Spectroscopic (^{119}Sn and ^{13}C NMR, ^{119m}Sn Mössbauer and IR) Studies of Tin(IV) Tetrahalide Adducts of Cyclic and Aromatic Ethers, in the Solid State and in Solution

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Abstract

The interaction of tin(IV) halides ($SnCl_4$ and $SnBr_4$) with a series of cyclic and aromatic ethers has been studied in the solid state and in solution. Nine solid adducts of composition, $SnX_4 \cdot 2$(ether) and $SnCl_4 \cdot$(ether), were isolated and their structures investigated by ^{119m}Sn Mössbauer and IR spectroscopy. The 1:2 adducts contain an octahedral tin atom geometry, with *trans*-coordinated ether ligands. ^{119}Sn and ^{13}C NMR studies on the SnX_4/ether systems showed that, in certain cases, it is possible to form hexacoordinate complexes in solution. The relative donor abilities of the various ethers towards the tin(IV) halides have been compared.

Introduction

Tin(IV) halides have been reported [1–3] to be effective coal liquefaction catalysts, but the mechanism of their catalytic action is not fully understood. As part of a programme investigating the interaction of stannic halides with various functional groups in coal, we now report a study of their complexation with a series of ethers modelling those found in coal [4–6]. The ethers chosen were: tetrahydrofuran (THF), tetrahydropyran (THP), 2-methyltetrahydrofuran (2-Me-THF), 3-methyltetrahydrofuran (3-Me-THF), 2,5-dimethyltetrahydrofuran (2,5-Me$_2$-THF), 2,2,5,5,-tetramethyltetrahydrofuran (2,2,5,5-Me$_4$-THF), dihydrobenzofuran (DHBF), dibenzyl ether (Bz$_2$O), diphenyl ether (Ph$_2$O), benzyl phenyl ether (BzPhO), furan (Fur), and 1,4-dioxan (diox).

Previous solid state studies have indicated the formation of 1:2 adducts, $SnX_4 \cdot 2L$ [7–11], with *trans* ether groups [7, 8], whereas, in solution, both 1:1 and 1:2 complexes have been observed [10, 12–16]. In addition, 1,4-dioxan has been reported to give solid products of the type, $SnX_4 \cdot L$ and $SnX_4 \cdot 2L$, with stannic chloride and stannic bromide [11, 17, 18].

Experimental

Syntheses

The complexes were prepared by adding the anhydrous tin tetrahalide (1 mol), in chloroform, toluene or light petroleum (b.p. range 60–80 °C) to a stirred solution of the appropriate ether (2 mol) in the same solvent, under dry nitrogen, and the resulting solid product was removed by filtration, dried *in vacuo*, and stored in a sealed tube. 1,4-Dioxan and 2,2,5,5-tetramethyltetrahydrofuran formed 1:1 adducts with stannic chloride under these conditions. The microanalytical data and melting points for the adducts are shown in Table I, and all of the compounds were found to hydrolyse readily on exposure to the air.

Spectroscopic Methods

^{119m}Sn Mössbauer spectra were recorded at 80 K using a constant acceleration microprocessor spectrometer described previously [20]. The experimental error in the measured values of isomer shift (δ) and quadrupole splitting (ΔEq) parameters is ±0.05 mm s^{-1}. Isomer shifts are relative to CaSnO$_3$.

^{119}Sn and ^{13}C NMR spectra were recorded in 10 mm tubes on a Jeol FX60Q spectrometer. Field frequency lock was to external D$_2$O. ^{119}Sn chemical shifts, $\delta(^{119}$Sn), are relative to Me$_4$Sn and are accurate to ±0.5 ppm; ^{13}C chemical shifts, $\delta(^{13}$C), are relative to TMS and are accurate to ±0.1 ppm.

Infrared spectra were obtained as nujol mulls on a Pye-Unicam SP 2000 instrument and the error in ν(C–O–C) is ±5 cm^{-1}.

Results and Discussion

^{119}Sn and ^{13}C NMR Studies

The interactions of $SnCl_4$ and $SnBr_4$ with the cyclic and aromatic ethers, in CCl$_4$ solution, were studied by ^{119}Sn and ^{13}C NMR spectroscopy. Solutions of the appropriate reagents were mixed at room

TABLE I. Melting Point and Analytical Data for Tin(IV) Halide Adducts.

