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The Unexpected Isolation of Bismuth Tris(carboxylate) Hydrates: Syntheses and Structures of $[\text{Bi}(\text{Hsal})_3(\text{H}_2\text{O})]$ and $[\text{Bi}(\text{Hanth})_3(\text{H}_2\text{O})]$ ($\text{H}_2\text{sal} = 2\text{-OH-C}_6\text{H}_4\text{CO}_2\text{H}$, $\text{Hanth} = 2\text{-NH}_2\text{-C}_6\text{H}_4\text{CO}_2\text{H}$)

Ish Kumar,^[a] Phil Andrews,^[b] and Kenton H. Whitmire*^[a]**Keywords:** Bismuth / Salicylates / Carboxylates / Hydrates / Hydrolysis

A complex of the composition $[\text{Bi}(2\text{-OH-C}_6\text{H}_4\text{CO}_2)_3(\text{H}_2\text{O})]$ (**1**) was isolated from the 1:3 reaction of BiPh_3 with H_2sal ($\text{H}_2\text{sal} = \text{salicylic acid} = 2\text{-OH-C}_6\text{H}_4\text{CO}_2\text{H}$) in wet xylene, and the analogous anthranilate compound $[\text{Bi}(2\text{-NH}_2\text{-C}_6\text{H}_4\text{CO}_2)_3(\text{H}_2\text{O})]$ (**2**) was obtained from the 1:3 reaction of $\text{Bi}(\text{OtBu})_3$ with Hanth ($\text{Hanth} = \text{anthranilic acid} = 2\text{-NH}_2\text{-C}_6\text{H}_4\text{CO}_2\text{H}$) in tetrahydrofuran. Compounds **1** and **2** were fully characterized spectroscopically and by single-crystal X-ray diffraction.

Compounds **1** and **2** crystallize in the triclinic space group and display the $\eta^2\text{-(O,O')}$ binding mode for the oxygen atoms of the carboxylate ligands. There are two independent molecules in the asymmetric units of **1** and **2** that are connected by a weak bridging interaction of the OH or NH_2 group to an adjacent molecule. Both bismuth atoms are bound to a H_2O molecule, but the distances are highly asymmetric, long $\text{Bi}\cdots\text{O}$ lengths ranging from 2.74 to 2.89 Å.

Introduction

The carboxylato complexes of bismuth(III) have received considerable attention owing to their potent antibacterial^[1,2] and antileishmanial activity.^[3] They are known to hydrolyze readily to give colloidal bismuth oxido clusters that have found medicinal use. Of all the bismuth(III) carboxylates reported, bismuth subsalicylate (BSS) is one of the best known. It is the main ingredient in Pepto-Bismol, an over-the-counter preparation used for the treatment of diarrhea, dyspepsia, and peptic and duodenal ulcers.^[4–6] Whereas bismuth subsalicylate itself is not well defined and may be a mixture of bismuth oxido clusters, there have recently been various models used to explain its structure. In 2002, the first structures of $\text{Bi}(\text{Hsal})_3$ ($\text{Hsal} = 2\text{-OH-C}_6\text{H}_4\text{CO}_2^-$) as adducts of 2,2'-bipyridine and 2,2'-phenanthroline were reported,^[7] in 2007 followed by the derivatives of $[\text{PhBi}(\text{Hsal})_2]$.^[8] Andrews et al. reported the synthesis and structures of Bi_9 and Bi_{38} oxido-salicylate clusters that provide a reasonable model for BSS.^[9] Recently, the simplest known member of the bismuth oxido-salicylate cluster series, $[\text{Bi}_4(\mu_3\text{-O})_2(\text{Hsal})_8(\text{solvent})_2]$, was described.^[10] Mehring examined the hydrolysis of bismuth

salicylates and nitrates^[11–14] and has compiled an excellent review regarding the chemistry of bismuth oxido clusters.^[15] The formation of bismuth thiocarboxylate clusters (formed by the reaction of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ with thiocarboxylic acids) was determined by using ESI-MS.^[16]

