

Dibromido(*N*-phenylbenzamidine- $\kappa N'$)tin(II)

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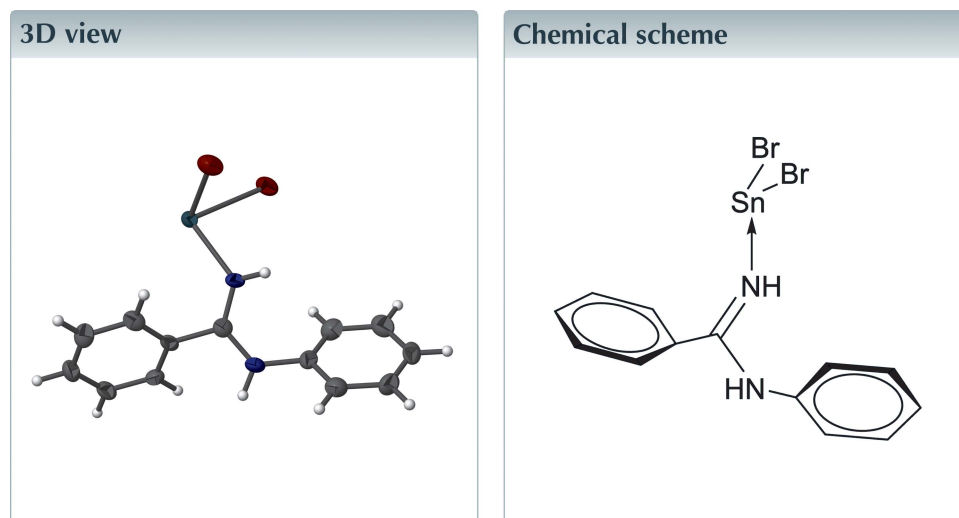
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Structural data: full structural data are available from iucrdata.iucr.org

The asymmetric unit of the title compound, $[\text{SnBr}_2(\text{C}_{13}\text{H}_{12}\text{N}_2)]$, contains an amidine ligand and tin(II) bromide moiety. In the amidine ligand, the phenyl rings present a head-to-tail configuration mode. The tin atom is coordinated by the terminal N atom of the amidine ligand, and the two Br atoms extend to both sides of the Sn atom in a V-shape. The phenyl rings are twisted from the mean N/C/N plane by 26.14 (18) and 79.50 (8)°. The crystal structure features N—H···Br hydrogen bonds.



Structure description

The representative amidinate ligand $[\text{RC}(\text{NR})_2]^-$ is four-electron monoanionic and has a typical conjugated N—C—N construction, through which the negative charge is able to be delocalized so as to form chelating surroundings (Bai *et al.*, 2010). Based on this backbone, amidinates have been widely ligated to transition metals (Edelmann, 1994), particularly the group 14 metallylenes tin(II). Tin(II) amidinates belong to the family of complexes bearing so-called spectator ligands which are commonly used for fine-tuning of the electronic as well as coordination properties of the metal atom (Chlupatý *et al.*, 2015). Interesting features in the title compound arise from the highly catalytic activity in the ring-opening polymerization of caprolactone and aryl isocyanates to perhydro-1,3,5-triazine-2,4,6-triones (isocyanurates) in a living fashion, under mild conditions. As part of our studies in this area, the title compound (Fig. 1) was prepared in a novel manner (reaction in Schlenk bottle by PhNH_2 , $t\text{-BuLi}$, SiMe_2Cl_2 , PhCN , SnCl_2 and Br_2) and we have determined its crystal structure. The compound is closely similar to the benzamidine with an *o*-tolyl substituent on the N atom, namely N^2 -*o*-tolylbenzamidine (Zhang *et al.*, 2008), which has no stannous bromine moiety attached.