| Compound	Solvent	M.p. (°C)	Analysis: Found (Calc.)		
			C	H	Hal.
SnCl₄·2THF	Petroleum ether	168–170 (165–175)[a]	23.22 (23.70)	3.83 (3.95)	34.92 (35.06)
SnBr₄·2THF	Petroleum ether	110–113 (120)[b]	16.46 (16.47)	2.75 (2.74)	55.66 (54.89)
SnCl₄·2THP	CHCl₃	159–165 (subl.)	25.20 (27.71)	4.33 (4.62)	32.77 (32.79)
SnBr₄·2THP	Petroleum ether	107–115 (subl.) (125)[b]	19.59 (19.64)	3.31 (3.27)	53.38 (52.37)
SnCl₄·2(2-Me-THF)	Petroleum ether	[c]	25.56 (25.62)	4.81 (5.16)	31.49 (30.25)
SnCl₄·2(3-Me-THF)	Petroleum ether	111–113	26.13 (27.75)	4.41 (4.66)	31.65 (32.77)
SnCl₄·2(2,5-Me₂-THF)	Toluene	[c]	28.51 (28.99)	5.02 (5.68)	31.15 (28.53)
SnCl₄·diox	Petroleum ether	200–203 (175–195)[a] (187)[d]	14.64 (13.80)	3.51 (2.31)	39.75 (40.68)
SnCl₄·(2,2,5,5-Me₄-THF)	CHCl₃	[c]	24.76 (24.72)	4.89 (4.15)	33.84 (36.48)

[a]Ref. 11.   [b]Ref. 9.   [c]M.p. not recorded, due to instability of the compound.   [d]Ref. 19.

temperature, and their ¹¹⁹Sn and ¹³C chemical shifts recorded (Table II).

¹¹⁹Sn NMR chemical shifts are indicative of coordination number, an increase of which is accompanied by a change in δ(¹¹⁹Sn) to low frequency [21]. In CCl₄ solution, SnCl₄ and SnBr₄ presumably exist as discrete four coordinate monomers and have δ(¹¹⁹Sn) values of −149 ppm and −637 ppm respectively. These shifts should be compared to those obtained from the same compounds in methanol solution (−600.5 ppm and −1307.0 ppm respectively), in which the species present is the 6-coordinate neutral adduct, SnX₄·2MeOH [11], the increase in coordination number being reflected by the change in δ(¹¹⁹Sn). From Table II, it may be seen that, in some cases, addition of the ether to a solution of the inorganic tin halide produces a shift in δ(¹¹⁹Sn) to low frequency. Obviously the magnitude of the change in δ(¹¹⁹Sn) does not reflect the presence of a 6-coordinate complex, but, instead, may be interpreted as an average chemical shift between free and complexed SnX₄. If the mole ratio of the ether to tin halide is increased, δ(¹¹⁹Sn) moves to even lower frequency, indicating that SnX₄ exists for a longer period of time in the complexed form. In fact, in the case of SnCl₄ with Bz₂O or 2-Me-THF, and SnBr₄ with the latter compound, when the ether was present in a 10:1 molar excess, δ(¹¹⁹Sn) values were obtained which are

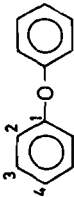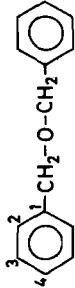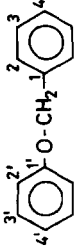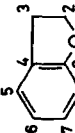consistent with the presence, in solution, of a 6-coordinate adduct, SnX₄·2L.

Since the formation of a donor complex results in a change in δ(¹¹⁹Sn), the magnitude of this change gives a direct indication of the relative strength of the interaction from each individual ether. Thus, by comparing values obtained (Table II) from solutions containing 1:1 mole ratios of SnX₄ to ether, it may be seen that, of the compounds studied, 2-Me-THF has the strongest interaction, whereas Ph₂O and Fur probably have no significant coordination to the tin. The relative strength of the donor interactions may therefore be summarised as follows:

2-Me-THF > DHBF > Bz₂O > BzPhO > Ph₂O ≈ Fur
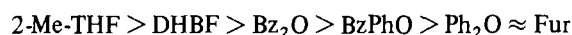
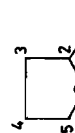¹³C chemical shift measurements (Table II) are in accord with the results discussed above. In cases where the ether forms a strong donor complex with the tin halide, the δ(¹³C) values are significantly different from those of the free ether. It might be expected that electron donation to tin would result in a deshielding of the carbon atoms adjacent to oxygen and a high frequency shift of δ(¹³C) would occur. However, this is not always the case, and, with Bz₂O, and C-2 of DHBF, complexation results in a low frequency shift of δ(¹³C) for the carbon adjacent to oxygen, as has been noted previously in related systems [22]. Comparison of δ(¹³C) values for

TABLE II. ^{119}Sn and ^{13}C NMR Chemical Shifts.

