(with decreasing *T*) associated with a first-order transition. In a differential scanning calorimetry study of the $\gamma \rightarrow \alpha$ transition of the manganese, iron, and cobalt bis(pyridyl) chloride compounds ($M(py)_2Cl_2$), we have observed endotherms for crystalline-solution preparations.[19] A final conclusion concerning the thermodynamic order of the transition must await further study. Solution preparations of a more crystalline, less defect-containing form of $Fe(bpy)(NCS)_2$ may be helpful in this regard and are being attempted.

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Registry No. $Fe(bpy)(NCS)_2$, 79803-24-0.

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Oxy and Thio Phosphorus Acid Derivatives of Tin. 8. Tin(II) Bis(dithiophosphate) Esters and Their Bipyridyl Adducts. X-ray Crystal and Molecular Structure of Bis(*O*,*O*′-diphenyl dithiophosphato)tin(II), a Bicyclic Dimer Held Together by Three-Coordinated Sulfur Atoms and by η^6-C_6H_5 Interactions Binding Tin(II) Lone Pairs to Phenoxy Ester Groups[1-3]

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Four tin(II) dithiophosphate esters, $Sn[S_2P(OR)_2]_2$, where R = CH_3, C_2H_5, *i*-C_3H_7, or C_6H_5, are synthesized in high yield by the action of the *O*,*O*′-diorganodithiophosphoric acids on dimethoxytin(II) in benzene to release methanol. The R = C_2H_5 product is a pale yellow oil, but the others are colorless crystalline solids soluble in nonpolar organic solvents. The 2,2′-bipyridyl adducts of the parent esters form immediately upon mixing. NMR coupling is observed from the ester groups to phosphorus, as $|^3J(^{31}P\text{–}O\text{–}C\text{–}^1H)| = 15.5$ Hz in the R = CH_3 derivative. Infrared spectral assignments can be made for the $\nu_{asym}(PS_2)$ (660–627 cm^{-1}), $\nu_{sym}(PS_2)$ (525–505 cm^{-1}), $\nu[(P)O\text{–}C]$ (1190–1150 cm^{-1}), $\nu[P\text{–}O(C)]$ (1030–1010 cm^{-1}), and $\nu(SnS)$ (355–332 cm^{-1}) modes. In the mass spectra parent molecular ions are found for all the species, but the fragments resulting from the loss of one ligand moiety are more abundant. The chief pathway for the decomposition is the successive loss of ligand moieties. Ditin-bearing ions are detected in the spectrum of the R = C_2H_5 derivative. The mass spectra of the bipyridyl adducts are the superposition of those of the parent tin(II) esters and of bipyridyl. The tin-119m Mössbauer isomer shifts (IS = 3.66–3.78 mm s^{-1}) confirm the presence of tin(II), and the barely resolvable quadrupole splittings (QS = 0.97–1.06 mm s^{-1}) do not increase on complexation by bipyridyl (1.03–1.15 mm s^{-1}), suggesting that the parent tin(II) esters themselves have higher coordination number in the solid state. Bis(*O*,*O*′-diphenyl dithiophosphato)tin(II), $C_{24}H_{20}O_4S_4P_2Sn$, crystallizes in the triclinic space group $P\bar{1}$ with a = 10.499 (5) Å, b = 13.948 (7) Å, c = 9.291 (4) Å, α = 99.18 (6)°, β = 95.71 (5)°, and γ = 91.80 (5)°, at 138 ± 2 K. The structure was determined by Patterson and Fourier techniques from 5517 reflections measured at 138 ± 2 K on an automatic diffractometer with monochromatic Mo Kα radiation and refined to a final R value of 0.029 for all data. The centrosymmetric dimer contains one ligand bridging two tin atoms intermolecularly, while simultaneously chelating one tin atom in an extremely anisobidentate fashion via a bifurcated, three-coordinated sulfur atom [S(4)]. A second ligand is involved in normal chelation. Completing the coordination sphere at the tin(II) atom and contributing to the formation of the dimer is an η^6-C_6H_5 interaction between the phenoxy ester group of the bridging ligand of the second molecular unit and the tin(II) lone pair to produce a ψ-6-coordinated metal center. A planar Sn_2S_2 ring is demanded by crystallographic symmetry and is seen to be circumscribed by an eight-membered $[SnSPS]_2$ ring in a chair conformation. The ester P(1)—S(1)—Sn(1) and P(2)—S(3)—Sn(1) systems are distinguished from the double-bonded, dative P(1)=S(2)→Sn(1), P(2)=S(4)→Sn(1), and P(2′)=S(4′)→Sn(1) systems on the basis of their P—S and S—Sn internuclear distances. The tin atom is 0.46 Å out of the plane formed by the S(1), S(2), S(4), and S(4′) atoms and is away from the S(3) atom, with the ester-bound sulfur atoms cis oriented [∠S(1)–Sn(1)–S(3) = 87.41°]. The smallest angle in the plane is formed by the terminally chelating sulfur atoms [∠S(1)–Sn(1)–S(2) = 74.28°]. Atom S(3) is opposite the expected direction of the tin(II)-lone-pair vector, which if extended strikes a perpendicularly oriented phenoxy group with tin to carbon distances at 3.457–4.317 Å. The distances to the center of the ring and to the plane of the ring are 3.66 and 3.46 Å, respectively. The ordering of the angles at the phosphorus atoms obeys the expected isovalent hybridization predictions: ∠S–P–S > ∠S–P–O > ∠O–P–O. The stability of the phenoxy ester to air oxidation is rationalized in terms of the additional η^6-C_6H_5 bonding contribution and by the steric blocking of the tin(II) lone pair by the phenoxy group.

In this series of papers we have been studying the synthetic routes to organotin(IV) derivatives of various oxy and thio phosphorus acids, and the spectroscopic properties and structures of the resulting products.[1] We have also had an interest in tin(II) chemistry extending over 20 years.[5] This paper is the issue of the marriage of these two themes. We report the synthesis of four tin(II) dithiophosphate esters, their adducts with 2,2′-bipyridyl, and the remarkable and unexpected crystal structure of the diphenyl ester derivative.

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[1] For part 7 of this series see: Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Cunningham, D.; Zuckerman, J. J. *Inorg. Chem.* **1981**, *20*, 2402.

