

Tetrakis(2,4,6-trimethylanilido)tin(IV)

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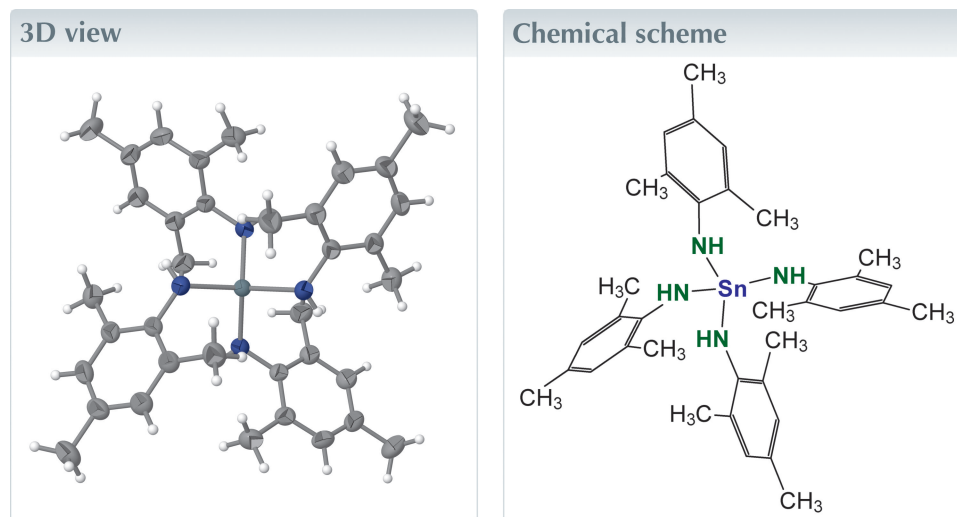
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Keywords: crystal structure; tin; amide.**CCDC reference:** 2357316**Structural data:** full structural data are available from iucrdata.iucr.org

Transamination of $\text{Sn}(\text{NMe}_2)_4$ with H_2NMes (Mes is 2,4,6-trimethylphenyl, C_9H_{11}) led to the formation of the title compound, $[\text{Sn}(\text{C}_9\text{H}_{12}\text{N})_4]$ or $\text{Sn}(\text{NHMe}_2)_4$, which crystallizes in the tetragonal space group $P4_21c$, with four formula units per unit cell. The molecular structure consists of a central tin(IV) atom, which is surrounded by four NHMe groups. $\text{Sn}(\text{NHMe}_2)_4$ possesses crystallographically imposed $\bar{4}$ symmetry. The SnN_4 coordination polyhedron is best described as a compressed bisphenoid.



Structure description

Contrary to homoleptic silicon amides $\text{Si}(\text{NHR})_4$ [e.g. $R = \text{methyl}$ (Andersch & Jansen, 1990), $R = \text{pentafluorophenyl}$ (Jansen *et al.*, 1992), $R = i\text{-propyl}$ (Engering *et al.*, 2003)], corresponding tin(IV) compounds have been studied much less. In 1998, Beswick and co-workers reported the crystal structure of $[\text{Li}_2(\text{THF})_2\text{Sn}(\text{NHCy})_6]$ (Cy = cyclohexyl), which represents a rare example of a homoleptic tin(IV) amide (Beswick *et al.*, 1998). In the context of our investigations on polynuclear organotin(IV) nitrogen compounds like $[(\text{MeSn})_4(\text{NPh})_4(\text{NPh})_4]$ (Lämmer & Merzweiler, 1999), we found that $\text{Sn}(\text{NMe}_2)_4$ reacts with 2,4,6-trimethylphenyl amine (H_2NMes) to give the title compound, (**1**) (Fig. 1).

