

Polymeric [μ_3 -(*N*-phosphonomethyl)-glycinato]tris(tributyltin)

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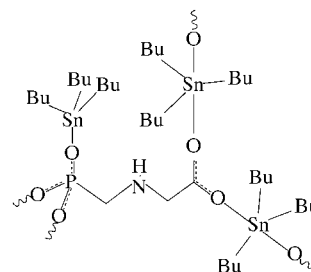
N-(Phosphonomethyl)glycine, glyphosate, reacts with bis(tributyltin) oxide to form a ligand–tin (1:3) complex in which all five O atoms are coordinated to tin. The complex, $[\text{Sn}_3(\text{C}_4\text{H}_9)_9(\text{C}_3\text{H}_5\text{NO}_5\text{P})]$, is polymeric, with the glyphosate and two tributyltin groups forming a two-dimensional network and with the third Sn atom alternately above and below the plane of the net. The Sn atoms in the network have a trigonal-bipyramidal coordination, with O atoms in the axial positions and C atoms in the equatorial positions; the pendant tributyltin group is tetrahedrally coordinated to one O atom and to three butyl groups. Sn–O distances vary from 2.030 (3) to 2.408 (3) Å. The Sn–O distances for O atoms *trans* to carboxylate groups are shorter than those *trans* to phosphonate groups and $d_{\text{Sn}-\text{O}}$ decreases with increasing $d_{\text{C/P}-\text{O}}$ ($\Delta_{\text{Sn}-\text{O}} \simeq -4.6\Delta_{\text{C/P}-\text{O}}$). The amino N atom in the ligand is neither protonated nor involved in coordination to the Sn atoms.

Comment

Organotin(IV) compounds have been used as marine anti-fouling agents, agricultural fungicides, miticides and surface disinfectants (Davies & Smith, 1982). An interesting development is the synthesis of organotin compounds in which the organotin moiety is bonded to ligands which exhibit biocidal activity. One such ligand system is the widely used commercial herbicide glyphosate, *N*-(phosphonomethyl)glycine, which forms complexes in which the carboxylate O atoms, the phosphonate O atoms or the N atom can coordinate to a metal atom (Appleton *et al.*, 1994; Franz *et al.*, 1997). The incorporation of organotin and phosphorus portions in one molecule leads to the possibility that each fragment may make a contribution to the overall biocidal activity of the compound. We report here the synthesis and crystal structure of the glyphosphate complex with bis(tributyltin) oxide, (I).

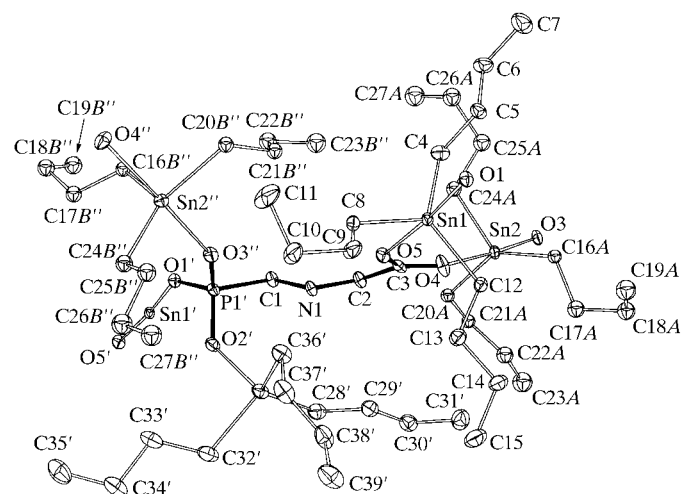
Regardless of the proportions of glyphosate and bis(tributyltin)oxide used, we obtained a product which was shown

by elemental microanalysis to be the 3:1 (tin–ligand) adduct $(n\text{-Bu}_3\text{Sn})_3(\text{OCOCH}_2\text{NHCH}_2\text{PO}_3)$. The structure determination showed all five O atoms of the glyphosate to be bonded to Sn atoms (Fig. 1) to give a polymeric structure. The glyphosate moiety, together with Sn1 and Sn2, forms a two-dimensional network, with the Sn3 atoms situated alternately above and below the plane of the network (Fig. 2). Sn1 and Sn2 are pentacoordinated to two O atoms and to three *n*-butyl groups at the corners of a trigonal bipyramid, with the O atoms