[2] The crystal structure of bis(*O*,*O*′-diphenyl dithiophosphato)tin(II) has been published in a preliminary form.[3]

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Chart I

R	g (mmol) of dithiophosphate	g (mmol) of 2,2′-bipyridyl	recrystn solvent	yield, g (%)
CH_3	2.16 (5.0) in benzene (10 mL)	0.80 (5.1) in hexane (10 mL)	hexane/benzene (2:1)	1.50 (50.9)
C_2H_5	2.45 (5.0) in hexane (10 mL)	0.80 (5.1) in hexane (10 mL)	hexane/benzene (5:1)	2.20 (68.2)
C_6H_5	1.60 (2.3) in benzene (10 mL)	0.38 (2.4) in hexane (10 mL)	benzene	0.75 (37.9)

Experimental Section

The dithiophosphoric acids used in this study were prepared by literature methods.[6-9] Tin(II) dimethoxide was prepared from the reaction of tin(II) chloride and dry methanol in the presence of triethylamine.[10]

All solvents were dried and distilled immediately before use. Reactions were carried out under an atmosphere of dry nitrogen with use of standard anaerobic techniques. With the exception of bis(diphenyl dithiophosphato)tin(II), which is stable to atmospheric moisture for up to ca. 7 days, all the tin(II) dithiophosphate esters slowly turn orange on exposure to air. Infrared spectra were recorded as Nujol mulls or neat liquids on CsI plates or as KBr disks on a Beckman 4250 spectrometer. Tin-119 Mössbauer spectra were recorded at 77 K on a Ranger Engineering constant-acceleration spectrometer equipped with a proportional counter and with a $Ca^{119m}SnO_3$ source (New England Nuclear Corp.) and $Ca^{119}SnO_3$ used as the zero isomer shift (IS) reference standard at room temperature. Mass spectra were recorded on a Hewlett-Packard 5985 GC/MS system at 70 eV. NMR spectra were run on a Varian T60 instrument. Carbon and hydrogen analyses and the molecular weight determination were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Bis(*O,O′*-dimethyl dithiophosphato)tin(II), $Sn[S_2P(OCH_3)_2]_2$. To a suspension of dimethoxytin(II) (4.07 g, 22.5 mmol) in benzene (50 mL) was added a solution of dimethoxydithiophosphoric acid (7.17 g, 45.3 mmol) in the same solvent (20 mL). During the course of a mildly exothermic reaction the insoluble starting material dissolved and small amounts of an insoluble brown product were formed. The mixture was stirred at room temperature for 48 h and filtered under N_2 and the clear filtrate evaporated to dryness at reduced pressure, to leave a colorless solid product. Recrystallization from benzene/hexane (1:1) yielded the title compound (8.48 g, 87%), mp 65.5–67.0 °C.

Bis(*O,O′*-diethyl dithiophosphato)tin(II), $Sn[S_2P(OC_2H_5)_2]_2$. A suspension of dimethoxytin(II) (5.44 g, 30.1 mmol) in benzene (40 mL) and a solution of diethyldithiophosphoric acid (11.39 g, 61.2 mmol) in the same solvent (15 mL) were stirred together at room temperature for 24 h. The resulting mixture was filtered and the solvent removed from the filtrate to leave the product as a pale yellow oil (14.6 g, 98.0%), which decomposed upon attempted distillation (ca. 80 °C, 0.005 torr).

Bis(*O,O′*-diisopropyl dithiophosphato)tin(II), $Sn[S_2P(OC_3H_7\text{-}i)_2]_2$. To a suspension of dimethoxytin(II) (3.62 g, 20 mmol) in benzene (20 mL) was added a solution of diisopropyldithiophosphoric acid (4.28 g, 40 mmol) in benzene (20 mL). After 24 h of stirring at room temperature, the mixture was filtered (to remove traces of brown precipitate) and concentrated in vacuo to yield an oil, which was then filtered again. On standing in vacuo at room temperature for ca. 3 weeks, the oil solidified to a colorless crystalline solid, which was washed with hexane (2 × 5 mL) at −78 °C and dried in vacuo (8.20 g, 75.2%); mp 55–58 °C.

Bis(*O,O′*-diphenyl dithiophosphato)tin(II), $Sn[S_2P(OC_6H_5)_2]_2$. Following the procedure outlined above, we reacted dimethoxytin(II) (5.89 g, 32.6 mmol) and diphenyldithiophosphoric acid (18.37 g, 65.1 mmol) in benzene (80 mL). After 48 h the mixture was filtered and concentrated to dryness. Recrystallization of the resulting solid from toluene/hexane (1:1) affords the title compound as a colorless, crystalline solid (22.0 g, 99.1%), mp 125.5–126.5 °C.

The syntheses of all the 1:1 adducts of tin(II) dithiophosphates and 2,2′-bipyridyl follow essentially the same procedure; the synthesis of bis(*O,O′*-diisopropyl dithiophosphato)tin(II)–2,2′-bipyridyl (1:1) is given as a typical example.

Table II. Tin-119m Mössbauer Data for the Tin(II) Dithiophosphate Esters and Their Adducts at 77 K

compd	IS[a]	QS[b]	Γ_+[a]	Γ_-[a]
$Sn[S_2P(OCH_3)_2]_2$	3.67	0.97	0.96	1.04
$Sn[S_2P(OC_2H_5)_2]_2$	3.60	1.11	1.01	1.03
$Sn[S_2P(OC_3H_7\text{-}i)_2]_2$	3.49	1.12	1.11	1.19
$Sn[S_2P(OC_6H_5)_2]_2$	3.78	1.06	1.04	1.09
$Sn[S_2P(OCH_3)_2]_2\cdot$bpy[c]	3.61	1.07	1.05	0.98
$Sn[S_2P(OC_2H_5)_2]_2\cdot$bpy	3.75	1.04	1.10	1.05
$Sn[S_2P(OC_3H_7\text{-}i)_2]_2\cdot$bpy	3.66	1.03	0.97	1.05
$Sn[S_2P(OC_6H_5)_2]_2\cdot$bpy	3.75	1.15	1.07	1.03

[a] ±0.03 mm s^{-1}. [b] ±0.06 mm s^{-1}. [c] bpy = 2,2′-bipyridyl.

Table III. ^1H NMR Data for the Tin(II) Dithiophosphate Esters, $Sn[S_2P(OR)_2]_2$[a-c]

R = CH_3	d, 3.50 (12 H, $POCH_3$), $|^3J(^{31}P\text{–}O\text{–}C\text{–}^1H)| = 15.5$
R = C_2H_5	dq, 4.13 (8 H, $POCH_2CH_3$), $|^3J(^{31}P\text{–}O\text{–}C\text{–}^1H)| = 10.0$, $|^3J(^1H\text{–}C\text{–}C\text{–}^1H)| = 7.0$; t, 1.13 (12 H, $POCH_2CH_3$), $|^3J(^1H\text{–}C\text{–}C\text{–}^1H)| = 7.0$
R = $i\text{-}C_3H_7$	m, 5.00 (4 H, $POCH(CH_3)_2$), $|^3J(^{31}P\text{–}O\text{–}C\text{–}^1H)| = 13.0$, $|^3J(^1H\text{–}C\text{–}C\text{–}^1H)| = 6.5$; d, 1.32 (2 H, $POCH(CH_3)_2$), $|^3J(^1H\text{–}C\text{–}C\text{–}^1H)| = 6.5$
R = C_6H_5	m, 6.84–7.55 (20 H, POC_6H_5)

[a] In C_6D_6. [b] d = doublet, dq = doublet of quartets, m = multiplet, t = triplet. [c] Shifts in ppm; coupling constants in Hz.

