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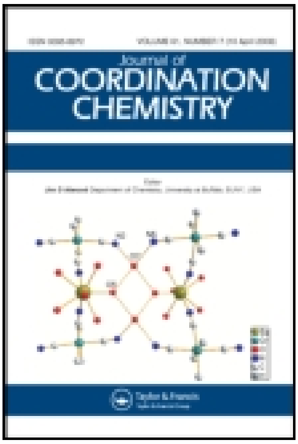

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Structural study on a sulfido-bridged dinuclear organotin(IV) complex with weak Sn···Sn bonding

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Structural study on a sulfido-bridged dinuclear organotin(IV) complex with weak Sn···Sn bonding

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A dinuclear anionic complex, $Bu_4N[Me_2SnCl(S)ClSnMe_2Br]$, has been synthesized in chloroform solution by reacting $(Me_2SnS)_3$, Me_2SnCl_2, and Bu_4NBr. Attempts to isolate the anionic complex using tetramethylammonium cation were unsuccessful. The anion possesses two five-coordinate tin(IV) units bridged by sulfide and bromide. X-ray diffraction study revealed the possibility of a weak Sn–Sn bond in the complex. Theoretical (DFT) studies have been carried out to analyze the nature of metal–metal interaction in the complex.

Keywords: Organotin sulfide; Weak interaction; Metal–metal bonding; Bimetallic complex

1. Introduction

Compounds containing weak metal–metal bonds have attracted attention due to their structural features, nature of bonding, and in a number of cases due to their interesting properties [1, 2]. Studies on weak metal–metal bonding have been carried out in complexes of both early and late transition metals [3–5]. There are some reports of such weak bonds in heavier main group metals as well [6–9]. In spite of these reports, studies on main group metal complexes containing weak M–M bonds are largely unexplored and the significance of such bonds are unrevealed [9]. Recently, we reported structural studies on a few di- and triorganotin compounds containing sulfide/hydrosulfide ligands [10–13]. We report herein, the synthesis and structure of an anionic diorganotin sulfide including the electronic structural details obtained by DFT calculations.

2. Experimental

2.1. *Starting materials*

All solvents were purified by standard methods. Dimethyltin dichloride and tetrabutylammonium bromide (Sigma-Aldrich) were used as received. $(Me_2SnS)_3$ has been synthesized according to the literature procedure [14].

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Table 1. Crystallographic data of **2**.

Empirical formula	$C_{20}H_{48}BrCl_2NSSn_2$
Formula weight	722.88
Crystal size (mm^3)	$0.26 \times 0.24 \times 0.10$
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å, °)	
a	11.867(3)
b	15.270(2)
c	17.557(15)
α	90.00
β	91.03(1)
γ	90.00
Volume (Å^3)	3181(3)
Calculated density (g cm^{-3})	1.464
Absorption coefficient (mm^{-1})	3.102
F(000)	1411
Limiting indices	$-14 \le h \le 14$; $-20 \le k \le 8$; $-24 \le l \le 20$
θ range for data collection (°)	2.32–29.34
R_{int}	0.0611
$R_1/wR(F^2)$	0.0755/0.1998
Goodness-of-fit on F^2	0.908

2.2. *Instrumentation*

Elemental analyses were performed using an Exeter Model E-440 CHN analyzer. ^{1}H, ^{13}C, and ^{119}Sn NMR spectra were recorded in $CDCl_3$ on a JEOL AL300 FT NMR spectrometer.

2.3. *X-ray crystallography*

Single-crystal X-ray data of **2** was collected on a Xcalibur Eos Oxford Diffractometer using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The data integration and reduction were processed with CrysAlisPro software [15]. The structure was solved by direct methods and then refined on F^2 by full-matrix least-squares with SHELX-97 software [16] using the WinGX (version 1.70.01) program package [17]. All non-hydrogen atoms were refined anisotropically. All hydrogens were treated as riding using SHELX default parameters. The details of crystallographic data are given in table 1.

2.4. *Theoretical calculations*

All theoretical calculations were performed with the GAUSSIAN 03W set of programs [18]. The basis set LANL2DZ was utilized for all atoms using B3LYP functional.

