Oxy- and Thio-phosphorus Acid Derivatives of Tin. Part 12.† A Mössbauer Spectroscopic Investigation of the Structures and Polymorphic Behaviour of Diorganotin(IV) Phenyl-phosphonates and -arsonates

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The phenylphosphonate and phenylarsonates $Me_2Sn[PhPO_3]$, $Me_2Sn[PhAsO_3]$, and $Bu^n{}_2Sn[PhAsO_3]$ are isolated as their α-modifications from the reaction of dimethyl- or di-n-butyl-tin dichloride with the monosodium salt of the appropriate acid. β-Modifications are obtained by removal of water from the monohydrates $Me_2Sn[PhPO_3]\cdot H_2O$, $Me_2Sn[PhAsO_3]\cdot H_2O$, and $Bu^n{}_2Sn[PhAsO_3]\cdot H_2O$, obtained in turn from the reaction of the diorganotin dichloride with the disodium salt of the appropriate acid. Only one form of $Ph_2Sn[PhPO_3]$ was isolated; this can be obtained either from the direct reaction of diphenyltin dichloride with phenylphosphonic acid or by removal of water from $Ph_2Sn[PhPO_3]\cdot H_2O$. On the basis of i.r. and variable-temperature Mössbauer spectroscopic and *X*-ray powder diffraction data it is suggested that the structures of the β-modifications and of $Ph_2Sn[PhPO_3]$ consist of infinite chains, and that chains with similar backbone structures occur in solid-state forms of their hydrate precursors. The α-modifications of $Me_2Sn[PhAsO_3]$ and $Bu^n{}_2Sn[PhAsO_3]$ appear to have two-dimensional sheet structures in which tin achieves five-co-ordination, but the data do not preclude the possibility that α-$Me_2Sn[PhPO_3]$ has a more associated three-dimensional network structure, with tin in highly distorted octahedral sites. The complexes $Me_2Sn[PhAs(OH)O_2]_2$, $Bu^n{}_2Sn[PhAs(OH)O_2]_2$, and $Bu^n{}_2Sn[PhP(OH)O_2]_2$, obtained by the reaction of a diorganotin dihalide with the appropriate acid, have structures in which tin is in octahedral sites. It is suggested that these are chain structures in which chains are linked by strong hydrogen bonds.

While there are numerous examples of phosphorus oxy-acid derivatives of organotin(IV), few of these are organophosphonates. Both di- and tri-organotin(IV) organophosphonates are known,[1-3] and all appear to have polymeric structures involving –O–P–O– bridging of organotin moieties. A recent crystallographic study [1] has confirmed an infinite chain structure for $Me_3Sn[PhP(OH)O_2]$. Diorganotin(IV) phenylarsonates and substituted phenylarsonates are well documented [4-8] and also appear to have polymeric structures.[6-8]

We have recently extended [9] earlier studies of divalent metal phenylphosphonates,[10] and shown that there is a pronounced tendency towards polymorphism in both these materials and their phenylarsonate analogues. More recently we have demonstrated that trimethyl(phenylphosphonato)tin(IV) exists in two crystal modifications.[1,11] Consequently, a particular point of interest in the present study of diorganotin(IV) derivatives of phenylphosphonic and phenylarsonic acids was whether polymorphic behaviour extended to these also.

This paper reports the synthesis of phenylphosphonates and phenylarsonates of dimethyl-, di-n-butyl-, and diphenyltin(IV). Complexes were isolated containing singly and doubly charged acid anions. In addition, the methods of synthesis led to the isolation of two forms each of $Me_2Sn[PhAsO_3]$, $Bu^n{}_2Sn[PhAsO_3]$, and $Me_2Sn[PhPO_3]$. The structures are discussed in the light of i.r., variable-temperature Mössbauer, and *X*-ray powder diffraction data.

