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Oxy and Thio Phosphorus Acid Derivatives of Tin. 6. Crystal and Molecular Structures of Bis(dimethyldithiophosphinato)dimethyltin(IV) and Bis(diethyldithiophosphinato)diiodotin(IV) at 138 K[1]

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Bis(dimethyldithiophosphinato)dimethyltin(IV), $C_6H_{18}P_2S_4Sn$, forms colorless crystals, mp 215–217 °C, in the orthorhombic space group $C222_1$ with $a = 6.218$ (2) Å, $b = 11.001$ (4) Å, $c = 22.347$ (20) Å, $V = 1528.6$ Å^3, $Z = 4$, and $\rho_{calcd} = 1.73$ g cm^{-3}. The structure was solved by three-dimensional Patterson and difference Fourier techniques from 914 reflections measured at 138 ± 2 K on an Enraf-Nonius CAD/4 automatic diffractometer using monochromated Mo K$\bar{\alpha}$ radiation to a final R value of 0.028 for the 786 reflections included in the least-squares sums. The molecule is six-coordinated in a distorted octahedral geometry with the four sulfur atoms of the anisobidentate chelating dithiophosphinato ligands lying in a plane with the central tin atom while the dimethyltin system makes a trans C–Sn–C angle of 122.6 (8)° (127.5° predicted from the tin-119m Mössbauer quadrupole splitting value of 3.00 mm s^{-1}). The ester (shorter) and dative (longer) pairs of Sn–S bonds are found on opposite sides of the girdle of the molecule, cis oriented. The tin atoms stack in a linear array along the a axis at a distance of 6.218 (2) Å, well within the bridging range of a dithiophosphinate ligand. Bis(diethyldithiophosphinato)diiodotin(IV), $C_8H_{20}I_2P_2S_4Sn$, forms red crystals, mp 174–176 °C, in the monoclinic space group $P2_1/a$ with $a = 14.817$ (4) Å, $b = 11.223$ (3) Å, $c = 13.170$ (5) Å, $\beta = 115.53$ (3)°, $V = 1976.2$ Å^3, and $\rho_{calcd} = 2.28$ g cm^{-3}. The structure was solved by three-dimensional Patterson and difference Fourier techniques from 4073 reflections measured at 138 ± 2 K on the above automatic diffractometer using monochromated Mo K$\bar{\alpha}$ radiation to a final R value of 0.058 for the 3746 reflections included in the least-squares sums. The molecule is octahedral at tin with *cis*-diiodotin system. Opposite each tin–iodine bond lies a longer Sn–S dative bond, while the sulfur atoms of the ester system are in a trans arrangement in contrast to the cis orientation of the corresponding atoms in the structure of the first title compound. The phosphorus atoms in the dithiophosphinate ligands are found at the center of a distorted tetrahedral system in both structures.

A series of diorgano- and dihalotin(IV) dithiophosphinates was prepared by us (F.P.M.), who brought to bear tin-119m Mössbauer, electric dipole moment, and infrared data on the question of the geometry about tin in these complexes.[2] Comparison with the analogous and better known dithiocarbamatotin(IV) complexes led to the view that the tin atom adopts a distorted octahedral geometry in the title compounds. The very large electric dipole moments in the dihalo derivatives require anisobidentate phosphinate ligand chelation and a cis arrangement of both the halogen atoms as well as the Sn←S dative bonds. Similarly, the dipole moments of the diorganotin derivatives, $R_2Sn[S_2PR'_2]_2$, were interpreted as demanding nonequivalent Sn–S bonds in a cis arrangement of Sn–S ester and Sn←S dative bonds with trans diorganotin groups. The difference in the infrared ν_{as}(P–S) and ν_s(P–S) stretching frequencies was used to infer the presence of nonequivalent P–S and, therefore, nonequivalent Sn–S bonds in these complexes. Tin-119m Mössbauer isomer shift (IS) and quadrupole splitting (QS) values for the diorganotin dithiophosphinates are similar to those for the analogous *trans*-diorganotin(IV) dithiophosphato, $S_2P(OR')_2$, and dithiocarbamato, $S_2CNR'_2$, complexes, suggesting a similar anisobidentate character in the chelating ligands and consequent distortion from 180° in the C–Sn–C bond angle, as is seen in, for example, $(CH_3)_2Sn[S_2CN(CH_3)_2]_2$.[3] The QS values for the dimethyltin derivatives of the dithiophosphinato, phosphato, and carbamato ligands are 3.00,[2] 3.35,[4] and 3.14[5] or 3.04,[6] respectively. The Mössbauer data for the dihalo complexes (IS = ca. 0.90 mm s^{-1}; QS = 0.0 mm s^{-1}) are consistent with a six-coordinated geometry at tin with cis halogen atoms.

Specific physical and spectroscopic properties for the title compounds are listed in Table I. The compounds were prepared from the reaction of the sodium salt of the dithiophosphinic acid and a diorganotin dihalide or tin(IV) halide in a 2:1 ratio.

$$(CH_3)_2SnCl_2 + 2(CH_3)_2PS_2Na \rightarrow (CH_3)_2Sn[S_2P(CH_3)_2]_2 + 2NaCl \quad (1)$$

$$SnI_4 + 2(C_2H_5)_2PS_2Na \rightarrow I_2Sn[S_2P(C_2H_5)_2]_2 + 2NaI \quad (2)$$

Pursuing our interest in the structural chemistry[7] of biocidal organotin compounds,[8] and in particular the derivatives of thio and oxy phosphorus acid,[1,4,9-11] we have investigated representatives of the diorgano- and dihalodithiophosphinatotin(IV) complexes to test whether the predicted geometries[2] would in fact be found.

