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REVIEW

Crown ethers in tin chemistry

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This article comprehensively reviews the literature concerning the adducts formed between crown ethers and organotin(IV), inorganic tin(IV) and inorganic tin(II) species, and it also covers organotin(II) complexes containing alkali metal–crown ether cations. The uses of crown ethers as co-catalysts in organic and organotin synthesis are surveyed and some potential industrial applications of crown ether/tin chemical systems are discussed.

Keywords: Organotin compounds, inorganic tin compounds, crown ethers, Mössbauer spectroscopy

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INTRODUCTION

Inorganic tin(IV) halides and inorganic tin(II) halides form addition complexes of the type $SnX_4.L_2^{1,2}$, $SnX_4.L^{1,2}$ and $SnX_2.L^2$ with simple ethers, whereas their organotin(IV) counterparts (R_nSnX_{4-n}), which are generally weaker Lewis acids, form a limited number of these adducts.[3–6]

In recent years there has been considerable interest in the reactions of crown ethers with organometallic and inorganic species,[6a] and in this paper the chemistry, structure and applications of compounds of this type involving tin are reviewed. The structures of the following common crown ethers are illustrated in Fig. 1:

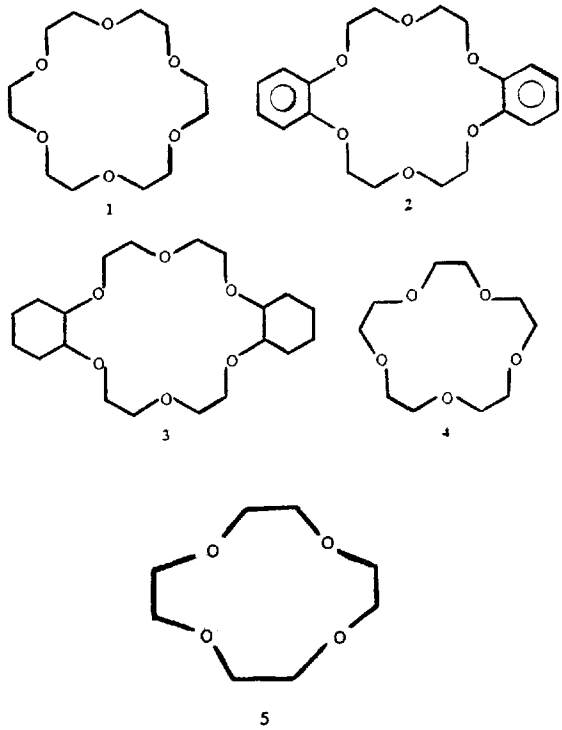


Figure 1 Structures of common crown ethers.

(**1**) 18-crown-6 (18-cr-6);
(**2**) dibenzo-18-crown-6 ($Bz_2$18-cr-6);
(**3**) dicyclohexano-18-crown-6 ($Cy_2$18-cr-6);
(**4**) 15-crown-5 (15-cr-5);
(**5**) 12-crown-4 (12-cr-4).

ORGANOTIN(IV) COMPLEXES OF CROWN ETHERS

Triphenyltin chloride and isothiocyanate form adducts of the type $[Ph_3SnX(H_2O)]_2.L$, with 18-cr-6 or 15-cr-5.[7] ^{119m}Sn Mössbauer spectroscopic

studies are indicative of trigonal bipyramidal stereochemistry for each tin atom, with planar Ph_3Sn units; the axial sites are occupied by a chlorine atom (or a pseudohalide group) and an oxygen atom from a water molecule, with the crown ether suggested to be bound to the resulting $Ph_3SnX(H_2O)$ units by hydrogen bonds. On the basis of the changes in their UV spectra, crown ethers derived from β-cyclodextrin were concluded[8] to interact with triphenyltin acetate and bis(trineophyltin) oxide (neophyl = $PhMe_2CCH_2$—), but no discrete complexes were isolated. It is interesting to note that triphenyltin trichloroacetate has recently been shown to form a solid 1:1 adduct with methanol ($Ph_3SnOCOCCl_3.MeOH$), in which the oxygen atom of the alcohol ligand is coordinated to the tin.[9]

Considering the diorganotin(IV) complexes of crown ethers, a number of these have been synthesized and their stoichiometry is summarized in Table 1.

