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Oxy and Thio Phosphorus Acid Derivatives of Tin. 5. X-ray Crystal and Molecular Structure of Bis(*O*,*O'*-diisopropyl dithiophosphato)diphenyltin(IV), a Monomeric, Molecular, Virtual Polymer

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Bis(*O*,*O'*-diisopropyl dithiophosphato)diphenyltin(IV), $C_{24}H_{38}O_4P_2S_4Sn$, crystallizes in the monoclinic space group $P2_1/n$ with $a = 17.517$ (7) Å, $b = 14.212$ (7) Å, $c = 6.341$ (8) Å, $\beta = 100.63$ (7)°, $V = 1551.6$ Å^3, $Z = 2$, $\rho_{calcd} = 1.497$ g cm^{-3}, and $\mu = 12.17$ cm^{-1}. The structure was determined by the heavy-atom technique from 3195 reflections measured at 138 ± 2 K on an automatic diffractometer using monochromatized Mo Kα radiation and refined to a final R value of 0.052. The tightly packed, centrosymmetric structure consists of *trans*-diphenyltin(IV) units octahedrally coordinated by symmetrically chelating dithiophosphate ester ligands. There are short (3.30 Å) intermolecular sulfur–sulfur contact distances, and the tin atoms, which are related by a unit translation along the c axis, lie at a distance of 6.341 Å, easily within the bridging range of a dithiophosphate ligand. The sulfur and phosphorus atoms that chelate each tin atom in the structure could be shifted by half a cell dimension to lie *between* instead of *about* the tin atoms, thereby linking the *trans*-diphenyltin units together at an equivalent distance into a polymer of equal dimensions and density. The structure has been termed a "virtual polymer".

In the fourth part of this series we described the preparation of a series of diorganotin dithiophosphate esters, $R_2SnSP({=}S)(OR')_2$, where R = CH_3 and C_6H_5 and R' = CH_3, C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9, i-C_4H_9, and C_6H_5, and their characterization by infrared, NMR, and ^{119m}Sn Mössbauer spectroscopies.[1] Such systems are of interest structurally[2] since the dithiophosphate ester ligand can adopt a monodentate configuration, as we have found for (*O*,*O'*-diethyl dithiophosphato)triphenyltin(IV), $(C_6H_5)_3SnSP({=}S)(OC_2H_5)_2$, which is described in part 2 of this series.[3] This configuration is extremely rare.[4] Virtually all other known complexes of these ligands engage the metal in chelating or bridging bidentate behavior.

The title compound, bis(*O*,*O'*-diisopropyl dithiophosphato)diphenyltin(IV), was synthesized by the action of diphenyltin dichloride on the ammonium salt of diisopropyldithiophosphoric acid (eq 1) or by the action of diphenyltin oxide on the free acid (eq 2). The white crystalline product

$$(C_6H_5)_2SnCl_2 + 2NH_4SP({=}S)(OC_3H_7\text{-}i)_2 \xrightarrow{88\%} (C_6H_5)_2Sn[SP({=}S)(OC_3H_7\text{-}i)_2]_2 + 2NH_4Cl \quad (1)$$

$$(C_6H_5)_2SnO + 2HSP({=}S)(OC_3H_7\text{-}i)_2 \xrightarrow{65\%} (C_6H_5)_2Sn[SP({=}S)(OC_3H_7\text{-}i)_2]_2 + H_2O \quad (2)$$

which melts at 108 °C was studied by tin-119m Mössbauer spectroscopy. The isomer shift (IS) (=1.40 ± 0.02 mm/s) and quadrupole splitting (QS) (=3.67 ± 0.04 mm/s) values (ρ = QS/IS = 2.62) specify a higher than four-coordinated situation at the tin atom.[5] The magnitude of the slope of the temperature dependence of the area under the Mössbauer resonance (-1.06×10^{-2} K^{-1}) between 77 and 155 K indicates that the tin atom is firmly held in the lattice,[6-8] more so than in the corresponding bis(*O*,*O'*-diethyl dithiophosphato)diphenyltin(IV), $(C_6H_5)_2Sn[SP({=}S)(OC_2H_5)_2]_2$, whose structure has recently been published. This latter material, which exhibits a slope of -1.92×10^{-2} K^{-1} between 77 and 150 K, exists as monomeric six-coordinated units with tin in a badly distorted octahedral environment with trans phenyl groups and anisobidentate dithiophosphate ligands occupying the remaining four sites. The two short Sn–S distances are cis oriented, which allows an alternative view of the structure as a badly distorted tetrahedron about tin involving the two phenyl groups and the nearest sulfur atoms.[9] However, the rather wide C–Sn–C angle (135°) and acute S–Sn–S angles (69.2 and 84.5°), along with the tin-119m Mössbauer evidence makes this interpretation seem less likely. Finally, a treatment of the Mössbauer and low-energy Raman data based upon the effective vibrating-mass model developed by Herber[10] yields a monomeric molecular weight for both compounds, calculated from the intermolecular, intraunit cell lattice mode observed at 28 and 34 cm^{-1} for the diethyl and diisopropyl derivatives, respectively, in the Raman spectra.

