Tin-119 'Mössbauer Titration' of Dimethyl- and Trimethyl-tin(IV) Hydroxides with Model Ligands mimicking Nucleic Acid Phosphate Sites, and with Deoxyribonucleic Acid

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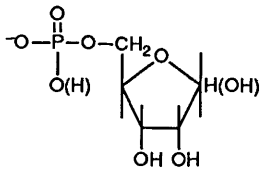
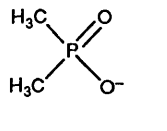
Aqueous systems at pH 7.4, consisting respectively of phosphate, D-ribose 5-phosphate, dimethylphosphinate, adenosine 3′:5′-cyclic monophosphate (Ado-3′:5′-*P*), and native DNA, as well as of either $SnMe_2(OH)_2$ or $SnMe_3(OH)(OH_2)$, have been investigated by ^{119}Sn Mössbauer spectroscopy, on samples frozen at 77.3 K. The trends in the variation of the Mössbauer parameters, as a function of the molar ratio ligand group: metal, have been determined for each system. The results are interpreted in terms of complex formation, which appears to be rather consistent for phosphate and D-ribose 5-phosphate with respect to both organotins. The effect due to dimethylphosphinate and Ado-3′:5′-*P* is quite limited, in a special way towards $SnMe_3(OH)(OH_2)$, and native DNA does not induce any interaction. The distorted 'average' configuration of the organotin moieties, as well as the nature of the complex species determining the distortions, have been inferred through the rationalization of the experimental nuclear quadrupole splittings by application of the point-charge model.

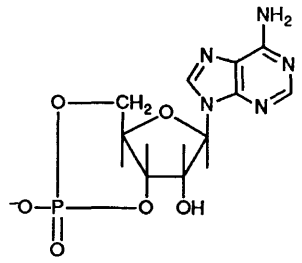
The interaction of $Sn^{IV}Me_2$ moieties with native DNA has recently been investigated, in the context of studies to provide a molecular basis for the understanding of the biological effects of organotin(IV) derivatives.[1] The formation of solid species $Sn^{IV}Me_2$–DNA (possibly 1:2 with respect to DNA phosphate), where the dimethyltin would assume a linear CSnC skeleton, has been proposed.[1] Subsequent work, reported in the present paper, has been devoted to the investigation of model systems $Sn^{IV}Me_2$– and $Sn^{IV}Me_3$–phosphate-containing ligands. The organotins were $SnMe_2(OH)_2$ and $SnMe_3(OH)(OH_2)$, *i.e.* the species formed in aqueous solution at the (physiological) pH value 7.4.[2,3] The phosphate ligands, at pH 7.4 in aqueous solutions, were $H_nPO_4^{(3-n)-}$ (n = 1 or 2, phosphate buffer), D-ribose 5-phosphate, dimethylphosphinate, and adenosine 3′:5′-cyclic monophosphate (Ado-3′:5′-*P*). Dimethylphosphinate would mimic the phosphodiester residue of nucleic acids, and this holds also for Ado-3′:5′-*P*, where, on the other hand, mononucleotide constituents are present; the monoester ribose phosphate has been selected as intermediate between inorganic phosphate and dimethylphosphinate, bearing also a component molecule of nucleic acids. In this context, the systems $SnMe_2(OH)_2$– and $SnMe_3(OH)(OH_2)$–DNA have also been investigated. Series of aqueous samples in each system, with varying ligand:organotin molar ratios, frozen at 77.3 K, have been monitored by ^{119}Sn Mössbauer spectroscopy, gradually following the eventual complex formation, whose possible nature has been inferred from the point-charge model treatment of the nuclear quadrupole splitting, ΔE.



D-Ribose 5-phosphate



Dimethylphosphinate



Adenosine 3′:5′-cyclic monophosphate

Experimental

The organotins $SnMe_2Cl_2$ and $SnMe_3Cl$ were from Schering A. G. (Bergkamen). Ciba-Geigy (Marienberg), and Strem Chemicals (Newburyport); compounds were recrystallized from benzene and light petroleum respectively. The phosphate buffer (KH_2PO_4 + Na_2HPO_4), dimethylphosphinic acid [$P(CH_3)_2(O)OH$], D-ribose 5-phosphate (disodium salt), adenosine 3′:5′-cyclic monophosphate, and the buffer Tris [*i.e.* tris(hydroxymethyl)amino methane] were from Aldrich (Milwaukee) and Sigma (St. Louis, Missouri) and were used as received. Native calf thymus DNA was from Serva Fenbiochemica (Heidelberg). Other reagents were from C. Erba (Milan).