X-ray crystal structures have been determined for five of these adducts, viz. $[Me_2SnCl_2(H_2O)]_2.L$, where L = 18-cr-6,[10] 15-cr-5[15] or $Cy_2$18-cr-6,[10] $Me_2Sn(NCS)_2(H_2O)_2$.18-cr-6[11] and $Me_2SnCl_2(H_2O)_2$.15-cr-5,[10] and these indicate that the crown ether oxygen atoms are not directly coordinated to tin, but are hydrogen-bonded to the water molecules (which are, in turn, complexed to the metal via oxygen).

The only monoalkyltin(IV) complexes of crown ethers so far reported[13] are $MeSnCl_3(H_2O)_2$.18-cr-6 and $[MeSnCl_3(H_2O)]_2$.$Cy_2$18-cr-6, which, on the basis of IR and Mössbauer data, were proposed to have an octahedral coordination geometry at the tin centre. It was not possible, however, to conclude whether the water or crown ether oxygen atoms were coordinated to the tin.

Table 1 Diorganotin(IV) complexes of crown ethers

Complex	R	X	L[a]	δ[b]	ΔE_Q[b]
$R_2SnX_2(H_2O)_2.L$	Ph	Cl	18-cr-6	1.20	3.82[7]
	Ph	NCS	18-cr-6	1.10	4.03[7]
	Me	Cl	15-cr-5[10]	—	—
	Me	NCS	18-cr-6[11]	1.34	4.37[12]
$[R_2SnX_2(H_2O)]_2.L$	Me	Cl	18-cr-6[10]	1.43	3.94[7]
				1.48	3.93[13]
				1.59	3.93[14]
	Me	Cl	$Cy_2$18-Cr-6[10]	1.37	3.46[13]
	Me	Cl	15-cr-5[15]	—	—
$[R_2Sn(H_2O)_4.L]X_2$	Me	ClO_4	18-cr-6	1.27	4.14[12]
$[R_2Sn(H_2O)_4.L_2]X_2$	Me	ClO_4	12-cr-4	1.30	4.52[12]
	Me	ClO_4	15-cr-5	1.31	4.42[12]
$R_2SnX_2(H_2O)_2.L_2$	Me	NCS	12-cr-4	1.35	4.22[12]
	Me	NCS	15-cr-5	1.28	4.07[12]

[a]Superscript indicates X-ray reference [b]Mössbauer data in mm s^{-1} (δ relative to SnO_2).

Table 2 Inorganic tin(IV) complexes of crown ethers

Complex	X	L[a]	δ[b]	ΔE_Q[b]
$SnX_4.L$	Cl	18-cr-6[16]	—	—
$(SnX_4)_2.L$[17]	Cl	$Bz_2$24-cr-8	—	—
$SnX_4(H_2O)_2.L$	Cl	18-cr-6	0.29	0.82[7]
			0.34	0.49[13]
	Br	18-cr-6	0.54	0.80[7]
	Cl	$Bz_2$18-cr-6	0.43	0.63[13]
	Cl	15-cr-5[18]	0.31	0.80[7]
	Br	15-cr-5	0.53	0.90[7]
	Cl	12-cr-4	0.28	0[7]
	Br	12-cr-4	0.62	0[7]
$[SnX_4(H_2O)]_2.L$	Cl	$Cy_2$18-cr-6	0.51	0.80[13]
$SnX_4(H_2O)_2.L.2H_2O$	Cl	18-cr-6[19]	0.27	0[7]
$SnX_4(H_2O)_2.L.2H_2O.CHCl_3$	Cl	18-cr-6[7]	0.26	0[7]
$(H_3O)_2(SnX_6).L$	Cl	18-cr-6[20]	—	—

[a]Superscript indicates X-ray reference. [b]Mössbauer data in mm s^{-1}

INORGANIC TIN(IV) COMPLEXES OF CROWN ETHERS

The known tin(IV) halide complexes of crown ethers are listed in Table 2.