Table VI. Crystal Data

formula	$C_{24}H_{20}O_4P_2S_4Sn$	α, deg	99.18 (6)[a]
fw	681.34	β, deg	95.71 (5)[a]
cryst syst	triclinic	γ, deg	91.80 (5)[a]
space group	$P\bar{1}$	V, Å^3	1334.8
a, Å	10.499 (5)[a]	Z	2
b, Å	13.948 (7)[a]	D_{calcd}, g cm^{-3}	1.70
c, Å	9.291 (4)[a]	μ, cm^{-1}	12.9

[a] Based upon ±2θ values of 48 reflections with Mo Kα_1 radiation (λ = 0.709 26 Å) at 138 (2) K.

Table VII. Data Collection Parameters

diffractometer	Enraf-Nonius CAD/4
radiation (λ, Å)	Mo K$\bar{\alpha}$ (0.710 69)
temp, K	138 ± 2
scan technique	θ–2θ
limit, deg	0 ≤ 2θ ≤ 53
max scan time, s	60
scan angle, deg	0.80 + 0.20 tan θ
aperture width, mm	2.50 + 0.86 tan θ
aperture height, mm	4
aperture dist, mm	173
monitor reflctn	224
intens monitor freq, s	5000
max fluctuation in monitor, %	4.5
orientation monitors	200 reflctns[a]
no. of unique data	5517
no. of obsd data[b]	5154
corrections	Lorentz, polarization, absorption, anomalous dispersion

[a] New orientation matrix used if angular change greater than 0.1°. Orientation matrix was based upon 17 reflections. [b] $I > 2[\sigma(I)]$; intensities assigned to unobserved data $1.4[\sigma(I)]$.

Bis(*O,O′*-diisopropyl dithiophosphato)tin(II)–2,2′-Bipyridyl (1:1), $Sn[S_2P(OC_3H_7\text{-}i)_2]_2\cdot C_{10}H_8N_2$. Solutions of the tin(II) dithiophosphate (2.00 g, 3.7 mmol) and 2,2′-bipyridyl (0.60 g, 3.8 mmol) in hexane (10 mL each) were mixed, with stirring, under a dry-nitrogen atmosphere. A yellow precipitate formed immediately and was isolated by filtration, washed with hexane, and recrystallized from hexane/benzene (ca. 20:1) to yield a 1:1 adduct as a yellow crystalline solid (1.90 g, 73.3%), mp 105–107 °C.

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Table VIII. Final Positional Parameters ($\times 10^4$) for Nonhydrogen Atoms in Bis(*O*,*O'*-diphenyl dithiophosphato)tin(II), $Sn[S_2P(OC_6H_5)_2]_2$[a]

atom	*x*	*y*	*z*
Sn(1)	4511.7 (1)	841.7 (1)	1899.7 (2)
P(1)	4049.5 (6)	2979.3 (4)	3662.2 (6)
P(2)	7426.8 (5)	1210.7 (4)	623.2 (6)
S(1)	2846.7 (5)	2208.0 (4)	2056.1 (6)
S(2)	5370.4 (6)	2180.7 (4)	4459.9 (6)
S(3)	5771.3 (5)	1858.2 (4)	267.0 (6)
S(4)	7260.7 (6)	−153.4 (4)	895.3 (7)
O(1)	3270 (2)	3566 (1)	4879 (2)
O(2)	4746 (2)	3877 (1)	3147 (2)
O(3)	8298 (2)	1394 (1)	−632 (2)
O(4)	8293 (2)	1778 (1)	2026 (2)
C(1)	2507 (2)	3116 (2)	5767 (3)
C(2)	1219 (3)	2957 (2)	5335 (3)
C(3)	451 (3)	2580 (2)	6272 (3)
C(4)	1001 (4)	2379 (2)	7604 (3)
C(5)	2292 (4)	2546 (2)	8010 (3)
C(6)	3074 (3)	2916 (2)	7088 (3)
C(7)	4027 (2)	4550 (2)	2443 (3)
C(8)	3566 (3)	5338 (2)	3284 (3)
C(9)	2906 (3)	6006 (2)	2564 (4)
C(10)	2734 (3)	5873 (2)	1051 (4)
C(11)	3216 (3)	5073 (2)	228 (3)
C(12)	3874 (3)	4404 (2)	924 (3)
C(13)	8215 (2)	790 (2)	−2015 (3)
C(14)	7289 (3)	927 (2)	−3113 (3)
C(15)	7289 (3)	347 (2)	−4477 (3)
C(16)	8192 (3)	−343 (2)	−4725 (3)
C(17)	9117 (3)	−458 (2)	−3602 (3)
C(18)	9132 (2)	105 (2)	−2236 (3)
C(19)	8714 (2)	2765 (2)	2167 (3)
C(20)	8112 (2)	3446 (2)	3080 (3)
C(21)	8586 (3)	4402 (2)	3315 (3)
C(22)	9628 (3)	4667 (2)	2639 (3)
C(23)	10211 (3)	3976 (2)	1727 (3)
C(24)	9755 (2)	3010 (2)	1488 (3)

[a] Estimated standard deviations in parentheses.

Details of other adducts, $Sn[S_2P(OR)_2]_2 \cdot C_{10}H_8N_2$, prepared by this method are tabulated in Chart I.

Analytical and physical data for the esters and their bipyridyl adducts are tabulated in Table I, tin-119m Mössbauer data in Table II, proton NMR data in Table III, infrared data in Table IV, and mass spectral data in Table V (Tables I, IV, and V are included in the supplementary material).

Crystal Data Collection and Structure Determination of Bis(*O*,*O'*-diphenyl dithiophosphato)tin(II), $Sn[S_2P(OC_6H_5)_2]_2$. Colorless, prismatic crystals were obtained by crystallization from a hexane/toluene (1:1) mixture at 0 °C. Crystal data are given in Table VI. Data were collected at 138 ± 2 K with a CAD-4 counter diffractometer (Enraf-Nonius) controlled by a PDP8/e computer and fitted with a low-temperature apparatus. Details of the method of data collection and data reduction have been reported previously.[11] Pertinent data collection parameters are given in Table VII. X-ray diffraction experiments showed the crystal system to be triclinic. The successful refinement showed the space group to be $P\bar{1}$.

