metal-organic compounds

Di-μ-hydroxido-bis[dimethyl(thio-cyanato-κN)tin(IV)]

Yaya Sow,[a]* Libasse Diop,[a] Kieran C. Molloy[b] and Gabriele Kociok-Köhn[b]

[a]Laboratoire de Chimie Minerale et Analytique (LACHIMIA), Departement de Chimie, Faculte des Sciences et Techniques, Universite Cheikh Anta Diop, Dakar, Senegal, and [b]Department of Chemistry, University of Bath, Bath BA2 7AY, England
Correspondence e-mail: yayasow81@yahoo.fr

The Sn[IV] atom in the centrosymmetric title complex, [Sn$_2$(CH$_3$)$_4$(NCS)$_2$(OH)$_2$], adopts a distorted trigonal–bipyramidal coordination environment defined by two methyl C atoms and one bridging hydroxide group in the equatorial plane while the other bridging hydroxide group and the N atom of the thiocyanate anion are in the apical >positions. The dinuclear species are linked through O—H···S and C—H···S hydrogen-bonding interactions into a three-dimensional network.

Related literature

For background to organotin(IV) chemistry, see: Davies (2004); Gielen *et al.* (1991); Gielen (1996); Kamruddin *et al.* (1996); Khoo & Ng (2001); Tsangaris & Williams (1992). For structures containing the four-membered distannoxane [Sn(μ-OH)]$_2$ unit, see: Chandrasekhar *et al.* (2007); Ng (1998). For related structures, see: Cox & Wardell (1996); Okio *et al.* (2003).
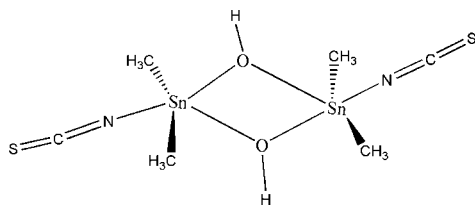
Experimental

Crystal data

[Sn$_2$(CH$_3$)$_4$(NCS)$_2$(OH)$_2$]	b = 12.5214 (3) Å
M_r = 447.69	c = 13.3871 (2) Å
Orthorhombic, $Pcab$	V = 1398.67 (5) Å^3
a = 8.3440 (2) Å	Z = 4

Mo $K\alpha$ radiation	T = 150 K
μ = 3.85 mm^{-1}	0.15 × 0.15 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer	20098 measured reflections
Absorption correction: multi-scan ($SORTAV$; Blessing, 1995)	1603 independent reflections
T_{min} = 0.596, T_{max} = 0.699	1333 reflections with $I > 2\sigma(I)$
	R_{int} = 0.055

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.056	
S = 1.11	$\Delta\rho_{max}$ = 1.06 e Å^{-3}
1603 reflections	$\Delta\rho_{min}$ = −0.64 e Å^{-3}
71 parameters	
1 restraint	

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O—H10···S^i	0.84 (2)	2.38 (2)	3.207 (3)	168 (4)
C2—H2C···S^{ii}	0.98	2.79	3.746 (4)	164

Symmetry codes: (i) $x - \frac{1}{2}, -y + \frac{1}{2}, z$; (ii) $x - \frac{1}{2}, -y + 1, -z + \frac{3}{2}$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Chandrasekhar, V., Singh, P. & Gopal, K. (2007). *Appl. Organomet. Chem.* **21**, 483–503.
Cox, P. J. & Wardell, J. L. (1996). *Acta Cryst.* C**52**, 317–319.
Davies, A. G. (2004). *Organotin Chemistry*, 2nd ed. Weinheim: Wiley-VCH.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Gielen, M. (1996). *Coord. Chem. Rev.* **151**, 41–51.
Gielen, M., Boualam, M., Biesemans, M., Mahieu, B. & Willem, R. (1991). *Main Group Met. Chem.* **14**, 271–281.
Kamruddin, S. K., Chattopadhyaya, T. K., Roy, A. & Tiekink, E. R. T. (1996). *Appl. Organomet. Chem.* **10**, 513–521.
Khoo, L. E. & Ng, S. W. (2001). *Main. Group. Met. Chem.* **24**, 445–446.
Ng, S. W. (1998). *Acta Cryst.* C**54**, 752–755.
Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
Okio, K. Y., Diop, L., Barry, A. H., Jouini, T. & Ortega, S. H. (2003). *Appl. Organomet. Chem.* **17**, 317–318.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C.W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tsangaris, J. M. & Williams, D. R. (1992). *Appl. Organomet. Chem.* **6**, 3–18.