The X-ray structure of the anhydrous adduct, $SnCl_4$.18-cr-6 (Fig. 2a), shows[16] that the macrocycle functions as a bidentate ligand, with the tin atom occupying an octahedral geometry; a similar stereochemistry at the tin centre has been proposed[17] for $(SnCl_4)_2.Bz_2$24-cr-6.

In contrast with these structures, a number of hydrated complexes of tin(IV) halides with crown ethers have been prepared and, in these, the water molecules are directly coordinated to the tin atom.

Interestingly, Mössbauer spectroscopy has proved to be informative in elucidating the disposition of the water ligands in these complexes; those complexes in which the water molecules are in a *cis* configuration give no resolvable quadrupole splitting, whereas *trans*-coordinated complexes give distinct two-line spectra (Table 2). This relationship has been confirmed by single

crystal X-ray determinations and (in Fig. 2b) the structure[7] of *cis*-$SnCl_4(H_2O)_2$.18-cr-6.$2H_2O$.$CHCl_3$ is illustrated.

Recent studies by Bel'skii and co-workers[21] have shown that the reaction of tin(IV) chloride ($SnCl_4$) with 15-cr-5 in anhydrous acetonitrile leads to cleavage of the crown ether ring, with elimination of $C_2H_4Cl_2$, to form an unusual bimetallic tin(IV) complex with a stoichiometry corresponding to $C_8H_{16}O_5.SnCl_2.SnCl_4.MeCN$. The X-ray structure[21] of this adduct reveals that one of the —OCH_2CH_2O—groups in the polyether macrocycle is replaced by a *cis* octahedral —$OSnCl_4O$— fragment and that the five oxygen atoms form donor bonds to a central *trans* Cl_2Sn^{2+} unit. The Mössbauer spectrum shows a single tin(IV) resonance, with $\delta = 0.15$ mm s^{-1}. The two Sn–O bond lengths involving the ring-substituted tin atom [2.149(8) Å][21] are shorter than those in the adduct, $SnCl_4$.18-cr-6 [2.212(4) and 2.237(4) Å],[16] due to the latter being donor bonds. This appears to be the only tin(IV)–crown ether complex which has been conclusively established to contain the metal atom inside the macrocycle.

INORGANIC TIN(II) COMPLEXES OF CROWN ETHERS

A series of ionic tin(II) complexes has been synthesized in which the tin(II) moiety interacts directly with the crown ligand (Table 3).

Herber and his co-workers[23,24] have used Mössbauer spectroscopy to show that the stoichiometry of the tin(II)–crown ether complexes formed is dependent on the chemical nature of the anion of the tin(II) salt. Tin(II) chloride and tin(II) isothiocyanate form complexes in which there are two distinct tin sites per molecule, comprising a cationic moiety bonded to the crown ether, with an anionic group (SnX_3^-), present as a gegenion. However, tin(II) perchlorate reacts with crown ethers to give products which contain only one tin site per molecule, and this is ascribed to the existence of a 'bare' tin(II) ion, which is bonded to either one or two crown ether molecules. This tin site is characterized by a sharp singlet Mössbauer spectrum and has an isomer shift which is among the most positive recorded for a tin(II) species. X-ray crystallographic studies have shown that the tin(II) atom can occupy either a hexagonal pyramidal site, in which the metal is bonded to the crown oxygens and an axial chlorine atom [for $(SnCl.18\text{-cr-}6)^+$],[22] or it is sandwiched between two polyether rings [for $Sn(15\text{-cr-}5)_2^{2+}$].[25] Extended X-ray absorption fine structure (EXFAS) studies on $SnCl_2$ complexes of 12-cr-4 and 15-cr-5 in methanol have recently been reported.[25a]

ORGANOTIN(II) COMPLEXES WITH ALKALI METAL–CROWN CATIONS

The addition of hexaphenylditin (PR_6Sn_2) to a mixture of sodium in liquid ammonia containing

