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SYNTHESIS AND ^{119m}Sn MÖSSBAUER STUDIES OF CATIONIC TRIBUTYLTIN COMPLEXES

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Summary

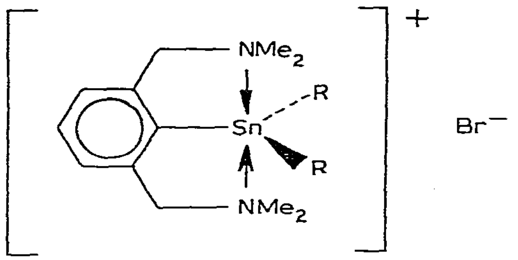
A series of cationic tributyltin complexes with a tetraphenylborate counter-anion, $[Bu_3SnL_2]^+BPh_4^-$, where L = DMSO, Ph_3PO, Ph_3AsO, pyO or DMF, and L_2 = diphosO_2, has been prepared and their ^{119m}Sn Mössbauer spectra investigated. These indicate that the triorganotin cation occupies a pentacoordinate trigonal bipyramidal geometry with equatorial organic groups when L = monodentate donor, whilst the bidentate diphosO_2 ligand produces a *mer*-R_3SnX_2 stereochemistry about tin.

Introduction

In the course of our investigations into the synthesis of water-soluble tributyltin biocides [1—4], we have previously prepared a number of anionic tributyltin complexes, $M^+[Bu_3SnCl_2]^-$, and it was found that a tetraorganophosphonium cation ($M^+ = Ph_4P^+$, n-Bu_4P^+ or $PhCH_2PPh_3^+$) was necessary to stabilise the organotin anion [1,2]. In the present paper, we extend this work to a number of novel cationic tributyltin salts.

Earlier studies have shown that pentacoordinate trimethyltin cations, $\{Me_3SnL_2\}^+$, where L = H_2O [5], DMSO, DMF, DMA, Ph_3AsO or $(C_6H_4Me\text{-}4)_3$-AsO [6,7]; L_2 = bipy [8], may be stabilised with a tetraphenylborate counter-anion and, more recently, an X-ray study [9] has demonstrated a double trimethyltin salt, $[Me_3Sn(HMPT)_2]^+[Me_3SnBr_2]^-$. There have been no previous reports of cationic tributyltin derivatives.

Although the cationic trimethyltin complexes appear to be largely insoluble in water, Noltes et al., have shown [10] that the mixed triorganotin salts (I),



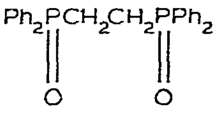
(I)

containing an intramolecularly pentacoordinate organotin cation show aqueous solubilities which are dependent upon the nature of the organic group. Thus, when R = methyl, the complex was extremely soluble in water, whilst when R = ethyl or phenyl, the complex was only moderately soluble or insoluble in water, respectively. The ionic nature of I was confirmed by an X-ray structural analysis of the dimethyltin derivative [10].

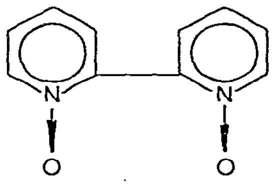
Experimental

Preparation of complexes

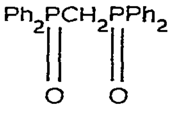
The complexes, $\{Bu_3SnL_2\}^+BPh_4^-$, were prepared in a similar manner to the trimethyltin analogues [6,7]. In the cases where the ligands were liquids, equimolar amounts of tributyltin chloride and sodium tetraphenylborate were dissolved in excess ligand, whilst, for the solid ligands, tributyltin chloride (1 mole) and the ligand (1 mole) were dissolved in methanol, followed by addition of methanolic sodium tetraphenylborate (1 mole). The complexes were precipitated as white solids by the addition of an ice/water slurry to the mixture. Attempts to prepare complexes with the bidentate oxygen donor ligands diphosO_2 (II), bipyO_2 (III) or oPo (IV) were achieved only with II and it was not possible to prepare any of the tributyltin salts with tetrafluoroborate


$Ph_2P(=O)CH_2CH_2P(=O)Ph_2$

(II)



(III)


$Ph_2P(=O)CH_2P(=O)Ph_2$

(IV)

(BF_4^-) or hexafluorophosphate (PF_6^-) counteranions. The new tributyltin complexes were all found to be insoluble in water and the melting points and analytical data are shown in Table 1.

