

# SYNTHESIS, CRYSTAL STRUCTURE AND HIRSHFELD SURFACE ANALYSIS OF A NEW COORDINATION POLYMER: STRONTIUM BENZILATE

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## ABSTRACT

A novel coordination polymer was synthesized from strontium carbonate and benzylic acid in aqueous solution and is formulated as  $\text{Sr}[(\text{C}_6\text{H}_5)_4(\text{COCOO})_2 \cdot 2\text{H}_2\text{O}]$ . This compound was characterized by FTIR spectroscopy and powder X-ray diffraction. The crystal structure was determined by single-crystal X-ray diffraction. The complex crystallizes in the monoclinic  $P2_1/n$  space group, with unit cell parameters  $a = 15.0224(9)$  Å,  $b = 7.5038(6)$  Å,  $c = 25.000(2)$  Å,  $\beta = 94.764(2)^\circ$ ,  $V = 2808.4$  Å<sup>3</sup>,  $Z = 4$ . In the structure, the metallic ion is coordinated to eight oxygen atoms, six from benzilate molecules, and two from water molecules, forming a distorted tetragonal antiprism. One of the benzilates is coordinated to the metal in a monodentate fashion (carboxylate only), while the other benzilate molecule does it in the bidentate from carboxylate and hydroxide. Strontium ions form infinite zig-zag chains along the [010] direction, which form a three-dimensional network via O–H···O hydrogen-bond interactions between the coordinated water molecules and the O atoms of the carboxylate groups. The intermolecular interactions were analyzed using Hirshfeld surface analysis.

**Keywords:** Benzilate, coordination polymer, X-ray diffraction, hydrogen bonds, Hirshfeld surface.

## 1. INTRODUCTION

$\alpha$ -Hydroxycarboxylic acids are organic compounds with two functional groups, carboxylic acid and an alcoholic in  $\alpha$ -position concerning the carboxylic acid group. These types of organic compounds containing a hydroxyl (-OH) and carboxylic (-COOH) moieties constitute suitable building blocks in generating a variety of supramolecular assemblies through strong O–H···O hydrogen bond interactions<sup>1</sup>. Meaningfully, the hydrogen bond is one of the most important intermolecular interactions, responsible for several of the main characteristics of these systems, and provides a powerful way to generate supramolecular architectures from simple building blocks<sup>2</sup>.

Both functional groups in  $\alpha$ -hydroxycarboxylic acids are capable of coordinating metal ions in a variety of modes and with numerous possibilities leading to the formation of assembly of supramolecular arrays through intermolecular interactions<sup>3</sup>. When these  $\alpha$ -hydroxycarboxylic acids act as a single ligand, three forms of coordination to a single cation have been observed: bidentate chelate through the carboxylate and alcoholic hydroxyl groups, bidentate chelate through the carboxylate group alone, and monodentate through the carboxylate<sup>3</sup>.

For some metal complexes of  $\alpha$ -hydroxy carboxylate ligands have been reported medicinal uses as antibacterial and antiulcer activities<sup>4,5</sup> and more recently as an anticancer agent<sup>6</sup>.

Benzilic acid, an aromatic  $\alpha$ -hydroxycarboxylic acid, has long been used in the preparation of antimuscarinic agents<sup>7-10</sup> and treatment against Alzheimer's disease since it can be a considerable inhibitor of acetylcholinesterase enzyme<sup>11,12</sup>.

From the supramolecular point of view, the benzilate moiety has two phenyl rings oriented as propeller blades, and hydroxyl and carboxylate groups, which have the potential to form hydrogen bonds and interact with the charged field of a counter-ion. This fact has been evidenced in the structural characterization of some metal complexes studied with benzylic acid acting as the only ligand with  $\text{Li}^{+13}$ ,  $\text{K}^{+14}$ ,  $\text{Tl}^{+15}$  and  $\text{Pb}^{2+16}$ , or in conjunction with other ligands<sup>6,17-20</sup>. In these complexes, packing in the solid-state should comprise diverse cohesive interactions such as O–H···O and aromatic ( $\pi \cdots \pi$ , C–H··· $\pi$ ), which allow the formation of coordination polymer around the metal ion.

