The unexpected isolation of bismuth tris(carboxylate) hydrates: syntheses and structures of [Bi(Hsal)₃(H₂O)] and [Bi(Hanth)₃(H₂O)] (H₂sal = 2-OH-C₆H₄CO₂H; Hanth = 2-NH₂-C₆H₄CO₂H)

Ish Kumar,^a Phil Andrews^b and Kenton H. Whitmire^{a,*}

^a*Department of Chemistry, Rice University*

6100 Main Street, MS-60,

Houston, Texas-77005, USA

^b*Department of Chemistry*

Monash University

Clayton, Melbourne, Victoria 3800 Australia

Email: whitmir@rice.edu; Fax: 713-348-5652, Tel: 713-348-5650

Abstract

A complex of the composition [Bi(2-OH-C₆H₄CO₂)₃(H₂O)] (**1**) was isolated from the 1:3 reaction of BiPh₃ with H₂sal (H₂sal = salicylic acid = 2-OH-C₆H₄CO₂H) in wet xylene and the analogous anthranilate compound [Bi(2-NH₂-C₆H₄CO₂)₃(H₂O)] (**2**) was obtained from the 1:3 reaction of Bi(O^{*t*}Bu)₃ with Hanth (Hanth = anthranilic acid = 2-NH₂-C₆H₄CO₂H) in tetrahydrofuran. Compounds **1** and **2** were fully characterized spectroscopically and by single crystal X-ray diffraction. **1** and **2** crystallize in the triclinic space group $\bar{P}1$ and display the η^2 -(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 on –OH or NH₂ group to an adjacent molecule. Both bismuth atoms are bind to a H₂O molecule but the distances are highly asymmetric long Bi---O distance ranging from 2.74-2.89 Å.

Introduction

The carboxylato complexes of bismuth(III) have received considerable attention due to their potent antibacterial¹⁻² and antileishmanial activity.³ They are known to hydrolyze readily to give colloidal bismuth oxido-clusters that found medicinal use. Of all the bismuth(III) carboxylates reported, bismuth sub-salicylate (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 While 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 has examined the hydrolysis of bismuth salicylates and nitrates¹¹⁻¹⁴ 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 earlier 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** has also been determined and was found to be isostructural **1**. Though they 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 $[\text{Bi}(\text{2-MeO-C}_6\text{H}_4\text{CO}_2)_3]_\infty$,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 There are very few aromatic bismuth(III) carboxylates known which 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 porphyrins²⁴ 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 (HSsal = 5-sulfosalicylate ion) that may be expected to be more stable to hydrolysis.

Results and discussion

The reaction of BiPh_3 with salicylic acid (1:3) in the absence of solvent affords a yellow amorphous powder $[\text{Bi}(\text{Hsal})_3]$ that yields bismuth oxido-clusters on dissolving in wet acetone. These clusters have been observed to have cores with nine or thirty eight bismuth atoms.⁹ However, the same reaction when carried out in undried xylene gives a monohydrated *tris*-salicylato bismuth(III) species **1**. This contrasts with the reaction of BiPh_3 and H_2sal in MeCN and MeNO_2 where the products are $[\text{Bi}_4\text{O}_2(\text{Hsal})_8(\text{solvent})_2]_\infty$.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 so obvious. Compound **1** has the appropriate ratio of water and salicylate ligands to produce the putative “ $\text{BiO}(\text{Hsal})$ ” upon elimination of two 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 coworkers²¹ recently demonstrated that BiCl_3 undergoes initial hydrate formation similarly before being converted to BiOCl in the solid state.

