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## Oxy and Thio Phosphorus Acid Derivatives of Tin. 2. Crystal and Molecular Structure of (*O,O'*-Diethyl dithiophosphato)triphenyltin(IV) at 138 K. A Unique, Monodentate Dithiophosphate Derivative

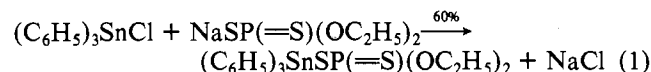
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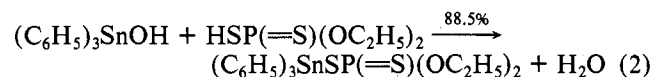
(*O,O'*-Diethyl dithiophosphato)triphenyltin(IV),  $C_{22}H_{25}O_2S_2PSn$ , crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 12.647$  (7) Å,  $b = 9.961$  (3) Å,  $c = 9.437$  (3) Å,  $\alpha = 98.59$  (3)°,  $\beta = 91.51$  (4)°,  $\gamma = 96.12$  (4)°,  $V = 1173$  Å<sup>3</sup>,  $Z = 2$ , and  $\rho_{\text{calcd}} = 1.63$  g cm<sup>-3</sup>. The structure was determined by the heavy-atom technique from 4838 reflections measured at  $138 \pm 2$  K on an automatic diffractometer using monochromated Mo  $K\alpha$  radiation, to a final  $R$  value of 0.039. The molecule contains a four-coordinated tin atom and a monodentate dithiophosphate ligand, an unusual example of a dithiophosphate ligand which is neither chelating nor bridging.

In the first paper of this series we described the preparation of a series of triorganotin dithiophosphate esters,  $R_3SnSP(=S)(OR')_2$ , where  $R = CH_3^-$ ,  $C_6H_{11}^-$ , and  $C_6H_5^-$ , and their characterization by infrared, NMR, mass and <sup>119m</sup>Sn Mössbauer spectroscopies.<sup>1</sup> These compounds have practical importance since they are a combination of the powerful triorganotin biocides<sup>2</sup> with the well-known organophosphorus biocides. Combining the dual biocidal activities in a single molecule could produce a potent and lasting effect, while retarding the development of tolerance. The systems are also of interest structurally<sup>3</sup> since the dithiophosphate ester ligand can potentially adopt a mono- or bidentate configuration, the latter in a monomeric chelate, a bridged, associated oligomer or one-dimensional polymer.

The title compound, (*O,O'*-diethyl dithiophosphato)triphenyltin(IV),<sup>4</sup> was synthesized by the action of triphenyltin chloride on the sodium salt of diethyldithiophosphoric acid in ethanol



or by the action of the organotin hydroxide on the free acid in ethanol



The white crystalline product which melts at 105 °C was subjected to Mössbauer study. The isomer shift (IS =  $1.26 \pm 0.02$  mm/s) and quadrupole splitting (QS =  $2.08 \pm 0.03$  mm/s) values specify a four-coordinated situation at tin, and this is corroborated by the magnitude of the slope of the temperature dependence of the area under the resonance ( $-1.43 \times 10^{-2}$  K<sup>-1</sup> between 77 and 150 K) which lies in a range usually associated with monomeric systems<sup>5</sup> (tetraphenyltin, for example, whose resonance has been recorded at ambient temperatures,<sup>6</sup> exhibits a slope of  $-1.659 \times 10^{-2}$  K<sup>-1</sup><sup>6,7</sup>). Finally, a treatment of the Mössbauer and low-energy Raman spectra based upon the effective vibrating mass model developed by Herber<sup>8</sup> yields a unit molecular weight for the intermolecular, intramolecular cell lattice mode observed at 34 cm<sup>-1</sup> in the Raman spectrum.<sup>1</sup>

The predicted monodentate, monomeric configuration would be rare among dithiophosphate derivatives,<sup>9</sup> and so it was decided to seek verification through a single-crystal X-ray diffraction study. We report the results in this paper.

### Experimental Section

**Crystal Data.** Colorless, prismatic crystals of the title compound were obtained by slow evaporation of a benzene solution and were

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Table I. Crystal Data

formula $C_{22}H_{25}O_2S_2PSn$	$F(000) = 540$
fw 577.35	$\mu(\text{Mo } K\alpha) = 13.49 \text{ cm}^{-1}$
space group $P\bar{1}$	$T = 138 \pm 2 \text{ K}$
$a = 12.647$ (7) Å	$D_{\text{calcd}} = 1.63 \text{ g cm}^{-3}$
$b = 9.961$ (3) Å	no. of independent reflections = 4838
$c = 9.437$ (3) Å	max $2\theta = 53^\circ$
$\alpha = 98.59$ (3)°	radiation Mo $K\alpha$ (0.7121 Å) for
$\beta = 91.51$ (4)°	intensity data, Mo $K\alpha_1$ (0.709 26 Å)
$\gamma = 96.12$ (4)°	for cell parameters
$V = 1173 \text{ Å}^3$	
$Z = 2$	

stable to both atmospheric moisture and X-rays. A crystal of approximate dimensions  $0.4 \times 0.4 \times 0.2$  mm was mounted on a glass fiber and used for the determination of the initial cell parameters and subsequent data collection.