The crystal structure of (**1**) consists of discrete $\text{Sn}(\text{NHMe}_2)_4$ molecules without any unusually short intermolecular contacts. The asymmetric unit consists of one tin(IV) atom on Wyckoff position $2a$ of space group $P4_21c$ with site symmetry $\bar{4}$, and one NHMe group on a general position. The tin(IV) atom exhibits a distorted tetrahedral (bisphenoidal) coordination ($\tau_4 = 0.83$, with extreme values of 1 for ideal tetrahedral and 0 for ideal square-planar coordination; Yang *et al.*, 2007) from four nitrogen atoms with Sn–N distances of 2.033 (2) Å and N–Sn–N angles from 104.22 (5) to 120.6 (1)° (Table 1). Similar Sn–N distances were observed in $(\text{Me}_3\text{Si})_3\text{CSn}(\text{NH}^i\text{Bu})_3$ (2.017–2.028 Å; Jansen *et al.*, 2003), $(^i\text{Bu}_2\text{Sn})_3(\text{NH})_3$ (2.030 Å; Puff *et al.*, 1989) and 2,4,6- $^i\text{Bu}_3\text{-C}_6\text{H}_2\text{-NHSnMe}_3$ (2.050 Å; Lichtscheidl *et al.*, 2015) that also exhibit four-coordinate tin(IV) atoms. In the case of $[\text{Li}_2(\text{THF})_2\text{Sn}(\text{NHCy})_6]$, which contains tin(IV) in a distorted octahedral coor-

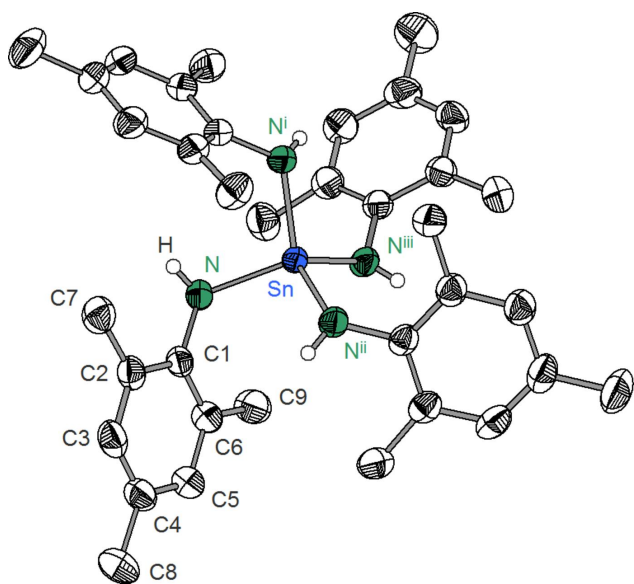


Figure 1
Molecular structure of compound (**1**) in the crystal. Displacement ellipsoids are drawn at the 50% probability level. H atoms except for the NH group are omitted for clarity. [Symmetry codes: (i) $y, -x + 1, -z + 1$; (ii) $-x + 1, -y + 1, z$; (iii) $-y + 1, x, -z + 1$.]

dination, the Sn–N distances are longer in average and vary from 2.06–2.27 Å (Beswick *et al.*, 1998). Regarding the NHMes group, bond lengths and angles are within the expected ranges. The N atom in (**1**) displays a slightly pyramidal coordination, as indicated by the sum of bond angles (345.1°).

The packing diagram (Fig. 2) indicates that the molecules of (**1**) are arranged in undulating layers parallel to (001) in the solid state. The NH groups do not participate in hydrogen bridges. This is obviously due to the steric shielding of the bulky mesityl residues.

Synthesis and crystallization

All manipulations were carried out under an argon atmosphere. *n*-Hexane was freshly distilled from lithium aluminium hydride. Sn(NMe₂)₄ was prepared according to the literature (Jones & Lappert, 1965).

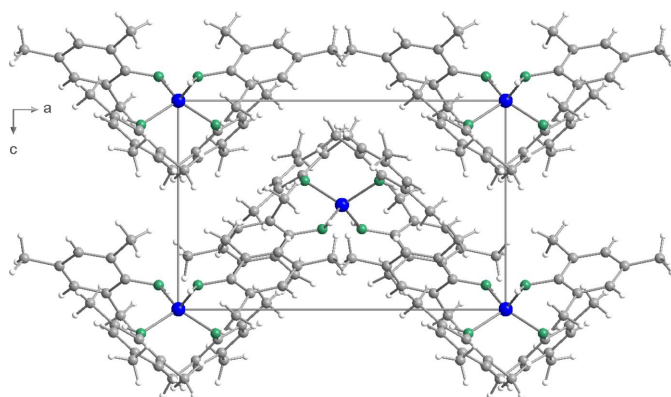


Figure 2
Crystal structure of compound (**1**), in a view along [010].

