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Synthesis and Spectroscopic Studies of Inorganic Tin(IV) Halide Adducts of Crown Ethers

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Although inorganic tin(II) complexes of crown ethers have recently been prepared [1, 2], there is only one report of an inorganic tin(IV) adduct, 2 $SnCl_4$·(dibenzo-24-crown-8), [3]. The tin(IV) halide complex was not isolated in the solid state, but it was suggested [3] that, in benzene solution, the crown ether functions as a neutral donor ligand, with each tin coordinated exocyclically to two oxygen atoms from the polyether. In this work, we report the syntheses of the first pure tin(IV) complexes of crown ethers.

Experimental

$SnCl_4$·18-crown-6·$2H_2O$ was prepared by the addition of anhydrous stannic chloride (2.3 g, 8.8 mmol), dissolved in methanol (25 ml), to a solution of 18-crown-6 (1.2 g, 4.4 mmol, in 25 ml) in the same solvent, at room temperature. The reaction mixture was refluxed, with constant stirring, for 2 hr and then concentrated to 25 ml on a rotary evaporator. On cooling to 0 °C, the white crystals which separated were collected by filtration and dried in air at room temperature.

The other inorganic tin(IV) crown ether complexes studied in this work were prepared in a similar manner, except that the syntheses of the adducts of the polyether, 12-crown-4, were carried out in 1:1 v/v methanol/chloroform solutions. The products were obtained as white crystalline solids. Attempts to isolate similar complexes of $SnCl_4$ or $SnBr_4$ with dicyclohexyl-18-crown-6 and dibenzo-18-crown-6 were unsuccessful, as were those to prepare the adducts of SnI_4 and $Sn(NCS)_4$ with 18-crown-6.

Analytical, infrared and ^{119m}Sn Mössbauer data for the new compounds are given in Table I.

TABLE I. Analytical, Infrared and ^{199m}Sn Mössbauer Data for the Inorganic Tin(IV) Crown Ether Complexes.

Compound	M.p. (°C)	Analysis: Found (Calc.)				IR Data	^{199m}Sn Mössbauer Data	
		C	H	Hal.	Sn	$\nu C-O-C^a$ (cm^{-1})	δ^b ($mm \cdot s^{-1}$)	ΔE_Q ($mm \cdot s^{-1}$)
(1) $SnCl_4$·18-crown-6·$2H_2O$	174–8	26.2 (25.7)	5.1 (5.0)	24.9 (25.3)	21.1 (21.2)	1104	0.29	0.82
(2) $SnBr_4$·18-crown-6·$2H_2O$	132–5	18.5 (19.5)	3.9 (3.8)	42.1 (43.3)	15.5 (16.1)	1105	0.54	0.80
(3) $SnCl_4$·15-crown-5·$2H_2O$	201–5	22.0 (23.2)	4.5 (4.7)	27.7 (27.4)	22.9 (23.0)	1100	0.31	0.80
(4) $SnBr_4$·15-crown-5·$2H_2O$	175–9	17.4 (17.3)	3.5 (3.5)	46.6 (46.0)	17.1 (17.1)	1100	0.53	0.90
(5) $SnCl_4$·12-crown-4·$2H_2O$	164–8	19.3 (20.3)	4.1 (4.3)	28.6 (30.0)	24.9 (25.1)	1088	0.28	0.00
(6) $SnBr_4$·12-crown-4·$2H_2O$	153–6	14.7 (14.8)	2.9 (3.1)	50.4 (49.1)	18.2 (18.2)	1086	0.62	0.00

[a] $\nu C-O-C$ in free crown ethers: 18-crown-6 (1110 cm^{-1}), 15-crown-5 (1134 cm^{-1}), and 12-crown-4 (1100 cm^{-1}). The spectra of the tin(IV) complexes all show a broad band at *ca.* 3400 cm^{-1} due to ν(O–H). [b] Relative to $Ca^{119}SnO_3$; error in δ and $\Delta E_Q = \pm 0.02$ $mm \cdot s^{-1}$.

Results and Discussion

The inorganic tin(IV) haldie crown ether adducts crystallise from solution as the dihydrates, and all

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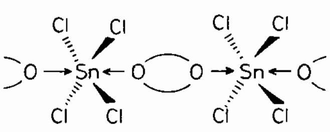
show a broad ν(O–H) stretching band in their infrared spectra at *ca.* 3400 cm^{-1}.. In agreement with the work of Herber and Smelkinson on tin(II) complexes of 18-crown-6 [1], the tin(IV) adducts show partial red shifts of the ν_{as}(C–O–C) stretching vibration (Table I), indicating that the metal atom interacts strongly with only two (or three) of the polyether oxygen atoms. Hence, the water molecules of hydration presumably do not enter the coordination sphere of the tin atom, as demonstrated crystallographically for $SnCl_4 \cdot Hpipox \cdot 2H_2O$ [4].

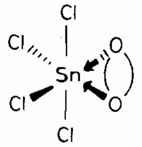
The ^{119m}Sn Mössbauer isomer shifts for the new compounds (Table I) are lower than those of the corresponding uncomplexed tin(IV) halides, *viz.* $\delta(SnCl_4)$ = 0.78 mm·s^{-1}, and $\delta(SnBr_4)$ = 1.05 mm·s^{-1} [5], and are consistent with adduct formation, involving oxygen donor atoms from the crown ether ligand. In addition, the values of δ are significantly lower than those generally observed for other SnX_4 adducts with O-donor ligands [6], implying that the O → Sn interactions are relatively strong.

Interestingly, the SnX_4 adducts with 18-crown-6 and 15-crown-5 (compounds 1–4) show a quadrupole split doublet in their Mössbauer spectra, whereas the complexes of 12-crown-4 (compounds 5 and 6) give rise to a single resonance. Gustavson and Zuckerman 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 [7]; a *trans*-configuration was therefore assigned to $SnCl_4 \cdot$diglyme for which the Mössbauer parameter are: $\delta = 0.49$; $\Delta E_Q = 1.10$ mm·s^{-1} [7]. Additionally, the Mössbauer resonance for the 1:1 complex of $SnCl_4 \cdot$diglyme for which the Mössbauer parameters ethane, shows a small splitting (δ = 0.51; ΔE_Q = 0.80 mm·s^{-1}), [8], and this is presumably indicative of a similar *trans*-octahedral stereochemistry. A parallel relationship appears to hold for octahedral tin(IV) halide adducts with hydroxyl donor ligands, $SnX_4 \cdot 2ROH$ [9].

The Mössbauer parameters for the tin(IV) crown ether complexes suggest that the larger polyether rings, 18-crown-6 and 15-crown-5, act as bridging ligands between planar SnX_4 units, to give the polymeric structure (A), in which the tin atoms are occupying a *trans*-octahedral geometry, whereas the less bulky crown ether molecule, 12-crown-4, is able to occupy *cis*-positions in the monomeric structure (B):



(A)



(B)

A similar tin atom environment (B) has been proposed for the 2:1 adduct of $SnCl_4$ with dibenzo-24-crown-8 in benzene solution, but, in this case, the polyether ligand furnishes two pairs of oxygen atoms for coordination to each tin [3]

In order to clarify this difference in structure, single crystal X-ray studies on two of the complexes are now in progress.

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