2820 reflections
208 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0501P)^2$
$+ 1.4214P]$
where $P = (F_o^2 + 2F_c^2)/3)$

Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. *Selected geometric parameters (Å, °)*

Sb—Cl(1)	2.460 (3)	P—O	1.492 (3)
Sb—Cl(2)	2.345 (3)	P—N(1)	1.621 (4)
Sb—Cl(3)	2.348 (3)	P—N(2)	1.613 (4)
Sb—O	2.396 (4)	P—Cl(4)	2.037 (3)
Cl(2)—Sb—Cl(3)	95.85 (10)	O—P—N(1)	117.4 (2)
Cl(2)—Sb—O	83.78 (12)	O—P—Cl(4)	106.3 (2)
Cl(3)—Sb—O	83.89 (13)	N(2)—P—Cl(4)	108.9 (2)
Cl(2)—Sb—Cl(1)	92.42 (11)	N(2)—P—N(1)	108.8 (2)
Cl(3)—Sb—Cl(1)	92.10 (12)	N(1)—P—Cl(4)	104.6 (2)
Cl(1)—Sb—O	174.15 (7)	P—O—Sb	133.4 (2)
O—P—N(2)	110.4 (2)		

X-ray data for (2) were collected after inserting the crystal into a Lindemann capillary. The structure was solved by conventional methods (*SHELX*86; Sheldrick, 1990) and refined by full-matrix least-squares methods (*SHELXL*93; Sheldrick, 1993). H atoms bonded to C atoms were placed in calculated positions using a riding model. They were assigned isotropic displacement parameters of 1.2 times that of the parent C atom; all non-H atoms were refined anisotropically.

Data collection: *DIF*4 (Stoe & Cie, 1988*a*). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1988*b*). Molecular graphics: *ORTEP* (Johnson, 1965).

We thank the Council of Scientific and Industrial Research (India) for a fellowship (MV). Generous donation of equipment from the AvH Foundation (Germany) is also acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: DE1057). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1791–1794

Piperidinium Diazidotriphenylstannate and Quinuclidinium Diazidotriphenylstannate

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(*Received 4 February 1997; accepted 27 June 1997*)

Abstract

Two triphenyltin–azide adducts with cyclic aliphatic amines are shown by X-ray diffraction to be $[LH][(C_6H_5)_3Sn(N_3)_2]$, where for (I), L = piperidine ($C_5H_{11}N$), and for (II), L = quinuclidine ($C_7H_{13}N$). The anions have quasi-trigonal-bipyramidal symmetry, with the azide groups occupying axial positions. In each case, the azide groups are non-equivalent due to one of them hydrogen bonding with the cation. In (I), the NH_2 of the cation hydrogen bonds with azides of adjacent anions forming chains through the lattice. For (II), the asymmetric unit has two cations and anions. One cation singly hydrogen bonds to an azide group of one anion, while the other cation forms a bifurcated hydrogen bond linked to azide groups on the two different anions. The cations have their usual geometries, the piperidinium ion having the expected chair conformation.

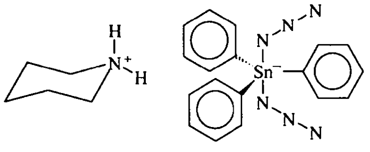
Comment

Following our earlier reports on adducts (1/1) of triphenyltin pseudo-halides with various O- and N-donor ligands, with particular reference to their Raman and far-IR spectra (Wharf, Piehler, Sailofsky, Onyszchuk & Simard, 1987, and references therein), we have recently completed a similar study on triphenyltin azide and its adducts (1/1) with a range of O- and N-donor ligands (Wharf, Wojtowski, Lebuis, Bowes & Onyszchuk, 1997). While many amines did form 1/1 adducts, some aliphatic amines [L = morpholine, triethylamine, 1,2-bis(dimethylamino)ethane, piperidine, quinuclidine] gave products that appeared from elemental analysis to contain two azide groups which, together with IR data [$\sim$2050 cm^{-1}, $\nu_{as}(N_3)$; $\sim$3400 cm^{-1}, ν(N—H)], suggested these compounds were perhaps $[LH^+][Ph_3Sn(N_3)_2^-]$, analogues of the $(CH_3)_4N^+$ and $(C_6H_5)_4As^+$ salts with the same anion [IR (cm^{-1}); $\nu_{as}(N_3)$, 2050*s*, 2070*sh* and 2040*s*, 2055*s*, respectively] reported by Barbieri, Bertazzi & Tomarchio (1975). In the same way, the compound having

