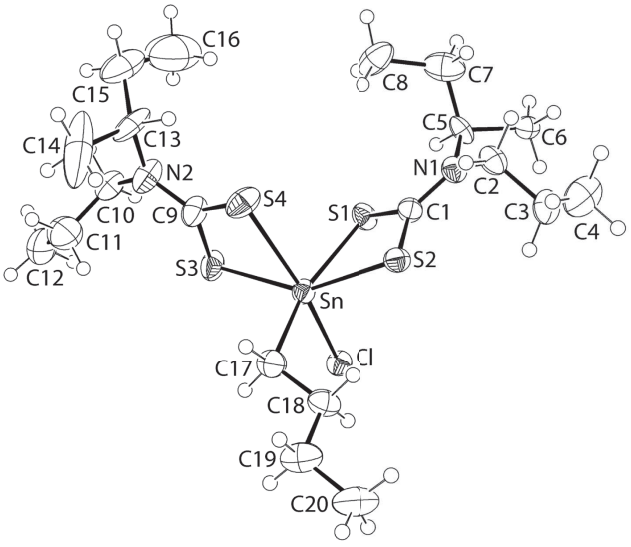
Open Access

Amirah Faizah Abdul Muthalib, Ibrahim Baba*, Siti Nadiah Abdul Halim and Edward R.T. Tiekink

Crystal structure of *n*-butyl-chlorido-bis[N-*sec*-butyl,N-*n*-propyl-carbamodithioato κ^2S,S']-tin(IV), $C_{20}H_{41}ClN_2S_4Sn$



DOI 10.1515/ncrs-2015-0055
Received November 24, 2015; accepted January 18, 2016; available online February 9, 2016

Abstract

$C_{20}H_{41}ClN_2S_4Sn$, triclinic, $P\bar{1}$ (no. 2), $a = 10.0750(3)$ Å, $b = 10.7593(7)$ Å, $c = 13.3097(6)$ Å, $\alpha = 74.619(5)°$, $\beta = 86.861(3)°$, $\gamma = 88.582(4)°$, $V = 1388.93(12)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.044$, $wR_{ref}(F^2) = 0.106$, $T = 100$ K.

CCDC no.: 1448005

The crystal structure is shown in the figure. Tables 1–3 contain details of the measurement method and a list of the atoms including atomic coordinates and displacement parameters.

***Corresponding author: Ibrahim Baba,** School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia, e-mail: aibi@ukm.my
Amirah Faizah Abdul Muthalib: School of Chemical Sciences and Food Technology, Universiti Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia
Siti Nadiah Abdul Halim: Department of Chemistry, University of Malaysia, 50603 Kuala Lumpur, Malaysia
Edward R.T. Tiekink: Faculty of Science and Technology, Sunway University, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia

Table 1: Data collection and handling.

Crystal:	Colourless, prism, size 0.18×0.20×0.30 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	13.26 cm^{-1}
Diffractometer, scan mode:	Agilent Technologies SuperNova Dual diffractometer with Atlas detector, ω scan
$2\theta_{max}$:	55°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	13831, 6362
$N(param)_{refined}$:	289
Programs:	CrysAlis [13], SHELXL-2014/7 [14], WinGX [15]

