

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

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

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Piperidinium Diazidotriphenylstannate and Quinuclidinium Diazidotriphenylstannate

IVOR WHARF,^a RYSZARD WOJTOWSKI,^a MARIO ONYSZCHUK^a AND MICHEL G. SIMARD^b

^a*Chemistry Department, McGill University, Montreal, Quebec, Canada H3A 2K6, and* ^b*Département de Chimie, Université de Montréal, CP 6128, Succ. Centre-ville, Montréal, Québec, Canada H3C 3J7. E-mail: wharf@omc.lan.mcgill.ca*

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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 (*SHELX86*; Sheldrick, 1990) and refined by full-matrix least-squares methods (*SHELXL93*; 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: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). Molecular graphics: *ORTEP* (Johnson, 1965).

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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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Abstract

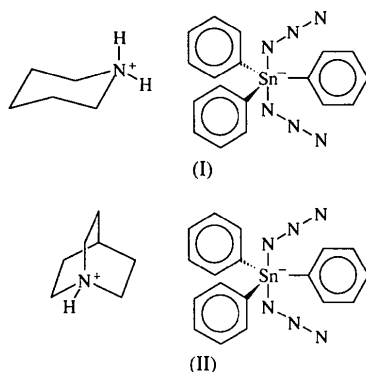
Two triphenyltin–azide adducts with cyclic aliphatic amines are shown by X-ray diffraction to be $[LH][(\text{C}_6\text{H}_5)_3\text{Sn}(\text{N}_3)_2]$, where for (I), L = piperidine ($\text{C}_5\text{H}_{11}\text{N}$), and for (II), L = quinuclidine ($\text{C}_7\text{H}_{13}\text{N}$). The anions have 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, Lebus, 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 [$\sim 2050\text{ cm}^{-1}$, $\nu_{\text{as}}(\text{N}_3)$; $\sim 3400\text{ cm}^{-1}$, $\nu(\text{N—H})$], suggested these compounds were perhaps $[LH^+][\text{Ph}_3\text{Sn}(\text{N}_3)_2^-]$, analogues of the $(\text{CH}_3)_4\text{N}^+$ and $(\text{C}_6\text{H}_5)_4\text{As}^+$ salts with the same anion [IR (cm^{-1}); $\nu_{\text{as}}(\text{N}_3)$, 2050s, 2070sh and 2040s, 2055s, respectively] reported by Barbieri, Bertazzi & Tomarchio (1975). In the same way, the compound having

the formula $L_2\text{Ph}_3\text{SnNCS.HNCS}$ [$L = 1\text{-(salicylidene-imino)-2-methoxybenzene}$] was found by analysis to be $[L_2\text{H}][\text{Ph}_3\text{Sn}(\text{NCS})_2]$ (Charland, Gabe, Khoo & Smith, 1989). The few tin systems with monodentate azide groups whose structures are given in the literature include $[\text{CpFe}(\text{CO})_2]_2\text{Sn}(\text{N}_3)_2$ (Hampden-Smith, Lei & Duesler, 1990) and $^t\text{Bu}_n\text{Sn}(\text{N}_3)_{4-n}$ (Hänssgen, Jansen, Leben & Oster, 1995), as well as the anions hexaazido-stannate (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 $[\text{LH}^+][\text{Ph}_3\text{Sn}(\text{N}_3)_2]^-$ [$L = \text{piperidine}$ in (I) and quinuclidine in (II)], presumably formed by reaction with water present in the incompletely dried solvent or ligand: $2\text{Ph}_3\text{SnN}_3 + L + \text{H}_2\text{O} \rightarrow [\text{LH}][\text{Ph}_3\text{Sn}(\text{N}_3)_2] + ^-\text{Ph}_3\text{SnOH}$.