To date, the pathway by which bismuth oxido-salicylate clusters are formed is not well understood, and the structure of $[\text{Bi}(\text{Hsal})_3]$ has not been published. A complex of the molecular composition $\text{Bi}(\text{Hsal})_3 \cdot 4\text{H}_2\text{O}$ has been reported, but its structure has not been confirmed.^[17] This paper reports the structure of hydrated tris-salicylato bismuth(III) $[\text{Bi}(\text{Hsal})_3(\text{H}_2\text{O})]$ (**1**), which can be viewed as the first step in the hydrolysis process that gives rise to polynuclear bismuth oxido clusters. The related structure of the monohydrated tris-carboxylato bismuth(III) complex of anthranilic acid, **2**, was also determined and was found to be isostructural to **1**. Though there are many examples of aromatic tris-carboxylato bismuth(III) complexes known, only a few of them have been characterized by single-crystal X-ray diffraction, including $[\text{Bi}(2\text{-MeO-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,^[18] $[\text{Bi}(2\text{-EtO-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,^[19] $[\text{Bi}(3\text{-Me-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,^[20] $[\text{Bi}(2\text{-OAc-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,^[21] and $[\text{Bi}(\text{C}_6\text{H}_5\text{CO}_2)_3]_\infty$.^[22] There are very few aromatic bismuth(III) carboxylates known that have one or more water molecules coordinated to the bismuth center, and this is attributed to the facile hydrolysis of these complexes to give oxido species. Those reported possess polyfunctional ligands such as polyaminocarboxylates,^[23] porphyrins,^[24] or sulfur-containing ligands including $[\text{PhBi}(\text{HSsal})\text{H}_2\text{O}]_\infty$ ¹ and $[\text{Bi}(\text{H}_2\text{Ssal})(\text{HSsal})(\text{H}_2\text{O})_3]_\infty$ ¹ ($\text{HSsal} = 5\text{-sulfosalicylate ion}$) that may be expected to be more stable to hydrolysis.

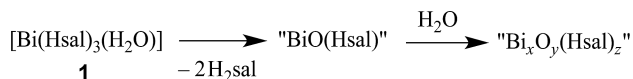
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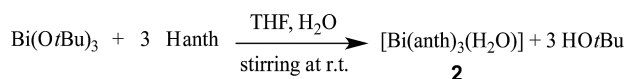
Results and Discussion

The reaction of BiPh_3 with salicylic acid (1:3) in the absence of solvent affords a yellow amorphous powder of $[\text{Bi}(\text{Hsal})_3]$ that yields bismuth oxido clusters upon dissolution in wet acetone. These clusters have been observed to have cores with 9 or 38 bismuth atoms.^[9] However, upon performing the same reaction in undried xylene, monohydrated tris-salicylato bismuth(III) species **1** is obtained. This contrasts with the reaction of BiPh_3 and H_2sal in MeCN and MeNO_2 , for which the products are $[\text{Bi}_4\text{O}_2(\text{Hsal})_8(\text{solvent})_2]$.^[10] The products of these reactions are strongly dependent upon the reaction solvents used, as the products obtained are those that crystallize from the solvent, but a clear understanding of what solvent properties determine the final product is not clear. Compound **1** has the appropriate ratio of water and salicylate ligands to produce putative “ $\text{BiO}(\text{Hsal})$ ” upon elimination of 2 equivalents of H_2sal (Scheme 1). No currently known Bi oxido-salicylate has this exact stoichiometry. The formation of a bismuth(III) oxido-salicylate complex was reported in 1926 by Picon, who reported $\text{Bi}(\text{Hsal})_3 \cdot 4\text{H}_2\text{O}$, which upon hydrolysis in acetone or ethanol yielded $[\text{Bi}_4\text{O}_3(\text{Hsal})_6 \cdot \text{H}_2\text{O}]$.^[17] Interestingly, Ruck and co-workers^[21] recently demonstrated that BiCl_3 undergoes initial hydrate formation similarly before it is converted into BiOCl in the solid state.



Scheme 1.

