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Oxy and Thio Phosphorus Acid Derivatives of Tin. 14. X-ray Crystal and Molecular Structure of the Dimeric Bis[bis(*O,O'*-diphenyl thiophosphato)diphenyltin(IV) hydroxide], $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$, at 138 K[1]

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Bis[bis(*O,O'*-diphenyl thiophosphato)diphenyltin(IV) hydroxide], $C_{48}H_{42}O_8P_2S_2Sn$, an intermediate in the hydrolysis of bis(*O,O'*-diphenyl thiophosphato)diphenyltin(IV), forms colorless crystals, mp 128–129 °C, in the monoclinic space group $P2_1/c$ with $a = 10.227$ (3) Å, $b = 14.252$ (5) Å, $c = 18.065$ (6) Å, $\beta = 118.22$ (2)°, $V = 2320.10$ Å^3 at 138 K, $Z = 2$, and $\rho_{calcd} = 1.589$ g cm^{-3}. The structure was solved by the heavy-atom method and refined to an R value of 0.034 for the 4751 reflections collected at 138 ± 2 K on an Enraf-Nonius CAD-4 automatic diffractometer with the use of Mo K$\bar{\alpha}$ radiation. The molecular units associate through double hydroxide bridges to form a centrosymmetric dimer with a planar, central Sn_2O_2 ring whose angles are acute at tin ($\angle$O(1)–Sn–O(1)' = 72.77 (7)°) and open at oxygen ($\angle$Sn–O–Sn = 107.23 (8)°). The sulfur–tin distances (d(Sn–S) = 3.947 (1) Å) are outside the range associated with dative interactions in chelated $P{=}S{\rightarrow}Sn$ systems. Thus the tin atoms are best described as being five-coordinated and lying at the center of a badly distorted trigonal bipyramid. The largest angle, and hence axial connection, is made to the ligand and bridging hydroxide oxygen atoms ($\angle$O(1)'–Sn–O(2) = 159.81 (7)°), while the two phenyl groups ($\angle$C(1)–Sn–C(7) = 132.16 (11)°) and the hydroxy group bonded with the shorter distance (d(Sn–O(1)) = 2.032 (2) Å) occupy the equatorial plane. The sum of the angles in this plane is 358.94°. The phenyl ring planes are twisted by 73.02 (3)° to accommodate themselves above and below the Sn_2O_2 plane. Within each molecular unit the sulfur and hydroxide oxygen atoms are brought together at d(O(1)—H- - -S=P) = 3.121 (2) Å by a hydrogen-bonding interaction.

In previous parts of this series we have reported the synthesis of the diphenyltin(IV) diphenyl phosphate (mp 250 °C) and *O,O'*-diphenyl dithiophosphate, (mp 145.5–146.5 °C) esters, $(C_6H_5)_2Sn[E_2P(OC_6H_5)_2]_2$, where E = O[2] and S.[3] These compounds can be prepared by straightforward condensation reactions, including those that release water, and the products are stable to air and moisture. Data from a battery of spectroscopic techniques suggest six-coordinated, *trans*-diphenyl geometries, and the tin-119m Mössbauer quadrupole splittings (QS) yield calculated angles of 175.2° (QS = 3.24 mm s^{-1}) and 142° (QS = 3.21 mm s^{-1}) for the E = O and S analogues, respectively. We have recently solved the structures of the related dimethyl- and diiodotin(IV) dialkyldithiophosphinates, $R_2Sn[S_2PR'_2]_2$, where R = CH_3 and I and R' = CH_3 and C_2H_5, which takes *trans*-dimethyl- and *cis*-diiodotin octahedral forms, respectively.[4] From our structural studies we have learned that the oxygenated derivatives have a greater propensity for employing the potentially bidentate phosphorus ligand fully, to chelate the central tin atom or to bind the tin atoms into an associated oligomer or polymer. Indeed, we have elucidated cyclic hexameric and helical structures in the E = O derivatives $(C_6H_5)_3SnO_2P(OC_6H_5)_2$[5] and $(CH_3)_3SnO_2P(C_6H_5)OH$,[6] while the E = S derivative, $(C_6H_5)_3SnS_2P(OC_2H_5)_2$, is monodentate with four-coordinated tin atoms.[7] However, the E = S diphenyltin(IV) *O,O'*-diethyl[8] and *O,O'*-diisopropyl dithiophosphate[9] ester derivatives form *trans*-diphenyltin chelated octahedral complexes.

Thus it was of interest to examine the structure of the mixed oxygen–sulfur phosphate ester ligand to test whether typical oxygen or sulfur behavior would predominate in determining the solid-state structure, i.e., whether an associated structure bridged through oxygen atoms or a monodentate or severely anisobidentate structure with weak sulfur to tin coordination would form. However, the crystal of bis[*O,O'*-diphenyl thiophosphato]diphenyltin(IV)[1] chosen for this study was instead an intermediate in its hydrolysis:

$$(C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]_2 + H_2O \rightarrow (C_6H_5)_2Sn[OP(S)(OC_6H_5)_2]OH + HOP(S)(OC_6H_5)_2 \quad (1)$$

The diphenyltin(IV) hydroxide product can be prepared directly by refluxing the parent compound in wet ether. The stability of the doubly bridged, μ-hydroxy structure described in this paper explains why the hydrolysis reaction does not proceed further to form diphenyltin(IV) oxide.

