

Dimethylbis(4-methylpiperidine-1-dithio-
carboxylato- κ^2S,S')tin(IV)Saira Shahzadi,^a Saqib Ali^{a*} and
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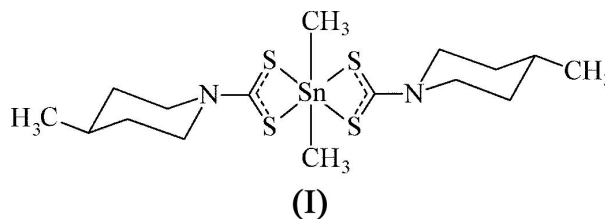
Key indicators

Single-crystal X-ray study
 $T = 295$ K
Mean $\sigma(C-C) = 0.009$ Å
 R factor = 0.058
 wR factor = 0.110
Data-to-parameter ratio = 26.4For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.The title compound, $[\text{Sn}(\text{CH}_3)_2(\text{C}_7\text{H}_{12}\text{NS}_2)_2]$, comprises Sn^{IV} coordinated by two 4-methylpiperidinedithiocarboxylate ligands and two methyl groups. The coordination geometry around Sn is distorted octahedral, with the methyl groups adopting an arrangement intermediate between a *cis* and *trans* configuration. There are two independent complexes in the asymmetric unit, with closely comparable geometries.

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Comment

The complexing ability of dithiocarbamates (DTCs) with metals has been known for many years. DTCs form chelates with metals through the two donor S atoms (Hulanicki, 1967). DTCs have been used for analytical applications, especially for the separation and determination of metals as metal chelates in thin-layer (Weissmahr *et al.*, 1998) and liquid (Riekkola *et al.*, 1983) chromatography. Some salts of DTCs have been used as antidotes in veterinary medicine (Shinobu *et al.*, 1984). Large quantities of water-soluble DTC complexes are used in agriculture as fungicides or pesticides (Montgomery, 1993) and have also been tested in various medical applications (Xie *et al.*, 1994).In the title compound, (I) (Fig. 1 and Table 1), there are two independent complexes in the asymmetric unit, with closely comparable geometries. The coordination geometry of Sn is highly distorted octahedral. The S atoms of the 4-methylpiperidinedithiocarboxylate ligands lie in the equatorial plane, with the S–Sn–S angles distorted significantly from 90° (Table 1). The angles are comparable with the S–Sn–S angles (65.4–149.7°) found in $[\text{Sn}(\text{CH}_3)_2(\text{S}_2\text{CN}(\text{CH}_2)_4)_2]$ (Lockhart *et al.*, 1986). The methyl groups define C–Sn–C angles of 138.5 (2) and 134.0 (2)° in the two independent molecules, intermediate between a *cis* and a *trans* configuration. These angles are similar to those in $[\text{Sn}(\text{CH}_3)_2(\text{S}_2\text{CN}(\text{CH}_3)_2)_2]$ (136°; Kimura *et al.*, 1972) and $[\text{Sn}(\text{CH}_3)_2(\text{S}_2\text{CN}(\text{CH}_2\text{CH}_3)_2)_2]$ (135.6–142.8° for three different crystalline modifications; Morris & Schlemper, 1979).

Each dithiocarboxylate ligand exhibits one short [in the range 2.5043 (14)–2.5364 (14) Å] and one long [2.8923 (15)–3.0397 (17) Å] Sn–S bond. The shorter Sn–S bond lengths

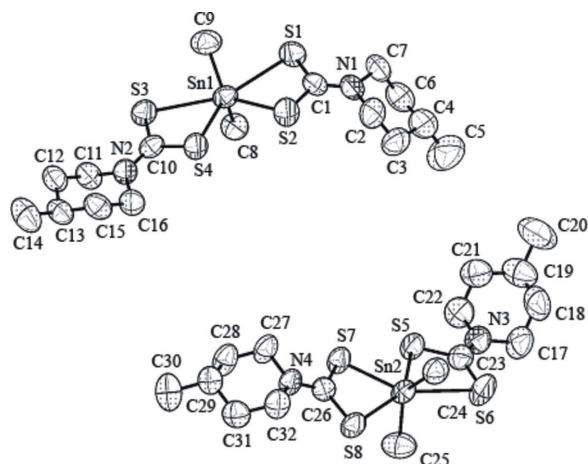


Figure 1

The asymmetric unit of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms have been omitted for clarity.

are close to the sum of the covalent radii of Sn and S (2.52 Å; Ma *et al.*, 2003), while the longer Sn–S distances are significantly less than the sum of the van der Waals radii (4.0 Å; Ma *et al.*, 2003). The effective coordination number is six (Lockhart *et al.*, 1985). The shorter Sn–S bonds are associated in each case with longer C–S bonds [in the range 1.742 (5)–1.754 (5) Å], while the longer Sn–S bonds are associated with shorter C–S bonds [1.687 (6)–1.710 (5) Å]. Previously, we have reported a chlorodimethyltin derivative of the same ligand, [Sn(CH₃)₂Cl(C₇H₁₂NS₂)] (Shahzadi *et al.*, 2006), which exhibits one short Sn–S bond [2.466 (7) Å] and one long Sn–S bond [2.739 (9) Å]. The dithiocarboxylate ligand is clearly coordinated unsymmetrically in both cases; the smaller difference between the Sn–S bond lengths in [Sn(CH₃)₂Cl(C₇H₁₂NS₂)] compared with (I) presumably reflects the presence of the electronegative chloride ligand, which increases the Lewis acidity of the Sn centre. The Sn–C distances in (I) and [Sn(CH₃)₂Cl(C₇H₁₂NS₂)] are similar.

