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Crystal structure of dichlorido-octamethyl-bis(μ_3 -oxido)-bis(μ_2 -2-(phenylamino)ethanolato- $\kappa^2 O:O$) tetratin(IV), $C_{24}H_{44}Cl_2N_2O_4Sn_4$

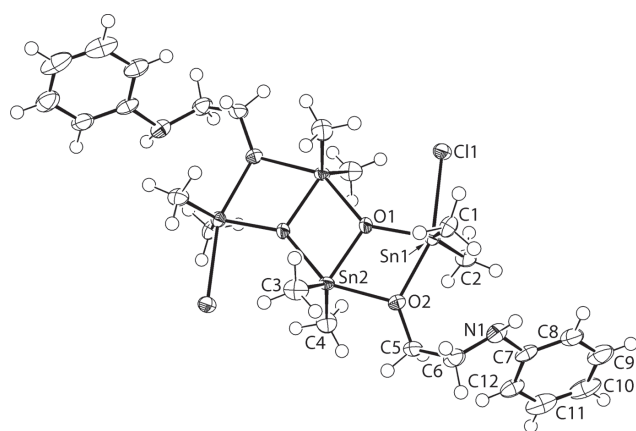


Table 1: Data collection and handling.

Crystal:	Colourless prism
Size:	0.16 × 0.12 × 0.06 mm
Wavelength:	Cu K α radiation (1.54178 Å)
μ :	25.0 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Synergy, ω
θ_{\max} , completeness:	67.1°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	21693, 3006, 0.042
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 2840
$N(\text{param})_{\text{refined}}$:	170
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3], WinGX/ORTEP [4]

<https://doi.org/10.1515/ncrs-2019-0567>

Received August 5, 2019; accepted September 22, 2019; available online October 9, 2019

Abstract

$C_{24}H_{44}Cl_2N_2O_4Sn_4$, orthorhombic, *Pbca* (no. 61), $a = 13.9593(2)$ Å, $b = 11.1227(2)$ Å, $c = 21.6656(3)$ Å, $V = 3363.91(9)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0252$, $wR_{\text{ref}}(F^2) = 0.0642$, $T = 100(2)$ K.

CCDC no.: 1955109

The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals and solvents were used as purchased without purification. The melting point of the compound was measured on a Mel-Temp II digital melting point apparatus and

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was uncorrected. The IR spectrum was recorded on a Perkin-Elmer RX1 spectrophotometer in the range 4000 to 400 cm⁻¹.

The dithiocarbamate salt, $K[S_2CN(Ph)CH_2CH_2OH]$, was prepared *in situ* (methanol) from the reaction of CS_2 (Merck, 0.25 mmol) with 2-anilinoethanol (Merck, 0.25 mmol) and KOH (0.03 mL; 50% w/v); CS_2 was added dropwise into the methanolic solution (10 mL). The resulting mixture solution was kept at 273 K for 0.5 h. Dimethyltin dichloride (0.25 mmol, 0.05 g) in methanol (10 mL) was added to the prepared salt. The resulting mixture was stirred and refluxed for 2 h. The filtrate was evaporated slowly until a white precipitate was formed. The precipitate was recrystallised from methanol and dimethylformamide. The title molecule was isolated as a side-product obtained from the slow evaporation of the solvent. Yield: 0.02 g (16%). **M.pt.**: >573 K. **IR** (cm⁻¹) 467 (w) $\nu(Sn-O)$, 1487 (m) $\nu(C-N)$, 1018 (s) $\nu(C-O)$.

Experimental details

The C-bound H atoms were geometrically placed ($C-H = 0.95-0.99$ Å) and refined as riding with $U_{\text{iso}}(H) = 1.2-1.5U_{\text{eq}}(C)$. The N-bound H-atom was located in a difference Fourier map but was refined with a distance restraint of $N-H = 0.88 \pm 0.01$ Å, and with $U_{\text{iso}}(H)$ set to $1.2U_{\text{eq}}(N)$.

Comment

Diorganotin dichloride molecules are well-known to be subject to hydrolysis [5, 6] and it was in this context the crystals of the title tetra-tin oxido-cluster $\{[(Me_2SnCl)(Me_2Sn)(OCH_2CH_2N(H)Ph)]O\}_2$, (I), was isolated.