Experimental

Infrared spectra were recorded with Perkin-Elmer 457 and Beckman 4 250 spectrometers. Variable-temperature Mössbauer spectra were recorded with a Ranger Engineering constant acceleration spectrometer equipped with an NaI scintillation counter using $Ca^{119}SnO_3$ (New England Nuclear Corporation) as source. The Ranger Engineering variable-temperature liquid nitrogen Dewar and controller was regulated by a variable bridge, silicon-controller–rectifier circuit, and was accurate to within ±1 K. Other Mössbauer data in Table 1 were recorded with a J & P Engineering (Reading) constant acceleration Mössbauer spectrometer equipped with an NaI scintillation counter using $Ca^{119}SnO_3$ (The Radiochemical Centre, Amersham) as source. The velocity calibration for both spectrometers was based on the spectrum of natural iron. The spectrum of $Ca^{119}SnO_3$ at room temperature was adopted as the isomer shift reference.

The organotin starting materials were of commercial grade (Fluka) and were used without further purification. The products of all the reactions described were highly insoluble in water and organic solvents, and were isolated by filtration followed by washing with ethanol and drying under vacuum at *ca.* 20 °C for upwards of 10 h. Elemental analyses are included in Table 1.

$Bu^n{}_2Sn[PhAs(OH)O_2]_2$.—When either bis(acetato)di-n-butyltin(IV) (0.01 mol) or di-n-butylbis(pentane-2,4-dionato)-tin(IV) (0.01 mol) and phenylarsonic acid (0.02 mol) were stirred in methanol (100 cm³) at room temperature for *ca.* 12 h, the product was obtained as a white solid in about 60% yield.

$Me_2Sn[PhAs(OH)O_2]_2$.—When a solution of dimethyltin dichloride (0.01 mol) in water (20 cm³) was added to a solution of phenylarsonic acid (0.02 mol) in water (50 cm³) at room temperature, a white precipitate formed almost immediately, in greater than 80% yield.

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† Part 11, D. Cunningham, L. A. Kelly, K. C. Molloy, and J. J. Zuckerman, *Inorg. Chem.*, 1982, **21**, 1416.

Table 1. Analytical data and Mössbauer parameters for diorganotin(IV) phenylphosphonates and phenylarsonates

Complex	% Found (required)		δ/mm s^{-1}	Δ/mm s^{-1}
	C	H		
$Me_2Sn[PhAs(OH)O_2]_2$	30.7(30.55)	3.3(3.3)	1.26	4.34
$Bu^n{}_2Sn[PhAs(OH)O_2]_2$	38.0(37.85)	4.7(4.5)	1.23	4.11
$Bu^n{}_2Sn[PhP(OH)O_2]_2$	44.2(43.9)	5.55(5.5)	1.24	3.79
α-$Me_2Sn[PhAsO_3]$	27.75(27.75)	3.2(3.2)	1.07	3.19
β-$Me_2Sn[PhAsO_3]$	27.8(27.75)	3.15(3.2)	0.92	2.92
$Me_2Sn[PhAsO_3]\cdot H_2O$	26.4(26.2)	3.1(3.55)	0.99	3.11
α-$Bu^n{}_2Sn[PhAsO_3]$	39.0(38.85)	5.25(5.3)	1.08	2.92
β-$Bu^n{}_2Sn[PhAsO_3]$	39.1(38.85)	5.3(5.3)	0.97	2.60
$Bu^n{}_2Sn[PhAsO_3]\cdot H_2O$	37.4(37.3)	5.6(5.55)	1.03	2.98
α-$Me_2Sn[PhPO_3]$	31.8(31.55)	3.75(3.65)	1.11	3.55
β-$Me_2Sn[PhPO_3]$	31.7(31.55)	3.65(3.65)	0.94	3.06
$Me_2Sn[PhPO_3]\cdot H_2O$	30.2(29.75)	3.9(4.05)	1.12	3.52
$Ph_2Sn[PhPO_3]$	50.2(50.4)	3.45(3.5)	1.11	2.81
$Ph_2Sn[PhPO_3]\cdot H_2O$	48.45(48.35)	3.8(3.8)	1.12	2.85

$Bu^n{}_2Sn[PhP(OH)O_2]_2$.—A solution of phenylphosphonic acid (0.02 mol) in water (50 cm^3) was added slowly with vigorous stirring to a solution of di-n-butyltin dichloride (0.01 mol) in methanol (100 cm^3), and stirring was continued for *ca.* 5 h at room temperature. The product was then isolated in *ca.* 50% yield.

