

**CRYSTAL STRUCTURE AND HIRSHFELD ANALYSIS OF (C<sub>7</sub>H<sub>5</sub>NS)<sub>2</sub>SNCL<sub>6</sub>·2H<sub>2</sub>O**

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**ABSTRACT**

The compound bisbenzothiazolium hexachloridostannate(II) dihydrate was obtained and structurally characterized by single-crystal X-ray diffraction techniques. The ionic compound crystallizes in the triclinic, space group P-1. The environment of the Sn ion is octahedral slightly deformed. Supramolecular architecture involves C—H...O, C—H...Cl and N—H...O hydrogen bonds and featuring  $\pi$ - $\pi$  stacking interactions link the molecules into a three-dimensional network. Hirshfeld analysis was performed to show the intermolecular interactions in the crystal structure.

**Keywords:** Benzothiazole stannate, hydrogen bonds, single-crystal, X-ray diffraction, Hirshfeld surface.

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**1. INTRODUCTION**

Studies of organic-inorganic hybrid materials have received great attention in recent years, because of their ionic, electrical, magnetic and optical properties [1-5]. The antitumor activity of organotin complexes is also known [6].

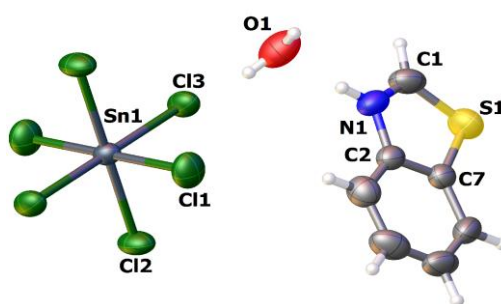


Benzothiazole (BZT) is a well-known class of organic compounds with a diverse range of biological activities [7]. The benzothiazole skeleton constitutes an important template for a wide variety of biologically active compounds. This molecule and its derivatives show antitumor [8], anti-infective and antifungal [9], and antimicrobial activities [10]. As part of our ongoing studies of benzothiazole-based coordination networks [11,12], we now report the structure of new organic– inorganic hybrid compound (1).

## 2. RESULTS AND DISCUSSION

### 2.1. Structural commentary

The title compound has been obtained and structurally characterized by single-crystal X-ray diffraction techniques. The compound (1) crystallizes in the triclinic, space group P-1 with  $z=2$  (table 1, figure 1). The Sn ions are located on an inversion center and adopt an environment octahedral slightly distorted. The Sn-Cl bonds are in the range of 2.4260(7)-2.4324(6) Å. All non-linear angles Cl-Sn-Cl are near 90° and are similar to those found in other octahedral  $\text{SnCl}_6^{2-}$  moieties [2-5]. The benzothiazolium cations are quasi planar and the distance between the mean parallel planes of the cations is 3.554 Å. The  $[\text{SnCl}_6]^{2-}$  octahedron and the water molecules alternate with the benzothiazolium ions to form organic and inorganic layers parallel to (001) (figure 2). The angle at the S atom in the thiazole ring is near 90° suggesting it is using unhybridized  $p$  orbitals for bonding.



**Fig.1.** Ortep of the title compound

**Table 1.** Crystal data and structure refinement for (1)

Empirical formula, Formula weight	C <sub>7</sub> H <sub>8</sub> Cl <sub>3</sub> NOSSn <sub>0.5</sub> , 319.90
Temperature/K	150.00
Crystal system, Space group	Triclinic, P-1
a/Å	7.1749(2)
b/Å	8.3623(2)
c/Å	10.3733(3)
α/°	92.4820(10)
β/°	109.7810(10)
γ/°	99.8490(10)
Volume/Å <sup>3</sup>	573.58(3)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.852
μ/mm <sup>-1</sup>	2.008
F(000)	314.0
Crystal size/mm <sup>3</sup>	0.13 × 0.07 × 0.05
Radiation	MoKα (λ = 0.71073
2θ range for data collection/°	6.112 to 53.998
Index ranges	-9 ≤ h ≤ 9, -10 ≤ k ≤ 10, -13 ≤ l ≤ 12
Reflections collected	10891
Independent reflections	2486 [R <sub>int</sub> = 0.0216, R <sub>sigma</sub> = 0.0183]
Data/restraints/parameters	2486/3/127
Goodness-of-fit on F <sup>2</sup>	1.070
Final R indexes [I ≥ 2σ (I)]	R <sub>1</sub> = 0.0236, wR <sub>2</sub> = 0.0574
Final R indexes [all data]	R <sub>1</sub> = 0.0263, wR <sub>2</sub> = 0.0586
Largest diff. peak/hole / e Å <sup>-3</sup>	0.51/-0.29

