general formulae $SnX_4{\cdot}L{\cdot}2H_2O$, $SnCl_4{\cdot}L{\cdot}4H_2O{\cdot}nCHCl_3$ (n = 0 or 1), $(SnR_2X_2)_n{\cdot}L{\cdot}2H_2O$ (n = 1 or 2), and $(SnPh_3X)_2{\cdot}L{\cdot}2H_2O$, have been synthesised. The structure and bonding in these adducts are discussed in terms of their i.r. and ^{119}Sn Mössbauer spectroscopic data. These suggest co-ordination to the tin either by one or more of the polyether O atoms, or by the water molecules of hydration (the crown ether acting as a second-sphere ligand). The latter structure is confirmed by a single-crystal *X*-ray determination of $Sn(OH_2)_2Cl_4{\cdot}18\text{-crown-}6{\cdot}2H_2O{\cdot}CHCl_3$. The crystals are monoclinic, space group $P2_1/n$, with a = 10.315(6), b = 13.630(8), c = 20.649(13) Å, and β = 94.68(5)°. The structure was solved using multisolution direct methods and refined by least squares to R = 0.062 (R' = 0.068) for 3 142 observed diffractometer data. The water molecules within the octahedral $Sn(OH_2)_2Cl_4$ units are found to be *cis* to each other and are involved in an extensive hydrogen-bonding scheme. The latter links together the 18-crown-6 molecules, unco-ordinated water molecules, and $Sn(OH_2)_2Cl_4$ octahedra, to give hydrogen-bonded chains which run parallel to the *b* axis.

Recent studies on adducts of transition-metal aqua and ammine complexes with crown ethers have shown [1] that the macrocyclic polyether is not directly co-ordinated to the metal atom, but acts as a second-sphere ligand, in which it interacts with either the co-ordinated water or ammonia molecules *via* hydrogen bonds.

There are very few reports on the interaction of tin compounds with crown ethers. Herber and his co-workers have suggested, on the basis of i.r. and Mössbauer spectroscopy, that various inorganic tin(II) salts furnish ionic complexes with 18-crown-6 [2] and 15-crown-5,[3,‡] in which the Sn^{2+} cation interacts strongly with two (or three) of the polyether oxygen atoms. The only work on inorganic tin(IV) complexes of crown ethers is by Gur'yanova *et al.*[4] who reported the existence of the neutral adduct $2SnCl_4{\cdot}$dibenzo-24-crown-8 in benzene solution. This adduct was not isolated in the solid state, but it was suggested that the crown ether functions as a quadridentate donor ligand, with each tin co-ordinated exocyclically to two oxygen atoms from the polyether ring.

We now report on a extension of our preliminary studies on inorganic tin(IV) [5] and organotin(IV) [6] complexes of crown ethers, including the first crystal structure determination of a representative of the former type. §

Experimental

Preparation of Complexes.—The reactions between a number of inorganic tin(IV) and organotin(IV) halides and pseudohalides, and the crown ethers, 18-crown-6, 15-crown-5, and 12-crown-4, have been studied. The types of product obtained are shown in the Scheme.

When a mixture of the appropriate tin(IV) halide (2 mol) and either 18-crown-6 or 15-crown-5 (1 mol) in methanol solution was refluxed for 2 h, followed by cooling to −20 °C, the neutral 1 : 1 adducts [compounds (1)—(4)] were obtained as the dihydrates (reactions A). A similar reaction of the tin(IV) halide (2 mol) with 12-crown-4 (1 mol), using methanol–chloroform (1 : 1 v/v) as the solvent, again resulted in the formation of the dihydrated 1 : 1 complexes [compounds (5) and (6)] (reactions D). Recrystallisation of compound (1) from methanol–chloroform (1 : 1 v/v) solution gave (7) (reaction B), and slow crystallisation of (1) from methanol at room temperature yielded (8) (reaction C).

When di- or tri-organotin halide or pseudohalide (1 or 2 mol) and crown ether (1 mol) were refluxed in methanol for 2 h, followed by cooling to −20 °C, the dihydrated complexes (9) (reaction E), (10) and (11) (reactions F), and (12)—(14) (reactions G) crystallised from solution.

All of the above products (white solids) were dried in air at room temperature, and their analytical, physical, and i.r. data are presented in Table 1. Microanalytical data for the elements, C, H, N, S, Cl, and Br were obtained by the Microanalytical Laboratory, University College London. Tin analyses were performed as follows. The samples were dissolved in dilute HCl, tin(IV) was reduced to tin(II) using nickel metal, and the total tin was determined volumetrically with potassium iodate–potassium iodide solution, using starch as indicator.