Table 1
Selected geometric parameters (Å, °).

Sn–N	2.0332 (19)	N–H	0.79 (3)
N–C1	1.422 (3)		
N–Sn–N ⁱ	104.22 (5)	C1–N–Sn	122.05 (15)
N–Sn–N ⁱⁱ	120.57 (12)	C1–N–H	114 (2)

Symmetry codes: (i) $y, -x + 1, -z + 1$; (ii) $-x + 1, -y + 1, z$.

Table 2
Experimental details.

Crystal data	[Sn(C ₉ H ₁₂ N) ₄]
Chemical formula	655.47
<i>M_r</i>	Tetragonal, $P\bar{4}2_1c$
Crystal system, space group	170
Temperature (K)	13.7000 (6), 8.7123 (5)
<i>a</i> , <i>c</i> (Å)	1635.21 (17)
<i>V</i> (Å ³)	2
<i>Z</i>	Mo <i>K</i> α
Radiation type	0.81
μ (mm ⁻¹)	0.50 × 0.35 × 0.30
Crystal size (mm)	
Data collection	Stoe <i>IPDS 2</i>
Diffraction	Integration [<i>X-RED32</i> (Stoe & Cie, 2016), by Gaussian integration analogous to Coppens (1970)]
Absorption correction	
<i>T_{min}</i> , <i>T_{max}</i>	0.735, 0.898
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	30518, 2205, 2049
<i>R_{int}</i>	0.053
($\sin \theta/\lambda$) _{max} (Å ⁻¹)	0.686
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, <i>S</i>	0.022, 0.057, 1.07
No. of reflections	2205
No. of parameters	100
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å ⁻³)	0.42, -0.21
Absolute structure	Flack <i>x</i> determined using 832 quotients [$(I^+) - (I^-)$]/ $[(I^+) + (I^-)]$ (Parsons <i>et al.</i> , 2013)
Absolute structure parameter	-0.036 (19)

Computer programs: *X-AREA* (Stoe & Cie, 2016), *SHELXT* (Sheldrick, 2015a), *SHELXL* (Sheldrick, 2015b), *DIAMOND* (Brandenburg, 2019) and *OLEX2* (Dolomanov *et al.*, 2009).

2.5 g (18.4 mmol) of mesityl amine were added to a solution of 1.36 g (4.61 mmol) of Sn(NMe₂)₄ in 30 ml of *n*-hexane. The reaction slowly turned pale yellow and a colourless precipitate was formed. After 12 h the reaction mixture was filtered and 300 mg of the product were received. The filtrate was stored at 253 K to give another 0.83 g of yellowish crystals of the title compound. Combined yield: 1.13 g (38%).

¹H NMR (C₆D₆) δ = 6.17 (*s*, C₆H₂), 3.38 (*s*, NH), 2.15 (*s*, *p*-CH₃), 2.07 (*s*, *o*-CH₃) p.p.m. ¹³C NMR (CDCl₃) δ = 142.1, 129.4, 128.7, 127.6, 20.4, 18.6 p.p.m. ¹¹⁹Sn NMR (CDCl₃) δ = -170.5 p.p.m.

Refinement

Crystal data, data collection, and structure refinement details are given in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2024). 9, x240479 [https://doi.org/10.1107/S2414314624004796]

Tetrakis(2,4,6-trimethylanilido)tin(IV)

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Tetrakis(2,4,6-trimethylanilido)tin(IV)

Crystal data

[Sn(C₉H₁₂N)₄]

$M_r = 655.47$

Tetragonal, $P4_21c$

$a = 13.7000$ (6) Å

$c = 8.7123$ (5) Å

$V = 1635.21$ (17) Å³

$Z = 2$

$F(000) = 684$

$D_x = 1.331$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 28663 reflections

$\theta = 29.7$ – 1.5°

$\mu = 0.81$ mm⁻¹

$T = 170$ K

Block, colourless

$0.50 \times 0.35 \times 0.30$ mm

Data collection

Stoe IPDS 2

diffractometer

rotation scans

Absorption correction: integration

[X-Red32 (Stoe & Cie, 2016), by Gaussian

integration analogous to Coppens (1970)]

