Table 2. *Selected geometric parameters* (Å, °)

Pb1—C7	2.183 (8)	C1—C6	1.361 (13)
Pb1—C13	2.196 (8)	C19—C20	1.388 (12)
Pb1—C1	2.213 (10)	C19—C21	1.395 (12)
Pb1—O1	2.659 (6)	C20—C21	1.368 (11)
Pb1—Br1	2.696 (1)	C20—C22	1.448 (12)
O1—C19	1.232 (10)	C21—C28	1.454 (11)
C7—Pb1—C13	122.5 (3)	C14—C13—Pb1	119.2 (7)
C7—Pb1—C1	115.9 (3)	C18—C13—Pb1	120.4 (6)
C13—Pb1—C1	116.4 (3)	O1—C19—C20	150.3 (9)
C7—Pb1—O1	81.4 (3)	O1—C19—C21	150.7 (9)
C13—Pb1—O1	79.8 (2)	C20—C19—C21	58.9 (6)
C1—Pb1—O1	86.2 (3)	C21—C20—C19	60.8 (6)
C7—Pb1—Br1	97.9 (2)	C21—C20—C22	148.0 (9)
C13—Pb1—Br1	95.7 (2)	C19—C20—C22	151.0 (9)
C1—Pb1—Br1	99.3 (3)	C20—C21—C19	60.3 (6)
O1—Pb1—Br1	174.10 (14)	C20—C21—C28	150.7 (9)
C19—O1—Pb1	132.7 (5)	C19—C21—C28	148.7 (9)
C6—C1—C2	118.5 (11)	C23—C22—C27	118.2 (9)
C6—C1—Pb1	119.5 (7)	C23—C22—C20	123.3 (9)
C2—C1—Pb1	122.1 (9)	C27—C22—C20	118.5 (9)
C8—C7—C12	119.0 (8)	C33—C28—C29	119.5 (9)
C8—C7—Pb1	120.5 (7)	C33—C28—C21	119.3 (9)
C12—C7—Pb1	120.4 (7)	C29—C28—C21	121.2 (9)
C14—C13—C18	120.4 (8)		

H atoms were generated and allowed to ride on their parent C atoms, with $U(H) = 1.5U_{eq}(C)$.

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC*. Data reduction: *Xtal*3.0 (Hall & Stewart, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Bis(tetraphenylphosphonium) Tetraazido-dimethylstannate(IV)

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Abstract

The structure of $[(C_6H_5)_4P]_2[Sn(N_3)_4(CH_3)_2]$ is ionic. In the anion the Sn atom lies at a centre of symmetry and has hexacoordination in which the angles differ slightly but significantly from those of exact octahedral symmetry. The difference between the two unique Sn—N distances is marginal but significant. The azide groups are linear and inclined at approximately 120° to the Sn—N direction. The cation is tetrahedral around the P atom but the orientation of the phenyl groups is unsymmetrical.

Comment

This investigation of the title compound, (I), is part of a study of the octahedral complexes of Sn^{IV} (*e.g.* Dillon, Halfpenny & Marshall, 1983, 1985). It also affords an opportunity to examine the configuration and symmetry of the azide group when coordinated in an organometallic complex. The structure is clearly ionic, as expected,

(I)
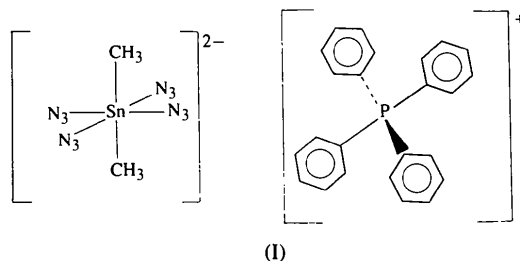
and the two ions are shown separately in the *SNOOPI* (Davies, 1983) diagrams of Fig. 1. The two methyl groups are *trans* – a necessary consequence of the Sn atom lying on a centre of symmetry. The two Sn—N

distances differ only marginally but significantly. As can be seen in Table 2, the bond angles around the Sn atom deviate slightly from exact octahedral, the differences being significant. Another way of looking at this is to note that the angle between the C—Sn—C^i direction and the normal to the plane of the four coordinated N atoms, N1, N4, $N1^i$ and $N4^i$ (planar because of the centre of symmetry) is $3.6\,(2)°$ [symmetry code: (i) $-x$, $-y$, $-z$]. In that plane the N1—Sn—N4 angle is $88.8\,(1)$ (Table 2) rather than 90°. Although the azide groups are positioned alternately up and down relative to the plane of N1, N4, $N1^i$ and $N4^i$, the symmetry is only very approximately fourfold alternating as the angles made by the groups N1–N3 and N4–N6 to the plane are $48.2\,(2)$ and $30.9\,(2)°$, respectively. Within the azide groups, which are essentially linear to within the limits of accuracy, the distances are not quite symmetrical (Table 2). In both cases the longer N—N distance involves the N atom coordinated to the Sn atom, as would be expected from simple valence theory. Both azide groups are coordinated with Sn—N—N angles

