Table 3. *Results of first-shell EXAFS fits of tetrakis-(imidazole)cobalt with a hexakis(imidazole)cobalt standard*

$\Delta\sigma^2$ = difference in Debye–Waller parameters (sample–standard). χ^2 = sum of residuals.

N	$R(\text{Å})$	$\Delta\sigma^2 \times 10^3 \ (\text{Å}^2)$	χ^2
Single-scatterer fit			
6·0 (1)	2·15 (1)	1·3 (1)	0·21
Two-scatterer fit*			
1·7 (2)	2·09 (1)	0	0·15
4·3 (2)	2·18 (1)	0	

* $\Delta\sigma^2$ fixed to 0.

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Dimethylbis(4,4,5,5-tetramethyl-2-thioxo-1,3,2-dioxaphospholane-2-thiolato)tin, (CH₃)₂Sn[SP(S)O₂C₂(CH₃)₄]₂

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Abstract. [Sn(C₆H₁₂O₂PS₂)₂(CH₃)₂], $M_r = 571\cdot3$, orthorhombic, *Pccn,* $a = 16\cdot830$ (9), $b = 11\cdot407$ (5), $c = 12\cdot829$ (9) Å, $V = 2463$ Å³, $Z = 4$, $D_x = 1\cdot541$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0\cdot7107$ Å, $\mu = 1\cdot51$ mm⁻¹, $F(000) = 1160$, $T = 291$ K, final $R = 0\cdot031$ for 1700 observed data [$I > 3\sigma(I)$]. Two anisobidentate dithiophosphate ligands and the two CH₃ groups [C(1)–Sn–C(1ⁱ) 133·9 (2)°] form a heavily distorted octahedron around Sn. The short Sn–S bonds [2·495 (1)Å] and the dative Sn–S bonds [3·130 (1) Å] are in the equatorial plane, each pair being *cis.*

Introduction. Knowledge of structures of organotin dithiophosphates is still rather limited and uncertainty exists mainly regarding the kind of bonding of the dithiophosphato group which is generally considered to act as a bidentate ligand. In fact, Ph₂Sn[SP(S)(OR)₂]₂ (R = isopropyl) consists of *trans* Ph₂Sn units octahedrally coordinated by symmetrically chelating S₂P(OR)₂ ligands (Molloy, Hossain, van der Helm, Zuckerman & Haiduc, 1980), but in Ph₃SnSP(S)(OEt)₂ the dithiophosphate ligand is monodentate (Molloy, Hossain, van der Helm, Zuckerman &

Haiduc, 1979) and in Ph₂Sn[SP(S)(OEt)₂]₂ apart from a normal covalent Sn–S(1) bond only an additional weak Sn–S(2) bond exists (Liebich & Tomassini, 1978). Of these compounds only Ph₂Sn[SP(S)(OR)₂]₂ (R = isopropyl) has short intermolecular sulfur–sulfur contact distances; it has been termed a 'virtual polymer' (Molloy, Hossain, van der Helm, Zuckerman & Haiduc, 1980).

In a recent paper, from spectroscopic data cyclic dithiophosphate ligands have been proposed to be chelating in diorganotin derivatives of Hdtpl [2-mercapto-4,4,5,5-tetramethyl-1,3,2-dioxaphospholane 2-sulfide, HSP(S)O₂C₂(CH₃)₄] (Rao, Srivastava, Mehrotra, Saraswat & Mason, 1984). We had independently studied analogous organometal dithiophosphates, in part the same, like Me₂Sn(dtpl)₂. From this compound we obtained single crystals and from X-ray diffractometer measurements we can report a more detailed structure.

Experimental. Me₂Sn(dtpl)₂ was obtained from Na(dtpl) (*in situ* from Hdtpl and Na in EtOH) and Me₂SnCl₂ in MeOH after separation of NaCl, con-

centrating the solution and solidifying the residue by adding petroleum ether; recrystallization from Et_2O gave white crystals, m.p. 472 K (lit. 468–469 K).