supporting information

Di-*μ*-hydroxido-bis[dimethyl(thiocyanato-*κN*)tin(IV)]

Yaya Sow, Libasse Diop, Kieran C. Molloy and Gabriele Kociok-Köhn

S1. Comment

Organotin complexes may interact with biological systems in many different ways as bactericides, fungicides, acaricides and industrial biocides (Davies, 2004; Gielen *et al.*, 1991; Gielen, 1996; Kamruddin *et al.*, 1996; Khoo & Ng, 2001; Tsangaris & Williams, 1992). Many tin compounds containing the $Sn(CH_3)_2$ residue tiogether with a four-membered distannoxane $[Sn(\mu\text{-}OH)]_2$ ring have been reported (Chandrasekhar *et al.*, 2007; Ng, 1998). In the context of new $Sn(CH_3)_2$-residue containing compounds we have initiated the structural study of the interactions between $(NH_4)SCN$ and $Sn(CH_3)_2Cl_2$, which has yielded the title complex, $[Sn(CH_3)_2(OH)(SCN)]_2$, (I).

The asymmetric unit of compound (I) is situated close to an inversion centre, which generates a dimer containing a central Sn_2O_2 ring; the tin(IV) atom is five-coordinated by two methyl groups, two bridging oxygen atoms and one nitrogen atom of the thiocyanate anion, forming a distorted trigonal bipyramid (Fig. 1). The sum of the angles at the tin atom, involving the carbon atoms and one O atom is 359.47 °; the nitrogen and the other oxygen atom O^i [(i) -x,-y + 1, -z + 1] are at the apical positions. The angles involving N and the atoms of the equatorial plane [N1—Sn1—C2 = 95.18 (12)°, N—Sn—C1 = 95.43 (13)°, N—Sn—O1 = 84.76 (10)°] show a significant deviation from the perfect trigonal-bipyramidal configuration. The bond lengths Sn—C [2.101 (4), 2.102 (4) Å] and Sn—N [2.220 (3) Å] are quite similar while the two Sn—O bond lengths [Sn—O1 = 2.032 (2), Sn—O^i = 2.198 (2) Å] are different but are in the range of typical Sn—O(bridging) distances (Ng, 1998; Chandrasekhar *et al.*, 2007). The Sn—N and Sn—C bond length are likewise in the range of reported values (Cox & Wardell, 1996; Ng, 1998; Okio *et al.*, 2003; Chandrasekhar *et al.*, 2007). The SCN⁻ anion is almost linear [N—C3—S = 178.1 (3)°], as in the structure of $[(CH_3)_4N][Sn(C_6H_5)_3(SCN)_2]$ (Okio *et al.*, 2003). The Sn—N—C angle deviates more from linearity [C3—N—Sn = 172.5 (3)°].

The dinuclear species are linked through O—H⋯S hydrogen bonds into layers parallel to (001) (Fig. 2); C—H⋯S hydrogen bonding interactions (Table 1) lead to the formation of a three-dimensional network.

S2. Experimental

All chemicals were purchased from Aldrich (Germany) and used without any further purification. The salt $(NH_4)SCN$ was obtained by mixing KSCN with NH_4Cl in ethanol 96%. The title compound (I) was synthesized by reacting $Sn(CH_3)_2Cl_2$ with $(NH_4)SCN$ in ethanol ($96_{wt\%}$) in a 1:1 ratio. After stirring for two hours a clear solution was obtained that was slowly evaporated, yielding colourless crystals with a melting point of 502 K.