Table I. Crystal Data for $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$

formula	$C_{48}H_{42}O_8P_2S_2Sn_2$
fw	1110.3
cryst syst	monoclinic
a, Å	10.227 (3)[a]
b, Å	14.252 (5)[a]
c, Å	18.065 (6)[a]
β, deg	118.22 (2)[a]
V, Å^3	2320.10
space group[b]	$P2_1/c$
Z	2
$F(000)$	2224
ρ_{calcd}, g cm^{-3}	1.589
μ, cm^{-1}	12.8

[a] Measured at 138 K, estimated standard deviations in parentheses. [b] Based upon systematic absences: $0k0$, $k = 2n + 1$; $h0l$, $l = 2n + 1$.

Experimental Section

Synthesis of Dimeric Bis[bis(*O,O'*-diphenyl thiophosphato)diphenyltin(IV) hydroxide], $[(C_6H_5)_2SnOP(S)(OC_6H_5)_2OH]_2$. To an ether solution (50 mL) of bis(*O,O'*-diphenyl thiophosphato)diphenyltin(IV)[1] (1.65 g, 0.001 mol) was added distilled water (0.04 g, 0.001 mol) and the mixture refluxed for 1 h. The *O,O'*-diphenylthiophosphoric acid was filtered, and excess solvent was removed under reduced pressure, yielding a pale, oily product that was recrystallized from methanol and filtered. The filtrate, after it was cooled overnight, gave the product as colorless crystals (1.0 g, 61%), mp 128–129 °C. Anal. Calcd for $C_{48}H_{42}O_8P_2S_2Sn_2$: C, 51.87; H, 3.78; Sn, 21.38. Found: C, 53.59; H, 3.70; Sn, 21.70.

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(1) For part 13 of this series see: Nasser, F. A. K.; Zuckerman, J. J. *J. Organomet. Chem.* **1983**, *244*, 17.

(2) Molloy, K. C.; Nasser, F. A. K.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 1711.

(3) Lefferts, J. L.; Molloy, K. C.; Zuckerman, J. J.; Haiduc, I.; Curtui, M.; Guta, C.; Ruse, D. *Inorg. Chem.* **1980**, *19*, 2861.

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

(5) Molloy, K. C.; Nasser, F. A. K.; Barnes, C. L.; van der Helm, D.; Zuckerman, J. J. *Inorg. Chem.* **1982**, *21*, 960.

(6) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Cunningham, D.; Zuckerman, J. J. *Inorg. Chem.* **1981**, *20*, 2402.

(7) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Haiduc, I. *Inorg. Chem.* **1979**, *18*, 3507.

(8) Lieblich, B. W.; Tomassini, M. *Acta Crystallogr., Sect. B* **1978**, *B34*, 944.

(9) Molloy, K. C.; Hossain, M. B.; van der Helm, D.; Zuckerman, J. J.; Haiduc, I. *Inorg. Chem.* **1980**, *19*, 2041.

0020-1669/83/1322-3107$01.50/0

Table II. Data Collection Parameters for $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$

diffractometer	Enraf-Nonius CAD-4
radiation	Mo K$\bar{\alpha}$ ($\lambda = 0.71069$ Å)
temp, K	138 ± 2
scan technique	θ–2θ
2θ limit, deg	$0 < 2\theta < 53$
max scan time, s	60
scan angle, deg	$0.7 + 0.2 \tan \theta$
aperture width, mm	$3.0 + 0.86 \tan \theta$
aperture height, mm	6
aperture dist, mm	173
monitor reflectn	3
orientation monitors	200 reflctns[a]
no. of unique data	4751
no. of obsd data[b]	4068
corrections	Lorentz-polarization, anomalous dispersion

[a] New orientation matrix if angular change >0.1°; orientation matrix based upon 16 reflections. [b] $I > 2\sigma(I)$.

Crystal Data. Colorless crystals of the title compound were obtained by slow evaporation of a methanol solution. A crystal of dimensions 0.38 × 0.138 × 0.15 mm was used for the determination of the cell parameters and subsequent data collection.

The space group was determined by diffractometry studies to be monoclinic, $P2_1/c$. The cell dimensions were determined by least squares from the $+2\theta$ and -2θ values of 48 reflections spaced throughout reciprocal space and measured at 138 K. All measurements were performed on an Enraf-Nonius CAD-4 automatic counter diffractometer controlled by a PDP 8/e computer and fitted with a low-temperature device. Crystal data are listed in Table I.