## 2.2. Supramolecular features

In the structure, the components are linked *via* intermolecular C—H...O, C—H...Cl and

N—H...O hydrogen bonds (table 2). The whole hydrogen-bonded ensemble makes an  $R_1^2(4)$  and  $R_4^4(10)$  supramolecular motif (figure 3). Additional stabilization is provided by  $\pi$ – $\pi$  stacking interactions:  $Cg1-Cg1 = Cg2-Cg2 = 4.809(00)$  Å,  $Cg1-Cg2 = 3.712(00)$  Å and  $Cg3-Cg3 = 3.644(00)$  Å, where  $Cg1$ ,  $Cg2$  and  $Cg3$  are the *centroid* of the thiazole, phenyl and benzothiazole rings respectively. These interactions link the components together and reinforce the cohesion of the ionic structure.

To understand the role of intermolecular interactions, a Hirshfeld surface analysis was performed [16] and the two-dimensional fingerprint plots were generated [17,18] with *Crystal Explorer17.5* [19].

The red spot on the surface represents a strong interaction, whereas the blue color represents a lack of interaction. The  $d_{\text{norm}}$  map of the title compound and their pure components is shown in figure 3, where individual molecular interactions were estimated.

Individually, for the water molecule, the H...H contact contributes 38.1%, Cl...H/H...Cl 36.5% and O...H/H...O 25.3% while the contribution of Cl...H/H...Cl 26.5% and H...H 17.3% in BZT. The contribution of Cl...H/H...Cl is 76.5% in  $\text{SnCl}_6$  ion. The water molecule is important for the crystal packing, as emphasized in figure 4.

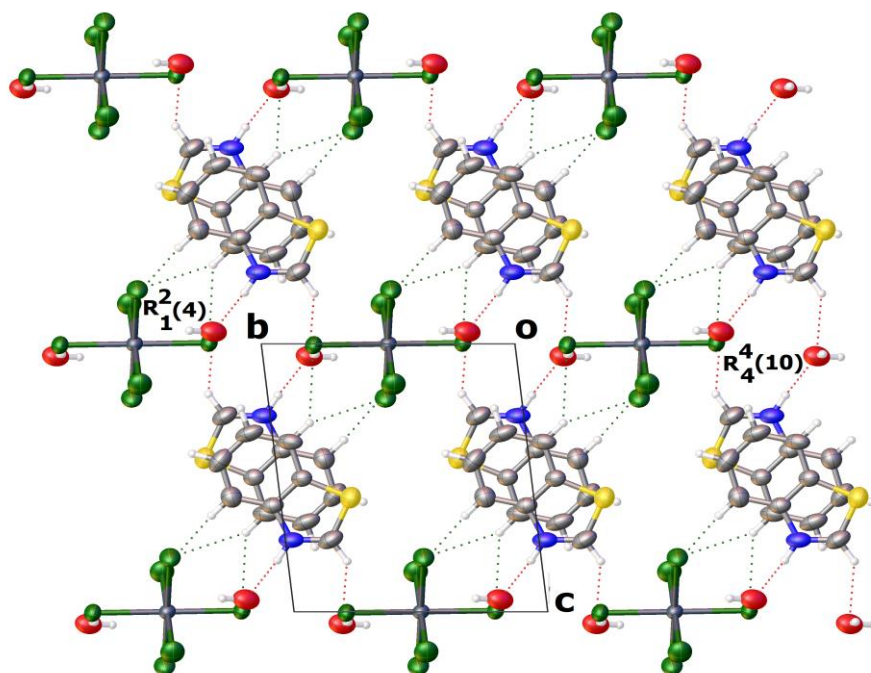
The fingerprint plot shows that H...H contribute the major part of the interaction in all components.

The presence of the adjacent red and blue triangles in figure 5 clearly illustrates the  $\pi$ – $\pi$  stacking interactions.