The anion of (I), like that of (II), has pseudo-trigonal-bipyramidal symmetry, with the azide ligands in axial positions (Fig. 1) generally having $d(\text{N}_\alpha - \text{N}_\beta) \geq d(\text{N}_\beta - \text{N}_\gamma)$ (Table 1). However, unlike the structure of the anion $\text{Ph}_3\text{Sn}(\text{NCS})_2^-$ 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_α angles

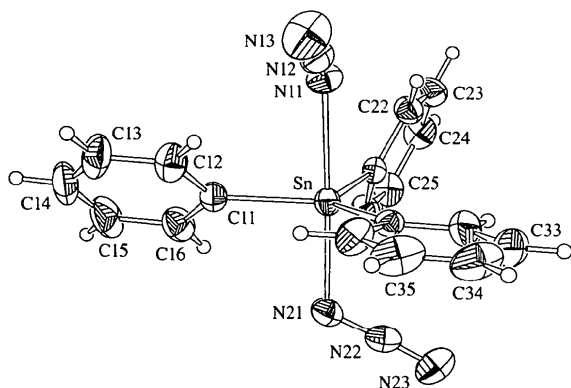


Fig. 1. ORTEP (Johnson, 1976) view of the anion of (I), showing the general numbering scheme adopted. Ellipsoids are drawn at the 40% probability level. H atoms are represented by spheres of arbitrary size.

and $d(\text{Sn}-\text{N}_\alpha)$ 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 $\text{N}-\text{H} \cdots \text{N}$ bonds with α - and γ -N atoms of azide groups on adjacent anions creating hydrogen-bonded chains through the lattice (Fig. 2).

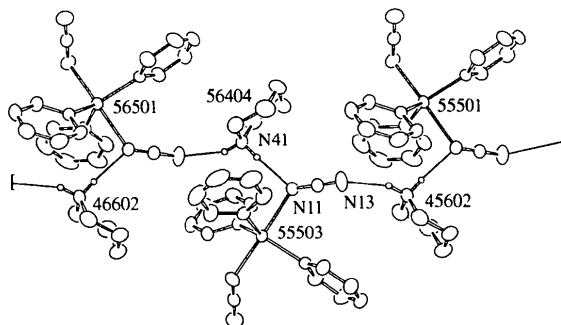


Fig. 2. Hydrogen-bonding network in (I). H atoms are in calculated positions. The site symmetry codes indicate the symmetry operations relating the various units.

In contrast, the asymmetric unit in (II) has two anions and cations (Fig. 3). One cation forms a single $\text{N}-\text{H} \cdots \text{N}$ 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 $\text{N}-\text{H}$ of the other cation. A search of the Cambridge Structural Database (Allen & Kennard, 1993) shows several examples of $\text{N}-\text{H} \cdots \text{N}$ 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.

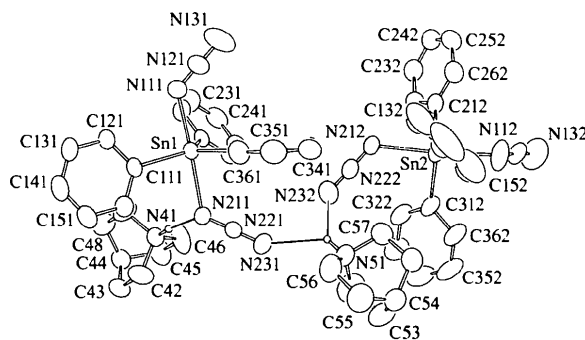


Fig. 3. ORTEP (Johnson, 1976) view of the asymmetric unit of (II), showing the full hydrogen-bonding network. H atoms are in calculated positions.

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 Ph₃SnNCO.pyO (Wharf *et al.*, 1987) and the Ph₃Sn(NCS)₂[−] anions referenced above, and may better represent the structure to be expected of the Ph₃Sn(N₃)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 C₂₃H₂₇N₇Sn 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 C₂₅H₂₉N₇Sn C 54.97, H 5.35, N 17.95%.