A similar product was obtained when either bis(acetato)di-n-butyltin(IV) (0.01 mol) or di-n-butylbis(pentane-2,4-dionato)tin(IV) (0.01 mol) and phenylphosphonic acid (0.02 mol) were stirred together in either methanol or acetone at room temperature. Reactions in methanol were complete after *ca.* 1 h but required several hours in acetone.

α-$Bu^n{}_2Sn[PhAsO_3]$.—A solution of di-n-butyltin dichloride (0.01 mol) in methanol (20 ml) was added slowly with vigorous stirring to a solution of monosodium phenylarsonate (0.01 mol) in water (80 cm^3). After stirring for 3 h a sticky product had formed. The solvent was decanted and acetone added to the product. After shaking for *ca.* 1 h the sticky material was converted into an insoluble powder.

$Bu^n{}_2Sn[PhAsO_3]\cdot H_2O$ *and* β-$Bu^n{}_2Sn[PhAsO_3]$.—A solution of di-n-butyltin dichloride (0.01 mol) in methanol (30 cm^3) was added dropwise with stirring to a solution of disodium phenylarsonate (0.01 mol) in water (60 cm^3). The hydrate was obtained in greater than 80% yield after stirring for 1 h at room temperature.

Heating the hydrate under vacuum at *ca.* 130 °C for several hours resulted in loss of water (as indicated by i.r. spectroscopy and elemental analysis) to yield β-$Bu^n{}_2Sn[PhAsO_3]$.

α-$Me_2Sn[PhAsO_3]$, β-$Me_2Sn[PhAsO_3]$, *and* $Me_2Sn[PhAsO_3]\cdot H_2O$.—A solution of dimethyltin dichloride (0.01 mol) in methanol (30 cm^3) was added to a solution of monosodium phenylarsonate (0.01 mol) in water (80 cm^3) to yield an immediate precipitate of α-$Me_2Sn[PhAsO_3]$ in almost quantitative yield. A similar reaction employing disodium phenylarsonate (0.01 mol) resulted in the immediate precipitation of $Me_2Sn[PhAsO_3]\cdot H_2O$ in almost quantitative yield. (I.r. and elemental analytical data supported the hydrate formulation.) When the hydrate was heated under vacuum at *ca.* 130 °C for several hours water was removed to yield β-$Me_2Sn[PhAsO_3]$.

α-$Me_2Sn[PhPO_3]$, β-$Me_2Sn[PhPO_3]$ *and* $Me_2Sn[PhPO_3]\cdot H_2O$.—These were prepared by the same procedures as the analogous arsonates. α-$Me_2Sn[PhPO_3]$ was also obtained by adding a solution of dimethyltin dichloride (0.01 mol) in methanol (30 cm^3) to a solution of phenylphosphonic acid (0.01 mol) in water (50 cm^3). The product precipitated rapidly in almost quantitative yield at room temperature.

$Ph_2Sn[PhPO_3]$.—A solution of diphenyltin dichloride (0.01 mol) in methanol (60 cm^3) was added to a solution of phenylphosphonic acid (0.01 mol) in methanol (60 cm^3) and the resulting solution was stirred at room temperature for 4 days. Insoluble $Ph_2Sn[PhPO_3]$ was isolated in greater than 80% yield at this stage.