The space group was determined by diffractometry studies to be triclinic,  $P\bar{1}$ . Cell dimensions were determined by least squares from the  $+2\theta$  and  $-2\theta$  values of 38 reflections spaced throughout reciprocal space. 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.** Intensities of all reflections with  $2\theta \leq 53^\circ$  were measured at  $138 \pm 2$  K on the above-described diffractometer using  $\theta-2\theta$  scan techniques with variable scan rates ( $\nu$ ) using monochromated Mo  $K\alpha$  radiation. The angular scan width was also variable and was obtained from  $(A + B \tan \theta)^\circ$  for each reflection, where  $A$  and  $B$  were taken as 0.8 and 0.08. A receiving aperture with a variable width of  $(5.00 + 0.86 \tan \theta)$  mm and a constant height of 6 mm was located at a distance of 173 mm from the crystal. The maximum scan time for a reflection was 60 s. For each reflection, two-thirds of the scan time was spent scanning the peak ( $P$ ) and one-sixth of the time scanning each of the right and left backgrounds (LB and RB). The unscaled intensity was calculated as  $I = [P - 2(LB + RB)]$ . These were then scaled according to their scan rate.

Reflection (135) was used as a standard, and its intensity was monitored every 20 measurements. Fluctuations in the intensity of the standard were within 3% for most (66%) of the data, the maximum fluctuation over all data being 6%. Three orientation control reflections were centered after every 200 observations. In case of any angular change greater than  $0.2^\circ$ , a new orientation matrix was automatically determined from a list of 11 reflections. In all, 4838 independent reflections were measured, 348 of which were considered indistinguishable from background [ $I < 2\sigma(I)$ ] and were assigned an intensity equal to  $1.4T^{1/2}$ , where  $T = [P + 2(LB + RB)]$ .

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

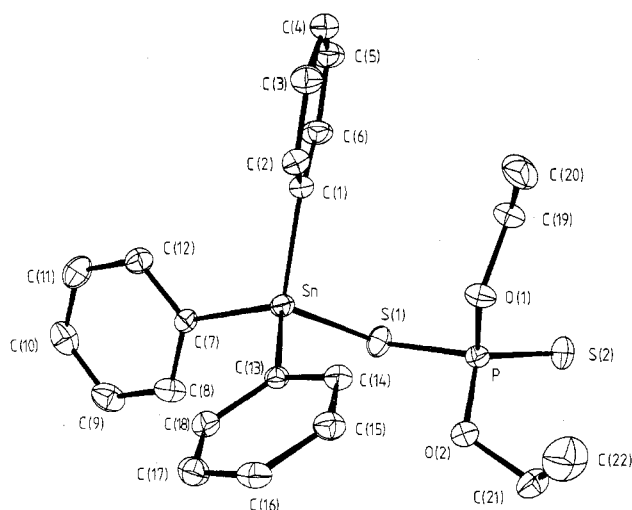
$$\sigma_{F^2} = \frac{1}{2} \left[ \frac{\sigma^2 + (0.04I\nu)^2}{(Lp)(I\nu)} \right] \quad (3)$$

and  $\sigma = T^{1/2}\nu$  and  $Lp$  is the product of the Lorentz and polarization

**Table II.** Final Fractional Atomic Coordinates and Isotropic Temperature Factors for Located Hydrogen Atoms in  $(C_6H_5)_3SnSP(=S)(OC_2H_5)_2^a$ 

atom	x	y	z	B, Å <sup>2</sup>
H(2)	0.613 (3)	0.271 (4)	-0.049 (4)	1.9 (8)
H(3)	0.787 (4)	0.328 (6)	-0.003 (6)	5.3 (13)
H(4)	0.859 (4)	0.400 (5)	0.220 (5)	3.1 (10)
H(5)	0.757 (4)	0.409 (5)	0.423 (5)	3.3 (10)
H(6)	0.574 (3)	0.348 (5)	0.379 (5)	2.6 (9)
H(8)	0.199 (3)	0.040 (4)	0.171 (4)	1.9 (8)
H(9)	0.160 (3)	-0.160 (4)	0.277 (5)	2.4 (9)
H(10)	0.288 (4)	-0.252 (5)	0.377 (5)	2.8 (9)
H(11)	0.464 (3)	-0.151 (4)	0.402 (5)	2.6 (9)
H(12)	0.499 (4)	0.047 (5)	0.310 (5)	2.9 (10)
H(14)	0.380 (4)	0.391 (5)	-0.144 (5)	3.2 (10)
H(15)	0.338 (4)	0.327 (5)	-0.391 (5)	3.8 (11)
H(16)	0.272 (4)	0.105 (5)	-0.480 (5)	3.1 (10)
H(17)	0.254 (4)	-0.054 (5)	-0.335 (5)	3.1 (10)
H(18)	0.304 (3)	-0.012 (4)	-0.088 (5)	2.6 (9)
H(19)	0.163 (3)	0.357 (5)	-0.055 (5)	3.1 (10)
H(20)	0.055 (4)	0.379 (5)	0.008 (5)	2.9 (9)
H(21)	0.107 (3)	0.266 (5)	0.558 (5)	2.7 (9)
H(22)	0.045 (4)	0.376 (5)	0.475 (5)	3.4 (10)

<sup>a</sup> Estimated standard deviations in parentheses.