The structure was determined by conventional Patterson and Fourier techniques. Refinement was concluded at an *R* factor of 0.029 over all data when shifts in the positional and thermal parameters of the nonhydrogen atoms were less than one-third the corresponding estimated standard deviation. A final difference Fourier map contained no peaks greater than 0.9 e Å^{-3}. Scattering factors were for neutral atoms and were taken from refs 12 (Sn, C, P, O, S) and 13 (H). The positional parameters for the nonhydrogen atoms are listed in Table VIII, the positional and isotropic thermal parameters for hydrogen in Table IX, and the anisotropic thermal parameters for the nonhydrogen atoms in Table X. Internuclear distances are listed in Tables XI and XII and angles in Tables XIII and XIV (Tables IX, X, XII, and XIV are included in the supplementary material).

Table XI. Final Intramolecular Distances (Å) in $Sn[S_2P(OC_6H_5)_2]_2$[a,b]

Sn(1)–S(1)	2.6230 (6)	O(1)–C(1)	1.408 (3)
Sn(1)–S(2)	2.8300 (6)	O(2)–C(7)	1.422 (3)
Sn(1)–S(3)	2.6510 (6)	O(3)–C(13)	1.413 (3)
Sn(1)–S(4)	3.3914 (6)	O(4)–C(19)	1.414 (3)
Sn(1)–S(4')[c]	3.0428 (7)		
		Sn(1)–C(13')	3.622 (2)
P(1)–S(1)	2.0016 (8)	Sn(1)–C(14')	3.457 (3)
P(1)–S(2)	1.9670 (8)	Sn(1)–C(15')	3.745 (3)
P(2)–S(3)	2.0064 (8)	Sn(1)–C(16')	4.168 (3)
P(2)–S(4)	1.9636 (8)	Sn(1)–C(17')	4.317 (3)
		Sn(1)–C(18')	4.065 (2)
P(1)–O(1)	1.596 (2)	Sn(1)–Sn(1')	4.1536 (2)
P(1)–O(2)	1.592 (2)		
P(2)–O(3)	1.598 (2)		
P(2)–O(4)	1.594 (2)		

[a] Estimated standard deviations in parentheses. [b] Carbon-carbon distances are found in Table XII (supplementary material). [c] Primed atoms are related to the corresponding unprimed atoms by the center of symmetry at (0, 0, 0).

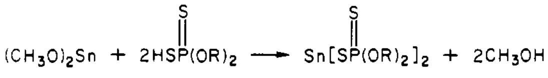
Table XIII. Final Intramolecular Angles (Deg) in $Sn[S_2P(OC_6H_5)_2]_2$[a,b]

S(1)–Sn(1)–S(2)	74.28 (2)	Sn(1)–S(3)–P(2)	94.33 (3)
S(1)–Sn(1)–S(3)	87.41 (2)	Sn(1)–S(4)–P(2)	74.76 (2)
S(1)–Sn(1)–S(4)	153.53 (2)	Sn(1)–S(4)–Sn(1')	80.21 (1)
S(1)–Sn(1)–S(4')[c]	79.23 (2)	Sn(1')–S(4)–P(2)	96.06 (3)
S(2)–Sn(1)–S(3)	91.14 (2)	S(3)–P(2)–S(4)	115.51 (4)
S(2)–Sn(1)–S(4)	102.85 (2)	S(3)–P(2)–O(3)	107.72 (7)
S(2)–Sn(1)–S(4')	153.40 (2)	S(3)–P(2)–O(4)	111.47 (7)
S(3)–Sn(1)–S(4)	66.21 (2)	S(4)–P(2)–O(3)	114.29 (7)
S(3)–Sn(1)–S(4')	85.34 (2)	S(4)–P(2)–O(4)	106.94 (7)
S(4)–Sn(1)–S(4')	99.79 (2)	O(3)–P(2)–O(4)	99.83 (9)
Sn(1)–S(1)–P(1)	87.88 (3)	P(1)–O(3)–C(13)	123.1 (1)
Sn(1)–S(2)–P(1)	82.88 (3)	P(1)–O(4)–C(19)	123.3 (1)
S(1)–P(1)–S(2)	112.32 (4)	O(1)–C(1)–C(2)	118.7 (2)
S(1)–P(1)–O(1)	110.50 (7)	O(1)–C(1)–C(6)	118.3 (2)
S(1)–P(1)–O(2)	112.45 (7)		
S(2)–P(1)–O(1)	113.75 (7)	O(2)–C(7)–C(8)	119.2 (2)
S(2)–P(1)–O(2)	108.33 (7)	O(2)–C(7)–C(12)	118.1 (2)
O(1)–P(1)–O(2)	98.78 (9)	O(3)–C(13)–C(14)	120.2 (2)
		O(3)–C(13)–C(18)	117.6 (2)
P(1)–O(1)–C(1)	123.6 (1)	O(4)–C(19)–C(20)	118.0 (2)
P(1)–O(2)–C(7)	120.8 (1)	O(4)–C(19)–C(24)	119.7 (2)

[a] Estimated standard deviations in parentheses. [b] Angles involving only carbon are found in Table XIV (supplementary material). [c] Primed atoms are related to the corresponding unprimed atoms by the center of symmetry at (0, 0, 0).

Results and Discussion

Syntheses and Properties. The tin(II) dithiophosphate esters, $Sn[S_2P(OR)_2]_2$, are prepared in high yield by the action of dimethoxytin(II) on the *O*,*O'*-diorganodithiophosphoric acids in a 1:2 molar ratio in benzene (a suspected carcinogen) to release methanol:



$$(CH_3O)_2Sn + 2HS\overset{S}{\overset{\|}{P}}(OR)_2 \longrightarrow Sn[S\overset{S}{\overset{\|}{P}}(OR)_2]_2 + 2CH_3OH \quad (1)$$

The R = C_2H_5 product is a pale yellow oil, but the others are colorless crystalline solids soluble in nonpolar organic solvents. Analytical and physical data are listed in Table I (supplementary material).

2,2'-Bipyridyl adducts of the tin(II) derivatives form immediately on mixing solutions of the tin compounds and the ligand.

The proton NMR spectra consist as expected of the pattern of the organic ester groups in the appropriate integrated areas and peak multiplicities. For example, in the spectrum of bis(*O*,*O'*-dimethyl dithiophosphato)tin(II), Sn[SP(S)(OC-

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Table XV. Selected Infrared Assignments for the Tin(II) Dithiophosphate Esters, $Sn[S_2P(OR)_2]_2$[a]

R = CH_3[b]	R = C_2H_5[c]	R = i-C_3H_7[b]	R = C_6H_5[b]	assignt
			1190 s	
1170 vs	1152 s	1180 s	1175 vvs	ν[(P)O–C]
			1150 vvs	
1030 vvs, br	1020 vvs	1015 vvs	1025 m	ν[P–O(C)]
			1010 m	
635 vs, br	645 vs	627 s, br	660 vs	$\nu_{asym}(PS_2)$
505 s	525 m, br	525 s, br	525 m	$\nu_{sym}(PS_2)$
340 s	355 w	332 vw	355 w	ν(SnS)

[a] Relative intensities are indicated by s = strong, m = medium, w = weak, v = very, br = broad. [b] Nujol mull on CsI plates. [c] Neat liquid on CsI plates.

