

C21	0.2461 (5)	0.4269 (5)	0.1914 (4)	0.041 (2)
F22	0.2263 (2)	0.3512 (3)	0.1459 (2)	0.0374 (9)
F23	0.2225 (3)	0.3960 (4)	0.2493 (2)	0.0721 (15)
F24	0.1854 (3)	0.4989 (3)	0.1640 (4)	0.098 (2)
N1	0.3632 (3)	0.2081 (3)	0.0878 (2)	0.0264 (12)
C22	0.2979 (4)	0.1201 (4)	0.0584 (3)	0.0293 (14)
C23	0.3286 (5)	0.0310 (5)	0.1093 (3)	0.037 (2)
C24	0.3076 (5)	0.0914 (5)	-0.0150 (3)	0.045 (2)
C25	0.1893 (4)	0.1446 (5)	0.0514 (4)	0.037 (2)
C26	0.1250 (5)	0.0537 (5)	0.0217 (4)	0.045 (2)
C27	0.1569 (5)	-0.0353 (5)	0.0714 (4)	0.045 (2)
C28	0.2638 (5)	-0.0603 (5)	0.0808 (4)	0.041 (2)
C29	0.2752 (6)	-0.0879 (6)	0.0063 (5)	0.065 (2)
C30	0.2400 (6)	-0.0004 (6)	-0.0456 (4)	0.052 (2)
C31	0.1345 (5)	0.0263 (6)	-0.0508 (4)	0.048 (2)

† Occupancy 0.85.

‡ Occupancy 0.15.

Table 2. Selected geometric parameters (Å, °)

Sn1—N1	1.698 (5)	Sn1—N1	2.037 (5)
Sn1—C1	1.760 (6)	Sn1—C13	2.179 (6)
C1—C3	1.324 (10)	Sn1—C4	2.187 (5)
C1—C2	1.483 (10)	N1—C22	1.501 (7)
Sn1—F6	1.938 (3)		
N1—S1—C1	107.2 (3)	F6—Sn1—C4	90.1 (2)
C3—C1—C2	121.6 (6)	N1—Sn1—C4	126.2 (2)
C3—C1—S1	117.0 (6)	C13—Sn1—C4	116.9 (2)
C2—C1—S1	120.8 (5)	C22—N1—S1	116.9 (4)
F6—Sn1—N1	103.8 (2)	C22—N1—Sn1	120.2 (3)
F6—Sn1—C13	107.7 (2)	S1—N1—Sn1	111.2 (3)
N1—Sn1—C13	107.7 (2)		

The *para*-trifluoromethyl group at the C4—C9 phenyl ring was found to be disordered. Two positions for each F atom were refined to occupancies of 0.85 and 0.15. Distance restraints for 1,2 and 1,3 distances were applied. The *U* values of F atoms opposite each other were constrained to be equal. H atoms were included in calculated positions and refined using a riding model. The *U* value of each H atom was fixed to 1.2*U*_{eq} of the corresponding C atom.

Data collection: *DIF4* (Stoe & Cie, 1988a). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988b). 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*.

Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the IUCr (Reference: NA1120). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Ahlemann, J. T. (1992). Diplomarbeit, Univ. of Göttingen, Germany.
Blom, R. & Haarland, A. (1985). *J. Mol. Struct.* **128**, 21–27.
Grützmacher, H., Pritzkow, H. & Edelman, F. T. (1991). *Organometallics*, **10**, 23–25.
May, A., Roesky, H. W., Stalke, D., Pauer, F. & Sheldrick, G. M. (1990). *Chem. Ber.* **123**, 1475–1478.
Rademacher, P. (1987). *Strukturen organischer Moleküle, Physikalische Organische Chemie*, Vol. 2, edited by M. Klessinger. New York: VCH.
Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
Sheldrick, G. M. (1991). *SHELXTL-Plus*. Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

- Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
Stoe & Cie (1988a). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
Stoe & Cie (1988b). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

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Dibromodiethylbis(3*H*-imidazole-2-thione-*S*)tin(IV)

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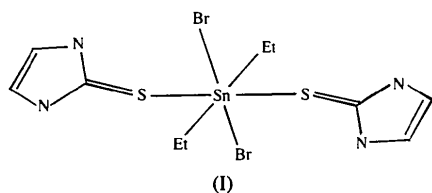
Abstract

The crystal structure of the title compound, [SnBr₂(C₂H₅)₂(C₃H₄N₂S)₂], comprises discrete all-*trans* octahedral [SnBr₂Et₂(Himt)₂] units (Himt = imidazol-2-thione) with the Sn atom coordinated to two ethyl C atoms [Sn—C = 2.158 (7) Å], two Br atoms [Sn—Br = 2.759 (3) Å] and two Himt S atoms [Sn—S = 2.771 (2) Å]. The structural parameters suggest the presence of an intermolecular N—H...Br hydrogen bond.