**Figure 1.** The asymmetric unit of  $(O,O'$ -diethyl dithiophosphato)-triphenyltin(IV), showing atomic labeling.

factors. All intensity data were scaled by a standard reflection and Lorentz and polarization corrections were applied. Because of the relatively cubic shape of the data crystal and the low  $\mu$  value ( $13.49 \text{ cm}^{-1}$ ), no absorption correction was applied.

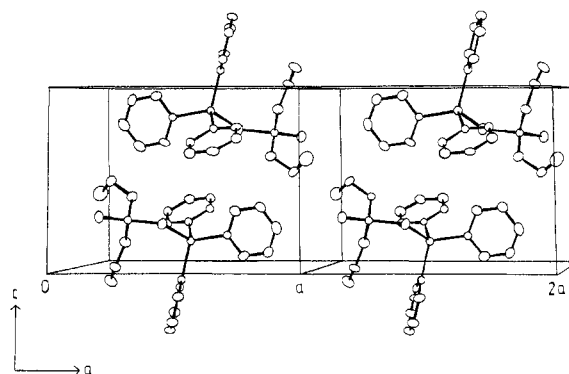
**Structure Determination and Refinement.** The position of the tin atom was determined from a three-dimensional Patterson map. Structure factors calculated with the tin parameters gave an  $R$  factor ( $R = \sum ||kF_o| - |F_c|| / \sum |kF_o|$ ) of 0.50 for all reflections. The parameters of the tin atom were refined, and a difference Fourier map was calculated by using the heavy-atom phases. From the difference map all nonhydrogen atoms were easily located. These atoms were first refined isotropically and then with anisotropic thermal parameters to an  $R$  factor of 0.052 for all 4838 reflections by using a block-diagonal least-squares program.<sup>10</sup> A difference Fourier map calculated at this stage revealed all hydrogen atom positions except those bonded to the terminal carbon of the aliphatic group, which appeared as highly diffuse peaks, presumably due to high thermal motion. Hydrogen parameters were refined isotropically. Refinement was discontinued when the maximum parameter shift for all nonhydrogen atoms was less than one-third of the corresponding standard deviation. The final  $R$  factor is 0.034 for the 4453 reflections that were included in the least-squares calculations and is 0.039 for all 4830 reflections.

In all least-squares refinements the quantity  $\sum w_F(|kF_o| - |F_c|)^2$  was minimized, where  $w_F$  is as defined above. The scattering factors for Sn, P, S, and C atoms were taken from ref 11 and those for the hydrogen atoms from ref 12. An analysis of the function  $w_F(k|F_o| - |F_c|)^2$  vs.  $|F_o|$  and  $\sin^2 \theta$  showed no significant variation of the average

**Table III.** Final Fractional Atomic Coordinates of Nonhydrogen Atoms in  $(C_6H_5)_3SnSP(=S)(OC_2H_5)_2^a$ 

atom	x	y	z
Sn	0.40361 (2)	0.24093 (2)	0.13019 (2)
P	0.17345 (7)	0.39080 (9)	0.25501 (9)
S(1)	0.33230 (7)	0.45137 (9)	0.23697 (10)
S(2)	0.08964 (7)	0.54314 (10)	0.27809 (11)
O(1)	0.1354 (2)	0.2747 (2)	0.1228 (2)
O(2)	0.1722 (2)	0.3044 (3)	0.3826 (3)
C(1)	0.5698 (3)	0.3029 (3)	0.1660 (4)
C(2)	0.6362 (3)	0.2981 (4)	0.0496 (4)
C(3)	0.7454 (3)	0.3361 (4)	0.0723 (4)
C(4)	0.7892 (3)	0.3796 (4)	0.2098 (5)
C(5)	0.7242 (3)	0.3843 (4)	0.3259 (4)
C(6)	0.6151 (3)	0.3472 (4)	0.3049 (4)
C(7)	0.3570 (3)	0.0676 (3)	0.2305 (3)
C(8)	0.2535 (3)	0.0027 (4)	0.2197 (4)
C(9)	0.2294 (3)	-0.1170 (4)	0.2778 (4)
C(10)	0.3093 (3)	-0.1734 (4)	0.3468 (4)
C(11)	0.4120 (3)	-0.1094 (4)	0.3576 (4)
C(12)	0.4361 (3)	0.0105 (4)	0.3010 (4)
C(13)	0.3554 (3)	0.1974 (4)	-0.0914 (3)
C(14)	0.3613 (3)	0.2963 (4)	-0.1819 (4)
C(15)	0.3295 (3)	0.2623 (4)	-0.3264 (4)
C(16)	0.2917 (3)	0.1284 (4)	-0.3815 (4)
C(17)	0.2853 (3)	0.0288 (4)	-0.2933 (4)
C(18)	0.3174 (3)	0.0628 (4)	-0.1486 (4)
C(19)	0.0999 (3)	0.3093 (4)	-0.0145 (4)
C(20)	0.0499 (4)	0.1785 (4)	-0.1035 (5)
C(21)	0.0769 (3)	0.2815 (5)	0.4653 (4)
C(22)	0.0028 (4)	0.1603 (6)	0.3929 (6)