$Ph_2Sn[PhPO_3]\cdot H_2O$.—A solution of diphenyltin dichloride (0.01 mol) in methanol (60 cm^3) was added to a solution of disodium phenylphosphonate (0.01 mol) in water (100 cm^3) and the resulting solution was stirred for 4 h. The insoluble hydrate $Ph_2Sn[PhPO_3]\cdot H_2O$ was isolated in greater than 90% yield after this time. The hydrate lost water at 100 °C under vacuum to yield $Ph_2Sn[PhPO_3]$ as obtained in the preceding preparation (confirmed by *X*-ray powder diffractometry).

Results and Discussion

Elemental analytical and Mössbauer data for the complexes prepared are listed in Table 1. They were obtained in aqueous or alcoholic media by treating the organo-tin(IV) species with the acid or with its mono- or di-sodium salt. In most cases the white products precipitated almost immediately at room temperature. Direct reaction of the diorganotin dichloride with the acids led to $Me_2Sn[PhAs(OH)O_2]_2$, $Bu^n{}_2Sn[PhAs(OH)O_2]_2$, and $Bu^n{}_2Sn[PhP(OH)O_2]_2$. However, attempts to isolate $Me_2Sn[PhP(OH)O_2]_2$ and $Ph_2Sn[PhP(OH)O_2]_2$ by this procedure were unsuccessful, yielding instead α-$Me_2Sn[PhPO_3]$ and $Ph_2Sn[PhPO_3]$. Complexes of composition $R_2Sn[PhEO_3]$ (R = Me, Bu^n, or Ph; E = P or As) were always obtained from reactions involving monosodium salts of the acids, and monohydrates of these were obtained from those reactions involving disodium salts. The hydrates lose water under vacuum at 100—150 °C to yield the anhydrous materials. Powder diffraction and i.r. data confirm that in some cases these latter anhydrous materials are different modifications from those obtained by direct reaction (see for example the diffraction patterns in Figure 4), as shown in equations (i) and (ii). Under such circumstances the form

$$R_2SnCl_2 + NaPhE(OH)O_2 \longrightarrow \alpha\text{-}R_2Sn[PhEO_3] \qquad (i)$$

$$\begin{tikzcd} R_2SnCl_2 + Na_2PhEO_3 \arrow[r] & R_2Sn[PhEO_3]\cdot H_2O \arrow[d, "\text{heat}"', "\text{vacuum}"] \\ & \beta\text{-}R_2Sn[PhEO_3] \end{tikzcd} \qquad (ii)$$

$$R = Me;\ E = P \text{ or } As$$
$$R = Bu^n;\ E = As$$

obtained by direct reaction is referred to as the α-form and the other as the β-form.

The complexes listed in Table 1 are essentially insoluble in water and organic solvents and have m.p.s greater than 250 °C. Largely as a result of low solubility, crystals which are suitable for single-crystal *X*-ray diffraction studies have not been obtained. The most illuminating structural information is derived from Mössbauer data and in the discussion which follows greatest attention will be focused on these data.

The large quadrupole splitting values (3.79—4.34 mm s^{-1}) observed for $Me_2Sn[PhAs(OH)O_2]_2$ and $Bu^n{}_2Sn[PhE(OH)O_2]_2$ (E = P or As) are almost certainly indicative of octahedral tin environments with organo groups *trans*. The most plausible structures consistent with octahedral geometry at tin and containing a single tin environment (only one doublet was observed in each Mössbauer spectrum and linewidths were normal) are: (*a*) a monomer in which acid groups have a bidentate chelating role; (*b*) a dimer $\{R_2Sn[PhE(OH)O_2]_2\}_2$ with two bridging acid groups linking tin atoms and a further terminal bidentate group on each tin, *i.e.* a structure of the type suggested for dimeric dialkyltin(IV) bis-phosphinates;[3] and (*c*) a more extensive polymer $\{R_2Sn[PhE(OH)O_2]_2\}_n$ ($n > 2$) which probably would adopt a chain or cyclic structure with acid groups doubly bridging neighbouring tin atoms.