Comment

Interest in the properties of Sn—S bonds is prompted by the desire to understand the biological behaviour of diorganotin(IV) compounds (Barbieri, 1992, and references therein). We have recently described the interaction of dimethyltin(IV) (García Martínez, Sánchez González, Casas, Sordo, Valle & Russo, 1993) and diphenyltin(IV) (García Martínez, Sánchez González, Casas, Sordo, Casellato, Graziani & Russo, 1993) derivatives with the ligand 1-methyl-2(3*H*)-imidazo-

linethione. In this paper we describe the crystal structure of [SnBr₂Et₂(Himt)₂], (I), where Himt is the related ligand, 3*H*-imidazole-2-thione.



Crystals of this complex consists of discrete all-*trans* [SnBr₂Et₂(Himt)₂] units with the Sn atom coordinated to two ethyl atoms, two Br atoms and two Himt S atoms in a slightly distorted octahedral arrangement. The plane containing the ethyl groups approximately bisects the S(1)—Sn—Br(1) angle [Br(1)—Sn—C(1)—C(2) torsion angle 42.8 (5)°]. Each coordinated Himt ligand is essentially in the thione form and is planar ($\chi^2 = 6.0$), with bond lengths and bond angles close to those observed in other metal—Himt complexes (Graziani, Peruzzo, Plazzogna & Casellato, 1993; Kahn, Rheingold & Shupack, 1993). The C—S bond length and the Sn—S(1)—C(3) angle are similar to those found in the organotin complexes of 1-methyl-2(3*H*)-imidazolinethione (Bandoli, Dolmella, Peruzzo & Plazzogna, 1993; García Martínez, Sánchez González, Casas,

Sordo, Valle & Russo, 1993; García Martínez, Sánchez González, Casas, Sordo, Casellato, Graziani & Russo, 1993).

The N(2)⋯Br(1ⁱ) distance and the N(2)—H(1)⋯Br(1ⁱ) angle (Table 2) suggest the presence of an intermolecular hydrogen bond, which could be partially responsible for the orientation of the ligand [Sn—S(1)—C(3)—N(1) 133.4 (4)°].

Experimental

The title compound was prepared by the dropwise addition of SnBr₂Et₂ in CH₂Cl₂ to a stirred solution of Himt in the same solvent. M.p. 409 K.

Crystal data

[SnBr₂(C₂H₅)₂(C₃H₄N₂S)₂]

M_r = 536.90

Triclinic

P $\bar{1}$

a = 8.641 (1) Å

b = 7.236 (1) Å

c = 7.337 (1) Å

α = 107.0 (1)°

β = 84.4 (1)°

γ = 96.8 (1)°

V = 434.7 (3) Å³

Z = 1

D_x = 2.05 Mg m⁻³

D_m = 2.043 Mg m⁻³

Mo *K*α radiation

λ = 0.71070 Å

Cell parameters from 25

reflections

θ = 8–13°

μ = 6.253 mm⁻¹

T = 293 K

Pseudo-rhombohedral

0.3 × 0.2 × 0.2 mm

Colourless

Data collection

Philips PW1100 diffractometer

θ –2 θ scans

Absorption correction:

none

1868 measured reflections

1868 independent reflections

1778 observed reflections

[*F* ≥ 2σ(*F*)]

θ_{\max} = 28.0°

h = –11 → 11

k = –9 → 9

l = 0 → 9

3 standard reflections

monitored every 50

reflections

intensity decay: 10%

Refinement

Refinement on *F*

R = 0.039

wR = 0.038

S = 0.584

1778 reflections

88 parameters

H-atom parameters not

refined

$w = 1/[\sigma^2(F) + 0.003933F^2]$

(Δ/σ)_{max} = 0.187

$\Delta\rho_{\max}$ = 2.488 e Å⁻³

(near Sn)

$\Delta\rho_{\min}$ = –1.87 e Å⁻³

(near Sn)

Extinction correction: none

Atomic scattering factors

from *SHELX76*

(Sheldrick, 1976)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
Sn	0	1	1	0.0310 (1)
Br(1)	0.10684 (5)	0.73499 (8)	0.67179 (7)	0.0513 (2)
S(1)	0.3036 (1)	1.1745 (2)	1.0174 (2)	0.0386 (4)