<sup>a</sup> Estimated standard deviations in parentheses.

**Figure 2.** The contents of adjacent unit cells, showing molecular packing.

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 parameters, both positional and thermal, are listed in Tables II, III, and IV. Atomic number schemes followed in these listings are identified in Figure 1. Hydrogen atoms in Table II are numbered according to the atoms to which they are bonded. Interatomic bond distances and angles calculated from the final parameters are given in Table V. Table VI lists the shortest nonbonding distances in the asymmetric unit shown in Figure 1.

### Description and Discussion of the Structure

The prediction based upon the tin-119m Mössbauer IS and QS data, the slope of the plot of the area under the resonance curve vs. temperature, and the molecularity of the vibrating unit from the effective vibrating mass model using low-energy, lattice-mode Raman data is borne out in the monomeric molecule shown in Figure 1 which contains a four-coordinated tin atom and a monodentate dithiophosphate ligand. The distance from tin to the nonbonded, intramolecular sulfur atom [S(2)] is 5.326 Å. The shortest intermolecular distance is 5.84 Å [Sn-S(1)], while intermolecular contacts to P, S(2), O(1), and O(2) are all in excess of 6 Å. The molecules in the unit cell are shown in Figure 2. So far as we are aware, only the

Table IV. Final Anisotropic Thermal Parameters<sup>a</sup> for Nonhydrogen Atoms in (C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>SnSP(=S)(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub><sup>b</sup>

atom	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
Sn	178 (1)	210 (1)	144 (1)	0 (1)	13 (1)	26 (1)
P	187 (4)	215 (4)	185 (4)	23 (3)	11 (3)	21 (3)
S(1)	206 (4)	219 (4)	291 (4)	2 (3)	45 (3)	-11 (3)
S(2)	225 (4)	242 (4)	380 (5)	47 (3)	37 (4)	24 (4)
O(1)	295 (13)	211 (12)	203 (11)	7 (10)	-29 (9)	30 (9)
O(2)	249 (12)	338 (14)	200 (11)	54 (10)	36 (9)	71 (10)
C(1)	204 (15)	205 (17)	209 (16)	13 (12)	16 (12)	39 (12)
C(2)	278 (18)	263 (18)	229 (17)	-5 (14)	23 (14)	24 (14)
C(3)	265 (18)	352 (21)	380 (22)	5 (16)	117 (16)	56 (16)
C(4)	215 (18)	330 (21)	483 (24)	-30 (15)	-37 (16)	111 (18)
C(5)	335 (20)	347 (21)	310 (20)	-59 (16)	-98 (16)	89 (16)
C(6)	297 (18)	330 (20)	205 (17)	-35 (15)	1 (14)	65 (14)
C(7)	220 (16)	197 (16)	155 (15)	36 (12)	11 (12)	18 (12)
C(8)	241 (17)	227 (17)	200 (16)	27 (13)	-9 (13)	37 (12)
C(9)	254 (18)	260 (18)	249 (17)	-27 (14)	7 (14)	44 (14)
C(10)	357 (19)	223 (17)	210 (17)	25 (14)	14 (14)	45 (13)
C(11)	295 (18)	271 (18)	217 (17)	85 (14)	-27 (14)	39 (13)
C(12)	208 (16)	279 (18)	217 (16)	15 (13)	10 (13)	1 (13)
C(13)	212 (16)	264 (17)	153 (15)	42 (13)	9 (12)	25 (12)
C(14)	375 (20)	243 (18)	210 (17)	60 (15)	17 (14)	32 (13)
C(15)	443 (22)	369 (22)	214 (18)	124 (17)	23 (16)	82 (15)
C(16)	330 (20)	457 (24)	173 (17)	122 (17)	-19 (14)	-19 (15)
C(17)	267 (18)	325 (20)	241 (18)	38 (15)	-8 (14)	-49 (14)
C(18)	253 (17)	272 (18)	218 (16)	48 (14)	24 (13)	31 (13)
C(19)	301 (18)	378 (21)	211 (17)	60 (16)	-30 (14)	60 (15)
C(20)	388 (23)	532 (28)	355 (23)	73 (20)	-140 (18)	-85 (19)
C(21)	317 (20)	480 (25)	288 (19)	113 (18)	131 (16)	145 (17)
C(22)	431 (27)	628 (34)	590 (32)	-149 (24)	128 (23)	171 (26)