The asymmetric unit of the title compound, $[\text{SnBr}_2(\text{C}_{13}\text{H}_{12}\text{N}_2)]$, contains an amidine ligand and tin(II) bromide. In the amidine ligand, the phenyl rings exhibit a head-to-tail configuration mode. The tin atom is coordinated by the terminal N atom of the amidine

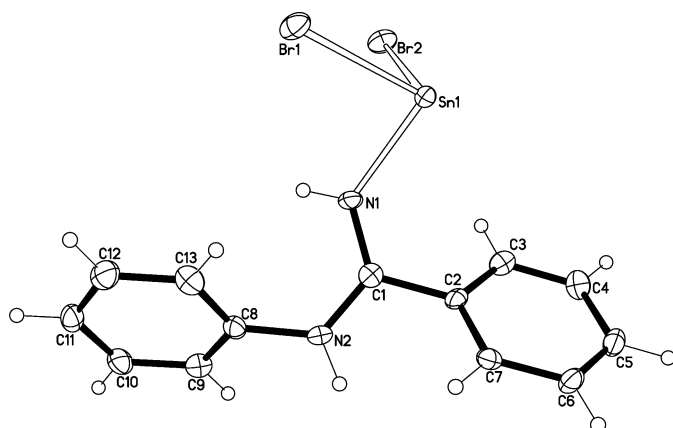


Figure 1
The molecular structure of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

ligand, and the two Br atoms extend to both sides of Sn in a V-shape (Fig. 1). The outward expansion configuration of the two bromine atoms is due to the large steric hindrance of the nearby substituents. The C2–C7 and C8–C13 phenyl rings are twisted from the N1/C1/N2 mean plane by 26.14 (18) and 79.50 (8)°, respectively. The two N atoms connect the central C atom with bond lengths of 1.315 (5) and 1.324 (5) Å, while the Sn–N bond length is 2.176 (3) and the Sn–Br bond lengths are 2.6286 (6) and 2.6313 (6) Å.

In the crystal, the molecules are linked into chains along [100] by N–H···Br hydrogen bonds (Fig. 2, Table 1).

Synthesis and crystallization

The title compound was prepared by a reaction of aniline, ⁿBuLi, SiMe₂Cl₂, PhCN, SnCl₂ and Br₂. To a solution of aniline (2.328 g, 5 mmol) in diethyl ether (30 ml) were added ⁿBuLi (2 ml, 2.5 M, 5 mmol) at 273 K and 0.5 equiv. of dimethyl dichlorosilane (0.3 ml, 2.5 mmol) 3 h later; the solution was stirred overnight and filtered to remove the white LiCl precipitate. ⁿBuLi (2 ml, 2.5 M, 5 mmol) was added again, then PhCN (0.5 ml, 5 mmol) was added by syringe in drops 4 h later. After stirring overnight, SnCl₂ (0.474 g, 2.5 mmol) was added at 273 K and the solution was stirred for 12 h. Then the

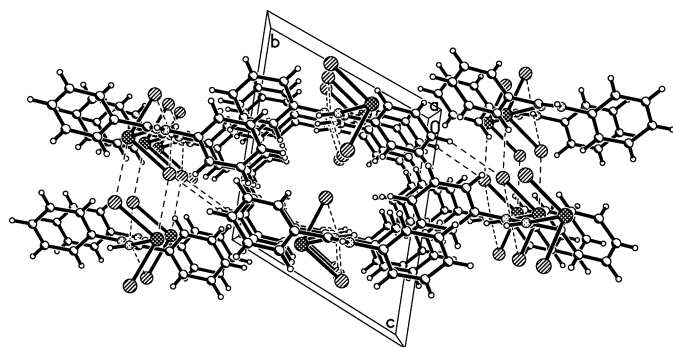


Figure 2
Part of the crystal structure, with hydrogen bonds drawn as dashed lines

Table 1
Hydrogen-bond geometry (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>
N2–H2···Br1 ⁱ	0.88	2.95	3.593 (4)	132
N2–H2···Br2 ⁱ	0.88	2.77	3.517 (3)	144

Symmetry code: (i) *x* + 1, *y*, *z*.

Table 2
Experimental details.