$H_3)_2]_2$, the methoxy group signal appears as a doublet at 3.50 ppm arising from coupling to phosphorus, $|^3J(^{31}P–O–C–^1H)|$ = 15.5 Hz, a value apparently unaffected by the oxidation state of the attached tin atom since the tri-[14] and diphenyltin(IV)[15] analogues display the same coupling constant. In the ethoxy derivative, however, the methylene protons appear as a doublet of quartets arising from a coupling to phosphorus-31 of 10.0 Hz and a coupling with the terminal/methyl protons, $|^3J(^1H–C–C–^1H)|$ = 7.0 Hz, again identical values with those found in the tri-[14] and diphenyltin(IV)[15] analogues.

In the infrared spectra it is unfortunately impossible to assign the positions of the ν(P—S) and ν(P═S) modes with confidence, and hence a discussion of the possible structural possibilities cannot be mounted on this basis. The infrared absorptions are listed in Table IV (supplementary material), and some selected assignments for the four dithiophosphate esters are presented in Table XV. The P–S absorptions, which appear in the 670–630 and 560–530 cm^{-1} ranges whether for the free acids, $HSP(S)(OR)_2$, for their esters, $RSP(S)(OR)_2$,[16-18] or for their transition-metal complexes, $M[S_2P(OR)_2]_n$, in which the bidentate ligands chelate,[19] can be found at 660–627 and 525–505 cm^{-1} in the tin(II) derivatives and are described as $\nu_{asym}(PS_2)$ and $\nu_{sym}(PS_2)$, respectively. The ν[(P)–O–C] and ν[P–O(C)] modes have been assigned to the 1190–1152 and 1025–1010 cm^{-1} ranges in our compounds, respectively, with reference to the data in ref 20. However, other authors claim that these modes absorb in the 1060–905 and 875–730 cm^{-1} regions, respectively, while bands occurring in the range 1240–1085 cm^{-1} arise from deformation vibrations involving the carbon atom of the P–O–C linkage.[21] The assignment of our $\nu(PS_2)$ modes is done by analogy with those reported for the corresponding organolead,[22] -thallium,[18] and -mercury[23] derivatives.

Mass spectral data for the four tin(II) compounds are listed in Table V (supplementary material) with suggested assignments. Odd-electron parent molecular ions are found in all the spectra, unlike our experience with the analogous di-[15] and triorganotin(IV)[14] species. Moreover, loss of a neutral alkene to form a further odd-electron ion in both cases where this is possible (R = C_2H_5, i-C_3H_7) is unusual in spectra normally dominated by even-electron species. The fragments resulting from the loss of one ligand moiety are the most abundant tin-bearing ions in all the spectra but that of the isopropoxy derivative, as with the di-[15] and triorganotin(IV)[14] species. Common fragments include the SnS_2PO^+ (m/e = 231) and $Sn^{+\cdot}$ (120) ions. The chief pathway for the decomposition of these esters is the successive loss of ligand moieties.

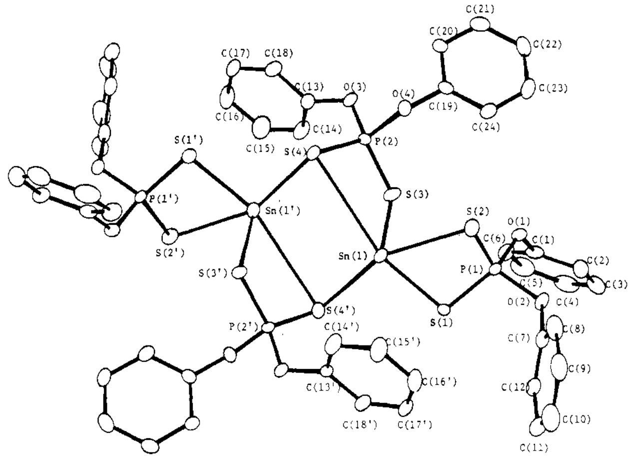

Figure 1. Molecular structure of dimeric bis(O,O'-diphenyl dithiophosphato)tin(II), $\{Sn[S_2P(OC_6H_5)_2]_2\}_2$, held together by bifurcated, three-coordinated sulfur atoms and η^6-C_6H_5 interactions with the tin(II) lone pairs. Primed atoms are related to the corresponding unprimed atoms by the center of symmetry at (0, 0, 0).

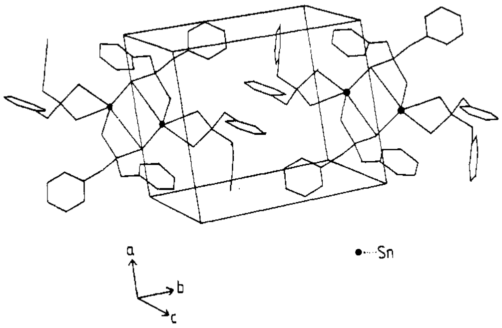

Figure 2. Contents of the unit cell showing the molecular packing.

Most interesting from a structural point of view are two even-electron ions of low relative abundance at m/e = 581 and 553 in the mass spectrum of the diethoxy ester. These fragments exhibit the characteristic patterns of a ditin-bearing ion and are assigned as $\{Sn_2L[S_2P(O)OC_2H_5]\}^+$ and $\{Sn_2L[S_2P(O)OH]\}^+$. This observation suggests an associated structure for the tin(II) esters (vide infra).

The mass spectra of the bipyridyl adducts are the superposition of the fragmentation patterns of the parent tin(II) dithiophosphate derivatives and of bipyridyl with only small differences in relative abundances. These data have thus not been separately tabulated.