Table I. Crystal Data

formula	$C_{24}H_{38}O_4P_2S_4Sn$	V, Å^3	1551.6
fw	699.49	space group	$P2_1/n$ (systematic absences: $h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$)[a]
cryst system	monoclinic		
a, Å	17.517 (7)		
b, Å	14.212 (7)		
c, Å	6.341 (8)	Z	2
β, deg	100.63 (7)	D_{calcd}, g cm^{-1}	1.497[b]
		μ, cm^{-1}	12.2

[a] Equivalent positions for $P2_1/n$: x, y, z; $-x, -y, -z$; $^1/_2 + x$, $^1/_2 - y$, $^1/_2 + z$; $^1/_2 - x$, $^1/_2 + y$, $^1/_2 - z$. [b] The title compound was found to be soluble in the usual solvents used for measuring density.

We report in this paper the results of a single-crystal X-ray diffraction investigation of the diisopropyl dithiophosphate ester to determine the manner in which this lattice is tightened with respect to its diethyl ester analogue.

Experimental Section

Crystal Data. Colorless needlelike crystals of the title compound suitable for intensity measurements were obtained by slow evaporation of a benzene solution. A crystal of approximate dimensions 0.15 × 0.15 × 0.40 mm was used in the initial diffractometry investigation and subsequent data collection. Data were obtained at 138 ± 2 K

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Table II. Final Positional ($\times 10^4$) Parameters for the Nonhydrogen Atoms in $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$ [a]

atom	*x*	*y*	*z*
Sn(1)	0	0	0
P(1)	1225 (1)	1537 (1)	−1173 (2)
S(1)	1030 (1)	1305 (1)	1789 (2)
S(2)	533 (1)	737 (1)	−3335 (2)
O(1)	2113 (2)	1415 (2)	−1313 (5)
O(2)	1158 (2)	2616 (2)	−1808 (5)
C(1)	−909 (2)	1030 (3)	−331 (7)
C(2)	−1037 (3)	1519 (3)	1478 (8)
C(3)	−1678 (3)	2119 (4)	1341 (9)
C(4)	−2180 (3)	2235 (4)	−608 (9)
C(5)	−2041 (3)	1768 (4)	−2412 (9)
C(6)	−1409 (3)	1168 (3)	−2271 (8)
C(7)	2474 (3)	478 (3)	−881 (7)
C(8)	2769 (3)	197 (4)	−2883 (8)
C(9)	3103 (3)	575 (4)	1093 (9)
C(10)	385 (3)	3064 (3)	−2258 (8)
C(11)	277 (3)	3441 (4)	−4531 (9)
C(12)	369 (4)	3819 (4)	−584 (9)

[a] Estimated standard deviations in parentheses.

with a CAD-4 counter diffractometer (Enraf-Nonius) controlled by a PDP8/e computer and fitted with a low-temperature apparatus. Crystal data are listed in Table I.

Collection and Reduction of Intensity Data. All reflections with $2\theta \leq 53°$ were measured at 138 ± 2 K on the above-mentioned diffractometer using θ–2θ scan techniques with variable scan rates (ν) using graphite-monochromatized Mo Kα radiation. The angular scan width was variable: $(0.70 + 0.35 \tan \theta)°$. An aperture of variable width $(3.50 + 0.86 \tan \theta)$ mm and a constant height (6 mm) was located 173 mm from the crystal. Each reflection was scanned for a maximum of 60 s, of which two-thirds was spent scanning the peak (P), the remaining time being divided equally between the left and right backgrounds (LB and RB, respectively). Scaled intensities (I) were obtained from $I = [P - 2(LB + RB)]/\nu$.