Scheme 1

The reaction of BiPh_3 with Hanth (1:3) in refluxing toluene and solvent free both produces 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 $\text{Bi}(\text{O}^t\text{Bu})_3$ 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 crystallographically characterized as **2**. The formation of the hydrate is attributed to the slow leakage of air into the system over the time of the crystallization. The formation of the hydrates as opposed to hydrolysis products is believed to occur due to 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, crystallizing in the triclinic space group $P\bar{1}$, and differ essentially only the replacement of the OH group on the salicylate ligand with the NH₂ function on the anthranilate. There are two Bi(O₂CR)₃(H₂O) molecules in the asymmetric unit of each structure (Figures 1 and 2) and the molecules display the η^2 -(O, O') binding mode for the oxygen atoms of the carboxylate ligands. The same numbering scheme has been used for **1** and **2**. The bidentate η^2 -(O, O') mode has been observed previously in [Bi(2-MeO-C₆H₄CO₂)₃]_∞,¹⁸ [Bi(2-EtO-C₆H₄CO₂)₃]_∞,¹⁹ [Bi(3-Me-C₆H₄CO₂)₃]_∞,²⁰ [Bi(2-OAc-C₆H₄CO₂)₃]_∞,²¹ and [Bi(C₆H₅CO₂)₃]_∞.²² The bismuth - oxygen (carboxylate) bond lengths in **1** vary from 2.272(4) Å to 2.574(5) Å on Bi(1) and from 2.249(4) Å to 2.534(4) Å Bi(2). Similarly in **2**, they vary from 2.282(6) Å to 2.581(7) Å and 2.258(6) Å to 2.536(7) Å, respectively. The bismuth-water distances are very asymmetrical between the two molecules. In **1** these are 2.734(5) Å and 2.880(5) Å and in **2** the corresponding values are 2.748(7) Å and 2.878(7) Å. This arises from two sources: first, the coordination environments of the two bismuth atoms are different because Bi(1) additionally binds to the -OH or NH₂ of an adjacent molecule. The O(H)-Bi distance in **1** is 2.911(4) Å and the Bi(1)-N distance in **2** is 2.920(6) Å. These additional interactions give overall coordination numbers at the Bi(1) centers of eight, and seven for Bi(2). Furthermore, the hydrogen bonding network around each coordinated water is different. The water molecules are hydrogen-bonded to the carboxylate oxygen and phenolic oxygen/amine nitrogen atoms either intra- or intermolecularly. In the case of the more weakly bound water, the hydrogen bonding environment also includes the phenol or amine group on a nearby ligand. For example, for the water on Bi(1) in **1**, there are four O...O separations of 2.788(6) to 2.993(6) Å and for the water on Bi(2), there are O...O hydrogen bonding separations

between 2.768(7) to 2.944(6) Å. Examination of the structures **1** and **2** for possible void areas 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 Ph groups support the formation of *tris*-carboxylato product. There was a broad peak observed at 3208 cm⁻¹ in **1** and 3346 cm⁻¹ in **2** confirming the presence of OH from the H₂O and phenol or NH₂ groups. A peak at 1234 cm⁻¹ in **1** also confirmed the presence of phenolic group. In complexes **1** and **2** the value of $\Delta\nu$ of < 200 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 show the shift in the carboxyl region that give rise to symmetric and asymmetric carboxylate stretching. The NMR spectra were unremarkable and 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 for **1** and **2** showed weight losses of 2.83% and 2.87%, respectively around 100-150 °C which is consistent with the theoretical weight loss of one water molecule (*calc.* 2.82 and 2.83 %). Interestingly, the water is lost without simultaneous loss of H₂sal or Hanth. This contrasts with the heating of BiCl₃·H₂O, upon which BiOCl is obtained. This highlights the fact that the hydrolysis process of bismuth salicylate is more complicated and, as already known from the literature, highly dependent upon the solvent which acts to control the extent of hydrolysis by solubility of the growing oxido clusters. The difference may be in part attributable to the extended network structure of bismuth halides as contrasted with the molecular nature of the bismuth carboxylate hydrates reported here.

Figure 1: Molecular structure of **1**. Selected bond lengths (Å): Bi(1)-O(111) 2.574(5), Bi(1)-O(112) 2.317(4), Bi(1)-O(121) 2.924(4), Bi(1)-O(122) 2.501(4), Bi(1)-O(131) 2.503(4), Bi(1)-O(132) 2.272(4), Bi(1)-O(100) 2.734(5), Bi(2)-O(211) 2.534(4) Bi(2)-O(212) 2.239(4), Bi(2)-O(221) 2.324(4), Bi(2)-O(222) 2.466(4), Bi(2)-O(231) 2.523(4), Bi(2)-O(232) 2.249(4), Bi(2)-O(200) 2.880(5), Bi(1)-O(223), 2.911(4). Anisotropic displacement ellipses are shown at the 50% level.

Figure 2. The molecular structure of compound **2**. Selected bond lengths: (Å): Bi(1)-O(111) 2.581(7), Bi(1)-O(112) 2.321(7), Bi(1)-O(121) 2.286(6), Bi(1)-O(122) 2.501(8), Bi(1)-O(131) 2.507(7), Bi(1)-O(132) 2.282(6), Bi(1)-O(100) 2.748(7), Bi(2)-O(211) 2.535(7), Bi(2)-O(212) 2.332(6), Bi(2)-O(221) 2.335(6), Bi(2)-O(222) 2.479(6), Bi(2)-O(231) 2.526(6), Bi(2)-O(232) 2.257(6), Bi(2)-O(200) 2.878(7), Bi(1)-N(223) 2.920(6). Anisotropic displacement ellipses are shown at the 50% level.