Collection and Reduction of Intensity Data. The intensities of all reflections with $2\theta \leq 53°$ were measured at 138 ± 2 K with use of θ–2θ scan techniques with variable scan rates using monochromatized Mo Kα radiation. For each reflection, two-thirds of the scan time was spent scanning the peak (P) and one-sixth of the time scanning the right and left backgrounds (LB and RB). The unscaled intensity was calculated as $I = [P - 2(\mathrm{LB} + \mathrm{RB})]$. These were then scaled according to their scan rate.

The intensities of three standard reflections were measured every 7200 s of X-ray exposure. In all, 4751 independent reflections were measured, 683 of which were considered indistinguishable from the background ($I < 2\sigma(I)$) and were assigned an intensity equal to $1.4T^{1/2}$, where $T = [P + 2(\mathrm{LB} + \mathrm{RB})]$. Intensities were corrected for Lorentz and polarization effects, but no absorption corrections were applied (the ratio of the maximum and minimum transmission factors was 1.4).

The structure factors for each reflection were assigned a weight given by $w_F = 1/\sigma_F^2$, where σ_F was obtained from counting statistics.

Specific parameters pertaining to the collection of the data set are summarized in Table II.

Structure Determination and Refinement. The positions of the tin atoms were determined from a three-dimensional Patterson map. The parameters of the tin atom were refined, and a difference Fourier map was calculated by using the heavy-atom phases. From the difference map all non-hydrogen atoms were easily located. These atoms were first refined with isotropic and then with anisotropic thermal parameters to an R factor of 0.032 by using a block-diagonal least-squares program.[10] A difference Fourier map calculated at this stage revealed all hydrogen atom positions. Hydrogen parameters were refined isotropically. Anomalous dispersion effects for the Sn, S, and P atoms were taken into account. Refinement was discontinued when the maximum parameter shift for non-hydrogen atoms was less than one-third of the corresponding standard deviation. The final R factor is 0.022 for the 4018 reflections that were included in the least-squares calculations and 0.034 for all 4751 reflections.

Table III. Final Positional Parameters (×10⁴) for $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$[a]

atom	x	y	z
Sn	291.7 (2)	975.5 (1)	603.1 (1)
S	4022 (1)	−301 (1)	2147.0 (4)
P	3111 (1)	611 (1)	2562.1 (4)
O(1)	775 (2)	−416 (1)	684 (1)
O(2)	1636 (2)	1029 (1)	1946 (1)
O(3)	4140 (2)	1500 (1)	2998 (1)
O(4)	2921 (2)	243 (1)	3345 (1)
C(1)	1578 (3)	1946 (2)	338 (2)
C(2)	1429 (3)	2020 (2)	−474 (2)
C(3)	2170 (3)	2727 (2)	−658 (2)
C(4)	3057 (3)	3360 (2)	−49 (2)
C(5)	3245 (3)	3262 (2)	759 (2)
C(6)	2515 (3)	2578 (2)	958 (2)
C(7)	−1755 (3)	1099 (2)	598 (2)
C(8)	−2042 (3)	565 (2)	1145 (2)
C(9)	−3432 (4)	612 (3)	1117 (2)
C(10)	−4519 (3)	1192 (3)	537 (2)
C(11)	−4253 (4)	1695 (3)	−27 (2)
C(12)	−2874 (3)	1653 (2)	−2 (2)
C(13)	5696 (3)	1409 (2)	3437 (2)
C(14)	6500 (3)	1838 (2)	3096 (2)
C(15)	8028 (3)	1776 (3)	3526 (2)
C(16)	8742 (3)	1296 (2)	4283 (2)
C(17)	7917 (3)	878 (2)	4617 (2)
C(18)	6372 (3)	940 (2)	4194 (2)
C(19)	1816 (3)	−419 (2)	3213 (2)
C(20)	519 (4)	−109 (2)	3178 (2)
C(21)	−576 (4)	−765 (3)	3064 (2)
C(22)	−320 (5)	−1714 (3)	2986 (2)
C(23)	988 (7)	−1999 (3)	3042 (3)
C(24)	2110 (5)	−1361 (2)	3170 (2)

[a] Estimated standard deviations in parentheses.

Table IV. Intramolecular Distances (Å) in $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$[a]

	Sn-Heteroatom Distances		
Sn–O(1)	2.032 (2)	Sn–C(1)	2.113 (3)
Sn–O(1)′[b]	2.198 (2)	Sn–C(7)	2.096 (3)
Sn–O(2)	2.151 (2)		
	Other Distances		
P–S	1.944 (1)	O(3)–C(13)	1.409 (3)
P–O(2)	1.511 (2)	O(4)–C(19)	1.402 (4)
P–O(3)	1.596 (2)	C–C in the Ph rings (av)	1.388 (5)
P–O(4)	1.604 (2)		

[a] Estimated standard deviations in parentheses. [b] Primed atom is related by a center of symmetry at (0, 0, 0).