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Sn1	0.53720(2)	0.28294(2)	0.47533(2)	0.01347(9)
Sn2	0.46391(2)	0.01011(2)	0.42686(2)	0.01254(9)
Cl1	0.59652(6)	0.30565(8)	0.58783(4)	0.01838(18)
O1	0.51453(17)	0.1109(2)	0.49898(11)	0.0165(5)
O2	0.47623(17)	0.1953(2)	0.39460(12)	0.0180(5)
N1	0.5083(2)	0.4455(3)	0.34412(15)	0.0203(7)
H1N	0.480(3)	0.510(2)	0.360(2)	0.024*
C1	0.4119(2)	0.3840(3)	0.49237(18)	0.0188(7)
H1A	0.3558	0.3315	0.4893	0.028*
H1B	0.4068	0.4487	0.4618	0.028*
H1C	0.4151	0.4188	0.5339	0.028*
C2	0.6758(2)	0.3090(4)	0.43797(17)	0.0200(8)
H2A	0.6890	0.2463	0.4074	0.030*
H2B	0.7234	0.3047	0.4711	0.030*
H2C	0.6791	0.3881	0.4181	0.030*
C3	0.3131(3)	0.0038(4)	0.42892(19)	0.0243(9)
H3A	0.2906	0.0202	0.4709	0.036*
H3B	0.2914	-0.0762	0.4161	0.036*
H3C	0.2871	0.0645	0.4007	0.036*
C4	0.5720(3)	-0.0579(4)	0.36759(19)	0.0238(8)
H4A	0.6352	-0.0416	0.3855	0.036*
H4B	0.5673	-0.0187	0.3272	0.036*
H4C	0.5637	-0.1449	0.3626	0.036*
C5	0.4829(3)	0.2247(3)	0.33104(18)	0.0216(8)
H5A	0.4448	0.1666	0.3067	0.026*
H5B	0.5505	0.2183	0.3176	0.026*
C6	0.4466(3)	0.3514(4)	0.31875(18)	0.0232(8)
H6A	0.4410	0.3632	0.2736	0.028*
H6B	0.3818	0.3598	0.3368	0.028*
C7	0.5856(3)	0.4890(3)	0.30925(18)	0.0200(8)
C8	0.6262(3)	0.6010(4)	0.32490(18)	0.0255(8)
H8	0.5995	0.6463	0.3579	0.031*
C9	0.7039(3)	0.6458(4)	0.2931(2)	0.0334(10)
H9	0.7300	0.7218	0.3040	0.040*
C10	0.7444(3)	0.5798(5)	0.2449(2)	0.0373(11)
H10	0.7984	0.6098	0.2231	0.045*
C11	0.7046(3)	0.4702(5)	0.2294(2)	0.0342(11)
H11	0.7320	0.4246	0.1968	0.041*
C12	0.6259(3)	0.4255(4)	0.26014(18)	0.0248(8)
H12	0.5988	0.3509	0.2478	0.030*

The difficulties associated with hydrolysis notwithstanding, recent work has highlighted the potential anti-tumour activity of related tetra-tin oxido clusters [7, 8], a well-documented attribute of organotin compounds [9]. Herein, the crystal and molecular structures of (I) are described.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids; unlabelled atoms are related by the symmetry operation (i) $1-x, -y, 1-z$); the entire molecule is generated by the application of a crystallographic centre of inversion. The molecule is constructed about a

central Sn₂O₂ core, containing endocyclic Sn₂ atoms. The μ₃-O1 oxido atom of the core also binds to an exocyclic Sn1 atom. Further links between the Sn1 and Sn2 atoms are provided by a μ₂-O2 alkoxide atom. The coordination geometry for the Sn1 atom is completed by two methyl groups and a chloride atom [Sn1–Cl1 = 2.5866(9) Å], while that of the Sn2 atom is completed by two methyl substituents. Within the core, the Sn2–O1, O1ⁱ bond lengths of 2.049(2) and 2.118(2) Å, respectively, and the O1–Sn2–O1ⁱ = 73.76(10)° and Sn2–O1–Sn2ⁱ = 106.24(10)° bond angles indicate the core has the shape of a distorted rhombus. The Sn1–O2 [2.176(3) Å] and Sn2–O2 [2.181(3) Å] bond lengths indicate the μ₂-O(alkoxide) bridge is symmetric. Each of the penta-coordinate geometries is highly distorted. For the Sn1 atom, the donor set is defined by C₂ClO₂ atoms with the widest angle defined by the Cl1 and O2 atoms [Cl1–Sn1–O2 = 157.89(7)°] whereas for the Sn2 atom, the widest angle in the C₂O₃ geometry is defined by the O2 and O1ⁱ atoms [O2–Sn2–O1ⁱ = 146.31(9)°]. The next widest angles are subtended by the tin-bound methyl substituents [Cl1–Sn1–C2 = 138.66(15)° and C3–Sn2–C4 = 135.40(16)°]. The value of τ is a parameter that quantifies five-coordinate geometries, equalling 0.0 for an ideal square-pyramidal coordination geometry and 1.0 for an ideal trigonal-bipyramid [10]. In (I), τ = 0.32 for the Sn1 atom and τ = 0.18 for the Sn2 atom, each indicative of tendencies towards a square-pyramidal coordination geometry. The sequence of three edge-shared Sn₂O₂ rhombi have the shape of a kinked ladder.

The most prominent feature of the molecular packing is the formation of amine-N–H···Cl hydrogen bonds [N1–H1n···Cl1ⁱⁱ: H1n···Cl1ⁱⁱ = 2.57(3) Å, N1···Cl1ⁱⁱ = 3.461(3) Å with angle at H1n = 177(2)° for (ii) $1-x, 1-y, 1-z$]. These give rise to a linear supramolecular chain along the *b*-axis direction. The chains are linked into a supramolecular layer in the *bc*-plane by weak methylene-C–H···π(phenyl) interactions [C5–H5···Cg(C7–C12)ⁱⁱⁱ: H5···Cg(C7–C12)ⁱⁱⁱ = 2.79 Å, C5···Cg(C7–C12)ⁱⁱⁱ = 3.766(4) Å with angle at H5 = 170° for (iii) $1-x, -1/2+y, 1/2-z$]. Layers stack along the *a*-axis without significant directional interactions between them.

Finally, the Hirshfeld surfaces and two-dimensional fingerprint (full and decomposed) plots were calculated on the entire tetra-tin oxido-cluster using Crystal Explorer 17 [11] and standard procedures [12]. This analysis points to the significance of H···H contacts which contribute 76.0% of all contacts to the Hirshfeld surface. The only other two contacts registered are C···H/H···C [12.7%] and Cl···H/H···Cl [10.9%].

Acknowledgements: Sunway University Sdn Bhd is thanked for financial support of this work through Grant no. STR-RCTR-RCCM-001-2019.

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