Precisely, in recent years, significant attention had been paid in designing and development of coordination polymers (CPs) which are certainly very promising as multifunctional materials<sup>21-23</sup>. The possibilities of packaging self-assembly mean that polymers can have unlimited structures and these varied structures can be prepared by choosing different metal ions or/and different ligands, and therefore these materials can have multiple applications in gas storage, heterogeneous catalysis, chemical sensors, energy conversion, drug delivery, among others<sup>23</sup>.

In continuation of our previous investigation on coordination polymers<sup>13,14,24-27</sup>, in this work, we present the synthesis, structural characterization and energetic properties of the new coordination polymer strontium benzilate. Hirshfeld surface analysis<sup>28</sup> was used for visually analyzing intermolecular interactions in the crystal structure.

## 2. EXPERIMENTAL SECTION

### 2.1 Synthesis and FT-IR spectroscopy

Strontium benzilate was prepared by reaction of benzylic acid ( $\text{C}_{14}\text{H}_{12}\text{O}_3$ ) and strontium carbonate ( $\text{SrCO}_3$ ) in a 1:1 ratio in water. The mixture was maintained under continuous stirring for 24 h. The resulting solution was filtered and allowed to evaporate slowly at ambient temperature. Colorless plates grew in the solution over one month.

The FT-IR absorption spectrum was obtained as KBr pellet using a Perkin-Elmer 1600 spectrometer. The FT-IR showed O-H stretching bands from coordination water molecules at  $3650\text{ cm}^{-1}$ , and lattice water at  $3358$  y  $3180\text{ cm}^{-1}$ . The aromatic ring  $\text{sp}^2$  carbons stretching band is at  $3059\text{ cm}^{-1}$ , while the  $\nu_a$  ( $\text{CO}_2^-$ ) and  $\nu_s$  ( $\text{CO}_2^-$ ) stretchings are located at  $1596$  and  $1389\text{ cm}^{-1}$ , respectively. The C-O stretching band appears at  $1053\text{ cm}^{-1}$ .