The reactions of BiPh_3 with anthranilic acid (Hanth, 1:3) in refluxing toluene and under solvent-free conditions both result in a complex of formula $[\text{Bi}(\text{anth})_3]$. This has been previously synthesized and spectroscopically characterized by Andrews et al., but it has not been structurally characterized.^[18] The repetition of the same reaction in a variety of different solvents produced yellow amorphous powders, and attempts to crystallize them repeatedly failed. However, the reaction of $\text{Bi}(\text{OtBu})_3$ with Hanth (1:3) overnight in THF (Scheme 2) produced a heterogeneous yellow solution. The solution was filtered, and a clear yellow filtrate was obtained. After a period of a few weeks, a few crystals were obtained from the filtrate, and they were crystallographically characterized as **2**. The formation of the hydrate is attributed to slow leakage of air into the system over the time of crystallization. The formation of the hydrates as opposed to hydrolysis products is believed to occur as a result of the fortuitous insolubility of the hydrates in the chosen solvents.



Scheme 2.

Complexes **1** and **2** were characterized by IR spectroscopy, NMR spectroscopy, elemental analysis, and single-crystal X-ray diffraction. The compounds are isomorphous and crystallize in the triclinic $P\bar{1}$ space group; they differ essentially only in the replacement of the OH group on the salicylate ligand with the NH_2 function on the anthranilate. There are two $\text{Bi}(\text{O}_2\text{CR})_3(\text{H}_2\text{O})$ molecules in the asymmetric unit of each structure (Figures 1 and 2), and the molecules display the $\eta^2-(O, O')$ binding mode for the oxygen atoms of the carboxylate ligands. The same number-

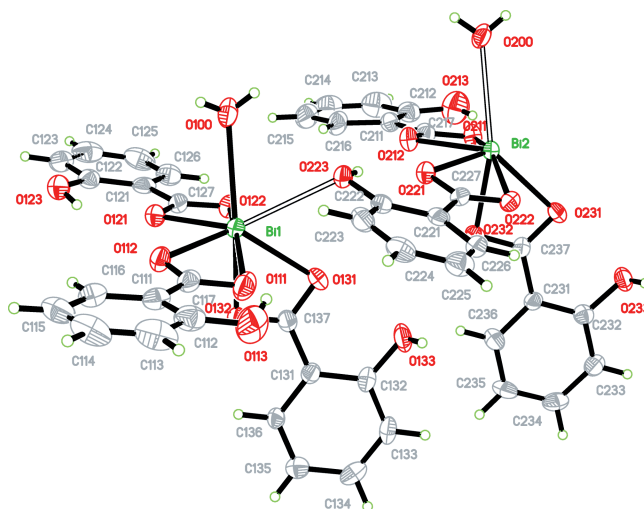


Figure 1. Molecular structure of **1**. Selected bond lengths [Å]: Bi1–O111 2.574(5), Bi1–O112 2.317(4), Bi1–O121 2.924(4), Bi1–O122 2.501(4), Bi1–O131 2.503(4), Bi1–O132 2.272(4), Bi1–O100 2.734(5), Bi2–O211 2.534(4), Bi2–O212 2.239(4), Bi2–O221 2.324(4), Bi2–O222 2.466(4), Bi2–O231 2.523(4), Bi2–O232 2.249(4), Bi2–O200 2.880(5), Bi1–O223, 2.911(4). Anisotropic displacement ellipsoids are shown at the 50% level.

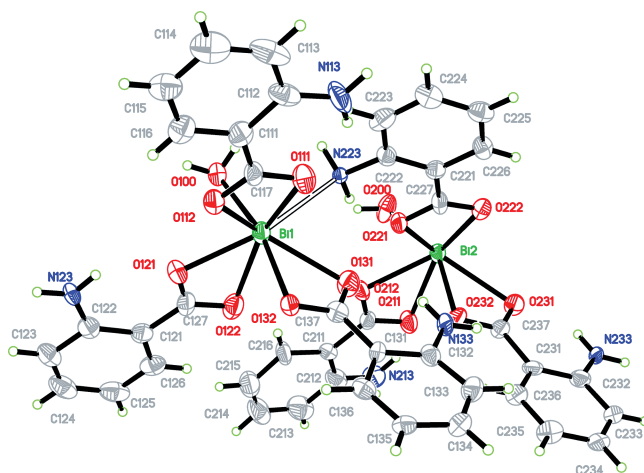


Figure 2. The molecular structure of compound **2**. Selected bond lengths [Å]: Bi1–O111 2.581(7), Bi1–O112 2.321(7), Bi1–O121 2.286(6), Bi1–O122 2.501(8), Bi1–O131 2.507(7), Bi1–O132 2.282(6), Bi1–O100 2.748(7), Bi2–O211 2.535(7), Bi2–O212 2.332(6), Bi2–O221 2.335(6), Bi2–O222 2.479(6), Bi2–O231 2.526(6), Bi2–O232 2.257(6), Bi2–O200 2.878(7), Bi1–N223 2.920(6). Anisotropic displacement ellipsoids are shown at the 50% level.