The tin-119m Mössbauer data gathered in Table II confirm that the tin(II) oxidation state is present.[24] The isomer shifts (IS) lie in the range 3.66–3.78 mm s^{-1}, and the quadrupole splittings (QS) are just resolvable (0.97–1.06 mm s^{-1}) and do not increase on complexation by bipyridyl. This suggests that the coordination number at the tin atom does not change on going from the dithiophosphate esters to their bipyridyl adducts and thus that the parent tin(II) esters are of higher coordination number in the solid state (vide infra). The coordination number at the tin atom in the bipyridyl adducts must be at least ψ-5 [with two monodentate dithiophosphate ester ligands, a bidentate nitrogenous ligand, and the lone pair about tin(II)], although higher coordinations are both possible and more likely

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Table XVI. Comparative Tin-Sulfur and Phosphorus-Sulfur Internuclear Distances (A) in Dithiophosphorus Derivatives

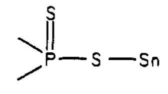
compd	ester[a] P–S–Sn		dative[a] P=S→Sn		ref
$[(C_6H_5O)_2PS_2]_2Sn(II)$	2.0016	2.6230[b]	1.9670	2.8300[b]	*c*
	2.0064	2.6510[d]	1.9636	3.0428[d]	
$(C_2H_5O)_2PS_2Sn(C_6H_5)_3$[e]	2.054	2.4582	1.931	5.326	25
$[(C_2H_5O)_2PS_2]_2Sn(C_6H_5)_2$[f]	2.04	2.48	1.92	3.20	28
	2.03	2.49	1.94	3.23	
$[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_6)_2$[f]	2.006	2.678	1.998	2.689	26
$[(CH_3)_2PS_2]_2Sn(CH_3)_2$[f]	2.047	2.482	1.969	3.334	27
$[(C_2H_5)_2PS_2]_2SnI_2$[g]	2.043	2.537	2.026	2.621	27
	2.044	2.533	2.032	2.593	

[a] The first number listed in each case is the P-S distance and the second is the S-Sn distance. [b] Data for the terminal ligands. [c] This work. [d] Data for the bridging ligands. [e] This compound is a rare example of a monodentate dithiophosphate ligand system. [f] *trans*-Diorganotin groups. [g] *cis*-Diiodotin configuration.

utilizing one or both dithiophosphate moieties in the usual bidentate mode.[19] Thus the coordination about the tin(II) atom in the parent esters must also be at least ψ-5, involving two bidentate sulfur ligands (vide infra).

Crystal and Molecular Structure of Bis(*O,O'*-diphenyl dithiophosphato)tin(II), $Sn[S_2P(OC_6H_5)_2]_2$.[2] The title compound exists as a centrosymmetric dimer as depicted in Figure 1 and shown packed into the unit cell in Figure 2. Each of the tin(II) atoms in the dimer is bound to two dithiophosphate ligands: one is bound to tin in a simple, chelating, anisobidentate fashion, while a second ligand is extremely skewed, with one of the sulfur atoms S(4) bridging to the tin(II) atom of an adjacent molecule to form a rectangular Sn_2S_2 ring, and at the same time chelating the tin(II) atom to which the ligand is ester bound (see Figure 1). Completing the coordination sphere of the tin(II) atom and contributing to the formation of the dimer is a η^6-C_6H_5 interaction between the phenoxy ester group of the bridging ligand of the second molecule and the tin(II) lone pair as depicted in Figure 1. This produces a distorted ψ-6 geometry at the metal center. The Sn_2S_2 ring, which by crystallographic symmetry must be perfectly planar with the sum of the four angles exactly 360°, contains triply bonded sulfur atoms seen in Figure 1 to be circumscribed by an eight-membered $[SnSPS]_2$ ring in a chair conformation.

We first discuss the simple, terminally chelated system whose understanding requires the identification of the sulfur atoms in terms of their belonging to the covalently bound ester system



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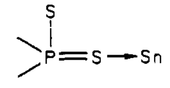

system. It is known for the dithiophosphate ester derivatives of the transition metals that the more tightly the sulfur atom is bound to the metal atom, then the longer is its bond with phosphorus.[19] Conversely, the shorter sulfur bonds to phosphorus can be written as P═S and are associated with the longer, coordinate-covalent sulfur–metal interaction. These shorter P═S distances are found in the range 1.85–1.95 Å for the dithiophosphate ester complexes, with the corresponding single P—S distances at 1.99–2.19 Å.[19] More direct comparison is made in Table XVI with the internuclear distances in the ester P—S—Sn and dative P═S→Sn linkages from four recent molecular structure determinations of dithiophosphate ester derivatives of tin(IV)[25–27] from this laboratory, plus another from the literature.[28] Except for bis(*O,O'*-diisopropyl dithiophosphato)diphenyltin(IV), $[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_5)_2$, in which the ligands chelate symmetrically,[26] the ester and dative portions of these chelating ligands can be easily distinguished.

The bonds that sulfur makes with tin(II) are expected to be longer than for their tin(IV) analogues, since their covalent radii have been assigned as 1.63 and 1.40 Å, respectively.[29] Examination of Table XVI, however, reveals no such apparent difference, since for both the ester and dative tin–sulfur bonds, longer tin(IV) examples are available in genuinely chelating systems. The title compound fits our model in that the long, dative S(2)—Sn(1) [2.8300 (6) Å] bond is associated with the shorter P(1)═S(2) [1.9670 (8) Å] bond, and the short S(1)—Sn(1) [2.6230 (6) Å] ester bond is contiguous to a longer P(1)—S(1) [2.0016 (8) Å] bond.

Turning to the bridging/chelating dithiophosphate ligand, with the same analysis, Table XVI reveals consistent behavior here, too, in that the longer, dative, chelating S(4)—Sn(1) [3.3914 (6) Å] bond is contiguous to the short P(2)═S(4) [1.9636 (8) Å] and the shorter S(3)—Sn(1) [2.6510 (6) Å] ester bond is associated with the long P(2)—S(3) [2.0064 (8) Å] bond. The bridging S(4)—Sn(1′) [3.0428 (7) Å] bond is significantly longer than the corresponding bond S(2)–Sn(1) [2.8300 Å] in the terminally chelating system, but the P═S distances are quite similar. The unexpectedly long P(2)═S(4) [1.9636 (8) Å] bond must arise because of electron withdrawal along the S(4)—Sn(1) vector at 3.3914 Å, thus confirming the chelating interaction between these two atoms and the existence of the inner Sn_2S_2 ring. Thus the sulfur atom S(4) is involved simultaneously in binding both the tin(II) atoms in the dimer in a bifurcated, three-coordinated manner. The three-coordinated sulfur atoms that bridge two metal centers in $\{CuS_2P[OCH(CH_3)_2]_2\}_4$, on the other hand, form equal or stronger sulfur–metal bonds than the sulfurs bonded to only a single metal atom. In this case electron withdrawal from the bridging P═S bond so lengthens this distance that it actually becomes longer than the adjacent P—S single bond.[30]

Precedent for the bifurcated association and our three-coordinated sulfur atom can be found in the structure of the dimeric bis(tetrathiotungstato)tin(II), which contains tridentate WS_4 ligands.[31] Planar, four-membered Sn_2S_2 rings are found in Sn_2S_3,[32] $(t\text{-}C_4H_9)_2SnS$,[33] and $(CH_3Sn)_4S_6$,[34] and the