Experimental Section

Crystal Data. Data were obtained at 138 ± 2 K with an Enraf-Nonius CAD-4 automatic counter diffractometer controlled by a PDP-8/e computer and fitted with a low-temperature apparatus. Crystal data are listed in Table II.

Details of our diffractometer and methods of data collection and data reduction have been outlined previously.[1] Specific parameters pertaining to the collection of the two data sets are summarized in Table III. For both compounds, the structure factors for each reflection were assigned individual weights.[1]

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Table I. Physical and Spectroscopic Data for the Two Title Compounds[2]

compd	color	mp, °C	ν_{as}(P-S), cm^{-1}	ν_s(P-S), cm^{-1}	QS,[a] mm/s	μ_{eff}, μ_B
$(CH_3)_2Sn[S_2P(CH_3)_2]_2$	colorless	215-217	601, 593	484	3.00	3.53
$I_2Sn[S_2P(C_2H_5)_2]_2$	red	174-176	581, 569	503, 484	0.00[b]	8.1

[a] ±0.06 mm s^{-1}. [b] The width at half-height, Γ, is 0.93 mm/s.

Table II. Crystal Data for the Two Title Compounds

	$(CH_3)_2Sn-[S_2P(CH_3)_2]_2$	$I_2Sn[S_2P-(C_2H_5)_2]_2$
formula	$C_6H_{18}P_2S_4Sn$	$C_8H_{20}I_2P_2S_4Sn$
fw	399.11	678.97
crystal system	orthorhombic	monoclinic
a, Å	6.218 (2)	14.817 (4)
b, Å	11.001 (4)	11.223 (3)
c, Å	22.347 (20)	13.170 (5)
β, deg[a]	90	115.53 (3)
V, Å^3	1528.6	1976.2
space group	$C222_1$[b]	$P2_1/a$[c]
Z	4	4
F(000)	792	1272
ρ_{calcd}, g cm^{-3}	1.73	2.28
μ, cm^{-1}	23.8	50.0
dimens of data crystal, mm	0.25 × 0.25 × 0.10	0.15 × 0.30 × 0.35

[a] From ±2θ values of 48 reflections with use of Mo K$\bar{\alpha}_1$ radiation (λ = 0.709 26 Å). [b] Based upon systematic absences: hkl, $h + k = 2n + 1$; $00l$, $l = 2n + 1$. [c] Based upon systematic absences: $h0l$, $h = 2n + 1$; $0k0$, $k = 2n + 1$.

Table III. Data Collection Parameters for $(CH_3)_2Sn[S_2P(CH_3)_2]_2$ and $I_2Sn[S_2P(C_2H_5)_2]_2$

	$(CH_3)_2Sn[S_2P(CH_3)_2]_2$	$I_2Sn[S_2P(C_2H_5)_2]_2$
diffractometer	Enraf-Nonius CAD/4	Enraf-Nonius CAD/4
radiation	Mo K$\bar{\alpha}$ (λ = 0.7121 Å)	Mo K$\bar{\alpha}$ (λ = 0.7121 Å)
temp, K	138 ± 2	138 ± 2
scan technique	θ-2θ	θ-2θ
2θ limit, deg	$0 \leq 2\theta \leq 53$	$1 \leq 2\theta \leq 53$
scan time, s	50	50
scan angle	0.8 + 0.2 tan θ	0.8 + 0.2 tan θ
aperture width	3.5 + 0.86 tan θ	3.0 + 0.86 tan θ
aperture height, mm	6	6
aperture dist, mm	173	173
monitor reflctn	314	$\bar{4}08$
intens monitor, s	3600	2500
max fluctuation in monitor	<2.5%	<3.5%
orientation monitors	200 reflections[a]	200 reflections[b]
no. of unique data	914	4073
no. of obsd data[c]	805	3816
cor	Lorentz-polarization anomalous dispersion	Lorentz-polarization, abs, anomalous dispersion

[a] New orientation matrix if angular change greater than 0.1°. Orientation matrix based upon 17 reflections. [b] New orientation matrix if angular change greater than 0.1°. Orientation matrix based upon 15 reflections. [c] $I > 2\sigma(I)$.

Table IV. Final Positional (×10^4) Parameters for $(CH_3)_2Sn[S_2P(CH_3)_2]_2$[a]

atom	*x*	*y*	*z*
Sn(1)	249.3 (8)	0 (0)	0 (0)
P(1)	1664 (3)	13 (10)	1506 (1)
S(1)	3310 (3)	16 (10)	713 (1)
S(2)	−1484 (3)	12 (11)	1412 (1)
C(1)	2689 (14)	1280 (9)	1912 (4)
C(2)	2660 (16)	−1306 (9)	1923 (4)
C(3)	−1397 (12)	1698 (7)	48 (20)

[a] Estimated standard deviations in parentheses.