<sup>a</sup>  $U_{ij}$ 's are of the form  $10^4 \exp[-2\pi^2(h^2U_{11}a^{*2} + k^2U_{22}b^{*2} + l^2U_{33}c^{*2} + 2hkU_{12}a^*b^* + 2klU_{23}b^*c^* + 2hlU_{13}a^*c^*)]$ . <sup>b</sup> Estimated standard deviations in parentheses.

tetragonal-pyramidal adduct of Ni[S<sub>2</sub>P(OCH<sub>3</sub>)<sub>2</sub>]<sub>2</sub> with 2,9-dimethyl-1,10-phenanthroline has been shown to contain a monodentate dithiophosphate ligand.<sup>13,14</sup> Curiously, the parent 1,10-phenanthroline complex is hexacoordinated with both dithiophosphato ligands bidentate.

There is slightly distorted tetrahedral geometry at tin with the angles to the phenyl carbons lying in the range 110.78 (13)–113.14 (13)° and the angles involving the directly bonded sulfur in the range 100.09 (9)–114.47 (9)°. Conventional isovalent hybridization arguments would lead to the expectation that the angles involving the more electronegative chalcogenide would close relative to those involving only carbon and tin, but only C(1)–Sn–S(1) (–100.09 (9)°) is found to do so, while the phenyl–tin angles are all approximately tetrahedral.

The phosphorus atom sits in a roughly tetrahedral environment among two oxygen and two sulfur atoms (one doubly bonded) with angles ranging from 101.02 (14) to 115.89 (11)°. As expected from isovalent hybridization arguments, in this case the angles involving the more electronegative oxygen are smaller [O–P–O [101.02 (14)°] < O–P–S [103.65 (11)°, 108.24 (101)°]], which are in turn smaller than those involving the terminal, double-bonded sulfur atom where by contrast S=P–S [112.29 (6)°] < S=P–O [114.59 (10)°, 115.89 (11)°].

It is said that the phosphorus to sulfur internuclear distances generally are sensitive to the environment of the sulfur atom—the more tightly bound to a given metal the sulfur atom is, then the longer the P–S distance. All but one of the dithiophosphate derivatives whose structures are known are chelated and contain anisobidentate ligands. The shorter P to S distances in these compounds lie in the range of 1.85–1.97 Å, with the longer P–S distances 1.99–2.19 Å.<sup>9</sup> Our noncoordinated P=S distance is 1.931 (1) Å, which is not particularly short compared with other shorter P to S distances in metal complexes or with the nonbonded P=S distances in the metal-free compounds [S<sub>2</sub>P(O-*i*-C<sub>3</sub>H<sub>7</sub>)<sub>2</sub>]<sub>2</sub> (1.908 Å)<sup>15</sup> or SCH<sub>2</sub>CH<sub>2</sub>SP(=S)Cl (1.910 Å).<sup>16</sup> The shorter P to S distance is 1.923 Å<sup>17</sup>

in bis(*O,O'*-dimethyl dithiophosphato)tellurium(II) in which the tellurium atom is said to be bound in a monodentate fashion in a recent review,<sup>9</sup> but contains intermolecular association through bridging sulfur–tellurium coordination at 3.31 Å to form two-dimensional polymeric layers instead. Our longer P–S distance of 2.054 (1) Å is, on the other hand, not particularly long when compared with the range of other longer P to S distances in the chelated metal complexes or with the bonded P to S distances in the disulfur dimer (2.072 Å)<sup>15</sup> or the cyclic phosphorus chloride (2.051 Å)<sup>16</sup> quoted above. Thus, nonutilization of the P=S bond in coordination is not reflected either in a very short P=S distance or in a very long P–S distance.

Our tin–sulfur distance is 2.4582 (9) Å. There are only two pentacoordinated tin Sn–S distances to choose from for comparison. The heavily distorted trigonal bipyramid formed by the diphenyltin derivative of the tridentate anion of 2-(2-hydroxyphenyl)benzothiazoline in the Schiff base form (SAT) contains a covalent tin–sulfur bond at 2.496 Å,<sup>18</sup> and the shorter tin–sulfur distance in the more directly relevant (*N,N*-diethyldithiocarbamato)triphenyltin, which is chelated, is at 2.449 Å.<sup>19</sup> More relevant still are the structures in which the tin atom is four-coordinated. A group of four structures of variously substituted triphenyltin thiophenols are available in which tin–sulfur distances lie in the range 2.41–2.44 Å,<sup>3</sup> and the cyclic trimer of diphenyltin sulfide contains a mean tin–sulfur distance of 2.42 Å.<sup>20</sup> Thus it appears that there is little to separate the four- and five-coordinated tin–sulfur internuclear distances and that our value could be ascribed to either situation on the basis of the currently available data.