The use of bidentate nitrogen donor ligands, e.g. 1,10-phenanthroline and 4,4′-bipyridyl, or phosphorous donors, such as triphenylphosphine, in the above reactions returned only starting materials. However, when a methanolic solution of 2,2′-bipyridyl (1 mole) was added dropwise to an equimolar mixture of tributyltin chloride and sodium tetraphenylborate in methanol, pale

TABLE 1

ANALYTICAL DATA FOR CATIONIC TRIBUTYLTIN COMPLEXES

	Analysis: Found(Calcd.)(%)						M.p.(%)
	C	H	Sn	P	S	N	
$[Bu_3Sn(DMSO)_2]^+BPh_4^-$	62.34 (62.75)	7.68 (7.71)	15.80 (15.56)	—	8.18 (8.37)	—	115—116
$[Bu_3Sn(pyO)_2]^+BPh_4^-$	68.28 (69.09)	7.31 (7.13)	14.20 (14.89)	—	—	3.10 (3.50)	99—100
$[Bu_3Sn(Ph_3PO)_2]^+BPh_4^-$	74.34 (74.16)	6.68 (6.61)	10.80 (10.21)	5.32 (5.32)	—	—	124—125
$[Bu_3Sn(Ph_3AsO)_2]^+BPh_4^-$	68.79 (68.95)	6.14 (6.15)	9.50 (9.50)	—	—	—	142
$[Bu_3Sn(DMF)_2]^+BPh_4^-$	65.82 (66.75)	8.23 (8.08)	16.20 (15.76)	—	—	3.60 (3.71)	83—84
$[Bu_3Sn(diphosO_2)]^+BPh_4^-$	70.84 (71.61)	6.94 (6.83)	11.00 (11.45)	5.70 (5.97)	—	—	120

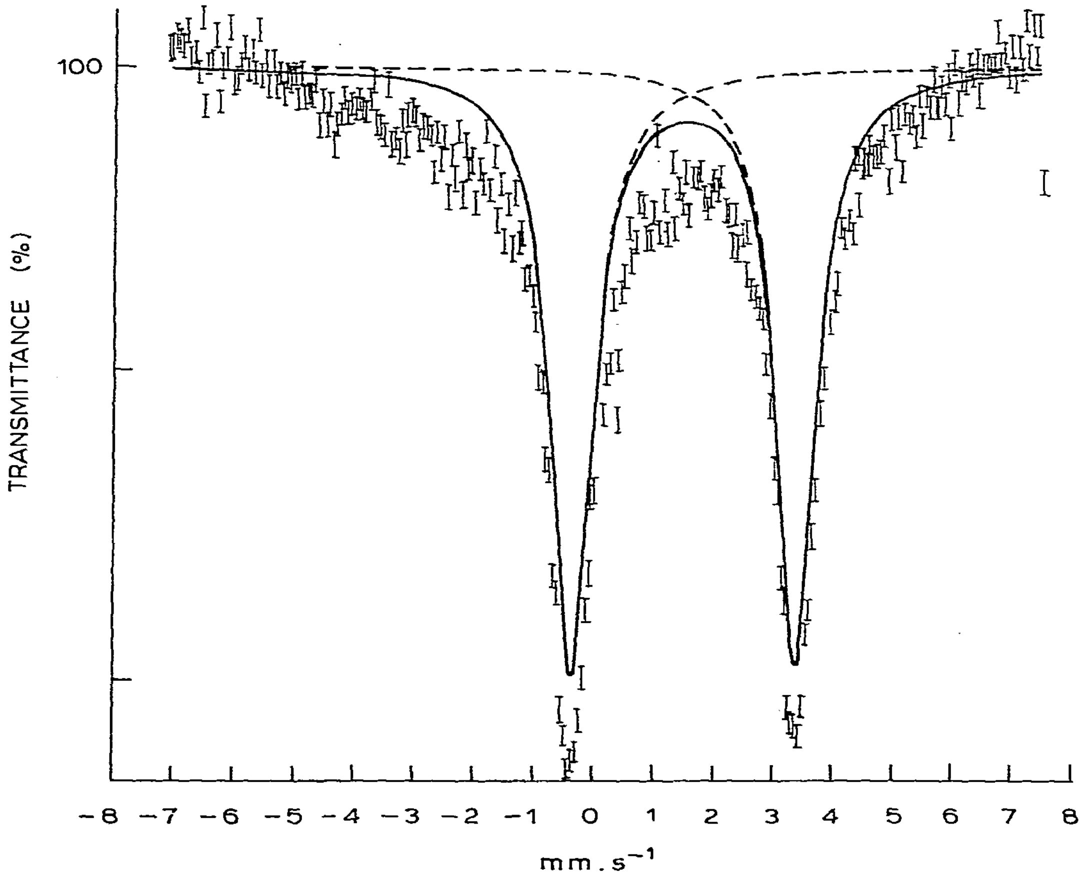


Fig. 1. ^{119m}Sn Mössbauer spectrum of $[Bu_3Sn(DMSO)_2]^+BPh_4^-$.

