

Oxy and Thio Phosphorus Acid Derivatives of Tin. Structural Contrasts¹

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The biocidal properties of organotin compounds have led, over the past decade, to a rapid increase in the commercial utilization of these species. Organotins are currently in use as agricultural fungicides and miticides, surface disinfectants, anthelmintics, and marine anti-fouling agents.²

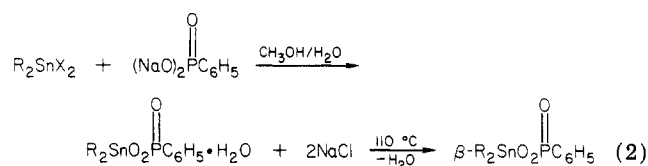
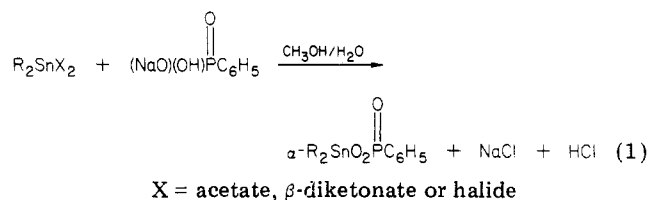
One intriguing development is the synthesis of compounds in which the organotin is bonded to ligands that exhibit biocidal activity, the effectiveness of the product being potentially greater than the sum of the components. Although several ligand systems suggest themselves for study, the oxy and thio phosphorus acids are particularly amenable. Esters of dithiophosphoric acids have, for example, found widespread use in the postwar years as pesticides, being marketed under such trade names as Ethion, Malathion, and Thimet,³ while the importance of phosphates in *in vivo* systems is well-documented.⁴ Moreover, specific evidence for the activity of miscellaneous organotin derivatives of the phosphorus acids is available^{5,6} and provides encouragement for more detailed studies. In particular, answers to the important structure-activity questions demand the availability of reliable structural data, the collection of which has formed the basis of our recent research efforts. This Account affords us the opportunity to compare in detail two structurally constraining classes of compounds and to evaluate those factors that determine the nature of the structures adopted.

Synthesis and Physical Properties

Both inorganic and organotin derivatives of the oxy and thio phosphorus acids can be synthesized by conventional metathesis reactions in which the coformation of stable, small molecules, which are removed from the reaction solution by either precipitation or distillation, enhances product formation. Typical of such reactions are the azeotropic distillation of water from benzene

solutions of an organotin oxide or hydroxide and the phosphorus acid and the precipitation of inorganic halides from solutions of organotin halides and a salt of the phosphorus acid in a suitable organic solvent.⁷⁻¹⁶

The most interesting systems from a synthetic viewpoint, however, are the organotin derivatives of phenylphosphonic acid, where different modifications are accessible by varying the synthetic routes:¹²



Similarly, two modifications of certain triorganotin phenylphosphonates can also be isolated:

(1) Oxy and Thio Phosphorus Acid Derivatives of Tin. Part 15. For Part 14, see F. A. K. Nasser, M. B., Hossain, D. van der Helm, and J. J. Zuckerman, *Inorg. Chem.*, in press.

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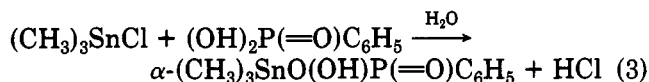
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Kieran C. Molloy was born in Birmingham in 1952 and took his B.Sc. and later his doctorate under P. G. Harrison at the University of Nottingham. He was a postdoctoral fellow with J. J. Zuckerman at Oklahoma (1977-1980) before taking a faculty position as Lecturer in the School of Chemical Sciences, National Institute for Higher Education in Dublin, Ireland.

J. J. Zuckerman was born on Leap Year Day, 1936, in South Philadelphia. His teachers were A. G. MacDiarmid at the University of Pennsylvania (undergraduate study; B.S., 1957) E. G. Rochow at Harvard (graduate work; A. M., 1959; Ph.D., 1960), and H. J. Emeléus at Cambridge (for a second Ph.D., 1962, and later a D.Sc., 1976). He taught at Cornell for 6 years and then at SUNY-Albany for 8 years. At SUNY-Albany he also served as campus Director for Research. He became department chairman (1976-1980) at the University of Oklahoma, where he is now Professor. He is a Fellow of the AAAS. He has been Gastprofessor at the Technical University of Berlin, Germany, and Senior Fellow of the Alexander von Humboldt Foundation (1973) and Professor Associé at the Université d'Aix Marseille III (1979, 1982), which awarded him a doctorate honoris causa (1982).



Rapid precipitation from a solution of the α -isomorph yields a second, β -modification, which can itself be independently synthesized from concentrated aqueous solutions of trimethyltin chloride and the monosodium salt of phenylphosphonic acid.¹⁷

These isomorphs are readily distinguishable by differences in the PO_3 stretching region of the IR.^{12,17} Specific spectroscopic data for other oxy¹⁰⁻¹² and thio phosphorus acid⁷⁻⁹ derivatives of tin are available.

A critical appraisal of these data reveals that they serve to assign molecular composition rather than shed light on molecular structure, and they will not be discussed further. In contrast, information derived from Mössbauer spectroscopy is structural in nature^{18,19} and thus merits further comment. Although the conventional applications of isomer shift (IS) and quadrupole splitting (QS) values to the assignment of oxidation state and coordination number, respectively, have been made,^{7-13,16} discussion is restricted to two less common applications of the technique.

