The Configuration and Lattice Dynamics of Complexes of Dialkyltin(IV) with Adenosine 5'-Monophosphate and Phenyl Phosphates

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The dialkyltin(IV) complexes of the mononucleotide adenosine 5'-monophosphate (AMP) and of phenyl phosphate, $SnR_2(AMP)\cdot 2H_2O$ (R = Me or Bu^n) and $SnR_2[PO_3(OPh)]$ (R = Me, Et, or Bu^n), have been prepared and structurally characterized in the solid state by means of ^{119}Sn Mössbauer spectroscopy, determination of lattice dynamics by temperature-dependent ^{119}Sn Mössbauer spectroscopy, and by vibrational studies using conventional and Fourier-transform i.r. spectroscopy. The known diphenyl phosphate complexes $SnR_2[PO_2(OPh)_2]_2$ (R = Me, Et, or Bu^n) have been similarly investigated, particularly with respect to their lattice dynamics. A distorted-octahedral configuration is proposed for the tin environment in the complexes $SnR_2(AMP)\cdot 2H_2O$ (which appear to be phosphate-only bonded species) and $SnR_2[PO_3(OPh)]$, involving a trifurcated oxygen atom and bent SnC_2 skeletons; these units appear to be embedded into two-dimensional solid-state polymers originating from intermolecular bridging of the phosphate groups. The regular octahedral structure, with linear SnC_2 skeletons, which has been inferred for the complexes $SnR_2[PO_2(OPh)_2]_2$, as well as their polymeric, sheet-like, nature, has been confirmed.

The present study is primarily concerned with the interaction between dialkyltin(IV) moieties and the nucleotide adenosine 5'-monophosphate (AMP^{2-}), which, by reaction in aqueous media, yield the solid products $SnR_2(AMP)\cdot 2H_2O$ (R = Me or Bu^n). These compounds appear to be the first examples of an organometal binding to nucleotides;[1,2] in this context, it should be noted that the complex $Pb_2(ATP)\cdot 2H_2O$ [ATP = adenosine 5'-triphosphate(4−)][3] is the only post-transition metal derivative of nucleotides so far reported.

Interest in the study of such complexes has been stimulated by recent reports of the antitumour activity of organotin(IV) salts, adducts, and complexes.[4–12] Diorganotin(IV) derivatives, and mainly dialkyltin(IV), appear to be the biologically most active examples.[4–6,8,10,12] In attempts to correlate the antitumour activity with the structure, it has been generally assumed that the eventually co-ordinated organic ligand would facilitate the transport of the complex across cell membranes, while the antitumour activity would be exerted by the dissociated diorganotin(IV) moieties.[4,5,9,10,12] These would interact with nucleic acids, in a manner somewhat analogous to that shown by cisplatin, *cis*-$[Pt^{II}Cl_2(NH_3)_2]$.[4,9,10] Moreover, metal ion–nucleotide complexes could also play a significant role in transport processes across membranes[13] affecting both the kinetics and thermodynamics of the interaction with the phase boundary.

The importance of detailed studies of the binding of dialkyltin(IV) to nucleic acid constituents thus becomes evident. In this context we have previously investigated interactions with purine bases (adenine and 6-thiopurine[14,15]) and the ribose moiety of adenosine.[16,17] We have extended these investigations to nucleotide–organotin(IV) systems, and report here our solid-state studies on the complexes $SnR_2(AMP)\cdot 2H_2O$ (R = Me or Bu^n) by variable-temperature Mössbauer spectroscopy, conventional i.r., and Fourier-transform (F.t.) i.r. spectroscopy. With the aim of defining as completely as possible the nature of the AMP derivatives, the new phenyl phosphate complexes $SnR_2[PO_3(OPh)]$, as well as the already known diphenyl phosphates $SnR_2[PO_2(OPh)_2]_2$[18] (R = Me, Et, or Bu^n), have been included in the present investigation.

Experimental

The compounds SnR_2Cl_2 (R = Me, Et, or Bu^n), $H_2AMP\cdot H_2O$, $Na_2(AMP)\cdot H_2O$, $Na_2[PO_3(OPh)]\cdot 2H_2O$, and $PO(OH)(OPh)_2$ were supplied by Alfa or Ega; other reagents and solvents were pure commerical products. The complexes were synthesized as described below. In agreement with literature reports on the syntheses of a number of metal ion–nucleotide complexes,[1] and in view of possible correlations between solid state and solution species[2] the present study concerns itself primarily with complexes formed in aqueous systems. In the latter context, the knowledge of the experimental conditions, and in particular of the pH range, where organotin(IV)–nucleotide complexes form in aqueous media is essential for further studies on complex formation in aqueous solution, which are presently underway in our laboratories.[19]

$SnMe_2(AMP)\cdot 2H_2O$ (**1**).—Solutions of $SnMe_2Cl_2$ and $H_2AMP\cdot H_2O$ (2 mmol of each reagent in *ca.* 100 cm^3 H_2O) were combined dropwise in the presence of aqueous $NaHCO_3$ while stirring. A white bulky precipitate was obtained at pH *ca.* 6, and this was filtered off, washed with H_2O, and dried under vacuum (Found: C, 27.6; H, 4.0; N, 13.4. Calc. for $C_{12}H_{22}N_5O_9PSn$: C, 27.2; H, 4.2; N, 13.2%). The presence of two molecules of H_2O in (**1**) [and (**2**) below] has been inferred from the analytical and i.r. spectroscopic data.