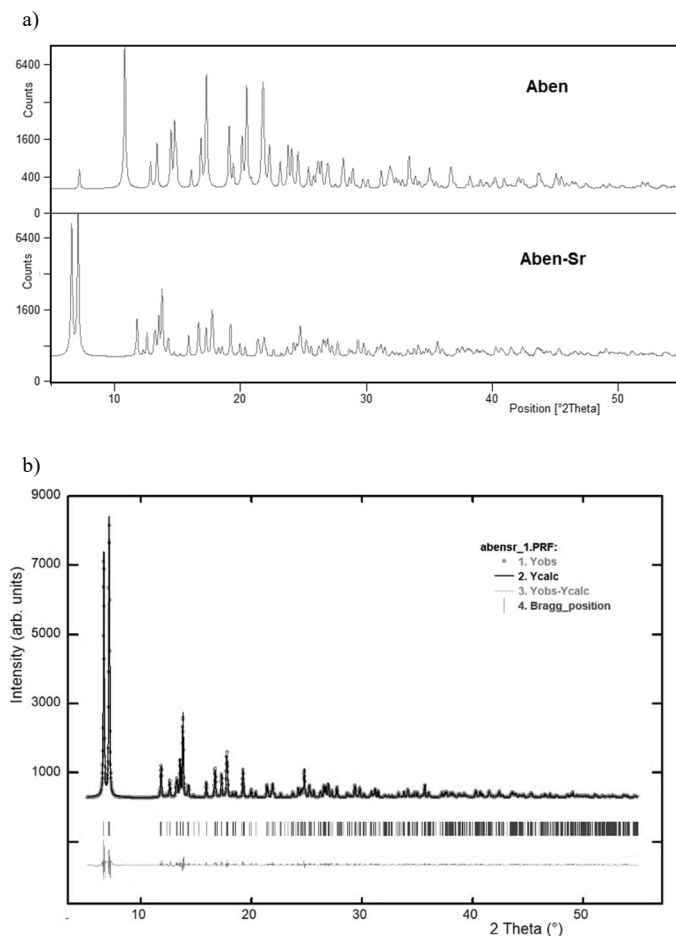
### 2.2 X-ray powder diffraction

The X-ray powder diffraction data of benzylic acid and strontium benzilate was collected at room temperature  $293(1)\text{ K}$ , in  $\theta/\theta$  reflection mode using a Siemens D5005 diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.5418$  Å). The diffractometer was worked at  $40\text{ kV}$  and  $25\text{ mA}$ . A small quantity of each compound was ground mechanically in an agate mortar and pestle and mounted

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on a flat holder covered with a thin layer of grease. The samples were scanned from 5° to 55° 2 $\theta$ , with a step size of 0.02° and counting time of 10 s per step. Quartz was used as an external standard.

X-ray powder patterns showed in Figure 1a evidence the formation of a new compound. For the complex powder pattern, the 20 first measured reflections were completely indexed, using Dico104 program<sup>29</sup>, which gave a unique solution in a monoclinic cell with parameters  $a = 15.05 \text{ \AA}$ ,  $b = 7.48 \text{ \AA}$ ,  $c = 25.01 \text{ \AA}$ ,  $\beta = 94.6^\circ$  in a  $P$ -type cell. This cell was confirmed employing single-crystal analysis. In order to check the unit cell parameters, a Le Bail refinement<sup>30</sup> was carried out using the Fullprof program<sup>31</sup>. The Figure 2b shows a very good fit between the observed and calculated patterns. This analysis is also indicative of the homogeneity of the crystallized sample and the single crystals appear to be representative of the bulk samples.



**Figure 1.** a) X-ray powder diffraction patterns of benzylic acid and strontium benzilate. b) Le Bail refinement of the complex.

### 2.3 X-ray single-crystal crystallography

A colorless rectangular crystal (0.50, 0.40, 0.20 mm) was used for data collection. X-ray diffraction data were collected at 295 K on a Bruker SMART CCD area-detector diffractometer<sup>32</sup> equipped with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The data were corrected for Lorentz-polarization and absorption effects<sup>33</sup>. The structure of were solved by direct methods<sup>34</sup> using the OLEX2 program<sup>35</sup> and refined by a full-matrix least-squares calculation on  $F^2$  using SHELXL<sup>36</sup>. All H atoms were placed at calculated positions and treated using the riding model with C-H distances of 0.97-0.98  $\text{\AA}$ . Non-hydrogen atoms were refined with anisotropic displacement parameters. The Cambridge Structural Database (CSD, version 5.41, Aug. 2020) was used for structure analysis<sup>37</sup>. Hydrogen bond interactions were verified using PLATON Software<sup>38</sup>. Diagrams were prepared using DIAMOND software<sup>39</sup>.

Table 1 summarizes the crystal data, intensity data collection, and refinement details for the title compound. Crystallographic data for the structure reported

here have been deposited with the Cambridge Crystallographic Data Centre (Deposition No. CCDC-2002517). These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 1.** Crystal data, data collection, and structure refinement of strontium benzilate.