$T_{\min} = 0.735$, $T_{\max} = 0.898$

30518 measured reflections

2205 independent reflections

2049 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.053$

$\theta_{\max} = 29.2^\circ$, $\theta_{\min} = 2.1^\circ$

$h = -18 \rightarrow 18$

$k = -18 \rightarrow 17$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.022$

$wR(F^2) = 0.057$

$S = 1.07$

2205 reflections

100 parameters

0 restraints

Hydrogen site location: mixed

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 0.2402P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 0.42$ e Å⁻³

$\Delta\rho_{\min} = -0.21$ e Å⁻³

Absolute structure: Flack x determined using

832 quotients $[(I^-)-(I)]/[(I^+)+(I)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: -0.036 (19)

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. The amino hydrogen atom was located from a difference-Fourier map and was refined freely.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn	0.500000	0.500000	0.500000	0.03205 (9)
N	0.38602 (14)	0.43981 (15)	0.3843 (2)	0.0398 (4)
H	0.337 (2)	0.464 (2)	0.414 (3)	0.058 (9)*
C9	0.51845 (19)	0.3557 (2)	0.1674 (3)	0.0523 (6)
H9A	0.485199	0.412240	0.122563	0.078*
H9B	0.547813	0.316490	0.085463	0.078*
H9C	0.569620	0.378157	0.237652	0.078*
C6	0.44600 (16)	0.29472 (16)	0.2542 (3)	0.0419 (4)
C5	0.44012 (18)	0.19474 (18)	0.2270 (3)	0.0479 (5)
H5	0.487138	0.165100	0.161838	0.057*
C4	0.36777 (19)	0.13675 (17)	0.2921 (3)	0.0508 (6)
C1	0.37965 (16)	0.33771 (16)	0.3564 (3)	0.0368 (4)
C8	0.3612 (3)	0.0293 (2)	0.2557 (5)	0.0782 (10)
H8A	0.406218	-0.007008	0.321874	0.117*
H8B	0.378659	0.018516	0.147944	0.117*
H8C	0.294318	0.006481	0.273615	0.117*
C3	0.30148 (17)	0.18170 (18)	0.3885 (3)	0.0478 (5)
H3	0.250913	0.143525	0.432859	0.057*
C2	0.30595 (18)	0.28038 (19)	0.4231 (3)	0.0407 (5)
C7	0.23079 (19)	0.3233 (2)	0.5301 (3)	0.0512 (6)
H7A	0.185274	0.363947	0.471476	0.077*
H7B	0.263505	0.363313	0.607882	0.077*
H7C	0.194779	0.270463	0.580599	0.077*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn	0.02775 (10)	0.02775 (10)	0.04063 (14)	0.000	0.000	0.000
N	0.0305 (9)	0.0343 (9)	0.0544 (11)	-0.0004 (7)	-0.0056 (8)	-0.0023 (8)
C9	0.0519 (14)	0.0485 (13)	0.0566 (13)	-0.0059 (10)	0.0118 (11)	-0.0064 (11)
C6	0.0410 (11)	0.0387 (10)	0.0461 (11)	-0.0019 (8)	-0.0044 (9)	-0.0037 (9)
C5	0.0462 (12)	0.0426 (11)	0.0548 (13)	-0.0015 (10)	-0.0049 (11)	-0.0089 (10)
C4	0.0508 (14)	0.0347 (11)	0.0668 (15)	-0.0026 (9)	-0.0158 (12)	-0.0035 (10)
C1	0.0334 (10)	0.0331 (10)	0.0440 (11)	-0.0022 (8)	-0.0081 (9)	0.0005 (8)
C8	0.074 (2)	0.0391 (13)	0.121 (3)	-0.0126 (13)	-0.007 (2)	-0.0154 (17)
C3	0.0429 (12)	0.0410 (11)	0.0596 (14)	-0.0117 (10)	-0.0119 (11)	0.0084 (11)
C2	0.0362 (11)	0.0399 (12)	0.0459 (13)	-0.0038 (9)	-0.0091 (10)	0.0047 (10)
C7	0.0431 (11)	0.0516 (13)	0.0591 (16)	-0.0067 (10)	0.0046 (10)	0.0035 (11)