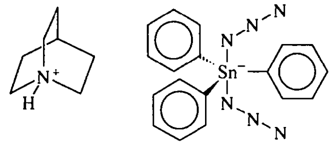
Acta Crystallographica Section C
ISSN 0108-2701 © 1997

the formula $L_2Ph_3SnNCS.HNCS$ [L = 1-(salicylideneimino)-2-methoxybenzene] was found by analysis to be $[L_2H][Ph_3Sn(NCS)_2]$ (Charland, Gabe, Khoo & Smith, 1989). The few tin systems with monodentate azide groups whose structures are given in the literature include $[CpFe(CO)_2]_2Sn(N_3)_2$ (Hampden-Smith, Lei & Duesler, 1990) and $^tBu_nSn(N_3)_{4-n}$ (Hänssgen, Jansen, Leben & Oster, 1995), as well as the anions hexaazidostannate (Fenske, Dörner & Dehnicke, 1983) and tetraazidodimethylstannate (Halfpenny, 1995).

An X-ray diffraction study of crystals of the two title compounds, (I) and (II), shows that both are indeed $[LH^+][Ph_3Sn(N_3)_2^-]$ [L = piperidine in (I) and quinuclidine in (II)], presumably formed by reaction with water present in the incompletely dried solvent or ligand: $2Ph_3SnN_3 + L + H_2O \rightarrow [LH][Ph_3Sn(N_3)_2]$ + 'Ph_3SnOH'.



(I)



(II)

The anion of (I), like that of (II), has pseudo-trigonal-bipyramidal symmetry, with the azide ligands in axial positions (Fig. 1) generally having $d(N_\alpha—N_\beta) \geq d(N_\beta—N_\gamma)$ (Table 1). However, unlike the structure of the anion $Ph_3Sn(NCS)_2^-$ noted above, as well as that with Et_4N^+ as the counterion (Cox & Wardell, 1996), the axial azide groups are not equivalent, the detailed geometry around the tin, including $CSnN_\alpha$ angles and $d(Sn—N_\alpha)$ values (Table 1), showing one azide group is acting as a weaker ligand than the other. This effect, which is more pronounced in (I), is clearly due to the hydrogen bonding in which this weaker donor azide group is involved (Table 2). In (I), the primary NH_2 group of the cation forms two N—H···N bonds with α- and γ-N atoms of azide groups on adjacent anions creating hydrogen-bonded chains through the lattice (Fig. 2).

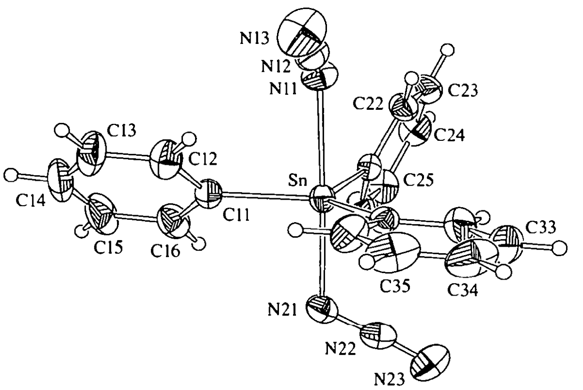


Fig. 1. *ORTEP*II (Johnson, 1976) view of the anion of (I), showing the general numbering scheme adopted. Ellipsoids are drawn at the 40% probability level. H atoms are represented by spheres of arbitrary size.