The organotin–ligand solutions were generally prepared from stock aqueous 20 mmol dm^{-3} solutions of $SnMe_2Cl_2$ and $SnMe_3Cl$, adjusted to pH around 7.4 by addition of 0.1 mol dm^{-3} NaOH (using a pH meter equipped with a glass electrode), which were added to aliquots of aqueous solutions of the ligands at pH 7.4. Aqueous stock DNA was, *e.g.*, 25.5 mmol dm^{-3} in DNA phosphate in 1 mmol dm^{-3} Tris buffer, 0.1 mmol dm^{-3} ethylenediaminetetra-acetate, pH ≈8; the concentration was determined by u.v. spectrophotometry using the absorption coefficient, ε = 7 000 dm^3 mol^{-1} cm^{-1} at 260 nm.[4] Only for the data point at $[L]/[SnMe_{2,3}]$ = 5, Table and Figure 1, was employed a stock solution 50 mmol dm^{-3}, in DNA monomers, which was obtained through sonication (and partial degradation). In some instances, weighed amounts of the compounds were dissolved in water and the pH adjusted to the required value. In the series of organotin–ligand samples investigated

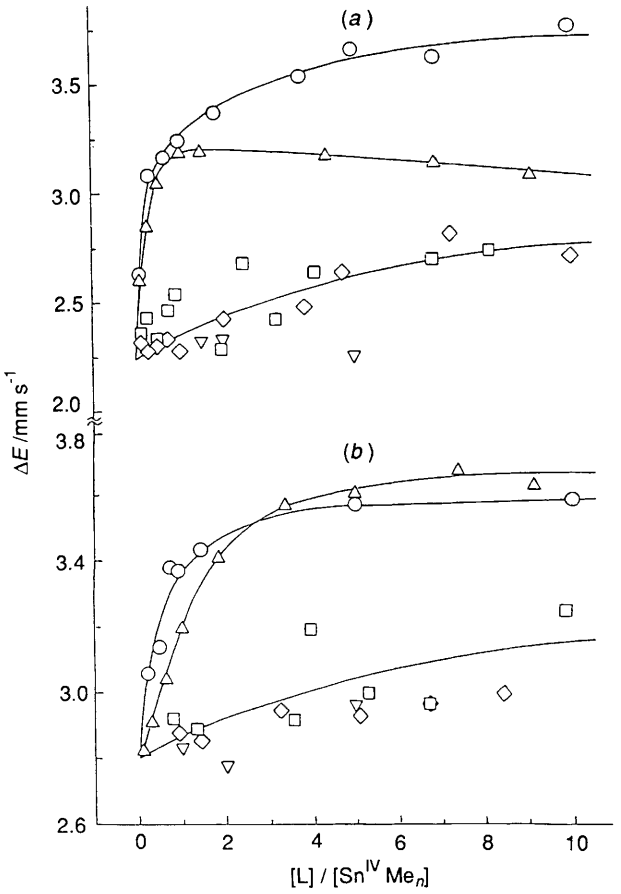


Figure 1. ^{119}Sn Mössbauer 'titrations' of (*a*) $SnMe_2(OH)_2$ and (*b*) $SnMe_3(OH)(OH_2)$, with the ligands L = $H_nPO_4^{(3-n)-}$ (*n* = 1 or 2) (○), D-ribose 5-phosphate (△), adenosine 3′:5′-cyclic monophosphate (□), dimethylphosphinate (◇), or DNA (▽). The experimental nuclear quadrupole splitting, ΔE, is plotted *vs.* the mole ratio [L]/[$SnMe_{2,3}$]. The data points at [L] = 0.0, taken as the origin of the curves, refer to $SnMe_2(OH)_2$ and $SnMe_3(OH)(OH_2)$ respectively; see Discussion section. For DNA systems, see the Table and footnotes

here the final concentration of organotins was in the range 9.59—12.85 mmol dm^{-3}, the pH ranging from 7.10 to 7.65. About 2 cm^3 of these solutions, in Polythene sample holders, were frozen by immersion in liquid nitrogen, thus possibly yielding glassy phases in the tin environments,[5] and placed in the Mössbauer spectrometer. The spectra were determined with the apparatus and data-reduction techniques reported previously.[5] The effect (ε) in the resonant doublets was in the range ε = 0.31—1.51%, suitable for computer fitting of the experimental points and calculation of the Mössbauer parameters. Data for representative terms in any series are reported in Table 1; the functions ΔE *vs.* [L]/[$SnMe_{2,3}$], obtained from all data points, are shown in Figure 1.

