Facile one-pot synthesis of triphenylbismuth (V) bis(carboxylate) complexes

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Supporting Information Placeholder

ABSTRACT: Triphenylbismuth(V) bis(carboxylates), $\text{Ph}_3\text{Bi}(\text{O}_2\text{CR})_2$ ($\text{R} = 5\text{-Br-2-OH-C}_6\text{H}_3\text{-}$ (**1**), $2\text{-OH-C}_6\text{H}_4\text{-}$ (**2**), $2,6\text{-(OH)}_2\text{-C}_6\text{H}_3\text{-}$ (**3**); $3\text{-Me-2-NH}_2\text{-C}_6\text{H}_3\text{-}$ (**4**); Ph- (**5**) and Me- (**6**)) were obtained from the reaction of triphenylbismuth with hydrogen peroxide and excess carboxylic acid in wet 2-propanol. The synthesis avoids the use of halogens as oxidants and the products crystallize directly from the solution as pure compounds. They crystallize from solution without further need of purification. The structures of **1** - **5** were confirmed by single crystal X-ray diffraction. Compounds **2** and **5** exhibit a different polymorph than that previously reported in the literature. While all of the Bi(V) compounds adopt a trans-axial trigonal-bipyramidal configuration with the carboxylates in the axial positions, there is considerable variation in the coordination of the carboxylate that ranges from simple monohapto to the mixture of mono- and bidentate chelating bonding modes.

Organobismuth compounds, particularly bismuth carboxylates, have antimicrobial properties and are commonly used as pharmaceutical agents in chemotherapy and in the treatment of *Helicobacter pylori* infections.¹ The versatility of these bismuth compounds in organometallic reactions also enables them to be extensively used in the synthesis of heterobimetallic complexes² and as catalysts.^{3,4} Triphenylbismuth undergoes reactions with three equivalents of carboxylic acids in the presence of polar and non-polar solvents to yield complete replacement of the aryl groups, but these compounds are often sensitive to hydrolysis and oxo-cluster compounds result.⁵⁻⁷ Nuclearities up to 38 bismuth atoms have been reported.^{5,8,9} It is possible to obtain monophenyl bismuth(III) dicarboxylato compounds by careful addition of stoichiometric amounts of the carboxylic acid.^{10,11} Interestingly, conducting these reactions in reagent-grade 2-propanol led to isolation of triphenylbismuth(V) bis(carboxylates), whose formation we were ultimately able to trace to the presence of peroxides in the solvent, which was confirmed by qualitative analysis. Normally, these compounds are prepared in a two-step process, first by reacting BiPh_3

with chlorine or bromine to produce Ph_3BiX_2 followed by reaction with an alkali metal salt of an appropriate anionic ligand.¹² Several examples of $\text{BiPh}_3(\text{O}_2\text{CR})_2$ have been reported previously ($\text{R} = \text{Me}$,^{13,14} Et ,¹⁴ Ph ,^{13,14} Bu ,¹³ CH-CH_2 ,¹³ $\text{Me}(\text{CH}_2)_8$,¹³ $\text{Me}(\text{CH}_2)_{10}$,¹³ oxalate,¹³ $p\text{-OHC}_6\text{H}_4\text{CH}_2\text{CH}_2$,¹⁵ Cl_3C ,¹⁶ ClCH_2 ,¹⁶ BrCH_2 ,¹⁶ F_3C ,¹⁷ $3\text{-MeC}_6\text{H}_4$,¹⁸ $4\text{-MeC}_6\text{H}_4$,¹⁸ $2\text{-AcOC}_6\text{H}_4$,¹⁸ F_5C_6 ,¹⁹ $3,4,5\text{-F}_3\text{C}_6\text{H}_2$,²⁰ C_3H_5 ²¹). Bi(V) compounds have been studied extensively as aryl transfer reagents in organic synthesis.²²⁻²⁶ We have presumed that the reaction proceeds through the intermediacy of Ph_3BiO , but attempts to isolate that compound or to detect it spectroscopically in solution were not successful. In the absence of the carboxylic acid we observed decomposition and side products rather than the formation of a stable complex.