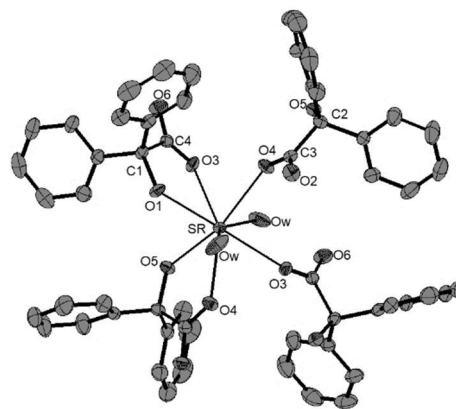
Chemical formula	C <sub>28</sub> H <sub>20</sub> O <sub>7</sub> Sr	CCDC	2002517
Formula weight	556.06	Radiation [ $\text{\AA}$ ]	0.71073
Crystal system	monoclinic	$\theta$ range [ $^\circ$ ]	1.6-23.3
Space group	P2 <sub>1</sub> /n (14)	hkl range	-16, 6; -8, 8; -27, 22
$a$ [ $\text{\AA}$ ]	15.0224(9)	Reflections	
$b$ [ $\text{\AA}$ ]	7.5038(6)	Collected	12184
$c$ [ $\text{\AA}$ ]	25.000(2)	Unique (Rint)	4058 (0.058)
$\beta$ [ $^\circ$ ]	94.764(2)	With $I > 2\sigma(I)$	3039
$V$ [ $\text{\AA}^3$ ]	2808.4(4)	R( $F^2$ ) [ $I > 2\sigma(I)$ ]	0.043
Z	4	wR( $F^2$ ) [ $I > 2\sigma(I)$ ]	0.123
dx [ $\text{g}\cdot\text{cm}^{-3}$ ]	1.315	Refinement method	Full-matrix least-squares on $F^2$
$\mu$ [ $\text{mm}^{-1}$ ]	1.960	Number of parameters	352
Crystal size [mm]	0.5 x 0.4 x 0.2	Goodness of fit on $F^2$	0.92
F [000]	1128	Max/min $\Delta\rho$ [ $\text{e}\cdot\text{\AA}^{-3}$ ]	0.73/-0.64

### 2.4 Hirshfeld surfaces analysis

For the title compound, Hirshfeld surfaces analysis<sup>28</sup> was performed with the aid of CrystalExplorer program<sup>40</sup>. The two-dimensional fingerprint plots were calculated for the crystal, as were the electrostatic potentials<sup>41</sup>. The electrostatic potentials were mapped on the Hirshfeld surfaces using the 3-21G basis set at the level of Hartree-Fock theory. The crystallographic information file (CIF) of the complex was used as input for the analysis. For the generation of fingerprint plots, the bond lengths of hydrogen atoms involved in interactions were normalized to standard neutron values (C-H = 1.083  $\text{\AA}$ , O-H = 0.983  $\text{\AA}$ ).

## 3. RESULTS AND DISCUSSION

The structure of strontium benzilate unit is depicted in Figure 2. This complex crystallizes in the monoclinic system with  $P2_1/n$  as space group, with 4 entities *per* unit cell. Table 2 shows the fractional atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms. Each of the central  $\alpha$ -C atoms bonds tetrahedrally to a hydroxyl, two phenyls, and a carboxylate with bond distances and angles shown in Table 3. All bond distances and angles are normal<sup>42</sup> and agree with the average values found in 90 entries with benzilate fragments found in the Cambridge Structural Database (CSD, version 5.41, Aug. 2020)<sup>37</sup>.

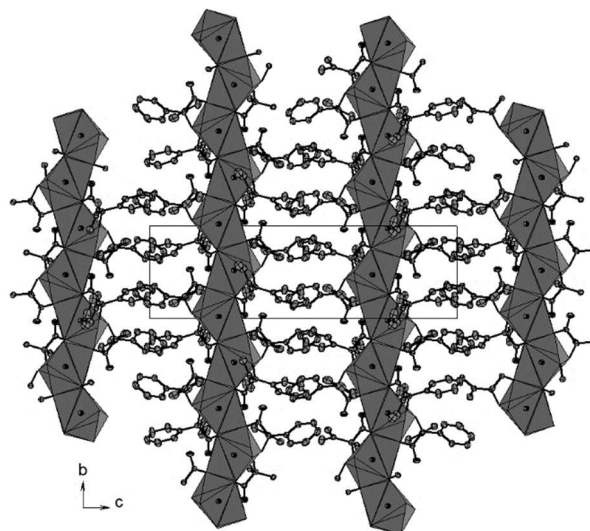


**Figure 2.** The coordination environment of the Sr ion in strontium benzilate. Displacement ellipsoids are shown at a 30% probability level.