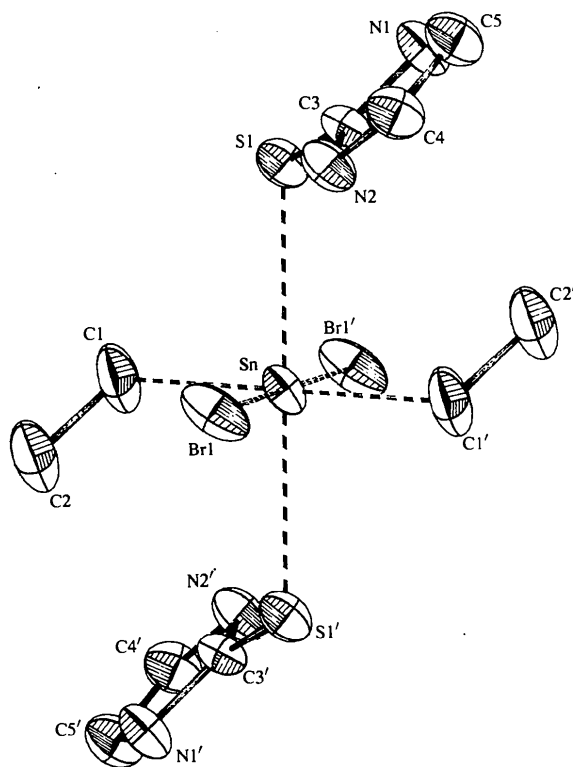


Fig. 1. Molecular structure of [SnBr₂Et₂(Himt)₂] showing the numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

N(1)	0.4866 (4)	1.1808 (6)	1.3026 (6)	0.041 (1)
N(2)	0.2711 (4)	1.3030 (6)	1.4092 (5)	0.040 (1)
C(1)	0.0434 (6)	0.8193 (9)	1.1737 (8)	0.056 (2)
C(2)	0.1891 (8)	0.7227 (9)	1.138 (1)	0.066 (3)
C(3)	0.3532 (5)	1.2195 (6)	1.2475 (6)	0.032 (1)
C(4)	0.3518 (6)	1.3152 (8)	1.5657 (7)	0.044 (2)
C(5)	0.4872 (5)	1.2406 (8)	1.4982 (7)	0.045 (2)

Table 2. Selected geometric parameters (Å, °)

Sn—Br(1)	2.759 (3)	S(1)—C(3)	1.711 (5)
Sn—C(1)	2.158 (7)	N(1)—C(5)	1.373 (6)
N(1)—C(3)	1.343 (6)	N(2)—C(4)	1.377 (7)
N(2)—C(3)	1.339 (6)	C(4)—C(5)	1.336 (7)
C(1)—C(2)	1.477 (9)	N(2)···Br(1 ⁱ)	3.341 (4)
Sn—S(1)	2.771 (2)		
S(1)—Sn—C(1)	92.3 (2)	Sn—S(1)—C(3)	107.0 (2)
Br(1)—Sn—S(1)	86.19 (8)	C(3)—N(2)—C(4)	110.5 (5)
C(3)—N(1)—C(5)	110.1 (5)	N(1)—C(3)—N(2)	105.6 (4)
Sn—C(1)—C(2)	119.9 (5)	S(1)—C(3)—N(1)	126.3 (4)
S(1)—C(3)—N(2)	128.1 (4)	N(1)—C(5)—C(4)	107.3 (5)
N(2)—C(4)—C(5)	106.5 (4)	N(2)—H(1)···Br(1 ⁱ)	145
Br(1)—Sn—C(1)	91.6 (2)		
Br(1)—Sn—C(1)—C(2)	42.8 (5)	Sn—S(1)—C(3)—N(1)	133.4 (4)

Symmetry code: (i) $-x, 2 - y, 2 - z$.

The crystal had a cylinder radius R of 0.1 mm. As $\mu R = 0.63$, no absorption correction was applied. The structure was solved by Patterson and subsequent difference Fourier methods. Anisotropic displacement parameters were used for all non-H atoms. H atoms were obtained from the F map except for those bonded to N atoms, which were fixed geometrically. The program used to solve and refine the structure was *SHELX76* (Sheldrick, 1976). Molecular graphics were drawn using *ORTEP* (Johnson, 1965).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and torsion angles have been deposited with the IUCr (Reference: NA1084). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- Bandoli, G., Dolmella, A., Peruzzo, V. & Plazzogna, G. (1993). *J. Organomet. Chem.* **452**, 47–53.
- Barbieri, R. (1992). *Inorg. Chim. Acta*, **191**, 253–259.
- García Martínez, E., Sánchez González, A., Casas, J. S., Sordo, J., Casellato, U., Graziani, R. & Russo, U. (1993). *J. Organomet. Chem.* In the press.
- García Martínez, E., Sánchez González, A., Casas, J. S., Sordo, J., Valle, G. & Russo, U. (1993). *J. Organomet. Chem.* **453**, 47–52.
- Graziani, R., Peruzzo, V., Plazzogna, G. & Casellato, U. (1993). *J. Organomet. Chem.* **396**, 19–23.
- Johnson, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
- Kahn, E. S., Rheingold, A. L. & Shupack, S. I. (1993). *J. Crystallogr. Spectrosc. Res.* **23**, 697–710.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