Further study of this reaction proved it to be general and applicable to a diverse set of carboxylic acids shown as illustrated in **Figure 1**. Salicylic acid and its derivatives were targeted because i) they display wide variety of chemotherapeutic properties such as antibacterial and antiparasitic activity^{27,28} and ii) they possess a wide variety of coordination modes^{29,30} which can be useful in the construction of organic frameworks. Our group has previously reported the structure of $\text{Bi}(\text{Hsal})_3$ adducts with nitrogen containing chelating ligands and monophenyl bismuth carboxylate complexes, $[\text{PhBi}(\text{O}_2\text{CR})]$, (where $\text{R} = 2\text{-OH-C}_6\text{H}_4\text{-}$, $4\text{-Me-2-OH-C}_6\text{H}_3\text{-}$).^{7,10} Recently we also reported the structure of the simplest oxo cluster, $[\text{Bi}_4(\mu_3\text{-O})_2(\text{Hsal})_8]$, containing a salicylate ligand.⁹ The yield and physical properties of all the complexes prepared synthesized are provided in supporting information. A detailed comparison of the bismuth(V) carboxylato complexes is presented here and shows systematic variation in the structural parameters of the compounds as a function of the carboxylate used.

Figure 1: Acids used in the present study: (A) 5-bromosalicylic acid, (B) salicylic acid, (C) 2,6-dihydroxy benzoic acid, (D) 3-methylantranilic acid, (E) benzoic acid and (F) acetic acid.

The complexes are stable in the solid state and are soluble in acetone and DMSO. All of the complexes were characterized by NMR spectroscopy, IR spectroscopy, elemental analyses and melting points. Molecular structures were confirmed using single crystal X-ray diffraction. Structures of **2**³¹ and **5**²⁰ have been previously determined although those reported here are new polymorphs. Pictures of the new compounds **1** and **4** are presented in **Figure 2** and **3**, respectively. Figures of the other molecules are given in the Supporting Information. The selected Bi-O(carboxylate), O-Bi-O and Bi-O-C angles of **1** - **5** are reported in Table 1.

Figure 2: Molecular structure of **1** (phenyl hydrogens have been omitted for clarity).

Figure 3: Molecular structure of [BiPh₃(3-CH₃-2-NH₂-C₆H₃CO₂)₂], **4** (phenyl hydrogens have been omitted for clarity).

Complexes **1** - **5** have distorted trigonal-bipyramidal geometry with the carboxylate oxygen atoms in the axial position and the carbon atoms of the phenyl groups in equatorial positions. One of the phenyl groups in **3** is disordered over two positions, and three carbons of another aryl group are slightly disordered and this could not be resolved. Both carboxylate ligands in **1** - **3** bind in an η^1 -(O) fashion, whereas for **4** both bind in symmetrical η^2 -(O, O') fashion. In **5**, there are two molecules in the asymmetric unit and in one of the molecules both the carboxylate ligands bind in a η^1 -(O) fashion whereas for the other molecule the carboxylate ligands bind in both η^2 -(O, O') and η^1 -(O) modes. The bonding modes of the oxygen atom of the carboxylate ligands vary from monodentate to a mixture of both monodentate and bidentate modes (Figure 4). The IR spectra of all the complexes show asymmetrical and symmetrical stretching carboxylate modes. Complexes **1**-**3** display a $\Delta\nu$ value ($\Delta\nu = \nu_{\text{asymm}} - \nu_{\text{symm}}$) greater than 200 cm⁻¹, indicating monodentate bonding mode as observed in the solid state structure, whereas complexes **4** and **5** exhibit $\Delta\nu$ values less than 200 cm⁻¹ consistent with the bidentate bonding mode observed in their solid state structures.