Firstly, a model²⁰ that relates the variation in the magnitude of the QS with the angle C-Sn-C for diorganotin compounds:

$$|\text{QS}| = 4\{\text{R}\}(1 - 3 \sin^2 \theta \cos^2 \theta)^{1/2} \quad (4)$$

where $\{\text{R}\}$ = partial QS for the group R and $\angle\text{C-Sn-C} = (180 - 2\theta)^\circ$, has been applied. The model assumes that contributions from the ligands are small enough compared to that of the R groups to be ignored.²⁰ Nevertheless, despite this crude approximation, the available data show a good correlation for derivatives of the thio phosphorus acids, and the model can be extended with confidence to estimate C-Sn-C angles in those compounds where crystallographic data are lacking.^{8,13} From this parameter it is then possible to infer the relative lengths of both the two distinct P-S bonds in the ligand and the two different pairs of Sn-S bonds in the molecule as a whole (vide infra).

Unfortunately, in the case of the oxy phosphorus acid derivatives, the model breaks down.^{10,11} Although eq 4 predicts a maximum QS value of ca. 4.00 mm s^{-1} (when $\angle\text{C-Sn-C} = 180^\circ$), values well in excess of this are encountered, e.g., for $(\text{CH}_3)_2\text{Sn}[\text{O}_2\text{P}(\text{C}_6\text{H}_5)(\text{OC}_6\text{H}_5)]_2$, $\text{QS} = 4.66 \text{ mm s}^{-1}$.¹⁰ Clearly, the contribution of the oxy phosphorus acid ligands to the QS here cannot be ignored, and structural assignment can go no further than a qualitative assessment of either cis or trans R_2Sn geometry.

Secondly, we have utilized of the area under the Mössbauer resonance, A_T , at varying temperatures T , to distinguish lattices comprised of discrete molecular or oligomeric units from those involving polymerization in one or more directions.^{7,8,12,13} The theoretical basis for the technique lies in the relationship between recoil-free fraction, f , and the mean-square amplitude of displacement, $\langle x^2 \rangle$, of the tin atom:

$$A_T \propto f = \exp(-\langle x^2 \rangle / \lambda^2) \quad (5)$$

(17) D. Cunningham, K. C. Molloy, and J. J. Zuckerman, unpublished work.

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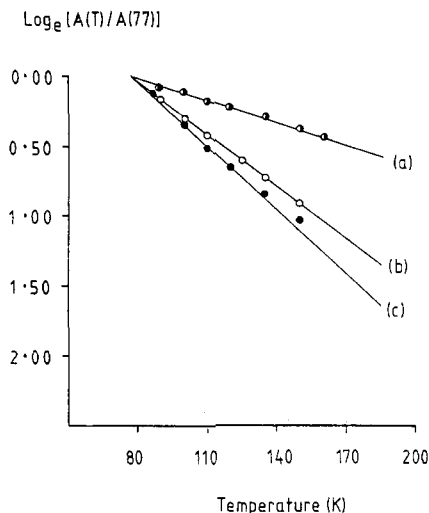


Figure 1. Plot of $\log_e A_T$ (normalized to the area under the resonance curve at 77 K) vs. temperature in Kelvin: (●) $\alpha\text{-(CH}_3)_2\text{SnO}_3\text{PC}_6\text{H}_5$, (●) $\beta\text{-(CH}_3)_2\text{SnO}_3\text{PC}_6\text{H}_5$, (○) $(\text{C}_6\text{H}_5)_2\text{SnO}_3\text{P-C}_6\text{H}_5$.

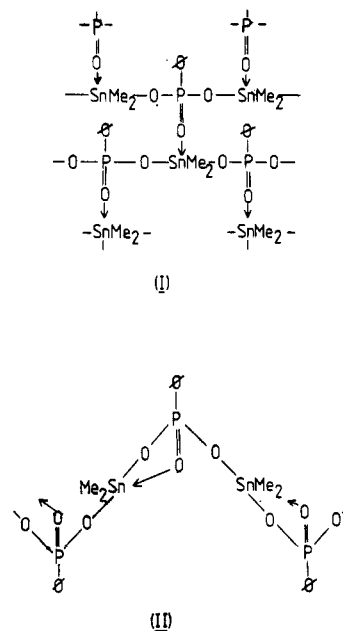


Figure 2. Proposed structures for $\alpha\text{-(CH}_3)_2\text{SnO}_3\text{PC}_6\text{H}_5$ (I) and $\beta\text{-(CH}_3)_2\text{SnO}_3\text{PC}_6\text{H}_5$ (II).

where λ is the wavelength of the Mössbauer γ ray divided by 2π . The experimentally more accessible parameter A_T , being linearly related to f , thus reflects the binding strength of the lattice. Since:

$$A_T \propto \exp(-6E_R T / k\theta_D^2) \quad (6)$$

where E_R is the Mössbauer recoil energy and θ_D is the Debye temperature of the solid, plots of $\log_e A_T$ against T yield straight lines whose slopes reflect the extent to which the tin is bound in the lattice, viz., the shallower the slope, the more firmly the tin atom is bound in the lattice.²¹⁻²⁶

(21) P. G. Harrison, R. C. Phillips, and E. W. Thornton, *J. Chem. Soc., Chem. Commun.*, 603 (1977).