close to 120°, indicating involvement of the sp^2 orbital. Only one other organometallic complex of Sn involving the azide group has been reported (Allman, Hohlfeld, Olejnik & Lorberth, 1981). Unfortunately that work is considerably less accurate, making comparison difficult, but the Sn—N distances are both greater [2.44 (2) and 2.61 (2) Å]. Comparable organometallic structures involving azide groups are uncommon, but Restivo, Ferguson, Hay & Piplani (1978) found similar azide geometry in a cobalt(III) complex. There was found to be hydrogen bonding with the terminal azide N atom as acceptor in both of those structures. In the present structure there are no close contacts between the ions, the shortest approach being N6$\cdots$H2 of 2.55 Å. In the cation, while the bonds around the P atom are tetrahedral, the phenyl groups show no symmetry in their relative orientation.

Experimental

The crystals were supplied by Dr K. B. Dillon and were suitable without further recrystallization.

Crystal data

$(C_{24}H_{20}P)_2[Sn(N_3)_4(CH_3)_2]$	Mo $K\alpha$ radiation
$M_r = 995.59$	$\lambda = 0.7107$ Å
Triclinic	Cell parameters from 15
$P\bar{1}$	reflections
$a = 12.38\,(1)$ Å	$\theta = 5$–25°
$b = 10.11\,(1)$ Å	$\mu = 0.592$ mm^{-1}
$c = 11.44\,(1)$ Å	$T = 286$ K
$\alpha = 123.2\,(1)°$	Oblique bipyramid
$\beta = 77.9\,(1)°$	$1.0 \times 0.3 \times 0.3$ mm
$\gamma = 100.0\,(1)°$	Pale yellow
$V = 1168.6\,(10)$ Å^3	
$Z = 1$	
$D_x = 1.414$ Mg m^{-3}	

Data collection

Stoe Stadi-2 two-circle diffractometer	$R_{int} = 0.048$
Variable ω scans, $2\theta'$ fixed	$\theta_{max} = 30.0°$
Absorption correction:	$h = -14 \rightarrow 15$
by integration from	$k = -11 \rightarrow 10$
crystal shape (SHELX76;	$l = 0 \rightarrow 9$
Sheldrick, 1976)	1 standard reflection per
$T_{min} = 0.748$, $T_{max} =$	layer monitored every
0.857	20 reflections
4059 measured reflections	intensity decay: 5%
3833 independent reflections	maximum, corrected
3451 observed reflections	by interpolation
[$I > 3\sigma(I)$]	

Refinement

Refinement on F	$(\Delta/\sigma)_{max} = 0.003$
$R = 0.038$	$\Delta\rho_{max} = 0.43$ e Å^{-3}
$wR = 0.038$	$\Delta\rho_{min} = -0.36$ e Å^{-3}
$S = 0.427$	Extinction correction: none
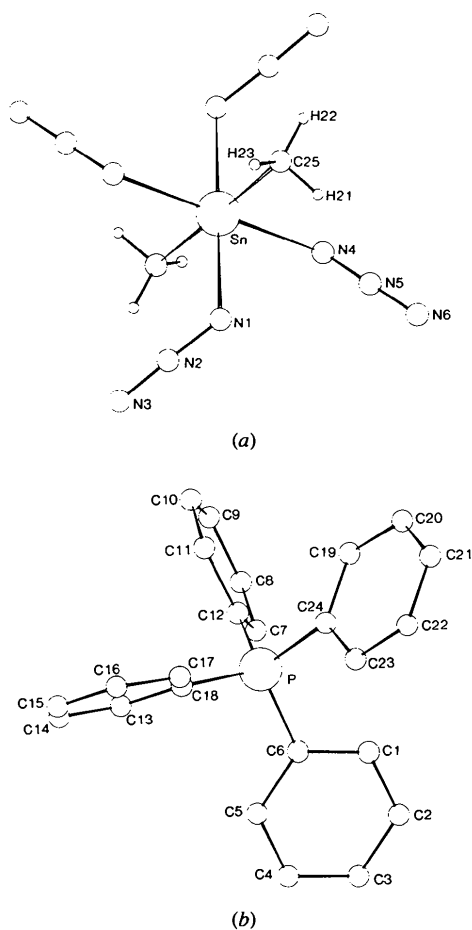
Fig. 1. (a) The centrosymmetric $[(CH_3)_2Sn(N_3)_4]^{2-}$ anion. (b) The $P(C_6H_5)_4^+$ cation.