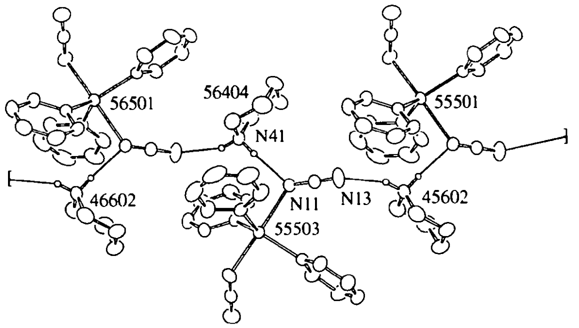


Fig. 2. Hydrogen-bonding network in (I). H atoms are in calculated positions. The site symmetry codes indicate the symmetry operations relating the various units.

In contrast, the asymmetric unit in (II) has two anions and cations (Fig. 3). One cation forms a single N—H···N bond with the α-N atom of an azide group in one anion, but then the γ-N atoms of this azide group and one in the adjacent anion together form a bifurcated hydrogen bond with the N—H of the other cation. A search of the Cambridge Structural Database (Allen & Kennard, 1993) shows several examples of N—H···N bonds with α-N and γ-N atoms of coordinated azide groups including one γ-N atom forming two such bonds, but (II) appears to have the first example of the reverse motif.

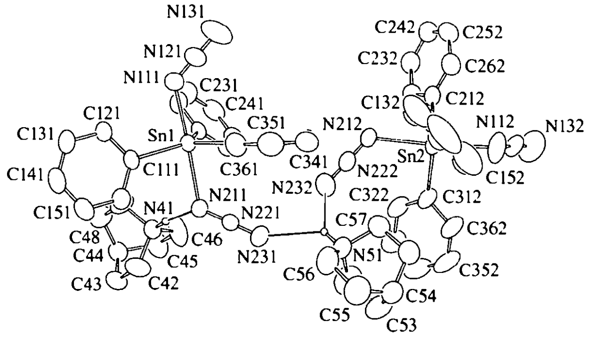


Fig. 3. *ORTEP*II (Johnson, 1976) view of the asymmetric unit of (II), showing the full hydrogen-bonding network. H atoms are in calculated positions.

The conformations around tin in the anions (I), (II1) and (II2) may reflect the effects of hydrogen bonding and crystal packing. Thus, inspection of the dihedral angles between the phenyl rings and the SnC_3 moiety of anion (I) [(1) 45.45 (11), (2) 66.64 (8), (3) 5.45 (17)°] or (II2) [(1) 49.32 (20), (2) 31.26 (19), (3) 53.08 (20)°] shows distorted propeller arrangements of phenyl rings, while the torsion angles (N13—N11—N21—N23), apparent by looking down the quasi-linear N_α—Sn—N_α axis, are −100.7 (2) and 105.8 (5)°, respectively. In case (I), there are two hydrogen bonds (at N_α and N_γ) to the weaker donor azide group, but in (II2), there is only one hydrogen bond at N_γ for the weaker donor azide group. In contrast, for (II1) with two hydrogen bonds (at N_α and N_γ) to the weaker donor azide group, the torsion angle is smaller [34.8 (5)°], while the dihedral angle values [(1) 81.56 (13), (2) 53.10 (14), (3) 12.98 (24)°] show that the plane of the phenyl ring *trans* to the azide groups is almost in line with the N_α—Sn—N_α axis. This overall conformation for the phenyl rings is similar to that found for $Ph_3SnNCO.pyO$ (Wharf *et al.*, 1987) and the $Ph_3Sn(NCS)_2^-$ anions referenced above, and may better represent the structure to be expected of the $Ph_3Sn(N_3)_2^-$ anion without hydrogen bonding.