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(25) K. C. Molloy, J. J. Zuckerman, H. Schumann, and G. Rodewald, *Inorg. Chem.*, 19, 1089 (1980).

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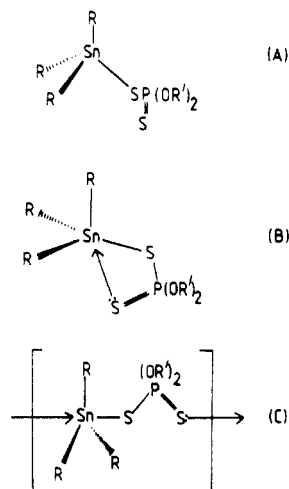


Figure 3. Possible structures for $R_3SnS_2P(OR')_2$. Reprinted with permission from J. L. Lefferts et al., *Inorg. Chem.*, 19, 1662 (1980).

By applying this technique to the study of isomorphous dimethyltin phenylphosphonate, α - and β - $(CH_3)_2SnO_3PC_6H_5$, we can detect structural differences¹² hitherto inaccessible. The tin atom in the α -modification is clearly more tightly bound into the lattice than its counterpart in the β -isomorph (Figure 1). On the basis of the available slope-structure systematics,²¹ the data imply a sheet structure for the α -form and a chain structure for the β -form, shown in Figure 2, as I and II, respectively. Moreover, the single modification of $(C_6H_5)_2SnO_3PC_6H_5$ that can be synthesized clearly adopts the chain structure of the β -type (Figure 1).

Crystallographic Studies

Three obvious candidates for the structure of a triorganotin derivative of a potentially bidentate ligand, typified by $R_3SnS_2P(OR)_2$, are given in Figure 3 A-C. A simple ionic form, $[R_3Sn]^+[S_2P(OR)_2]^-$, is also possible. For a diorganotin moiety bonded to two potentially bidentate ligands, the problem is magnified. The molecule could possess none, one, or two ligands behaving in a bidentate mode, each of which could either chelate a tin atom or form a bridge between tin atoms. In such cases, the inability of spectroscopic data to distinguish unambiguously the correct structure from the plethora of possibilities is the driving force for crystallographic analysis.

Thio Phosphorus Acid Derivatives.

We begin with a consideration of (*O,O'*-diethyl dithiophosphato)triphenyltin(IV), which, because of its simplicity, represents one extreme of the structural spectrum.²⁷ The tetrahedral, four-coordinated complex, which incorporates a monodentate dithiophosphate ligand (Figure 4), has a twofold importance. Firstly, only the adduct of $Ni[S_2P(OCH_3)_2]_2$ with 2,9-dimethyl-1,10-phenanthroline has hitherto been shown to contain a monodentate dithiophosphate ligand.²⁸ Secondly, the compound serves to establish typical values of the Sn-S [2.4582 (9) Å], S-P single [2.054 (1) Å], and S=P double [1.931 (1) Å] bonds.²⁷ A review of dithiophosphate structures³ reveals the ranges

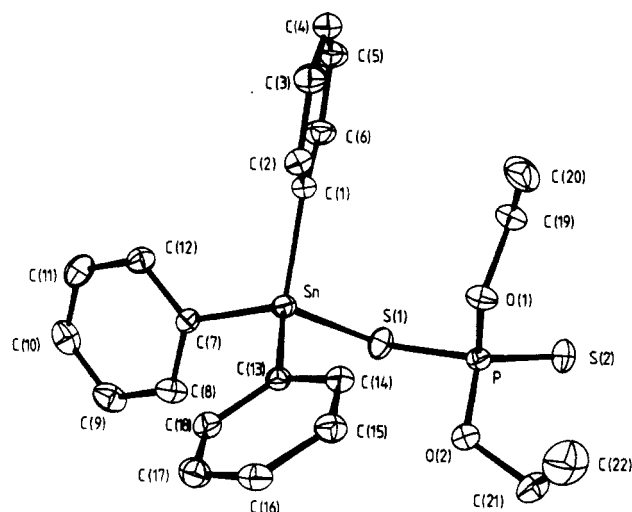


Figure 4. The asymmetric unit of (*O,O'*-diethyl dithiophosphato)triphenyltin(IV). Reprinted with permission from K. C. Molloy et al., *Inorg. Chem.*, 18, 3507 (1979).

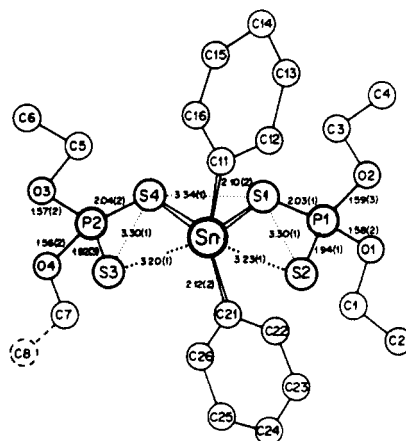


Figure 5. The asymmetric unit of bis(*O,O'*-diethyl dithiophosphato)diphenyltin(IV). Reprinted with permission from B. W. Lieblich and M. Tamassini, *Acta Crystallogr., Sect. B*, 34, 944 (1978). Copyright 1978, Munksgaard.

1.85–1.97 and 1.99–2.19 Å for the shorter and longer P-S bonds, respectively, although electron delocalization often brings into question the exact order of the P-S bond.