Spectroscopic Measurements.—Infrared spectra were recorded as Nujol mulls on a Pye Unicam SP 2000 spectrophotometer. ^{119}Sn Mössbauer spectra were obtained using a constant-acceleration microprocessor spectrometer (Cryophysics Ltd., Oxford), with a 512-channel data store. A 2-mCi $Ca^{119m}SnO_3$ source was used at room temperature and

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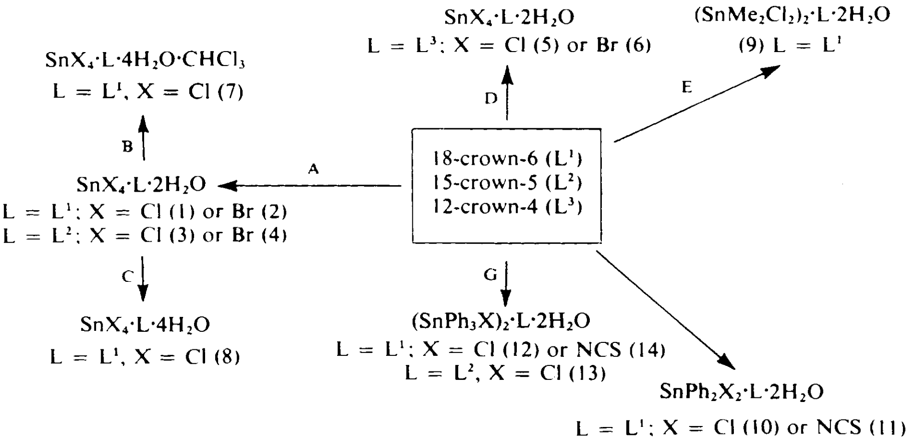
† *Supplementary data available* (No. SUP 23884, 17 pp.): thermal parameters, H-atom co-ordinates, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

‡ 18-crown-6 = 1,4,7,10,13,16-Hexaoxacyclo-octadecane; 15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane; dibenzo-24-crown-8 = 6,7,9,10,12,13,20,21,23,24,26,27-dodecahydrodibenz-[*b*,*n*][1,4,7,10,13,16,18,22]octaoxacyclotetracosine; 12-crown-4 = 1,4,7,10-tetraoxacyclododecane; diglyme = bis(2-methoxyethyl) ether; terpy = 2,2′:6′,2″-terpyridyl.

§ *Note added in proof*: since this paper was submitted the *X*-ray structure of $SnCl_4{\cdot}18\text{-crown-}6{\cdot}4H_2O$ (8) has been reported independently (G. Valle, A. Cassol, and U. Russo, *Inorg. Chim. Acta*, 1984, **82**, 81) and an additional series of tin(IV) halide complexes of crown ethers has also been prepared (U. Russo, A. Cassol, and A. Silvestri, *J. Organomet. Chem.*, 1984, **260**, 69).



Scheme. Synthetic routes to tin(IV) complexes of crown ethers

Table 1. Analytical, physical, and i.r. data for tin(IV) complexes of crown ethers

Complex	M.p. (°C)	Analysis [a] (%)				ν_{asym}(C–O–C) [b]/cm^{-1}
		C	H	Halogen	Sn	
(1) SnCl$_4$·18-crown-6·2H$_2$O	174—178	26.2 (25.7)	5.1 (5.0)	24.9 (25.3)	21.1 (21.2)	1 104
(2) SnBr$_4$·18-crown-6·2H$_2$O	132—135	18.5 (19.5)	3.9 (3.8)	42.1 (43.3)	15.5 (16.1)	1 105
(3) SnCl$_4$·15-crown-5·2H$_2$O	201—205	22.0 (23.2)	4.5 (4.7)	27.7 (27.4)	22.9 (23.0)	1 100
(4) SnBr$_4$·15-crown-5·2H$_2$O	175—179	17.4 (17.3)	3.5 (3.5)	46.6 (46.0)	17.1 (17.1)	1 100
(5) SnCl$_4$·12-crown-4·2H$_2$O	164—168	19.3 (20.3)	4.1 (4.3)	28.6 (30.0)	24.9 (25.1)	1 088
(6) SnBr$_4$·12-crown-4·2H$_2$O	153—156	14.7 (14.8)	2.9 (3.1)	50.4 (49.1)	18.2 (18.2)	1 086
(7) SnCl$_4$·18-crown-6·4H$_2$O·CHCl$_3$	175—183	22.0 (21.8)	4.4 (4.7)	32.7 (34.6)	*c*	1 105
(8) SnCl$_4$·18-crown-6·4H$_2$O	172—179	23.5 (24.1)	5.3 (5.4)	24.0 (23.8)	*c*	1 105
(9) (SnMe$_2$Cl$_2$)$_2$·18-crown-6·2H$_2$O	119—123	26.1 (26.0)	5.3 (5.5)	18.8 (19.2)	32.8 (32.1)	1 107
(10) SnPh$_2$Cl$_2$·18-crown-6·2H$_2$O	88—95	44.2 (44.7)	5.8 (6.0)	11.2 (11.0)	18.9 (18.4)	1 104
(11) SnPh$_2$(NCS)$_2$·18-crown-6·2H$_2$O	140—148	44.7 (45.3)	5.4 (5.6)	*d*	17.8 (17.2)	1 100
(12) (SnPh$_3$Cl)$_2$·18-crown-6·2H$_2$O	117—120	52.8 (53.8)	5.6 (5.5)	6.4 (6.6)	21.3 (22.2)	1 102
(13) (SnPh$_3$Cl)$_2$·15-crown-5·2H$_2$O	99—105	53.5 (53.8)	5.6 (5.3)	6.8 (6.9)	23.2 (23.1)	1 105
(14) [SnPh$_3$(NCS)]$_2$·18-crown-6·2H$_2$O	110—132	51.6 (53.8)	5.5 (5.2)	*e*	20.3 (21.3)	1 107