S3. Refinement

Hydrogen atoms bonded to the O atom have been located in difference Fourier maps and have been freely refined. The other hydrogen atoms have been placed onto calculated position and refined using a riding model, with C—H distances of 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$.
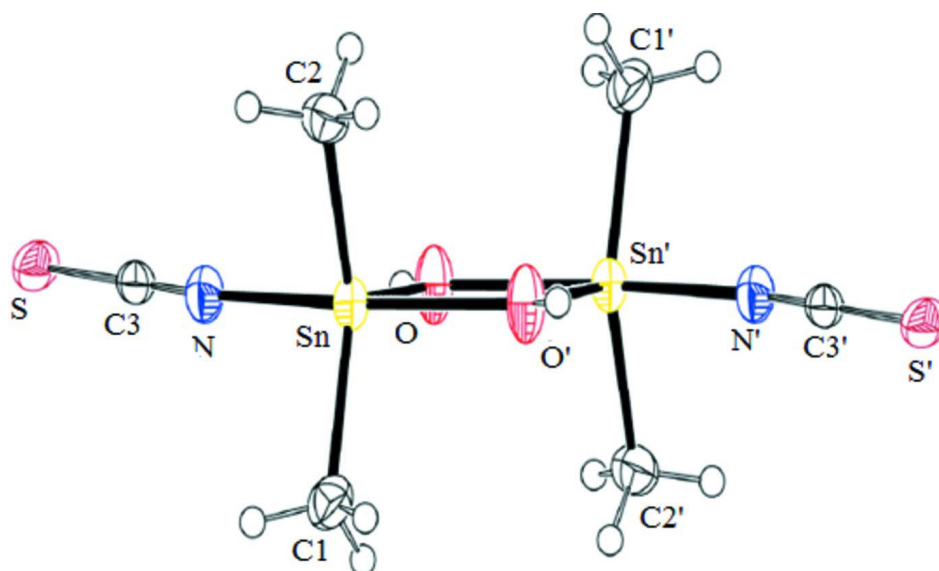
Figure 1

The dinuclear complex of compound (I). Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (′) -*x*,-*y* + 1, -*z* + 1.]
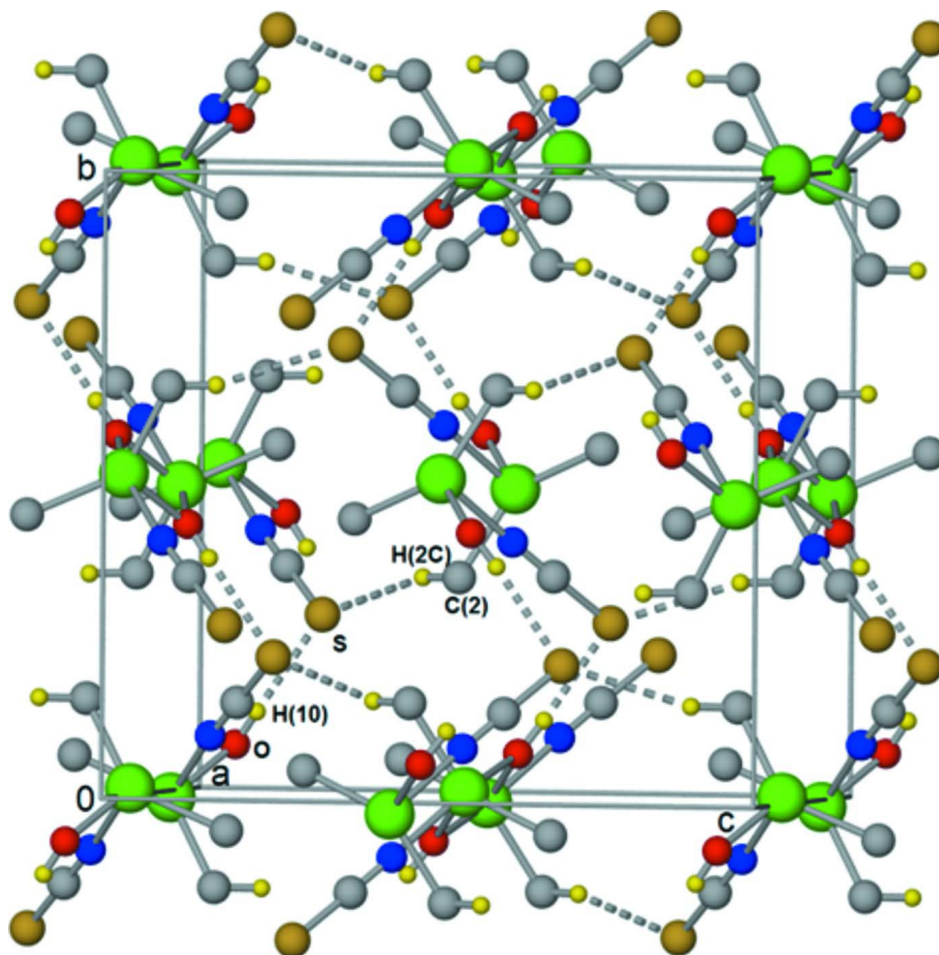
Figure 2