2.5. *Synthesis of $Bu_4N[Me_2SnCl(S)ClSnMe_2Br]$ (2)*

Me_2SnCl_2 (0.182 g, 0.827 mmol) in chloroform (15 mL) and solid tetrabutylammonium bromide (0.267 g, 0.829 mmol) were added to a stirred solution of $(Me_2SnS)_3$

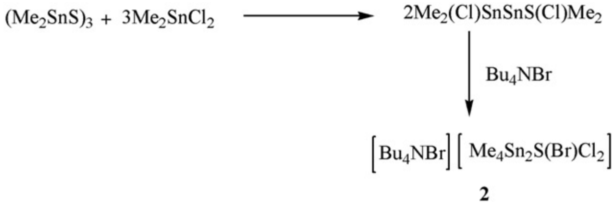
(0.150 g, 0.276 mmol) in chloroform (15 mL). The reaction mixture was refluxed for 12 h [19] and then left at room temperature for crystallization. After a few days, block-shaped colorless single crystals of the compound were obtained. Yield 75%. Anal. Calcd for $C_{20}H_{48}BrCl_2NSSn_2$ (%): C, 33.23; H, 6.69; N, 1.94. Found (%): C, 33.30; H, 6.71; N, 1.92. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.20$ ppm (*s*, 3H, Me–H)], 1.1 (*t*, 3H, Me–H), 1.45–1.49 (*q*, 2H, methylene–H), 1.57–1.68 (*m*, 2H, 70 methylene–H), 3.23–3.29 (*t*, 2H, methylene–H), ^{13}C NMR (75.45 MHz, $CDCl_3$): $\delta = 13.55$, 13.69, 19.80, 24.09, 59.19 ppm, ^{119}Sn NMR: $\delta = -40.35$ ppm.

2.6. *Attempted synthesis of $(Me)_4N[Me_2SnCl(S)ClSnMe_2]Cl$*

Me_2SnCl_2 (0.200 g, 0.912 mmol) in chloroform (15 mL) and solid tetramethylammonium chloride (0.100 g, 0.912 mmol) were added to a solution of $(Me_2SnS)_3$ (0.165 g, 0.304 mmol) in chloroform (15 mL). The reaction mixture was refluxed for 12 h. The expected reaction did not proceed on refluxing for 12 h and the reactants could be identified as such.

3. Results and discussion

When dimethyltin sulfide was reacted with dimethyltin dichloride in 1 : 3 stoichiometric ratio, an adduct $Me_2(Cl)Sn(S)Sn(Cl)Me_2$ (**1**) was formed. The latter when refluxed for 12 h with equimolar tetrabutylammonium bromide in chloroform gave **2**, which could be isolated as colorless crystals after slow evaporation of solvent (equation 1). The complex anion of **2** could not be obtained when a smaller cation (Me_4N^+) was used in place of Bu_4N^+. Compound **2** was quite stable under ambient conditions.



2

Equation 1. Synthesis of **2**.

In the ^{1}H NMR spectrum of the complex, four signals for $-CH_3$, two $-CH_2$ groups adjacent to methyl, and one $-CH_2$ directly attached to nitrogen have been recorded at 1.1 ($-CH_3$), 1.45–1.49 (CH_2), 1.57–1.68 (CH_2), and 3.23–3.29 (CH_2). A singlet for methyl directly attached to Sn has also been recorded at 1.2 ppm. In the ^{13}C NMR spectrum, signals at 13.55 (CH_3Sn), 13.69 (CH_3), 19.80 (CH_2), 24.09 (CH_2), and 59.19 (CH_2) are for methyls directly attached to tin and carbons of the butyl group, respectively. ^{119}Sn NMR spectrum of the compound showed a single resonance at -40.36 ppm, indicating the presence of a five-coordinate tin [11]. The peak position remained unaltered in the temperature range from +23°C to +45°C, indicating the stability of structure in the solution.

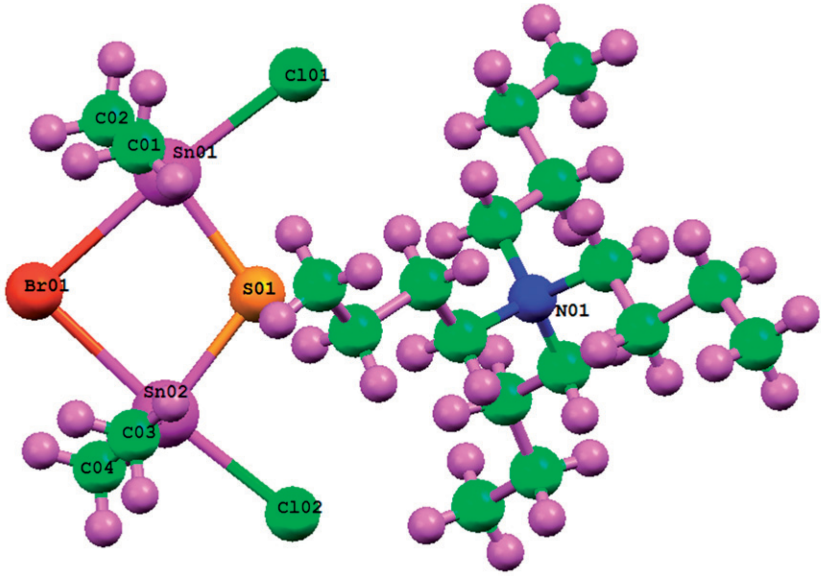


Figure 1. Structure of **2**.