Experimental

Triphenyltin azide (1.0 g) was stirred at room temperature with a toluene (20 ml) solution of piperidine (2.0 g) to yield an oil which began to solidify after 2–3 h. The solid was filtered after 24 h and recrystallized from toluene to give (I): yield 61%, m.p. 410 K. Analysis: found C 53.69, H 5.39, N 19.33%; calculated for $C_{23}H_{27}N_7Sn$ C 53.10, H 5.23, N 18.85%. Treatment of triphenyltin azide (1.0 g) with quinuclidine (2.0 g) in hexane (40 ml) in the same way gave (II) after recrystallization of the crude from acetone–ether: yield 87%, m.p. 428 K. Analysis: found C 55.17, H 5.40, N 17.98%; calculated for $C_{25}H_{29}N_7Sn$ C 54.97, H 5.35, N 17.95%.

Compound (I)

Crystal data

$(C_5H_{12}N)[Sn(N_3)_2(C_6H_5)_3]$
$M_r = 520.21$
Orthorhombic
$P2_12_12_1$
$a = 11.5345\ (1)$ Å
$b = 13.7765\ (2)$ Å
$c = 15.1022\ (1)$ Å
$V = 2399.82\ (4)$ Å^3
$Z = 4$
$D_x = 1.440$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6069 reflections
$\theta = 2.00$–$26.39°$
$\mu = 1.088$ mm^{-1}
$T = 300\ (2)$ K
Plate
0.40 × 0.18 × 0.05 mm
Colourless

Data collection

Siemens SMART/*P*4 diffractometer
ω scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996*a*)
$T_{min} = 0.779$, $T_{max} = 0.928$
19 640 measured reflections
4840 independent reflections

4349 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 26.39°$
$h = -14 \rightarrow 9$
$k = -17 \rightarrow 17$
$l = -18 \rightarrow 18$
300 standard reflections intensity decay: 7.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.048$
$S = 1.066$
4840 reflections
281 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0196P)^2 + 0.6055P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.361$ e Å^{-3}
$\Delta\rho_{min} = -0.433$ e Å^{-3}
Extinction correction: *SHELXL*96 (Sheldrick, 1996*b*)
Extinction coefficient: 0.00129 (16)
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = −0.05 (2)

Table 1. *Selected geometric parameters (Å, °) for (I)*

Sn—N11	2.396 (2)	Sn—N21	2.216 (3)
Sn—C11	2.123 (3)	Sn—C21	2.140 (3)
Sn—C31	2.135 (2)	N11—N12	1.187 (3)
N12—N13	1.163 (4)	N21—N22	1.201 (4)
N22—N23	1.146 (4)		
N11—Sn—N21	178.37 (9)	N12—N11—Sn	120.9 (2)
N22—N21—Sn	117.29 (19)	C11—Sn—C21	115.07 (10)
C21—Sn—C31	123.41 (11)	C11—Sn—C31	120.82 (11)
C11—Sn—N11	86.65 (10)	C21—Sn—N11	86.43 (10)
C31—Sn—N11	88.47 (9)	C11—Sn—N21	91.91 (11)
C21—Sn—N21	93.49 (10)	C31—Sn—N21	92.92 (11)

Table 2. *Hydrogen-bonding geometry (Å, °) for (I)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N41—H41*A*···N11^{i}	0.90	2.02	2.909 (3)	168.0
N41—H41*B*···N13^{ii}	0.90	2.00	2.848 (4)	157.1

Symmetry codes: (i) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (ii) $\frac{1}{2} - x, -y, \frac{1}{2} + z$.

Compound (II)

Crystal data

$(C_7H_{14}N)[Sn(N_3)_2(C_6H_5)_3]$
$M_r = 546.24$
Monoclinic
$P2_1/c$
$a = 27.1533\ (4)$ Å
$b = 9.9162\ (2)$ Å
$c = 19.0714\ (1)$ Å
$\beta = 98.284\ (1)°$
$V = 5081.54\ (13)$ Å^3
$Z = 8$
$D_x = 1.428$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 8192 reflections
$\theta = 0.76$–$26.42°$
$\mu = 1.032$ mm^{-1}
$T = 300\ (2)$ K
Plate
0.45 × 0.15 × 0.06 mm
Colourless