ing scheme has been used for both **1** and **2**. The bidentate $\eta^2\text{-(O,O')}$ mode has been observed previously in $[\text{Bi}(\text{2-MeO-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,^[18] $[\text{Bi}(\text{2-EtO-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,^[19] $[\text{Bi}(\text{3-Me-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,^[20] $[\text{Bi}(\text{2-OAc-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,^[21] and $[\text{Bi}(\text{C}_6\text{H}_5\text{CO}_2)_3]_\infty$.^[22] The bismuth–oxygen (carboxylate) bond lengths in **1** vary from 2.272(4) to 2.574(5) Å on Bi1 and from 2.249(4) to 2.534(4) Å on Bi2. Similarly in **2**, they vary from 2.282(6) to 2.581(7) Å and from 2.258(6) to 2.536(7) Å, respectively. The bismuth–water distances are very asymmetrical between the two molecules. In **1**, these are 2.734(5) and 2.880(5) Å, and in **2** the corresponding values are 2.748(7) and 2.878(7) Å. This arises from two sources: one, the coordination environments of the two bismuth atoms are different because Bi1 additionally binds to the OH or NH_2 group of an adjacent molecule. The O(H)–Bi distance in **1** is 2.911(4) Å, and the Bi1–N distance in **2** is 2.920(6) Å. These additional interactions give overall coordination numbers at the Bi1 centers of eight and seven for Bi2. Furthermore, the hydrogen-bonding network around each coordinated water molecule is different. The water molecules are hydrogen bonded to the carboxylate oxygen atom and phenolic oxygen/amine nitrogen atoms either intra- or intermolecularly. In the case of the more weakly bound water molecule, the hydrogen-bonding environment also includes the phenol or amine group on a nearby ligand. For example, for the water molecule on Bi1 in **1**, there are four O \cdots O separations of 2.788(6) to 2.993(6) Å, and for the water molecule on Bi2, there are O \cdots O hydrogen-bonding separations between 2.768(7) to 2.944(6) Å. Examination of the structures **1** and **2** for possible void areas by using Platon (version 161012)^[22] showed there was no additional lattice solvent present.

The absence of infrared absorption bands corresponding to C–H out-of-plane deformations and C–Bi out-of-plane deformations expected for the Ph groups supports the formation of a tris-carboxylato product. A broad band observed at 3208 cm^{-1} in the spectrum **1** and a band at 3346 cm^{-1} in the spectrum of **2** confirm the presence of an OH group from H_2O and the phenol or NH_2 group. A band at 1234 cm^{-1} in the spectrum of **1** also confirms the presence of the phenolic group. In complexes **1** and **2**, the value of $\Delta\nu$ of $< 200\text{ cm}^{-1}$ for the carboxylate bands indicates a bidentate bonding mode. This is consistent with structure in the solid state. The IR spectra of both compounds show a shift in the carboxyl region that gives rise to symmetric and asymmetric carboxylate stretching. The NMR spectra are unremarkable and are consistent with the presence of a single environment for the salicylate or anthranilate ligands. Given the weak interactions of the two molecules in the solid state, it is likely that the dimeric association does not persist in solution.

Thermogravimetric analyses of **1** and **2** showed weight losses of 2.83 and 2.87%, respectively, at approximately $100\text{--}150^\circ\text{C}$, which is consistent with the theoretical weight loss of one water molecule (calcd. 2.82 and 2.83%, respectively). Interestingly, the water molecule is lost without simultaneous loss of H_2sal or Hanth . This contrasts with the heating of $\text{BiCl}_3\cdot\text{H}_2\text{O}$, upon which BiOCl is obtained. This

highlights the fact that the hydrolysis process of bismuth salicylate is more complicated and is, as already known from the literature, highly dependent upon the solvent that acts to control the extent of hydrolysis by solubility of the growing oxido clusters. The difference may in part be attributable to the extended network structure of bismuth halides, as contrasted with the molecular nature of the bismuth carboxylate hydrates reported herein.