Reflection $(\bar{6}51)$ was used as the standard and its intensity monitored every 30 min. The maximum variation in the standard was ca. 7%, although, for most of the data (80%), the variation was less than 4%. Centering was based upon three reflections monitored every 200 data points; for angular changes larger than 0.15°, a new orientation matrix was automatically determined from a list of 15 reflections. This occurred eight times during total data collection and the maximum angular change was 0.191°. In all, 3195 independent reflections were measured, of which 557 were considered indistinguishable from the background ($I < 2\sigma(I)$) and were assigned an intensity of $T^{1/2}$ where $T = P + 4(LB + RB)$.

Structure factors for each reflection were assigned a weight $w_F = 1/\sigma_{F^2}$, where σ_{F^2} is given by

$$\sigma_{F^2} = \frac{1}{2}\left[\frac{\sigma^2 + (0.04I\nu)^2}{(Lp)(I\nu)}\right] \tag{3}$$

$\sigma = T^{1/2}\nu$ and Lp is the Lorentz and polarization factor. Corrections for absorption were also made.

Structure Determination and Refinement. The position of the tin atom, indicated as lying on a special position from the density calculation, was confirmed by solution of a Patterson map and located on the unit cell origin (0, 0, 0, the crystallographic center of symmetry). The positions of the nonhydrogen, light atoms were located by a succession of difference Fourier syntheses. In subsequent cycles of least-squares refinement, the thermal parameters were allowed to vary isotropically, initially, and anisotropically in later stages, yielding an R factor of 0.054 for all data. At this point, correction was made for the anomalous dispersion of tin and the structure further refined before all nonmethyl hydrogen atoms were located from a final difference Fourier synthesis. Refinement was concluded when shifts in all parameters were less than one-third of their corresponding standard deviation. The final R factor was 0.033 for the 2599 reflections included in the least-squares calculations and 0.052 over all data. A logical routine[12] was used to decide which structure amplitudes to include in the least-squares computations. An amplitude was excluded when one of the following conditions prevailed: $|\Delta F|/|kF_o| < 2$ for $|kF_o| < F_{min}$; $1.5|F_c| < |kF_o|^2$ for $F_{min} < |kF_o| < 2F_{min}$; $1.8|F_c| < |kF_o|$ for $2F_{min} < |kF_o| < 3F_{min}$; $2.0|F_c| < |kF_o|$ for $3F_{min} < |kF_o| < 4F_{min}$; $2.5|F_c| < |kF_o|$ for $4F_{min} < |kF_o|$; $|F_c| - |kF_o| < 12.5$ while $(\sin^2 \theta)/\lambda^2 < 0.012$. The value of F_{min} was set at 5.0, which is close to the amplitudes of the observed reflections with the lowest intensities. Application of the first condition means that unobserved reflections are included only when $|F_c| > 2|kF_o|$, while the last condition excludes reflections which are affected by extinction.

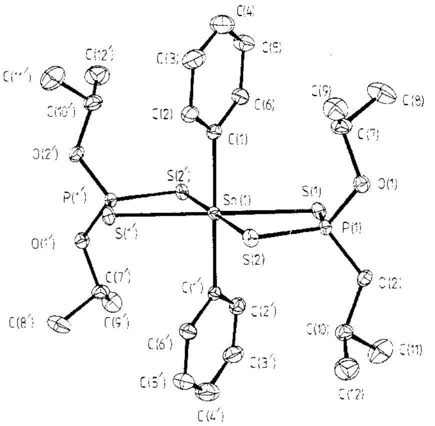

Figure 1. The molecular structure of bis(O,O'-diisopropyl dithiophosphato)diphenyltin(IV) showing the atomic labeling. Primed atoms are related to the corresponding unprimed atoms by an inversion center at Sn(1).