Solid Products.—These have been obtained from aqueous solutions of $Sn^{IV}Me_2$ and phosphate. The compound $SnMe_2(HPO_4)$ precipitates soon after the preparation of a solution, at pH ≈ 2, of 25 mmol dm^{-3} $SnMe_2Cl_2$ and 50 mmol dm^{-3} phosphate (Found: C, 10.15; H, 3.05. Calc. for $C_2H_7O_4PSn$: C, 9.80; H, 2.90%). Mössbauer parameters (average data from experiments at 77.3 K and at room temperature): δ = 1.14, ΔE = 3.55 mm s^{-1}. The same product was obtained at pH 2.5 (Found: C, 9.90; H, 2.85%), δ = 1.11, ΔE = 3.49 mm s^{-1}. From solutions of $SnMe_2(OH)_2$ and phosphate buffer, both 50 mmol dm^{-3}, at pH 7.7, $SnMe_2O$ was precipitated on standing at room temperature for about 10 d (Found: C, 14.90; H, 3.70. Calc. for C_2H_6OSn: C, 14.60; H, 3.65%), δ = 0.88, ΔE = 2.06 mm s^{-1}.

Calculations of Partial Nuclear Quadrupole Splitting (p.q.s.).—The configuration of the organotin moieties in the model systems, as well as the nature of the complexes possibly formed, were investigated in this work by the point-charge model formalism.[6] For this purpose, calculations of p.q.s. parameters[7–9] for phosphate oxygen atoms, not reported in the literature, were made on the basis of experimental ΔE data for phosphate derivatives of $Sn^{IV}R_2$ and $Sn^{IV}R_3$, as follows.

(*a*) The p.q.s. of phosphate oxygen in octahedral structures, p.q.s. $[PO_2(XY) - \text{halide}]^{oct}$ = +0.11 mm s^{-1} (weighed average), was obtained from experimental ΔE data for complexes $SnR_2[PO_2(XY)]_2$,[10–17] having structure (**1**),[10–17] Figure 2 (X = Y = H, Cl, OPh, OEt, or C_6H_{13}; X = H, Y = Ph; X = OPh, Y = Ph). The data for $\Delta E_{exptl.av.}$ are: R = alkyl, 4.60 mm s^{-1} (average of 18 values[11–17]); R = Ph, 4.08 mm s^{-1} (average of three values[10,15,16]).

(*b*) The p.q.s. of phosphate oxygen in trigonal-bipyramidal axial structures, p.q.s. $[PO_2(XY)]^{tba}$ = +0.13 mm s^{-1} (weighted average), was obtained from experimental ΔE data for complexes $SnR_3[PO_2(XY)]$[11,14–16,18–21] having structure (**2**), Figure 2, according to reported molecular structures.[19,22,23] (X = Y = H, Cl, Ph, OPh, $OSnBu_3$, Me, or C_6H_{13}; X = Me, Y = $OSnBu_3$; X = Ph, Y = $OSnBu_3$,OPh, or H). The data for $\Delta E_{exptl.av.}$ are: R = alkyl, 3.90 mm s^{-1} (average of 16 values[11,14–16,18–21]); R = Ph, 3.49 mm s^{-1} (average of three values[15,16,21]).

(*c*) The p.q.s. of phosphate oxygen in trigonal-bipyramidal equatorial structures, p.q.s. $[PO_2(XY)]^{tbe}$ = +0.37 mm s^{-1}, was calculated from $[PO_2(XY)]^{tba}$ according to the literature.[9]

The ΔE data for the following complexes have not been taken into account in the calculations under (*a*) and (*b*): (*i*) derivatives of $PO_2F_2^-$,[12] the ligand p.q.s. value being particularly large due to the electronegativity of the fluorine atoms; (*ii*) $SnR_2(PO_3X)$, where both co-ordination numbers five and six have been advanced;[3,17,24] (*iii*) $(SnMe_2)_3(PO_4)_2$,[13] also indicated as $SnMe_2(HPO_4)$,[25] with distorted structures according to *X*-ray[26] and n.m.r.[25] studies; (*iv*) $(SnR_3)_2(HPO_3)$ and $(SnMe_3)_3(PO_4)$, in which three-co-ordinate oxygen would occur.[18]