More typically, the structures of both bis(diethyl-²⁹ and diisopropyl³⁰ dithiophosphato)diphenyltin(IV) contain bidentate phosphorus acid ligands bonded to a six-coordinated tin, with the R groups disposed in a trans manner about the central atom. Although in both cases the bidentate ligands chelate the tin to produce a monomeric species, there are subtle but important differences. The four coplanar sulfur atoms in the ethyl analogue (Figure 5) are nonequivalent. Instead, pairs of sulfur atoms form either short, covalent [Sn-S(1) = 2.49(1), Sn-S(4) = 2.481 (8) Å] or long, coordinate [Sn-S(2) = 3.23(1), Sn-S(3) = 3.20 (1) Å]²⁹ bonds to tin. The weakness of the coordinate Sn-S bonds manifests itself in the C-Sn-C angle of 135 (1)°, which is opened from the tetrahedral but falls well short of the 180° expected in a perfectly octahedral geometry. The anisobidentate chelation is also reflected in the retention

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Table I
Phosphorus-Sulfur and Sulfur-Tin Internuclear Distances (Å) in Tin Dithiophosphorus Acid Derivatives

compd	covalent P-S-Sn ^a	coordinate P-S-Sn ^a	ref
(C ₆ H ₅) ₂ SnS ₂ P(OC ₂ H ₅) ₂	2.054, 2.4582	1.931, 5.326	27
(C ₆ H ₅) ₂ Sn[S ₂ P(OC ₂ H ₅) ₂] ₂	2.03, 2.49	1.94, 3.23	29
	2.04, 2.48	1.92, 3.20	
(C ₆ H ₅) ₂ Sn[S ₂ P(OC ₃ H ₇ -i) ₂] ₂	2.006, 2.678	1.998, 2.689	30
(CH ₃) ₂ Sn[S ₂ P(CH ₃) ₂] ₂	2.047, 2.482	1.969, 3.334	31
I ₂ Sn[S ₂ P(C ₂ H ₅) ₂] ₂	2.043, 2.537	2.026, 2.621	31
	2.044, 2.533	2.032, 2.593	
{Sn[S ₂ P(OC ₆ H ₅) ₂] ₂ } ₂	2.0016, 2.6230 ^b	1.9670, 2.8300 ^b	9
	2.0064, 2.6510 ^c	1.9636, 3.0428 ^c	
{(C ₆ H ₅) ₂ Sn(OH)[O(S)P(OC ₆ H ₅) ₂] ₂ }		1.944, 3.947	1

^a The first number listed in each case is the P-S distance and the second is the S-Sn distance. ^b Data for terminal ligands. ^c Data for bridging ligands.

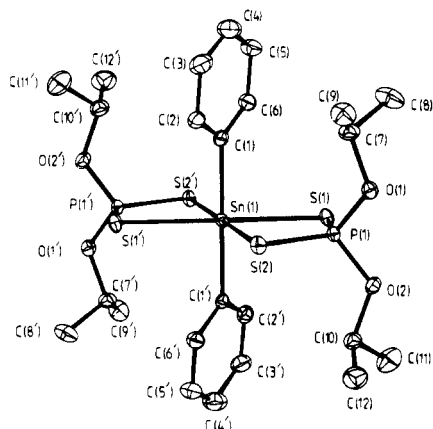


Figure 6. The molecular structure of bis(*O,O'*-diisopropyl dithiophosphato)diphenyltin(IV). Primed atoms are related to the corresponding unprimed atoms by an inversion center at Sn(1). Reprinted with permission from K. C. Molloy et al., *Inorg. Chem.*, 19, 2041 (1980).

of distinct P-S bonds within the ligand. In this and subsequent examples involving bidentate thio phosphorus acid ligands, the long, essentially single S-P bond lies adjacent to the short, covalent Sn-S bond, while the shorter, nominally S=P double bond is associated with the long, coordinate Sn-S interaction (Table I).

The corresponding isopropyl compound (Figure 6) differs in two respects. Firstly, the molecule, which is centrosymmetric at tin, contains four, virtually identical Sn-S bonds [Sn(1)-S(1) = 2.689 (1), Sn(1)-S(2) = 2.678 (1) Å]. Furthermore, this isobidentate chelation involves a \angle C-Sn-C of 180° (by symmetry) and equal S-P bonds [P(1)-S(1) = 1.998 (2), P(1)-S(2) = 2.006 (2) Å]. This reflects extensive delocalization within the S-P-S moiety.³⁰ Note that a consequence of this delocalization is a lengthening of the Sn-S covalent bond (ca. 2.68 Å) relative to the Sn-S bond (2.4582 Å) arising from the interaction of tin with a completely localized, monodentate dithiophosphate ligand.²⁷

The second important difference arises in the lattice structure of the two compounds. In the ethyl ester, the molecules pack with no apparent regularity into the unit cell,²⁹ but the isopropyl molecules stack along the *c* axis to produce a linear tin-tin array (Figure 7). Moreover, the relatively short Sn-Sn distance [6.341 (8) Å] is within the bridging range for the dithiophosphate ligand (Figure 8). That is, the four sulfur and two phosphorus atoms that chelate each tin could be rearranged to lie *between* rather than *about* the tin atoms, thereby producing a polymer of equal dimensions and density.