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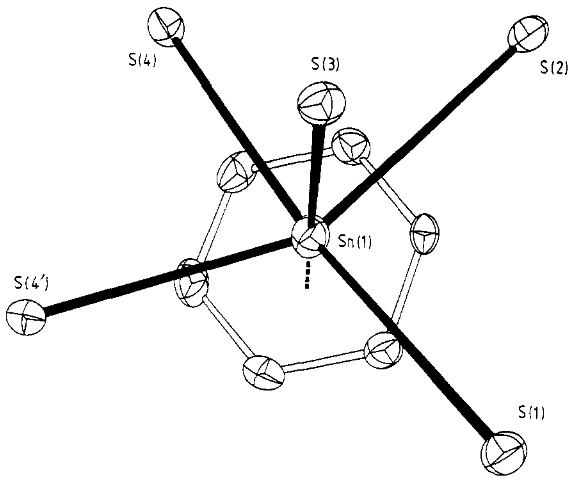

Figure 3. η^6-C_6H_5–tin(II) interaction along the S(3)–Sn(1) vector. The distance to the center of the ring is 3.655 Å.

dimeric $[Cl_3SnPO_2Cl_2{\cdot}POCl_3]_2$ contains an eight-membered centrosymmetric ring formed by the tin(IV) atoms and dichlorophosphate groups,[35] like our $[SnSPS]_2$ system. Simple sulfur chelation of tin(II) atoms is found in the dithiocarbonate,[36] $Sn[S_2COCH_3]_2$, and carbamate,[37] $Sn[S_2CN(C_2H_5)_2]_2$. The structure of the title compound contrasts with those adopted by lead(II) diethyl dithiophosphate, in which the metal atoms are chelated in monomers,[38] and its diisopropyl analogue, in which the metal atom is coordinated by six sulfur atoms, two of which are bonded intermolecularly to create a polymeric lattice.[39]

The sulfur atom coordination sphere about the tin(II) atom creates a ψ-6 situation with a distorted octahedral geometry and the lone pair of electrons occupying the sixth coordination site. The planar girdle of this octahedron can be considered to be formed by the four sulfur atoms S(1), S(2), S(4), and S(4'), with the tin atom 0.457 Å out of the least-squares plane and away from sulfur atom S(3). The sulfur atoms making ester bonds to the tin(II) atom in our analysis (vide supra) are cis to one another [∠S(1)–Sn(1)–S(3) = 87.41°]. The largest angle between adjacent (cis) sulfur atoms is formed by S(2) and S(4') at 102.85°, while the smallest angle in the plane is formed by the terminally chelating system[∠S(1)–Sn(1)–S(2) = 74.28°]. The sulfur atom normal to this plane [S(3)] leans in the direction of S(4), making a rather acute angle [∠S(3)–Sn(1)–S(4) = 66.21°].

Sulfur atom S(3) is opposite the expected direction of the tin(II)–lone-pair vector. This S(3)–Sn(1) vector when extended strikes near to the center of one of the phenyl groups of an ester of the bridging ligand of a second monomeric unit. This phenyl group is oriented in a spacially significant position nearly perpendicular to the assumed lone-pair vector. A view of the tin coordination sphere looking roughly along the S(3)–Sn(1) bond is found in Figure 3 and approximately perpendicular to this vector in Figure 4. The phenyl group appears approximately centered over the lone pair, with tin to carbon distances ranging from 3.457 to 4.317 Å (mean 3.896 Å). The distance from the tin atom to the least-squares center of the ring is 3.66 Å and is perpendicularly 3.46 Å from the least-squares plane of the ring. These distances are long when compared with those in η^6-C_6H_6 transition-metal complexes[40] but are (in part) within the sum of the van der Waals radii (4.00 Å).[41,42]

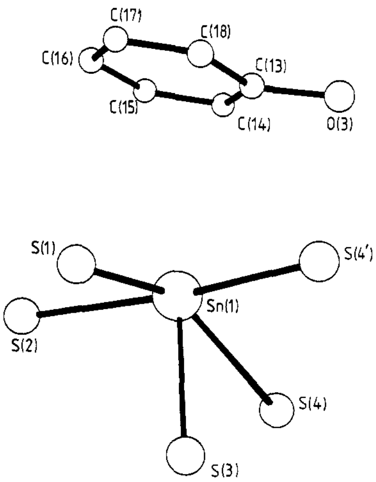

Figure 4. η^6-C_6H_5–tin(II) interaction viewed perpendicular to the S(3)–Sn(1) vector.

Table XVII. π-Sn(II)-Carbon Ring Interactions

compd	d(Sn–COR), Å[a]	range of d(Sn–C), Å	ref
η^6-$C_6H_6Sn(AlCl_4)_2{\cdot}C_6H_6$	2.74	3.06 ± 0.02	43
η^6-$C_6H_6SnCl(AlCl_4)$	2.90	3.05–3.39	44
η^6-p-$(CH_3)_2C_6H_4SnCl(AlCl_4)$	2.77	2.92–3.27	44
$(\eta^5$-$C_5H_5)_2Sn$[b]		2.71 ± 0.02	45
$(\eta^5$-$C_5H_5)SnCl$		2.45–2.75	46
$Sn[S_2P(OC_6H_5)_2]_2$	3.66	3.46–4.32	*c*

[a] COR = center of the six-membered ring. [b] From electron diffraction data. [c] This work.

Known π-Sn(II) to aromatic ring interactions are listed in Table XVII. Especially relevant are the structures of the polymeric materials of the composition η^6-$C_6H_6Sn(AlCl_4)_2{\cdot}C_6H_6$,[43] $C_6H_6SnCl(AlCl_4)$, and η^6-$(CH_3)_2C_6H_4SnCl(AlCl_4)$.[44] The first consists of pentagonal-bipyramidal arrangements of six chlorine atoms about each tin with the last coordination site occupied by a symmetrically placed benzene molecule. An additional benzene molecule of solvation fits into a cleft of the structure. The coordination number at the tin(II) atom is thus ψ-7.[43] In the latter two materials there are five chlorine atoms about each tin(II) with the sixth coordination site occupied by the aromatic moiety. The coordination number in this case is ψ-6, and the geometry is distorted octahedral.[44] In all three cases the tin(II)–carbon distances are regular and the local symmetry of the aromatic ring interaction is C_{6v}. A qualitative MO model that accommodates the tin(II) 5s and 5p electrons and those from six chlorines and the benzene ring in η^6-$C_6H_5Sn(AlCl_4)_2{\cdot}C_6H_6$ leads to a diamagnetic, closed-shell electronic structure. The principal interaction in this scheme between the tin(II) atom and the benzene ring is an e_1 MO

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formed by overlap of p orbitals lying in a plane parallel to the benzene ring, rationalizing the rather long tin–carbon distance.[43] This scheme contrasts with the generally accepted bonding model for transition-metal aromatic complexes where metal d orbitals are directed toward the carbon atoms. In the tin(II) case, only the $5p_x$ and $5p_y$ orbitals are available for interaction with the benzene e_1 electrons.