Owing to the high Lewis acidity of bismuth ions, they often exhibit high coordination numbers. For this reason, most of the bismuth(III) carboxylates reported are dimeric or polymeric in nature.^[23] However, in both **1** and **2** polymer formation is hindered because of the coordinated water molecule, which satisfies the coordination requirements of the bismuth atom. The presence of the coordinated water molecule in **1** and **2** could be due to the use of wet solvents or to prolonged exposure to the atmosphere. These compounds can be viewed as the first step in the bismuth carboxylate hydrolysis process and are surprisingly stable given the facile hydrolysis of bismuth tris(carboxylates) in other solvents.

Conclusions

Two new homoleptic hydrated tris-bismuth(III) carboxylates, $[\text{Bi}(\text{2-OH-C}_6\text{H}_4\text{CO}_2)_3(\text{H}_2\text{O})]$, **1**, and $[\text{Bi}(\text{2-NH}_2\text{-C}_6\text{H}_4\text{CO}_2)_3(\text{H}_2\text{O})]$, **2**, were synthesized and fully characterized. Both the salicylate and anthranilate ligands show similar bonding patterns of the carboxylate functionality. The bismuth atoms display pentagonal bipyramidal coordination in both complexes, and the seventh coordination sites are occupied by an oxygen atom from a water molecule. These two compounds can be viewed as useful starting synthons for studying other hydrolysis reactions that can lead to the formation of novel bismuth oxido species of interest in pharmaceutical applications.

Experimental Section

Materials and Equipment: All reagents and chemicals, unless otherwise stated, were purchased from commercial sources. NMR spectra were collected at room temperature in CD_3CN with a Bruker Avance 500 spectrometer, and the ^1H and ^{13}C chemical shifts are reported relative to tetramethylsilane. Melting points were obtained in sealed capillaries with an Electrothermal melting point instrument. IR spectra were recorded with a Perkin–Elmer FTIR spectrometer. $\text{Bi}(\text{O}i\text{Bu})_3$ was prepared according to a literature procedure.^[25] Thermogravimetric analysis and differential scanning calorimetry (TGA–DSC) was performed by using a Q-600 simultaneous TGA/DSC instrument under an argon atmosphere (50 mL min^{-1}) between 0 and 800°C with a temperature ramp rate of 5°C min^{-1} . Elemental analyses (C, H) were performed at Galbraith Laboratories. Bismuth analysis was done by the acid digestion of the corresponding bismuth complex and titration against EDTA by using xylenol orange as an indicator and hexamethylenetetramine as a buffer.

Synthesis of 1: A sample vial was charged with BiPh_3 (0.33 mmol, 0.146 g), salicylic acid (1 mmol, 0.138 g), and undried xylene

(6 mL). The contents were heated and stirred for a few minutes until the mixture became homogeneous. The mixture was exposed briefly to the atmosphere and was left undisturbed; after a few days, block crystals had deposited on the side walls of the vial. The crystals were identified as $[\text{Bi}(\text{Hsal})_3(\text{H}_2\text{O})]$ (**1**), yield 0.124 g (59%), m.p. 330 °C (decomp.). ^1H NMR (500 MHz, CD_3CN , 30 °C): δ = 7.84 (dd, J = 7.8 Hz, 3 H, Ar-*H*), 7.43 (m, 3 H, Ar-*H*), 6.88 (m, 6 H, Ar-*H*), 3.27 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, CD_3CN , 30 °C): δ = 162.9 (C-OH), 136.2 (Ar-C), 131.9 (Ar-C), 120.0 (Ar-C), 118.1 (Ar-C) ppm. IR: $\tilde{\nu}$ = 3208 (br.), 1625 (m), 1584 (m), 1525 (m), 1477 (m), 1380 (m), 1234 (m), 1143 (m), 1029 (m), 877 (s), 822 (m), 746 (s), 667 (m) cm^{-1} . $\text{C}_{21}\text{H}_{17}\text{BiO}_{10}$ (638.34): calcd. Bi 32.7; found Bi 31.8.