$(C_{24}H_{20}P)_2[Sn(N_3)_4(CH_3)_2]$

3451 reflections
326 parameters (2 blocks)
Only H-atom U's refined
Unit weights applied

Atomic scattering factors from *SHELX*76 (Sheldrick, 1976)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* ($Å^2$)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
P	0.3226 (1)	0.6102 (1)	0.4064 (1)	0.042 (1)
Sn	0	0	0	0.045 (1)
N1	0.1633 (3)	0.1346 (4)	0.0804 (4)	0.059 (4)
N2	0.2212 (3)	0.0745 (4)	0.1063 (4)	0.056 (3)
N3	0.2790 (3)	0.0206 (5)	0.1315 (5)	0.088 (5)
N4	0.0572 (3)	0.0088 (4)	−0.1958 (4)	0.060 (3)
N5	0.1080 (3)	0.1213 (5)	−0.1909 (4)	0.062 (4)
N6	0.1584 (4)	0.2288 (6)	−0.1898 (6)	0.099 (6)
C1	0.2757 (3)	0.4892 (5)	0.5717 (5)	0.057 (4)
C2	0.2148 (4)	0.3987 (5)	0.6214 (5)	0.064 (5)
C3	0.1186 (3)	0.3138 (5)	0.5694 (5)	0.061 (4)
C4	0.0821 (3)	0.3174 (5)	0.4687 (5)	0.065 (4)
C5	0.1422 (3)	0.4092 (5)	0.4187 (4)	0.055 (4)
C6	0.2397 (3)	0.4950 (4)	0.4707 (4)	0.043 (3)
C7	0.4511 (3)	0.3502 (4)	0.2405 (4)	0.048 (3)
C8	0.5409 (3)	0.2729 (5)	0.1420 (5)	0.060 (4)
C9	0.6101 (3)	0.3429 (5)	0.0781 (4)	0.060 (4)
C10	0.5901 (3)	0.4891 (6)	0.1095 (5)	0.065 (4)
C11	0.4999 (3)	0.5661 (5)	0.2053 (5)	0.059 (4)
C12	0.4308 (3)	0.4974 (4)	0.2725 (4)	0.044 (3)
C13	0.2092 (3)	0.5514 (5)	0.2039 (4)	0.055 (4)
C14	0.1494 (3)	0.5923 (6)	0.1429 (5)	0.066 (5)
C15	0.1245 (3)	0.7480 (7)	0.2083 (6)	0.070 (5)
C16	0.1562 (3)	0.8620 (6)	0.3352 (6)	0.070 (5)
C17	0.2144 (3)	0.8239 (5)	0.4004 (5)	0.058 (4)
C18	0.2419 (3)	0.6676 (4)	0.3335 (4)	0.046 (4)
C19	0.5002 (3)	0.8102 (5)	0.5415 (5)	0.060 (4)
C20	0.5451 (4)	0.9383 (6)	0.6555 (6)	0.076 (6)
C21	0.4769 (5)	1.0373 (6)	0.7727 (6)	0.082 (6)
C22	0.3629 (5)	1.0098 (5)	0.7813 (5)	0.072 (5)
C23	0.3164 (3)	0.8801 (5)	0.6694 (4)	0.060 (4)
C24	0.3854 (3)	0.7804 (4)	0.5482 (4)	0.046 (3)
C25	−0.0663 (4)	0.2255 (5)	0.1089 (6)	0.061 (5)

Table 2. *Selected geometric parameters* (Å, °)

C6—P	1.777 (5)	C25—Sn	2.130 (5)
C12—P	1.789 (3)	N2—N1	1.187 (7)
C18—P	1.764 (6)	N3—N2	1.134 (8)
C24—P	1.789 (3)	N5—N4	1.179 (6)
N1—Sn	2.288 (3)	N6—N5	1.150 (8)
N4—Sn	2.250 (5)		

C6—P—C12	110.0 (2)	N1—Sn—C25	86.8 (2)
C6—P—C18	110.6 (2)	N4—Sn—C25	91.6 (2)
C6—P—C24	108.9 (2)	Sn—N1—N2	118.3 (3)
C12—P—C18	108.6 (2)	Sn—N4—N5	121.3 (3)
C12—P—C24	108.1 (2)	N1—N2—N3	177.9 (4)
C18—P—C24	110.7 (2)	N4—N5—N6	178.2 (5)
N1—Sn—N4	88.8 (1)		

Intensity measurements were made with a two-circle diffractometer employing equi-inclination Weissenberg geometry. The angle θ' referred to above is the projection of θ onto the equatorial plane. The crystal was set to rotate around the c axis. A separate standard is required for each layer measured; at a late stage, interlayer scale factors were refined and thereafter fixed. The structure was solved by the use of Patterson and difference syntheses. During refinement, H atoms were included at calculated positions with individually refined values of U_{iso}. The standard reduced cell [$a = 10.11$, $b = 10.32$, $c = 12.38$ Å, $\alpha = 93.5$, $\beta = 100.0$, $\gamma = 111.9°$] can be obtained using the reorientation matrix $0\bar{1}0/011/\bar{1}00$.

Data collection: Stoe Stadi-2 diffractometer software. Data reduction: *DATR* (Small, 1977). Program(s) used to solve structure: *SHELX*76 (Sheldrick, 1976). Program(s) used to refine structure: *SHELX*76. Molecular graphics: *SNOOPI* (Davies, 1983).

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