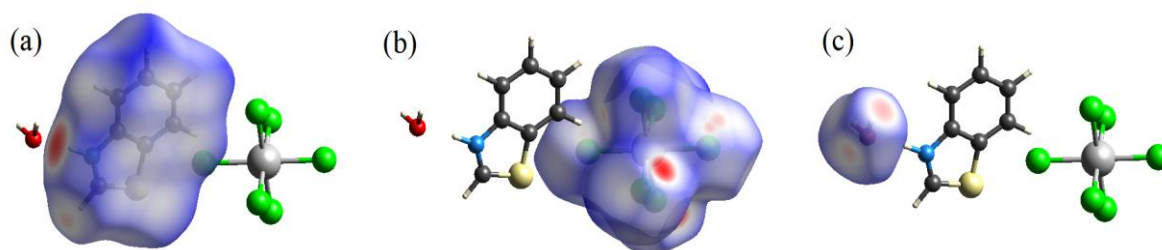
**Table 2.** Hydrogen Bonds for (1)

D H A	d(D-H)/Å	d(H-A)/Å	d(D-A)/Å	D-H-A/°
N1 H1 O1	0.88	1.81	2.687(3)	173.4
C6 H6 Cl3	0.95	2.85	3.633(3)	139.9
C6 H6 Cl3	0.95	2.90	3.633(3)	135.1
C3 H3 Cl1 <sup>1</sup>	0.95	2.98	3.741(3)	138.5
C1 H1A Cl2 <sup>2</sup>	0.95	2.82	3.368(3)	117.9
C1 H1A O1 <sup>3</sup>	0.95	2.50	3.239(4)	134.6

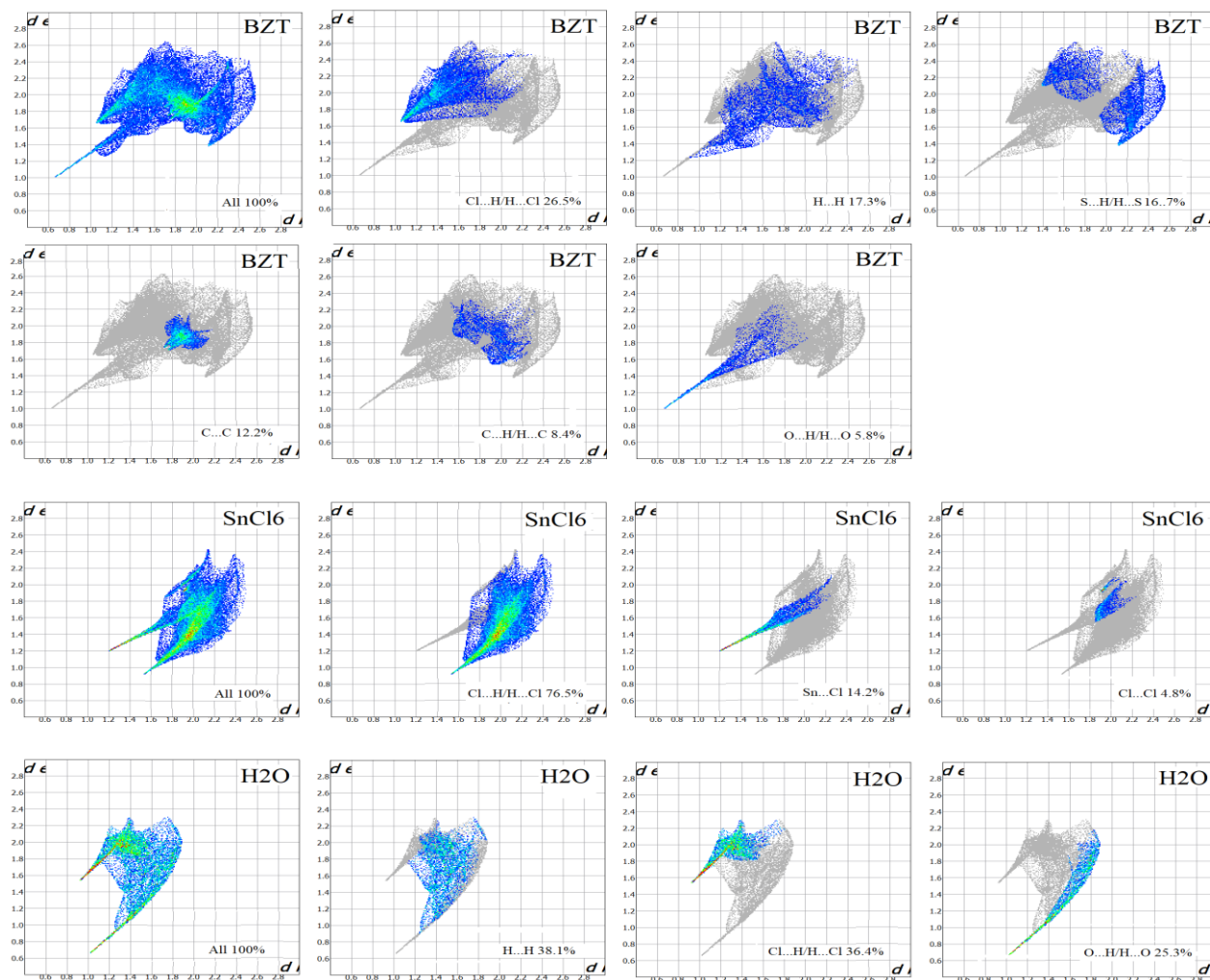
<sup>1</sup>2-x,-y,-z; <sup>2</sup>1-x,-1-y,-z; <sup>3</sup>2-x,-y,1-z