Discussion

From Figure 1 and the Table it clearly appears that the ^{119}Sn 'Mössbauer titration' of $SnMe_2(OH)_2$ (δ = 0.94, ΔE = 2.24 mm s^{-1})[5] and $SnMe_3(OH)(OH_2)$ (δ = 1.24, ΔE = 2.80 mm s^{-1})[27] with phosphate and D-ribose 5-phosphate causes consistent changes in the parameters (in a special way for ΔE), the effect due to dimethylphosphinate and Ado-3′:5′-*P* being instead quite limited, mainly with respect to $SnMe_3(OH)(OH_2)$. No changes occur due to DNA. These facts suggest gradual complex formation by the phosphate anions and the monoester of ribose only. This is in line with predictions based upon literature values of hydrolysis and stability constants,[3,28] according to which *e.g.* the following molar ratios would be established at pH 7.4 and at 0.1 mol dm^{-3} free ligand: $[SnMe_3(H_2PO_4)]/[SnMe_3(OH)(OH_2)_n]$ = 0.35; $[SnMe_3\{H\text{-}(Ado\text{-}5'\text{-}P)\}]/[SnMe_3(OH)(OH_2)_n]$ = 0.62 (Ado-5′-*P* = adenosine 5′-monophosphate). As far as phosphate complexes of $Sn^{IV}Me_2$ are concerned, for which no stability constants are available, complex formation clearly occurs in aqueous solution at acid pH, where *e.g.* the solid $SnMe_2(HPO_4)$ is formed; instead, $SnMe_2(OH)_2$ predominates at pH 7.4, according to the precipitation of $SnMe_2O$ (see Experimental section; the Mössbauer parameters there reported strictly correspond to $SnMe_2O$ literature data[13,29]). The formation of complex species, in equilibrium with the (predominant) hydrolysis

Table. Selected ^{119}Sn Mössbauer parameters (mm s^{-1}) of frozen aqueous systems, ligand species–$SnMe_2(OH)_2$ and –$SnMe_3(OH)(OH_2)$[a]

Ligand	[Ligand]/[$Sn^{IV}Me_{2,3}$]	δ[b]	ΔE[c]	Γ_1[d]	Γ_2[d]	Angle CSnC[e] (°)
(*a*) Ligand–$SnMe_2(OH)_2$						
Phosphate buffer[f]	0.10	1.06	2.62	1.13	0.88	
	10.0	1.23	3.75	1.18	1.01	oct, 152; tbe, 140
D-Ribose 5-phosphate	0.12	1.07	2.60	0.95	0.92	
	1.50	1.17	3.19	1.01	0.80	oct, 134; tbe, 125
	9.08	1.11	3.06	1.02	0.81	oct, 130; tbe, 122
Dimethylphosphinate	0.15	0.92	2.32	0.90	0.78	
	9.97	1.02	2.70	0.87	0.88	tbe, 113
Ado-3′:5′-*P*[g]	0.11	0.96	2.35	1.04	0.82	
	8.14	1.04	2.72	0.87	0.78	tbe, 113
DNA[h]	1.50	0.92	2.32	0.94	1.03	*i*
	5.00	0.93	2.24	0.98	0.79	*i*
(*b*) Ligand–$SnMe_3(OH)(OH_2)$						Angle CSnA[e] (°)
Phosphate buffer[f]	0.22	1.29	3.06	1.14	0.80	
	10.0	1.36	3.59	0.83	0.87	102
D-Ribose 5-phosphate	0.11	1.24	2.82	0.81	0.79	
	9.14	1.31	3.63	1.00	0.90	101
Dimethylphosphinate	0.93	1.24	2.88	1.02	0.77	
	8.46	1.26	3.02	1.04	0.93	107
Ado-3′:5′-*P*[g]	0.82	1.21	2.92	0.85	0.91	
	9.85	1.27	3.26	0.94	0.81	105
DNA[h]	1.00	1.24	2.83	0.93	0.75	*j*
	5.00	1.26	2.96	0.92	0.91	*j*