The Mössbauer spectra of the solids display an asymmetry which appears to originate from the Goldanskii–Karyagin effect; in the case of $Me_2Sn[PhAs(OH)O_2]_2$ a spectrum is readily accumulated at room temperature.* Such features are symptomatic of structures in which tin nuclei are rigidly bound, and in the absence of hydrogen bonding could be cited as strong evidence for associated structures as in (*c*). However, i.r. spectra indicate the presence of strong hydrogen bonding in each of the solids, and this in itself could account for both the Goldanskii–Karyagin effect and the enhanced recoil-free fraction at room temperature. Nonetheless, in view of the highly intractable nature of the materials and the pronounced tendency for ⁻O⁻P⁻O⁻ and ⁻O⁻As⁻O⁻ bridging of tin atoms to occur both in the solid state and in solution,† a structure composed of monomeric units [as in (*a*)] seems highly unlikely. More specifically, in view of the infinite chain polymeric structure of $Me_3Sn[PhP(OH)O_2]$,[1] it seems likely that the dialkyltin(IV) complexes also adopt infinite chain structures [as proposed in (*c*)] with hydrogen bonding occurring as it does in the trimethyltin(IV) complex holding neighbouring chains together into sheet-like structures.

The structures of $R_2Sn[PhEO_3]$ (E = P or As; R = Me, Bu^n, or Ph) are of particular interest in view of the dimorphic behaviour of the butyl- and methyl-tin analogues. Since the previously reported $Bu^n{}_2Sn[RPO_3]$ (R = C_6H_{11}, n-octyl, CH_2Ph, or Ph)[2,3] are highly associated in solution, it is virtually certain that all the present less tractable complexes are also polymeric. With the exception of α-$Me_2Sn[PhPO_3]$, their Mössbauer isomer shift (δ) and quadrupole splitting (Δ) values are clearly indicative of structures in which tin has a co-ordination always less than six. Unfortunately, the Mössbauer data in themselves do not give more specific information regarding co-ordination about tin. However, α-modifications consistently have significantly greater δ and Δ values than β-modifications; this could be interpreted on the basis of α-structures having greater co-ordination about tin than β-structures.[12] If this interpretation is correct, β-modifications of $Me_2Sn[PhAsO_3]$ and $Bu^n{}_2Sn[PhAsO_3]$ must contain four-co-ordinate tin, since the Δ values for their α-analogues cannot be rationalized in terms of a tin co-ordination greater than five. On the other hand, since α-$Me_2Sn[PhPO_3]$ has a Δ value which could result from an octahedral tin environment in which the C⁻Sn⁻C bond deviates markedly from 180°, β-$Me_2Sn[PhPO_3]$ may contain either four- or five-co-ordinate tin. The suggested co-ordination numbers would have important implications for the nature of the polymers.

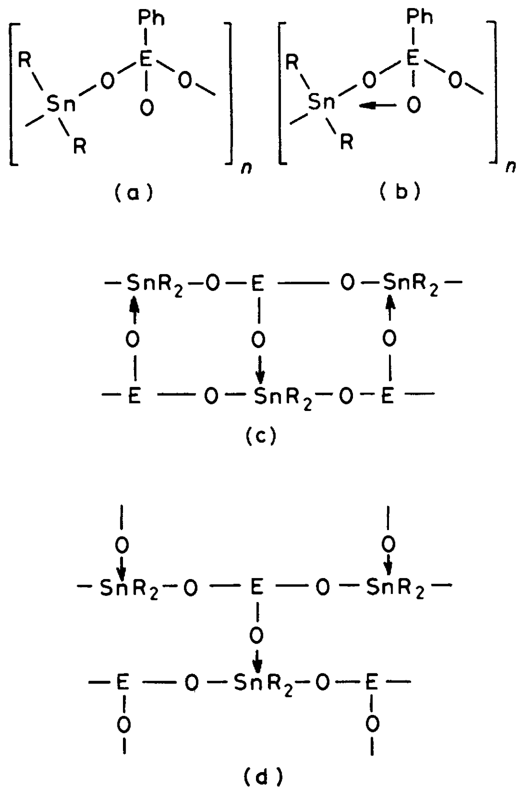

Figure 1. Possible structures for complexes $R_2Sn[PhEO_3]$ (R = Me, Bu^n, or Ph; E = P or As)