The Bi-O(carboxylate) bond lengths, O-Bi-O and Bi-O-C bond angles of complexes **1** - **5** are consistent with the corresponding distances and angles of other triphenylbismuth(V) bis(carboxylate) complexes reported in the literature.¹⁵⁻¹⁷ The structural data show a correlation between the pK_a of the carboxylate ligands and Bi-O bond lengths, with the weaker acids having the shorter Bi-O distances. Interestingly, the average Bi-O distance is the same for both independent molecules in spite of the variation in Bi-carboxylate binding. The Bi-O-C bond angles, where the O atom is the one in the axial position that always has the shorter Bi-O distance, were also considered as this value should correlate with a tilt of the carboxylate group, a smaller angle corresponding to a greater tilt. The less acidic carboxylates exhibit a greater angle (See **supporting information Table S2**), which corresponds to increased interaction between the Bi and the second oxygen atom of the carboxylate ligand. **Figures S6** and **S7** have been provided in the supporting information in correlation with the above statement. A high correlation ($R^2 = 0.91$) exists between the average Bi-O bond lengths and their corresponding Bi-O-C angles (**Figure S8 in the supporting information**). This is a logical consequence of higher charge localization on the carboxyl group with increasing pK_a orienting both oxygen atoms of the carboxyl group towards the metal center. Complexes **1**-**3** the OH groups are intramolecularly H-bonded to an oxygen atom of the carboxylate, and these secondary interactions can explain the larger deviations of **1** and **3** in the plot. In the case of the bromo derivative **1**, the acidity of the OH group would

be enhanced allowing it to more strongly internally hydrogen bond to the carboxylate ligand while the presence of the second OH group in **3** would tend to offset the tilting effect.

Figure 4. Variation in the bonding modes of the carboxylate oxygen.

The distances between the non-bonded oxygen atoms and the bismuth atom (i.e. Bi---O(=C)) in **1** - **3** and **5** are 3.016(4) and 2.997(3) Å, **1**; 2.869(3) and 2.859(3) Å, **2**; 2.916(3) and 2.863(3) Å, **3**; and 2.893(5), 2.856(5) and 2.795(4) Å, **5**, indicating substantially weaker interactions between the second oxygen atoms and the metal

center. Comparison of the Bi---O(=C) distances in **1** - **5** indicates that the degree of bidentate coordination is slightly greater in **4** than the others whereas it is a minimum in **1**. This may be due to the presence of electron withdrawing group in **1**. The Bi---O(=C) in **1** is similar to that reported for BiPh₃(CF₃CO₂)₂ (2.980 Å).¹⁷ The O-Bi-O angle is expected to be 180° for an idealized trigonal bipyramid but these compounds show significant deviation from linearity with values ranging from 170.3° to 172.6° (supporting information Table S2). This distortion exhibits itself further in the C-Bi-C angles, which show a bimodal range: 106.5(2)-139.8(2) (**1**), 106.9(2)-140.3(2) (**2**), 105.1(2)-141.4(2) (**3**), 102.9(3)-148.8(3) (**4**) and 105.8(2)-144.4(2) (for Bi1); 103.9(2)-148.3(2) (for Bi2) (**5**). One angle is substantially larger than the other two to accommodate the demands of the weaker binding to the second carboxylate oxygen atoms. Nevertheless, the sum of C-Bi-C angles (i.e. C-Bi-C) (°) still indicates a planar arrangement of these groups: 359.8 (**1**), 359.7 (**2**), 360.0 (**3**), 360.0 (**4**), 360.0 and 359.7 (**5**).

Examination of the structure **5** for possible void areas using Platon (version 161012)³² was consistent with the presence of water. The total potential solvent area volume was found to be 69.5 Å³.