[a] At liquid-nitrogen temperature. The data concern samples with the lesser and larger value of the molar ratio [ligand]/[$Sn^{IV}Me_{2,3}$] investigated in the present work, except for D-ribose 5-phosphate–$SnMe_2(OH)_2$ (see Discussion section). See Figure 1, and Experimental section for the preparation of the absorber samples. [b] Isomer shift with reference to room-temperature $Ca^{119}SnO_3$ (±0.03 mm s^{-1}, standard error, measured from $CaSnO_3$ spectra determined during this work). [c] Nuclear quadrupole splitting, ±0.01 mm s^{-1} (standard error related to g_1 of spectra of iron foil in the period concerning the present work [5]). [d] Full width at half-height of the resonant peaks at the lesser and larger velocity of the spectrum centroid, respectively. [e] Estimated from the point-charge model treatment of ΔE, as a function of the contribution only of the organic groups, bound to the metal, to the electric field gradient at the nucleus (see Discussion Section). oct = *trans*-R_2 octahedral; tbe = trigonal bipyramidal with equatorial Me groups; these configurations are correlated to the estimated CSnC values. Angles CSnA refer to tetrahedral species [32] (A being a donor atom from a general ligand); we have determined, by the point-charge model calculations mentioned above, that CSnA data from tba species $SnMe_3A_2$ (axial A_2) and from tetrahedral $SnMe_3A$ correspond perfectly, the function ΔE *vs.* angle [32] being coincident. [f] $H_nPO_4^{(3-n)-}$, n = 1 or 2. [g] Data are averages of multiple determinations. [h] From calf thymus. The ratios [L]/[$Sn^{IV}Me_{2,3}$] refer to L = DNA phosphate. Native DNA has been employed in the experiments with [L]/[$Sn^{IV}Me_{2,3}$] = 1.0, 1.3, and 2.0:1, while DNA degraded by sonication was used for ratio 5.0:1. See Figure 1 and text. The data referring to $SnMe_2(OH)_2$–DNA are from ref. 1. [i] δ and ΔE are as those for tetrahedral $SnMe_2(OH)_2$.[5] [j] δ and ΔE are as those for $SnMe_3(OH)(OH_2)$.[27]

product, would then take place also in the systems $Sn^{IV}Me_2$–phosphates and related ligands, at pH 7.4. It seems worth noting, in the present context, that these deductions are supported by the Mössbauer linewidths Γ, which lie randomly around the values reported in the Table, while *e.g.* a net and regular variation of Γ occurs [27] for the gradual formation of a complex with a high stability constant such as $Sn^{IV}Me_3$–cysteinate.[28]

Turning now to the possible configuration of the organotin moieties in the systems investigated, it is first recalled that the Mössbauer isomer shift, δ, of $Sn^{IV}R_2$ (R = alkyl) derivatives is a function of the CSnC angle. Tetrahedral species SnR_2L_2 (L being an electronegative donor atom) are characterized by δ < 1 mm s^{-1} [*e.g.*, 0.94 mm s^{-1} for $SnMe_2(OH)_2$[5]]; the same order of magnitude is shown by δ of *cis*-R_2 configurations in octahedral complexes SnR_2L_4, while the related *trans*-R_2 species are characterized by δ values as large as 1.61 mm s^{-1}.[30] The trend shown by the δ values in the Table suggests a gradual, and consistent, opening of the CSnC angle of $SnMe_2(OH)_2$ due to complex formation with phosphate and D-ribose 5-phosphate, and a lesser effect due to the other ligands. The δ values of the $Sn^{IV}Me_3$ systems are practically invariant with respect to δ = 1.24 mm s^{-1} of $SnMe_3(OH)(OH_2)$,[27] for which a distorted trigonal-bipyramidal configuration has been assumed;[27] this suggests that the same type of configuration pertains also to the phosphate complexes. A regular trigonal-bipyramidal structure, for example, implies a larger δ value, such as δ = 1.50 mm s^{-1} for $[SnMe_3(H_2O)_2]^+$.[27]

The distortions discussed are quantified by the estimation of CSnC angles in $Sn^{IV}Me_2$ derivatives, and of CSnA in $Sn^{IV}Me_3A$ moieties (A being a ligand atom), through point-charge model calculations of nuclear quadrupole splittings, ΔE, as a function only of the organic groups bound to the metal.[31,32] Representative results are reported in the Table. The values of the angles refer to the 'average' configurations occurring in frozen solutions, as reflected by the experimental values of ΔE.