Synthesis of 2: A Schlenk flask was charged with $\text{Bi}(\text{O}t\text{Bu})_3$ (0.33 mmol, 0.143 g), anthranilic acid (1 mmol, 0.137 g), and dry THF (10 mL). The mixture was stirred overnight at room temperature and appeared to be a heterogeneous, yellow slurry. The mixture was filtered, and the yellow filtrate was placed in a vial and left undisturbed for several days. The yellow powder left behind was dried under vacuum and was characterized as $[\text{Bi}(\text{Hanth})_3(\text{H}_2\text{O})]$ (**2**). After several weeks, very few crystals were obtained from the clear yellow filtrate. The crystals were also identified and characterized as **2**, which is consistent with all the other analyses, yield 0.10 g (50%), m.p. 275–80 °C. ^1H NMR (500 MHz, CD_3CN , 30 °C): δ = 7.83 (dd, J = 8.0 Hz, 3 H, Ar-*H*), 7.23 (t, J = 6.9 Hz, 3 H, Ar-*H*), 6.67 (d, J = 8.5 Hz, 3 H, Ar-*H*), 6.55 (t, J = 7.4 Hz, 3 H, Ar-*H*), 5.60 (s, 6 H, NH_2), 3.38 (s, 1 H, OH) ppm. ^{13}C NMR (125 MHz, CD_3CN , 30 °C): δ = 164.6 (C=O), 149.0 (C- NH_2), 137.0 (Ar-C), 131.4 (Ar-C), 120.4 (Ar-C), 117.4 (Ar-C), 113.8 (C-COO) ppm. IR: $\tilde{\nu}$ = 3446 (br.), 3346 (br.), 1614 (s), 1576 (m), 1501 (s), 1457 (w), 1369 (s), 1254 (s), 1156 (s), 1030 (s), 867 (s), 799 (s), 751 (s), 705 (m), 668 (s) cm^{-1} . $\text{C}_{21}\text{H}_{20}\text{BiO}_7\text{N}_3$ (619.381207): calcd. C 39.70, H 3.17, Bi 32.9; found C 39.94, H, 4.18, Bi 32.3.

X-ray Crystallography: Single crystals of **1** and **2** suitable for X-ray crystallography were separated as blocks directly from the aforementioned reactions. Intensities were measured at 173 K with a Rigaku SCX Mini diffractometer by using a CCD area detector with Mo- K_α radiation (λ = 0.71073 Å). Empirical absorption correction with the use of the program SADABS was applied to the data. The structures were solved by direct methods and were refined against F^2 with the SHELXTL software package.^[26] All non-hydrogen atoms in the complexes were refined anisotropically. Hydrogen atoms were idealized throughout the convergence process.

CCDC-1030373 (for **2**) and -1030374 (for **1**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): Crystallographic data of **1** and **2**, tables of selected bond lengths and angles, thermogravimetric analysis plots for **1** and **2**.

Acknowledgments

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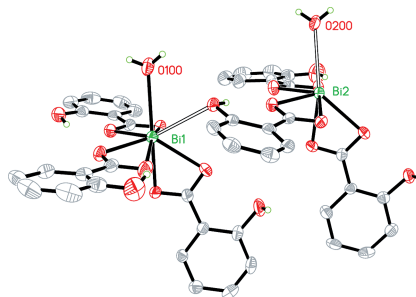
Bismuth Drugs

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The Unexpected Isolation of Bismuth Tris-(carboxylate) Hydrates: Syntheses and Structures of $[\text{Bi}(\text{Hsal})_3(\text{H}_2\text{O})]$ and $[\text{Bi}(\text{Hanth})_3(\text{H}_2\text{O})]$ ($\text{H}_2\text{sal} = 2\text{-OH-C}_6\text{H}_4\text{CO}_2\text{H}$, $\text{Hanth} = 2\text{-NH}_2\text{-C}_6\text{H}_4\text{CO}_2\text{H}$)

Keywords: Bismuth / Salicylates / Carboxylates / Hydrates / Hydrolysis



Treatment of BiPh_3 with salicylic acid in xylene in the presence of air leads to the unexpected isolation of the tris(salicylato)-bismuth(III) hydrate.