$SnBu^n{}_2(AMP)\cdot 2H_2O$ (**2**).—This complex was prepared from $SnBu^n{}_2Cl_2$ and H_2AMP essentially as for (**1**). Larger volumes of H_2O, or CH_3OH–H_2O (1:1), were employed as solvent, owing to the smaller solubility of $SnBu^n{}_2Cl_2$. The precipitate formed immediately after mixing, even from H_2O solutions at pH *ca.* 3, adjusted by the addition of aqueous HCl (Found: C, 35.1; H, 5.2; N, 11.2. Calc. for $C_{18}H_{34}N_5O_9PSn$: C, 35.2; H, 5.6; N, 11.4%).

$SnR_2[PO_3(OPh)]$ [R = Me (**3**), Et (**4**), *or* Bu^n (**5**)].—$Na_2[PO_3(OPh)]\cdot 2H_2O$ (2 mmol in *ca.* 50 cm^3 H_2O) was added dropwise with stirring to solutions of SnR_2Cl_2 (2 mmol in 50—100 cm^3 H_2O) resulting in the immediate precipitation of white solids, which were washed with H_2O and/or MeOH and dried

Table 1. Summary of ^{119}Sn Mössbauer data

Compound	δ^a/mm s^{-1}	Δ^b/mm s^{-1}	$10^2\{-\mathrm{d}\ln[A(T)/A(78)]/\mathrm{d}T\}$/K^{-1}	Γ^c/mm s^{-1}	T range/K
(**1**) $SnMe_2(AMP)\cdot 2H_2O$	1.228	3.803	0.95	0.99	78—295
(**2**) $SnBu^n{}_2(AMP)\cdot 2H_2O$	1.274	3.355	1.28	0.98	78—228
(**3**) $SnMe_2[PO_3(OPh)]$	1.279	3.899	1.303	0.98	78—215
(**4**) $SnEt_2[PO_3(OPh)]$	1.330	3.681	1.025	0.90	78—165.5
(**5**) $SnBu^n{}_2[PO_3(OPh)]$	1.275	3.466	1.947	0.99	78—195
(**6**) $SnMe_2[PO_2(OPh)_2]_2{}^d$	1.406	4.779	1.042	0.89	78—125
(**7**) $SnEt_2[PO_2(OPh)_2]_2{}^d$	1.506	4.753	0.969	0.86	78—137
(**8**) $SnBu^n{}_2[PO_2(OPh)_2]_2{}^d$	1.515	4.781	1.627	0.94	78—210

[a] With respect to $CaSnO_3$ at 295 ± 2 K. Temperature independent within experimental error (±0.006 mm s^{-1}) over the indicated range. [b] Temperature independent within experimental error (±0.010 mm s^{-1}) over the indicated range. [c] Temperature independent within experimental error (±0.018 mm s^{-1}) over the indicated range. The data for compounds (**6**), (**7**), and (**8**) were acquired using a slightly narrower linewidth source compared to the other results herein reported. [d] Ref. 18, at 77 K: (**6**), $\delta = 1.38$, $\Delta = 4.91$; (**7**), $\delta = 1.50$, $\Delta = 4.86$; (**8**), $\delta = 1.54$, $\Delta = 4.58$ mm s^{-1}.

under vacuum. Analogous syntheses were also carried out from MeOH solutions [Found for (**3**): C, 29.3; H, 3.5. Calc. for $C_8H_{11}O_4PSn$: C, 29.9; H, 3.45%. Found for (**4**): C, 35.8; H, 4.5. Calc. for $C_{10}H_{15}O_4PSn$: C, 34.4; H, 4.3%. Found for (**5**): C, 41.3; H, 5.9. Calc. for $C_{14}H_{23}O_4PSn$: C, 41.5; H, 5.7%].

$SnR_2[PO_2(OPh)_2]_2$ [R = Me (**6**), Et (**7**), *or* Bu^n (**8**)].[18]—These compounds were prepared from SnR_2Cl_2 and $PO(OH)(OPh)_2$ as for (**3**)—(**5**) above, using MeOH as solvent.