View of the hydrogen bonding system (dashed lines) between the sulfur atom of the SCN⁻ anion and the H atom of the bridging OH group, as well as C—H···S interactions. O atoms are red, S atoms olive, N atoms blue, Sn atoms green, H atoms yellow and C atoms grey.

Di-µ-hydroxido-bis[dimethyl(thiocyanato-κN)tin(IV)]

Crystal data

$[Sn_2(CH_3)_4(NCS)_2(OH)_2]$	$F(000) = 848$
$M_r = 447.69$	$D_x = 2.116$ Mg m^{-3}
Orthorhombic, $Pcab$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2bc 2ac	Cell parameters from 30989 reflections
$a = 8.3440$ (2) Å	$\theta = 2.9–27.5°$
$b = 12.5214$ (3) Å	$\mu = 3.85$ mm^{-1}
$c = 13.3871$ (2) Å	$T = 150$ K
$V = 1398.67$ (5) Å^3	Block, colourless
$Z = 4$	$0.15 \times 0.15 \times 0.10$ mm

Data collection

Nonius KappaCCD diffractometer	20098 measured reflections
Radiation source: fine-focus sealed tube	1603 independent reflections
Graphite monochromator	1333 reflections with $I > 2\sigma(I)$
584 1.0 degree images with φ and ω scans	$R_{int} = 0.055$
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)	$\theta_{max} = 27.5°$, $\theta_{min} = 4.1°$
$T_{min} = 0.596$, $T_{max} = 0.699$	$h = -10 \rightarrow 10$
	$k = -16 \rightarrow 16$
	$l = -17 \rightarrow 17$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.026$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.056$	
$S = 1.11$	$w = 1/[\sigma^2(F_o^2) + (0.0224P)^2 + 1.8745P]$ where $P = (F_o^2 + 2F_c^2)/3$
1603 reflections	
71 parameters	$(\Delta/\sigma)_{max} < 0.001$
1 restraint	$\Delta\rho_{max} = 1.06$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.64$ e Å^{-3}
	Extinction correction: *SHELXL97* (Sheldrick, 2008), Fc*=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$
Secondary atom site location: difference Fourier map	Extinction coefficient: 0.0026 (2)