Ether	SnX$_4$	Ratio Ether:SnX$_4$	$\delta(^{119}\text{Sn})$ (ppm)	$\delta(^{13}\text{C})$ (ppm)
Diphenyl ether (Ph–O–Ph)	SnCl$_4$		−149	157.2 (C-1), 129.4 (C-3), 122.8 (C-4), 118.8 (C-2)
	SnBr$_4$		−637	157.2, 129.4, 122.8, 118.8
Ar–CH$_2$–O–CH$_2$–Ar (positions 1,2,3,4)	SnCl$_4$	1:1	−150	138.3 (C-1), 128.0 (C-3), 127.3 (C-2/4), 127.2 (C-2/4), 71.6 (CH$_2$)
		10:1	−602	136.8, 128.2, 128.0, 127.8, 71.2
	SnBr$_4$	1:1	−181 / −696	136.6, 128.2, 128.0, 127.8, 71.2
		10:1	−835	138.1, 128.1, 127.4, 127.3, 71.6
				138.1, 128.1, 127.4, 127.3, 71.6
Ar–O–CH$_2$–Ar' (positions 1,2,3,4 and 1',2',3',4')	SnCl$_4$	1:1	−637.6	158.6 (C-1'), 137.0 (C-1'), 129.2 (C-3), 120.7 (C-4), 128.3 (C-3'), 127.5 (C-4'), 127.0 (C-2'), 114.7 (C-2), 69.5 (CH$_2$)
	SnBr$_4$			127.5 (C-4'), 137.1 (C-2'), 129.2, 120.6, 114.7, 69.4
Furan (O-1, positions 2,3)	SnCl$_4$	1:1	−153	142.1 (C-2), 109.2 (C-3)
	SnCl$_4$	1:1	−149	142.1, 109.2
	SnBr$_4$	1:1	−637	142.1, 109.2
2,3-Dihydrobenzofuran / isochroman (O-1, positions 4,5,6,7,8,9)	SnCl$_4$	1:1	−163	159.7 (C-9), 127.7^a (C-8), 126.2 (C-4), 124.4^a (C-3), 120.1^a, 109.4 (C-8), 70.4 (C-2), 29.7 (C-3)
	SnBr$_4$	1:1	−641.4	160.0, 127.7, 126.2, 124.4, 119.9, 109.3, 70.2, 29.7
				159.9, 127.7, 126.2, 124.4, 120.1, 109.4, 70.3, 29.7
2-Methyltetrahydrofuran (O-1, positions 2,3,4,5, CH$_3$)	SnCl$_4$	1:1	−334	74.6 (C-5), 67.1 (C-2), 33.2 (C-4), 25.9 (C-3), 21.0 (CH$_3$)
		10:1	−604	80.9, 70.4, 32.0, 24.3, 21.1
	SnBr$_4$	1:1	−755	80.9, 70.4, 32.0, 24.3, 21.1
		10:1	−1317	76.1, 67.7, 32.7, 25.2, 21.3
				76.1, 67.7, 32.7, 25.2, 21.3

^{a} Assignment of this resonance was uncertain.

TABLE III. Mössbauer and IR Data for the Complexes.

Compound	^{119m}Sn Mössbauer Parameters		IR Data	
	δ (mm s^{-1})	ΔEq (mm s^{-1})	ν(C–O–C) (cm^{-1})[a]	$\Delta\nu$(C–O–C) (cm^{-1})
SnCl$_4$·2THF	0.41	1.23	1005	65
SnCl$_4$·2THF	0.43[b]	1.14[b]	–	–
SnCl$_4$·2THF	0.43[c]	1.29[c]	–	–
SnCl$_4$·2THF	0.47[d]	1.23[d]	–	–
SnCl$_4$·2THF	0.43[e]	1.26[e]	–	–
SnBr$_4$·2THF	0.70	1.27	1005	65
SnBr$_4$·2THF	0.76[e]	1.34[e]	–	–
SnCl$_4$·2THP	0.45	1.36	1005	90
SnBr$_4$·2THP	0.76	1.46	1000	100
SnCl$_4$·2(2-Me-THF)	0.49	1.26	1040	60
SnCl$_4$·2(3-Me-THF)	0.44	1.12	1015	85
SnCl$_4$·2(2,5-Me$_2$-THF)	0.54	1.19	1060	45
SnCl$_4$·(2,2,5,5-Me$_4$-THF)	0.62	0.00	–	–
SnCl$_4$·diox	0.41	0.90	1055	85
SnCl$_4$·diox	0.49[f]	1.48[f]	–	–
SnCl$_4$·2diox	0.45[b]	1.10[b]	–	–
SnCl$_4$(H$_2$O)$_2$·2diox	0.26[g]	0.00[g]	–	–

[a]ν(C–O–C) in free ethers: THF (1070 cm^{-1}), THP (1095 cm^{-1}), 2-Me-THF (1100 cm^{-1}), 3-Me-THF (1100 cm^{-1}), 2,5-Me$_2$-THF (1105 cm^{-1}), diox (1130 cm^{-1}). [b]Ref. 25. [c]Ref. 26. [d]Ref. 27. [e]Ref. 28. [f]Ref. 19. [g]Ref. 29.

complexes formed with SnCl$_4$ and SnBr$_4$ with those of the free ether, shows that the largest change occurs with the former tin halide, indicating, as would be expected on the grounds of Lewis acidity, that the stronger interactions occur with SnCl$_4$.