3.1. *Molecular structure of 2*

Compound **2** crystallized in the monoclinic crystal system with space group $P2_1/c$. An ORTEP view of the ion pair is shown in figure 1. Selected bond lengths and angles are listed in table 2.

The structure has a tetrabutylammonium cation and a tin complex anion. There are extensive hydrogen bonds involving Cl, Br, and S resulting in a sheet-like structure in the lattice (figure 2). The CH···Cl distance of 2.937 Å falls under the intermediate category of hydrogen bonding [19], while the S···H distance of 2.935 Å and Br···H distance of 2.831 Å are indicative of fairly strong hydrogen bonding [20, 21]. There is no unusual feature in the cationic part that merits any comments. In the anion each tin is five coordinate having a chloride and two Me groups as terminal ligands, bridged by a sulfide and a bromide. The sulfur symmetrically bridges the two tin centers with equal Sn–S distances. Similarly, the two Sn–Br distances [2.809(2) and 2.820(2) Å] are also similar. Thus, there is an approximate C_2 axis passing through the bridging S and Br. The geometry around each tin is trigonal bipyramidal having two methyl groups and the bridging sulfur at the equatorial positions. The Cl–Sn–Br angles being 174.72(8)° and 175.41(8)° place the Cl^- and μ-Br^- at axial sites. All the equilateral angles [C01–Sn01–C02 = 126.6(6), C01–Sn01–S05 = 114.4(4), C02–Sn01–S05 = 117.6(4)] around Sn01 slightly deviate from the ideal angle of 120°.

An interesting feature of the structure of the anion is the Sn–Sn distance of 3.800 Å, which is significantly shorter than two of the van der Waals' radii of tin (4.34 Å). Such a short distance could arise due to weak Sn–Sn bond or may be due to constraints imposed by the bridging sulfide and bromide.

Table 2. Selected geometrical parameters of the **2**.

Bond lengths (Å)		Experimental (X-ray)	Calculated	
S1	Sn2	2.400(2)	2.50	
S1	Sn1	2.404(2)	2.50	
Br1	Sn1	2.809(2)	3.15	
Br1	Sn2	2.820(2)	3.15	
Cl1	Sn1	2.541(2)	2.50	
Cl3	Sn2	2.552(2)	2.52	
Sn1	C1	2.08(1)	2.13	
Sn1	C2	2.05(1)	2.13	
Sn2	C3	2.09(1)	2.13	
Sn2	C4	2.07(1)	2.13	
Bond angles (°)			Experimental (X-ray)	Calculated
Sn2	S1	Sn1	104.54(9)	108.53
Sn1	Br1	Sn2	84.91(7)	80.103
C1	Sn1	C2	126.6(6)	124.703
C3	Sn2	C4	123.2(5)	124.720
C1	Sn1	S1	117.6(4)	116.490
C2	Sn1	S1	114.4(4)	116.507
C3	Sn2	S1	114.6(4)	116.491
C4	Sn2	S1	120.2(4)	116.513
C1	Sn1	Cl1	95.4(4)	94.447
C2	Sn1	Cl1	95.1(4)	94.445
C1	Sn1	Br1	87.1(4)	84.639
C2	Sn1	Br1	86.4(4)	84.634
S1	Sn1	Cl1	90.63(8)	96.338
S1	Sn1	Br1	84.80(8)	85.666