At this point, we may seek to identify the series of complexes formed in each solution phase, possibly in equilibrium, contributing to the apparent distortions referred to. This may be effected through rationalization of experimental ΔE values by literal interpretation of the point-charge model where the calculation of ΔE involves all bonds to the metal, in conjunction with essentially regular geometries.[8] In phosphate- and D-ribose 5-phosphate–$Sn^{IV}Me_2$ systems a large increase of ΔE takes place for molar ratios ligand:metal ranging from 0 to 2:1, Figure 1(*a*), and this could be explained with the formation *e.g.* of the 1:1 complexes (**3**), and then of the 2:1 complexes (**4**) and/or (**5**), Figure 2.*

* It is worth noting that the structures (**3**)—(**5**) and (**7**), Figure 2, obey the Muetterties rule, which states that, in trigonal-bipyramidal configurations, the most electronegative groups are located in apical positions.[33] This rule is still valid, according to a number of *X*-ray diffractometric studies.

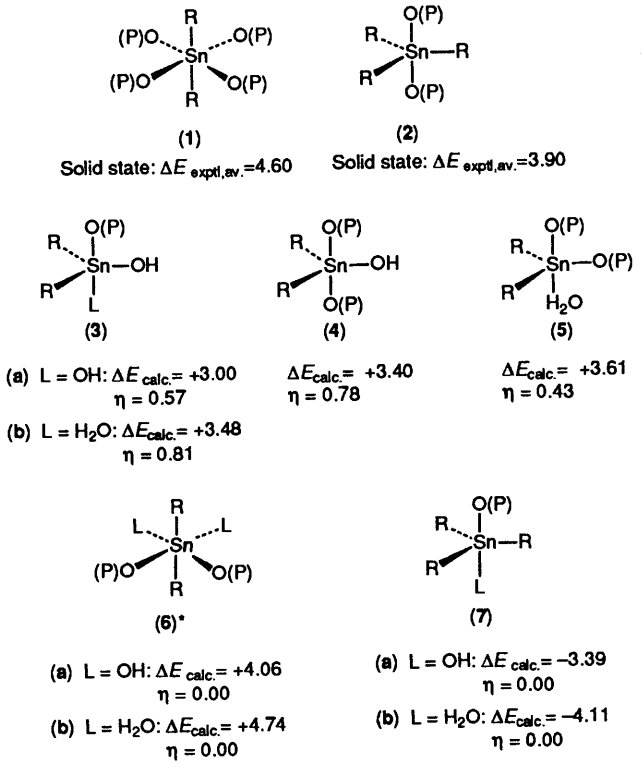


Figure 2. Schemes of the tin environments in phosphate complexes in the solid state, (**1**) and (**2**), and in species possibly formed in aqueous solutions of organotins and ligands, (**1**)—(**7**) (see Experimental and Discussion Sections, Figure 1, and the Table). Idealized regular configurations are generally considered. Calculated values of the nuclear quadrupole splittings, ΔE, and of the asymmetry parameter $\eta = (V_{xx} - V_{yy})/V_{zz}$, have been obtained by the literal point-charge model approach, using tabulated values for p.q.s.[5,7–9] in conjunction with p.q.s. data extracted in this work for phosphate ligands (see Experimental section). * Equatorial ligands in *trans* configuration yield slightly larger $\Delta E_{calc.}$ values

The adduct (**3a**) corresponds to $SnMe_2(OH)_2(N_{amino})$, assumed to be formed by co-ordination of 4-(2-hydroxyethyl)-piperazine-2-ethanesulphonic acid (hepes) buffer in aqueous solution.[5] Octahedral species like (**6**), Figure 2, could subsequently be formed by co-ordination of phosphates (HPO_4^{2-}, $H_2PO_4^-$), being possibly distorted in the CSnC angle, as has been detected in the polymeric solids $(SnMe_2)_3(PO_4)_2$[26] [ΔE = (+)3.10 mm s^{-1} [13]] and $SnMe_2(HPO_4)$ (ΔE = 3.62 mm s^{-1} [13]). Only the complex (**3a**), Figure 2, would occur in the dimethylphosphinate– and Ado-3′:5′-*P*–$Sn^{IV}Me_2$ systems, in equilibrium with $SnMe_2(OH)_2$, according to the experimental ΔE values in the Table. Adducts like (**7**) and (**2**), Figure 2 (the latter being considered a monomeric species in aqueous solution), would gradually form in phosphate– and D-ribose 5-phosphate–$Sn^{IV}Me_3$ systems, and perhaps (**7a**) only in dimethylphosphinate– and Ado-3′:5′-*P*–$Sn^{IV}Me_3$, in equilibrium with $SnMe_3(OH)(OH_2)$ (in line with the experimental ΔE data in the Table). A configuration of type (**7a**) has previously been advanced for $SnMe_3(OH)$ (N_{amino}), assumed to form in aqueous hepes.[27]

