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Preliminary communication

SYNTHESIS AND SPECTROSCOPIC STUDIES OF ORGANOTIN COMPLEXES OF CROWN ETHERS

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Summary

A series of neutral adducts of di- and tri-organotin halides and pseudohalides with crown ethers, of general formula, $(Ph_3SnCl)_2 \cdot L \cdot 2H_2O$, where L = 18-crown-6 or 15-crown-5, and $(R_2SnX_2)_n \cdot$ 18-crown-6 $\cdot$ $2H_2O$, when R = Me, X = Cl, n = 2; R = Ph, X = Cl or NCS, n = 1, has been synthesised; The ^{119m}Sn Mössbauer and IR data suggest that the crown ethers are functioning as bidentate bridging ligands towards the metal atoms, which have coordination numbers of five, in the triphenyltin adducts, and six, in the diorganotin complexes.

Although crown ethers are known to form complexes with a wide variety of metals, they have only very recently been shown to interact with inorganic tin(II) [1,2] and tin(IV) [3,4] species. In this communication, we report the synthesis of the first organotin complexes of these polyethers.

The di- and tri-organotin halide and pseudohalide adducts of 18-crown-6 and 15-crown-5 were prepared by refluxing the appropriate starting materials in methanol for 2 h, and, on cooling to −20°C, the products separated as white crystalline solids. The melting points and spectroscopic data are shown in Table 1.

The reaction of triphenyltin chloride with 18-crown-6 or 15-crown-5 in methanol, in a 1/1 molar ratio, was found to give 2/1 adducts (Table 1), whereas Ph_2SnCl_2 or $Ph_2Sn(NCS)_2$ reacted with the former ether to give 1/1 complexes, regardless of the mole ratios used; dimethyltin dichloride and 18-crown-6 in methanol, in a 1/1 or 2/1 molar ratio, were found to give a 2/1 adduct, $(Me_2SnCl_2)_2 \cdot$18-crown-6$\cdot 2H_2O$.

The organotin complexes crystallise from solution as the dihydrates, as do the inorganic tin(IV) halide adducts [3], and show a broad ν(O—H) stretching band in their IR spectra in the region 3200—3400 cm^{-1}. In agreement with the work of Herber and Smelkinson on tin(II) complexes of 18-crown-6 [1], the organotin(IV) adducts show shifts of the ν_{as}(C—O—C) stretching vibration to lower fre-

TABLE 1

MELTING POINTS AND INFRARED AND ^{119m}Sn MOSSBAUER DATA FOR THE COMPLEXES[a]

Complex	M.p. ($^\circ$C)	ν_{as}(COC)[b] (cm^{-1})	δ[c] (mm s^{-1})	ΔE_Q (mm s^{-1})
$(Me_2SnCl_2)_2$·18-crown-6·$2H_2O$	119—123	1107	1.43	3.94
Ph_2SnCl_2·18-crown-6·$2H_2O$	88—95	1104	1.20	3.82
$Ph_2Sn(NCS)_2$·18-crown-6·$2H_2O$	140—148	1100	1.10	4.03
$(Ph_3SnCl)_2$·18-crown-6·$2H_2O$	117—120	1102	1.26	3.13
$(Ph_3SnCl)_2$·15-crown-5·$2H_2O$	99—105	1105	1.27	3.14

[a] Satisfactory C, H, Sn and Cl (or N) analyses were obtained in all cases. [b] ν_{as}(COC) in free crown ethers: 18-crown-6 (1110 cm^{-1}), 15-crown-5 (1134 cm^{-1}); the spectra all show a band in the region 3200—3400 cm^{-1}, due to ν(O—H). [c] Relative to $Ca^{119}SnO_3$; error in δ and ΔE_Q = ±0.02 mm s^{-1}.

quencies (Table 1), indicating that the metal atom interacts with one (or more) of the polyether oxygen atoms*.

The two triphenyltin complexes show, in their Mössbauer spectra (at 80 K), ΔE_Q values which are indicative of trigonal bipyramidal stereochemistries for each tin atom, with planar R_3Sn units; the two axial sites are, therefore, each occupied by an oxygen atom from a bridging crown ether ligand, and a chlorine atom, cf. $(Ph_3SnCl)_2 \cdot Ph_2P(O)CH_2CH_2P(O)Ph_2$ [5]. The diorganotin complexes show ΔE_Q values in the range 3.82—4.03 mm s^{-1}, which are characteristic of octahedral tin atom geometries, with *trans*-organic groups, and, in the case of the diphenyltin dichloride adduct, the presence of a single ν(Sn—Cl) IR stretching vibration at 258 cm^{-1} suggests a linear Cl—Sn—Cl unit. Hence, this complex (and probably $Ph_2Sn(NCS)_2$·18-crown-6·$2H_2O$) in the solid state is likely to consist of polymeric chains of linear Ph_2Sn units linked by bidentate bridging crown ether ligands, through their oxygens, and *trans*-chlorine (or NCS) atoms occupying the equatorial plane containing the oxygen atoms, cf. $Me_2SnCl_2 \cdot$ salenH_2 [6]. Similar *trans*-octahedral tin atom environments are likely to exist in $(Me_2SnCl_2)_2$·18-crown-6·$2H_2O$, which shows a single ν(Sn—Cl) band at 263 cm^{-1}, but, in this case, the structure is probably not polymeric and the plane perpendicular to each linear Me_2Sn fragment is occupied by two *trans*-chlorine atoms, a coordinated water molecule and an oxygen atom from the bridging bidentate crown ether ligand. Further structural studies are under way on these complexes and will be reported at a later date.

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**Note added in proof (January 1983).* Preliminary structural studies on $SiCl_4$·18-crown-6·$4H_2O$·$CHCl_3$, have indicated that two water molecules are coordinated to tin, and, therefore this possibility cannot be completely ruled out for the organotin adducts [I.W. Nowell and D.W. Allen, personal communication].