Clear crystals, $0.27 \times 0.38 \times 0.38$ mm. Data collection on a CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation using $\omega/2\theta$ scan technique and scan speed between 1.2 and $4.0°$ min^{-1} in ω; cell parameters determined from 21 reflexions in the range $20.3° < \theta < 24.1°$; 2533 intensities measured up to $(\sin\theta)/\lambda = 0.59$ Å^{-1}; $1° \leq \theta \leq 25°$, hkl: $h\,0\rightarrow13$, $k\,0\rightarrow15$, $l\,0\rightarrow20$; ω scans of reflexions 400, 040, 002 showed a width at half-height of $0.29°$; three standard reflexions were recorded every 3 h and showed only random deviations; intensities corrected for Lorentz and polarization effects and for absorption via ψ scans; max./min. transmission $1.00/0.87$; systematic absences $0kl$ $l = 2n + 1$, $h0l$ $l = 2n + 1$, $hk0$ $h + k = 2n + 1$ indicated space group $Pccn$ (No. 56); 1700 observed [466 unobserved, $I \leq 3\sigma(I)$] unique reflexions with $I > 3\sigma(I)$ were used in the refinements; structure was solved via Patterson function, ΔF syntheses and full-matrix least-squares refinement for 115 parameters with anisotropic temperature factors for non-H atoms and one common isotropic temperature factor for H atoms; H atoms were placed in calculated positions (C—H 0.95 Å); function minimized $\sum w(F_o - F_c)^2$, weights given as $w^{-1} = [\sigma^{-2}(I) + (0.1F_o^2)^2]^{1/2}$; complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); final R

$= 0.031$, $wR = 0.051$ and $S = 0.94$; $(\Delta/\sigma)_{max} = 0.04$ in the final cycle; largest peak in final ΔF synthesis ± 0.7 (2) e Å^{-3}; programs: Enraf–Nonius *Structure Determination Package* (Frenz, 1981), *ORTEP*II (Johnson, 1976), *PLUTO* (Motherwell & Clegg, 1978).

Discussion. The structure of the title compound is shown in Fig. 1 (*ORTEP*) and a stereoscopic view of the unit cell in Fig. 2 (*PLUTO*). Positional parameters of the non-H atoms and the equivalent values of the anisotropic temperature factors β_{ij} are given in Table 1,* bond lengths and angles in Table 2. The Sn atom of

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* Lists of structure factors, anisotropic thermal parameters, and a complete list of atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42818 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Fractional atomic coordinates and temperature factors* (Å$^2 \times 10^3$)

$$U_{eq} = \frac{1}{24\pi^2} \sum_i \sum_j \beta_{ij} \mathbf{a}_i \cdot \mathbf{a}_j.$$

	x	y	z	U_{eq}
Sn(1)	0.250	0.250	0.09013 (2)	41
S(1)	0.28232 (7)	0.11170 (8)	0.23468 (7)	59
S(2)	0.30777 (8)	0.0116 (1)	−0.00388 (8)	79
P(1)	0.33460 (7)	−0.00972 (8)	0.14134 (7)	50
O(1)	0.4276 (2)	−0.0121 (3)	0.1628 (2)	61
O(2)	0.3148 (2)	−0.1332 (2)	0.1924 (2)	56
C(1)	0.3582 (3)	0.3105 (4)	0.0256 (3)	66
C(2)	0.4490 (3)	−0.1101 (4)	0.2323 (4)	70
C(3)	0.3863 (3)	−0.2018 (3)	0.2127 (3)	67
C(4)	0.4425 (3)	−0.0649 (5)	0.3464 (4)	80
C(5)	0.5352 (3)	−0.1382 (6)	0.2102 (5)	104
C(6)	0.3708 (4)	−0.2893 (4)	0.2951 (4)	104
C(7)	0.4047 (5)	−0.2685 (5)	0.1084 (5)	125