Due 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 due to the coordinated water molecule satisfying 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 from prolonged exposure to 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 the bismuth tris(carboxylates) in other solvents.

Conclusions

The two new homoleptic hydrated *tris*-bismuth(III) carboxylates [Bi(2-OH-C₆H₄CO₂)₃(H₂O)], **1**, and [Bi(2-NH₂-C₆H₄CO₂)₃(H₂O)], **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 the complexes, and the seventh coordination sites are occupied by an oxygen atom of a water molecule. These two compounds can be viewed as useful as starting synthons for studying further hydrolysis reactions that can lead to the formation of novel bismuth oxido species that can be of interest in pharmaceutical applications.

Experimental

Materials and Equipment

All reagents and chemicals, unless otherwise stated, were purchased from commercial sources. NMR spectra were collected at room temperature in d₃-CD₃CN on Bruker Avance 500 spectrometer, and the ¹H and ¹³C chemical shifts were reported to tetramethylsilane (TMS). Melting points were obtained in sealed capillaries on an Electrothermal melting point

instrument. IR spectra were recorded on Perkin Elmer FTIR spectrometer. $\text{Bi}(\text{O}^t\text{Bu})_3$ was prepared according to the literature procedure.²⁵ Thermogravimetric analysis and differential scanning calorimetry (TGA-DSC) was carried out using a Q-600 simultaneous TGA/DSC instrument in an argon atmosphere (50ml/min) between 0 and 800°C with a temperature ramp rate of 5°C/min. Elemental analyses (C, H) were performed at Galbraith Laboratories. The bismuth analysis was done by the acid digestion of the corresponding bismuth complexes and titration against EDTA using xylenol orange as an indicator and hexamethylenetetramine as a buffer.

Synthesis of **1**

BiPh_3 (0.33 mmol, 0.146 g) and salicylic acid, H_2sal (1 mmol, 0.138 g) were taken in a sample vial and 6 mL of undried xylene was added. The contents were heated and stirred for few minutes until the reaction mixture became homogeneous. The reaction was exposed briefly to the atmosphere and left undisturbed and after few days block of crystals were seen to be 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%) Melting point: decomposes over 330 °C. IR (ν , cm^{-1}): 3208(br.), 1625(m), 1584(m), 1525(m), 1477(m), 1380(m), 1234(m), 1143(w), 1029(m), 877(s), 822(m), 746(s), 667(m). ^1H -NMR (500 MHz, $\text{d}^3\text{-CD}_3\text{CN}$, 30 °C): δ = 7.84 (d of d, 3H, J = 7.8 Hz, Ar-*H*), 7.43 (m, 3H, Ar-*H*), 6.88(m, 6H, Ar-*H*), 3.27 (s, 1H, OH). ^{13}C -NMR (125 MHz, $\text{d}^3\text{-CD}_3\text{CN}$, 30 °C): δ = 162.9 (C-OH), 136.2 (Ar-C), 131.9 (Ar-C), 120.0 (Ar-C), 118.1 (Ar-C). Elemental Analysis (%): Found for $\text{C}_{21}\text{H}_{17}\text{BiO}_{10}$: Bi 31.8; Calc: 32.7 Bi.

Synthesis of **2**

$\text{Bi}(\text{O}^t\text{Bu})_3$ (0.33 mmol, 0.143 g) and anthranilic acid, Hanth (1 mmol, 0.137 g) were taken in a Schlenk flask and 10 mL of dry THF was added. The reaction contents were stirred

overnight at room temperature and the reaction appeared to be heterogeneous yellow slurry. The reaction 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 characterized as [Bi(Hanth)₃(H₂O)], **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%). Melting point: 275-80 °C. IR (ν, cm⁻¹): 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). ¹H-NMR (500 MHz, d³-CD₃CN, 30 °C): δ = 7.83 (d of d, 3H, *J* = 8.0 Hz, Ar-*H*), 7.23 (t, 3H, *J* = 6.9 Hz, Ar-*H*), 6.67 (d, 3H, *J* = 8.5 Hz, Ar-*H*), 6.55 (t, 3H, *J* = 7.4 Hz, Ar-*H*), 5.60 (s, 6H, NH₂), 3.38 (s, 1H, OH). ¹³C-NMR (125 MHz, d³-CD₃CN, 30 °C): δ = 164.6 (C=O), 149.0 (C-NH₂), 137.0 (Ar-C), 131.4 (Ar-C), 120.4 (Ar-C), 117.4 (Ar-C), 113.8 (C-COO). Elemental Analysis (%): Found for C₂₁H₂₀BiO₆N₃: C 39.94, H, 4.18, Bi 32.3; Calc: C 39.68, H 3.64, 32.9 Bi.