Complexes (**1**)—(**8**) are white, air-stable solids, very slightly soluble in water and in common organic solvents. Decomposition occurs at temperatures above *ca.* 200 °C. The two water molecules per formula weight in the AMP complexes (**1**) and (**2**) are retained even upon heating at 110 °C overnight *in vacuo*, as inferred from the elemental analyses as well as from the vibrational spectra in the 3 000 cm^{-1} region (see later). Variable-temperature ^{119}Sn Mössbauer spectra of the subject compounds were acquired using the constant acceleration transmission mode spectrometer described earlier.[20] In order to avoid saturation corrections at low temperatures, optically thin samples were prepared by pressing weighed quantities of the sample compounds, and of an inert carbohydrate dispersant, into self-supporting weighable pellets, which could then be mounted into the copper cold-finger of an Air Products Helitran cryostat. Temperatures were monitored using NBS calibrated thermocouples. Spectrometer calibration was effected using the magnetic hyperfine interaction of metallic iron at room temperature. All isomer shifts reported are with respect to the centre of the $CaSnO_3$ (or $BaSnO_3$) absorber spectrum at 295 ± 2 K.

Midrange (1 800—400 cm^{-1}) i.r. spectra were obtained using an IBM Instruments model 32 Fourier-transform spectrometer which had been purged with dry nitrogen to remove CO_2 and H_2O in the sample compartment. Typically 100 interferometer scans at 2-cm^{-1} resolution were co-added and ratioed against a background of the KBr blank. The samples were *ca.* 1% by weight solutes in thoroughly dried spectroscopic grade KBr. I.r. spectra in the range 4 000–200 cm^{-1} were also obtained using Perkin-Elmer 938 and 580 instruments, as Nujol and hexachlorobutadiene mulls between CsI discs.

Results and Discussion

The results of the variable-temperature ^{119}Sn Mössbauer experiments are summarized in Table 1. All of the compounds examined gave rise to doublet resonance spectra with component linewidths of 0.86—0.99 mm s^{-1}, and there is little doubt that their structures involve a metal atom bonded to the oxygen atoms of the phosphate moiety which give rise to a Mössbauer spectrum characteristic of a unique lattice site. The isomer shifts (at 78 K) are typical of diorganotin(IV) compounds, and are otherwise unremarkable. Because of the relatively large temperature dependence of the recoil-free fractions (see later), which limits the accessible temperature range over which measurements can be made, and the intrinsically small temperature dependence of the isomer shift parameter (δ) of organotin complexes, it is not possible to extract any meaningful information from $\mathrm{d}(\delta)/\mathrm{d}T$ data, and the isomer shift values reported in Table 1 are average values over the indicated temperature range.

The large quadrupole hyperfine interactions observed in the resonance spectra of the bis(diphenyl phosphate) complexes (**6**)—(**8**) are characteristic of *trans* octahedral ligand symmetry about the metal atom, with the two alkyl groups in the axial positions. The magnitude of the quadrupole splitting parameters (Δ) is insensitive to the size of the alkyl group. The observation that these 2:1 (ligand to metal) complexes are insoluble white solids having no definite melting point below *ca.* 250 °C[18] suggests a polymeric structure, which can be envisaged as involving bidentate diphenyl phosphate groups bridging adjacent metal atoms by occupying *cis* equatorial sites in the octahedral positions around Sn.[18] It seems worth noting that complexes (**6**)—(**8**) fit quite well into the pattern described by the class of complexes $SnR_2[PO_2(XY)]_2$, *i.e.*, bis(fluorophosphate) (X = Y = F),[21] bis(phosphinate) (X = Y = H),[22] and bis(phenyl phenylphosphonate) (X = Ph, Y = OPh)[23] derivatives.

In the case of the AMP [(**1**) and (**2**)] and the monophenyl phosphate [(**3**)—(**5**)] complexes of diorganotin, the quadrupole hyperfine interaction is appreciably smaller than for the diphenyl phosphate homologues, suggesting an appreciable distortion of the ligand symmetry from an ideal O_h configuration. In contrast to the observations for (**6**)—(**8**), Δ values appear to depend on the size (length) of the alkyl ligands bonded to the metal atom, and are suggestive of a steric interaction between the (asymmetric) phosphate ligand and the organic group. Such an interaction would result in a pronounced departure from linearity of the C–Sn–C configuration and its concomitant reflection in the magnitude of Δ, as observed experimentally. In this context, it is interesting to note that the decrease in Δ for R = Bu^n compared to R = Me is approximately the same for the pairs (**1**),(**2**) and (**3**),(**5**), in contrast with the constancy of this parameter for the pair (**6**),(**8**).