Crystal data	
Chemical formula	[SnBr ₂ (C ₁₃ H ₁₂ N ₂)]
<i>M</i> _r	474.76
Crystal system, space group	Triclinic, <i>P</i> $\bar{1}$
Temperature (K)	200
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.0315 (11), 9.7147 (14), 10.7577 (15)
α , β , γ (°)	111.205 (4), 90.226 (5), 109.381 (4)
<i>V</i> (Å ³)	730.81 (18)
<i>Z</i>	2
Radiation type	Mo <i>K</i> α
μ (mm ⁻¹)	7.20
Crystal size (mm)	0.06 × 0.06 × 0.05
Data collection	
Diffractometer	Bruker SMART area-detector
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 1996)
<i>T</i> _{min} , <i>T</i> _{max}	0.672, 0.715
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	7880, 2558, 2278
<i>R</i> _{int}	0.023
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.595
Refinement	
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.025, 0.055, 1.05
No. of reflections	2558
No. of parameters	164
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	0.64, -0.57

Computer programs: *SMART* and *SAINT* (Bruker, 2000), *SHELXS97* (Sheldrick, 2008) and *SHELXL2014* (Sheldrick, 2015).

solvent was removed under vacuum followed by extraction with dichloromethane and filtration to remove the white LiCl precipitate. To the filtrate was added Br₂ (0.13 ml, 2.52 mmol) and the solution was concentrated *in vacuo* to ca 15 ml about 24 h later. Colorless crystals (0.151 g, 76% yield) were obtained in toluene.

¹H NMR (300 MHz, CDCl₃): δ 6.59–7.68 (*m*, 11H; phenyl, C=N), 11.04 (*s*, 1H, C–N). ¹³C NMR (75 MHz, CDCl₃): δ 122.03, 124.32, 124.68, 127.68, 128.21, 128.67, 130.08 (phenyls), Elemental analysis (calculated %) for C₁₃H₁₂Br₂N₂Sn: C, 30.81; H, 2.45; N, 6.09%. Found: C, 31.89; H, 2.55; N, 5.90%.

Refinement

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

Funding information

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full crystallographic data

IUCrData (2017). 2, x170316 [https://doi.org/10.1107/S2414314617003169]

Dibromido(*N*-phenylbenzamidine- κ *N'*)tin(II)

Xiuming Ma

Dibromido(*N*-phenylbenzamidine- κ *N'*)tin(II)*Crystal data*

[SnBr₂(C₁₃H₁₂N₂)]

M_r = 474.76

Triclinic, *P* $\bar{1}$

a = 8.0315 (11) Å

b = 9.7147 (14) Å

c = 10.7577 (15) Å

α = 111.205 (4)°

β = 90.226 (5)°

γ = 109.381 (4)°

V = 730.81 (18) Å³

Z = 2

F(000) = 448

D_x = 2.157 Mg m⁻³

Mo *K* α radiation, λ = 0.71073 Å

Cell parameters from 5984 reflections

θ = 2.9–28.3°

μ = 7.20 mm⁻¹

T = 200 K

Block, colorless

0.06 × 0.06 × 0.05 mm

Data collection

Bruker SMART area-detector
diffractometer

φ and ω scan

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996)

T_{min} = 0.672, *T_{max}* = 0.715

7880 measured reflections

2558 independent reflections

2278 reflections with *I* > 2 σ (*I*)

R_{int} = 0.023

θ_{\max} = 25.0°, θ_{\min} = 2.9°

h = -9→9

k = -11→10

l = -12→12

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2 σ (*F*²)] = 0.025

wR(*F*²) = 0.055

S = 1.05

2558 reflections

164 parameters

0 restraints

Hydrogen site location: inferred from
neighbouring sites

H-atom parameters constrained

w = 1/[$\sigma^2(F_o^2) + (0.0169P)^2 + 1.8927P$]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} = 0.001

$\Delta\rho_{\max}$ = 0.64 e Å⁻³

$\Delta\rho_{\min}$ = -0.57 e Å⁻³

Extinction correction: SHELXL2014

(Sheldrick, 2015),

*F_c** = *kF_c*[1 + 0.001 × *F_c*² × $\lambda^3/\sin(2\theta)$]^{-1/4}

Extinction coefficient: 0.0035 (4)

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.

