***Crystal Structure Theory and Applications*, 2013, 2, 28-33**
http://dx.doi.org/10.4236/csta.2013.21004 Published Online March 2013 (http://www.scirp.org/journal/csta)

Synthesis and Structural Study of Triphenylbismuth Bis (Salicylate)

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Received October 29, 2012; revised December 5, 2012; accepted December 18, 2012

ABSTRACT

The crystal of triphenylbismuth bis (Salicylate) pentavalent was synthesized from the reaction of triphenylbismuth dichloride with salicylic acid dissolved in methylene chloride at room temperature. The molecular and crystal structures of triphenylbismuth bis (Salicylate) were determined by X-ray diffraction analysis. This compound crystallizes in the triclinic space group $P\overline{1}$ with crystallographic parameters: a = 11.2937 (3) Å, b = 14.6516 (3) Å, c = 17.8253 (4) Å, α = 78.2958 (7)˚, β = 76.232 (6)˚, γ = 85.351 (6)˚, $\mu = 6.332\ \text{mm}$, V = 2803.59 (11) Å, $Z = 2$, $Dc = 1.693\,\text{g/cm}$, $F(000) = 1392$, $T = 293(2)\,\text{K}$. The final residual factor is 0.0602 for 5806 reflexions with $I > 2\sigma(I)$. The bismuth atom of the compound has a distorted trigonal-bipyramidal configuration.

Keywords: Organobismuth; Structure; X-Ray Diffraction; Salicylate; Synthesis

1. Introduction

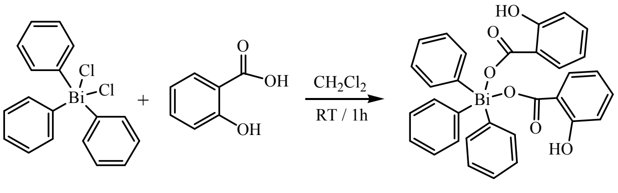
Bismuth is nontoxic and relatively cheap, and bismuth compounds have been widely used in catalysis and organic synthesis [1]. Inorganic bismuth compounds such as bismuth halides have been used as Lewis acid catalysts in a number of organic reactions [1-5]. However, the utilization of organobismuth compounds trivalent and pentavalent for organic synthesis is rarely reported partly due to the unstable nature of the Bi-C bonds [6,7]. Recent developments show that the incorporation of a bulky substituent in pentavalent organobismuth complex can result of organobismuth compounds that have stable Bi-C bonds [8-10]. In our research group, we have been working on the synthesis of stable pentavalent organobismuth compounds. In previous works we have synthesized organobismuth compounds such as pentavalent triphenylbismuth dichloride, triphenylbismuth diacetate and triphenylbismuth bis (thiophene carboxylate) [7,11]. In this work, we report synthesis and structure determination of the organobismuth compound triphenylbismuth bis (salicylate), **I**, where **I** is the pentavalent complex, bulky and more stable at room temperature.

2. Materials and Methods

2.1. Synthesis

The compound triphenylbismuth bis (salicylate) **I** was prepared from the triphenyl dichloride and salicylic acid in solution of methylene chloride. The mixture is heated to react for one hour of stirring. At the end of the reaction, the mixture is removed and then recrystallized from dichloromethane/pentane (1.1) [12] (**Scheme 1**).

The obtained compound has the empirical formula $C_{32}H_{25}BiO_6$ containing an OH and carboxylate groups that were chosen for our investigation for the following considerations: 1) the hydroxyl group can act as both proton acceptor to promote the formation of intermolecular hydrogen bond; 2) the oxygen atoms of the car-



I

Scheme 1. The synthetic route of the triphenylbismuth bis (salicylate) compound, I.

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bismuth (V) centre, hence it could act as a proton acbonyl of carboxylate ligand is weakly associated with theceptor and participate in the formation of hydrogen bonds; 3) The oxygen atom of the carboxylate links to the central atom of bismuth, forming a stable coordination bond. The resulting compound is studied using X-ray diffraction to obtain molecular crystal structure.