Table V. Intramolecular Angles (deg) in $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$[a]

Sn–O(1)–Sn′[b]	107.23 (8)	O(1)–Sn–C(7)	106.88 (9)
O(1)–Sn–O(1)′[b]	72.77 (7)	C(1)–Sn–C(7)	132.16 (11)
O(1)′–Sn–O(2)	159.81 (7)	Sn–O(2)–P	134.38 (12)
O(1)′–Sn–C(1)	92.78 (1)	S–P–O(2)	118.27 (9)
O(1)′–Sn–C(7)	91.76 (1)	S–P–O(3)	113.35 (8)
O(2)–Sn–O(1)	87.13 (7)	S–P–O(4)	113.66 (9)
O(2)–Sn–C(1)	95.63 (9)	O(2)–P–O(3)	104.22 (11)
O(2)–Sn–C(7)	96.09 (9)	O(2)–P–O(4)	106.46 (11)
O(1)–Sn–C(1)	119.90 (9)	O(3)–P–O(4)	98.70 (11)

[a] Estimated standard deviations in parentheses. [b] Primed atoms are related by a center of symmetry at (0, 0, 0).

In all least-squares refinements the quantity $\sum w_F(|KF_o| - |F_c|)^2$ was minimized. The scattering factors for Sn, P, S, and C atoms and $\Delta f'$ and $\Delta f''$ for the Sn, S, and P atoms were taken from ref 11 and those for the hydrogen atoms from ref 12. An analysis of the function of $w_F(K|F_o| - |F_c|)^2$ vs. $|F_o|$ and $\sin^2 \theta$ showed no significant variation of the average values of $\sum w_F \Delta F^2$ for various ranges of F_o and $\sin^2 \theta$, demonstrating the validity of the weighting scheme used.

The final atomic positional parameters are listed in Table III. The atomic numbering schemes followed in these listings are identified

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(10) Ahmed, F. R. "SFLS Program", Report NCR-10; National Research Council: Ottawa, Canada, 1966.

(11) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, pp 72, 149.

(12) Stewart, R. F.; Davidson, E. R.; Simpson, W. J. *J. Chem. Phys.* **1965**, *42*, 3175.

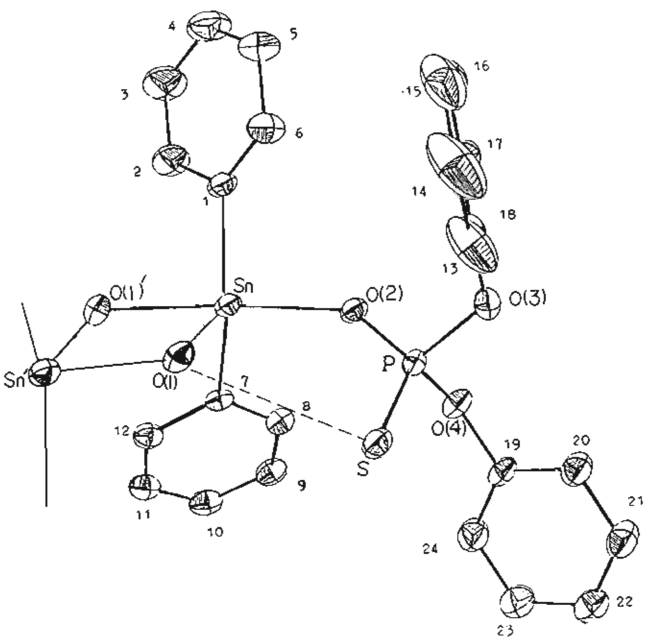


Figure 1. Asymmetric unit of $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$ plus the Sn′–O(1)′ atoms showing the atomic numbering.

Table VI. Shortest Intramolecular Nonbonding Distances (Å) in $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$[a]

Sn–Sn′[b]	3.4068 (2)	O(1)–O(1)′	2.513 (3)
Sn–S	3.947 (1)	S–O(1)	3.121 (2)[c]
Sn–P	3.385 (1)		

[a] Estimated standard deviations in parentheses. [b] Primed atoms are related by a center of symmetry at (0, 0, 0). [c] Hydrogen bond.

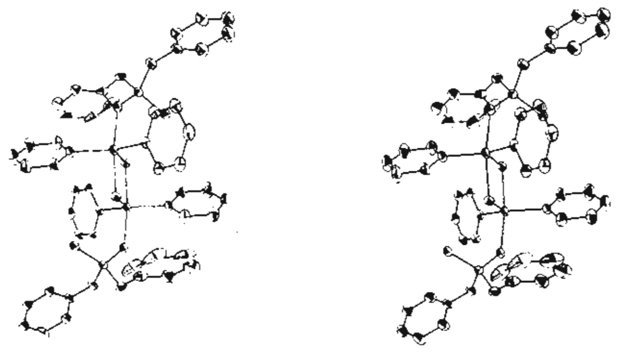


Figure 2. Stereoscopic view of the dimer $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$.