The crystal structure of the related compound bis(*O,O'*-diethyl dithiophosphato)diphenyltin(IV) is octahedral with chelating, anisobidentate dithiophosphate ester ligands in which two of the tin–sulfur distances are 2.48, 2.49 Å and other two are 3.20, 3.23 Å. The diphenyltin system exhibits a C–Sn–C angle of 135° about the six-coordinated tin atom, with the four sulfur atoms in an equatorial plane.<sup>21</sup> The structure of the corresponding bis(*O,O'*-diethyl dithiophosphato)lead(II) is

**Table V.** Final Intramolecular Bond Distances (Å) and Angles (deg) in  $(C_6H_5)_3SnSP(=S)(OC_2H_5)_2^a$ 

A. Distances			
Sn-S(1)	2.4582 (9)	C(13)-C(14)	1.394 (5)
Sn-C(1)	2.129 (3)	C(14)-C(15)	1.392 (5)
Sn-C(7)	2.127 (3)	C(15)-C(16)	1.386 (6)
Sn-C(13)	2.131 (3)	C(16)-C(17)	1.384 (6)
S1-P	2.054 (1)	C(17)-C(18)	1.396 (5)
P-S(2)	1.931 (1)	C(18)-C(13)	1.397 (5)
P-O(1)	1.595 (3)	C(2)-H(2)	0.95 (4)
P-O(2)	1.581 (3)	C(3)-H(3)	0.89 (6)
O(1)-C(19)	1.461 (4)	C(4)-H(4)	0.89 (5)
C(19)-C(20)	1.507 (6)	C(5)-H(5)	0.99 (5)
O(2)-C(21)	1.469 (5)	C(6)-H(6)	0.89 (4)
C(21)-C(22)	1.511 (7)	C(8)-H(8)	0.96 (4)
C(1)-C(2)	1.399 (5)	C(9)-H(9)	0.93 (4)
C(2)-C(3)	1.395 (5)	C(10)-H(10)	0.89 (5)
C(3)-C(4)	1.386 (6)	C(11)-H(11)	0.94 (4)
C(4)-C(5)	1.385 (6)	C(12)-H(12)	0.83 (5)
C(5)-C(6)	1.392 (6)	C(14)-H(14)	0.96 (5)
C(6)-C(1)	1.405 (5)	C(15)-H(15)	0.95 (5)
C(7)-C(8)	1.391 (5)	C(16)-H(16)	0.94 (5)
C(8)-C(9)	1.393 (5)	C(17)-H(17)	0.90 (5)
C(9)-C(10)	1.399 (5)	C(18)-H(18)	1.00 (4)
C(10)-C(11)	1.378 (5)	C(19)-H(19)	1.00 (4)
C(11)-C(12)	1.387 (5)	C(19)-H(20)	0.95 (5)
C(12)-C(7)	1.402 (5)	C(21)-H(21)	0.98 (5)
		C(22)-H(22)	1.05 (5)
B. Angles			
S(1)-Sn-C(1)	100.09 (9)	C(2)-C(3)-C(4)	120.57 (37)
S(1)-Sn-C(7)	114.47 (9)	C(3)-C(4)-C(5)	119.83 (38)
S(1)-Sn-C(13)	108.77 (9)	C(4)-C(5)-C(6)	120.27 (37)
C(1)-Sn-C(7)	110.78 (13)	C(5)-C(6)-C(1)	120.43 (34)
C(1)-Sn-C(13)	113.14 (13)	Sn-C(7)-C(8)	122.88 (24)
C(7)-Sn-C(13)	109.41 (13)	Sn-C(7)-C(12)	118.14 (24)
Sn-S(1)-P	103.80 (4)	C(8)-C(7)-C(12)	118.79 (31)
S(1)-P-S(2)	112.29 (6)	C(7)-C(8)-C(9)	120.37 (32)
S(1)-P-O(1)	108.24 (10)	C(8)-C(9)-C(10)	120.20 (33)
S(1)-P-O(2)	103.65 (11)	C(9)-C(10)-C(11)	119.59 (34)
S(2)-P-O(1)	114.59 (10)	C(10)-C(11)-C(12)	120.39 (34)
S(2)-P-O(2)	115.89 (11)	C(11)-C(12)-C(7)	120.66 (32)
O(1)-P-O(2)	101.02 (14)	Sn-C(13)-C(14)	123.14 (25)
P-O(1)-C(19)	121.13 (22)	Sn-C(13)-C(18)	118.17 (25)
P-O(2)-C(21)	121.84 (24)	C(14)-C(13)-C(18)	118.69 (32)
O(1)-C(19)-C(20)	106.97 (31)	C(13)-C(14)-C(15)	120.88 (35)
O(2)-C(21)-C(22)	111.35 (35)	C(14)-C(15)-C(16)	119.75 (37)
Sn-C(1)-C(2)	119.74 (25)	C(15)-C(16)-C(17)	120.22 (37)
Sn-C(1)-C(6)	121.47 (25)	C(16)-C(17)-C(18)	120.00 (35)
C(2)-C(1)-C(6)	118.79 (32)	C(17)-C(18)-C(13)	120.46 (33)
C(1)-C(2)-C(3)	120.11 (34)		