It seems opportune to comment on the particular aspects of some 'titration curves' in Figure 1. The line shape of the function for D-ribose 5-phosphate–$Sn^{IV}Me_2$, Figure 1(*a*), and the data in the Table, indicate the occurrence of an additional reaction, at ligand to metal ratios larger than 1:1 with respect to those advanced for phosphate–$Sn^{IV}Me_3$ systems. The compound $SnMe_2(OH)_2$ could react with ribose hydroxyls, as suggested by the reaction of $SnMe_2O$ and related species with a series of carbohydrates, nucleosides, and nucleotides;[34–36] the solid products obtained show $\Delta E \approx 3.00$ mm s^{-1}, consistent with five- and six-co-ordinated structures.[36–38] It seems worth recalling that, for example, the $Sn^{IV}Bu_2$ derivatives of glucose and mannose show the following values of CSnC angles (by *X*-ray diffractometry) and Mössbauer parameters: glucose,[36,39] CSnC 126, 139°, δ = 1.13, ΔE = 2.72 mm s^{-1}; mannose,[36,40] CSnC 126, 138° (average values), δ = 1.15, 1.27, ΔE = 2.38, 3.44 mm s^{-1}.

Moreover, in the systems Ado-3′:5′-*P*–$Sn^{IV}Me_2$ and –$Sn^{IV}Me_3$, Figure 1(*a*) and (*b*), data points are consistently scattered; this effect could be ascribed to the eventual co-ordination of the metal by donor atoms of adenine, besides phosphate oxygen, supposedly depending upon the experimental procedures employed in the preparation of the absorber samples (although no definite correlations of this type have been observed during this work). The limited interaction of organotins, at pH 7.4, with the molecule Ado-3′:5′-*P*, which is involved in a number of biochemical processes, is anyway remarkable.

In conclusion, the phosphodiester groups of DNA, and the related model ligands, do not show a consistent affinity for the tin centres in $SnMe_2(OH)_2$ and $SnMe_3(OH)(OH_2)$, which are formed at physiological pH. The interaction with DNA requires a consistent Lewis-acid character of the metal atom, such as in the solvated species $SnMe_2Cl_2(EtOH)_n$, with formation of solids containing both DNA and linear $Sn^{IV}Me_2$ moieties[1] (ΔE = 4.35—4.44 mm s^{-1}). Solutions in organic solvents appear to be required also for the interaction of $Sn^{IV}Et_3$ with phospholipids.[41] Inorganic phosphate, and the monoester D-ribose 5-phosphate, are instead quite efficient in co-ordinating tin of both hydrolyzed species, which is in line with the inhibition by phosphate of the antimicrobial action of tripropyltin(IV).[41]

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References

1 R. Barbieri and A. Silvestri, *J. Inorg. Biochem.*, 1990, in the press.
2 R. S. Tobias, I. Ogrins, and B. A. Nevett, *Inorg. Chem.*, 1962, **1**, 638.
3 R. S. Tobias, *Organomet. Chem. Rev.*, 1966, **1**, 93.
4 S. D. Kennedy and R. G. Bryant, *Biophys. J.*, 1986, **50**, 669.
5 R. Barbieri and M. T. Musmeci, *J. Inorg. Biochem.*, 1988, **32**, 89.
6 M. G. Clark, *Mol. Phys.*, 1971, **20**, 257.
7 G. M. Bancroft and R. H. Platt, *Adv. Inorg. Chem. Radiochem.*, 1972, **15**, 59.
8 M. G. Clark, A. G. Maddock, and R. H. Platt, *J. Chem. Soc., Dalton Trans.*, 1972, 281.
9 G. M. Bancroft, V. G. Kumar Das, T. K. Sham, and M. G. Clark, *J. Chem. Soc., Dalton Trans.*, 1976, 643.
10 B. W. Fitzimmons, N. J. Seeley, and A. W. Smith, *Chem. Commun.*, 1968, 390.
11 R. E. Ridenour and E. E. Flagg, *J. Organomet. Chem.*, 1969, **16**, 393.
12 T. H. Tan, J. R. Dalziel, P. A. Yeats, J. R. Sams, R. C. Thompson, and F. Aubke, *Can. J. Chem.*, 1972, **50**, 1843.
13 T. Chivers, J. H. G. van Roode, J. N. R. Ruddick, and J. R. Sams, *Can. J. Chem.*, 1973, **51**, 3702.
14 K. Denicke, R. Schmitt, A. F. Shihada, and J. Pebler, *Z. Anorg. Allg. Chem.*, 1974, **404**, 249.
15 D. Cunningham, L. A. Kelly, K. C. Molloy, and J. J. Zuckerman, *Inorg. Chem.*, 1982, **21**, 1416.
16 K. C. Molloy, F. A. K. Nasser, and J. J. Zuckerman, *Inorg. Chem.*, 1982, **21**, 1711.