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

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Sn1	0.48568 (3)	0.62191 (3)	0.83884 (3)	0.02458 (11)
Br1	0.26091 (5)	0.38582 (5)	0.88757 (5)	0.03684 (14)
Br2	0.28771 (6)	0.53282 (5)	0.60875 (4)	0.03595 (13)
N1	0.6254 (4)	0.4638 (4)	0.7385 (3)	0.0280 (8)
H1	0.5592	0.3670	0.6847	0.034*
N2	0.8777 (4)	0.3932 (4)	0.7203 (4)	0.0335 (8)
H2	0.9950	0.4287	0.7302	0.040*
C1	0.7990 (5)	0.4990 (5)	0.7505 (4)	0.0272 (9)
C2	0.9223 (5)	0.6672 (5)	0.7996 (4)	0.0259 (9)
C3	0.8896 (6)	0.7654 (5)	0.7439 (4)	0.0314 (9)
H3	0.7885	0.7267	0.6781	0.038*
C4	1.0049 (6)	0.9195 (5)	0.7847 (4)	0.0347 (10)
H4	0.9844	0.9870	0.7457	0.042*
C5	1.1505 (6)	0.9767 (5)	0.8821 (4)	0.0337 (10)
H5	1.2298	1.0832	0.9096	0.040*
C6	1.1808 (5)	0.8802 (5)	0.9391 (4)	0.0337 (10)
H6	1.2801	0.9206	1.0069	0.040*
C7	1.0680 (5)	0.7248 (5)	0.8987 (4)	0.0294 (9)
H7	1.0893	0.6579	0.9380	0.035*
C8	0.7869 (5)	0.2245 (5)	0.6727 (4)	0.0293 (9)
C9	0.8323 (6)	0.1320 (5)	0.5586 (5)	0.0378 (11)
H9	0.9193	0.1796	0.5124	0.045*
C10	0.7519 (6)	-0.0305 (5)	0.5106 (5)	0.0396 (11)
H10	0.7858	-0.0942	0.4324	0.048*
C11	0.6239 (6)	-0.1008 (5)	0.5743 (5)	0.0368 (11)
H11	0.5689	-0.2126	0.5406	0.044*
C12	0.5753 (6)	-0.0076 (6)	0.6882 (5)	0.0415 (11)
H12	0.4847	-0.0556	0.7318	0.050*
C13	0.6583 (6)	0.1562 (5)	0.7394 (5)	0.0386 (11)
H13	0.6271	0.2202	0.8190	0.046*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn1	0.02065 (15)	0.02166 (15)	0.02717 (17)	0.00595 (11)	0.00258 (11)	0.00613 (12)
Br1	0.0261 (2)	0.0444 (3)	0.0472 (3)	0.00800 (19)	0.00491 (19)	0.0299 (2)
Br2	0.0282 (2)	0.0485 (3)	0.0305 (3)	0.0105 (2)	0.00397 (18)	0.0173 (2)
N1	0.0163 (16)	0.0294 (18)	0.033 (2)	0.0086 (14)	-0.0015 (14)	0.0061 (15)
N2	0.0177 (17)	0.0324 (19)	0.050 (2)	0.0091 (15)	0.0042 (15)	0.0151 (17)
C1	0.029 (2)	0.030 (2)	0.022 (2)	0.0103 (17)	0.0048 (17)	0.0093 (17)
C2	0.0183 (19)	0.026 (2)	0.025 (2)	0.0056 (16)	0.0083 (16)	0.0036 (17)
C3	0.028 (2)	0.037 (2)	0.026 (2)	0.0080 (18)	0.0033 (17)	0.0114 (19)
C4	0.045 (3)	0.031 (2)	0.030 (2)	0.013 (2)	0.007 (2)	0.0142 (19)
C5	0.031 (2)	0.025 (2)	0.035 (3)	0.0023 (18)	0.0034 (19)	0.0075 (19)
C6	0.023 (2)	0.032 (2)	0.034 (2)	0.0039 (18)	-0.0029 (18)	0.0048 (19)