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

Atom	Site	*x*	*y*	*z*	U_{iso}
H(2A)	2*i*	1.2990	0.5807	0.6449	0.044
H(2B)	2*i*	1.3985	0.5893	0.7321	0.044
H(3A)	2*i*	1.3223	0.7983	0.7280	0.051
H(3B)	2*i*	1.2117	0.7897	0.6478	0.051
H(4A)	2*i*	1.4925	0.7828	0.6019	0.101
H(4B)	2*i*	1.3974	0.9030	0.5545	0.101
H(4C)	2*i*	1.3832	0.7712	0.5221	0.101
H(5A)[a]	2*i*	1.1667	0.4761	0.9418	0.042
H(6A)[a]	2*i*	1.3991	0.6384	0.8903	0.047
H(6B)[a]	2*i*	1.3433	0.5731	1.0069	0.047
H(6C)[a]	2*i*	1.2589	0.6839	0.9315	0.047
H(7A)[a]	2*i*	1.3811	0.3739	0.9744	0.073
H(7B)[a]	2*i*	1.4184	0.4220	0.8520	0.073
H(8A)[a]	2*i*	1.2090	0.2431	0.9420	0.087
H(8B)[a]	2*i*	1.3480	0.2047	0.8936	0.087
H(8C)[a]	2*i*	1.2432	0.2928	0.8192	0.087
H(5B)[b]	2*i*	1.1827	0.4868	0.9505	0.042
H(6D)[b]	2*i*	1.3521	0.3458	0.9962	0.047
H(6E)[b]	2*i*	1.4348	0.4042	0.8885	0.047
H(6F)[b]	2*i*	1.2997	0.3287	0.8894	0.047
H(7C)[b]	2*i*	1.3583	0.6873	0.8733	0.073
H(7D)[b]	2*i*	1.3213	0.6307	0.9941	0.073
H(8D)[b]	2*i*	1.0953	0.7074	0.9592	0.087
H(8E)[b]	2*i*	1.1497	0.7806	0.8440	0.087
H(8F)[b]	2*i*	1.2033	0.8186	0.9428	0.087

Table 2: (continued)

Atom	Site	x	y	z	U_{iso}
H(10A)	2*i*	0.7316	−0.1123	0.8889	0.070
H(10B)	2*i*	0.6796	0.0202	0.9115	0.070
H(11A)	2*i*	0.5568	0.0576	0.7528	0.082
H(11B)	2*i*	0.5915	−0.0894	0.7538	0.082
H(12A)	2*i*	0.4953	−0.1558	0.9268	0.110
H(12B)[b]	2*i*	0.3882	−0.0857	0.8454	0.110
H(12C)	2*i*	0.4525	−0.0093	0.9185	0.110
H(13A)[a]	2*i*	0.9908	0.0342	0.7057	0.067
H(14A)[a]	2*i*	0.9097	−0.1254	0.6185	0.209
H(14B)[a]	2*i*	0.8493	0.0176	0.5835	0.209
H(14C)	2*i*	0.7649	−0.0946	0.6623	0.209
H(15A)[a]	2*i*	0.9080	−0.1992	0.8520	0.093
H(15B)[a]	2*i*	1.0498	−0.1778	0.7901	0.093
H(16A)[a]	2*i*	1.0785	−0.0078	0.8700	0.192
H(16B)[a]	2*i*	1.0858	−0.1516	0.9440	0.192
H(16C)[a]	2*i*	0.9536	−0.0664	0.9458	0.192
H(13B)	2*i*	0.8028	−0.1723	0.6824	0.067
H(14D)[b]	2*i*	0.8781	−0.1064	0.7985	0.209
H(14E)[b]	2*i*	0.9630	0.0123	0.7287	0.209
H(14F)[b]	2*i*	0.8325	−0.0320	0.6846	0.209
H(15C)[b]	2*i*	1.0022	−0.0223	0.5310	0.093
H(15D)[b]	2*i*	0.8864	−0.1158	0.5041	0.093
H(16D)[b]	2*i*	0.7197	0.0285	0.6089	0.192
H(16E)[b]	2*i*	0.8134	−0.0070	0.5193	0.192
H(16F)[b]	2*i*	0.8660	0.0871	0.5832	0.192
H(17A)	2*i*	0.7472	0.4648	0.5227	0.048
H(17B)	2*i*	0.6206	0.5098	0.5825	0.048
H(18A)	2*i*	0.7092	0.7184	0.5497	0.051
H(18B)	2*i*	0.8391	0.6740	0.4932	0.051
H(19A)	2*i*	0.7138	0.6476	0.3571	0.068
H(19B)	2*i*	0.5794	0.6804	0.4152	0.068
H(20A)	2*i*	0.6357	0.8924	0.3850	0.109
H(20B)	2*i*	0.6679	0.8578	0.2764	0.109
H(20C)	2*i*	0.7858	0.8645	0.3506	0.109

[a]Disordered, occupancy factor: 0.732(5); [b]Disordered, occupancy factor: 0.268(5).