The Δ values of compounds (**1**)—(**5**) essentially correspond to

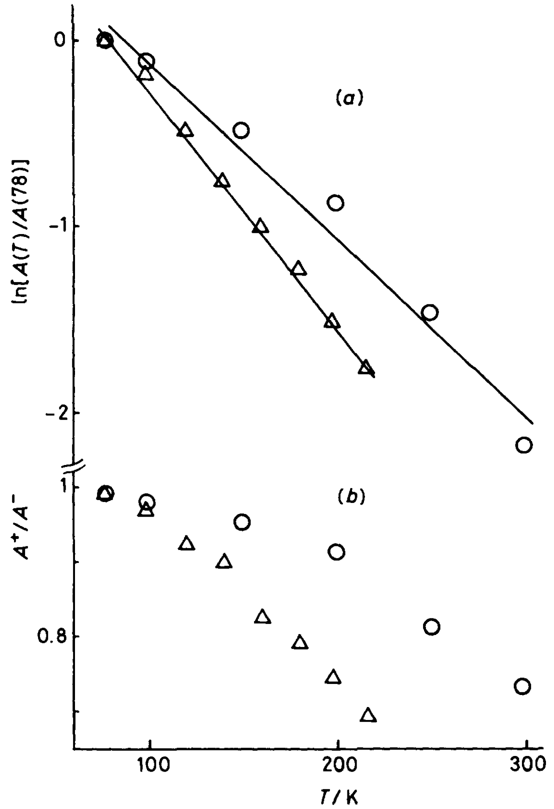

Figure 1. Temperature dependence of the ^{119}Sn Mössbauer parameters for $SnMe_2(AMP)\cdot 2H_2O$ (○) and $SnMe_2[PO_3(OPh)]$ (△) as examples of the trends detected for the $Sn^{IV}R_2$ complexes investigated in the present study. (*a*) ^{119}Sn Mössbauer recoil-free fraction as given by the temperature dependence of the normalized areas under the resonance peaks. Full lines are the linear least-squares fits to the experimental data points, the related equations being $\ln[A(T)/A(78)] = 0.852 - 9.46 \times 10^{-3}T$ (correlation coefficient $r = 0.990$) and $1.09 - 1.33 \times 10^{-2}T$ ($r = 0.998$). A small departure from linearity of the data for (**1**) is evident, but has been neglected in the data analysis. (*b*) Area ratio of the two components of the quadrupole doublet located at isomer shifts more (A^+) and less (A^-) positive than the spectrum centroid

those of complexes $SnR_2(PXO_3)$, *i.e.*, phosphonate (X = H),[22] phosphate (X = OH),[22] and phenylphosphonate (X = Ph)[24] derivatives; moreover, the quadrupole coupling observed in the ^{119}Sn Mössbauer spectra of the phosphonates is a function of the nature of R.[22] Polymeric structures have been suggested for these complexes, although an uncertainty remains concerning the co-ordination number of tin (five or six) and the exact nature of the polymer chain.[22,24]

There are two interesting observations relating to the lattice dynamics of the tin atom in the compounds studied. The first of these relates to the temperature dependence of the recoil-free fraction of the Mössbauer transition.[25] For thin absorbers, this is equivalent to the temperature dependence of the normalized area under the resonance curve,[25] and such data are included in Table 1, while Figure 1(*a*) reports the data points for the $Sn^{IV}Me_2$ complexes (**1**) and (**3**) as an example of the quality of the observed correlations. In both data sets it is noted that $\ln[A(T)/A(78)]$ is not strictly a linear function of temperature, but that a small amount of curvature is evident in the data. This curvature, which presumably arises from anharmonicity effects in the metal atom vibrational temperature dependence, has been neglected in the use of linear regression fits to the data in the present analysis. More significant is the observation that these temperature dependences are moderately large for (presumably) polymeric compounds,[25] being of the magnitudes determined for β-$SnMe_2(PPhO_3)$ and $SnPh_2(PPhO_3)$.[24] Typically the area under the resonance curve at 300 K is only *ca.* 0.1 or less of its value at liquid-nitrogen temperature, an observation which is consistent with the postulated chain polymeric nature of the subject compounds. For organometallic compounds of relatively compact structure, where only metal atom–nearest neighbour bonding forces need to be considered, it might be expected that there would be a simple correlation between the mass of the ligands and the temperature dependence of the recoil-free fraction. However, for more complex structures, such as those under discussion, the relationship between these two parameters is by no means straightforward and involves both electronic (bond strength) and steric (space-filling) aspects of the metal–ligand environment. Thus, it is observed that $-\mathrm{d}\ln f/\mathrm{d}T$ (f = recoil-free fraction) does not decrease monotonically with increasing mass (length) of the organic ligands bonded to the metal atom, but appears to reach a minimal value for the ethyl-substituted compounds, and is presumably a reflection of the influence of the size of the organic ligand on the mean-square amplitude of the tin atom in its octahedral environment. The present data suggest that in the bonding environment of the metal atom in these complexes, a relatively large displacement of the tin can be associated with both a small organic ligand occupying the 'axial' positions (where mass effects are expected to dominate) and large organic ligands (where relatively weak intermolecular forces are expected to dominate).