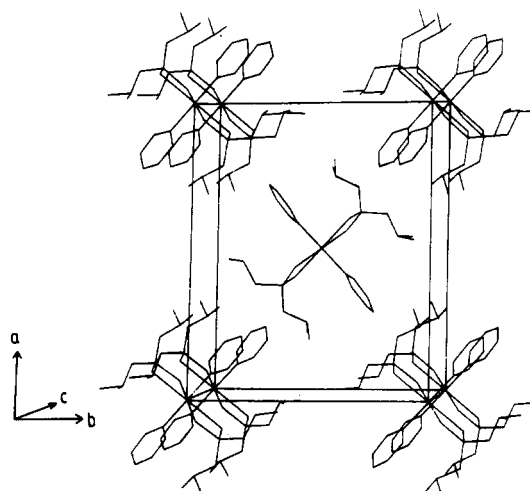


Figure 7. The unit cell of (C₆H₅)₂Sn[S₂P(OC₃H₇-i)₂]₂ showing the molecular packing. Reprinted with permission from K. C. Molloy et al., *Inorg. Chem.*, 19, 2041 (1980).

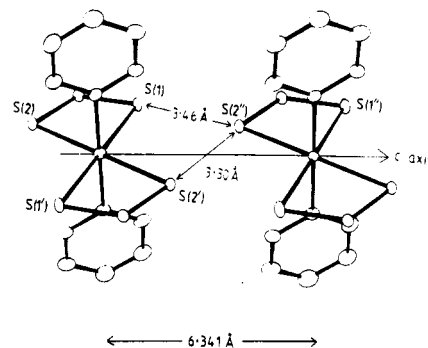


Figure 8. A view of the *c* axis of propagation in (C₆H₅)₂Sn[S₂P(OC₃H₇-i)₂]₂ showing the nearest intermolecular sulfur-sulfur contacts and the tin-tin distance. Reprinted with permission from K. C. Molloy et al., *Inorg. Chem.*, 19, 2041 (1980).

Indeed, in the variable-temperature Mössbauer experiment (vide supra) this compound behaves as a polymer,⁸ a situation for which we have coined the phrase "virtual polymer".³⁰

The two dithiophosphate compounds, (CH₃)₂Sn[S₂P(CH₃)₂]₂ and I₂Sn[S₂P(C₂H₅)₂]₂, both adopt distorted octahedral structures involving the now familiar chelating, bidentate thio phosphorus acid ligand.³¹ In the organometallic derivative, distortion from regular octahedral geometry is particularly severe, the weak, coordinate Sn-S bond [3.334 (2) Å] inducing a trans C-Sn-C angle of only 122.6 (8)°. In contrast, the purely

(31) K. C. Molloy, M. B. Hossain, D. van der Helm, J. J. Zuckerman, and F. P. Mullins, *Inorg. Chem.*, 20, 2172 (1981).

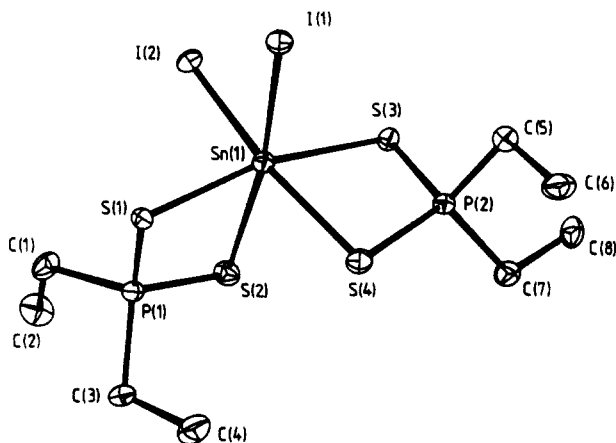


Figure 9. The molecular structure of $I_2Sn[S_2P(C_2H_5)_2]_2$. Reprinted with permission from K. C. Molloy et al., *Inorg. Chem.*, **20**, 2172 (1981).

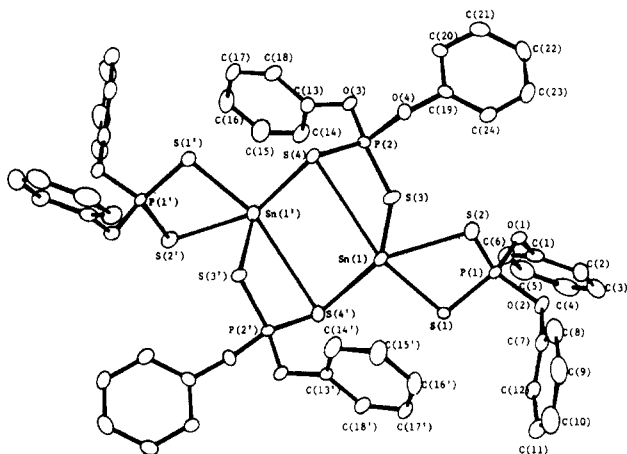


Figure 10. The molecular structure of dimeric $\{Sn[S_2P(OC_6H_5)_2]_2\}_2$, held together (in part) by bifurcated, three-coordinated sulfur atoms. Primed atoms are related to the corresponding unprimed atoms by the inversion center at the center of the $Sn(1)S(4)Sn(1')S(4')$ ring. Reprinted with permission from J. L. Lefferts et al., *Inorg. Chem.*, **21**, 1410 (1982).

inorganic species adopts a *cis*- I_2Sn arrangement (Figure 9); a configuration generally preferred by inorganic A_2SnB_4 systems,³² and a more regular array of almost isobidentate ligands (Table I).