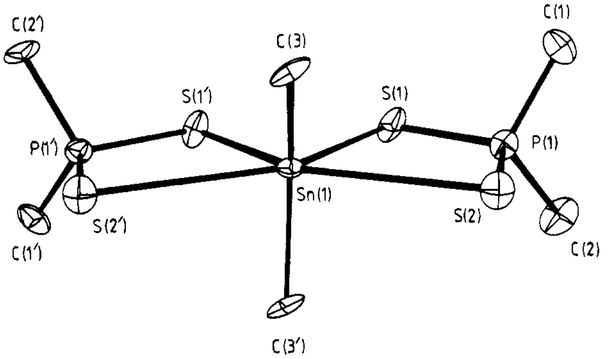

Figure 1. Asymmetric unit of bis(dimethyldithiophosphinato)dimethyltin(IV) showing the atomic labeling. Primed atoms are related to the corresponding unprimed atoms by a 2-fold axis passing through the tin atom and lying along the *a* axis of the unit cell.

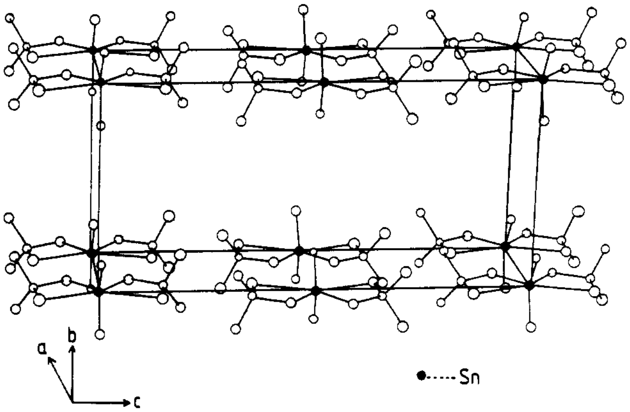

Figure 2. Unit cell contents of bis(dimethyldithiophosphinato)dimethyltin(IV).

Structure Determination and Refinement. Bis(dimethyldithiophosphinato)dimethyltin(IV), $(CH_3)_2Sn[S_2P(CH_3)_2]_2$. From an inspection of the three-dimensional Patterson map, the tin atom was found to occupy the special position *x*, 0, 0 (that is, lying on a 2-fold axis). The Patterson map was interpreted to yield the positions of all the remaining nonhydrogen atoms. Following three cycles of least-squares isotropic refinement,[12] the atomic thermal parameters were allowed to vary anisotropically and refinement continued for a further four cycles. At this point anomalous dispersion corrections for tin, phosphorus, and sulfur were included, and anisotropic refinement was continued for six additional cycles to give a final *R* value of 0.028 for the 786 reflections included in the least-squares sums and 0.037 over all data.

A final difference Fourier indicated some residual electron density (ca. 1 e/Å^3) in the vicinity of the tin atom and several smaller peaks (ca. 0.5 e/Å^3), corresponding to the probable positions of hydrogen atoms, although no systematic attempt was made to locate the latter.

An attempt to determine the polarity of the space group proved inconclusive. The *R* values for the two polarities (differing in the sign of *z*, U_{23}, and U_{13}) are identical, and corresponding bond lengths and angles differ by no more than one standard deviation. This may

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(12) Ahmed, F. R., SFLS Program NRC-10, National Research Council, Ottawa, Canada, 1966.

Table V. Final Anisotropic Thermal Parameters[a] (×10^4) for $(CH_3)_2Sn[S_2P(CH_3)_2]_2$[b]

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	108 (4)	129 (4)	192 (4)	−16 (4)	16 (26)	2 (21)
P(1)	147 (8)	205 (9)	218 (8)	40 (40)	3 (6)	24 (47)
S(1)	150 (8)	380 (12)	235 (8)	−91 (30)	−7 (6)	122 (34)
S(2)	135 (8)	412 (10)	299 (8)	28 (56)	2 (6)	−55 (60)
C(1)	197 (44)	321 (48)	281 (43)	41 (39)	18 (37)	−101 (38)
C(2)	302 (52)	267 (46)	415 (51)	167 (42)	−23 (44)	143 (41)
C(3)	171 (31)	180 (34)	336 (121)	59 (26)	4 (70)	191 (99)

[a] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] Estimated standard deviations in parentheses.

Table VI. Final Intramolecular Distances (Å) in $(CH_3)_2Sn[S_2P(CH_3)_2]_2$[a]

P(1)-S(1)	2.047 (2)	Sn(1)-S(1)	2.482 (2)
P(1)-S(2)	1.969 (2)	Sn(1)-S(2)	3.334 (2)
P(1)-C(1)	1.781 (13)	Sn(1)-C(1)	2.132 (8)
P(1)-C(2)	1.832 (13)		

[a] Estimated standard deviations in parentheses.

Table VII. Final Intramolecular Angles (Deg) in $(CH_3)_2Sn[S_2P(CH_3)_2]_2$[a]

S(1)-Sn(1)-S(2)	68.9 (1)	S(1)-P(1)-S(2)	113.8 (3)
S(1)-Sn(1)-S(2′)	148.8 (1)	S(1)-P(1)-C(1)	105.1 (4)
S(1)-Sn(1)-S(1′)	79.9 (2)	S(1)-P(1)-C(2)	105.8 (4)
S(1)-Sn(1)-C(3)	109.2 (5)	S(2)-P(1)-C(1)	114.2 (4)
S(1)-Sn(1)-C(3′)	114.0 (5)	S(2)-P(1)-C(2)	113.0 (4)
S(2)-Sn(1)-S(2′)	142.3 (1)	C(1)-P(1)-C(2)	103.9 (5)
S(2)-Sn(1)-C(3)	78.1 (5)		
S(2)-Sn(1)-C(3′)	84.0 (5)	Sn(1)-S(1)-P(1)	99.9 (2)
C(3)-Sn(1)-C(3′)	122.6 (8)	Sn(1)-S(2)-P(1)	77.3 (2)

[a] Estimated standard deviations in parentheses.