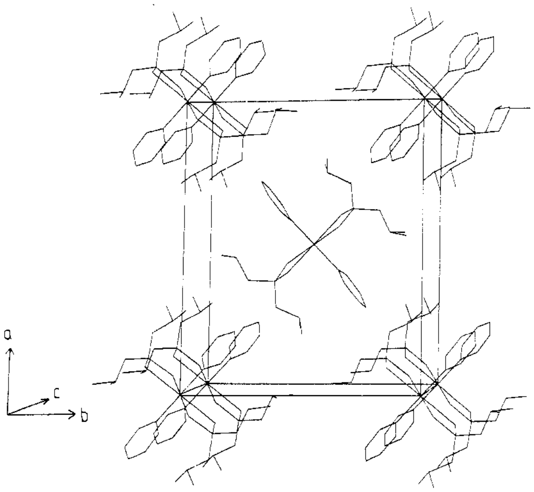

Figure 2. The contents of the unit cell showing the molecular packing.

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

Final positional and thermal parameters for nonhydrogen atoms are listed in Tables II and III, respectively. Standard deviations are calculated from $\Sigma w(\Delta F)_2$ for all 3195 data. The corresponding parameters for the located hydrogen atoms, which are numbered according to the carbon to which they are bonded, are given in Table IV. Final intramolecular distances and angles are listed in Tables V and VI. Figure 1 and 2 show the asymmetric unit, with atomic numbering, and the contents of the unit cell, respectively.

Description and Discussion of the Structure

The title compound exists as a six-coordinated, trans octahedral R_2SnX_4, symmetrical, monomeric species as depicted in Figure 1 and shown packed into the unit cell in Figure 2. The apparent tightening of the lattice in the title compound

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Table III. Final Anisotropic Thermal Parameters[a] (×10^4) for Nonhydrogen Atoms in $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$[b]

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	93 (2)	120 (2)	125 (2)	−2 (2)	23 (1)	4 (2)
P(1)	119 (5)	143 (5)	140 (5)	−22 (4)	35 (4)	−8 (4)
S(1)	152 (5)	200 (5)	111 (5)	−39 (4)	19 (4)	−32 (4)
S(2)	162 (5)	167 (5)	95 (5)	−22 (4)	23 (4)	−6 (4)
O(1)	131 (15)	168 (15)	279 (18)	−16 (12)	86 (13)	28 (13)
O(2)	194 (17)	137 (15)	284 (18)	−15 (12)	69 (13)	16 (13)
C(1)	150 (21)	128 (20)	213 (23)	0 (17)	52 (17)	40 (18)
C(2)	183 (23)	180 (24)	261 (25)	4 (18)	42 (18)	20 (19)
C(3)	315 (27)	212 (26)	380 (31)	47 (22)	95 (23)	15 (22)
C(4)	267 (27)	298 (29)	489 (35)	133 (23)	60 (24)	90 (26)
C(5)	239 (27)	342 (30)	347 (30)	68 (22)	−49 (22)	85 (24)
C(6)	188 (23)	230 (25)	259 (26)	15 (19)	7 (19)	32 (10)
C(7)	171 (23)	193 (25)	273 (25)	25 (18)	77 (18)	2 (20)
C(8)	305 (27)	419 (35)	272 (27)	43 (23)	86 (21)	−60 (23)
C(9)	264 (27)	535 (39)	285 (29)	126 (25)	−26 (22)	15 (26)
C(10)	228 (24)	149 (24)	340 (28)	21 (18)	115 (20)	−6 (20)
C(11)	399 (30)	385 (33)	334 (30)	43 (25)	33 (24)	132 (26)
C(12)	560 (38)	268 (30)	412 (33)	51 (26)	219 (29)	−124 (25)

[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 IV. Final Positional (×10^3) and Isotropic Thermal Parameters for Located Hydrogen Atoms in $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$[a]

atom	x	y	z	B, Å^2
H(2)	−68 (3)	142 (3)	296 (7)	1.9 (10)
H(3)	−173 (4)	236 (5)	291 (11)	6.1 (18)
H(4)	−263 (3)	271 (4)	−73 (9)	3.7 (14)
H(5)	−240 (3)	186 (4)	−384 (9)	3.1 (13)
H(6)	−136 (3)	81 (3)	−361 (7)	1.1 (9)
H(7)	206 (3)	5 (4)	−54 (9)	2.8 (12)
H(10)	0 (2)	254 (3)	−215 (7)	0.7 (9)

[a] Estimated standard deviations in parentheses.