[a] Calculated values are given in parentheses. [b] Values of ν_{asym}(C–O–C) in free crown ethers: 18-crown-6 (1 110 cm^{-1}); 15-crown-5 (1 134 cm^{-1}); and 12-crown-4 (1 100 cm^{-1}). The i.r. spectra all show a broad band in the region 3 200—3 400 cm^{-1} due to ν(O–H). [c] Not determined. [d] N, 4.1 (4.1); S, 9.0 (9.3)%. [e] N, 2.4 (2.5); S, 6.3 (5.7)%.

the samples were packed in Perspex discs and cooled to 80 K. Isomer shifts (δ) are relative to CaSnO$_3$, and the experimental error in the measured values of isomer shift and quadrupole splitting (Δ) parameters is ± 0.02 mm s^{-1}. Mössbauer data for the complexes are given in Table 2.

Crystal Structure Determination of Complex (7).—A crystal of approximate dimensions 0.10 × 0.15 × 0.38 mm was mounted with the *c* axis coincident with the ω axis of a Stöe Stadi 2 two-circle diffractometer.

Crystal data. $C_{13}H_{33}Cl_7O_{10}Sn$, $M = 716.3$, monoclinic, space group $P2_1/n$, $a = 10.315(6)$, $b = 13.630(8)$, $c = 20.649(13)$ Å, $\beta = 94.68(5)°$, $U = 2\,893.3$ Å^3, $D_m = 1.66$, $Z = 4$, $D_c = 1.64$ g cm^{-3}, $F(000) = 1\,440$, λ(Mo-K_α) = 0.710 69 Å, $\mu = 1.45$ mm^{-1}.

Data collection. Data were collected using the background–ω scan–background technique. Corrections for Lorentz and polarisation effects were applied, but not for absorption. Of the 4 578 unique reflections collected, 3 142 had $I \geqslant 3\sigma(I)$, and were used in the subsequent structure analysis.

Structure determination and refinement. Multisolution direct methods enabled the Sn(OH$_2$)$_2$Cl$_4$ unit to be located

Table 2. ^{119}Sn Mössbauer data (mm s^{-1})

Complex	δ	Δ	Complex	δ	Δ
(1) $SnCl_4 \cdot 18$-crown-$6 \cdot 2H_2O$	0.29	0.82	(10) $SnPh_2Cl_2 \cdot 18$-crown-$6 \cdot 2H_2O$	1.20	3.82
(2) $SnBr_4 \cdot 18$-crown-$6 \cdot 2H_2O$	0.54	0.80	(11) $SnPh_2(NCS)_2 \cdot 18$-crown-$6 \cdot 2H_2O$	1.10	4.03
(3) $SnCl_4 \cdot 15$-crown-$5 \cdot 2H_2O$	0.31	0.80	(12) $(SnPh_3Cl)_2 \cdot 18$-crown-$6 \cdot 2H_2O$	1.26	3.13
(4) $SnBr_4 \cdot 15$-crown-$5 \cdot 2H_2O$	0.53	0.90	(13) $(SnPh_3Cl)_2 \cdot 15$-crown-$5 \cdot 2H_2O$	1.27	3.14
(5) $SnCl_4 \cdot 12$-crown-$4 \cdot 2H_2O$	0.28	0.00	(14) $[SnPh_3(NCS)]_2 \cdot 18$-crown-$6 \cdot 2H_2O$	1.21	3.27
(6) $SnBr_4 \cdot 12$-crown-$4 \cdot 2H_2O$	0.62	0.00	$SnCl_4$	0.78 [a]	0.00 [a]
(7) $SnCl_4 \cdot 18$-crown-$6 \cdot 4H_2O \cdot CHCl_3$	0.26	0.00	$SnBr_4$	1.05 [a]	0.00 [a]
(8) $SnCl_4 \cdot 18$-crown-$6 \cdot 4H_2O$	0.27	0.00	$SnCl_4 \cdot$diglyme	0.49 [b]	1.10 [b]
(9) $(SnMe_2Cl_2)_2 \cdot 18$-crown-$6 \cdot 2H_2O$	1.43	3.94	$SnCl_4 \cdot MeO(CH_2)_2OMe$	0.51 [c]	0.80 [c]