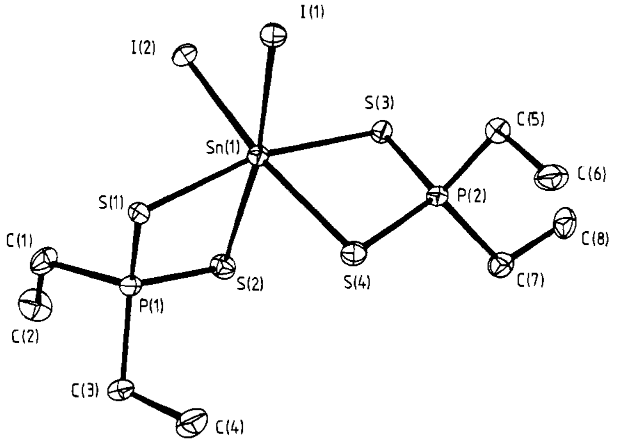

Figure 3. Molecular structure of bis(diethyldithiophosphinato)diiodotin(IV) showing the atomic labeling.

Table VIII. Final Positional Parameters (×10^4) for $I_2Sn[S_2P(C_2H_5)_2]_2$[a]

atom	*x*	*y*	*z*
Sn(1)	2700.4 (3)	−194.4 (5)	2514.3 (4)
I(1)	3499.4 (4)	1821.2 (5)	1928.4 (4)
I(2)	790.8 (3)	834.2 (5)	1708.5 (4)
P(1)	2600 (2)	−851 (2)	4805 (2)
P(2)	3575 (2)	−1949 (2)	1268 (2)
S(1)	3379 (2)	520 (2)	4536 (2)
S(2)	2157 (2)	−1942 (2)	3450 (2)
S(3)	2134 (1)	−1358 (2)	695 (2)
S(4)	4320 (2)	−1366 (2)	2879 (2)
C(1)	1528 (6)	−264 (8)	4956 (7)
C(2)	932 (7)	−1249 (8)	5206 (9)
C(3)	3391 (6)	−1633 (8)	6099 (7)
C(4)	3644 (7)	−848 (9)	7131 (7)
C(5)	3652 (6)	−3564 (8)	1213 (7)
C(6)	3195 (8)	−4210 (9)	1902 (9)
C(7)	4095 (6)	−1371 (8)	342 (7)
C(8)	5188 (6)	−1717 (9)	713 (9)

[a] Estimated standard deviations in parentheses.

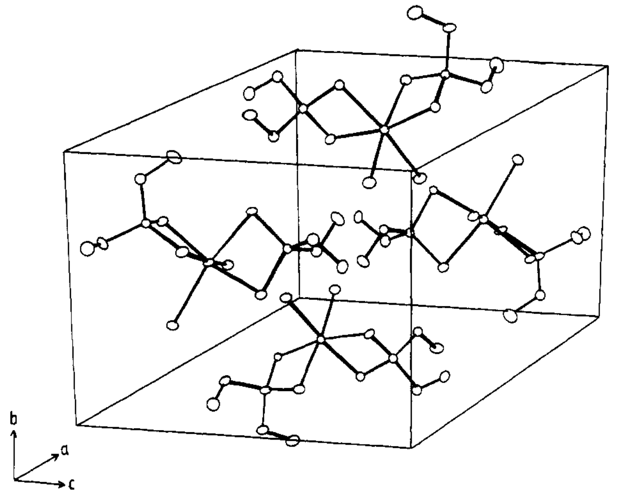

Figure 4. Unit cell contents of bis(diethyldithiophosphinato)diiodotin(IV).

be accounted for by the general centrosymmetric nature of the molecule.

Final atomic parameters (positional and thermal) are given in Tables IV and V; final interatomic distances and angles are given in Tables VI and VII, respectively. The asymmetric unit (with atom numbering scheme) is shown in Figure 1, and the arrangement of molecules within the unit cell in Figure 2.

Bis(diethyldithiophosphinato)diiodotin(IV), $I_2Sn[S_2P(C_2H_5)_2]_2$. The positions of the three heavy atoms [Sn(1), I(1), I(2)] were located from a three-dimensional Patterson map and were used to phase the initial structure factor calculations. Sequential refinement[12] followed by difference Fourier syntheses was used to locate the positions of the nonhydrogen light atoms. All atoms were refined first isotropically and then anisotropically to an *R* factor of 0.060 for the 3742 reflections included in the least-squares sums. Since a difference Fourier synthesis indicated areas of electron density remaining about the tin, iodine, sulfur, and phosphorus atoms, an anomalous dispersion correction was made for each of these atom types. Anisotropic least-squares refinement was continued to a final *R* factor of 0.058 for the 3746 reflections included in the least-squares sums and 0.064 over all data.

A final difference Fourier synthesis still contained large areas of electron density (ca. 2.5 e/Å^3) in the proximity of the three heavy atoms. No attempt was made to locate hydrogen atoms.

Final positional and thermal atomic parameters and intermolecular distances and angles are given in Tables VIII, IX, X and XI, respectively. The asymmetric unit (with atom numbering) and unit cell contents are shown in Figures 3 and 4, respectively.

