$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.3933P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Co1—C2	2.014 (3)	C2—C3	1.495 (5)
Co1—C1	2.015 (3)	C3—C4	1.314 (6)
Co1—C5	2.024 (3)	C4—C5	1.485 (6)
Co1—C6	2.029 (3)	C5—C6	1.426 (5)
C1—C2	1.418 (5)	C6—C7	1.492 (6)
C1—C8	1.494 (5)	C7—C8	1.342 (5)
C2—C1—C8	121.2 (3)	C6—C5—C4	120.7 (3)
C1—C2—C3	122.0 (3)	C5—C6—C7	121.6 (3)
C4—C3—C2	117.8 (3)	C8—C7—C6	117.6 (3)
C3—C4—C5	118.2 (3)	C7—C8—C1	117.1 (3)

Data collection: *DIF*4 (Stoe & Cie, 1989a). Cell refinement: *DIF*4. Data reduction: *REDU*4 (Stoe & Cie, 1989c). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*97.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1269). Services for accessing these data are described at the back of the journal.
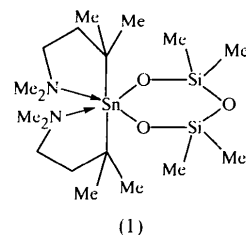
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6,6-Bis[3-(dimethylamino)-1,1-dimethylpropyl]-2,2,4,4-tetramethyl-1,3,5-trioxa-2,4-disila-6-stannacyclohexane

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Abstract

The title compound, bis(3-dimethylamino-1,1-dimethyl-propyl-C^1,N)(disiloxanediolato-O,O')tin(IV), [Sn($C_4H_{12}O_3Si_2$)($C_7H_{16}N$)$_2$], is the first stannasiloxane with hexacoordinate tin. The intramolecular Sn—N distances are 2.879 (3) and 2.957 (3) Å.

Comment

In an attempt to synthesize [Me$_2$N(CH$_2$)$_2$CMe$_2$]$_2$SnO as a functionally substituted analogue of (^{t}Bu$_2$SnO)$_3$ (Puff *et al.*, 1984) by reaction of [Me$_2$N(CH$_2$)$_2$CMe$_2$]$_2$SnCl$_2$ (Jurkschat *et al.*, 1989) with sodium hydroxide, we obtained the title compound, [Me$_2$N(CH$_2$)$_2$CMe$_2$]$_2$Sn(OSiMe$_2$)$_2$O, (1). The synthesis of (1) can be rationalized by reaction of sodium hydroxide and silicon grease, accidentally present in the reaction mixture, with [Me$_2$N(CH$_2$)$_2$CMe$_2$]$_2$SnCl$_2$. The formation of stannasiloxanes from reactions in the presence of silicon grease has been noticed by other groups (Churchill *et al.*, 1993; Eaborn *et al.*, 1995; Cervantes-Lee *et al.*, 1998).

(1)

The molecular structure of (1) is shown in Fig. 1. The Sn atom is coordinated by two C, two O and two N atoms, resulting in a distorted octahedral configuration. The C atoms are in mutually *trans* positions, whereas the O and N atoms are *cis*. This configuration at tin is the same as in the structure determined for [Me$_2$N(CH$_2$)$_3$]$_2$Sn(OPh)$_2$ (Pieper *et al.*, 1998), but it is different from the all-*trans* configuration observed for the Sn atoms in the related derivatives [Me$_2$N(CH$_2$)$_2$CMe$_2$]$_2$SnCl$_2$ (Schollmeyer *et al.*,

1991) and [Me₂N(CH₂)₃]₂SnF₂.2H₂O (Pieper *et al.*, 1997). The intramolecular Sn1—N1 and Sn1—N2 distances of 2.879 (3) and 2.957 (3) Å, respectively, are rather long. They are comparable with those found in (C₅H₅FeC₅H₃-2-CH₂NMe₂)₂SnCl₂ [Sn—N 2.89 (1) Å; Krüger *et al.*, unpublished], [{CH₂N(Et)CH₂CH₂CH₂}₂-SnS]₂ [Sn—N 2.766 (9) and 2.859 (9) Å; Schollmeyer *et al.*, 1988] and [{Me₂N(CH₂)₃}₂SnS]₂ [Sn—N 2.810 (3) and 3.158 (5) Å; Jurkschat *et al.*, 1992]. The Sn—C, Sn—O, Si—C and Si—O bond distances are as expected and comparable to those of related compounds (Beckmann *et al.*, 1997).