2.2. Single Crystal X-Ray Analysis

The crystal structure of **I** was determined by single crystal X-ray diffraction method. X-ray data were collected at room temperature (293 K) on a Kappa CCD diffractometer (Bruker Nonius, 1998) [13] using MoK$_\alpha$ radiation (k = 0.71073 Å), at a voltage of 50 kV and current of 20 mA. Cell parameters were obtained from refinement of 25 reflections collected from a random searching. Data reduction was performed with Denzo and Scalepack software [14]. Data obtained were processed with the WinGX integrated system software package for single crystal X-ray diffraction data solution, refinement and analysis [15]. The crystal structure was solved by direct methods and was refined by full-matrix least-squares refinement on F^2 using the software package SHELX-97 [16]. Molecular graphics were done with ORTEP-3 [17]. In the absence of significant anomalous scattering effects Friedel pairs have been merged. The crystal data and structure refinement details are listed in **Table 1**.

3. Results and Discussion

3.1. Bond Length and Angles

In **Figure 1**, the central bismuth-containing part exhibits a distorted pseudo-trigonal-bipyramidal structure.

Table 1. Crystal data and structure refinement details for $C_{32}H_{25}BiO_6$ compound.

Chemical formula	$C_{32}H_{25}BiO_6$
CCDC deposit	737,905
Colour	colourless
Crystal dimensions (mm)	0.15 × 0.10 × 0.10
Formula weight	1429
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	
a (Å)	11.2937 (3)
b (Å)	14.6516 (3)
c (Å)	17.8253 (4)
α (˚)	78.2958 (7)
β (˚)	76.232 (6)
γ (˚)	85.351 (6)
Cell volume (Å^3)	2803.59 (11)
Z	2
Temperature (K)	293 (2)
Density $(\mathrm{g/cm^3})$	1.693
Absorption coefficient $(\mathrm{mm^{-1}})$	6.332
Diffractometer	Kappa CCD
Radiation, λ (Å)	MoK$_\alpha$, 0.71073
Theta min-max (˚)	1.68 - 27.89
Reflections collected/unique	32748/12722
Range of h, k, l	$-13 \le h \le 14$, $-18 \le k \le 19$, $0 \le l \le 23$
Absorption correction	Sortav (Blessing, 1997)
Data/restraints/parameters	5806/0/712
Goodness of fit on F^2	0.857
Final R indices $R\left[F^2 > 2\sigma\left(F^2\right)\right]$	0.0602
R indices (all data)	0.1564

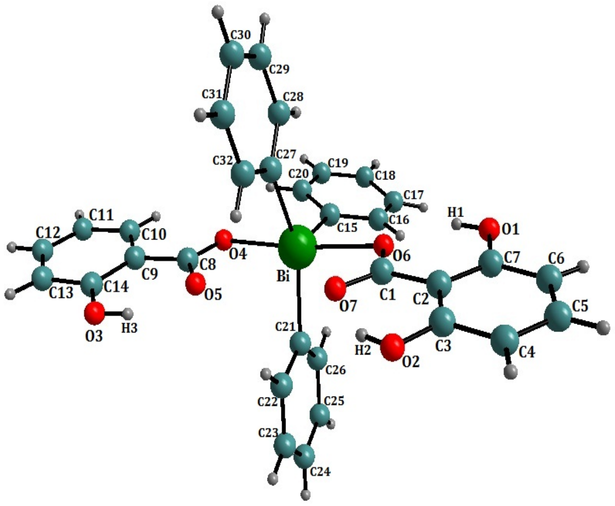

Figure 1. Perspective view of the molecule of triphenylbismuth bis (salicylate), I showing the labelling scheme.

The average values of bond distances and angles in different aryl rings are in agreement with the literature values [18]. The bond distances and valence angles of molecule **I** are shown in **Table 2**.

According to X-ray diffraction data of compound **I** and as shown in **Figure 2**, Bi atom has distorted trigonal-bipyramidal coordination with oxygen atoms in apical positions. The O(1) and O(4) atoms are located at the apical positions and the C(21), C(27) and C(15) atoms are at the equatorial positions. The sum of angles in

Table 2. Bond distances and bond angles for non-hydrogen atoms (e.s.d.'s are given in parenthesis).