The scattering factors used in both determinations were for neutral atoms and were taken from ref 13 (Sn, C, P, S, and I) and 14 (H).

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

Table IX. Final Anisotropic Thermal Parameters[a] (×10⁴) for $I_2Sn[S_2P(C_2H_5)_2]^b$

atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	158 (2)	107 (3)	140 (2)	−2 (2)	64 (2)	−6 (2)
I(1)	216 (3)	155 (3)	228 (3)	−24 (2)	95 (2)	32 (2)
I(2)	157 (2)	166 (3)	215 (2)	11 (2)	63 (2)	−2 (2)
P(1)	209 (9)	144 (11)	165 (10)	6 (8)	88 (8)	0 (8)
P(2)	170 (9)	144 (10)	177 (9)	12 (8)	75 (8)	4 (8)
S(1)	245 (9)	156 (10)	180 (9)	−45 (8)	80 (8)	−13 (8)
S(2)	292 (10)	157 (10)	220 (10)	−49 (8)	130 (8)	−28 (8)
S(3)	170 (8)	174 (10)	182 (9)	10 (8)	67 (7)	−22 (8)
S(4)	193 (9)	193 (11)	203 (9)	19 (8)	51 (8)	−11 (9)
C(1)	266 (40)	182 (43)	220 (41)	37 (33)	145 (34)	24 (35)
C(2)	344 (48)	170 (45)	508 (60)	59 (38)	305 (46)	89 (44)
C(3)	243 (40)	205 (44)	178 (39)	25 (34)	75 (33)	26 (35)
C(4)	296 (43)	277 (52)	147 (38)	7 (36)	83 (34)	17 (36)
C(5)	254 (40)	151 (42)	233 (41)	22 (33)	114 (34)	31 (35)
C(6)	457 (57)	227 (53)	412 (58)	21 (43)	242 (49)	96 (46)
C(7)	219 (38)	227 (47)	273 (44)	−10 (33)	139 (35)	75 (38)
C(8)	201 (40)	320 (54)	389 (53)	−18 (36)	171 (40)	−10 (44)

[a] Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$. [b] Estimated standard deviations in parentheses.

Table X. Final Intramolecular Distances (Å) in $I_2Sn[S_2P(C_2H_5)_2]_2^a$

Sn(1)–I(1)	2.8110 (8)	Sn(1)–S(2)	2.621 (2)
Sn(1)–I(2)	2.8065 (7)	Sn(1)–S(3)	2.533 (2)
Sn(1)–S(1)	2.537 (2)	Sn(1)–S(4)	2.593 (2)
P(1)–S(1)	2.043 (3)	P(2)–S(3)	2.044 (3)
P(1)–S(2)	2.026 (3)	P(2)–S(4)	2.032 (3)
P(1)–C(1)	1.808 (10)	P(2)–C(5)	1.820 (9)
P(1)–C(3)	1.824 (9)	P(2)–C(7)	1.820 (10)
C(1)–C(2)	1.538 (14)	C(5)–C(6)	1.529 (15)
C(3)–C(4)	1.524 (13)	C(7)–C(8)	1.526 (13)

[a] Estimated standard deviations in parentheses.

Table XI. Final Intramolecular Angles (Deg) in $I_2Sn[S_2P(C_2H_5)_2]_2^a$

I(1)–Sn(1)–I(2)	92.32 (2)	I(2)–Sn(1)–S(4)	168.60 (6)
I(1)–Sn(1)–S(1)	93.60 (5)	S(1)–Sn(1)–S(2)	78.83 (7)
I(1)–Sn(1)–S(2)	169.23 (6)	S(1)–Sn(1)–S(3)	167.30 (7)
I(1)–Sn(1)–S(3)	99.34 (5)	S(1)–Sn(1)–S(4)	92.82 (7)
I(1)–Sn(1)–S(4)	89.62 (5)	S(2)–Sn(1)–S(3)	90.87 (7)
I(2)–Sn(1)–S(1)	98.39 (5)	S(2)–Sn(1)–S(4)	88.89 (7)
I(2)–Sn(1)–S(2)	91.24 (5)	S(3)–Sn(1)–S(4)	79.44 (7)
I(2)–Sn(1)–S(3)	89.16 (5)		
Sn(1)–S(1)–P(1)	86.89 (10)	S(2)–P(1)–C(1)	110.48 (32)
Sn(1)–S(2)–P(1)	85.00 (10)	S(2)–P(1)–C(3)	111.47 (32)
S(1)–P(1)–S(1)	107.20 (14)	C(1)–P(1)–C(3)	108.27 (43)
S(1)–P(1)–C(1)	109.47 (32)	P(1)–C(1)–C(2)	112.05 (66)
S(1)–P(1)–C(3)	109.93 (31)	P(1)–C(3)–C(4)	111.55 (64)
Sn(1)–S(3)–P(2)	87.17 (10)	S(4)–P(2)–C(5)	110.30 (32)
Sn(1)–S(4)–P(2)	85.81 (10)	S(4)–P(2)–C(7)	112.85 (33)
S(3)–P(2)–S(4)	106.96 (13)	C(5)–P(2)–C(7)	106.05 (43)
S(3)–P(2)–C(5)	112.48 (32)	P(2)–C(5)–C(6)	113.41 (69)
S(3)–P(2)–C(7)	108.29 (32)	P(2)–C(7)–C(8)	113.10 (68)

[a] Estimated standard deviations in parentheses.