Table 2. *Bond lengths* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

|			
Sn(1)—S(1)	2.495 (1)	C(2)—O(1)	1.474 (5)
Sn(1)—S(2)	3.130 (1)	C(2)—C(3)	1.507 (6)
Sn(1)—C(1)	2.116 (4)	C(2)—C(4)	1.556 (7)
P(1)—S(1)	2.031 (1)	C(2)—C(5)	1.512 (6)
P(1)—S(2)	1.932 (1)	C(3)—O(2)	1.457 (5)
P(1)—O(1)	1.589 (3)	C(3)—C(6)	1.477 (7)
P(1)—O(2)	1.589 (3)	C(3)—C(7)	1.571 (7)
C(1)—Sn(1)—C(1^i)	133.9 (2)	O(1)—P(1)—O(2)	96.9 (1)
C(1)—Sn(1)—S(1)	108.0 (1)	P(1)—O(1)—C(2)	111.0 (2)
C(1)—Sn(1)—S(1^i)	105.8 (1)	P(1)—O(2)—C(3)	112.1 (2)
C(1)—Sn(1)—S(2)	82.3 (1)	O(1)—C(2)—C(3)	104.7 (3)
C(1)—Sn(1)—S(2^i)	80.4 (1)	O(1)—C(2)—C(4)	107.5 (3)
S(1)—Sn(1)—S(1^i)	83.97 (3)	O(1)—C(2)—C(5)	106.4 (4)
S(1)—Sn(1)—S(2)	70.68 (3)	C(3)—C(2)—C(4)	109.7 (4)
S(1)—Sn(1)—S(2^i)	154.64 (3)	C(3)—C(2)—C(5)	119.6 (4)
S(2)—Sn(1)—S(2^i)	134.68 (3)	C(4)—C(2)—C(5)	108.3 (4)
Sn(1)—S(1)—P(1)	95.01 (4)	O(2)—C(3)—C(2)	103.6 (3)
Sn(1)—S(2)—P(1)	79.07 (4)	O(2)—C(3)—C(6)	110.2 (4)
S(1)—P(1)—S(2)	112.43 (6)	O(2)—C(3)—C(7)	105.7 (4)
S(1)—P(1)—O(1)	109.7 (1)	C(2)—C(3)—C(6)	118.3 (4)
S(1)—P(1)—O(2)	105.7 (1)	C(2)—C(3)—C(7)	109.8 (4)
S(2)—P(1)—O(1)	113.5 (1)	C(6)—C(3)—C(7)	108.5 (4)
S(2)—P(1)—O(2)	117.4 (1)		
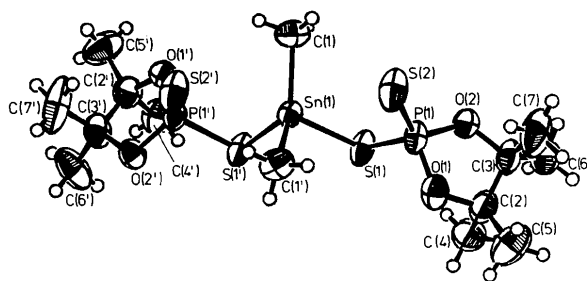
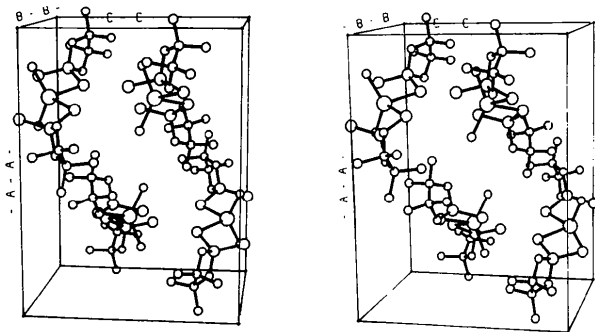Fig. 1. General view of the molecule [symmetry code: (i) $\frac{1}{2} - x$, $\frac{1}{2} - y, z$].