[a] D. E. Williams and C. W. Kocher, *J. Chem. Phys.*, 1970, **52**, 1480. [b] Ref. 9. [c] Ref. 10.

Table 3. Bond distances (Å) and angles (°) for $Sn(OH_2)_2Cl_4 \cdot 18$-crown-$6 \cdot 2H_2O \cdot CHCl_3$, with estimated standard deviations in parentheses

Sn–Cl(1)	2.400(3)	Sn–Cl(4)	2.391(3)	Cl(1)–Sn–Cl(2)	93.3(1)	Cl(2)–Sn–O(2)	172.2(2)
Sn–Cl(2)	2.392(3)	Sn–O(1)	2.113(6)	Cl(1)–Sn–Cl(3)	169.7(1)	Cl(3)–Sn–Cl(4)	92.8(1)
Sn–Cl(3)	2.393(3)	Sn–O(2)	2.115(6)	Cl(1)–Sn–Cl(4)	93.3(1)	Cl(3)–Sn–O(1)	87.5(2)
C(16′)–O(11)	1.417(12)	C(26″)–O(21)	1.416(13)	Cl(1)–Sn–O(1)	85.8(2)	Cl(3)–Sn–O(2)	85.8(2)
O(11)–C(11)	1.388(12)	O(21)–C(21)	1.411(13)	Cl(1)–Sn–O(2)	85.6(2)	Cl(4)–Sn–O(1)	175.9(2)
C(11)–C(12)	1.485(17)	C(21)–C(22)	1.507(16)	Cl(2)–Sn–Cl(3)	94.4(1)	Cl(4)–Sn–O(2)	92.4(2)
C(12)–O(12)	1.441(14)	C(22)–O(22)	1.436(15)	Cl(2)–Sn–Cl(4)	95.3(1)	O(1)–Sn–O(2)	83.5(2)
O(12)–C(13)	1.409(12)	O(22)–C(23)	1.441(12)	Cl(2)–Sn–O(1)	88.8(2)	Cl(5)–C(1)–Cl(6)	107.9(7)
C(13)–C(14)	1.501(15)	C(23)–C(24)	1.444(17)	Cl(5)–C(1)–Cl(7)	107.3(7)	Cl(6)–C(1)–Cl(7)	108.3(8)
C(14)–O(13)	1.425(11)	C(24)–O(23)	1.407(12)	C(16′)–O(11)–C(11)	111.5(7)	C(26″)–O(21)–C(21)	111.6(9)
O(13)–C(15)	1.442(13)	O(23)–C(25)	1.469(15)	O(11)–C(11)–C(12)	109.0(9)	O(21)–C(21)–C(22)	111.4(9)
C(15)–C(16)	1.537(15)	C(25)–C(26)	1.477(17)	C(11)–C(12)–O(12)	110.1(9)	C(21)–C(22)–O(22)	108.2(9)
C(1)–Cl(5)	1.752(14)	C(1)–Cl(6)	1.792(15)	C(12)–O(12)–C(13)	114.6(7)	C(22)–O(22)–C(23)	113.3(8)
C(1)–Cl(7)	1.746(16)			O(12)–C(13)–C(14)	109.7(8)	O(22)–C(23)–C(24)	108.6(9)
				C(13)–C(14)–O(13)	109.1(8)	C(23)–C(24)–O(23)	112.0(10)
				C(14)–O(13)–C(15)	109.3(7)	C(24)–O(23)–C(25)	112.5(9)
				O(13)–C(15)–C(16)	108.9(9)	O(23)–C(25)–C(26)	107.8(10)
				C(15)–C(16)–O(11′)	109.9(8)	C(25)–C(26)–O(21″)	110.3(10)

Symmetry codes: (′) $1 - x, -y, 1 - z$; (″) $1 - x, 1 - y, 1 - z$.

and revealed the presence of two independent crown ether molecules, each containing a centre of symmetry. Thus, in the early stages of the analysis, the asymmetric unit appeared to consist of $Sn(OH_2)_2Cl_4$ and two half-crown fragments. However, successive difference electron-density maps revealed the presence of two further water molecules and a chloroform molecule in the asymmetric unit. Only the ether hydrogen atoms could be satisfactorily located and they were not refined, but included in positions calculated from the geometry of the molecule. Common isotropic thermal parameters were applied to the sets of hydrogen atoms associated with the crown ether molecules and refined to final values of $U = 0.085(10)$ and 0.103(12) Å^2. Scattering factors were calculated using an analytical approximation,[7] and the weighting scheme adopted was $w = 2.1249/[\sigma^2(F_o) + 0.0019(F_o)^2]$. Full-matrix refinement with anisotropic thermal parameters for all non-hydrogen atoms gave the final $R = 0.062$ and $R' = 0.068$.