Table XII. Phosphorus–Sulfur and Sulfur–Tin Internuclear Distances (Å) in Dithiophosphate Ester Derivatives and the Title Compounds

compd	ester[a] P–S–Sn		dative[a] P–S→Sn		ref
$[(C_6H_5O)_2PS_2]_2Sn^{II\,b}$	2.0016	2.6230	1.9670	2.8300	9
$(C_2H_5O)_2PS_2Sn(C_6H_5)_3^c$	2.054	2.4582	1.931	5.326	10
$[(C_2H_5O)_2PS]_2Sn(C_6H_5)_2^d$	2.04	2.48	1.92	3.20	18
	2.03	2.49	1.94	3.23	
$[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_5)_2^d$	2.006	2.678	1.998	2.689	1
$[(CH_3)_2PS_2]_2Sn(CH_3)_2^d$	2.047	2.482	1.969	3.334	*e*
$[(C_2H_5)_2PS_2]_2SnI_2^f$	2.043	2.537	2.026	2.621	*e*
	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] Distorted ψ-6 octahedron. [c] This compound is a rare example of a monodentate dithiophosphate ligand system. [d] *trans*-Diorganotin groups. [e] This work. [f] *cis*-Diiodotin configuration.

Description and Discussion of the Structures

The predictions on the basis of previous physical and spectroscopic data[2] are entirely borne out in the structures of the title compounds. Both are six-coordinated, distorted octahedral in geometry[15] with chelating anisobidentate phosphinato ligands. The diorganotin derivative shown in Figure 1 has *trans*-dimethyl groups while the diiodo analogue in Figure 3 has a *cis*-SnI_2. The respective molecules in their unit cells are shown in Figures 2 and 4.

Understanding these and related chelated structures involves first an analysis to determine the identity of the sulfur atoms, that is, whether belonging to the covalently bound ester system, >P(=S)—S—Sn, or to the datively bound >P(—S)=S→Sn system. In the analogous dithiophosphate ester derivatives of the metals, it has been noted that the more tightly the sulfur atom is bound to the metal atom, then the longer is its bond with phosphorus.[17] Put the other way around, the shorter bonds to phosphorus can be written in each case as P=S and are associated with the longer, coordinate covalent sulfur–tin interaction. These shorter, P=S distances are found for the dithiophosphate ester complexes to lie in the range 1.85–1.95 Å, with the corresponding single-bonded, P–S distances at 1.99–2.19 Å.[17] Direct comparison can be made to three recent molecular structure determinations of dithiophosphate ester derivatives of tin(II)[9] and di-[1] and triphenyltin(IV)[10] from this laboratory, plus another from the literature.[18] The internuclear distances in the ester P–S–Sn and dative P=S→Sn linkages are listed in Table XII. Except for bis(*O,O'*-diisopropyl dithiophosphato)diphenyltin(IV), $[(i\text{-}C_3H_7O)_2PS_2]_2Sn(C_6H_5)_2$, which contains symmetrically che-

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

(15) The geometry of the *trans*-dimethyltin bis(dimethylphosphinate) derivative can alternatively be described as skew-trapezoidal bipyramidal, a description generally less favored.[16]

(16) Kepert, D. L. *Prog. Inorg. Chem.* **1977**, *23*, 1.

(17) Wasson, J. R.; Woltermann, G. M.; Stoklosa, H. J. *Fortschr. Chem. Forsch.* **1973**, *35*, 65.

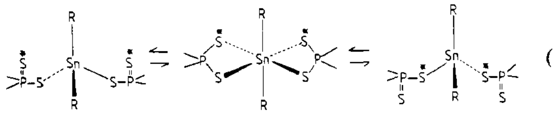
(18) Lieblich, B. W.; Tomassini, M. *Acta Crystallogr., Sect. B* **1978**, *B34*, 944.

lating ligands and must, therefore, involve extensive electron delocalization within the -S$\overline{\cdot\cdot}$P$\overline{\cdot\cdot}$S system, it is easy to distinguish the ester from the dative portion of these chelating ligands.

Comparison of the tin–sulfur interatomic distances in the dimethyltin derivative with the analogous chelated systems listed in Table XII, reveals that the dative S→Sn bonds in the title compound are the longest, while the covalent S–Sn bonds are the shortest [excluding $(C_2H_5O)_2PS_2Sn(C_6H_5)_3$ in which the dithiophosphato ligand is monodentate]. In addition, the short ester S–Sn bond is associated with a contiguous P–S bond which is the longest observed, again with the exception of the monodentate $(C_2H_5O)_2PS_2Sn(C_6H_5)_3$. The distances found for the P–S and S–Sn bonds do not seem to be affected by the change of substituent at the phosphorus atom from the alkoxy and phenoxy groups of the dithiophosphates to the aliphatic methyl and ethyl residues of the title compounds. The P═S bond in the monodentate $(C_2H_5O)_2PS_2Sn(C_6H_5)_3$ is shorter than in the title compounds since the dative S–Sn bond is longer, or nonexistent, but the P═S bond in the more closely related octahedral $(C_2H_5O)_2PS_2Sn(C_6H_5)_2$ is also shorter, while the dative S→Sn bond in the latter is shorter than in our dimethyltin derivative as well.