Fig. 2. Stereoscopic view of the unit cell.

the monomeric molecule resides on the special position c of space group Pccn (No. 56) and therefore the molecule has a twofold symmetry axis lying along the c axis of the unit cell.

The Sn—S(1) bond length corresponds to that of 2·482 (2) Å in $Me_2Sn[SP(S)Me_2]_2$ (Molloy, Hossain, van der Helm, Zuckerman & Mullins, 1981) and to those of 2·49 (1) and 2·481 (8) Å, respectively, in $Ph_2Sn[SP(S)(OEt)_2]_2$ (Liebich & Tomassini, 1978). In these compounds the ligands are unsymmetrically chelating, Sn being in a heavily distorted environment. A somewhat shorter bond of 2·4582 (9) Å was found in $Ph_3SnSP(S)(OEt)_2$, which contains tetrahedral tin (Molloy et al., 1979), while in $Ph_2Sn[SP(S)(OR)_2]_2$ ($R = i-C_3H_7$) with octahedral tin the Sn—S bonds with lengths of 2·689 (1) and 2·678 (1) Å are appreciably longer (Molloy et al., 1980). The Sn—S(2) bond length of 3·130 (1) Å in the present compound is well below the sum of the van der Waals radii of Sn and S (2·16 and 1·80 Å) and is shorter than the analogous bonds in $Ph_2Sn[SP(S)(OEt)_2]_2$ of 3·20 (1) and 3·23 (1) Å, respectively (Liebich & Tomassini, 1978). Considering the angles at tin, mainly $C(1)—Sn—C(1^i)$ 133·9 (2)°, being appreciably greater than tetrahedral, one has to assume weak intramolecular interaction between Sn and S(2), extending the primary tetrahedron around Sn [formed by C(1), $C(1^i)$, S(1), $S(1^i)$] to a heavily distorted octahedron. The two types of Sn—S bonds are each in cis positions. In accordance with this view of aniso-bidentate chelating dithiophosphate ligands the bond distances P—S(1) and P—S(2) are distinctly different.

They lie in the ranges 1·85 to 1·95 Å and 1·99 to 2·19 Å, respectively, which have been found in dithiophosphate complexes and which can be ascribed to P—S bonds with predominant double- and single-bond characters, respectively (Molloy et al., 1981, and references therein). Between the molecules there are no interactions exceeding van der Waals forces.

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Structure of Bis[tetraphenylarsonium] Bis(1,2-dithiooxalato-S,S')zincate(II)

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Abstract. $[As(C_6H_5)_4]_2[Zn(C_2O_2S_2)_2]$, $M_r = 1072·4$, triclinic, $P\bar{1}$, $a = 10·427$ (1), $b = 12·654$ (1), $c = 18·639$ (2) Å, $\alpha = 94·55$ (1), $\beta = 97·27$ (1), $\gamma = 81·48$ (1)°, $V = 2408·0$ Å^3, $Z = 2$, $D_m = 1·484$ (by flotation), $D_x = 1·479$ Mg m^{-3}, $\lambda(Mo\,K\alpha) = 0·71069$ Å, $\mu = 2·092$ mm^{-1}, $F(000) = 1088$, $T = 293$ (1) K, final $R = 0·044$ for 4693 observed reflections. The central Zn ion is tetrahedrally coordinated by the four sulfur atoms from two dithiooxalate ligands with Zn—S distances in the range 2·304 (2) to 2·334 (2) Å. The dithiooxalate ligands are not planar, having torsion angles along the C—C axes of 31·7 (2)° for S(1)—C(1)—C(2)—S(2) and 43·3 (2)° for S(3)—C(3)—C(4)—S(4), respectively.

Introduction. The major portion of structural work on dithiooxalate (dto) complexes has been done with compounds containing transition-metal central ions in