In the context of the above discussion, it is to be noted that Zuckerman and co-workers[18] have reported the observation of a resonance effect in room temperature spectra of $SnMe_2[PO_2(OPh)_2]_2$. Inference of the temperature dependence of the recoil-free fraction from the temperature dependence of the area under the resonance curve is only valid if the 'thin absorber approximation' is valid; that is, if saturation and self-absorption effects are negligible. In order to insure the validity of this approximation, the present study has concerned itself with optically thin samples only, thus limiting the temperature over which the data analysis can be carried out. Thus, the present results, and those cited earlier[18] are in no way inconsistent with each other, although the differences in synthetic procedures (aqueous *versus* toluene media, for example) used in the two studies should not be ignored.

The second unexpected observation relates to the vibrational anisotropy associated with the motion of the metal atom in these complexes. As already noted above, the values of the quadrupole splitting parameters suggest that the ligand geometry around the metal atom in the diorganotin(IV) bis(diphenyl phosphate) complexes [(**6**), (**7**), and (**8**)] is approximately that of a regular octahedral structure.[18] Coupled with the relatively large mean square amplitude of vibration of the metal atom when R = Me this leads to the expectation that anisotropy of this metal atom motion should be observable as a Goldanskii–Karyagin effect (*i.e.*, as reflected in the temperature dependence of the relative areas of the two components of a quadrupole-split doublet).[26] However, experimentally it is observed that over the temperature range $78 \leqslant T \leqslant 170$ K there is no observable temperature-dependent asymmetry in these spectra, the area ratios being 0.986 ± 0.013 when R = Me and 0.982 ± 0.019 when R = Et. When R = Bu^n, there appears to be a small temperature-dependent intensity ratio observable in the quadrupole-split Mössbauer spectra of complex (**8**), but whether this observation is related to the increase in the temperature dependence of the recoil-free fraction, as discussed above, or not, cannot be decided on the basis of the presently available data.

For all of the other compounds included in Table 1, with the

Table 2. Relevant i.r. absorptions of AMP derivatives in the regions 1 150—950, 800, and 650—200 cm^{-1} [a]

$Na_2(AMP)\cdot H_2O$	$SnBu^n{}_2(AMP)\cdot 2H_2O$ (**1**)	$SnBu^n{}_2(AMP)\cdot 2H_2O$ (**2**)	Assignments [b]
	1 130vs	1 125br,vs	$\nu(PO_3)$ (deg)
1 100br,vs	1 105vs		
	1 080vs	1 075vs	
	1 010s	1 010s	
975vs	995s	1 000s	$\nu_{sym}(PO_3)$
	965m	955m	
800m	800m	800m	$\nu[P–O–(C)]$
650m	650mw		$\delta(NH_2)$
	630w		
		630br,m	$\nu_{sym} + \nu_{asym}(SnC_2)$(II)
		590m	[$\delta(NH_2)$ + PO_3 (sym def)?]
	590vw		$\nu_{asym}(SnC_2)$
570 (sh)	560vw		PO_3 (sym def)
		535ms	$\nu_{sym} + \nu_{asym}(SnC_2)$(I) [$PO_3$ (deg def) + PO_3 (rock)?]
540m	535w		PO_3 (deg def) + PO_3 (rock)?
		520m	$\nu_{sym} + \nu_{asym}(SnC_2)$(I)?
	510w		$\nu_{sym}(SnC_2)$
500 (sh)	495mw	505vw	PO_3 (sym def + deg def) + PO_3 (rock)
	450w		
400 (sh)	395w		[PO_3 (deg def) + PO_3 (rock)?]
	315mw	320w	
	250m	240mw	[PO_3 (rock) + C–O–P (bend)?]

[a] s = Strong, m = medium, w = weak, br = broad, deg = degenerate, def = deformation. [b] Tentative; effected according to refs. 28, 29, 32 (phosphate modes) and 31, 33 ($Sn^{IV}R_2$ modes). See also the text.

exception of (**4**) (the area ratio being 1.011 ± 0.0230), there appears to be a non-negligible Goldanskii–Karyagin effect observable in the Mössbauer spectra, as shown in Figure 1(*b*) for the $Sn^{IV}Me_2$ derivatives (**1**) and (**3**). However, since these molecules presumably lack the four-fold symmetry axis present in the bis(diphenyl phosphate) compounds, no direct connection betwen this observation and the difference in the mean-square amplitude parallel and perpendicular to the principal field gradient axis can be extracted from these results. The apparent absence of a Goldanskii–Karyagin effect in (**4**), in which $d\ln A/dT$ is a minimum relative to (**3**) and (**5**), again appears to reflect the dependence of the metal atom motion both on the inter- and the intra-molecular forces in these complexes.