(I)

in the axial positions, whereas Sn3 is tetrahedrally coordinated to one O atom and to three *n*-butyl groups. The *n*-butyl groups around Sn2 are disordered. There is a wide spread in the Sn–O bond distances, 2.030 (3) to 2.408 (3) Å, the P–O distances are in the range 1.508 (3)–1.543 (3) Å and the C–O distances are 1.239 (4) and 1.263 (4) Å. The Sn–O distances for O atoms *trans* to carboxylate groups are shorter than those *trans* to phosphonate groups and $d_{\text{Sn}-\text{O}}$ decreases with increasing $d_{\text{C/P}-\text{O}}$ ($\Delta_{\text{Sn}-\text{O}} \simeq -4.6\Delta_{\text{C/P}-\text{O}}$). Only one H atom was observed on the N atom, in agreement with the observation of an NH stretching frequency of 3300 cm^{-1} together with the absence of $\nu(\text{NH})$ bands. The intramolecular contacts $\text{N1}\cdots\text{O5}(-1-x, \frac{1}{2}+y, 1-z)$ [2.643 (4) Å] and $\text{N1}\cdots\text{O3-}$


Figure 1

View of the title adduct showing the labelling of the non-H atoms. Displacement ellipsoids are shown at 50% probability levels. The disordered butyl groups C16A–C27A are shown bonded to Sn2, while C16B–C27B are shown bonded to Sn2ⁱⁱ. [Symmetry codes: (i) $x-1, y, z$; (ii) $x-1, \frac{1}{2}+y, 1-z$.]

$(-1-x, \frac{1}{2}+y, 1-z)$ [3.018 (4) Å] can be attributed to hydrogen bonding. The backbone of the glyphosate group is a non-planar zigzag chain; O1–P1–C1–N1–C2 and N1–C2–C3–O4 form nearly planar groups with the C1–N1–C2–C3 torsion angle being $-154.1(3)^\circ$. Comparison of the IR spectrum with that observed by Rajendram & Hoggard (1994) for glyphosate shows that the symmetric and asymmetric C–O stretching vibrations are lowered on bonding from 1734 to 1578 cm^{-1} and from 1485 to 1404 cm^{-1} , respectively. Similarly, the symmetric and asymmetric P–O stretching frequencies and the O–P–O bending–stretching frequencies are lowered from 1160, 917 and 1095 cm^{-1} to 1138, 877 and 1065 cm^{-1} , respectively. The sharp $\nu(\text{N–H})$ stretching band observed at 3300 cm^{-1} (3230 cm^{-1} for glyphosate) and the absence of $\nu(^+\text{NH})$ indicate that the amino N atom in the ligand is neither protonated nor involved in coordination to the Sn atoms. $\Delta\nu = \nu_{\text{asym}}(\text{OCO}) - \nu_{\text{sym}}(\text{OCO})$ is expected to be about 200 cm^{-1} for a bridging of the chelating carboxyl group (Deacon & Phillips, 1980; Micera *et al.*, 1984), the value found here is 174 cm^{-1} .

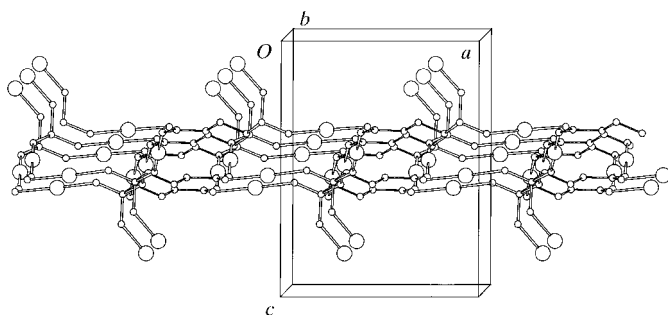


Figure 2
Packing diagram showing part of the two-dimensional network. Sn atoms are represented by large circles and the butyl groups have been omitted.

Experimental

Bis(tri-*n*-butyltin) oxide was purchased from the Aldrich Chemical Co. and used without further purification. *N*-(Phosphonomethyl)glycine was isolated by acidifying a solution of commercial 'Roundup' with concentrated HCl and allowing the free acid to crystallize. IR spectra were recorded as KBr pellets on a Perkin–Elmer Model 1725 FT–IR instrument. The elemental analyses were performed at the School of Chemical Sciences, Universiti Sains Malaysia, Penang. To a stirred solution of glyphosate (0.85 g, 5 mmol) in 95% ethanol (50 ml) was added dicyclohexylamine (1 ml) followed by bis(tri-*n*-butyltin) oxide (4.5 g, 7.5 mmol). After refluxing for 3–4 h, the mixture was concentrated to *ca* 10 ml with a rotary evaporator before allowing it to stand in a freezer overnight. A white solid (3.1 g, 60%) was obtained on filtration. Recrystallization from methanol afforded crystals (m.p. 359–361 K) of (I) which were suitable for X-ray crystallographic studies. Elemental analysis, calculated (found) for $\text{C}_{39}\text{H}_{86}\text{NO}_5\text{PSn}_3$: C 45.20 (45.23), H 8.38 (8.43), N 1.35% (1.18%). IR (KBr, ν , cm^{-1}): 1578 (*s*, $\text{CO}_{2\text{asym}}$), 1404 ($\text{CO}_{2\text{sym}}$), 1138 ($\text{PO}_{3\text{asym}}$), 877 ($\text{PO}_{3\text{sym}}$), 1065 (O–P–O bending–stretching), 3300 (NH stretch).