Table 1. Selected bond lengths (Å) and angles (°) for **1** - **5**

	1	2	3	4	5	
Bi(X) - O(X11)	2.292(3)	2.290(3)	2.291(3)	2.263(6)	2.254(4)	2.290(4)
Bi(X) - O(X12)	3.016(4)	2.859(3)	2.916(3)	2.755(7)	2.886(5)	2.752(4)
Bi(X) - O(X21)	2.278(3)	2.247(3)	2.329(3)	2.283(6)	2.270(4)	2.272(4)
Bi(X) - O(X22)	2.997(3)	2.869(3)	2.862(3)	2.699(7)	2.795(4)	2.893(4)
O(X11)-Bi(1)-O(X21)	172.6(1)	170.6(1)	170.7(1)	170.7(2)	170.3(1)	172.2(1)
Bi(X)-O(X11)-C(X17)	112.0(3)	108.2(3)	110.2(2)	105.9(5)	108.9(3)	103.9(3)
Bi(X)-O(X21)-C(X27)	111.4(3)	109.2(3)	107.1(3)	103.5(5)	104.9(3)	107.7(3)

Conclusions

A facile and general one pot synthesis of bismuth(V) bis(carboxylate) complexes was developed that gives good yields of pure, crystalline products without the use of chlorine or bromine. The average Bi-O bond lengths tend to be shorter and the Bi-O-C angles smaller for the less acidic RCO₂H acids, indicating that these ligands are more strongly bound and tend to have both oxygen atoms of the carboxylate ligand interacting with the metal center.

Experimental

Materials and Equipment

All reagents and chemicals, unless otherwise stated, were purchased from commercial sources. NMR spectra were recorded at room temperature in d₆-acetone on BrukerAvance 500 spectrometer, and the ¹H and ¹³C chemical shifts were referenced to tetramethylsilane (TMS). Melting points were obtained in sealed capillaries on an Electrothermal melting point instrument. Elemental analyses (C, H, N) were performed at Gal-

braith Laboratories. IR spectra were recorded on Perkin Elmer FTIR spectrometer.

General synthetic procedure

BiPh₃ (0.33 mmol) and the appropriate carboxylic acid (1.00 mmol) were combined and dissolved in 8.0 mL of reagent grade 2-propanol (used as received from Fisher Scientific) by stirring on low heat for 2 minutes. The homogeneous solutions were stored at room temperature for 2-3 days while crystals formed. The crystals were isolated, dried and identified as Bi(V) complexes. The composition of these complexes is given in Table 1. The analytical data has been provided in the supporting information. The experiment was repeated by performing the reaction in distilled 2-propanol with the addition of 30% H₂O₂ solution (5 µL). The results obtained were the same but the yield obtained through this synthetic method was generally higher than when not conducted with added peroxide. There was a trace amount of 2-propanol (< 1%) present in the NMR spectrum for some of the Bi(V) complexes.

Analytical data for complexes 1-6

[BiPh₃(5-Br-2-OH-C₆H₃CO₂)₂].1

Elemental Analysis (%): Found for C₃₂H₂₅BiBr₂O₆: C 43.43; H 2.76; Calc: C 43.96; H 2.88. ¹H NMR (500 MHz, d⁶-acetone, 30 °C): δ = 8.36 (d of d, 6H, *J* = 8.5 Hz, *o*-PhH), 7.92 (s, 2H, *ArH*), 7.82 (m, 6H, *m*-PhH), 7.65 (m, 3H, *p*-PhH), 7.51 (d, 2H, *J* = 9 Hz, *Ar-H*), 6.79 (d, 2H, *J* = 9 Hz, *Ar-H*). ¹³C-NMR (125 MHz, d⁶-acetone, 30 °C): 161.4(C=O), 159.4(C-OH), 138.3(Ar-C), 135.1(Ph-C), 133.0(Ph-C), 132.8(Ph-C), 131.3(Ar-C), 120.0(Ar-C), 117.5(C-COO), 110.5(C-Br). IR (ν, cm⁻¹): 3211(br.), 1643(m), 1576(m), 1483(m), 1442(m), 1403(m), 1363(m), 1292(m), 1267(m), 1220(s), 1129(m), 1033(m), 820(s), 698(s), 627(m), 573(m).