The information extracted from the i.r. study is in accord with that inferred from the analytical and Mössbauer data discussed above. In the spectra of the compounds $SnR_2(AMP)\cdot 2H_2O$, (**1**) and (**2**), a very strong and broad band, due to ν(OH) in hydrogen-bonded H_2O, occurs in the range 3 600—2 600 cm^{-1},[27] and obscures other vibrational modes expected in this region.[16,27–30] Moreover, the frequency and intensity of the bands detected in the range 1 655—1 200 cm^{-1}, and of the band at 725—720 cm^{-1}, correspond well with those reported for adenosine and $Na_2(AMP)\cdot H_2O$, and are assigned to modes involving adenine and ribose;[16,28–30] the possible (in principle) bonding to Sn by adenine heterocyclic nitrogen atoms is consequently ruled out.[16,29] In the regions 910—810 and 780—730 cm^{-1} the expected ribose vibrations, as well as the butyl rocking modes for the $Sn^{IV}Bu^n{}_2$ complex (**2**), have been adequately identified.[16,29–31]

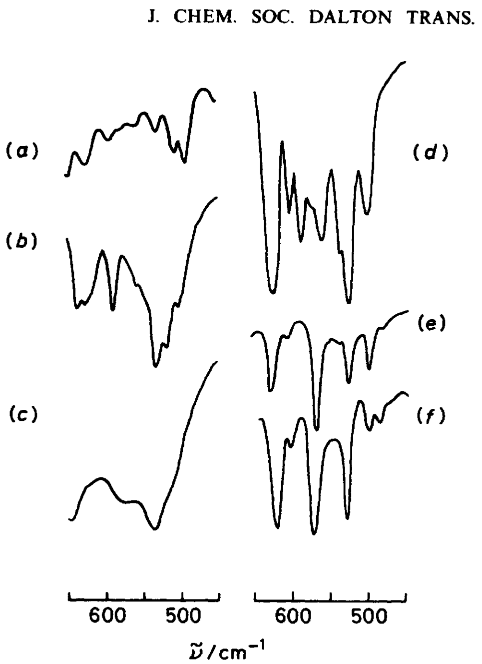

Figure 2. I.r. spectra in the 500—600 cm^{-1} region of (*a*) $SnMe_2(AMP)\cdot 2H_2O$, (*b*) $SnBu^n{}_2(AMP)\cdot 2H_2O$, (*c*) $Na_2(AMP)\cdot H_2O$, (*d*) $SnMe_2[PO_3(OPh)]$, (*e*) $SnEt_2[PO_3(OPh)]$, and (*f*) $SnBu^n{}_2[PO_3(OPh)]$

In the complexes $SnR_2(AMP)\cdot 2H_2O$, (**1**) and (**2**), the occurrence of $-PO_3{}^{2-}$ bonding to Sn, as well as the presence of a bent CSnC skeleton in (**1**), is evidenced by the following trends observed for the phosphate[28,29,32] and $Sn^{IV}R_2$[31,33] vibrational modes: (*i*) the shifting and splitting of $\nu(PO_3)$ (degenerate) and $\nu_{sym}(PO_3)$ in (**1**) and (**2**) with respect to $Na_2(AMP)\cdot H_2O$ (Table 2); (*ii*) the identification of two bands attributed to $\nu_{sym}(SnC_2)$ and $\nu_{asym}(SnC_2)$ in complex (**1**) (Table 2), which appears to be reliable on the basis of a careful comparison and assignment of the bands (of both their frequency and relative intensity) occurring in the spectra of $Na_2(AMP)\cdot H_2O$ and complexes (**1**) and (**2**) in the 500—600 cm^{-1} region [Figure 2(*a*)—(*c*)].

The invariance of the ν[P–O–(C)] mode in $Na_2(AMP)\cdot H_2O$[28,29,32] and in complexes (**1**) and (**2**) (Table 2) strongly suggests that the ester oxygen is not involved in co-ordination to the metal centre, in accord with earlier results on a series of metal complexes of nucleotides.[1]

The bonding and configuration of the SnC_2 skeleton in the complexes $SnR_2[PO_3(OPh)]$, (**3**)—(**5**), as inferred from i.r. spectroscopic data, appear to correspond to those occurring for (**1**) and (**2**) discussed above, while being substantially different in the derivatives $SnR_2[PO_2(OPh)_2]_2$, (**6**)—(**8**). The i.r. spectra of complexes (**3**)—(**8**) are practically identical for the mono-substituted phenyl absorptions, which occur at the expected frequency values;[27,34] within each homologous series, *i.e.*, (**3**)—(**5**) and (**6**)—(**8**), the bands related to the mono- and di-ester phosphate groups[28,34] respectively, again coincide, the spectra obviously differing for modes inherent to the $Sn^{IV}Me_2$,[33] $Sn^{IV}Et_2$,[35] and $Sn^{IV}Bu^n{}_2$[31] moieties. The F.t.–i.r. absorptions attributed to phosphate and skeletal SnC_2 vibrations in the $Sn^{IV}Me_2$ complexes (**3**) and (**6**) are listed in Table 3 as examples, and also serve to indicate the quality of the results we obtained by the F.t.–i.r. technique.