Our derivative is unusual and different from the materials discussed above in two ways: to our knowledge we have here, first, the only example of an η^6-C_6H_5 main-group π interaction and, second, the only known example of such an interaction contributing to the formation of a dimer from the constituent monomers.

The two phenyl rings that appear overlayed in the center of the cell in Figure 2 in fact occupy front and back regions and are separated by more than 12 Å.

The phosphorus atoms in the dithiophosphate ester ligands are found at the center of a distorted tetrahedral system with two oxygen atoms and two sulfur atoms, one of the latter double bonded. As we have found in other dithiophosphate ester derivatives of tin(IV),[25,26] the angles involving the more electronegative oxygen atoms are, as expected on the basis of isovalent hybridization arguments, smaller than those involving the sulfur atoms. We find that in both the chelating and bridging ligands $\angle$S–P–S > $\angle$S–P–O(mean values) > $\angle$O–P–O.

Of the tin(II) dithiophosphate esters, only the phenoxy derivative is stable to air oxidation. The other analogues we have prepared turn orange on exposure to air, and the surface oxidation to produce an unidentified tin(IV) product, presumably of the $[(RO)_2PS_2]_2SnO$ variety, can be followed by Mössbauer spectroscopy. The structure–reactivity relation that can rationalize the chemical stability of the phenoxy ester derivative must have to do either with additional lattice energy provided by the η^6-C_6H_5 bonding interaction with the tin(II) atom or with the protection of the tin(II) lone pair of electrons by the steric bulk of the phenyl ring, or with both.

Our observation, discussed above, that the magnitude of the QS values remains unchanged in going from the tin(II) dithiophosphate esters to their bipyridyl adducts can now be understood in terms of the structure we have solved. If the coordination number at the tin(II) center is the same in the bipyridyl adduct as in the parent solids from which they are derived, then with the presumption that the bipyridyl donor is itself bidentate, one of the dithiophosphate ester ligands must be monodentate in these adducts to produce the ψ-6 situation. Such a monodentate ligand is found in the structure of triphenyltin(IV) diethyl dithiophosphate.[11] The more reasonable ψ-7 alternative, employing all ligands in a bidentate manner, is known for tin(II) in the structure η^6-$C_6H_6Sn(AlCl_4)_2 \cdot C_6H_6$.[43]

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Registry No. $Sn[S_2P(OCH_3)_2]_2$ (salt form), 80301-45-7; $Sn[S_2P(OCH_3)_2]_2$ (coordination form), 80327-00-0; $Sn[S_2P(OC_2H_5)_2]_2$ (salt form), 80301-46-8; $Sn[S_2P(OC_2H_5)_2]_2$ (coordination form), 80327-01-1; $Sn[S_2P(OC_3H_7\text{-}i)_2]_2$ (salt form), 80301-47-9; $Sn[S_2P(OC_3H_7\text{-}i)_2]_2$ (coordination form), 80327-09-9; $Sn[S_2P(OC_6H_5)_2]_2$ (salt form), 73286-41-6; $Sn[S_2P(OC_6H_5)_2]_2$ (coordination form), 73296-25-0; $Sn[S_2P(OC_3H_7\text{-}i)_2]_2 \cdot C_{10}H_8N_2$, 80327-68-0; $Sn[S_2P(OCH_3)_2]_2 \cdot C_{10}H_8N_2$, 80327-67-9; $Sn[S_2P(OC_2H_5)_2]_2 \cdot C_{10}H_8N_2$, 80327-66-8; $Sn[S_2P(OC_6H_5)_2]_2 \cdot C_{10}H_8N_2$, 80327-69-1.

Supplementary Material Available: Analytical and physical (Table I), infrared (Table IV), and mass spectral data (Table V) for the tin(II) dithiophosphate esters and positional and isotropic thermal parameters for hydrogen atoms (Table IX), anisotropic thermal parameters for nonhydrogen atoms (Table X), carbon–carbon distances (Table XII), intramolecular angles involving only carbon (Table XIV), and a listing of structure factor amplitudes for $Sn[S_2P(OC_6H_5)_2]_2$ (32 pages). Ordering information is given on any current masthead page.

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Oxy and Thio Phosphorus Acid Derivatives of Tin. 11. Synthesis and Properties of Di- and Triorganotin(IV) Derivatives of Phenylphosphonic Acid Phenyl Ester[1]

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Seven di- and triorganotin(IV) phenylphosphonic acid phenyl esters, $R_2Sn[O_2P(C_6H_5)OC_6H_5]_2$, where R = CH_3, n-C_4H_9, n-C_8H_{17}, or C_6H_5, and $R_3SnO_2P(C_6H_5)OC_6H_5$, where R = CH_3, n-C_4H_9, or C_6H_5, are synthesized in quantitative yield by the action of the corresponding organotin(IV) chlorides or acetates upon the free acid in water or methanol, respectively. The products are colorless, insoluble solids. The diorganotin(IV) derivatives are infusible. In the mass spectra no ions having mass greater than the parent or containing more than one tin atom are detected, but parent molecular ions are found in the spectra of the trimethyl- and triphenyltin(IV) derivatives. The ion of highest abundance arises in all the triorganotins from loss of an organo group from the tin, while for the triphenyl derivative the triphenyltin fragment is most abundant. Successive loss of organic groups from tin is seen, and even-electron ions are preferred. The identity of the phenyl groups lost from the ligands in both series is unknown. No monoorganotin fragments are seen in the spectra of the diorganotin(IV) derivatives. Infrared and Raman data in the ν(Sn–C) region are used to assign a linear C–Sn–C configuration and a planar SnC_3 configuration in the di- and trimethyltin(IV) derivatives, respectively. Bands at 1080–1063 and 1000–993 cm^{-1} are also assigned to the ν_{asym}- and $\nu_{sym}(PO_2)$ modes, respectively. Tin-119m Mössbauer isomer shift (IS) values (1.12–1.47 mm s^{-1}) confirm the presence of tetravalent tin; the ρ [ratio of quadrupole splitting (QS) to IS] values (2.73–3.74) and QS values (3.60–4.66 mm s^{-1}) specify higher than four-coordination at tin. The particularly high QS values for the diorganotin(IV) series suggest a six-coordinated, trans-octahedral geometry. Ambient-temperature Mössbauer spectra for this series indicate intermolecular association, while the absence in the triorganotin analogues suggests an oligomeric structure where five units are the minimum for ring formation accommodating trigonal-bipyramidal and –O–P–O–bridges.

Previous reports in this series have described the syntheses of the di-[3] and triorganotin(IV) dithiophosphate[4] and diphenyl phosphate[1] esters. These studies are directed toward developing the basis for more powerful biocidal activity[5] through

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