Source of material

Carbon disulfide (0.015 mol) was added drop-wise to an ethanol solution (20 mL) of *N*-*sec*-butyl-*N*-*n*-propylamine (0.015 mol). The solution was kept at 277 K for 2 h. *n*-Butyltin trichloride (0.005 mol) dissolved in ethanol (20 mL) was added to give a white precipitate. This was collected and recrystallized from a methanol/dichloromethane (1/2) mixture. Yield: 72%. m.p.: 363 K. Elemental analysis. Found: C, 41.1; H, 7.9; N, 4.7. Calc.: C, 40.6; H, 7.0; N, 4.7. ^{1}H NMR ($CDCl_3$, ppm): δ Sn–Bu: 3.35 *t* (Sn–CH_2); 1.94 *m*, 1.53 *m* (CH_2CH_2); 0.91 *t* (Bu–CH_3); *n*-Pr: 3.50 *t* (N–CH_2); 1.68 *m* (CH_2CH_3); 0.88 *t* (CH_3); *sec*-Bu: 4.63 *m* (N–CH_2), 1.68 *m* ($CHCH_2$), 1.22 *d* ($CHCH_3$), 0.88 *t* (CH_2CH_3). ^{13}C NMR ($CDCl_3$, ppm): δ Sn–Bu: 46.7 (Sn–CH_2), 28.3, 25.3 (CH_2CH_2), 10.9 (CH_3); *n*-Pr: 51.0 (N–CH_2), 18.3 (CH_2CH_3), 13.8 (CH_3); *sec*-Bu: 64.0 (N–CH), 27.9 ($CHCH_2$), 21.6 ($CHCH_3$), 11.3 (CH_2CH_3); 198.3 (NCS_2). IR (KBr, cm^{-1}): 1484 ν(C—N), 991 ν(C—S_2), 328 ν(Sn—S). UV–Vis ($CHCl_3$, nm): 247 (π—π*transition from NCS_2).

Experimental details

The C-bound H atoms were geometrically placed (C—H = 0.98–1.00 Å) and refined as riding with $U_{iso}(H) = 1.2–1.5U_{eq}(C)$. Disorder was noted in both sec-butyl groups and modelled over two sites with site occupancy factors of 0.732(5) and 0.268(5) (not shown in the figure). Equivalent atoms were refined with the same anisotropic displacement parameter and equivalent bonds were restrained to be equal to each other. Finally, the anisotropic displacement parameters of atoms C13—C16 were restrained to be nearly isotropic. The maximum and minimum residual electron density peaks of 1.26 and 1.08 e Å^{-3}, respectively, were located 0.79 Å and 0.74 Å from the Sn atom.