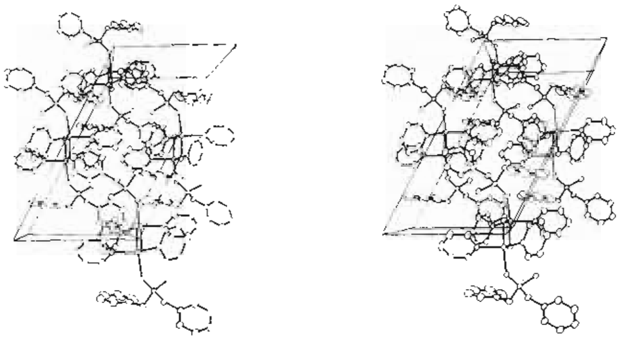
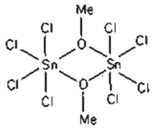
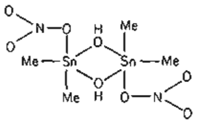
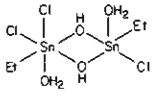
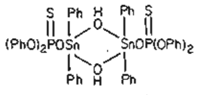


Figure 3. Stereoview of the packing diagram of $[HO(C_6H_5)_2SnOP(S)(OC_6H_5)_2]_2$.

in Figure 1. Figure 2 shows a stereoview of the dimer. Intramolecular distances calculated from the final parameters are given in Table IV. Table V lists the intramolecular angles, and Table VI lists the shortest nonbonding distances in the asymmetric unit. A comparison of molecular structure data for hydroxy-bridged Sn_2O_2 systems is given in Table VII, and P–S and S–Sn distances in related structures are compared in Table VIII. Thermal parameters are listed in Table IX, C–C distances and C–C–C angles in the phenyl rings in Tables X and XI, respectively, and least-squares planes in Table XII. Hydrogen parameters are found in Table XIII (Tables IX–XIII are

Table VII. Comparison Molecular Structure Data for Hydroxy-Bridged Sn_2O_2 Systems

compd	CN at tin	d(Sn---Sn), Å	d(Sn–O), Å	d(Sn–O), Å	∠Sn–O–Sn, deg	∠O–Sn–O, deg	d(OH---OH), Å
	6[a]	3.300	1.8	2.0			
	5[b]	3.44	2.06	2.18	108.6	71.4	
	6[c]	3.438	2.067	2.153	109.1	70.9	2.45
$[Sn_2Cl_6(OH)_2(H_2O)_2]\cdot nL$	6[d]						
(i) $nL = 3C_4H_8O_2$		3.358	2.056	2.086	108.3	71.7	
(ii) $nL = 4C_{10}H_{18}O$		3.318	2.044	2.042	108.6	71.4	
(iii) $nL = 4C_{10}H_{18}O$ (X = Br)		3.348	2.028	2.076	108.3	71.7	
(iv) $nL = 4H_2O$ (X = Cl)		3.368	2.077	2.078	108.3	71.7	
$(SnCl_3OH\text{-}H_2O)_2\cdot 3C_4H_8O_2$	6[e]	...	2.04	2.10	110.8	69.2	
$[SnCl_3(OC_2H_5)\cdot C_2H_5OH]_2$	6[f]	3.390	2.08 2.11	2.18	108.1	71.9	
$[h^5\text{-}C_5H_5Fe(CO)_2Sn(C_6H_5)(O_2SC_6H_5)OH]_2$	5[g]	3.49	2.054	2.206	109.2	70.8	
	5[h]	3.4068 (2)[i]	2.032 (2)	2.198 (2)	107.23 (8)	72.77 (7)	2.513 (3)

[a] Reference 14. [b] Reference 17. [c] Reference 19. [d] Reference 20. [e] Reference 16. [f] Reference 18. [g] Reference 15. [h] This work. [i] Estimated standard deviations in parentheses.

Table VIII. Phosphorus-Sulfur and Sulfur-Tin Internuclear Distances (Å) in Dithiophosphate Derivatives and the Title Compound

compd	ester[a] P-S-Sn	dative[a] P=S→Sn	ref
	Bonded		
$[(C_6H_5O)_2PS_2]_2Sn^{II}$[b]	2.0016, 2.623	1.967, 2.830	24
$[(C_2H_5O)_2PS_2]_2Sn(C_6H_5)_2$[c]	2.04, 2.48	1.92, 3.20	8
	2.03, 2.49	1.94, 3.23	
$[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_5)_2$[c]	2.006, 2.678	1.998, 2.689	9
$[(CH_3)_2PS_2]_2Sn(CH_3)_2$[c]	2.047, 2.482	1.969, 3.334	4
$[(C_2H_5)_2PS_2]_2SnI_2$[d]	2.043, 2.537	2.026, 2.621	4
	2.044, 2.533	2.032, 2.593	
	Nonbonded[a]		
$(C_2H_5O)_2PS_2Sn(C_6H_5)_3$[e]	2.054, 2.4582	1.931, 5.326	7
$[(C_6H_5O)_2PO(S)Sn(C_6H_5)_2OH]_2$[f]		1.944 (1), 3.947 (1)	*f*

[a] The first number listed in each case is the P-S distance, and the second is the S-Sn distance. [b] Distorted ψ-6 octahedron. [c] *trans*-Diorganotin groups. [d] *cis*-Diiodotin configuration. [e] A rare example of a monodentate dithiophosphate ligand system. [f] This work.

deposited as supplementary material).