[BiPh₃(2-OH-C₆H₄CO₂)₂].2

Elemental Analysis (%): Found for C₃₂H₂₅BiO₆: C 53.67; H 3.69; Calc: C 53.78; H 3.50. ¹H NMR (500 MHz, d⁶-DMSO, 30 °C): δ = 8.36 (d of d, 6H, *J* = 8.4 Hz, *o*-PhH), 7.85 (d of d, 6H, *J* = 8.1 Hz, *ArH*), 7.79 (m, 6H, *m*-PhH), 7.62 (m, 3H, *p*-PhH), 7.37 (m, 2H, *ArH*), 6.80 (m, 2H, *ArH*). ¹³C-NMR (125 MHz, d⁶-acetone, 30 °C): δ = 162.3(C=O), 159.9(C-OH), 135.7(Ar-C), 135.0(Ph-C), 132.8(Ph-C), 132.6(Ph-C), 132.0(Ar-C), 119.4(Ar-C), 117.6(Ar-C), 115.7(Ar-C). IR (ν, cm⁻¹): 3060(br.), 1740(m), 1625(m), 1688(m), 1481(s), 1445(w), 1375(s), 1308(w), 1247(m), 1217(m), 1158(w), 1091(w), 1032(w), 866(m), 815(m), 757(s), 701(s), 666(s).

[BiPh₃{2,6-(OH)₂-C₆H₃CO₂}₂].3

Elemental Analysis (%): Found for C₃₂H₂₅O₈Bi: C 50.89; H 3.35; Calc: C 51.34; H 3.64. ¹H NMR (500 MHz, d⁶-acetone, 30 °C): δ = 8.13 (d, 6H, *J* = 7.6 Hz, *o*-PhH), 7.85 (m, 6H, *m*-PhH), 7.68 (m, 3H, *p*-PhH), 7.06 (t, *J* = 8 Hz, 2H, *ArH*), 6.15 (d, *J* = 8.1 Hz, 4H, *ArH*). ¹³C-NMR (125 MHz, d⁶-acetone, 30 °C): δ = 162.5(C=O), 159.5 (C-OH), 138.4(Ar-C), 135.1(Ph-C), 133.4(Ar-C), 133.2(Ar-C), 131.3(Ph-C), 128.6(Ar-C), 107.6(C-COO). IR (ν, cm⁻¹): 3224(br.), 1638(s), 1579(m), 1442(m), 1360(m), 1269(s), 1219(s), 1154(m), 1126(m), 1032(s), 852(m), 818(m), 768(w), 674(m), 648(w), 605(m).

[BiPh₃(3-CH₃-2-NH₂-C₆H₃CO₂)₂].4

Elemental Analysis (%): Found for C₃₄H₃₃BiN₂O₄: C 55.24; H 4.28; N 3.89; Calc: C 54.99; H 4.48; N 3.77. ¹H NMR (500 MHz, d⁶-acetone, 30 °C): δ = 8.34 (d of d, *J* = 7 Hz, 6H, *o*-PhH), 7.75 (d of d, 2H, *J* = 7.1 Hz, *m*-PhH), 7.68 (t, 6H, *m*-PhH), 7.54 (m, 3H, *p*-PhH), 7.06 (d, *J* = 7.2 Hz, 2H, *Ar-H*), 6.42 (t, *J* = 7.5 Hz, 2H, *ArH*), 6.27(s(br.), 4H, NH₂), 2.08 (s, 6H, CH₃). ¹³C-NMR (125 MHz, d⁶-acetone, 30 °C): δ = 160.3(C=O), 150.2 (C-NH₂), 134.8(Ar-C), 134.7(Ph-C), 132.2(Ph-C), 131.7(Ph-C), 131.3(Ar-C), 123.6(Ar-C), 115.4 (Ar-C), 113.4(Ar-C), 17.7 (Ar-CH₃). IR (ν, cm⁻¹): 3488(w), 3346(m), 1605(m), 1532(s), 1468(s), 1434(s), 1374(m), 1350(m), 1319(s), 1285(m), 1252(s), 1083(s), 983(s), 780(s), 728(vs), 677(s), 632(s).