The structures of β-forms of the arsonates containing four-co-ordinate tin would almost certainly be as depicted in Figure 1(a), which represents a section of either an infinite chain or a cyclic polymer. Five-co-ordination about tin (in the α-forms) could result from the free oxygen atoms of Figure 1(a) becoming co-ordinated to neighbouring tin atoms in the same structural unit as depicted in Figure 1(b). However, it is unrealistic to assume that α- and β-forms of $Me_2Sn[PhAsO_3]$ and $Bu^n{}_2Sn[PhAsO_3]$ differ merely with respect to this latter mode of co-ordination of oxygen, since it is hardly likely that if the co-ordination in question could exist in the α-structures it could be prevented in the β-structures. Thus, the five-co-ordinate tin in α-modifications is more likely to arise as a result of acid groups adopting a more extensive bridging role, and the likely structures are the double chain or sheet polymers shown diagrammatically in Figure 1(c) and (d). On the other hand, if α-$Me_2Sn[PhPO_3]$ contains six-co-ordinate tin it almost certainly possesses some form of three-dimensional network structure.

The difference in Mössbauer parameters between crystal modifications can be accounted for in another way which does not involve different co-ordination numbers at tin. One modification could adopt a structure with the anions displaying the limited bridging role as shown in Figure 1(b) and the other a structure in which they display the more extensive bridging role as in Figure 1(c) or (d). The structures could clearly have five-co-ordinate tin sites sufficiently different to account for the differences in Mössbauer parameters.

From the foregoing argument, there is a strong possibility that the α- and β-modifications differ in the extent of association of their lattices. Since Mössbauer recoil-free fractions are so inherently dependent on lattice type, these structural differences should be readily detected by measurement of the temperature dependence of the recoil-free fractions of some key complexes.

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* The intensity asymmetry which is observed in the low temperature spectrum of $Me_2Sn[PhAs(OH)O_2]_2$ is markedly more pronounced in the room temperature spectrum. For all the complexes neither sample grinding nor sample orientation had any noticeable effect on the asymmetry.

† See refs. 1—10 and refs. therein.

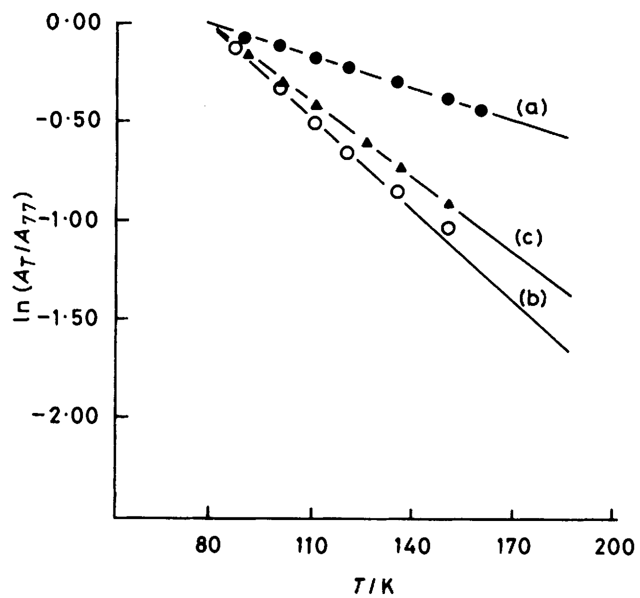

Figure 2. Plots of ln (A_T/A_{77}) for (a) α-$Me_2Sn[PhPO_3]$, (b) β-$Me_2Sn[PhPO_3]$, and (c) $Ph_2Sn[PhPO_3]$