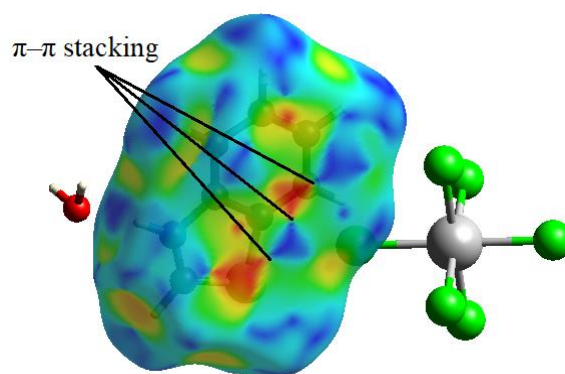
**Fig.2.** Projection of the crystal packing of (1) towards a-axis. The green and red dotted lines indicate hydrogen bond interactions



**Fig.3.** Hirshfeld surfaces plotted on  $d_{\text{norm}}$  mapped over BZT (-0.7184, 1.1723) (a),  $\text{SnCl}_6$  (-0.2251, 1.0292) (b) and  $\text{H}_2\text{O}$  (-0.7190, 0.8798) (c) molecules



**Fig.4.** Two-dimensional fingerprint plots and relative contributions of various interactions to the Hirshfeld surface of the BZT (a), SnCl<sub>6</sub> (b) and H<sub>2</sub>O (c) molecules



**Fig.5.** Curvedness surface of the title compound showing the  $\pi$ - $\pi$  stacking

### 3. EXPERIMENTAL

#### 3.1. Synthesis

All solvents and chemicals were used as received. Tin<sup>II</sup> chloride dihydrate (Sigma Aldrich, 98%) (45 mg, 0.2 mmol) in ethanol (10 ml) was added dropwise to a solution of benzothiazole (Alfa Aesar, 97%) (0.5 ml, 4.6 mmol) in ethanol/water (10ml/10ml). The mixture was then refluxed with stirring for 3 h and the resulting solution was left to stand at room temperature. Light yellow crystals were obtained after several days.

#### 3.2. Characterization techniques

Single crystal X-ray diffraction experiments were carried out at 150 K on a Bruker Apex 2 diffractometer using Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Using Olex2 [13], the structure was solved with the SHELXT [14] structure solution program using Intrinsic Phasing and refined with the SHELXL [15] refinement package using Least Squares minimisation. The H atoms were placed in calculated positions, with C—H = 0.95, N—H = 0.88 and 0.87 Å for O—H (water). They were refined with riding models with fixed isotropic displacement parameters, with  $U_{iso}(H) = 1.5U_{eq}(C)$  for OH groups and  $1.2U_{eq}(C)$  for CH and NH groups.

### 4. CONCLUSION

The compound (**1**) is hybrid and crystallizes in the triclinic, space group P-1 with  $z=2$ . The Sn ions adopt an environment octahedral slightly distorted. The benzothiazolium cations are quasi planar 3.554 Å interplanar distance. The components are linked *via* intermolecular C—H...O, C—H...Cl and N—H...O hydrogen bonds generating  $R_1^2(4)$  and  $R_4^4(10)$  supramolecular motif. Additional stabilization is provided by  $\pi$ - $\pi$  stacking interactions.

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## 6. SUPPLEMENTARY MATERIALS

Supplementary data for this paper are available from the electronic archives (CSD 2170567).

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