The molecular structure of compound (7) is shown in the Figure. The bond distances and angles are given in Table 3, short O · · · O contacts in Table 4, and the final fractional atomic co-ordinates in Table 5.

Results and Discussion

Inorganic Tin(IV) *Complexes*.—The inorganic tin(IV) halide crown ether adducts crystallise from methanol or methanol–chloroform (1 : 1 v/v) solution as the dihydrates (1)—(6), and all show a broad ν(O–H) stretching band in their i.r. spectra at *ca.* 3 400 cm^{-1}. However, recrystallisation of (1), either from methanol-chloroform (1 : 1 v/v) solution or from methanol, results in further hydration to give the compounds (7) and (8), respectively (Table 1).

Table 4. Short O · · · O contacts (Å); estimated standard deviations *ca.* 0.008 Å

O(1) · · · O(4)	2.520	O(2) · · · O(3)	2.569
O(1) · · · O(12′)	2.667	O(2) · · · O(22″)	2.647
O(4) · · · O(11)	2.884	O(3) · · · O(21)	2.888
O(4) · · · O(12)	3.053	O(3) · · · O(22)	3.097
O(4) · · · O(13)	2.848	O(3) · · · O(23)	2.967

The ^{119}Sn Mössbauer isomer shifts for the new compounds (1)—(8) are lower than those of the corresponding uncomplexed tin(IV) halide (Table 2), and are consistent with adduct formation involving oxygen donor atoms, either from the crown ether ligand or from the water molecules of hydration. In addition, the values of δ are significantly lower than those which are generally observed for other SnX_4 adducts with O-donor ligands,[8] implying that the O→Sn interactions are relatively strong in these complexes.

Interestingly, compounds (1)—(4) show a quadrupole-split doublet in their Mössbauer spectra, whereas the 12-crown-4 complexes (5) and (6) and the recrystallised 18-crown-6 adducts (7) and (8) give rise to a single resonance. Gustavson and Zuckerman [9] have suggested that, for octahedral tin(IV) halide adducts with O-donor ligands, a *cis* configuration of the oxygen atoms leads to an unresolved Mössbauer quadrupole splitting, but a *trans* arrangement gives a resolvable doublet; a *trans* configuration was therefore assigned [9] to $SnCl_4 \cdot$diglyme, which gives a Δ value of 1.10 mm s^{-1} (Table 2). Additionally, the Mössbauer resonance for the 1 : 1 complex of $SnCl_4$ with the aliphatic diether 1,2-dimethoxyethane shows a small splitting (Table 2), and this is presumably

Table 5. Final fractional co-ordinates (Sn, × 10^5; other atoms, × 10^4) for non-hydrogen atoms, with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Sn	18 714(6)	24 124(4)	37 943(3)	O(22)	5 657(7)	5 160(5)	6 425(3)
Cl(1)	3 000(3)	2 602(2)	2 831(1)	O(23)	6 931(7)	3 865(5)	5 622(3)
Cl(2)	562(3)	1 091(2)	3 345(1)	C(1)	7 094(14)	2 275(10)	1 515(7)
Cl(3)	1 122(3)	2 263(2)	4 857(1)	C(11)	4 692(12)	84(9)	6 780(4)
Cl(4)	328(3)	3 670(2)	3 483(1)	C(12)	5 761(12)	805(9)	6 737(5)
Cl(5)	8 221(4)	2 271(3)	2 197(2)	C(13)	7 528(11)	1 208(7)	6 099(5)
Cl(6)	6 220(6)	1 138(5)	1 504(3)	C(14)	8 231(10)	863(8)	5 532(4)
Cl(7)	5 997(6)	3 227(5)	1 618(2)	C(15)	8 014(11)	515(9)	4 420(5)
O(1)	3 333(7)	1 382(4)	4 089(3)	C(16)	7 099(12)	613(9)	3 798(5)
O(2)	3 228(7)	3 436(4)	4 220(3)	C(21)	3 779(13)	6 179(8)	6 428(5)
O(3)	4 057(8)	3 932(5)	5 380(3)	C(22)	4 571(12)	5 395(9)	6 790(5)
O(4)	4 707(7)	1 295(5)	5 154(3)	C(23)	6 378(13)	4 314(7)	6 670(5)
O(11)	3 916(7)	86(5)	6 198(3)	C(24)	7 412(12)	4 125(8)	6 256(5)
O(12)	6 594(6)	506(4)	6 246(3)	C(25)	7 966(13)	3 780(10)	5 176(6)
O(13)	7 351(7)	864(5)	4 963(3)	C(26)	7 376(14)	3 390(9)	4 553(6)
O(21)	3 343(8)	5 868(5)	5 795(4)				