In the severely anisobidentate bis(*O,O′*-diethyl dithiophosphato)diphenyltin(IV), $[(C_2H_5O)_2PS_2]_2Sn(C_6H_5)_2$, the ester and dative pairs of S–Sn bonds are found on opposite sides of the girdle of the molecule, cis oriented.[18] This is also the case for the title compound, bis(dimethyldithiophosphinato)dimethyltin(IV), $[(CH_3)_2PS_2]_2Sn(CH_3)_2$. The geometry at the tin atom can be described as a badly distorted tetrahedron in which the C–Sn–C angle made by the dimethyltin system has opened to 122.6 (8)°, while the angle at tin between the two ester-bound sulfur atoms [S(1)–Sn(1)–S(1′)] has closed to 79.2 (2)°. The compound is, however, unambiguously six-coordinated, with the four sulfur atoms about the central tin atom around the girdle of the molecule lying in a plane defined by the equation $-11.001y + 0.110z = 0.000$. The maximum deviation from the plane is ±0.009 Å for the S(1) and S(1′) atoms. The sum of the four relevant S–Sn–S angles [S(1)–Sn(1)–S(2) = S(1′)–Sn(1)–S(2′) = 68.9 (1)°; S(1)–Sn(1)–S(1′) = 79.9 (2)°; S(2)–Sn(1)–S(2′) = 142.3 (1)°] is 360.0°.

Alternatively, it is possible to think of the structure as a frozen intermediate in the intramolecular exchange reaction which would scramble the tin–sulfur linkages[19] (eq 3). Our structural studies thus far conducted on dithiophosphatotin systems have elucidated a four-coordinated, monodentate starting material,[10] the diorganotin(IV) title complex, on its way toward the exchange depicted in eq 3 and the symmetrical system lying almost precisely between starting material and product in the complex bis(*O,O′*-diisopropyl dithiophosphato)diphenyltin(IV).[1] The usual nomenclature of kinetics is confusing for this process. Equilibrations of the kind depicted in eq 3 would retain configuration. If one S* enters as one S leaves the tin atom coordination sphere, then the reaction would be considered an S_N2 rearrangement. However, since both S and S* belong to the same molecule, first-order kinetics would be followed, and in this sense the reaction is S_N1. The process reflected in the structure of the title compounds is the simultaneous addition of two ligand atoms, S*, to a tetrahedral R_2SnS_2 molecule to give the octahedral intermediate for a disubstitution reaction. Dunitz has termed this double addition–elimination an S_N3 reaction,[19] but since both S* atoms belong to the same molecule, first-order kinetics would again be followed. Sommer discussed long ago the mechanisms and intermediates in reactions of organosilyl derivatives which lead to retention of configuration in terms of front-side attack.[20]



(3)

The Mössbauer QS value measured for the dimethyltin derivative is 3.00 mm/s.[2] A simple point charge model can be used to rationalize the changes in the magnitude of the QS values as a function of the C–Sn–C angle in six-coordinated, $(CH_3)_2Sn(IV)$ structures.[21] According to this treatment, the splitting is generated by the $(CH_3)_2Sn(IV)$ unit only, the contribution of the other ligands being negligible, and it is assumed that there will be no sign inversion over the range of sysems compared. Nevertheless, the relationship

$$|QS| = 4\{CH_3\}[1 - 3\sin^2\theta\cos^2\theta]^{1/2} \tag{4}$$

where $\{CH_3\}$ is $(^1/_2)e^2Q[CH_3]$, the partial QS, taken as −1.03 mm/s, and the angle C–Sn–C is $(180 - 2\theta)°$,[21] is supported by abundant structural data for six-coordinated, dimethyltin(IV) compounds.[7] The QS value of 3.00 mm/s for our dimethyltin(IV) derivative gives a C–Sn–C angle of 127.5° vs. the angle of 122.6 (8)° observed. We consider this result as further support for the concept of using QS values to predict structure in the diorganotin(IV) systems.

The diiodotin(IV) derivative, being cis oriented, is a special case and must be discussed separately. Here the question of which type of S–Sn bond is found trans to the Sn–I linkage is of interest. As can be seen in Figure 3, in each it is a long, dative S→Sn bond [Sn(1)–S(2) = 2.621 (2); Sn(1)–S(4) = 2.593 (2) Å] that is so located. The arrangement of atoms about the tin atom describes a distorted octahedron in which the cis angle I(1)–Sn(1)–I(2) is 93.32 (2)°, and the angle at the tin atom between the sulfur atoms of the ester system, S(1)–Sn(1)–S(3), is 167.30 (7)°, describing a trans arrangement in contrast to the cis orientation of the corresponding atoms in the dimethyltin derivative. The mean trans angle is 168.38°, and the mean cis angle is 90.38°. Clearly, this structure represents a position further along the pathway of the sulfur atom scrambling reaction analogous to eq 3 than in the dimethyltin case, but now involving a cis oriented intermediate.

The phosphorus atoms in the dithiophosphinate ligands are found at the center of a distorted tetrahedral system in each case with two carbon and two sulfur atom nearest neighbors, one of the latter double bonded. In the analogous dithiophosphate ligand, the angles involving the more electronegative oxygen atoms are, as expected on the basis of isovalent hybridization, smaller than those involving the double-bonded P═S sulfur atoms.[1,10] In the dimethyltin dithiophosphinate case, the relative magnitudes of the angles at phosphorus are S–P–S > C–P–S > C–P–C, except for the S(2)–P(1)–C(1) angle which is greatest. In the diiodo case it is S–P–C > S–P–S ≈ C–P–C. Hence, in the dimethyltin case, sulfur is behaving in a weakly electronegative fashion, that is, less electronegative than carbon. Thus it is perhaps not surprising that the dative bonds it forms to tin are relatively long. Identifying the relative electronegativities of carbon and sulfur in the diiodotin case is less straightforward, but it appears from the similarity in the S–P–S and C–P–C angles that the electronegativities are approximately equal. This is reflected in rather similar dative and covalent S–Sn bond lengths (Table

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[19] Britton, D.; Dunitz, J. D., private communication, 1980.