C7	0.025 (2)	0.030 (2)	0.038 (3)	0.0141 (17)	0.0087 (18)	0.0144 (19)
C8	0.028 (2)	0.026 (2)	0.034 (2)	0.0109 (17)	-0.0025 (18)	0.0104 (18)
C9	0.030 (2)	0.039 (2)	0.046 (3)	0.013 (2)	0.007 (2)	0.017 (2)
C10	0.040 (3)	0.030 (2)	0.043 (3)	0.017 (2)	0.004 (2)	0.004 (2)
C11	0.035 (2)	0.026 (2)	0.043 (3)	0.0060 (19)	-0.011 (2)	0.011 (2)
C12	0.037 (3)	0.046 (3)	0.049 (3)	0.011 (2)	0.004 (2)	0.030 (2)
C13	0.044 (3)	0.039 (3)	0.037 (3)	0.020 (2)	0.008 (2)	0.015 (2)

Geometric parameters (Å, °)

Sn1—N1	2.176 (3)	C5—H5	0.9500
Sn1—Br2	2.6286 (6)	C6—C7	1.380 (6)
Sn1—Br1	2.6313 (6)	C6—H6	0.9500
N1—C1	1.315 (5)	C7—H7	0.9500
N1—H1	0.8800	C8—C9	1.367 (6)
N2—C1	1.324 (5)	C8—C13	1.385 (6)
N2—C8	1.441 (5)	C9—C10	1.381 (6)
N2—H2	0.8800	C9—H9	0.9500
C1—C2	1.492 (5)	C10—C11	1.368 (7)
C2—C3	1.384 (6)	C10—H10	0.9500
C2—C7	1.394 (6)	C11—C12	1.381 (7)
C3—C4	1.376 (6)	C11—H11	0.9500
C3—H3	0.9500	C12—C13	1.392 (6)
C4—C5	1.383 (6)	C12—H12	0.9500
C4—H4	0.9500	C13—H13	0.9500
C5—C6	1.371 (6)		
N1—Sn1—Br2	89.80 (9)	C5—C6—C7	120.5 (4)
N1—Sn1—Br1	87.49 (9)	C5—C6—H6	119.8
Br2—Sn1—Br1	90.618 (18)	C7—C6—H6	119.8
C1—N1—Sn1	126.3 (3)	C6—C7—C2	119.1 (4)
C1—N1—H1	116.8	C6—C7—H7	120.4
Sn1—N1—H1	116.8	C2—C7—H7	120.4
C1—N2—C8	125.3 (3)	C9—C8—C13	120.3 (4)
C1—N2—H2	117.4	C9—C8—N2	117.8 (4)
C8—N2—H2	117.4	C13—C8—N2	121.9 (4)
N1—C1—N2	124.3 (4)	C8—C9—C10	120.0 (4)
N1—C1—C2	120.4 (4)	C8—C9—H9	120.0
N2—C1—C2	115.2 (3)	C10—C9—H9	120.0
C3—C2—C7	120.4 (4)	C11—C10—C9	120.8 (4)
C3—C2—C1	118.5 (4)	C11—C10—H10	119.6
C7—C2—C1	121.1 (4)	C9—C10—H10	119.6
C4—C3—C2	119.4 (4)	C10—C11—C12	119.4 (4)
C4—C3—H3	120.3	C10—C11—H11	120.3
C2—C3—H3	120.3	C12—C11—H11	120.3
C3—C4—C5	120.4 (4)	C11—C12—C13	120.4 (4)
C3—C4—H4	119.8	C11—C12—H12	119.8
C5—C4—H4	119.8	C13—C12—H12	119.8

C6—C5—C4	120.2 (4)	C8—C13—C12	119.1 (4)
C6—C5—H5	119.9	C8—C13—H13	120.4
C4—C5—H5	119.9	C12—C13—H13	120.4

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
N2—H2 \cdots Br1 ⁱ	0.88	2.95	3.593 (4)	132
N2—H2 \cdots Br2 ⁱ	0.88	2.77	3.517 (3)	144

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