Attempts to study the reaction of the tin tetrahalides with THF and THP in solution were precluded by the immediate formation of a precipitate on mixing.

^{119}Sn Mössbauer and IR Studies

The quadrupole splitting values for the 1:2 complexes (Table III) fall in the range 1.12–1.46 mm s^{-1}. It has been proposed [23] that, for octahedral tin(IV) halide adducts with O-donor ligands, a *trans* configuration of oxygen atoms results in a resolvable quadrupole splitting in the Mössbauer spectrum, whilst no ΔEq is observed for those complexes with a *cis* arrangement of the oxygen ligands. Hence, it is likely that the ether molecules are occupying *trans* positions in the octahedral SnX$_4$·2L adducts. The isomer shifts are lower than those [24] of the parent stannic halide (SnCl$_4$, δ = 0.78 mm s^{-1}; SnBr$_4$, δ = 1.06 mm s^{-1}), due to a reduction in s-electron density at the tin nucleus on complexation.

The Mössbauer parameters for the 1:1 adduct of stannic chloride with dioxan are similar to those observed for the 1:2 complexes and suggest that, in this case, the *trans* octahedral tin atom geometry is maintained by a polymeric structure, in which the difunctional ether ligand bridges planar SnCl$_4$ units, as noted earlier [14, 19]. Ichiba *et al.* reported [25] Mössbauer data for a 1:2 adduct, SnCl$_4$·2diox

(although the microanalyses were not quoted for this compound), but the parameters (Table III) are similar to those which we find for the 1:1 adduct. Interestingly, the hydrolysis product, SnCl$_4$(H$_2$O)$_2$·2diox, which is known by X-ray crystallography [30] to contain an octahedral tin atom geometry, with the two water molecules occupying *cis* positions, shows a single line Mössbauer spectrum.

For these *trans* octahedral adducts, the lower δ values may be associated with the more strongly interacting ligands [19], and, accordingly, the following approximate donor order may be established:

THF $\simeq$ diox > 3-Me-THF $\simeq$ THP > 2-Me-THF

> 2,5-Me$_2$-THF
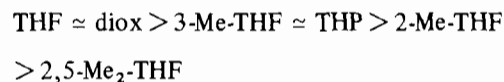
This is in good agreement with the results of previous workers [12, 15] for similar systems in benzene solution, and this order is presumably determined by steric considerations, as proposed by Cioffi and Zenchelsky [12]. In the IR spectra of the adducts (Table III), the largest shifts of the ν(C–O–C) band result from the strongest donor ligands and this gives the following order:

THP $\simeq$ diox $\simeq$ 3-Me-THF > THF > 2-Me-THF

> 2,5-Me$_2$THF
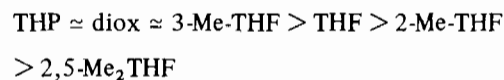
The reason for the reversal of THP and THF is not clear. However, it is possible that the ν(C–O–C) bands assigned for the THP adducts (Table III), although the strongest in the C–O–C stretching region, could consist of two overlapping absorptions,

and may, therefore, have given rise to an error in the quoted values of $\Delta\nu$. In this respect, the order of donor abilities obtained from the Mössbauer data is considered to be more reliable.

It was found that, with the sterically hindered ether, 2,2,5,5-Me_4-THF and stannic chloride, a 1:1 adduct was formed, and the significantly higher value of δ (0.62 mm s^{-1}), is indicative of a pentacoordinate trigonal bipyramidal structure. No quadrupole splitting was observed in the Mössbauer spectrum of this complex, and, in accord with this, it has been found that the five coordinate complexes $SnCl_4 \cdot Ph_3PO$ [19], $SnCl_4 \cdot NMe_3$ [31] and $SnBr_4 \cdot NMe_3$ [31] show single Mössbauer resonances.

Conclusions

In view of these results, the following overall order of donor abilities of the various ethers studied towards the tin(IV) halides has been established:

THF $\simeq$ diox > 3-Me-THF $\simeq$ THP > 2-Me-THF > 2,5-Me_2-THF > DHBF > Bz_2O > BzPhO > Ph_2O $\simeq$ Fur

Acknowledgement

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