Geometric parameters (\AA , $^\circ$)

Sn—N	2.0332 (19)	C5—H5	0.9500
Sn—N ⁱ	2.0332 (19)	C4—C3	1.382 (4)
Sn—N ⁱⁱ	2.0332 (19)	C4—C8	1.509 (3)
Sn—N ⁱⁱⁱ	2.0332 (19)	C1—C2	1.405 (3)

N—C1	1.422 (3)	C8—H8A	0.9800
N—H	0.79 (3)	C8—H8B	0.9800
C9—C6	1.502 (3)	C8—H8C	0.9800
C9—H9A	0.9800	C3—C2	1.386 (3)
C9—H9B	0.9800	C3—H3	0.9500
C9—H9C	0.9800	C2—C7	1.509 (4)
C6—C5	1.392 (3)	C7—H7A	0.9800
C6—C1	1.402 (3)	C7—H7B	0.9800
C5—C4	1.391 (4)	C7—H7C	0.9800
N—Sn—N ⁱ	104.22 (5)	C5—C4—C8	121.0 (3)
N—Sn—N ⁱⁱ	120.57 (12)	C6—C1—C2	119.6 (2)
N ⁱ —Sn—N ⁱⁱ	104.22 (5)	C6—C1—N	118.8 (2)
N—Sn—N ⁱⁱⁱ	104.22 (5)	C2—C1—N	121.6 (2)
N ⁱ —Sn—N ⁱⁱⁱ	120.57 (12)	C4—C8—H8A	109.5
N ⁱⁱ —Sn—N ⁱⁱⁱ	104.22 (5)	C4—C8—H8B	109.5
C1—N—Sn	122.05 (15)	H8A—C8—H8B	109.5
C1—N—H	114 (2)	C4—C8—H8C	109.5
Sn—N—H	109 (2)	H8A—C8—H8C	109.5
C6—C9—H9A	109.5	H8B—C8—H8C	109.5
C6—C9—H9B	109.5	C4—C3—C2	122.5 (2)
H9A—C9—H9B	109.5	C4—C3—H3	118.7
C6—C9—H9C	109.5	C2—C3—H3	118.7
H9A—C9—H9C	109.5	C3—C2—C1	119.2 (2)
H9B—C9—H9C	109.5	C3—C2—C7	118.9 (2)
C5—C6—C1	118.9 (2)	C1—C2—C7	121.9 (2)
C5—C6—C9	120.0 (2)	C2—C7—H7A	109.5
C1—C6—C9	121.0 (2)	C2—C7—H7B	109.5
C4—C5—C6	122.3 (2)	H7A—C7—H7B	109.5
C4—C5—H5	118.9	C2—C7—H7C	109.5
C6—C5—H5	118.9	H7A—C7—H7C	109.5
C3—C4—C5	117.5 (2)	H7B—C7—H7C	109.5
C3—C4—C8	121.5 (3)		
C1—C6—C5—C4	3.2 (4)	Sn—N—C1—C2	114.2 (2)
C9—C6—C5—C4	-173.1 (2)	C5—C4—C3—C2	-1.0 (4)
C6—C5—C4—C3	-1.1 (4)	C8—C4—C3—C2	-179.7 (3)
C6—C5—C4—C8	177.7 (3)	C4—C3—C2—C1	0.9 (4)
C5—C6—C1—C2	-3.2 (3)	C4—C3—C2—C7	-179.7 (2)
C9—C6—C1—C2	173.1 (2)	C6—C1—C2—C3	1.2 (3)
C5—C6—C1—N	179.8 (2)	N—C1—C2—C3	178.2 (2)
C9—C6—C1—N	-3.9 (3)	C6—C1—C2—C7	-178.2 (2)
Sn—N—C1—C6	-68.8 (3)	N—C1—C2—C7	-1.2 (4)

Symmetry codes: (i) $y, -x+1, -z+1$; (ii) $-x+1, -y+1, z$; (iii) $-y+1, x, -z+1$.