TABLE 2

TIN-119 MOSSBAUER PARAMETERS AND ν(E=O) STRETCHING FREQUENCIES FOR CATIONIC TRIALKYLTIN COMPLEXES

Complex	Isomer Shift (δ mm s^{-1})	Quadrupole Splitting (ΔE_q mm s^{-1})	ν(E=O)(cm^{-1})	
			Free Ligand	Complex
$[Bu_3Sn(DMSO)_2]^+BPh_4^-$	1.51	3.74	1040	980
$[Bu_3Sn(pyO)_2]^+BPh_4^-$	1.54	3.53	1243	1190
$[Bu_3Sn(Ph_3PO)_2]^+BPh_4^-$	1.52	3.98	1190	1142
$[Bu_3Sn(Ph_3AsO)_2]^+BPh_4^-$	1.45	3.60	880	840, 852
$[Bu_3Sn(DMF)_2]^+BPh_4^-$	1.57	3.77	1684	1640
$[Bu_3Sn(diphosO_2)]^+BPh_4^-$	1.55	4.06	1188 [a]	1181, 1144, 1126, 1092
$[Me_3Sn(DMSO)_2]^+BPh_4^-$	1.30 [b]	3.63 [b]	1053 [c]	950 [c]
$[Me_3Sn(Ph_3PO)_2]^+BPh_4^-$	1.28 [b]	3.87 [b]	1190	1144 [d]
$[Me_3Sn(Ph_3AsO)_2]^+BPh_4^-$	1.18 [b]	3.29 [b]	880	870 [d]
$[Me_3Sn(diphosO_2)]^+BPh_4$	1.31 [b]	3.90 [b]	1188 [a]	1183, 1150 1141, 1094 [a]
$[Me_3Sn(DMF)_2]^+BPh_4^-$	1.34 [d]	3.90 [b]	1673 [c]	1645 [c]

[a] Ref. 12. [b] Ref. 13. [c] Ref. 6. [d] Ref. 14

orange crystals of bipyridinium tetraphenylborate, $[bipyH]^+BPh_4^-$, m.p. 168°C, separated on standing (Found: C, 85.34; H, 6.26; N, 5.88. $C_{34}H_{29}N_2B$ calcd.: C, 85.71; H, 6.09; N, 5.88%).

Mössbauer spectra

The Mössbauer spectrometer has been described elsewhere [11]. Spectra were recorded as finely powdered samples at 77 K vs. $Ca^{119m}SnO_3$ (The Radiochemical Centre, Amersham). Data reduction was accomplished by fitting to Lorentzian line shapes, employing usual least-squares methods. The data are listed in Table 2, and a typical spectrum is illustrated in Fig. 1. Isomer shifts are quoted with respect to SnO_2. The error in δ and ΔE_q is ± 0.03 and ± 0.06 mm s^{-1} respectively.

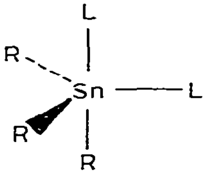
Infrared spectra

Infrared spectra were recorded as Nujol mulls on a Grubb-Parsons Mark 1 instrument. Potassium bromide plates were used. The element—oxygen stretching frequencies, ν(E=O) (cm^{-1}) (E = C, S, P, As or N), for the complexes and for the free ligands are listed in Table 2.

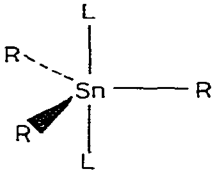
Discussion

The isomer shift values observed for the cationic tributyltin complexes (1.45—1.57 mm s^{-1}) are higher than those of their trimethyltin analogues [13], reflecting the greater *s*-electron density at the tin nucleus in the tributyltin salts (due to the greater electron-donating power of the butyl groups).

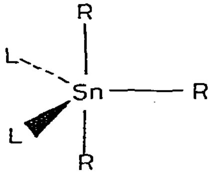
The pentacoordinate organotin cation may assume one of three possible isomeric forms: the *cis*-isomer (V), the *trans*-form (VI) or the *mer*-geometry (VII). The *cis*-isomer V may be ruled out immediately, since it would lead to a quadrupole splitting value of ~2.00 mm s^{-1}, e.g. $Me_3SnO{\cdot}NPh{\cdot}CO{\cdot}Ph$ [15],



(V)



(VI)



(VII)

which shows [16] ΔE_q = 2.36 mm s^{-1}. The similarity of the ΔE_q values of the tributyltin complexes with monodentate donor ligands (Table 2) to those of their trimethyltin analogues, which adopt the *trans*-structure VI [13], suggest that the two series are isostructural. Coordination of the ligands to tin is accompanied by a reduction in ν(E=O), which is most pronounced for the DMSO and triphenylphosphine oxide ligands. Bancroft et al., assigned the *mer*-structure VII to $[Me_3Sn(diphosO_2]^+BPh_4^-$ [13], although this geometry has yet to be demonstrated crystallographically for tin(IV). The analogous tributyltin complex shows similar Mössbauer parameters and a similar pattern of ν(P=O) bands and is thus tentatively assigned structure VII.

An additional signal was observed in the Mössbauer spectra of $[Bu_3Sn(pyO)_2]^+BPh_4^-$ and $[Bu_3Sn(DMF)_2]^+BPh_4^-$ at 1.38 mm s^{-1} and 1.42 mm s^{-1}, respectively, and this may be due to tetrabutyltin (δ 1.35 mm s^{-1} [17]), which could be formed by the following disproportionation reaction *:

$$2\{Bu_3SnL_2\}^+BPh_4^- \rightarrow Bu_4Sn + \{Bu_2SnL_4\}^{2+}(BPh_4^-)_2$$

Acknowledgements

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* An alternative decomposition pathway is as follows [7,14]: $\{Bu_3SnL_2\}^+BPh_4^- \rightarrow Bu_3SnPh + Ph_3B{\cdot}L + L$.