The orientations of the phenyl rings in the benzilate moieties are those of propeller blades, as found in lithium benzilate<sup>13</sup>, potassium benzilate<sup>14</sup>, and the various benzilate derivatives found in the CSD Database<sup>37</sup>. This conformation minimizes the repulsive interactions between the geminal phenyl rings.

In the structure, the metallic ion is coordinated to eight oxygen atoms, six from benzilate molecules, and two from water molecules, forming a distorted tetragonal antiprism. One of the benzilates is coordinated to the metal in a monodentate fashion (carboxylate only), while the other benzilate molecule does it in the bidentate from carboxylate and hydroxide. Strontium ions lies close to screw  $2_1$  axis (with  $x, y, z = 0.746, 0.976, 0.275$ , respectively) generating an

infinite *zig-zag* chains along the [010] direction with translational symmetry:  $3/2-x, 1/2+y, 1/2-z$  (Figure 3). The resulting one-dimensional chains are supramolecular related by O-H...O hydrogen-bond interactions between the coordinated water molecules and the O atoms of the carboxylate groups with graph set motifs<sup>43</sup> R(6) and  $C_2^2(7)$  along those (see Table 4).



**Figure 3.** Part of the crystal structure showing the *zig-zag* chains of {SrO8} polyhedra in the structure of strontium benzilate.

**Table 2.** Fractional atomic coordinates ( $\times 10^4$ ) and Equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for title compound.  $U_{eq}$  is defined as  $1/3$  of the trace of the orthogonalised  $U_{ij}$  tensor.

Atoms	x	y	z	$U_{eq}$
Sr	0.74624(3)	0.52442(5)	0.27496(1)	0.0315(2)
O1	0.8450(2)	0.5615(4)	0.3640(1)	0.042(1)
O2	0.9391(2)	0.5437(4)	0.1916(1)	0.051(1)
O3	0.7283(2)	0.3367(4)	0.1839(1)	0.038(1)
O4	0.8408(2)	0.7317(4)	0.2214(1)	0.042(1)
O5	0.6159(2)	0.4966(3)	0.3359(1)	0.037(1)
O6	0.6548(2)	0.5346(4)	0.1318(1)	0.054(1)
O7	0.6428(2)	0.7477(5)	0.2184(2)	0.073(2)
C1	0.8739(3)	0.7282(6)	0.3884(2)	0.034(1)
C2	0.5622(3)	0.3410(5)	0.3433(2)	0.034(2)
C3	0.9036(3)	0.6933(6)	0.1924(2)	0.033(2)
C4	0.6750(3)	0.3771(5)	0.1458(2)	0.033(2)
C11	0.8428(3)	0.7418(6)	0.4452(2)	0.038(2)
C12	0.7689(3)	0.6488(7)	0.4584(2)	0.051(2)
C13	0.7378(4)	0.6634(8)	0.5079(3)	0.069(2)
C14	0.7809(5)	0.7741(9)	0.5466(2)	0.074(3)
C15	0.8541(5)	0.8669(8)	0.5341(2)	0.065(2)
C16	0.8849(4)	0.8539(6)	0.4836(2)	0.050(2)
C17	0.9745(3)	0.7423(6)	0.3857(2)	0.041(2)
C18	1.0332(4)	0.6664(7)	0.4255(2)	0.056(2)
C19	1.1248(4)	0.6687(8)	0.4198(3)	0.075(3)
C21	0.5775(3)	0.2849(6)	0.4023(2)	0.035(2)
C22	0.5170(4)	0.3153(8)	0.4397(2)	0.065(2)