Experimental

A solution of 4-methylpiperidinecarbodithioic acid (C₇H₁₃NS₂, 1.0 g, 5.71 mmol) and triethylamine (0.79 ml, 5.71 mmol) in dry toluene (50 ml) was added to a solution of dimethyltin dichloride (0.62 g, 2.85 mmol) in anhydrous toluene (50 ml). The reaction mixture was refluxed for 4 h and then filtered. The filtrate was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was recrystallized from chloroform–petroleum ether (1:1) (yield 83%, m.p. 415–416 K).

Crystal data

[Sn(CH ₃) ₂ (C ₇ H ₁₂ NS ₂) ₂]	<i>Z</i> = 16
<i>M_r</i> = 497.41	<i>D_x</i> = 1.459 Mg m ^{−3}
Orthorhombic, <i>Pbca</i>	Mo <i>K</i> α radiation
<i>a</i> = 19.432 (3) Å	<i>μ</i> = 1.50 mm ^{−1}
<i>b</i> = 12.512 (2) Å	<i>T</i> = 295 K
<i>c</i> = 37.267 (6) Å	Needle, colourless
<i>V</i> = 9061 (2) Å ³	0.33 × 0.09 × 0.07 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	76764 measured reflections
<i>ω</i> scans	11153 independent reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	5552 reflections with <i>I</i> > 2σ(<i>I</i>)
<i>T</i> _{min} = 0.638, <i>T</i> _{max} = 0.900	<i>R</i> _{int} = 0.104
	<i>θ</i> _{max} = 28.3°

Refinement

Refinement on <i>F</i> ²	<i>w</i> = 1/[σ ² (<i>F</i> _o ²) + (0.0381 <i>P</i>) ² + 1.2271 <i>P</i>]
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.058	where <i>P</i> = (<i>F</i> _o ² + 2 <i>F</i> _c ²)/3
<i>wR</i> (<i>F</i> ²) = 0.110	(Δσ) _{max} = 0.001
<i>S</i> = 1.00	Δρ _{max} = 0.37 e Å ^{−3}
11153 reflections	Δρ _{min} = −0.32 e Å ^{−3}
423 parameters	
H-atom parameters constrained	

Table 1

Selected geometric parameters (Å, °).

Sn1–C8	2.111 (5)	Sn2–C25	2.106 (5)
Sn1–C9	2.114 (5)	Sn2–C24	2.114 (5)
Sn1–S2	2.5196 (15)	Sn2–S7	2.5043 (14)
Sn1–S4	2.5364 (14)	Sn2–S5	2.5330 (15)
Sn1–S3	2.9167 (15)	Sn2–S8	2.8923 (15)
Sn1–S1	2.9187 (16)	Sn2–S6	3.0397 (17)
S1–C1	1.702 (5)	S5–C23	1.747 (6)
S2–C1	1.742 (5)	S6–C23	1.687 (6)
S3–C10	1.710 (5)	S7–C26	1.754 (5)
S4–C10	1.743 (5)	S8–C26	1.700 (5)
C8–Sn1–C9	138.5 (2)	C25–Sn2–C24	134.0 (2)
C8–Sn1–S2	100.70 (16)	C25–Sn2–S7	110.36 (18)
C9–Sn1–S2	107.86 (17)	C24–Sn2–S7	106.16 (15)
C8–Sn1–S4	104.66 (15)	C25–Sn2–S5	102.41 (17)
C9–Sn1–S4	107.62 (16)	C24–Sn2–S5	108.91 (15)
S2–Sn1–S4	84.05 (5)	S7–Sn2–S5	83.21 (4)
C8–Sn1–S3	85.19 (15)	C25–Sn2–S8	84.56 (16)
C9–Sn1–S3	85.29 (17)	C24–Sn2–S8	85.57 (15)
S2–Sn1–S3	149.19 (4)	S7–Sn2–S8	66.00 (4)
S4–Sn1–S3	65.27 (4)	S5–Sn2–S8	148.79 (4)
C8–Sn1–S1	82.13 (15)	C25–Sn2–S6	83.99 (17)
C9–Sn1–S1	83.24 (16)	C24–Sn2–S6	81.03 (15)
S2–Sn1–S1	65.25 (4)	S7–Sn2–S6	146.02 (4)
S4–Sn1–S1	149.30 (4)	S5–Sn2–S6	63.33 (4)
S3–Sn1–S1	145.36 (4)	S8–Sn2–S6	147.81 (4)

H atoms bound to C atoms were positioned geometrically and allowed to ride during subsequent refinement, with C–H distances of 0.98 (C_{cy}–H), 0.97 (C_{cy}–H₂) and 0.96 Å (CH₃), and with *U*_{iso}(H) = 1.2*U*_{eq}(C) for C_{cy}–H and C_{cy}–H₂, or 1.5*U*_{eq}(C) for CH₃. The methyl groups were also allowed to rotate about their local threefold axes.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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