The vibrational modes $\nu(PO_3)$[28] essentially correspond in complexes (**1**) and (**2**) (Table 2), and (**3**)—(**5**) (Table 3, see above); the spectra of compounds (**3**)—(**5**) in the 500—600 cm^{-1} region [Figure 2(*d*)—(*f*)] strongly suggest the presence of both $\nu_{sym}(SnC_2)$ and $\nu_{asym}(SnC_2)$ in the spectra of the $Sn^{IV}Me_2$ derivative (**3**) (Table 3). No evidence for $\nu_{sym}(SnC_2)$, expected around 520 cm^{-1},[33] is observed in the spectrum of

Table 3. Relevant F.t.-i.r. absorptions of $Sn^{IV}Me_2$ phenyl- and diphenylphosphates, attributable to phosphate and SnC_2 vibrational modes

$SnMe_2[PO_3(OPh)]$ (3)		$SnMe_2[PO_2(OPh)_2]_2$ [6)		
$\tilde{\nu}/cm^{-1}$	%*T*	$\tilde{\nu}/cm^{-1}$	%*T*	Assignments[a]
1 230	14			$\nu[(P)–O–C]$
1 201	23			
		1 219	1	$\nu_{asym}(O\cdots P\cdots O)$ $+\nu[(P)–O–C]$
		1 200	1	
1 134	3			$\nu(PO_3)$ (deg)
1 117	3			
1 190	6			
		1 107	1	$\nu_{sym}(O\cdots P\cdots O)$
1 017	8			$\nu[P–O–(C)]$
		949	5	
936	12			$\nu_{sym}(PO_3)$
		779	16	$\nu_{asym}(O\cdots P\cdots O)$
		758	22	$\nu_{sym}(O\cdots P\cdots O)$
590	47	595	*b*	$\nu_{asym}(SnC_2)$
563	45			PO_3 (sym def)
540	38			PO_3 (deg def) + PO_3 (rock)
527	35			$\nu_{sym}(SnC_2)$
		542	20	$\delta(PO_2)$?
		521	44	

[a] Tentative, effected according to refs. 28, 33, and 34. [b] Medium-weak band, detected in the spectra but not reported in the computer output.

$SnMe_2[PO_2(OPh)_2]_2$ (**6**) (Table 3). In fact, the spectra of compounds (**6**)—(**8**) in the region 500—550 cm^{-1} each show three bands at 505, 520, and 540 cm^{-1}. The absorption at 505 cm^{-1} in (**7**), and at 540 cm^{-1} in (**8**), are consistently more intense than the corresponding bands in complex (**6**), and this may be attributed to the contribution of the respective tin–organic residue vibrations;[31,35] on the other hand, the bands at 520 cm^{-1} show comparable intensity in the three complexes (**6**)—(**8**). Only the $\nu_{asym}(SnC_2)$ vibration is present in the spectrum of $SnMe_2[PO_2(OPh)_2]_2$ (**6**) (Table 3), consistent with a linear C–Sn–C skeleton in this complex.

F.t.-i.r. spectra of $SnBu^n_2(AMP)\cdot 2H_2O$ (**2**) and $SnMe_2[PO_2(OPh)_2]_2$ (**6**) have been examined in the range 1 200—450 cm^{-1} at both 300 and 80 K. Except for the usual band sharpening as the temperature is lowered, which permits the resolution of some closely spaced absorptions into individual bands, there are no major qualitative differences in the spectra at the two temperatures thus validating the structural inferences deduced from the low-temperature ^{119}Sn Mössbauer data, on the one hand, and the room-temperature i.r. data, on the other. However, it should be noted that in the spectra of (**6**), the room-temperature absorption at 478 cm^{-1} is split into a doublet at 485 and 477 cm^{-1} at 80 K, and that the temperature dependence of such spectral changes may provide additional clues to the structural integrity of organometallic compounds between room and cryogenic temperatures, as well as of the strength of intermolecular forces which affect ligand interactions between metal centres.[36]