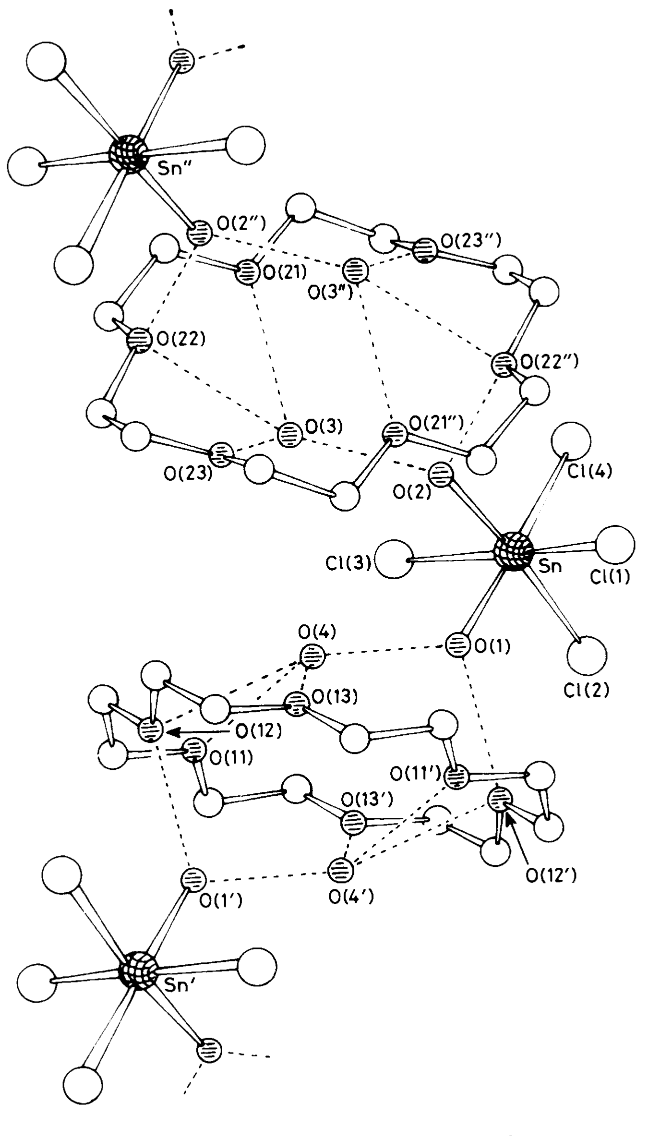


Figure. Part of the crystal structure of $Sn(OH_2)_2Cl_4$·18-crown-6·$2H_2O$·$CHCl_3$, in which the dotted lines indicate short oxygen–oxygen contacts (Table 4). For clarity, hydrogen atoms and the chloroform molecules have been omitted

indicative of a similar *trans*-octahedral stereochemistry.[10] A parallel relationship appears to hold for octahedral tin(IV) halide adducts with alcohol donor ligands, SnX_4·2ROH.[11]

Hence, the Mössbauer parameters for the tin(IV) crown ether adducts (1)—(4) indicate a *trans*-SnX_4L_2 arrangement, where L may be *either* (*a*) an oxygen atom of a crown ether ligand *or* (*b*) a water molecule, which may then be involved in hydrogen bonding with the crown ether molecule as in the case of the *cis*-diaqua compound (7) described below. It is difficult on the available evidence to distinguish between these possibilities. However, in all known examples of the type $SnX_4(OH_2)_2$ a *cis*-diaqa configuration has been established.[12] Hence, in the above case, it is possible that the water molecules do not enter into the co-ordination sphere of the tin [as has been demonstrated crystallographically [13] for $SnCl_4$·Hpipox·$2H_2O$ (Hpipox = *N*-pyridoxylidene-*N'*-picolinoylhydrazine*)], and that the polyethers 18-crown-6 and 15-crown-5 act as bridging ligands between planar SnX_4 units to give a polymeric structure, in which the tin atoms occupy *trans*-octahedral sites, as proposed for $SnCl_4$·diglyme.[9]