Compound (I)

Crystal data

(C₅H₁₂N)[Sn(N₃)₂(C₆H₅)₃]

M_r = 520.21

Orthorhombic

*P*2₁2₁2₁

a = 11.5345 (1) Å

b = 13.7765 (2) Å

c = 15.1022 (1) Å

V = 2399.82 (4) Å³

Z = 4

D_x = 1.440 Mg m^{−3}

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 6069 reflections

θ = 2.00–26.39°

μ = 1.088 mm^{−1}

T = 300 (2) K

Plate

0.40 × 0.18 × 0.05 mm

Colourless

Data collection

Siemens SMART/P4 diffractometer

ω scan

Absorption correction:

multi-scan (SADABS; Sheldrick, 1996a)

T_{min} = 0.779, *T_{max}* = 0.928

4349 reflections with *I* > 2σ(*I*)

R_{int} = 0.029

θ_{max} = 26.39°

h = −14 → 9

k = −17 → 17

l = −18 → 18

19 640 measured reflections
4840 independent reflections

Refinement

Refinement on *F*²

R[*F*² > 2σ(*F*²)] = 0.025

ω*R*(*F*²) = 0.048

S = 1.066

4840 reflections

281 parameters

H-atom parameters

constrained

w = 1/[σ²(*F_o*²) + (0.0196*P*)² + 0.6055*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

300 standard reflections
intensity decay: 7.3%

Δρ_{max} = 0.361 e Å^{−3}
Δρ_{min} = −0.433 e Å^{−3}

Extinction correction:

SHELXL96 (Sheldrick, 1996b)

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)

<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>
N41—H41A...N11 ⁱ	0.90	2.02	2.909 (3)	168.0
N41—H41B...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

(C₇H₁₄N)[Sn(N₃)₂(C₆H₅)₃]

M_r = 546.24

Monoclinic

*P*2₁/*c*

a = 27.1533 (4) Å

b = 9.9162 (2) Å

c = 19.0714 (1) Å

β = 98.284 (1)°

V = 5081.54 (13) Å³

Z = 8

D_x = 1.428 Mg m^{−3}

D_m not measured

Mo *K*α radiation

λ = 0.71073 Å

Cell parameters from 8192 reflections

θ = 0.76–26.42°

μ = 1.032 mm^{−1}

T = 300 (2) K

Plate

0.45 × 0.15 × 0.06 mm

Colourless

Data collection

Siemens SMART/P4 diffractometer

ω scan

Absorption correction:

multi-scan (SADABS; Sheldrick, 1996a)

T_{min} = 0.818, *T_{max}* = 0.928

39 976 measured reflections

10 206 independent reflections

reflections

7244 reflections with *I* > 2σ(*I*)

R_{int} = 0.038

θ_{max} = 26.42°

h = −33 → 33

k = −12 → 8

l = −23 → 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 $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.004$
 $\Delta\rho_{\max} = 0.877 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.746 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 SHELXL96
 Extinction coefficient:
 0.00058 (8)
 Scattering factors from
 International Tables for
 Crystallography (Vol. C)

Table 3. Selected geometric parameters ($\text{\AA}$, $^\circ$) 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 ($\text{\AA}$, $^\circ$) for (II)

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N41—H41 $\cdots$ N211 ⁱ	0.91	1.93	2.838 (5)	172.2
N51—H51 $\cdots$ N231	0.91	2.26	2.949 (6)	132.0
N51—H51 $\cdots$ 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: SHELXS86 (Sheldrick, 1985); program(s) used to refine structures: NRCVAX (Gabe, Le Page, Charland, Lee & White, 1989) and SHELXL96; molecular graphics: ORTEPII (Johnson, 1976) in NRCVAX; software used to prepare material for publication: NRCVAX and SHELXL96.

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

DANIEL RABINOVICH,^a GEORGE L. SCHIMEK,^b WILLIAM T. PENNINGTON,^b JON B. NIELSEN^c AND KENT D. ABNEY^a

^aLos Alamos National Laboratory, CST-11, Mail Stop J514, Los Alamos, New Mexico 87545, USA, ^bDepartment of Chemistry, Clemson University, Clemson, South Carolina 29634, USA, and ^cLos Alamos National Laboratory, MST-5, Mail Stop G730, Los Alamos, New Mexico 87545, USA.
 E-mail: xray@xray.clemson.edu

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Abstract

The title compound, [ThBr₂(η^5 -C₁₀H₁₅)₂] or Cp^{*}₂ThBr₂ [Cp^{*} = η^5 -C₅(CH₃)₅], presents a pseudo-tetrahedral 'bent-metallocene' geometry in the solid state, with the