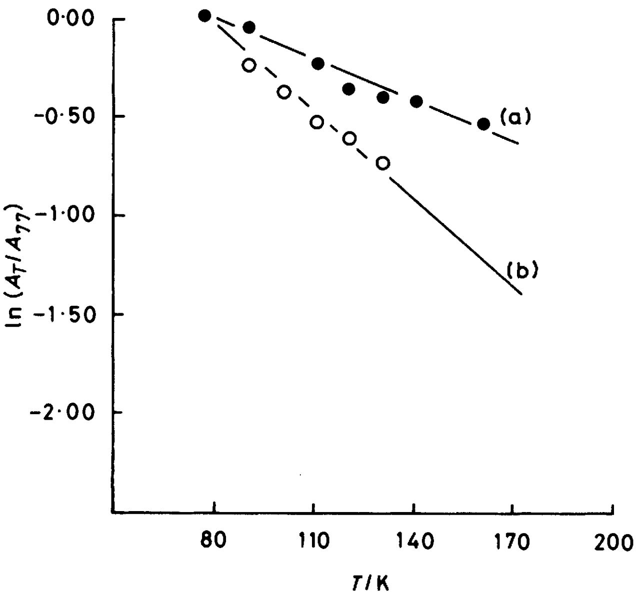

Figure 3. Plots of ln (A_T/A_{77}) for (a) α-$Me_2Sn[PhAsO_3]$ and (b) β-$Me_2Sn[PhAsO_3]$

Although the Mössbauer recoil-free fraction is not a readily accessible parameter from Mössbauer spectra, its temperature dependence can be monitored from the temperature dependence of the total area under the resonance peaks.[13,14] Following this procedure, plots of ln (A_T/A_{77}) (areas A_T at temperatures T are normalized to areas A_{77} at 77 K for purposes of intersample comparison) *vs.* T have been made for α- and β-forms of $Me_2Sn[PhAsO_3]$ and $Me_2Sn[PhPO_3]$ (see Figures 2 and 3 and Table 2). The most significant feature of the data for each complex is the large difference between the values of the slopes for α- and β-forms, indicating that tin atoms are much more rigidly bound in the α-lattices. The results are consistent with the α-modifications having the more associated lattices. In the absence of hydrogen bonding, it must be assumed that the greater degree of association results from more extensive bridging of tin atoms by acid groups. A three-dimensional polymeric structure would inevitably result in a tin co-ordination greater than five, and is thus a highly unlikely structure for α-$Me_2Sn[PhAsO_3]$ (in view of its Δ value of 3.19 mm s^{-1}). Therefore, the most reasonable interpretation of the recoil-free fraction data for the arsonates is that the α-form has the sheet structure of Figure 1(d) while the β-form has the chain or cyclic structure of either Figure 1(a) or (b). Powder diffraction data strongly suggest that the structures of β-forms of $Me_2Sn[PhAsO_3]$ and $Me_2Sn[PhPO_3]$ are closely related, and the recoil-free fraction data are consistent with this suggestion.[14] However, there is no suggestion from diffraction data of a structural similarity in the case of the α-modifications. The Δ value for α-$Me_2Sn[PhPO_3]$ is not inconsistent with six-co-ordinate tin and thus with a three-dimensional polymeric structure. There are clear similarities in the i.r. spectra (in regions associated with stretching and deformation modes of the $^-AsO_3$ moiety[6,15]) of α-forms of $Me_2Sn[PhAsO_3]$ and $Bu^n{}_2Sn[PhAsO_3]$ which suggest that they are isostructural. A similar type of i.r. evidence suggests that β-forms are isostructural.*