Table 3: Atomic displacement parameters (Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn	2*i*	0.81750(2)	0.46615(3)	0.71037(2)	0.0270(1)	0.0291(2)	0.0339(2)	−0.0023(1)	0.0031(1)	−0.0099(1)
Cl(1)	2*i*	0.67063(9)	0.6121(1)	0.78751(7)	0.0347(5)	0.0346(5)	0.0355(5)	0.0010(4)	0.0029(4)	−0.0123(4)
S(1)	2*i*	0.9690(1)	0.4564(1)	0.85712(8)	0.0306(5)	0.0455(6)	0.0337(5)	−0.0066(4)	0.0004(4)	−0.0032(4)
S(2)	2*i*	1.03716(9)	0.5911(1)	0.63757(8)	0.0286(5)	0.0321(5)	0.0336(5)	0.0002(4)	0.0010(4)	−0.0039(4)
S(3)	2*i*	0.6943(1)	0.2629(1)	0.81307(9)	0.0379(5)	0.0334(6)	0.0563(7)	−0.0098(4)	0.0098(5)	−0.0149(5)
S(4)	2*i*	0.9356(1)	0.2618(1)	0.6768(1)	0.0572(7)	0.0361(6)	0.0501(7)	0.0086(5)	0.0147(5)	−0.0105(5)
N(1)	2*i*	1.2081(3)	0.5558(3)	0.7883(3)	0.029(2)	0.037(2)	0.035(2)	−0.003(1)	0.003(1)	−0.010(2)
N(2)	2*i*	0.8095(4)	0.0479(4)	0.7828(3)	0.069(3)	0.031(2)	0.062(3)	−0.002(2)	0.008(2)	−0.014(2)
C(1)	2*i*	1.0864(4)	0.5368(4)	0.7640(3)	0.028(2)	0.032(2)	0.037(2)	−0.000(2)	0.001(2)	−0.011(2)
C(2)	2*i*	1.3092(4)	0.6153(4)	0.7058(3)	0.026(2)	0.048(3)	0.036(2)	−0.004(2)	0.005(2)	−0.016(2)
C(3)	2*i*	1.3023(4)	0.7615(4)	0.6699(3)	0.043(2)	0.043(3)	0.044(2)	−0.011(2)	0.012(2)	−0.018(2)
C(4)	2*i*	1.4028(6)	0.8088(5)	0.5790(5)	0.067(3)	0.051(3)	0.072(4)	−0.005(3)	0.036(3)	−0.003(3)
C(5)[a]	2*i*	1.248(2)	0.506(1)	0.895(2)	0.027(5)	0.052(3)	0.029(5)	−0.009(3)	−0.008(3)	−0.013(2)
C(6)[a]	2*i*	1.3188(6)	0.6100(6)	0.9347(5)	0.029(3)	0.032(3)	0.031(3)	0.002(2)	0.000(2)	−0.005(2)

Table 3: (continued)