Description and Discussion of the Structure

Dimeric bis[bis(*O,O'*-diphenyl thiophosphato)diphenyltin(IV) hydroxide] crystallizes in a centrosymmetric unit with a planar, central Sn_2O_2 ring formed by double μ-hydroxy bridges. The sulfur atoms of the ligand do not coordinate to the tin atoms, which are thus five-coordinated in a badly distorted trigonal bipyramid in which the monodentate ligand oxygen atom and one of the bridging hydroxy groups make the largest angle (∠O(1)–Sn–O(2) = 159.81 (7)°) and can thus be identified as the axial connections. The two phenyl groups then as expected occupy the equatorial plane with the hydroxide group bonded with the shorter distance. The angles in this plane sum to 358.94 (6)°. The hydroxide bonded with the shortest distance makes a hydrogen bond with the sulfur of the ligand in the same molecular unit at 3.121 (2) Å.

The synthesis of the parent bis-ligand tin derivative from which the hemihydrolysis title product is derived proceeds from the triethylammonium salt of the acid $[HN(C_2H_5)_3]^+[OP(S)(OC_6H_5)_2]^-$, and the structure shown in Figure 1 confirms that the tin atom is connected to the oxygen atom in the P–O–Sn system and not to the sulfur atom through a rearrangement of the salt or the bis-ligand tin compound in the course of the preparation or the hydrolysis.

The Sn_2O_2 ring, the center of which lies on a crystallographic center of symmetry, is formed with acute angles at the tin atoms (∠O(1)–Sn–O(1)′ = 72.77 (7)°) and open angles at the bridging hydroxide oxygen atoms (∠Sn–O–Sn′ = 107.23 (8)°). As a consequence the two tin atoms are separated by 3.4068 (2) Å across the parallelogram with the hydroxide oxygen atoms brought closer at 2.513 (3) Å. The phenyl rings are connected approximately perpendicularly, with the plane containing the C(1), C(7), and O(1) atoms forming an angle of 88.93 (1)° with the Sn_2O_2 ring plane. The planes of the phenyl rings themselves are twisted by 73.02 (3)° with respect to each other above and below the Sn_2O_2 ring to minimize steric interference.

Inorganic tin(IV) is found in several dimeric structures of the general formula $[Cl_3SnOR{\cdot}ROH]_2$, which are formed by the action of alcohols with the tetrachloride. The common feature of these systems is a facial-octahedral arrangement of ligand atoms in the Cl_3SnO_3 polyhedron. The dimers studied thus far are centrosymmetric with tin–tin distances of ca. 3.4 Å across the Sn_2O_2 rings.[13] Comparison data for the nine structures related to ours[14-20] are gathered in Table VII, but only two of these, the $[\eta^5\text{-}C_5H_5Fe(CO)_2Sn(C_6H_5)(O_2SC_6H_5)OH]_2$ and $[(CH_3)_2Sn(NO_3)OH]_2$ dimers, contain five-coordinated tin atoms like those in the title compound. The centrosymmetric Sn_2O_2 ring in the latter is formed by unidentate nitrate groups to give a very distorted trigonal-bipyramidal geometry at tin with the two methyl groups (∠C–Sn–C = 139.9°) and the hydroxy group held by the shorter bond in the equatorial plane,[17] just as in the title compound. The former carbonyliron derivative also forms a centrosymmetric Sn_2O_2 ring with axial oxygen bonds and the phenyl group in the equatorial plane.[15]

So far as we are aware, the only structural data available for the $-O-(S)P(OR)_2$ system acting as a ligand to a metal atom[21] contains a tetrakis(pyridine)magnesium center[22] to which further bonding by a chelating or bridging sulfur atom would be impossible. The nonbonded Mg- - -S═P distance is 7.209 Å. In addition, there are two examples of dithiophosphate ligands which are neither chelating nor bridging. One is the tetragonal-pyramidal adduct of $Ni[S_2P(OCH_3)_2]_2$ with 2,9-dimethyl-1,10-phenanthroline,[23] and the other is (*O,O'*-diethyl dithiophosphato)triphenyltin(IV), in which the nonbonding tin–sulfur distance is 5.326 Å.[7] The sulfur–nickel distance in the former is 5.502 Å,[23] while in the title compound the sulfur is 3.947 (1) Å from the tin atom. Data for six dithiophosphate derivatives of tin(II)[24] and tin(IV),[4,7-9] all but one[7] chelated, are compared to those for the title compound in Table VIII. In the situations in which the dithiophosphate ligand is clearly chelating, the sulfur–tin coordinate bonds (the longer of the two such bonds) range from 2.621[4] to 3.334 Å.[4] Our distance is longer than this by 0.6 Å but shorter than the obviously nonbonded sulfur–tin distance of 5.326 Å in the monodentate $(C_6H_5)_3SnS_2P(OC_2H_5)_2$.[7]