<sup>a</sup> Estimated standard deviations in parentheses.**Table VI.** Shortest Intramolecular Nonbonding Distances (Å)<sup>a</sup>

Sn-O(1)	3.444 (3)	Sn-P	3.5596 (9)
Sn-O(2)	3.867 (3)	Sn-S(2)	5.326

<sup>a</sup> Estimated standard deviations in parentheses.

likewise monomeric and chelated in an anisobidentate fashion with the lead(II) atom in a pseudopentacoordinated geometry.<sup>22</sup> Other related structures include the bis(*O,O'*-dimethyl dithiophosphato)tellurium(II)<sup>17</sup> and bis(*O,O'*-diisopropyl dithiophosphato)zinc(II) and -cadmium(II),<sup>23</sup> all of which are also chelated in an anisobidentate fashion.

It is interesting to note that the structure of bis(*O,O'*-diisopropyl dithiophosphato)lead(II) 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 a pentagonal-bipyramidal geometry about the lead atom.<sup>24</sup> This polymeric structure contrasts with that of the *O,O'*-diethyl dithiophosphato derivative which is monomeric.<sup>22</sup> In the case of the diisopropyl ester derivative in the triphenyltin series, the slope of the plot of the tin-119m Mössbauer resonance area vs. temperature ( $-1.40 \times 10^{-2} \text{ K}^{-1}$ ) is identical within experi-

mental error with that of the diethyl ester. The IS ( $=1.28 \pm 0.02 \text{ mm/s}$ ) and QS ( $=2.03 \pm 0.03 \text{ mm/s}$ ) are also within experimental error. In addition, the treatment of the low-energy, lattice-mode Raman data in the effective vibrating mass model yields a monomeric result.<sup>1</sup> We are forced to conclude that in our series these two esters are isostructural. In the zinc(II) series, on the other hand, the diethyl ester is a polymer held by bridging dithiophosphate moieties,<sup>25</sup> while the diisopropyl derivative contains dimeric units.<sup>23</sup>

The triphenyltin moiety alone is not responsible for imposing the monodentate nature upon the dithiophosphate ligand, since three triphenyltin derivatives containing chelated structures have now been established by X-ray crystallography: the 1,3-diphenyl-1,3-propanedione,<sup>26</sup> the *N*-benzoyl-*N*-phenylhydroxylamine,<sup>27</sup> and the diethyldithiocarbamate.<sup>19</sup> In the latter, the two sulfur atoms make an acute angle ( $62.8^\circ$ ) at tin with very unequal (2.449 and 3.118 Å) distances. The C-Sn-C angles lie in the range  $104.2$ – $106.6^\circ$  in the distorted trigonal bipyramid which contains one axial-sulfur atom and one axial-phenyl ring. Only in tetrakis(*N,N*-diethyldithiocarbamato)tin(IV) are there found two monodentate dithiocarbamate groups giving rise to a distorted trans octahedral geometry about the tin atom.<sup>28</sup> Other triphenyltin structures contain bridging ligands that give rise to infinite, zigzag chains such as those found in the triphenyltin 4-thiopyridone,  $(C_6H_5)_3SnSC_6H_4N$ ,<sup>29,30</sup> isocyanate,<sup>31</sup> and hydroxide.<sup>32</sup> However, the recently published triphenyltin bromide<sup>33</sup> is, like the corresponding chloride,<sup>34</sup> monomeric.

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**Registry No.** (*O,O'*-Diethyl dithiophosphato)triphenyltin(IV), 2117-78-4.

**Supplementary Material Available:** A listing of structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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## Superoxide and Manganese(III).<sup>†</sup> Reactions of Mn-EDTA and Mn-CyDTA Complexes with O<sub>2</sub><sup>-</sup>. X-ray structure of KMnEDTA·2H<sub>2</sub>O