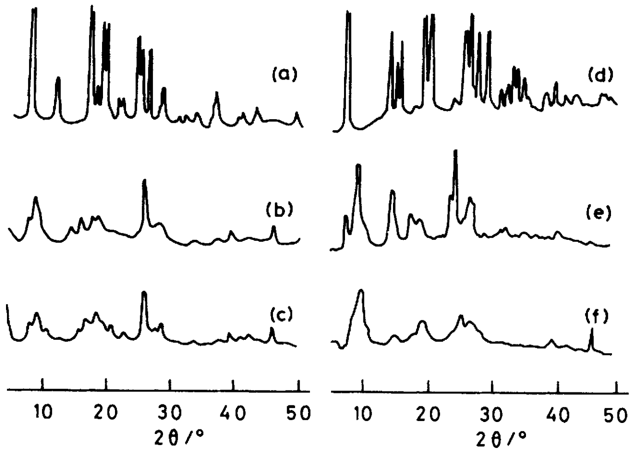

Figure 4. Powder diffraction patterns (Cu-K_α radiation) of (a) α-$Me_2Sn[PhPO_3]$, (b) $Me_2Sn[PhPO_3]\cdot H_2O$, (c) β-$Me_2Sn[PhPO_3]$, (d) α-$Me_2Sn[PhAsO_3]$, (e) $Me_2Sn[PhAsO_3]\cdot H_2O$, and (f) β-$Me_2Sn[PhAsO_3]$

Table 2. Recoil-free fraction temperature coefficients

Compound	$10^2a/K^{-1}$ [a]	n [b]	r [c]
α-$Me_2Sn[PhPO_3]$	−0.51	8	0.999
β-$Me_2Sn[PhPO_3]$	−1.44	7	0.998
$Ph_2Sn[PhPO_3]$	−1.24	7	0.999
α-$Me_2Sn[PhAsO_3]$	−0.69	7	0.979
β-$Me_2Sn[PhAsO_3]$	−1.37	6	0.988

[a] a = ln (A_T/A_{77}). [b] n = number of experimental points. [c] r = correlation coefficient.

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* As a general rule the most significant differences in the spectra of α- and β-modifications were observed in those regions associated with stretching and deformation modes of the $^-EO_3$ (E = P or As) moiety. The spectra are generally quite complex in these regions and consequently band assignments were not attempted.

(The α- and β-modifications were prepared by identical procedures for the two compounds.) Only one form of $Ph_2Sn[PhPO_3]$ was isolated (see Experimental section). Its i.r. spectrum (in regions associated with the stretching and deformation modes of the $^-PO_3$ moiety [3,10,16]) closely resembles that of β-$Me_2Sn[PhPO_3]$; furthermore, its variable-temperature Mössbauer data (see Figure 2 and Table 2) much more closely parallel those for β-$Me_2Sn[PhPO_3]$ than they do those for the α-form. It thus appears to have a β-type structure. The apparent inability of $Ph_2Sn[PhPO_3]$ to adopt the α-type structure may be related to the steric influence of the phenyl groups attached to tin.

I.r. spectra indicate that essentially the same mode of bonding of anionic groups occurs in both the hydrated and related anhydrous materials, and in the case of the dimethyl- and diphenyl-tin complexes *X*-ray powder diffraction data indicate that the broad structural features of the hydrates are retained on removal of water (compare, for example, relevant diffraction patterns of Figure 4). It is clear, therefore, that the same polymeric units exist in both the hydrates and the anhydrous materials, and that the water (in the hydrate structures) is either bonded to tin or present as lattice water. The role of the water is uncertain. The fact that hydrates of the dimethyl- and dibutyl-tin complexes have greater δ and Δ values than their anhydrous counterparts may indicate a greater co-ordination of tin in the hydrates and thus that water is bound to tin. However, the similarity of the δ and Δ values for $Ph_2Sn[PhPO_3]\cdot H_2O$ and $Ph_2Sn[PhPO_3]$ suggests that water is not co-ordinated to tin in $Ph_2Sn[PhPO_3]\cdot H_2O$.

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