**Table 3.** Selected geometrical parameters ( $\text{\AA}, ^\circ$ ) for the strontium benzilate.

O1-C1	1.442(5)	C1-C11	1.535(6)	Sr-O1	2.587(3)
O2-C3	1.244(5)	C2-C21	1.532(6)	Sr-O3	2.672(3)
O3-C4	1.230(5)	C1-C17	1.522(6)	Sr-O4	2.558(3)
O4-C3	1.271(5)	C2-C27	1.529(6)	Sr-O5	2.587(3)
O5-C2	1.440(5)	C1-C4	1.554(6)	Sr-Ow	2.619(4)
O6-C4	1.263(5)	C210-C211	1.364(12)	Sr-Ow	2.659(4)
O1-Sr-O3	143.18(9)	O1-Sr-O4	94.67(10)	O1-Sr-O5	84.84(9)
O1-Sr-O7	131.95(11)	Sr-O4-C3	129.2(3)	O3-Sr-O4	84.02(9)
Sr-O3-C4	122.9(3)	Sr-O1-C1	126.0(2)	Sr-O5-C2	127.0(2)
O3-Sr-O5	115.55(9)	O1-C1-C11	110.1(3)	O1-C1-C17	107.9(3)
C11-C1-C17	114.6(4)	O5-C2-C21	107.9(3)	O5-C2-C27	110.2(3)

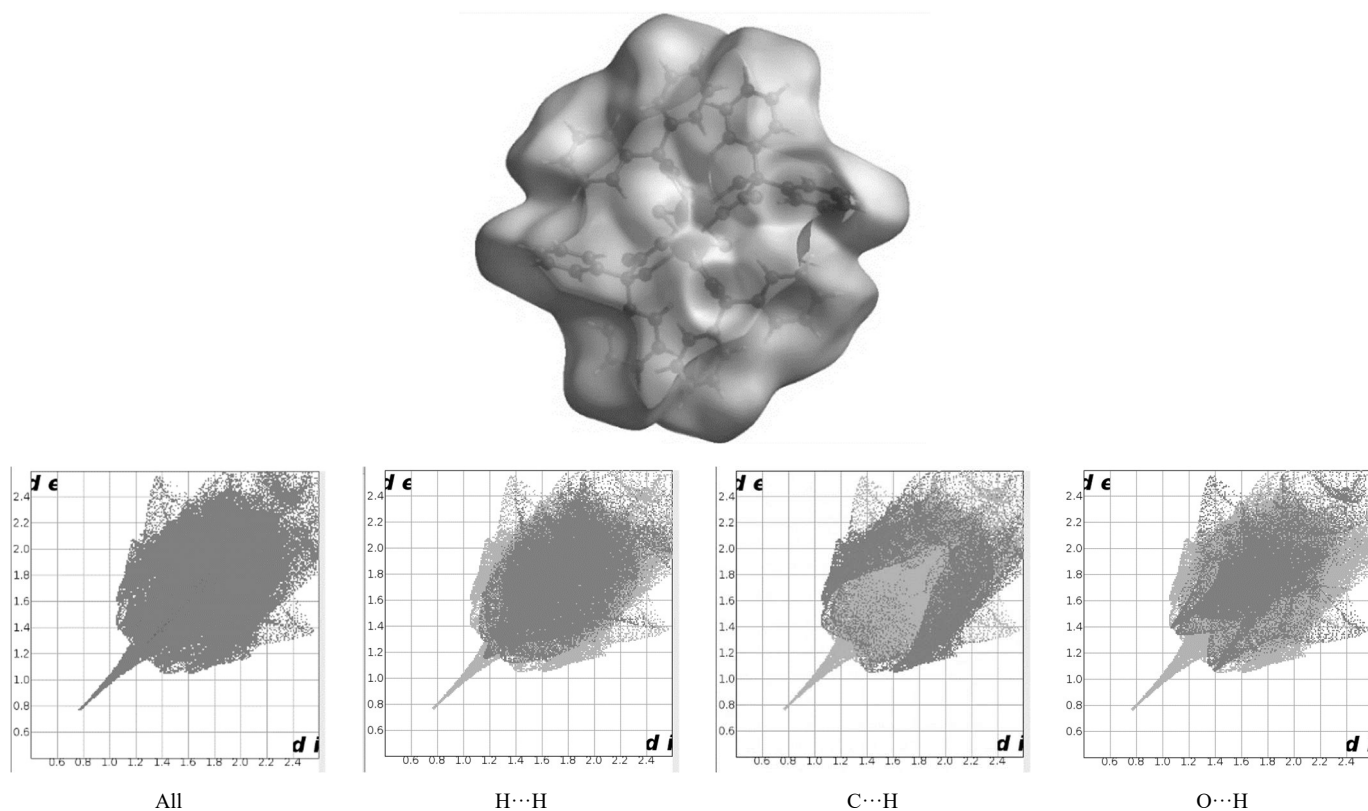
**Table 4.** Hydrogen bond interactions of the title compound.