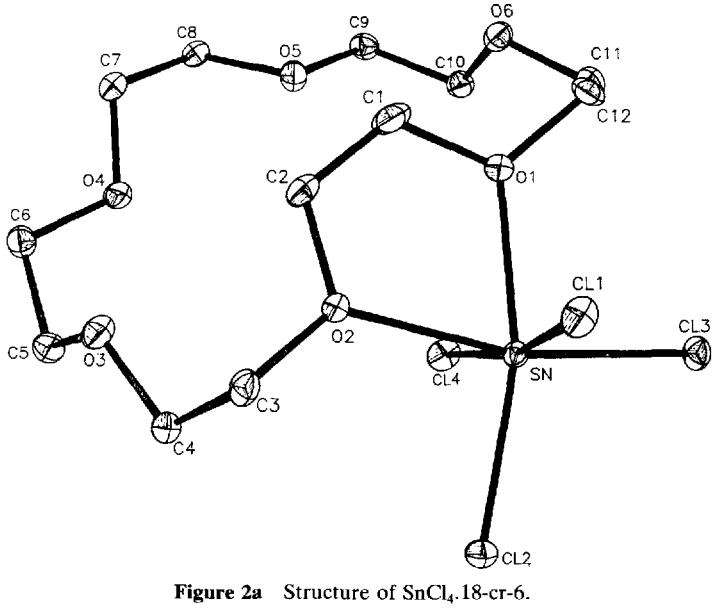


Figure 2a Structure of $SnCl_4$.18-cr-6.

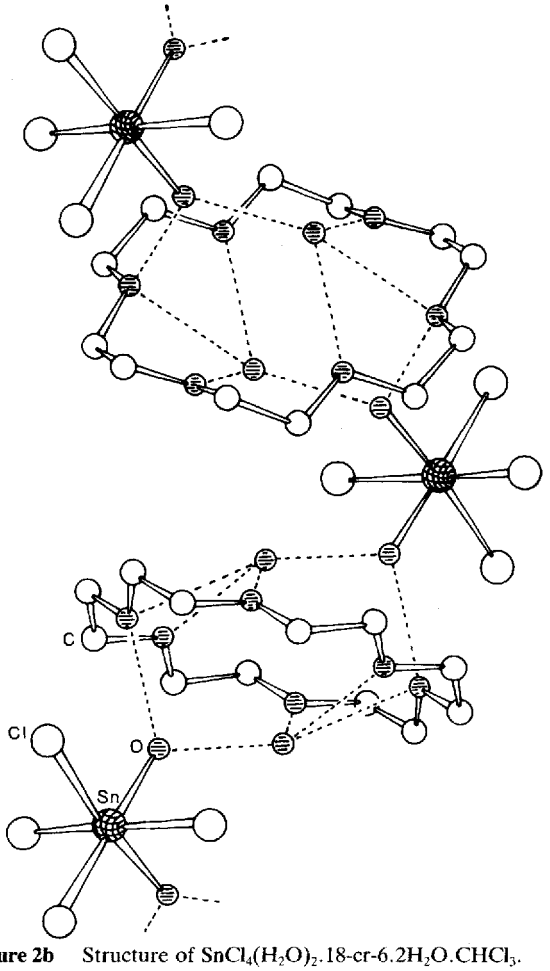


Figure 2b Structure of $SnCl_4(H_2O)_2.18\text{-cr-}6.2H_2O.CHCl_3$.

15-cr-5 gave[26] the complex, [Na(15-cr-5)]$SnPh_3$ (Eqn[1]):

$$(Ph_3Sn)_2 + 2Na \xrightarrow{NH_3} + 2(15\text{-cr-}5) \rightarrow 2[Na(15\text{-cr-}5)]SnPh_3 \; [1]$$

The complex [K(18-cr-6)]$SnPh_3$ was prepared[26] in a similar manner and a subsequent investigation[27] of its structure by X-ray crystallography showed the presence of pyramidal $Ph_3Sn(II)$ anions, together with cations in which the six crown ether oxygen atoms are coordinated to the potassium ion. A closely related, 'naked', triorganotin(II) anion has been demonstrated[28] recently in the complex $[Li(diox)_4]^+[Sn(2\text{-furyl})_3Li(2\text{-furyl})_3Sn]^-$. The Mössbauer spectrum of the triphenylstannide ion in the complex [K(18-cr-6)]$SnPh_3$ consists[27] of a symmetrical doublet with $\delta = 2.13\ mm\ s^{-1}$ and $\Delta E_Q = 1.86\ mm\ s^{-1}$, the large quadrupole splitting being consistent with the low symmetry at the tin nucleus. The X-ray structure of a related inorganic tin(IV) complex containing an alkali metal–crown cation, [Na(15-cr-5)][$PhC(NSiMe_3)_2$-$SnCl_3F$], has recently been determined.[28a]