A collective description of the structures discussed thus far is as representing positions along the pathway of a tin-sulfur linkage scrambling reaction.³³ (Diethyl dithiophosphato)triphenyltin(IV) is analogous to the four-coordinated starting material; the distorted octahedral bis(dimethyl dithiophosphinato)dimethyltin(IV) and bis(diethyl dithiophosphato)diphenyltin(IV) correspond to positions of increasing energy along the reaction pathway toward the transition state, while the symmetrical transition state itself is represented by bis(diisopropyl dithiophosphato)diphenyltin(IV). Analogously, the diiodotin dithiophosphinate represents a position well-advanced along the scrambling reaction pathway but now toward a *cis*-oriented transition state.

Another structure variation emerges from the richer and less predictable structural chemistry of divalent tin.^{32,53} Bis(diphenyl dithiophosphato)tin(II),⁹ $Sn[S_2P(OC_6H_5)_2]_2$, adopts a centrosymmetric, dimeric struc-

(32) J. A. Zubieta and J. J. Zuckerman, *Prog. Inorg. Chem.*, **24**, 251 (1978); P. J. Smith, *J. Organomet. Chem. Libr.*, **12**, 98 (1981).

(33) D. Britton and J. D. Dunitz, *J. Am. Chem. Soc.*, **103**, 2971 (1981).

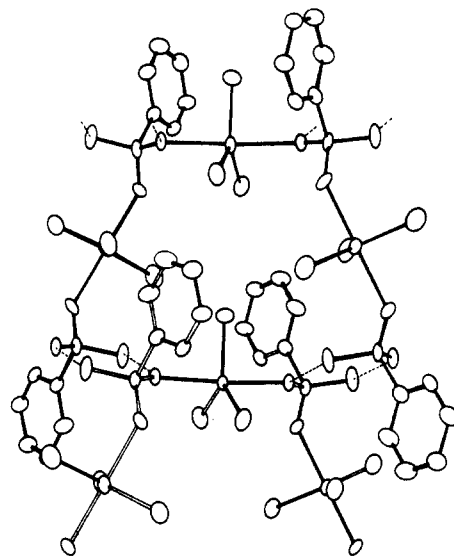


Figure 11. The helical, chain structure of $\alpha-(CH_3)_3SnO_2P(OH)C_6H_5$. Adjacent helices are of opposite hand and are linked by a network of hydrogen bonds (dotted lines). Reprinted with permission from K. C. Molloy et al., *Inorg. Chem.*, **20**, 2402 (1981).

ture, in which each tin is bonded to a terminal, chelating ligand in the normal fashion (Figure 10). Additionally, one ligand on each tin bridges to the adjacent tin in the dimer, while simultaneously chelating the tin from which the ligand emanates. Precedent for the bifurcated association and a three-coordinated sulfur atom can be found in the structure of dimeric bis(tetrathio tungstato)tin(II), which contains tridentate WS_4 ligands.³⁴ This is apparently the first instance of a bridging thiophosphate bonded to tin, although this bonding mode is common for transition-metal derivatives.³

Another feature of this tin(II) structure is the disposition of the phenyl ring of one of the phenoxy groups relative to the assumed position of the tin lone pair. The latter presumably lies approximately along an extension of the $Sn(1)-S(3)$ vector (Figure 10) and occupies the remaining vacant site in a badly distorted octahedron about tin. Although long and rather asymmetric by comparison with related structures,^{35,36} the stereochemistry of the ring and the presumed lone-pair position strongly suggests a π -interaction between these two molecular components.

Whether electronic or merely steric, this interaction reduces the reactivity of the compound, which alone among the tin(II) dithiophosphate esters is stable to air oxidation.⁹ The other members of this series turn orange in air, with surface oxidation producing a tin(IV) product, presumably of the $[(RO)_2PS_2]_2SnO$ type. The solid-state stability of the phenoxy compound arises from the blocking of access to the tin by the capping C_6H_5 ring, thereby precluding oxidation.

Oxy Phosphorus Acid Derivatives

Crystallographic data for this class of compounds are scarce, owing mainly to physical properties that tend to preclude crystal formation. The low solubility and

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associated high melting points^{10,11} of these compounds themselves suggest associated structures, an inference borne out by structure determinations.

The α -modification of (phenylphosphonato)trimethyltin(IV), $(\text{CH}_3)_3\text{SnO}_2\text{P}(\text{OH})(\text{C}_6\text{H}_5)$ forms a one-dimensional polymer, in which planar trimethyltin units are axially bridged by a three-atom $-\text{O}-\text{P}-\text{O}-$ linkage (Figure 11).³⁷ Although the axial $\text{O}-\text{Sn}-\text{O}$ bonds require linearity of the polymer in the vicinity of the tin atoms, the chains are bent through the tetrahedrally coordinated phosphorus atoms of the ligand [$\text{O}(1)-\text{P}(1)-\text{O}(2) = 115.3(3)^\circ$]. This results in chains that propagate through the crystal in a 4_1 -helical fashion, with adjacent helices turning in opposite directions. Adjacent helices are cross-linked by a network of hydrogen bonds, which we assume are binding the POH and $\text{O}=\text{P}$ groups in adjacent ligands, to form two-dimensional sheets. The phenyl groups point outward from the propagating helices, separating independent sheets of helices from one another.