On the basis of the Mössbauer and i.r. spectroscopic studies discussed above, it is concluded that complexes (**1**)—(**5**) can be considered to be solid-state polymeric species in which the tin atoms are six-co-ordinated by phosphate oxygen atoms and the carbon atoms of the alkyl radicals, giving rise to a non-linear CSnC skeleton. In fact, the coincidence of the spectral data for the two classes of compounds would rule out co-ordination of H_2O in the AMP complexes (**1**) and (**2**), so that H_2O molecules are assumed to be involved only in hydrogen bonding, analogous to that occurring in a series of metal complexes of nucleotides.[1] Moreover, the four Sn–O–P bonds presumably originate from the interaction of three oxygen atoms of each phosphate group with a Sn atom, since the ester oxygen appeared not to be involved in co-ordination. Phosphate-only bonding to metal ions has been detected for a series of pyrimidine and purine nucleotide complexes,[1,37] and four-co-ordination of tin by three oxygen atoms would involve one trifurcated oxygen (between two tin atoms and one phosphorus), such as in $SnHPO_4$.[38]

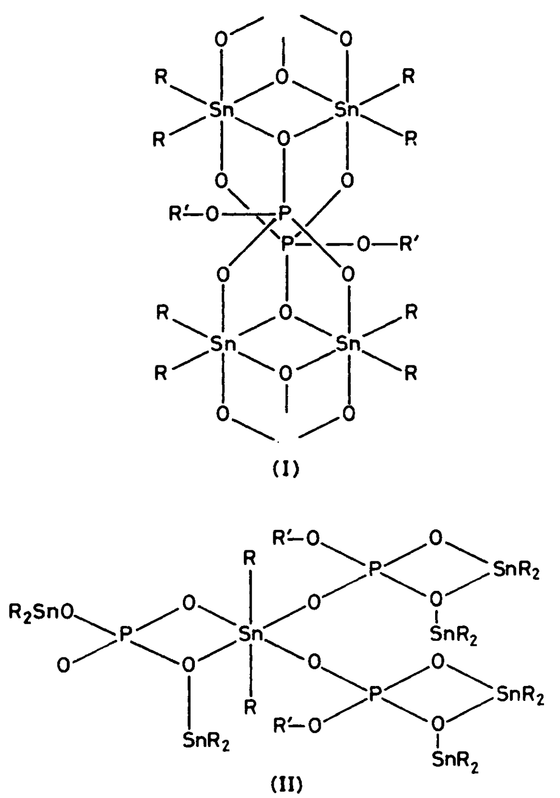

Figure 3. Phosphate-only bonding of AMP^{2-} and $PO_3(OPh)^{2-}$ to $Sn^{IV}R_2$, inferred on the basis of the present spectroscopic study (see text) as well as on known molecular structures of metal-ion complexes of mononucleotides: (**I**), a two-dimensional polymer;[39,40] (**II**), a three-dimensional polymer.[41-44] R′ = phenyl or adenosyl

Consequently it seems possible to suggest the structures of the type sketched in Figure 3. Structure (**I**) consists of a two-dimensional polymer with columns of metal–phosphate clusters, as detected for $[\{Co_2(H_2O)_4(UMP)_2\}_n]$[39] and $[\{Cd_2(H_2O)_4(UMP)_2\}_n]$ [UMP = uridine 5′-monophosphate(2−)];[40] the two *cis* H_2O molecules in the nearly regular octahedral Co and Cd complexes would be substituted by two alkyl groups bound to the metal in the $Sn^{IV}R_2$ complexes, and the C–Sn–C skeleton would obviously be bent (~140° as dictated by the Δ values, Table 1)[25b] into a severely distorted six-co-ordinated environment. Structure (**II**) involves a three-dimensional polymer, in which the phosphate–tin bonding reflects that detected in, *e.g.*, $[Mn(CMP)(H_2O)]\cdot 1.5H_2O$,[41] $[\{Cd(CMP)(H_2O)\}_n]$,[42] $[\{Cu(IMP)\}_n]$,[43] and $[\{Cd(dCMP)(H_2O)\}_n]$ [CMP, dCMP = cytosine 5′-monophosphate(2−) and its deoxy derivative; IMP = inosine 5′-monophosphate(2−)].[44] On the basis of the lattice dynamics of our compounds, a two-dimensional polymeric structure of type (**I**) would be preferred for compounds (**1**)—(**5**), thus in some aspects corresponding to the sheet-like polymeric structure[22] already proposed for the diphenyl phosphate complexes (**6**)—(**8**).[18] On the other hand, tin environments such as that in (**II**) would be better suited to the requirements of rather large C–Sn–C angles as dictated by the Δ values. Lastly, it should be noted that, in case of the occurrence of five-co-ordinate tin in compounds (**1**)—(**5**), instead of the assumed six-co-ordination, the actual structure would be consistent with previous assumptions for compounds $SnR_2(PPhO_3)$ (R = Me or Ph),[24] corresponding to (**I**) and/or (**II**) without three-centre-bonded phosphate oxygen atoms.

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