SYNTHETIC INTERMEDIATES

Crown ethers as co-catalysts

The alkali metal ion-crown chelates described in the previous section form the basis of the alkali metal salt–crown ether phase-transfer catalysts[29,30] and these have found a number of synthetic applications in organotin (and organic) chemistry.

(a) Crown ether + potassium iodide

Ugo *et al.* have shown[31] that, using a catalytic system formed by $Bz_2$18-cr-6, 18-cr-6 or $CR_2$18-cr-6 and potassium iodide, the direct reaction of metallic tin with alkyl halides in dimethylformamide to form dialkyltin dihalides (Eqn [2]) occurs at relatively low temperatures (80–120°C) and with selectivities as high as 95–99%. If activated alkyl halides, such as ethyl bromoacetate

Table 3 Inorganic tin(II) complexes of crown ethers

Complex	X	Y	L[a]	δ^b	ΔE_Q^b	δ^c	ΔE_Q^c
$(SnX.L)^+(SnX_3)^-$	Cl	—	18-cr-6[22]	3.89	2.11	3.30	0.99[23]
	NCS	—	18-cr-6	4.14	1.42	3.26	1.70[23]
	NCS	—	$Bz_2$18-cr-6	3.81	1.93	3.45	1.22[23]
$(SnX.L)^+Y^-$	Cl	ClO_4	18-cr-6[22]	—	—	—	—
$(Sn.L_2)^{2+}2Y^-$	—		18-cr-6	4.45	0[23]	—	—
	—	ClO_4	15-cr-5	4.53	0[24]	—	—
$(Sn.L_2)^{2+}(SnX_3)_2^-$	Cl	—	15-cr-5[25]	4.59	0	3.43	1.16[24]
	NCS	—	15-cr-5	4.54	0	3.43	1.16[24]

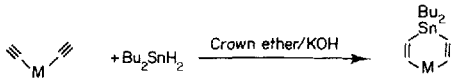
[a]Superscript indicates X-ray reference. [b]Mössbauer data for cation, in $mm\ s^{-1}$. [c]Mössbauer data for anion, in $mm\ s^{-1}$.

or allyl bromide, are employed, the crown ether alone will function as an effective catalyst for the synthesis of the corresponding dialkyltin dibromides.[32]

$$Sn + 2RX \xrightarrow[R=Bu,Oct;X=Cl,Br]{\text{Crown ether/KI}} R_2SnX_2 \quad [2]$$

(b) Crown ether + potassium hydroxide (or sodium hydroxide)

The phase-transfer catalysed interfacial reaction of the polysaccharide, dextran, with dibutyltin dichloride, in the presence of 18-cr-6/NaOH or $Bz_2$18-cr-6/NaOH, to form *O*-dibutylstannylated carbohydrate polymers, has been demonstrated by Carraher and his co-workers,[33] whilst Märkl *et al.* found[34] that the cycloaddition of dibutyltin dihydride to carbon or heteroatom penta-1,4-diynes is catalysed by 18-cr-6/KOH (Eqn[3]).



$$M = CR(OMe),\ P^tBu \text{ or } SiR_2 \quad [3]$$

(c) Crown ether + potassium fluoride (or caesium fluoride)

In the presence of potassium fluoride and a catalytic amount of 18-cr-6, *C*-trimethylstannylimines react with organic halides to form the corresponding ketimines[35] (Eqn [4]).

$$Ph(Me_3Sn)C{:}NPh + RX \xrightarrow{\text{Crown ether/KF}} PhCR{:}NPh + Me_3SnX \quad [4]$$

Caesium fluoride and a catalytic amount of 18-cr-6 will fluorodestannylate bis(triorganotin) chalcogenides [$(R_3Sn)_2Y$ where Y = O, S or Se] to liberate the nucleophilic chalcogenide anion(Y^{2-}) which, in the presence of alkyl halides, generates ethers, thioethers or organic selenides[36,37] (Eqn [5]):