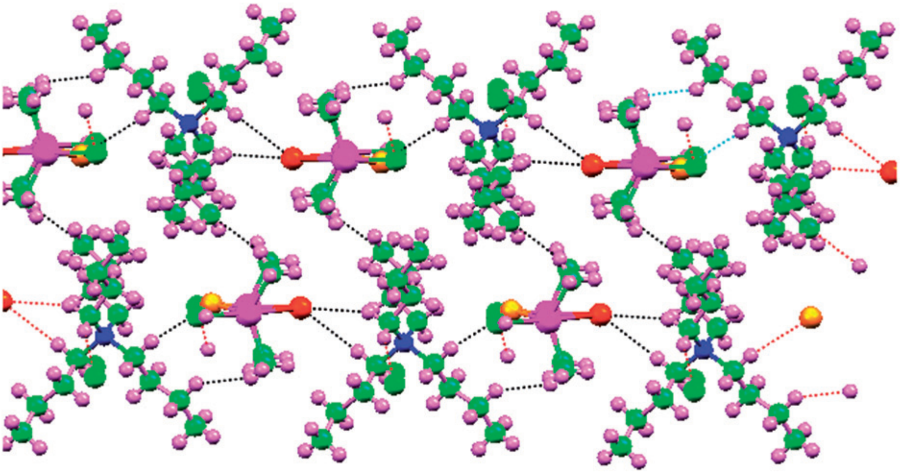


Figure 2. Portion of lattice showing hydrogen bonding.

3.2. *Theoretical studies*

Geometry of the anion was fully optimized by density functional calculations. The initial atomic coordinates used for the optimization were obtained from the X-ray structure. Selected geometrical parameters of the energy optimized anion are given

Table 3. Natural charges on different atoms of **2**.

	Charges	
Atom	A	B
C	−1.10	−1.21
C	−1.14	−1.21
C	−1.12	−1.21
C	−1.11	−1.21
S	−0.86	−0.86
Sn	+1.75	+1.83
Sn	+1.79	+1.83
Br	−0.58	−0.66
Cl	−0.63	−0.61
Cl	−0.63	−0.61

A, atomic coordinates were obtained from X-ray data; B, atomic coordinates were obtained from the optimized geometry.

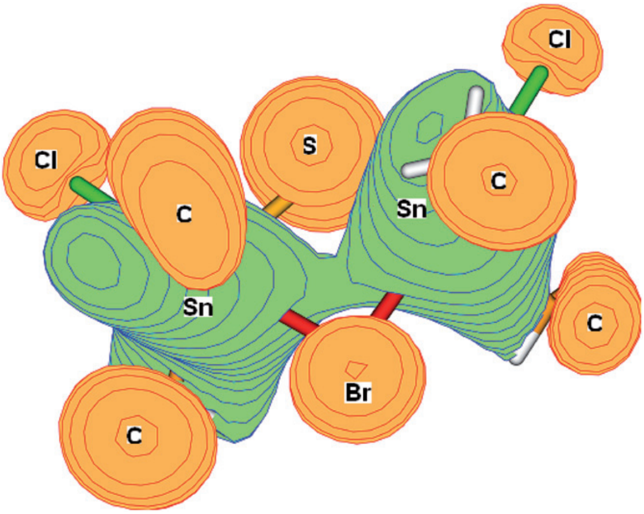


Figure 3. Contour diagram showing orbital overlap.

in table 2. It is evident that both experimental and calculated structures are identical with minor differences in atomic positions. Though the Sn · · · Sn distance in optimized structure (4.05 Å) is slightly larger than that observed crystallographically, still it is shorter than twice the van der Waals radius of Sn. To investigate the cause of a short Sn–Sn distance, we have carried out natural bond orbital (NBO) analysis calculations.

The NBO [22] charges on different atoms are listed in table 3. As expected, the NBO charges on various atoms of the optimized structure are similar to those calculated for the crystallographically obtained structure. The bonding features in the former would represent those existing in the crystalline phase. Though there is no direct Sn–Sn bonding (which is not expected), a close look at the various molecular orbitals reveals a small overlap between the σSn–C orbitals involving the two tins (figure 3). As shown in the table, the two tins possess high positive charges and interaction between the two tins is very weak. Further calculations to find out the extent of overlap and bond order revealed that the Wiberg bond index [23] for the Sn–Sn bond is only 0.01 and atom–atom overlap-weighted natural atomic orbital (NAO) bond order is 0.06.

4. Conclusion

We have synthesized an anionic organotin(IV) complex, $[Me_2SnCl(S)ClSnMe_2Br]^-$, in which two five-coordinate Sn(IV) centers are bridged by S^{2-} and Br^-. The two Sn(IV)s are separated by 3.800 Å, shorter than twice the van der Waals radius of tin. Density functional calculations reveal a weak overlap of two σSn–C orbitals to be responsible for the short Sn–Sn distance. In an earlier study [10] it was found that π–π stacking along with second-order perturbation was responsible for a short Sn–Sn distance in $(Ph_3Sn)_2S$. Further studies on other dinuclear compounds of heavier main group metals are expected to throw light on the nature and importance of various $M\cdots M$ interactions and would be helpful for generalization.

Supplementary material

CCDC 787633 contains the supplementary crystallographic data for **2**. This data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (+44) 1223-336-033; or Email: deposit@ccdc.cam.ac.uk.

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