Because the two tin-oxygen distances at each tin atom are symmetry related, and must, therefore, be equal, the conventional bridging arrangement such as that shown in Figure 3C is ruled out. Instead, the tin atoms make alternately two long or two short bonds to oxygen, and the structure is best represented by the complex ionic formulation $\{(\text{CH}_3)_3\text{Sn}\}^+\{(\text{CH}_3)_3\text{Sn}[\text{O}_2\text{P}(\text{OH})\text{C}_6\text{H}_5]_2\}^-$. This is the only authentic example³² of an associated organotin polymer in which the chains consist of alternating tin environments. Two determinations of the structure of $(\text{CH}_3)_3\text{SnO}_2\text{SCH}_3$ show that it contains two independent tin sites bridged by sulfinate ligands in an alternating, one-dimensional array. Each tin atom here also lies on a twofold axis and is bonded to two identical oxygen atoms that differ in the two sites. However, the difference between pairs of tin-oxygen bond distances was found to be only 3 standard deviations in one study³⁸ and zero in the other,³⁹ thereby making the tin environments indistinguishable. These polymer chains also adopt helical configurations, but there is no hydrogen bonding to associate the helices into sheets.

The local geometry at tin in $(\text{C}_6\text{H}_5)_3\text{SnO}_2\text{P}(\text{OC}_6\text{H}_5)_2$,⁴⁰ the oxygen analogue of the tetrahedral dithiophosphate that began this discussion, follows a similar pattern: planar triphenyltin moieties axially bridged through the oxygen of the bidentate oxy phosphorus acid ligand (Figure 12). The extended structure, however, differs dramatically from the phosphonate. Here, short chains lock together to form hexameric rings incorporating a 24-atom heterocycle⁴⁰ rather than propagate linearly or helically through the crystal. This hexameric ring structure is apparently unique among tin compounds.³²

The formation of a hexamer rather than a ring of larger or smaller size can be rationalized on geometric grounds. In order to facilitate efficient packing of molecules into the lattice, preference is given to structures containing a nearly planar ring. Additionally, polygons with nearly T_d internal angles, which minimize

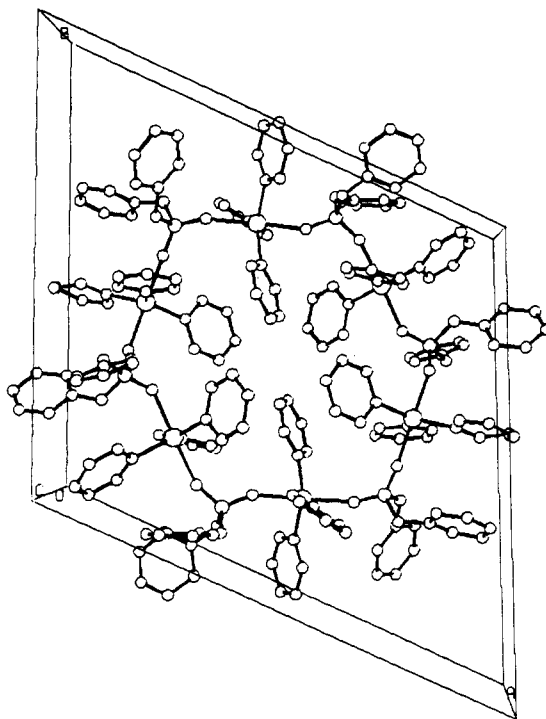


Figure 12. The unit cell contents of $(\text{C}_6\text{H}_5)_3\text{SnO}_2\text{P}(\text{OC}_6\text{H}_5)_2$. Reprinted with permission from K. C. Molloy et al., *Inorg. Chem.*, 21, 960 (1982).

angular distortions at phosphorus, will also be favored. Clearly, a pentamer (internal angles = 108°) best fits these criteria but is ruled out by its inability to accommodate the five phenyl rings (one per tin) that protrude into its center. A hexameric ring can, however, accommodate the six, internal phenyl groups, with only minimal deviations from ring planarity arising from the change in the vertex angle from 120° (for a planar ring) to the tetrahedral angle preferred by phosphorus.⁴⁰

In addition to these two organotin oxy phosphorus acid structures, a number of other reported structures, mainly inorganic tin(II) derivatives, confirm the bridging preference of the oxy ligand. Thus, bis[diethyltin(IV)] bis(orthophosphate) octahydrate consists of infinite ribbons in which octahedral, *trans*-diethyltin(IV), *cis*-diaquo groups are linked by PO_4 tetrahedra to give eight-membered rings in chair conformations.⁴¹ In the divalent tin series, the hydrogen phosphate (SnHPO_4) ,⁴²⁻⁴⁴ bis(dihydrogen phosphate) $[\text{Sn}(\text{H}_2\text{PO}_4)_2]$,⁴⁵ phosphite (SnHPO_3) ,⁴⁴ $\text{Sn}(\text{OH})\text{PO}_4$,^{44,46} $\text{Sn}_3(\text{PO}_4)_2$,^{44,47} $\text{Sn}(\text{O})(\text{OH})\text{PO}_3$,^{44,48} the two halophosphites $\text{Sn}_3\text{PO}_4\text{F}_3$ ^{44,49} and SnFPO_3 ,^{44,50} and ClSn