The six-membered SnO₃Si₂ ring is almost planar, with a maximum deviation from the least-squares plane of 0.072 (2) Å for Si2. It seems that the intramolecular Sn—N interactions in (1) prevent its polymerization in the solid state. For the related stannasiloxane ᵗBu₂Sn(OSiPh₂)₂O (Beckmann *et al.*, 1997), with no intramolecular donor function, a polymeric structure was observed in the solid state. Further systematic studies on this subject are in progress.
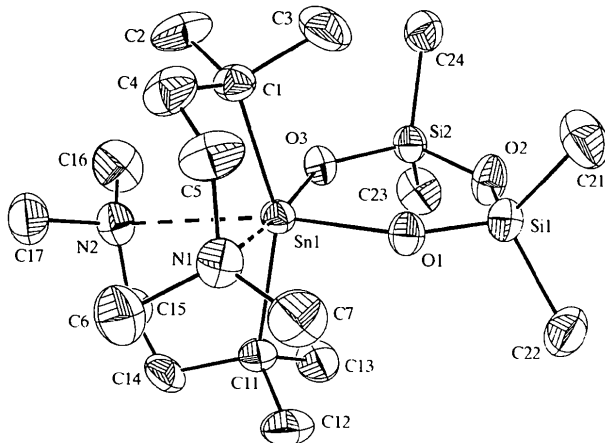

Fig. 1. View of the title compound showing the atom labelling. Displacement ellipsoids are shown at 30% probability levels and H atoms have been omitted for clarity.

Experimental

Reaction of [Me₂N(CH₂)₂C(Me₂)]₂SnCl₂ with two mole equivalents of NaOH in the presence of silicon grease (Baysilone-Paste, *mittelviskos*, Bayer AG Leverkusen) resulted in the formation of (1). A solution of NaOH (100 mg, 2.50 mmol) in water (3 ml) was added to a boiling solution of [Me₂N(CH₂)₂CMe₂]₂SnCl₂ (500 mg, 1.12 mmol) in toluene (25 ml). This mixture was refluxed for 30 min. The water was removed with a Dean–Stark-type water trap. Compound (1) crystallized from the solution overnight and was recrystallized from hexane solution to give colourless crystals (m.p. 358 K). Analysis calculated (found) (%) for C₁₈H₄₄N₂O₃Si₂Sn: C 42.12 (42.27), H 8.64 (8.95), N 5.46 (5.49); MS *m/e*: 496 (C₁₈H₄₄N₂Si₂SnO⁺₃), 397 (C₁₁H₂₈NSi₂SnO⁺₃), 284 (C₄H₁₂Si₂-SnO⁺₃), 268 (C₄H₁₂Si₂SnO⁺₂); ¹H NMR (CDCl₃): δ (p.p.m.) 0.06 (*s*, 3H, SiCH₃), 1.36 [*s*, 3H, CCH₃, ³*J*(¹H–¹¹⁹Sn) =

104 Hz], 1.68 (*t*, 1H, CCH₂), 2.25 (*s*, 3H, NCH₃), 2.34 (*t*, 1H, NCH₂); ¹³C NMR (CDCl₃): δ (p.p.m.) 2.18 (SiCH₃), 28.37 (CCH₃), 40.98 (SnC), 42.62 (CCH₂), 46.70 (NCH₃), 57.99 (NCH₂); ²⁹Si NMR (CDCl₃): δ (p.p.m.) −14 [²*J*(²⁹Si–O–¹¹⁹Sn) = 36 Hz]; ¹¹⁹Sn NMR (CDCl₃): δ (p.p.m.) −242.

Crystal data

[Sn(C₄H₁₂O₃Si₂)(C₇H₁₆N)₂]	Mo *Kα* radiation
Mᵣ = 511.42	λ = 0.71069 Å
Orthorhombic	Cell parameters from 30 964
*P*2₁2₁2₁	reflections
a = 9.095 (1) Å	θ = 4.44–25.68°
b = 15.624 (1) Å	μ = 1.088 mm⁻¹
c = 18.372 (1) Å	*T* = 291 (1) K
V = 2610.7 (4) Å³	Block
Z = 4	0.45 × 0.35 × 0.35 mm
Dₓ = 1.301 Mg m⁻³	Colourless
Dₘ not measured	

Data collection

Nonius Kappa-CCD diffractometer	3937 reflections with *I* > 2σ(*I*)
360 frames *via* ω rotation	*R*ᵢₙₜ = 0.045
(Δω = 1°) and 2 × 2 s	θₘₐₓ = 25.68°
per frame	*h* = −10 → 10
Absorption correction: none	*k* = −19 → 19
30 964 measured reflections	*l* = −22 → 22
4926 independent reflections	

Refinement

Refinement on *F²*	Δρₘₐₓ = 0.249 e Å⁻³
R[*F²* > 2σ(*F²*)] = 0.028	Δρₘᵢₙ = −0.433 e Å⁻³
wR(*F²*) = 0.055	Extinction correction: none
S = 0.940	Scattering factors from
4926 reflections	*International Tables for*
248 parameters	*Crystallography* (Vol. C)
H atoms: see below	Absolute structure: Flack
w = 1/[σ²(*F²ₒ*) + (0.0239*P*)²]	(1983)
where *P* = (*F²ₒ* + 2*F²c*)/3	Flack parameter = −0.03 (2)
(Δ/σ)ₘₐₓ = −0.001	