Bond distance (Å)		Bond angles (˚)	
Bi-O1	2.303 (6)	O1-Bi-O4	172.6 (2)
Bi-O4	2.313 (6)	O1-Bi-C15	93.4 (3)
Bi-C15	2.215 (9)	O1-Bi-C21	87.8 (3)
Bi-C21	2.238 (8)	O1-Bi-C27	87.5 (3)
Bi-C27	2.200 (9)	O4-Bi-C15	91.9 (3)
O1-C1	1.303 (11)	O4-Bi-C21	86.0 (3)
O2-C1	1.246 (12)	O4-Bi-C27	91.1 (3)
O3-C3	1.380 (14)	C15-Bi-C21	104.1 (4)
O4-C8	1.289 (11)	C15-Bi-C27	144.4 (4)
O5-C8	1.239 (11)	C21-Bi-C27	111.5 (4)
O6-C10	1.358 (13)	Bi-O1-C1	105.4 (6)
C1-C2	1.501 (14)	B-O4-C8	107.9 (4)
C2-C3	1.415 (15)	O1-C1-O2	121.0 (9)
C2-C7	1.386 (16)	O1-C1-C2	114.5 (11)
C3-C4	1.395 (17)	O2-C1-C2	124.3 (11)
C4-C5	1.33 (2)	C1-C2-C3	117.0 (12)
C5-C6	1.36 (2)	C1-C2-C7	122.8 (11)
C6-C7	1.365 (16)	O3-C3-C2	121.7 (11)
C8-C9	1.472 (13)	O3-C3-C4	119.0 (14)
C9-C10	1.368 (14)	C2-C3-C4	119.3 (14)
C9-C14	1.403 (13)	C3-C4-C5	119.5 (17)
C10-C11	1.393 (17)	C4-C5-C6	120.5 (16)
		C-C6-C7	123.9 (16)
		C2-C7-C6	116.5 (14)
		O4-C8-O5	120.5 (9)
		O4-C8-C9	116.3 (10)
		O5-C8-C9	123.2 (10)
		C8-C9-C10	118.1 (10)
		C10-C9-C14	119.6 (10)

The Bi atom does not almost extend from the equatorial plan as we can view in **Figure 2**.

However, the (Bi-C(15), Bi-C(21), Bi-C(27)) distances are (2.215 (9), 2.238 (8) and 2.200 (9) Å) respectively. The Bi-O(1) and Bi-O(4) distances are (2.303 (6) Å) and (2.313 (6) Å) respectively. We note that, from **Figure 3** that the ligands of carboxylate groups are in cis-position compared to the phenyl group. In the other hand, intermolecular interaction between the bismuth atom and the two carbonyl groups forms the Van-Der-Waals bond.

The distances between valence-non-bonded Bi-O(2) and Bi-O(5) are respectively 2.814 (4) and 2.861 (3) Å (**Figure 3**) which indicate that oxygen atoms are weakly coordinated with the bismuth atom and form a cis conformation together.

This conformation apparently causes significant deviation of the C-Bi-C angles from 120˚ in the equatorial plan.

However, **Figure 4** shows, in the equatorial plane, that the two aromatic rings A and B are perpendicular to equatorial plan and the axial angle O-Bi-O for the title compound are 360˚ (144.4˚, 104.1˚ and 111.5˚) and 172.6˚, respectively.

$$w = 1\Big/\left[\sigma^2\left(Fo^2\right) + \left(0.0437P\right)^2 + 2.0512P\right]$$

where

$$P = \left(Fo^2 + 2Fc^2\right)\Big/3 .$$

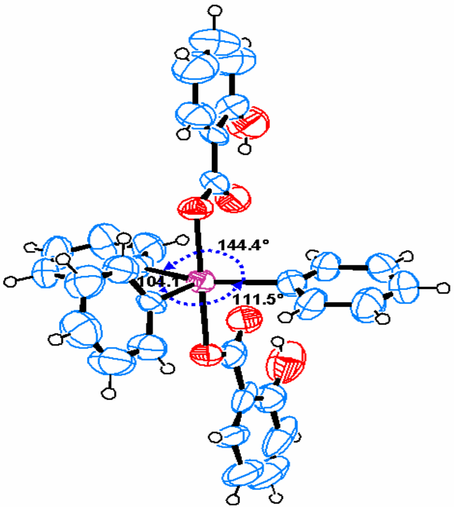

Figure 2. Three dimensional structure of compound I showing different angles in equatorial plan.

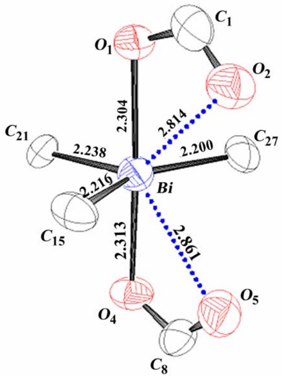

Figure 3. Bond lengths of atoms surrounding the bismuth atom.