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The reactions of Mn<sup>III</sup>EDTA<sup>-</sup>, Mn<sup>II</sup>EDTA<sup>2-</sup>, and Mn<sup>III</sup>CyDTA<sup>-</sup> with superoxide have been studied in both aqueous and nonaqueous solvents. In anhydrous Me<sub>2</sub>SO, the reduction of Mn<sup>III</sup>EDTA<sup>-</sup> to Mn<sup>II</sup>EDTA<sup>2-</sup> by superoxide has been characterized by stopped-flow kinetic measurements, rapid-scan spectrophotometry, electron paramagnetic resonance, and cyclic voltammetry. The reaction is second order with a rate constant of  $5 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$  at 20 °C. The reaction of Mn<sup>III</sup>CyDTA<sup>-</sup> is analogous, having a rate constant of  $\sim 1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ . Addition of superoxide to a Mn<sup>II</sup>EDTA<sup>2-</sup> solution in Me<sub>2</sub>SO produces a green intermediate which changes to a yellow-brown final product. Although manganese aminocarboxylate complexes do not catalyze the dismutation of superoxide in aqueous solution, the complexes do react with superoxide. Mn<sup>III</sup>EDTA<sup>-</sup> is reduced to Mn<sup>II</sup>EDTA<sup>2-</sup> by superoxide in water. Mn<sup>II</sup>EDTA<sup>2-</sup> and superoxide interact to form a blue intermediate which dissociates to regenerate Mn<sup>II</sup>EDTA<sup>2-</sup> and the spontaneous dismutation products. The reactions of manganese aminocarboxylate complexes with hydrogen peroxide, sodium peroxide, and dioxygen in Me<sub>2</sub>SO are also discussed. The crystal and molecular structure of KMnEDTA·2H<sub>2</sub>O has been determined by single-crystal X-ray diffraction techniques by using 1684 unique reflections in the range  $2^\circ \leq 2\theta \leq 50^\circ$ . KMnEDTA·2H<sub>2</sub>O crystallizes in the orthorhombic space group *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, with  $a = 6.579$  (1) Å,  $b = 23.161$  (7) Å, and  $c = 10.054$  (3) Å. There are four molecules in the unit cell. Refinement of the nonhydrogen atoms by least-squares procedures gave a final  $R_1$  value of 0.065. In the complex anion, the manganese is coordinated by the hexadentate EDTA ligand producing a distorted octahedral MnN<sub>2</sub>O<sub>4</sub> geometry. The closest water molecule is greater than 4 Å away from the manganese. The potassium counterion is coordinated to six oxygens from carboxylate and water groups. Average Mn-N and Mn-O (two types) bond lengths are 2.22 (1), 2.03 (1), and 1.90 (1) Å. The presence of two short Mn-O bonds and four long Mn-O and Mn-N bonds is opposite to the distortions observed in the 3d<sup>9</sup> CuN<sub>2</sub>O<sub>4</sub> complexes, wherein the metal-oxygen bonds are generally longest, a result thought to be consistent with Jahn-Teller effects. The diffusion coefficients of chemically prepared O<sub>2</sub><sup>-</sup> solutions and of dioxygen in Me<sub>2</sub>SO have been determined by single-step chronoamperometry. These values,  $1.1 \times 10^{-5}$  and  $2.93 \times 10^{-5} \text{ cm}^2/\text{s}$ , respectively, are in good agreement with less accurate values reported previously by other workers. We also report the electrochemistry of the aforementioned manganese aminocarboxylate complexes.

### Introduction

The presence of the manganese(III) ion in biological redox reactions has become increasingly apparent in recent years. It is known that manganese ions are required for the photosynthetic evolution of dioxygen from green plant chloroplasts.<sup>1</sup> A manganese metalloenzyme, superoxide dismutase, is responsible for the disproportionation of superoxide anion to molecular oxygen and hydrogen peroxide in procaryotes and in the mitochondria of eucaryotes.<sup>2</sup> The results of circular dichroism,<sup>3</sup> electron spin resonance and magnetic susceptibility,<sup>4</sup> and electron absorption spectroscopy,<sup>2</sup> suggest that the enzyme contains manganese(III) in its resting state. The protein has also been the subject of nuclear magnetic resonance<sup>5</sup> and pulse radiolysis<sup>6,58</sup> examination of its mechanism of catalysis.

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Although a chemical model for superoxide dismutase is potentially useful, the problems encountered in studying various manganese(III) species have resulted in only a few investigations to date. Kono et al.<sup>8</sup> have reported that a manganese(II) pyrophosphate complex is oxidized to Mn(III) by superoxide although this result has recently been refuted by Bielski and Chan.<sup>9</sup> Di- and trivalent manganese quinolinol complexes have been proposed as a redox model for mitochondrial superoxide dismutase.<sup>10</sup> Valentine<sup>11</sup> has studied the reaction of superoxide with Mn<sup>III</sup>TPP (TPP = tetraphenylporphyrin) and has shown that Mn<sup>III</sup>TPP is reduced by superoxide. Our continued interest in the structural chemistry of manganese(III) species and the relationships between dynamic behavior and structure, particularly with Jahn-Teller and pseudo-Jahn-Teller systems,<sup>12</sup> has prompted these studies.

The reactions of manganese complexes with hydrogen peroxide and dioxygen have received considerable study. Mn<sup>III</sup>CyDTA<sup>-</sup> (CyDTA<sup>-</sup> = diaminocyclohexane-*N,N,N',N'*-tetraacetic acid) is reduced by hydrogen peroxide in acidic