[BiPh₃(PhCO₂)₂].H₂O.5

Elemental Analysis (%): Found for C₃₂H₂₇BiO₄: C 54.05; H 3.70; Calc: C 54.8; H 3.85. ¹H NMR (500 MHz, d⁶-acetone, 30 °C): δ = 8.37(m, 6H, *o*-PhH), 7.96 (m, 2H, *Ar-H*), 7.70 (m, 6H, *m*-PhH), 7.55(m, 3H, *p*-PhH), 7.49 (m, 2H, *Ar-H*), 7.37 (m, 2H, *Ar-H*), 6.83(s, 1H, OH). ¹³C-NMR (125 MHz, d⁶-acetone, 30 °C): δ = 161.4(C=O), 134.1(Ph-C), 133.3(Ar-C), 132.0(Ar-C), 131.5(Ph-C), 131.2(Ar-C), 130.0 (Ar-C), 128.2(Ph-C). IR (ν, cm⁻¹): 3430 (br), 1603(m), 1564(m), 1489(m), 1446(m), 1397(m), 1339(s), 1298(m), 1261(m), 1226(m), 1171(w), 1132(w), 1068(m), 1022(m), 847(m), 803(w), 741(m), 717(s), 681(s). The IR band at 3430 cm⁻¹ is consistent with the presence of water in the sample, although the water molecule could not be located in the X-ray structure.

[BiPh₃(MeCO₂)₂].6

Elemental Analysis (%): Found for C₃₂H₂₅BiBr₂O₆: C 46.65; H 3.72; Calc: C 47.15; H 4.14. ¹H NMR (500 MHz, d⁶-acetone, 30 °C): δ = 8.15(d of d, *J* = 8.4 Hz, 6H, *o*-PhH), 7.67 (m, 6H, *m*-PhH), 7.56 (m, 3H, *p*-PhH), 1.72 (s, 6H, CH₃). ¹³C-NMR (125 MHz, d⁶-acetone, 30 °C): δ = 134.7(Ph-C), 131.9(Ph-C), 131.7(Ph-C). IR (ν, cm⁻¹): 1586(m), 1559(m), 1470(s), 1438(m), 1383(s), 1327(s), 1251(m), 1166(w), 1086(w), 1053(m), 1011(m), 984(s),

935(w), 780(w), 746(m), 728(s), 678(m), 666(s), 622(m).

X-Ray Structural Determinations

Single crystals of **1–5** suitable for X-Ray crystallography were separated as thin needles directly from the aforementioned reactions. Intensities were measured at 173 K on Rigaku SCX Mini diffractometer using a CCD area detector using Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). Empirical absorption correction using the program SADABS was applied to the data. The structures were solved using direct methods and refined against F^2 with the SHELXTL software package.³³ All non-hydrogen atoms in the complexes were refined anisotropically. Hydrogen atoms were idealized throughout the convergence process. Figures presented in this publication were created with the programs in the Diamond (version 3.2i) software package.³⁴

Supporting Information. Table for yield, melting point, and colour of $\text{Ph}_3\text{Bi}(\text{O}_2\text{CR})_2$. Table for pK_a , Bi-O bond lengths ($\text{\AA}$) and Bi-O-C bond angles ($^\circ$). Crystallographic data for **1–5** in CIF format, Tables of full bond lengths and angles, fully labeled anisotropic displacement ellipsoid diagrams of all compounds and Figures for correlation between pK_a and Bi-O bond lengths/Bi-O-C bond angles. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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A facile, general synthesis of triphenylbismuth *bis*-carboxylates has been developed based on the reaction of BiPh₃ with hydrogen peroxide and the appropriate carboxylic acid in 2-propanol. (green, bismuth; red, oxygen; blue, nitrogen; black, carbon; gray, hydrogen)