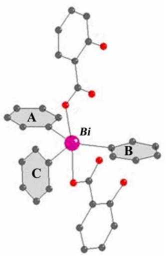

Figure 4. A, B and C rings compared to Bi-O bond apical position. A and B rings are in the same plan.

Bi-O bond while the third aromatic ring C is parallel to Bi-O. The axial positions are occupied by electronegative atoms and the equatorial ones by carbon atoms of the aromatic groups. The distortion of the coordination geometry at bismuth is mainly due to the restrictions imposed by the chelate rings.

The bond distances and valence angles of carbon (C15, C21 and C27) and oxygen (O2 and O4) atoms surrounding the bismuth central atom are shown in **Figure 5**.

3.2. Dihedral Angles

Torsion angles are reported in **Table 3**. We can see that, the carboxyl groups are coplanar (Bi-O(1)-C(1)-O(2) and Bi-O(4)-C(8)-O(5)). These two dihedral angles are about −8.01˚ and −1.83˚ respectively (**Table 3**).

3.3. Hydrogen Bonds

The bond distance between hydrogen and carbon, hydrogen and oxygen noted X-H (Å) and the possible intramolecular interactions by hydrogen bonds noted X-H (Å) of molecule **I** is shown in **Table 4**.

These different hydrogen bonds showed in **Figure 6** are responsible of the molecular packing in the unit cell.

3.4. Crystal Packing

Hydrogen bonds played crucial roles in the crystal packing. **Figure 7** shows the presence of two molecules in the unit cell $(Z = 2)$ which corresponds to the centrosymmetric triclinic space group $P1$ with two general positions (x, y, z) and $(-x, -y, -z)$.

4. Conclusions

The new pentavalent triphenylbismuth bis (salicylate) was synthesized with a good yield and its crystal structure was determined by X-ray diffraction analysis at room temperature. This work shows that coordination by the salicylate group is more stable, when compared to pentaphenylbismuth.

This is caused by rigidity of the ligand between the bismuth and oxygen atoms, and the presence of hydrogen bonding and the Van-Der-Waals bonding. The three-di-

Table 3. Dihedral angles in degrees with e.s.d.'s given in parenthesis.

Dihedral angles (˚)	
O4-Bi-O1-C1	−148.12
C15-Bi-O1-C1	75.50
C21-Bi-O1-C1	179.52
C27-Bi-O1-C1	−68.82
O1- Bi-O4-C8	155.21
C15-Bi-O4-C8	−68.34
C21-Bi-O4-C8	−172.36
C27-Bi-O4-C8	76.14
O1-Bi-C15-C16	−101.51
O1-Bi-C15-C20	77.26
O4-Bi-C15-C16	83.58
O4-Bi-C15-C20	−97.65
C21-Bi-C15-C16	169.89
C21-Bi-C15-C20	−11.34
C27-Bi-C15-C16	−11.01
C27-Bi-C15-C20	167.76
O1-Bi-C21-C22	−165.63
O1-Bi-C21-C26	10.43
O4-Bi-C21-C22	18.32
O4-Bi-C21-C26	−165.61
C15-Bi-C21-C22	−72.63
C15-Bi-C21-C26	103.44
C27-Bi-C21-C22	107.94
C27-Bi-C21-C26	−76.00
O1-Bi-C27-C32	−76.02
O4-Bi-C27-C28	−85.34
O4-Bi-C27-C32	96.72
C21-Bi-C27-C28	−171.43
C21-Bi-C27-C32	10.62
Bi-O4-C8-O5	−1.83
Bi-O4-C8-C9	178.75
O1-C1-C2-C3	177.38
O1-C1-C2-C7	−4.16
O2-C1-C2-C3	1.62
O2-C1-C2-C7	−179.92
C1-C2-C3-O3	3.34
C1-C2-C3-C4	−179.12
C7-C2-C3-O3	−175.16
C7-C2-C3-C4	2.37
C1-C2-C7-C6	178.78
C3-C2-C7-C6	−2.81
O3-C3-C4-C5	175.31
C2-C3-C4-C5	−2.29