Atom	Site	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(7)[a]	2*i*	1.344(2)	0.395(2)	0.905(1)	0.059(4)	0.082(7)	0.041(6)	0.021(4)	−0.014(5)	−0.016(5)
C(8)[a]	2*i*	1.2802(8)	0.2727(6)	0.8883(5)	0.097(5)	0.037(3)	0.039(3)	0.011(3)	−0.013(3)	−0.008(3)
C(5')[b]	2*i*	1.265(5)	0.516(3)	0.906(5)	0.027(5)	0.052(3)	0.029(5)	−0.009(3)	−0.008(3)	−0.013(2)
C(6')[b]	2*i*	1.345(3)	0.387(3)	0.921(3)	0.029(3)	0.032(3)	0.031(3)	0.002(2)	0.000(2)	−0.005(2)
C(7')[b]	2*i*	1.286(2)	0.646(2)	0.924(2)	0.059(4)	0.082(7)	0.041(6)	0.021(4)	−0.014(5)	−0.016(5)
C(8')[b]	2*i*	1.173(2)	0.747(2)	0.917(1)	0.097(5)	0.037(3)	0.039(3)	0.011(3)	−0.013(3)	−0.008(3)
C(9)	2*i*	0.8125(5)	0.1757(4)	0.7584(4)	0.050(3)	0.035(2)	0.049(3)	−0.002(2)	0.003(2)	−0.017(2)
C(10)	2*i*	0.7008(5)	−0.0235(5)	0.8557(5)	0.066(3)	0.031(2)	0.076(4)	0.002(2)	−0.013(3)	−0.007(2)
C(11)	2*i*	0.5783(6)	−0.0287(6)	0.7980(5)	0.065(4)	0.071(4)	0.075(4)	0.010(3)	−0.008(3)	−0.032(3)
C(12)	2*i*	0.4692(6)	−0.0738(6)	0.8791(5)	0.067(4)	0.050(3)	0.099(5)	−0.015(3)	−0.001(3)	−0.013(3)
C(13)[a]	2*i*	0.9176(8)	−0.0279(7)	0.7356(6)	0.070(5)	0.025(3)	0.065(4)	0.010(3)	0.036(4)	−0.010(3)
C(14)[a]	2*i*	0.854(2)	−0.061(2)	0.641(1)	0.16(1)	0.12(1)	0.17(1)	−0.07(1)	0.05(1)	−0.10(1)
C(15)[a]	2*i*	0.9770(9)	−0.1343(8)	0.8211(8)	0.074(5)	0.051(4)	0.097(6)	0.018(4)	0.031(5)	−0.008(4)
C(16)[a]	2*i*	1.028(1)	−0.086(1)	0.902(1)	0.090(7)	0.121(9)	0.16(1)	0.028(7)	0.003(7)	−0.010(8)
C(13')[b]	2*i*	0.863(3)	−0.096(2)	0.662(2)	0.070(5)	0.025(3)	0.065(4)	0.010(3)	0.036(4)	−0.010(3)
C(14')[b]	2*i*	0.873(5)	−0.022(4)	0.747(3)	0.16(1)	0.12(1)	0.17(1)	−0.07(1)	0.05(1)	−0.10(1)
C(15')[b]	2*i*	0.913(2)	−0.061(2)	0.549(2)	0.074(5)	0.051(4)	0.097(6)	0.018(4)	0.031(5)	−0.008(4)
C(16')[b]	2*i*	0.812(3)	0.011(4)	0.588(3)	0.090(7)	0.121(9)	0.16(1)	0.028(7)	0.003(7)	−0.010(8)
C(17)	2*i*	0.7173(4)	0.5220(4)	0.5670(3)	0.043(2)	0.044(3)	0.038(2)	0.005(2)	−0.006(2)	−0.018(2)
C(18)	2*i*	0.7421(4)	0.6610(5)	0.5064(3)	0.030(2)	0.051(3)	0.043(2)	0.005(2)	−0.001(2)	−0.009(2)
C(19)	2*i*	0.6755(5)	0.6995(5)	0.4030(4)	0.062(3)	0.062(3)	0.045(3)	0.022(3)	−0.006(2)	−0.014(2)
C(20)	2*i*	0.6928(6)	0.8410(6)	0.3490(5)	0.065(4)	0.074(4)	0.065(4)	0.026(3)	−0.007(3)	0.004(3)

[a]Disordered, occupancy factor: 0.732(5); [b]Disordered, occupancy factor: 0.268(5).

Discussion

Owing to promising biological activities and their usefulness as molecular synthetic precursors for tin sulfide nanoparticles, the chemistry of organotin dithiocarbamates continues to attract attention; these applications have been reviewed [1]. In continuation of ongoing studies of the structural chemistry of molecules of the general formula $RSn(S_2CNR'R'')_2Cl$, R, R′, R″ = alkyl and/or aryl [2], the structure of the R = *n*-butyl, R′ = *n*-propyl and R″ = *sec*-butyl derivative, has been investigated. The structural motif adopted by the title molecule is common to all other molecules having this generic formula [2–12]. Thus, the Sn atom exists within a C, Cl, S_4 donor set that describes a distorted octahedral geometry, being coordinated by *n*-butyl-C [2.144(4) Å], Cl [2.5069(10) Å] and four S atoms derived from two almost symmetrically coordinating dithiocarbamate ligands [Sn—S1–S4 = 2.5230(11), 2.6201(10), 2.5601(11) and 2.6043(12) Å]. The butyl-C and Cl atoms are *cis* to each other. The ranges of *cis*- and *trans*-angles are 69.78(4)–107.33(3)° and 151.45(4)–164.42(12)°, respectively, with the acute angles being due to the chelating ligands. No directional intermolecular contacts are noted in the crystal packing.