Table V. Final Intramolecular Distances (Å) in $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$[a]

Sn(1)–S(1)	2.689 (1)	C(1)–C(2)	1.394 (6)
Sn(1)–S(2)	2.678 (1)	C(2)–C(3)	1.399 (7)
Sn(1)–C(1)	2.145 (4)	C(3)–C(4)	1.388 (8)
P(1)–S(1)	1.998 (2)	C(4)–C(5)	1.383 (8)
P(1)–S(2)	2.006 (2)	C(5)–C(6)	1.387 (7)
P(1)–O(1)	1.584 (3)	C(6)–C(1)	1.386 (6)
P(1)–O(2)	1.584 (3)	C(2)–H(2)	1.04 (5)
O(1)–C(7)	1.476 (6)	C(3)–H(3)	1.07 (2)
O(2)–C(10)	1.476 (6)	C(4)–H(4)	1.03 (6)
		C(5)–H(5)	1.01 (6)
C(7)–C(8)	1.510 (7)	C(6)–H(6)	1.00 (4)
C(7)–C(9)	1.514 (7)		
C(10)–C(11)	1.517 (8)	C(7)–H(7)	1.00 (5)
C(10)–C(12)	1.514 (8)	C(10)–H(10)	1.02 (4)

[a] Estimated standard deviations in parentheses.

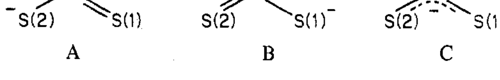
compared to its ethyl ester analogue[9] was predicted by the tin-119m Mössbauer IS and QS data, by the slope of the plot of the area under the resonance curve vs. temperature, and by the molecularity of the vibrating unit from the effective vibrating-mass model using low-energy, lattice-mode Raman data. The structure is centrosymmetric about the tin atom. The *trans*-diphenyltin octahedron with bidentate *O,O'*-diisopropyl dithiophosphate ligands about the equatorial plane formed by the tin and four virtually equidistant sulfur atoms contrasts with the severely anisobidentate ligands in the diethyl ester analogue. The angles at tin between oppositely placed sulfur atoms are all 180°, by symmetry, and the tin–sulfur distances are 2.689 (1) (Sn(1)–S(1)) and 2.678 (1) Å (Sn(1)–S(2)). The $Sn(SPS)_2$ moiety is essentially planar (equation of least-squares plane $0.0012x - 0.096y - 0.115z = 0$) with deviations from this plane having a minimum of 0.00 Å (for Sn(1)) and a maximum of ±0.027 Å (for P(1) and P(1')).

Table VI. Final Intramolecular Bond Angles (Deg) in $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$[a]

C(1)–Sn(1)–C(1')	180	O(1)–C(7)–C(8)	106.52 (37)
S(1)–Sn(1)–S(1')	180	O(1)–C(7)–C(9)	107.01 (38)
S(2)–Sn(1)–S(2')	180	C(8)–C(7)–C(9)	114.16 (42)
S(1)–Sn(1)–S(2)	76.03 (3)	O(2)–C(10)–C(11)	106.57 (39)
S(1)–Sn(1)–C(1)	89.92 (11)	O(2)–C(10)–C(12)	107.73 (39)
S(2)–Sn(1)–C(1)	90.94 (12)	C(11)–C(10)–C(12)	113.61 (44)
Sn(1)–S(1)–P(1)	86.26 (5)	Sn(1)–C(1)–C(2)	119.27 (32)
Sn(1)–S(2)–P(1)	85.38 (5)	Sn(1)–C(1)–C(6)	121.29 (32)
S(1)–P(1)–S(2)	111.26 (7)	C(2)–C(1)–C(6)	119.24 (41)
S(1)–P(1)–O(1)	111.98 (12)	C(1)–C(2)–C(3)	120.11 (43)
S(1)–P(1)–O(2)	112.38 (13)	C(2)–C(3)–C(4)	119.78 (48)
S(2)–P(1)–O(1)	112.04 (13)	C(3)–C(4)–C(5)	120.03 (51)
S(2)–P(1)–O(2)	111.57 (13)	C(4)–C(5)–C(6)	120.14 (49)
O(1)–P(1)–O(2)	96.88 (17)	C(5)–C(6)–C(1)	120.67 (44)
P(1)–O(1)–C(7)	118.65 (27)		
P(1)–O(2)–C(10)	119.28 (27)		

[a] Estimated standard deviations in parentheses.