In contrast to these results, the 12-crown-4 complexes (5) and (6) and the recrystallised 18-crown-6 adducts (7) and (8), which show a single Mössbauer line, presumably contain a *cis*-octahedral SnX_4L_2 unit, in which the less sterically hindered water molecules are co-ordinated to the tin atom. Similar tin atom environments are found in $SnCl_4(OH_2)_2$·2(1,4-dioxane) [14] and $SnCl_4(OH_2)_2$·$3H_2O$,[15] both of which display single Mössbauer resonances.[11]

The i.r. spectra of complexes (1)—(8) show shifts of the ν_{asym}(C–O–C) stretching vibration to lower frequency (Table 1), indicating that (*a*) the tin atom interacts with two (or more) of the polyether oxygen atoms or (*b*) significant hydrogen bonding occurs between the oxygen atoms and the water molecules in the complex. A similar reduction in ν_{asym}(C–O–C) has been observed by Herber and Smelkinson [2] for tin(II) complexes of 18-crown-6.

In an attempt to isolate crystals of the dihydrate (1) for single-crystal *X*-ray analysis, recrystallisation of this complex from methanol–chloroform (1 : 1 v/v) led to the formation of a chloroform solvate (7), and, from methanol, gave the tetrahydrate (8). Crystals of the former, (7), were found to be suitable for the *X*-ray study. The *X*-ray analysis of complex

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* *N*-(3-hydroxy-5-hydroxymethyl-2-methylpyridyl)methylidene-*N'*-(2-pyridylcarbonyl)hydrazine.

(7) confirms that the sample recrystallised from methanol–chloroform solution does contain octahedral $Sn(OH_2)_2Cl_4$ units, in which the two water molecules occupy *cis* positions (Figure). The co-ordination polyhedron about tin is somewhat distorted, in that the angles between the *cis* ligands range from 83.5(2) to 95.3(1)°, while those between the *trans* ligands vary from 169.7(1) to 175.9(2)° (Table 3). The Sn–Cl bond lengths are in the range 2.391(3)—2.400(3) Å and the Sn–O distances are 2.113(6) and 2.115(6) Å, which are similar to those in $SnCl_4·5H_2O$,[15] *viz.* Sn–Cl 2.383(5)—2.401(4) Å and Sn–O 2.098(14) Å, which also contains a *cis*-$Sn(OH_2)_2Cl_4$ unit.

The water molecules co-ordinated to tin appear to be involved in an extensive hydrogen-bonding scheme (Figure). Thus, O(1) and O(2) are each involved in two short oxygen–oxygen contacts (Table 4), one to an ether oxygen [O(1) ··· O(12′) 2.667, O(2) ··· O(22″) 2.647 Å] and the other to an unco-ordinated water molecule [O(1) ··· O(4) 2.520, O(2) ··· O(3) 2.569 Å]. The oxygens in the unco-ordinated water molecules [O(3) and O(4)] are, in addition, each found to be almost equidistant from three of the oxygen atoms within adjacent crown ether ligands. Although these O ··· O distances, which range from 2.848 to 3.097 Å, are considerably longer than those to O(1) and O(2), they nevertheless indicate the presence of significant hydrogen bonding. The centrosymmetric nature of both crown ethers is such that each macrocyclic unit is associated with four water molecules (Figure), linked *via* hydrogen bonding, to give chains which run parallel to the *b* axis. The chloroform molecules are located in the channels between these hydrogen-bonded chains.

Although crystallographically independent, the two crown ether molecules adopt very similar conformations, and the values of the C–O–C–C and O–C–C–O torsion angles [58.4—75.7(12) and 171.0—178.9(9)°, respectively] would indicate that both conformations are relatively strain-free.

Hence, the structure of this inorganic tin(IV) crown ether complex is clearly very similar to those of the transition metal–water–crown ether adducts,[1] in which the macrocyclic polyether is functioning as a second-sphere ligand.

Organotin(IV) *Complexes.*—The organotin(IV) crown ether complexes crystallise from methanol solution as the dihydrates (9)—(14), and show a broad ν(O–H) stretching band in their i.r. spectra in the region 3 200—3 400 cm^{-1}.