Crystal data

$[\text{Sn}_3(\text{C}_4\text{H}_9)_9(\text{C}_3\text{H}_5\text{NO}_5\text{P})]$
 $M_r = 1036.20$
Monoclinic, $P2_1$
 $a = 10.2144(7)$ Å
 $b = 18.018(1)$ Å
 $c = 13.1304(9)$ Å
 $\beta = 90.177(1)^\circ$
 $V = 2416.6(2)$ Å³
 $Z = 2$

$D_x = 1.424$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6517 reflections
 $\theta = 1.9\text{--}29.8^\circ$
 $\mu = 1.607$ mm^{-1}
 $T = 120$ K
Needle, colourless
 $0.47 \times 0.16 \times 0.15$ mm

Data collection

Siemens SMART CCD diffractometer
 ω rotation scans with narrow frames
Absorption correction: by integration (*XPREP*; Siemens, 1995)
 $T_{\text{min}} = 0.501$, $T_{\text{max}} = 0.799$
28299 measured reflections

13624 independent reflections
12628 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.032$
 $\theta_{\text{max}} = 29.8^\circ$
 $h = -14 \rightarrow 14$
 $k = -25 \rightarrow 25$
 $l = -18 \rightarrow 18$

Refinement

Refinement on F^2
 $R(F) = 0.029$
 $wR(F^2) = 0.071$
 $S = 1.122$
12628 reflections
431 parameters
H-atom parameters constrained
 $w = 1/[\sigma_{\text{calc}}(F^2) + 0.03F^2]^2$
 $(\Delta/\sigma)_{\text{max}} = 0.002$

$\Delta\rho_{\text{max}} = 2.2(1)$ e Å⁻³
 $\Delta\rho_{\text{min}} = -1.1(1)$ e Å⁻³
Extinction correction: *B–C* type 1
Lorentzian isotropic (Becker & Coppens, 1974)
Extinction coefficient: 56 (6)
Absolute structure: Rogers (1981)
Rogers parameter = 0.73 (3)

Table 1

Selected bond lengths (Å).

Sn1–C4	2.144 (4)	Sn2–C20B	2.095 (7)
Sn1–C8	2.135 (4)	Sn2–C24B	2.149 (8)
Sn1–C12	2.142 (3)	Sn2–O3	2.160 (3)
Sn1–O1	2.205 (2)	Sn2–O4	2.408 (3)
Sn1–O5	2.292 (2)	Sn3–C28	2.136 (5)
Sn2–C16A	2.093 (6)	Sn3–C32	2.147 (5)
Sn2–C20A	2.217 (8)	Sn3–C36	2.134 (4)
Sn2–C24A	2.124 (8)	Sn3–O2	2.030 (3)
Sn2–C16B	2.174 (7)		

Table 2

N–H···O contacts (Å, °).

<i>D</i> –H··· <i>A</i>	<i>D</i> –H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> –H··· <i>A</i>
N1–HN1···O5	0.95	2.21	2.643 (4)	107
N1–HN1···O3 ⁱ	0.95	2.60	3.018 (4)	107

Symmetry code: (i) $-1-x, y-\frac{1}{2}, 1-z$.

The butyl groups coordinated to Sn2 were disordered and were modelled by pairs of isotropic atoms with occupation 0.5. The H atoms were constrained to have C–H = 0.95 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the atom to which they were attached. The largest peaks and holes in the final difference map were close to the Sn atoms.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structure: *SIR97* (Casarano *et al.*, 1996) and *KRYSTAL* (Hazell, 1995); program(s) used to refine structure: modified *ORFLS* (Busing *et al.*, 1962) and *KRYSTAL*; molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *KRYSTAL*; software used to prepare material for publication: *KRYSTAL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1061). Services for accessing these data are described at the back of the journal.

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