In principle, another test of whether the sulfur atom is coordinated is based upon a comparison of the P═S distances; the stronger the dative interaction with a metal atom, the longer the P═S distance should be. The ester P-S-Sn and dative P═S→Sn distances in Table VIII are easily distinguished, but the apparently uncoordinated P═S distance of 1.944 (1) Å in our compound is not particularly short compared with 1.931 Å in the unidentate $(C_6H_5)_3SnS_2P(OC_2H_5)_2$ or in the metal-free compounds $[S_2P(OC_3H_7\text{-}i)_2]_2$ (1.908 Å)[25]

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(13) Zubieta, J. A.; Zuckerman, J. J. *Prog. Inorg. Chem.* **1978**, *24*, 251. Smith, P. J. *J. Organomet. Chem. Libr.* **1981**, *12*, 98.
(14) Sterr, G.; Mattes, R. *Z. Anorg. Allg. Chem.* **1963**, *322*, 319.
(15) Restivo, R.; Bryan, R. F. *J. Chem. Soc. A* **1971**, 3364.
(16) Bokii, N. G.; Struchkov, Yu. T. *J. Struct. Chem. (Engl. Transl.)* **1971**, *12*, 277.
(17) Domingos, A. M.; Sheldrick, G. M. *J. Chem. Soc., Dalton Trans.* **1974**, 475.
(18) Webster, M.; Collins, P. H. *Inorg. Chim. Acta* **1974**, *9*, 157.
(19) Lecomte, C.; Protas, J. *Acta Crystallogr., Sect. B* **1976**, *B32*, 923.
(20) Barnes, J. C.; Sampson, H. A.; Weakley, T. J. R. *J. Chem. Soc., Dalton Trans.* **1980**, 949.
(21) Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch.* **1973**, *35*, 65.
(22) Schwalbe, C. H.; Goody, R.; Saenger, W. *Acta Crystallogr., Sect. B* **1973**, *B29*, 2264.
(23) Shetty, P. S.; Fernando, Q. *J. Am. Chem. Soc.* **1970**, *92*, 3964.
(24) Lefferts, J. L.; Hossain, M. B.; Molloy, K. C.; van der Helm, D.; Zuckerman, J. J. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 309; *Inorg. Chem.* **1982**, *21*, 1410.
(25) Lawton, S. L. *Inorg. Chem.* **1970**, *9*, 2269.

or $S(CH_2)_2SP(S)Cl$ (1.910 Å).[26] A particularly short P═S distance of 1.923 Å is found in bis(*O,O'*-dimethyl dithiophosphato) tellurium(II), in which the sulfur bonds to the tellurium atoms at 3.31 Å.[27] In another group of organic structures containing the metal-free $(RO)_3P{=}S$ system, the free P═S group distances range from 1.89 to 2.00 Å.[28-35] Thus the *d*(P═S) data cannot be used to decide whether the sulfur is coordinated to tin.

An additional test to decide the coordination number at tin involves examining the expected approach vector of the sulfur atom to the tin center. From Figures 1 and 2 it can be seen that a sulfur-tin dative bond would approach the O(1)′-O(1)-O(2) plane from the side on which the C(7) atom is attached. But neither ∠O(1)-Sn-O(2) nor ∠O(2)-Sn-C(7) is significantly opened, nor do the connected atoms seem particularly displaced away from the expected point of contact of the sulfur vector with the tin atom.

Because of these facts, and especially the length that the expected dative bond would be required to span for sulfur-tin coordination, we regard the tin atom in the title compound as five-coordinated (see below).

Substituting the more electronegative oxygen for sulfur in the dithiophosphate ester ligand should withdraw electron density along the O—P═S-->Sn system and weaken the coordinating ability of the P-S unit toward tin, probably accounting for the monodentate nature of the ligand in the title compound. The chelated form is probably also somewhat less favored because of the increased resistance to valence angle distortion arising from the smaller tin-oxygen internuclear distance. Thus chelation in the dithiophosphate ligands generally gives way to bridging in the completely oxygenated series.

Finally, the magnitude of the tin-119m Mössbauer quadrupole splitting (QS = 2.98 ± 0.06 mm s^{-1})[1] cannot be used to distinguish among higher coordination numbers at the tin atom since it is related to the carbon-tin-carbon angle predominantly, and there is no rule available linking this angle to coordination number in the diphenyltin(IV)series. However, models are available that link the magnitude of the QS to this angle.[36-38] Using the measured QS value yields a prediction of 134.2° for the ∠C(1)-Sn-C(7), which is measured to be 132.16 (11)°.