The more tightly the sulfur atom in the dithiophosphate ester is bound to the metal atom, then the longer is the bond the sulfur atom makes with phosphorus.[4] All the complexes of this ligand but (*O,O'*-diethyl dithiophosphato)triphenyltin(IV), whose structure we have recently solved,[3] and the adduct of $Ni[S_2P(OCH_3)_2]_2$ with 2,9-dimethyl-1,10-phenanthroline, both of which contain monodentate ligands,[15] are chelated and contain anisobidentate arrangements of the ligand sulfur atoms. The longer sulfur–metal internuclear distances in those complexes are ascribed to coordinate-covalent bonding, with the adjacent sulfur to phosphorus interaction written as a double P═S bond. These shorter P═S distances are found to lie in the range 1.85–1.95 Å, with the corresponding single P—S distances at 1.99–2.19 Å.[4] The sulfur to phosphorus distances in the title compound (P(1)—S(1) = 1.998 (2) Å, P(1)—S(2) = 2.006 (2) Å) lie outside the P═S range, and at the low end of the single-bond range. This is interpreted as reflecting extensive delocalization within the S–P–S moiety; that is, almost equal contributions from canonical resonances A and B to the overall electron distribution of the system C.



Direct comparison may be made with the monomeric structure of the corresponding diethyl ester, bis(*O,O'*-diethyl dithio-

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Table VII. Sn–S Distances (Å) and C–Sn–C Angles (Deg) in $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$ and Related Compounds

compd	Sn–S (short)	Sn–S (long)	C–Sn–C	ref
$(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$	2.678 (1)	2.689 (1)	180 (0)	this work
$(C_6H_5)_2Sn[S_2P(OC_2H_5)_2]_2$	2.481 (8), 2.490 (10)	3.20 (1), 3.34 (1)	135 (1)	9
$(C_6H_5)_2Sn[S_2CN(C_2H_5)_2]_2$	2.548 (5), 2.613 (5)	2.637 (5), 2.790 (6)	101.4 (6)	23
$(CH_3)_2Sn[S_2CN(CH_3)_2]_2$	2.497 (7), 2.515 (8)	2.954 (7), 3.061 (8)	136 (1)	20
$(CH_3)_2Sn[S_2CN(CH_2)_4]_2$	2.522 (4)	2.936 (5)	129.7 (18)	26

phosphato)diphenyltin(IV), which is a distorted octahedron with chelating anisobidentate dithiophosphate ester ligands, where resonance form A dominates the electron distribution. The four sulfur atoms lie in an equatorial plane and the diphenyltin system makes a C–Sn–C angle of 135°. The shorter sulfur–tin distances of 2.48 and 2.49 (shorter than ours) are on the same side of the plane, with the larger distances opposite at 3.20 and 3.23 Å (longer than ours). This structure may be considered to be midway between tetrahedral and octahedral geometrics at tin (see Table VII). The sulfur–phosphorus distances found in the title compound (1.998 (2) and 2.006 (2) Å) are midway between those found for the P=S (1.92 (3) and 1.94(1) Å) and P—S (2.03 (1) and 2.04 (2) Å) bonds in the ethyl ester analogue. The average of the two sets of sulfur–tin distances in the latter complex (2.85 Å)[9] is larger than in the title compound (2.684 Å).

It has been noted that in diorganotin systems, the magnitude of the Mössbauer QS parameter is a function of the s-electron content of the Sn–C bonds and, hence, the C–Sn–C angle. Moreover, the QS values are found to increase from ca. 2.0 mm s^{-1} for the cis isomer (C–Sn–C = 90°) to ca. 4.00 mm s^{-1} for the trans isomer (C–Sn–C = 180°).[5] We find that the QS value increases from 3.12 to 3.67 mm s^{-1} in going from the diethyl to the diisopropyl ester, reflected in the observed opening of the C–Sn–C angle from 135 to 180°.