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

Sn1—O1	2.012 (2)	Si1—O2	1.638 (3)
Sn1—O3	2.029 (2)	Si1—C21	1.846 (4)
Sn1—C1	2.196 (4)	Si1—C22	1.862 (4)
Sn1—C11	2.205 (4)	Si2—O3	1.602 (2)
Sn1—N1	2.879 (3)	Si2—O2	1.628 (3)
Sn1—N2	2.957 (3)	Si2—C24	1.848 (4)
Si1—O1	1.608 (3)	Si2—C23	1.865 (4)
O1—Sn1—O3	94.53 (9)	O1—Si1—O2	110.40 (1)
O1—Sn1—C1	101.0 (1)	O1—Si1—C21	110.7 (2)
O3—Sn1—C1	96.4 (1)	O2—Si1—C21	109.0 (2)
O1—Sn1—C11	97.2 (1)	O1—Si1—C22	110.7 (2)
O3—Sn1—C11	100.1 (1)	O2—Si1—C22	107.5 (2)
C1—Sn1—C11	154.3 (1)	C21—Si1—C22	108.5 (2)
O1—Sn1—N1	81.74 (9)	O3—Si2—O2	110.5 (1)
O3—Sn1—N1	167.9 (1)	O3—Si2—C24	111.6 (2)
C1—Sn1—N1	73.2 (1)	O2—Si2—C24	108.3 (2)
C11—Sn1—N1	91.8 (1)	O3—Si2—C23	111.4 (2)
O1—Sn1—N2	167.5 (1)	O2—Si2—C23	107.4 (2)
O3—Sn1—N2	81.20 (9)	C24—Si2—C23	107.4 (2)
C1—Sn1—N2	91.1 (1)	Si1—O1—Sn1	133.9 (1)
C11—Sn1—N2	72.2 (1)	Si2—O2—Si1	136.0 (2)
N1—Sn1—N2	104.7 (1)	Si2—O3—Sn1	133.5 (1)

Sn1—O1—Si1—O2	4.3 (3)	Sn1—N1—C5—C4	38.7 (4)
O1—Si1—O2—Si2	8.1 (4)	C1—Sn1—N1—C5	−10.7 (3)
Si1—O2—Si2—O3	−14.0 (4)	N1—Sn1—C1—C4	−18.5 (3)
O2—Si2—O3—Sn1	9.1 (3)	Sn1—C11—C14—C15	53.3 (5)
Si2—O3—Sn1—O1	−1.3 (2)	C11—C14—C15—N2	−67.5 (5)
O3—Sn1—O1—Si1	−6.4 (2)	C11—Sn1—N2—C15	−10.5 (3)
Sn1—C1—C4—C5	51.7 (5)	Sn1—N2—C15—C14	39.1 (4)
C1—C4—C5—N1	−65.9 (5)	N2—Sn1—C11—C14	−19.8 (3)

The data collection covered almost the whole sphere of reciprocal space with a completeness of 98.4% up to θ_{max}. The crystal-to-detector distance was 2.6 cm. Crystal decay was monitored by repeating the initial frames at the end of data collection. Analysing the duplicate reflections, there was no indication of any decay. The structure was solved by direct methods and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods. The H atoms were placed in geometrically calculated positions and refined with a common isotropic displacement parameter [C—H(methylene) 0.97 Å, C—H(methyl) 0.95 Å and U_{iso} 0.118 (3) Å^2].

Data collection: Nonius Kappa-CCD software. Cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997). Data reduction: *DENZO* and *SCALEPACK*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL93*.

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Aqua(1,10-phenanthroline-N,N')(μ3-thiosulfato-S:S:O)cadmium(II) Hydrate

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Abstract

The structure of [Cd(S$_2$O$_3$)(C$_{12}$H$_8$N$_2$)(H$_2$O)].H$_2$O is reported. It consists of polymeric chains evolving along the 2$_1$ symmetry axis, interconnected by hydrogen bonds. The Cd^{2+} environment is a distorted octahedron which presents a rather long Cd—O distance [2.549 (4) Å]. The thiosulfate ion binds to three different cationic sites, through one singly coordinated O atom and one S atom acting in a bridging mode.

Comment

Cadmium thiosulfates have been the subject of our interest in the last few years and as a result three related crystal structures have been reported, all of which display the thiosulfate group acting as a polydentate ligand, *viz* [Cd$_2$(S$_2$O$_3$)$_2$(C$_{14}$H$_{12}$N$_2$)$_2$] [(I); Baggio *et al.*, 1996], [Cd(S$_2$O$_3$)(C$_{10}$H$_8$N$_2$)] [(II); Baggio, Pardo, Baggio & Garland, 1997] and Cd(S$_2$O$_3$).2H$_2$O [(III); Baggio, Pardo, Baggio & González, 1997].

As usual in complexes of d^{10} ions, the size of the accompanying ligands [2,9-dimethyl-1,10-phenanthroline (dmph) in (I), 2,2′-bipyridine (bpy) in (II) and H$_2$O in (III)] leads to different environments around the cadmium center which affect the way in which the thiosulfate bonds to the metal. These different types of coordination, in turn, influence the