Data collection

Siemens SMART/*P*4 diffractometer
ω scan
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996*a*)
$T_{min} = 0.818$, $T_{max} = 0.928$
39 976 measured reflections
10 206 independent reflections

7244 reflections with $I > 2\sigma(I)$
$R_{int} = 0.038$
$\theta_{max} = 26.42°$
$h = -33 \rightarrow 33$
$k = -12 \rightarrow 8$
$l = -23 \rightarrow 23$
418 standard reflections intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.088$
$S = 1.047$
10206 reflections
596 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 5.4307P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.004$
$\Delta\rho_{\max} = 0.877$ e Å^{-3}
$\Delta\rho_{\min} = -0.746$ e Å^{-3}
Extinction correction: *SHELXL*96
Extinction coefficient: 0.00058 (8)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 3. *Selected geometric parameters (Å, °) for (II)*

Sn1—N111	2.226 (4)	Sn2—N112	2.244 (5)
Sn1—N211	2.371 (4)	Sn2—N212	2.343 (4)
Sn1—C111	2.144 (4)	Sn2—C112	2.131 (5)
Sn1—C211	2.131 (4)	Sn2—C212	2.131 (5)
Sn1—C311	2.129 (4)	Sn2—C312	2.131 (5)
N111—N121	1.137 (5)	N112—N122	1.094 (6)
N121—N131	1.145 (7)	N122—N132	1.137 (7)
N211—N221	1.186 (5)	N212—N222	1.165 (6)
N221—N231	1.139 (5)	N222—N232	1.156 (6)
N111—Sn1—N211	177.54 (14)	N112—Sn2—N212	175.7 (2)
N121—N111—Sn1	123.4 (3)	N122—N112—Sn2	126.7 (4)
N221—N211—Sn1	121.5 (3)	N222—N212—Sn2	125.1 (3)
C111—Sn1—C211	123.70 (14)	C112—Sn2—C212	118.3 (2)
C111—Sn1—C311	120.83 (15)	C112—Sn2—C312	117.91 (19)
C211—Sn1—C311	115.28 (15)	C212—Sn2—C312	123.58 (18)
C111—Sn1—N111	89.73 (16)	C112—Sn2—N112	86.7 (2)
C211—Sn1—N111	92.24 (16)	C212—Sn2—N112	93.21 (18)
C311—Sn1—N111	92.41 (16)	C312—Sn2—N112	94.1 (2)
C111—Sn1—N211	88.17 (15)	C112—Sn2—N212	90.53 (19)
C211—Sn1—N211	87.88 (14)	C212—Sn2—N212	85.14 (17)
C311—Sn1—N211	89.76 (14)	C312—Sn2—N212	90.16 (18)

Table 4. *Hydrogen-bonding geometry (Å, °) for (II)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N41—H41···N211^{i}	0.91	1.93	2.838 (5)	172.2
N51—H51···N231	0.91	2.26	2.949 (6)	132.0
N51—H51···N232^{i}	0.91	2.43	3.140 (7)	135.3

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

For both compounds, data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Siemens, 1995); data reduction: *SAINT*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and *SHELXL*96; molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX*; software used to prepare material for publication: *NRCVAX* and *SHELXL*96.

The authors are most grateful to the Fonds FCAR [Programmes 'Actions spontanés and ACC' (IW) and 'Équipes et Séminaires' (MO)] of the Gouvernement du Québec for financial support, while one of us (IW) thanks the administration of Dawson College for release time to undertake this research.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1297). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1794–1797

Dibromobis(η^5-pentamethylcyclopentadienyl)thorium(IV)

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(*Received 1 April 1997; accepted 9 July 1997*)

Abstract

The title compound, $[ThBr_2(\eta^5\text{-}C_{10}H_{15})_2]$ or $Cp^*_2ThBr_2$ [$Cp^* = \eta^5\text{-}C_5(CH_3)_5$], presents a pseudo-tetrahedral 'bent-metallocene' geometry in the solid state, with the

Acta Crystallographica Section C
ISSN 0108-2701 © 1997