Atoms	D-H	H...A	D...A	D-H...A
O1-H1...O7 <sup>i</sup>	0.75	1.97	2.174(4)	170
O1-H7A...O2 <sup>ii</sup>	0.85	1.94	2.782(4)	173
O12-H12B...O8 <sup>iii</sup>	0.97	1.96	2.820(18)	147
O12A-H12C...O8 <sup>i</sup>	0.97	1.91	2.555(17)	121

<sup>i</sup> $x, 1-y, z$ ; <sup>ii</sup> $3/2-x, 1/2+y, 1/2-z$ ; <sup>iii</sup> $3/2-x, -1/2+y, 1/2-z$

The Hirshfeld surfaces mapped over  $d_{norm}$  (Figure 4) indicates the locations of the strongest intermolecular contacts (dark areas), and fingerprint plots indicates the contributions of interatomic contacts to the Hirshfeld surface. Table 5 summarizes the main intermolecular contacts and their percentage distributions on the Hirshfeld surface for the strontium benzilate.

The weak intermolecular interactions are mainly constituted by H...O, H...N, H...C and H...H, where the reciprocal contacts appear as a symmetrical wings for H...O, with  $d_e + d_i \sim 2.4 \text{ \AA}$ . The H...C as symmetrical clamp with  $d_e + d_i \sim 2.7 \text{ \AA}$ . The interatomic contacts of H...H have a majority of the all contribution in the surface generated showing a wide stain with  $d_e + d_i \sim 2.4 \text{ \AA}$ , denoting H...H short contacts generating no significant effect over molecular packing in the crystal structure stabilization.



**Figure 4.** Hirshfeld  $d_{\text{norm}}$  surface map and the bi-dimensional fingerprint plots of the title compound [ $d_e$  and  $d_i$  represent the distances from a point on the Hirshfeld surface to the nearest atoms outside (external) and inside (internal) the surface, respectively].

**Table 5.** Contributions of interatomic contacts to the Hirshfeld surface for the title compound\*.

Contact Contribution	H...H	C...H	O...H	C...C	Sr...O
(%)	42.2	22.9	15.8	4.9	3.6

\*Reciprocal contacts

## CONCLUSIONS

The new coordination polymer strontium benzilate has been synthesized and its crystal structure was determined using X-ray single-crystal diffraction. The complex crystallizes in the monoclinic  $P2_1/n$  space group. The strontium ion is coordinated to eight oxygen atoms in a distorted tetragonal antiprism and forming an infinite zig-zag chains along the [010] direction. These chains form a three-dimensional network via O--H...O hydrogen-bond interactions between the coordinated water molecules and the O atoms of the carboxylate groups. Two dimensional fingerprint plot calculations displayed the H...H, C...H, and O...H pair of contacts that were the most significant interaction to the Hirshfeld surface.

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