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Sn	0.20586 (3)	0.512859 (18)	0.486833 (17)	0.02446 (10)
S	0.55735 (12)	0.27972 (7)	0.69604 (7)	0.0356 (2)
O	0.0319 (3)	0.4300 (2)	0.5594 (2)	0.0365 (6)
N	0.3739 (3)	0.4101 (2)	0.5723 (2)	0.0301 (6)
C1	0.2597 (4)	0.4461 (3)	0.3467 (3)	0.0337 (8)
H1A	0.1938	0.3823	0.3361	0.051*
H1B	0.3733	0.4264	0.3445	0.051*
H1C	0.2371	0.4985	0.2942	0.051*
C2	0.2640 (4)	0.6541 (3)	0.5634 (3)	0.0326 (8)
H2A	0.2317	0.7159	0.5233	0.049*
H2B	0.3799	0.6566	0.5751	0.049*
H2C	0.2076	0.6556	0.6276	0.049*
C3	0.4481 (4)	0.3549 (3)	0.6243 (2)	0.0247 (7)
H10	0.054 (4)	0.377 (2)	0.596 (2)	0.033 (10)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Sn	0.01938 (14)	0.02506 (15)	0.02894 (15)	0.00034 (9)	−0.00069 (9)	0.00358 (8)
S	0.0431 (5)	0.0317 (5)	0.0319 (5)	0.0115 (4)	−0.0139 (4)	−0.0056 (3)
O	0.0234 (13)	0.0358 (15)	0.0501 (16)	0.0009 (11)	−0.0028 (12)	0.0229 (12)
N	0.0249 (15)	0.0311 (16)	0.0342 (16)	0.0036 (13)	−0.0038 (13)	0.0023 (12)
C1	0.032 (2)	0.034 (2)	0.036 (2)	−0.0050 (16)	−0.0056 (15)	−0.0037 (15)
C2	0.034 (2)	0.033 (2)	0.0311 (19)	0.0002 (15)	0.0040 (15)	−0.0044 (15)
C3	0.0200 (17)	0.0275 (18)	0.0266 (16)	−0.0032 (14)	0.0030 (14)	−0.0071 (13)

Geometric parameters (Å, º)

Sn—O	2.032 (2)	N—C3	1.160 (4)
Sn—C2	2.101 (4)	C1—H1A	0.9800
Sn—C1	2.102 (4)	C1—H1B	0.9800
Sn—O^i	2.198 (2)	C1—H1C	0.9800
Sn—N	2.220 (3)	C2—H2A	0.9800
S—C3	1.625 (4)	C2—H2B	0.9800
O—Sn^i	2.198 (2)	C2—H2C	0.9800
O—H10	0.842 (18)		
O—Sn—C2	111.20 (13)	Sn—C1—H1A	109.5
O—Sn—C1	112.11 (13)	Sn—C1—H1B	109.5
C2—Sn—C1	136.11 (15)	H1A—C1—H1B	109.5
O—Sn—O^i	69.90 (10)	Sn—C1—H1C	109.5
C2—Sn—O^i	94.13 (12)	H1A—C1—H1C	109.5
C1—Sn—O^i	94.06 (13)	H1B—C1—H1C	109.5
O—Sn—N	84.76 (10)	Sn—C2—H2A	109.5
C2—Sn—N	95.18 (12)	Sn—C2—H2B	109.5
C1—Sn—N	95.43 (13)	H2A—C2—H2B	109.5
O^i—Sn—N	154.66 (10)	Sn—C2—H2C	109.5
Sn—O—Sn^i	110.10 (10)	H2A—C2—H2C	109.5
Sn—O—H10	122 (3)	H2B—C2—H2C	109.5
Sn^i—O—H10	128 (3)	N—C3—S	178.1 (3)
C3—N—Sn	172.5 (3)		

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

Hydrogen-bond geometry (Å, º)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O—H10⋯S^{ii}	0.84 (2)	2.38 (2)	3.207 (3)	168 (4)
C2—H2*C*⋯S^{iii}	0.98	2.79	3.746 (4)	164

Symmetry codes: (ii) *x*−1/2, −*y*+1/2, *z*; (iii) *x*−1/2, −*y*+1, −*z*+3/2.