Continued

C3-C4-C5-C6	2.76
C4-C5-C6-C7	−3.45
C5-C6-C7-C2	3.39
O4-C8-C9-C10	−177.60
O4-C8-C9-C14	2.98
O5-C8-C9-C10	3.00
C8-C9-C10-O6	2.49
C8-C9-C10-C11	−179.81
C14-C9-C10-O6	−178.08
C14-C9-C10-C11	−0.37
C8-C9-C14-C13	−179.33
C10-C9-C14-C13	1.26
O6-C10-C11-C12	177.42
C9-C10-C11-C12	−0.40
C10-C11-C12-C13	0.29
C11-C12-C13-C14	0.60
C12-C13-C14-C9	−1.36
Bi-C15-C16-C17	−179.16
C20-C15-C16-C17	2.17
Bi-C15-C20-C19	178.95
C16-C15-C20-C19	−2.24
C15-C16-C17-C18	−0.17
C16-C17-C18-C19	−1.73
C17-C18-C19-C20	1.64
C18-C19-C20-C15	0.29
Bi-C21-C22-C23	175.91
C26-C21-C22-C23	−0.20
Bi-C21-C26-C25	−176.08
C22-C21-C26-C25	−0.05
C21-C22-C23-C24	0.53
C22-C23-C24-C25	−0.62
C23-C24-C25-C26	0.37
C24-C25-C26-C21	−0.04
Bi-C27-C28-C29	178.00
Bi-C27-C32-C31	−178.10

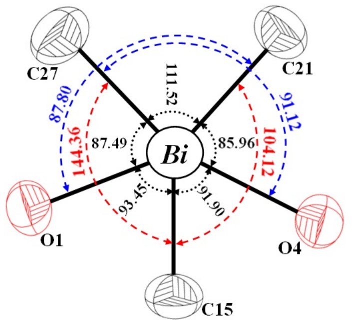

Figure 5. Bond distances and valence angles around the bismuth atom.

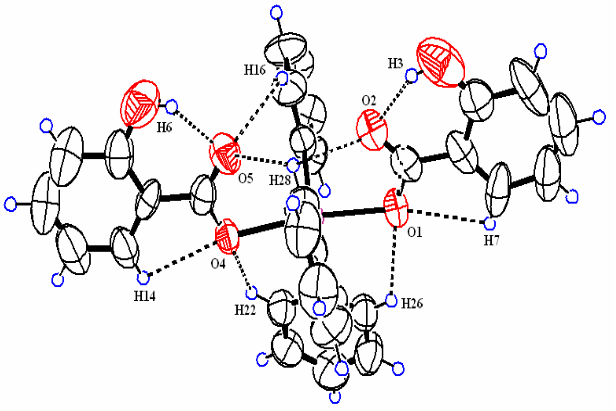

Figure 6. Hydrogen bonds representation ensuring the molecular packing in the unit cell of compound I.

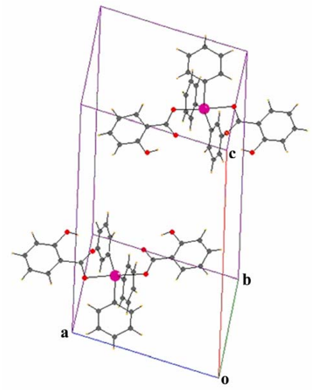

Figure 7. Molecular packing in the unit cell showing two molecules in symmetric positions (*x*, *y*, *z*) and (−*x*, −*y*, −*z*). Hydrogen atoms are shown as small spheres for clarity.

Table 4. Hydrogen bonds X-H and X···H of molecule I.

Distance of virtual bond **X···H (Å)**		Distance of actual bond **X-H (Å)**	
H3…O2	1.822	O3-H3	0.820
H6…O5	1.798	O6-H6	0.820
H7…O1	2.533	C7-H7	0.929
H14…O4	2.513	C14-H14	0.930
H16…O5	2.556	C16-H16	0.931
H22…O4	2.369	C22-H22	0.930
H26…O1	2.453	C26-H26	0.929
H28…O2	2.777	C28-H28	0.930
H28…O5	2.636		

bonding and the Van-Der-Waals bonding. The three-dimensional representation of the molecule shows the axial position of the two salicylate groups and the equatorial position of the three phenyls. This shows that the crystal structure of triphenylbismuth bis (Salicylate) pentavalent has a shape distorted trigonal-bipyramid.

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