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A Trinuclear Terbium(III)–Carborane Cluster, $[C_{61}H_{159}B_{24}Li_6O_5Si_{12}Tb_3].C_6H_6$

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Abstract

The title compound, $[\{\mu_3\text{-methoxy-tris}[\mu\text{-}2,3\text{-bis}(\text{trimethylsilyl})\text{-}2,3\text{-dicarba-1-lithia-closo-heptaborane(6)]\text{-Tb}\kappa^2B^4, B^5 : \text{Tb}'\kappa^2B^5, B^6 ; \text{Tb}\kappa^2B^4, B^5 : \text{Tb}''\kappa^2B^5, B^6 ; \text{Tb}'\kappa^2B^4, B^5 : \text{Tb}''\kappa^2B^5, B^6\}\mu_3\text{-oxo-tris}[\mu\text{-}2,3\text{-bis}(\text{trimethylsilyl})\text{-}2,3\text{-dicarba-1-terba-closo-heptaborane(6)]\text{-Li}^{\text{THF}}\kappa^2B^4, B^5 : \text{Li}^{\text{THF}'}\kappa^2B^5, B^6 ; \text{Li}^{\text{THF}}\kappa^2B^4, B^5 : \text{Li}^{\text{THF}''}\kappa^2B^5, B^6 ; \text{Li}^{\text{THF}'}\kappa^2B^4, B^5 : \text{Li}^{\text{THF}''}\kappa^2B^5, B^6\}\text{-tris}(\text{tetrahydrofuranlithium})\text{ benzene solvate}$, $[\{\mu_3\text{-OMe-}[\mu\text{-}1\text{-Li-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4\text{]}_3\}\text{-}\{\mu_3\text{-O-}[\mu\text{-}1\text{-Tb-}2,3\text{-}(\text{SiMe}_3)_2\text{-}2,3\text{-C}_2\text{B}_4\text{H}_4\text{]}_3\}\text{-}[\text{Li}(\text{C}_4\text{H}_8\text{O})_3]\text{-}].C_6H_6$, crystallized in the triclinic space group $P\bar{1}$. The structure of this cluster consists of three *closo*-terbacarboranes, three cage-bridged Li(THF) units, and three Tb-bridged *closo*-lithiacarboranes that form a tricapped trigonal prism with Tb atoms in the capping positions. A centrally located O atom triply bridges the Tb atoms [Tb—O = 2.185 (3), 2.170 (3) and 2.173 (3) Å], forming a nearly coplanar arrangement [Tb—O—Tb = 118.9 (2), 119.0 (2) and 120.1 (2)°]. The methoxy group in the cluster is linked to the apical Li atoms of the three *closo*-lithiacarboranes in a distorted tetrahedral fashion [average Li—O—Li = 105.9 (5)° and average C—O—Li = 112.8 (5)°].

Comment

Most of the organolanthanides that have been reported contain cyclopentadienides as ligands (Rogers & Rogers, 1991; Evans, 1985, 1987; Evans, Gonzales & Ziller, 1991; Wilkinson, Stone & Abel, 1982; Wilkinson, Gillard & McCleverty, 1987; Cotton & Wilkinson, 1988). On the other hand, the chemistry of lanthanide complexes of the $C_{2}B_{10}$, $C_{2}B_9$ and $C_{2}B_4$ carborane-ligand systems has just begun to be explored and, consequently, the carborane sandwich and half-sandwich complexes of Sm, Eu, Gd and Yb have recently been synthesized and structurally characterized (Manning, Knobler & Hawthorne, 1988; Khattar, Knobler, Johnson & Hawthorne, 1991; Manning, Knobler, Khattar & Hawthorne, 1991; Khattar, Manning, Knobler, Johnson & Hawthorne, 1992; Oki, Zhang & Hosmane, 1992). Our report on the synthesis and crystal structure of