The prismatic crystals of the ethyl ester analogue contrast with the needlelike appearance of the crystals of the title compound, and the much less severe dependence of the area of the tin-119m Mössbauer resonances with temperature of the latter would lead to the expectation of a polymeric structure. Indeed, in the lead(II) system the bis(*O,O*′-diethyl dithiophosphate) derivative is a chelated monomer,[16] while its diisopropyl analogue is a polymer whose structure involves anisobidentate chelation from two dithiophosphate ester ligands which lie in a plane containing the lead(II) lone pair along with short, out-of-plane interactions with neighboring sulfur atoms to create pentagonal-bipyramidal geometry about the lead atom.[17] However, in the zinc(II) series the diethyl ester forms a polymer,[18] while its diisopropyl analogue contains dimeric units in the solid.[19] Anisobidentate bridging is the rule in these and other related structures involving the dithiophosphate ester group.[4]

The dithiocarbamate ligand is also of interest. Here the dimethyltin(IV) derivatives are trans octahedral,[20-22] but the structure of bis(*N*-diethyl dithiocarbamato)diphenyltin(IV) contains a *cis*-diphenyltin system with a C–Sn–C angle of 101.4°[23] (Table VII). This change has been discussed in terms of the effect of the size of the phenyl group upon the minimization of the interligand repulsions and the maximization of the tin–carbon and tin–sulfur bonding. In the present study, on the other hand, the change in the structure at tin from the ethyl analogue is produced by differences on the periphery of the molecule.

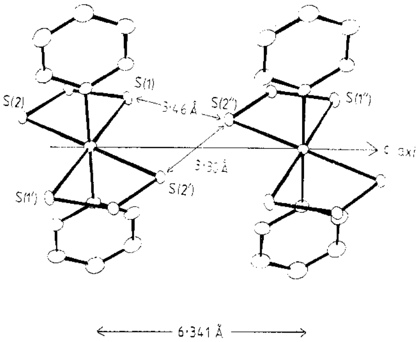

Figure 3. A view of the *c* axis of propagation showing the nearest intermolecular sulfur–sulfur atom contacts and the tin–tin distance. Singly primed atoms are related to the corresponding unprimed atoms by the inversion center at Sn(1). Doubly primed atoms are related to the corresponding unprimed atoms by a translation of one unit cell length along the *c* axis.

The molecules stack along the *c* axis to give rise to the observed, needlelike habit. Figure 2 shows the arrangement of the ligands which produces the linear tin–tin array along *c*. In Figure 3 this arrangement is viewed from the side to show that the S–P–S units are not perpendicular to this axis (that is, the P(1)–Sn(1)–P(1′) vector is not normal to *c*) but rather that the ligand system is somewhat rotated about the tin atom to bring pairs of sulfur atoms on the opposite sides of alternating molecules together. The van der Waals radius of sulfur is given as 1.73 Å;[24] the covalent radius as 1.04 Å.[25] The shortest intermolecular sulfur–sulfur contact in this crystal at 3.30 Å (S(2″)–S(2′), Figure 3) may thus reflect a weak interaction between the sulfur atoms of adjacent molecules.

We note a remarkable fact. The relatively short tin–tin distance along the *c* axis (6.341 (8) Å) is within the bridging range for dithiophosphate ligand. For example, the distance between dithiophosphate-bridged zinc atoms in the $Zn[S_2P(OC_2H_5)_5]_2$ one-dimensional polymer is 6.82 Å.[17] That is, the four sulfur and two phosphorus atoms that chelate each tin in this structure could be rearranged to lie *between* instead of *about* the tin atoms, thereby linking together diphenyltin units at an equivalent distance into a polymer of equal dimensions and density. The anisotropic thermal parameters from the X-ray data and the slope of the plot of Mössbauer resonance area vs. temperature would not be expected to differ in the resulting polymer from those in the array of monomers actually found. The factors which determine how tightly the tin atoms are held include, inter alia, (i) the number of nearest neighbor atoms and their distance, (ii) the strength of the interactions arising from the packing of molecules in the lattice which may be bonding (as in a true polymer) or nonbonding (van der Waals forces), and (iii) the mass of these neighboring units. None could be expected to change in the polymer corresponding to our structure. Our structure may best be described then as a "virtual polymer" created by the packing forces

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which can operate more powerfully in this isopropyl ester derivative than in its ethyl analogue. These packing factors are reflected in the anomalously small slope of the Mössbauer resonance area vs. temperature plot. Interpretation of variable temperature Mössbauer data should take this possibility into account. So far as we are aware, the structure of the title compound is the first example of a monomeric tin species with the same expected dimensions as its corresponding polymeric form, although information concerning the location of the next-nearest molecule and the shortest contact distances are surprisingly difficult to obtain from published structure reports.[2]

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Registry No. $(C_6H_5)_2Sn[S_2P(OC_3H_7\text{-}i)_2]_2$, 73453-95-9.