17 R. Barbieri, G. Alonzo, and R. H. Herber, *J. Chem. Soc., Dalton Trans.*, 1987, 789.
18 T. Chivers, J. H. G. van Roode, J. N. R. Ruddick, and J. R. Sams, *Can. J. Chem.*, 1976, **54**, 2184.
19 K. C. Molloy, M. B. Hossain, D. vander Helm, D. Cunningham, and J. J. Zuckerman, *Inorg. Chem.*, 1981, **20**, 2402.
20 S. J. Blunden, R. Hill, and D. G. Gillies, *J. Organomet. Chem.*, 1984, **270**, 39.
21 K. C. Molloy and K. Quill, *J. Chem. Soc., Dalton Trans.*, 1985, 1417.
22 K. C. Molloy, F. A. K. Nasser, C. L. Barnes, D. vander Helm, and J. J. Zuckerman, *Inorg. Chem.*, 1982, **21**, 960.
23 F. Weller and A. F. Shihada, *J. Organomet. Chem.*, 1987, **322**, 185.
24 D. Cunningham, P. Firtear, K. C. Molloy, and J. J. Zuckerman, *J. Chem. Soc., Dalton Trans.*, 1983, 1523.
25 T. P. Lockhart and W. F. Manders, *Inorg. Chem.*, 1986, **25**, 1068.
26 J. P. Ashmore, T. Chivers, K. A. Kerr, and J. H. G. van Roode, *Inorg. Chem.*, 1977, **16**, 191.
27 R. Barbieri, A. Silvestri, M. T. Lo Giudice, G. Ruisi, and M. T. Musmeci, *J. Chem. Soc., Dalton Trans.*, 1989, 519.
28 M. J. Hynes and M. O'Dowd, *J. Chem. Soc., Dalton Trans.*, 1987, 563.
29 P. J. Smith, *Organomet. Chem. Rev. A*, 1970, **5**, 373.
30 R. V. Parish, *Prog. Inorg. Chem.*, 1972, **15**, 101.
31 T. K. Sham and G. M. Bancroft, *Inorg. Chem.*, 1975, **14**, 2281.
32 R. V. Parish, in 'Mössbauer Spectroscopy applied to Inorganic Chemistry,' ed. G. J. Long, Plenum, New York, 1984, vol. 1, pp. 527–575.
33 E. L. Muetterties and R. A. Schunn, *Q. Rev. Chem. Soc.*, 1966, **20**, 245.
34 D. Wagner, J. P. H. Verheiden, and J. G. Moffatt, *J. Org. Chem.*, 1974, **39**, 24.
35 C. J. Cardin and A. Roy, *Inorg. Chim. Acta*, 1986, **125**, 63.
36 A. G. Davies, A. J. Price, H. M. Dawes, and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, 1986, 297.
37 L. Pellerito, G. Ruisi, and R. Barbieri, *Inorg. Chim. Acta*, 1977, **21**, L33.
38 G. Ruisi, M. T. Lo Giudice, and L. Pellerito, *Inorg. Chim. Acta*, 1984, **93**, 161.
39 S. David, C. Pascard, and M. Cesario, *Nouv. J. Chim.*, 1979, **3**, 63.
40 C. W. Holzapfel, J. M. Koeckemoer, C. F. Marais, G. J. Kruger, and J. A. Pretorius, *S. Afr. J. Chem.*, 1982, **35**, 81.
41 J. Yamada, K. Oishi, K. Tatsuguchi, and T. Watanabe, *Agric. Biol. Chem.*, 1979, **43**, 1015.

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