[20] Sommer, L. H. "Stereochemistry, Mechanism and Silicon"; McGraw-Hill: New York, 1965.

[21] Sham, T. K.; Bancroft, G. M. *Inorg. Chem.* **1975**, *14*, 2281.

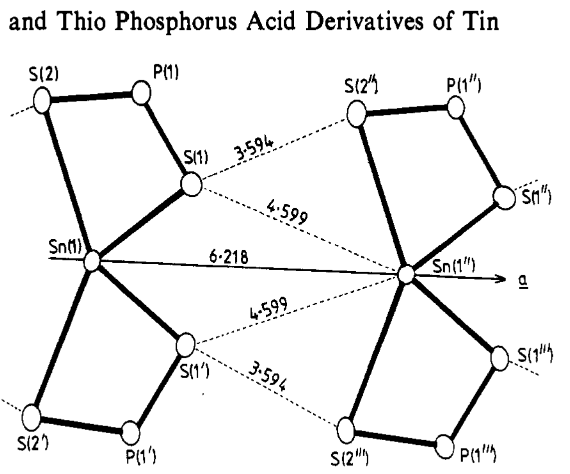

Figure 5. View of the close packing of molecules along the *a* axis, showing the closest intermolecular distances (methyl groups have been omitted for clarity). Singly primed atoms are related to unprimed atoms by the 2-fold axis along *a*. Doubly primed atoms are related to unprimed atoms by a translation of 100; the same translation relates singly and triply primed atoms.

XII), arising from a relatively strong coordinate S→Sn interaction.

In bis(dimethyldithiophosphinato)dimethyltin(IV), the molecules stack along the *a* axis. Figure 2 shows the arrangement of the molecules in the unit cell which produces a linear tin–tin array with an intermetallic distance of 6.218 (2) Å along the *a* axis. Figure 5 shows the dithiophosphinate ligand systems about two adjacent tin atoms along this axis, with the shortest intermolecualr contacts (excluding carbon). The shortest intermolecular sulfur–sulfur contact [S(1)–S(2'') and S(1')–S(2''')] is 3.594 Å which occurs above and below the tin–tin axis of propogation. The van der Waals radius of sulfur has been quoted as 1.73 Å,[22] and thus these intermolecular contact distances can at best only reflect a weak interaction between the sulfur atoms of adjacent molecules.

We have recently noted a similar situation in the corresponding bis(*O*,*O*'-diiospropyl dithiophosphato)diphenyltin(IV) where the tin atoms lie at 6.341 Å intervals along the *c* axis and the sulfur atoms of adjacent molecules are brought within 3.46 Å above and below this axis. In this case, however, the P–Sn–P vector is not normal to the *c* axis, but instead the ligand system is rotated somewhat about the tin atom to bring pairs of sulfur atoms on opposite sides of alternating molecules together at 3.30 Å.[1]

In both cases, however, the relatively short tin–tin intermetallic distances along the axes is within the expected bridging capability for a dithiophosphorus ligand. This means that the four sulfur and two phosphorus atoms that chelate each tin atom in these structures could be rearranged to lie *between* instead of *about* the tin atom, thus linking the diorganotin(IV) units together at an equivalent distance into an isomeric polymer of equal dimensions and density to the assemblage of monomers actually found. In the analogous bis(*O*,*O*'-diisopropyl dithiophosphato)diphenyltin(IV) system referred to above, we termed this structure a virtual polymer. The metal complexes of the parent phosphinates themselves generally adopt bridged structures to give actual polymers,[23,24] and the zinc(II) and cobalt(II) diethyldithiophosphinates are dimers in which there are both terminal chelating and bridging dithiophosphinate ligands. In the zinc(II) solid, however, the metal–metal distance is 4.25 Å (mean) and the S–P–S angle in the bridging ligand opens to 115.7° (mean) compared to the 109.6° (mean) value for the terminal chelating ligands. However, this angle opening is apparently accompanied by a twist in the bridging ligands which has the effect of bringing the zinc atoms closer together.[25]

The realization of the true polymeric isomer of the dimethyltin(IV) title compound must await the discovery of methods capable of directing synthesis and separation toward this end.

We conclude by noting that the unstructured iodine atom substituent with its longer bond to the central tin atom [2.8088 Å mean] can be accommodated in the cis configuration which is preferred in these octahedral, SnX_4B_2 systems, whenever possible,[7] while the structured methyl group which is held closer to the central tin atom [2.132(8) Å] is forced into a less favorable trans configuration.

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Registry No. $(CH_3)_2Sn[S_2P(CH_3)_2]_2$, 72467-26-6; $I_2Sn[S_2P(C_2H_5)_2]_2$, 72476-20-1.

Supplementary Material Available: Listings of structure factor amplitudes for $Me_2Sn[S_2PMe_2]_2$ and $I_2Sn[S_2PEt_2]_2$ (21 pages). Ordering information is given on any current masthead page.

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