The triphenyltin chloride and isothiocyanate adducts (12)—(14) show, in their Mössbauer spectra, Δ values (3.13—3.27 mm s^{-1}) which are indicative[16] of trigonal-bipyramidal stereochemistries for each tin atom, with planar Ph_3Sn units; the axial sites are therefore occupied by a chlorine atom and an oxygen from a water molecule, with the crown ether presumably being bound to the resulting $Ph_3SnX(H_2O)$ units by hydrogen bonds. It is interesting to note that the same $Ph_3SnX(H_2O)$ grouping has recently been identified crystallographically in $SnPh_3Cl·terpy·H_2O$[17] and in $SnPh_3(NCS)·terpy·H_2O$.[18] The dimethyl- and diphenyl-tin adducts (9)—(11) show Δ values in the range 3.82—4.03 mm s^{-1}, which are characteristic[16] of octahedral tin atom geometries, with *trans* organic groups, and, in the case of the diphenyltin dichloride derivative (10), the presence of a single Sn–Cl i.r. stretching vibration (at 258 cm^{-1}) suggests a linear Cl–Sn–Cl unit. Hence, this complex, and probably its isothiocyanate analogue (11), in the solid state, are likely to consist of *trans*-octahedral $Ph_2SnX_2(H_2O)_2$ molecules, which are linked to the crown ethers *via* a network of hydrogen bonds. A similar *trans*-R_2SnX_4 octahedral tin atom environment is indicated for the dimethyltin compound (9), which shows a single ν(Sn–Cl) band at 263 cm^{-1} in its i.r. spectrum. Recent *X*-ray studies[19] on the dimethyltin dichloride adduct $(SnMe_2Cl_2)_2·18\text{-crown-}6·2H_2O$ have confirmed that the crown ether molecules are not directly co-ordinated to the tin atom, but are held by hydrogen bonds to dimeric, chlorine-bridged, octahedral *trans*-$Me_2SnCl_2(H_2O)$ units. The isomer-shift values of the isothiocyanate complexes (11) and (14) are lower than those of their corresponding organotin chloride analogues (10) and (12), in accordance with the stronger electron-withdrawing power of the NCS group. The organotin complexes show, in their i.r. spectra, similar reductions in the ν_{asym}(C–O–C) stretching frequency to those observed for the inorganic tin(IV) adducts (Table 1).

Acknowledgements

We thank the International Tin Research Council, London, for permission to publish this paper, Professor J. J. Zuckerman, Oklahoma State University, for generously communicating *X*-ray structural results in advance of publication, the S.E.R.C. for an equipment grant (to I. W. N.), and the Analytical Department, International Tin Research Institute, for tin analyses.

References

1 H. M. Colquhoun, D. F. Lewis, J. F. Stoddart, and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1983, 607 and refs. therein.
2 R. H. Herber and A. E. Smelkinson, *Inorg. Chem.*, 1978, **17**, 1023.
3 R. H. Herber and G. Carrasquillo, *Inorg. Chem.*, 1981, **20**, 3693.
4 E. N. Gur'yanova, L. A. Ganyushin, I. P. Romm, E. S. Scherbakova, and M. Movsum-zade, *J. Gen. Chem. USSR*, 1981, **51**, 356.
5 P. A. Cusack, B. N. Patel, and P. J. Smith, *Inorg. Chim. Acta*, 1983, **76**, L21.
6 P. J. Smith and B. N. Patel, *J. Organomet. Chem.*, 1983, **243**, C73.
7 'International Tables for *X*-Ray Crystallography,' 2nd edn., Kynoch Press, Birmingham, 1974, vol. 4.
8 J. N. R. Ruddick, *Rev. Silicon, Germanium, Tin, Lead Cmpd.*, 1976, **2**, 115.
9 W. A. Gustavson and J. J. Zuckerman, *Synth. React. Inorg. Metal-Org. Chem.*, 1981, **11**, 47.
10 J. Philip, M. A. Mullins, and C. Curran, *Inorg. Chem.*, 1968, **7**, 1895.
11 S. J. Blunden, P. A. Cusack, P. J. Smith, and P. W. C. Barnard, *Inorg. Chim. Acta*, 1983, **72**, 217.
12 P. A. Cusack, P. J. Smith, J. D. Donaldson, and S. M. Grimes, 'A Bibliography of X-ray Crystal Structures of Tin Compounds,' No. 588, International Tin Research Institute, 1981.
13 P. Domiano, A. Musatti, M. Nardelli, C. Pelizzi, and G. Predieri, *Inorg. Chim. Acta*, 1980, **38**, 9.
14 J. C. Barnes and T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.*, 1976, 1786.
15 J. C. Barnes, H. A. Sampson, and T. J. R. Weakley, *J. Chem. Soc., Dalton Trans.*, 1980, 949.
16 A. G. Davies and P. J. Smith, in 'Comprehensive Organometallic Chemistry,' ed. G. Wilkinson, Pergamon Press, Oxford, 1982, vol. 2, p. 519.
17 L. Prasad, F. L. Lee, Y. Le Page, and F. E. Smith, *Acta Crystallogr., Sect. B*, 1982, **38**, 259.
18 L. Prasad and F. E. Smith, *Acta Crystallogr., Sect. B*, 1982, **38**, 1815.
19 J. J. Zuckerman, personal communication, 1983.

Received 15*th September* 1983; *Paper* 3/1623