Supplementary Material Available: Listing of structure factor amplitudes (13 pages). Ordering information is given on any current masthead page.

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Reagents for Asymmetric Epoxidations. Molecular Structure of a Molybdenum(VI)–Oxodiperoxo Complex Containing a Chiral Bidentate Lactamide Ligand

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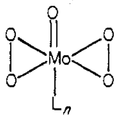
The molecular structure and absolute configuration of $MoO(O_2)_2\cdot(S)\text{-}MeCH(OH)CONMe_2$ have been determined from three-dimensional X-ray diffractometer data collected by counter methods. The molecule crystallizes in the orthorhombic space group $P2_12_12_1$ with four formula units per cell. The unit cell dimensions are $a = 6.651$ (2), $b = 9.567$ (3), and $c = 15.504$ (8) Å. The structure has been solved by the heavy-atom technique and refined to $R = 0.0549$ (3091 unique reflections). In the slightly distorted pentagonal-bipyramidal coordination sphere of molybdenum the two peroxo groups are located in equatorial positions; the chiral lactamide ligand is bidentate, being coordinated through the carbonyl oxygen at the fifth equatorial position and through the hydroxylic oxygen on the axial position opposite to the doubly bonded oxo group. The geometry of the amide group is significantly altered upon coordination to molybdenum. Crystal packing is determined by a three-dimensional network of hydrogen bonds between the hydroxyl group of the lactamide ligand and peroxo atoms of neighboring molecules. The absolute configuration at the asymmetric carbon atom of the coordinated lactamide derived from (−)-ethyl lactate has been determined by the Bijvoet method to be *S* in agreement with the classical assignment. The hydroxylic hydrogen was located and refined, establishing *S* chirality for the asymmetric oxygen atom which is formed upon coordination to molybdenum.

Introduction

Molybdenum(VI)–oxodiperoxo complexes of the general formula **1** (n = 1–2; L = H_2O, DMF, HMPA, pyr) are stoichiometric reagents for the oxidation of various organic substrates such as sulfides, aliphatic amines, ketones, and olefins.[1] The epoxidation of olefins by **1** is of considerable interest since metal peroxo species of molybdenum are claimed to be involved as key intermediates in the hydroperoxide oxidation of olefins catalyzed by salts of this metal.[1] Recently, some of us have demonstrated that asymmetric epoxidation of simple prochiral olefins (e.g., propene, 1-butene, *trans*-2-butene) can be achieved with stoichiometric quantities of **1** in which L represents the chiral bidentate ligand (*S*)-*N*,*N*-dimethyllactamide. In order to clarify the exact molecular structure of the novel chiral oxidizing agent,[2] we have carried out an X-ray crystallographic analysis of the compound $MoO(O_2)_2$·*N*,*N*-dimethyllactamide, **2**.



1

Table I. Crystal Data for **2** at 23 °C

cryst color: yellow
cryst size: 0.15 × 0.22 × 0.31 mm^3
cryst system: orthorhombic
space group: $P2_12_12_1$
cell dimensions: $a = 6.651$ (2) Å, $b = 9.567$ (3) Å, $c = 15.504$ (8) Å, $V = 986.52$ $Å^3$, $Z = 4$, $d_{\text{calcd}} = 1.973$ g cm^{-3}, $d_{\text{exptl}} = 1.94$ g cm^{-3}
μ(Mo Kα): 12.04 cm^{-1}

Experimental Section

Preparation of 2. A solution of $H_2Mo_2O_{11}$ is prepared by dissolving MoO_3 (5 g, 34.7 mmol) in 30% H_2O_2 (25 mL) at 40 °C according to the general procedure.[1,3] (The necessary care when preparing and handling peroxometal compounds should be observed, although no incidence of a violent decomposition of **2** occurred during synthesis, storage, and use; cf. ref 3, p 189). (*S*)-*N*,*N*-Dimethyllactamide (4.1 g, 35 mmol) prepared from (−)-(*S*)-ethyl lactate[4] is added with stirring to the filtered solution of $H_2Mo_2O_{11}$. The solution is concentrated in vacuo at 40 °C to three-fourths its initial volume, and after addition of 15 mL of methanol, the compound crystallized at 20 °C. The crystals are collected by suction, washed with methanol and diethyl

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*Authors to whom correspondence should be addressed (W.W.: X-ray analysis).

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