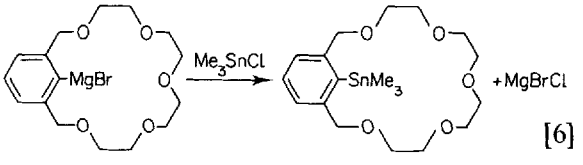
$$(R_3Sn)_2Y + 2R'X + 2CsF \xrightarrow{\text{Crown ether}} R'_2Y + 2R_3SnF + 2CsX \quad [5]$$

(d) Crown ether + tributyltin chloride

Alkyl and aryl halides may be reduced by suspensions of sodium borohydride in toluene to yield hydrocarbons in high yield by utilizing benzo-15-crown-5 and tributyltin chloride (rather than an alkali metal halide) as co-catalysts.[38] The crown ether acts as a phase-transfer catalyst to form tributyltin hydride from tributyltin chloride in toluene and the organotin hydride[39] reduces the organic halide. This work has recently been extended by binding the organotin chloride to polyethylene or polystyrene and the resulting polymer-bound tin halide is used as a co-catalyst with benzo-15-crown-5 for the sodium borohydride reduction.[40]

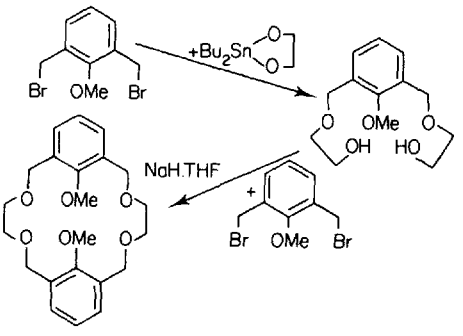
Crown ether chemistry

Treatment of the Grignard reagent derived from 2-bromo-1,3-xylyl-18-crown-5 with trimethyltin chloride for 3 h at 50°C gave 2-trimethylstannyl-1, 3-xylyl-18-crown-5 in 17% yield.[41] This reaction did not occur at 25°C, which was taken as an indication of steric hindrance in the starting material (Eqn [6]).



[6]

Organotin compounds may be utilized as intermediates for the synthesis of macrocyclic polyethers, particularly the dibutylstannylene derivatives of vicinal diols. Treatment[42] of 2.6-bis(bromomethyl)anisole with the dibutylstannylene derivative of ethylene glycol in a 2:1 molar ratio in hot dimethylformamide (DMF), followed by an aqueous work-up, furnished the intermediate diol in high yield. In the second step, this unpurified diol was exposed to sodium hydride, followed by the anisole dibromide, in tetrahydrofuran (THF) to produce the dimeric macrocycle in 60% yield (Scheme 1).



Stannic chloride has been shown[43,44] to be an effective homogeneous catalyst for cyclopolymerization reactions to form various types of polymers containing crown ether units.

APPLICATIONS

Although (to the authors' knowledge) the various crown ether/tin chemical combinations described in this review are not currently used in industry, a number of possible applications for these systems have been proposed.

In the synthesis of halogenated polymers, for example, it has been found[45] that formulations containing a tin(IV) tetramercaptide and a crown ether are effective heat stabilisers for poly(vinyl chloride) (PVC). Tetraphenyltin and 18-cr-6 mixtures have potential applications in formulations for the manufacture of perfluoroelastomer blends.[46]

Various crown ethers containing amino-substituted aromatic groups have been shown[47] to be useful as ion-exchange materials for the selective separation of metal ions, such as tin(II) and lead(II) ions (Sn^{2+} and Pb^{2+}). Tin(IV) has been quantitatively extracted with 4×10^{-2} M 18-cr-6 in dichloromethane from 1.5M sulphuric acid containing 1.65M potassium iodide.[48] The probable composition of the extracted species was found to be 1:1:4 tin:crown ether:potassium iodide and the tin could be separated from a large number of ions associated with it. Japanese workers have reported[49] on potential oscillations during the electrocrystallization of tin in the presence of crown ethers under galvanostatic conditions.

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