Acknowledgements: The authors thank Universiti Kebangsaan Malaysia and the Ministry of Science, Technology and Innovation (MOSTI), Malaysia, for supporting this research through grants DPP-2014–064 and 06–01–02-SF0887, respectively.

References

1. Tiekink, E. R. T.: Tin dithiocarbamates: applications and structures. Appl. Organomet. Chem. **22** (2008) 533–550.
2. Faizah, A.; Muthalib, A.; Baba, I.; Khaledi, H.; Ali; H. Md.; Tiekink, E. R. T.: Structural systematics of $RSn(S_2CNR'R'')_2Cl$ compounds. Z. Kristallogr. Cryst. Mat. **229** (2014) 39–46.
3. Harrison, P. G.; Mangia, A.: Structural studies in main group chemistry: XVII. The crystal and molecular structure of phenylchlorobis-(diethyldithiocarbamato)tin(IV). J. Organomet. Chem. **120** (1976) 211–216.
4. Jung, O. -S.; Jeong, J. H.; Sohn, Y. S.: Structure of chlorobis(*N*,*N*-dimethyldithiocarbamato)(3-methoxy-3-oxopropyl)tin(IV). Acta Crystallogr. **C46** (1990) 31–33.
5. Seth, N.; Gupta, V. D.; Nöth, H.; Thomann, M.: Synthesis and molecular structure of tin(IV) 1-pyrrolecarbodithioates. Chem. Ber. **125** (1992) 1523–1528.
6. Vrábel, V.; Kellö, E.; Holeček, J.; Sivý, J. Lokaj, J.: Chlorobis(*N*,*N*-diethyldithiocarbamato)(vinyl)tin(IV). Acta Crystallogr. **C51** (1995) 70–72.
7. Hibbert, T. G.; Mahon, M. F.; Molloy, K. C.: Organotin dithiocarbamate chlorides: X-ray structures of $n\text{-}BuSn(S_2CNEt_2)Cl_2$ and $n\text{-}BuSn(S_2CNEt_2)_2Cl$. Main Group Met. Chem. **22** (1999) 235–241.

8. Clarke, D. J.; Dakternieks, D.; Tiekink, E. R. T.: X-ray structure of chloro-bis(diisobutyldithiocarbamato)phenyltin(IV). Main Group Met. Chem. **24** (2001) 303–304.
9. Clarke, D. J.; Dakternieks, D.; Tiekink, E. R. T.: X-ray structure of n-butyl-chloro-bis(diisobutyldithiocarbamato)tin(IV). Main Group Met. Chem. **24** (2001) 307–308.
10. Clarke, D. J.; Dakternieks, D.; Tiekink, E. R. T.: X-ray structure of n-butyl-chloro-bis(diisopropyldithiocarbamato)tin(IV). Main Group Met. Chem. **24** (2001) 385–386.
11. Lébl, T.; Zoufalá, P.; Bruhn, C.: A comparative assessment of the effect of the Lewis acidity of the central tin atom on intramolecular coordination of (3-methoxypropyl)stannanes. Eur. J. Inorg. Chem. (2005) 2536–2544.
12. Li, Y. -X.; Zhang, R. -F.; Ma, C. -L.: Chlorobis(*N*,*N*-di-n-butyldithiocarbamato)phenyltin(IV). Acta Crystallogr. **E61** (2005) m2365–m2366.
13. Agilent Technologies (2010) CrysAlis PRO. Agilent Technologies, Santa Clara, CA, U.S.A.
14. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallog. **C71** (2015) 3–8.
15. Farrugia, L. J. WinGX and ORTEP for Windows: an update. J. Appl. Cryst. **45** (2012) 849–854.