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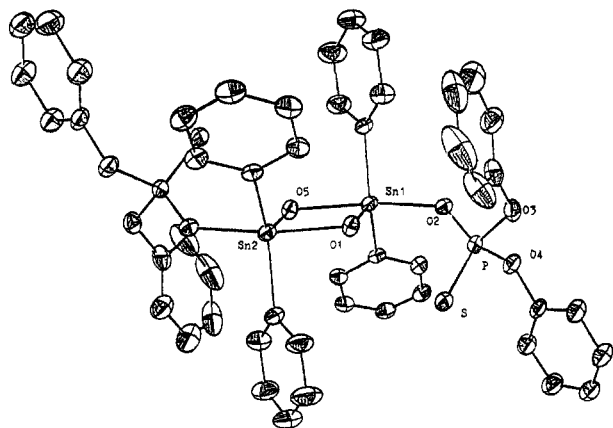


Figure 13. The structure of dimeric $\{(\text{C}_6\text{H}_5)_2\text{Sn}(\text{OH})[\text{OP}(\text{S})(\text{OC}_6\text{H}_5)_2]\}_2$.

$\text{H}_2\text{PO}_2^{51}$ are all bridged by three-atom $-\text{O}-\text{P}-\text{O}-$ linkages.

In such associated compounds, the overall nature of the structure chosen, be it linear, zig-zag, or helical polymer or, as above, a cyclic oligomer, appears to depend on minimizing the energy of the lattice as a whole. This is achieved by either secondary bond formation or efficient molecular packing. For the polymeric tin(IV) phosphonate, bonding energy is maximized by joining individual polymers into sheets by hydrogen bonds. To bring components of this secondary bond into juxtaposition requires a kinking of the polymer and hence helix formation. For the cyclic hexamer, packing efficiency dominates to produce an elegant arrangement of rings. Within each hexameric ring, one of the phenyl groups on each tin protrudes alternately above and below the ring plane to produce a staggered arrangement of the triphenyltin moieties around the ring (Figure 12). The hexameric units themselves nestle together in a stack along the c axis, where downward tilting phenyl groups of one hexamer fit between upward tilting phenyls of the hexamer below.⁴⁰

Unlike any of the other commonly encountered hydrocarbon groups, the structured phenyl ring is, apparently, able to induce packing effects that have a considerable contribution to the overall lattice structure. This is clear not only from the hexameric structure discussed above, but also, for example, in the stacking of phenyl groups along the c axis in $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{S}_2\text{P}(\text{OC}_3\text{H}_7\text{-}i)_2]_2$.³⁰

Mixed Ligands

Given the contrasting bonding modes for the two classes of ligands, compounds containing mono thio

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phosphorus acid ligands should prove structurally interesting. Spectroscopic studies⁵² indicate a preference for Sn–O rather than Sn–S covalent bond formation, and this is confirmed in the one available structure to date, that of $\{(\text{C}_6\text{H}_5)_2\text{Sn}(\text{OH})[\text{OP}(\text{S})(\text{OC}_6\text{H}_5)_2]\}_2$.¹

Synthesized by hydrolysis of $(\text{C}_6\text{H}_5)_2\text{Sn}[\text{OP}(\text{S})(\text{OC}_6\text{H}_5)_2]_2$ in wet ether, crystals of $(\text{C}_6\text{H}_5)_2\text{Sn}(\text{OH})[\text{OP}(\text{S})(\text{OC}_6\text{H}_5)_2]$, are dimeric with double hydroxy bridges (Figure 13). The tin–ligand covalent bond [2.153 (3), 2.199 (3) Å] is too short to arise from an Sn–S interaction and is comparable to other Sn–O distances [e.g., Sn–O in $(\text{C}_6\text{H}_5)_3\text{SnO}_2\text{P}(\text{OC}_6\text{H}_5)_2 = 2.129$ (8) Å⁴⁰]. Interestingly, the ligand sulfur atom does not coordinate to the tin (which remains five-coordinated), forming instead a hydrogen bond with a hydroxide within the same monomeric unit. Thus, in direct competition, the tin atom is hydroxy oxygen bridged in preference to being chelated through the P=S system. This oxygen bridge, in conjunction with an $\text{OH}\cdots\text{S}=\text{P}$ hydrogen bond, helps rationalize why hydrolysis does not proceed directly to diphenyltin oxide.¹

Conclusions

The contrast between the chelating of the dithio-phosphorus acid groups and the bridging of the corresponding oxygenated ligands can be rationalized on two counts. Firstly, the Sn–O bond is at least 0.2 Å shorter than the corresponding Sn–S bond. Thus, when chelation occurs, the angular strain within the resulting four-membered SnE_2P ($\text{E} = \text{O}, \text{S}$) heterocycle is greater for oxygen, rendering chelation less favorable. The relative electronegativities of C (2.50), S (2.44), and O (3.50) underlie the second rationale. In a trigonal bipyramid, for example, competition between carbon and sulfur for p- or s-dominated orbitals on tin will be negligible. The sulfur atoms show no preference for either the equatorial (s-dominated) or axial (p-dominated) position. Chelation is thus favored over bridging simply on the grounds of proximity—the second sulfur in the ligand is more likely to interact with the tin atom in whose environment it already exists than with the tin atom of a second molecule whose movement into the requisite position for such bridging bond formation to occur is governed by the relatively random nature of solution dynamics. Conversely, the increased electronegativity of oxygen over carbon directs it into the axial positions of the trigonal bipyramid. With the ligand unable to span both axial sites in the same molecule, bridging is thus observed.

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