Of the three tin-oxygen distances, the axial one to the bridging hydroxy group of the second molecular unit is longest, with *d*(Sn-O(1)′) = 2.198 (2) Å. The second axial connection, to the ligand, *d*(Sn-O(2)) = 2.151 (2) Å, is intermediate in length. The equatorial hydroxide belonging to the same molecular unit is held closest, with *d*(Sn-O(1)) = 2.032 (2) Å. The distance to the ligand oxygen is much shorter than those listed in Table VIII for the tin-sulfur esters, P-S-Sn, which lie in the 2.46-2.68-Å range.

The phosphorus atom is found at the center of a distorted tetrahedron in which the angles involving sulfur are all larger than 109°28′ while those involving only oxygen are all smaller, in accord with the expectations of the principle of isovalent hybridization.

Examination of the orientation of the ligand reveals that it is rotated so as to bring the sulfur atom into juxtaposition with the hydroxide group in the same molecular unit to which it makes a hydrogen bond of *d*(O(1)-H---S) = 3.121 (2) Å, *d*(O-H) = 0.83 (4) Å, *d*(S---H) = 2.32 (4) Å, and ∠O(1)-H---S) = 164 (4)°. Hydrogen bonds of the O-H---S variety are relativey rare,[39-41] but of the 22 examples whose structures are known,[40] the average length is 3.31 Å.[39] We are intrigued by the question of why the ligand is not rotated to the opposite side of the molecule, where it can hydrogen bond with the incoming *μ*-OH group and contribute to holding the dimer together. Presumably, the longer distance required or the unfavorable orientation of the proton would make too weak a bond. Hydrogen bonding helps to rationalize why the sulfur atom does not coordinate to the tin atom instead, raising the coordination number of tin to 6, and also why the hydrolysis reaction stops at the intermediate stage instead of proceeding to give diphenyltin(IV) oxide.

Related to this is the observation of the large angle at O(2) (∠Sn-O(2)-P = 134.38 (12)°, whose magnitude may prevent the sulfur atom from coordinating to the tin, even if the ligand were rotated to the opposite side of the molecule. Alternatively, this angle may be forced open to allow the formation of the hydrogen bond P═S---H—O.

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Registry No. $[(C_6H_5)_2SnOP(S)(OC_6H_5)_2OH]_2$, 85919-35-3; bis(*O,O'*-diphenyl thiophosphato)diphenyltin(IV), 85913-92-4.

Supplementary Material Available: Listings of observed and calculated structure amplitudes, thermal parameters (Table IX), carbon-carbon distances and carbon-carbon-carbon angles in the phenyl rings (Tables X and XI, respectively), least-squares planes (Table XII), and hydrogen positional and thermal parameters (Table XIII) (23 pages). Ordering information is given on any current masthead page.

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(26) Lee, J. D.; Goodacre, G. W. *Acta Crystallogr., Sect. B* **1971**, *B27*, 1055.

(27) Husebye, S. *Acta Chem. Scand.* **1966**, *20*, 24.

(28) Andersen, P.; Hjortaas, K. E. *Acta Chem. Scand.* **1960**, *14*, 829.

(29) Bally, R. *Acta Crystallogr., Sect. B* **1970**, *B26*, 477.

(30) Saenger, W.; Eckstein, F. *J. Am. Chem. Soc.* **1970**, *92*, 4712.

(31) Saenger, W.; Suck, D.; Eckstein, F. *Eur. J. Biochem.* **1974**, *46*, 559.

(32) Grand, A.; Robert, J. B. *Acta Crystallogr., Sect. B* **1975**, *B31*, 2502.

(33) Baughman, R. G.; Jacobson, R. A. *J. Agric. Food Chem.* **1976**, *24*, 1036.

(34) Clardy, J. C.; Milbrath, D. S.; Verkade, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 631.

(35) Baughman, R. G.; Jorgensen, S. K.; Jacobson, R. A. *J. Agric. Food Chem.* **1978**, *26*, 576.

(36) Bancroft, G. M.; Kumar Das, V. G.; Sham, T. K.; Clark, M. G. *J. Chem. Soc., Dalton Trans.* **1976**, 643.

(37) Sham, T. K.; Bancroft, G. M. *Inorg. Chem.* **1975**, *14*, 2281.

(38) Clark, M. G.; Maddock, A. G.; Platt, R. H. *J. Chem. Soc., Dalton Trans.* **1972**, 281.

(39) Pimentel, G. C.; McClellan, A. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 2532.

(40) Kuleshova, L. N.; Zorkii, P. M. *Acta Crystallogr., Sect. B* **1981**, *B37*, 1363.

(41) Srinivasan, R.; Chacko, K. K. In "Conformation of Biopolymers"; Ramachandran, G. N., Ed.; Academic Press: New York, 1967; Vol. 2, p 607.