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 on Rigaku SCX Mini diffractometer using a CCD area detector using Mo-Kα radiation (λ = 0.71073 Å). Empirical absorption correction using the program SADABS was applied to the data. The structures were solved using direct methods and refined against F² with the SHELXTL software package.²⁶ All non-hydrogen atoms in the complexes were refined anisotropically. Hydrogen atoms were idealized throughout the convergence process. X-ray crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC# 1030373 and 1030374).

Supplementary Material Available: Crystallographic data for **1** and **2**, Tables of selected bond distances and angles. Thermogravimetric analysis plots for **1** and **2**.

Acknowledgements: The Robert A. Welch Foundation (C-0976) is gratefully acknowledged for support of this work.

References

- (1) Andrews, P. C.; Deacon, G. B.; Ferrero, R. L.; Junk, P. C.; Karrar, A.; Kumar, I.; MacLellan, J. G. *Dalton Trans* **2009**, 6377.
- (2) Andrews, P. C.; Ferrero, R. L.; Junk, P. C.; Kumar, I.; Luu, Q.; Nguyen, K.; Taylor, J. W. *Dalton Trans* **2010**, 2861.
- (3) Andrews, P. C.; Frank, R.; Junk, P. C.; Kedzierski, L.; Kumar, I.; MacLellan, J. G. *J. Inorg. Biochem.* **2011**, 105, 454.
- (4) Sadler, P. J.; Li, H.; Sun, H. *Coord. Chem. Rev.* **1999**, 689.
- (5) Briand, G. G.; Burford, N. *Chem. Rev.* **1999**, 99, 2601.
- (6) Bierer, D. W.; Klapötke, T. *Biol. Met.* **1988**, 1, 69.
- (7) Thurston, J. H.; Marlier, E. M.; Whitmire, K. H. *J. Chem. Soc., Chem. Comm.* **2002**, 2834.
- (8) Stavila, V.; Fettingner, J. C.; Whitmire, K. H. *Organometallics* **2007**, 26, 3321.
- (9) Andrews, P. C.; Deacon, G. B.; Forsyth, C. M.; Junk, P. C.; Kumar, I.; Maguire, M. *Angew. Chem. Int. Ed.* **2006**, 45, 5638.
- (10) Boyd, T. D.; Kumar, I.; Wagner, E. E.; Whitmire, K. H. *Chem. Commun.*

2014, 50, 3556.

- (11) Mansfeld, D.; Miersch, L.; Rueffer, T.; Schaarschmidt, D.; Lang, H.; Boehle, T.; Troff, R. W.; Schalley, C. A.; Mueller, J.; Mehring, M. *Chem. - Eur. J.* **2011**, 17, 14805.
- (12) Miersch, L.; Ruffer, T.; Schlesinger, M.; Lang, H.; Mehring, M. *Inorg. Chem.* **2012**, 51, 9376.
- (13) Schlesinger, M.; Pathak, A.; Richter, S.; Sattler, D.; Seifert, A.; Rueffer, T.; Andrews, P. C.; Schalley, C. A.; Lang, H.; Mehring, M. *Eur. J. Inorg. Chem.* **2014**, 2014, 4218.
- (14) Schlesinger, M.; Weber, M.; Rueffer, T.; Lang, H.; Mehring, M. *Eur. J. Inorg. Chem.* **2014**, 2014, 302.
- (15) Mehring, M. *Coord. Chem. Rev.* **2007**, 251, 974.
- (16) Phillips, H. A.; Burford, N. *Inorg. Chem.* **2008**, 47, 2428.
- (17) Picon, M. *J. Pharm. Chim.* **1926**, 8, 145.
- (18) Andrews, P. C.; Deacon, G. B.; Junk, P. C.; Kumar, I.; Silberstein, M. *Dalton Trans.* **2006**, 4852.
- (19) Andrews, P. C.; Deacon, G. B.; Jackson, W. R.; Maguire, M.; Scott, N. M.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Dalton Trans.* **2002**, 4634.
- (20) Sharutin, V. V.; Egorova, I. V.; Ivanenko, T. K.; Sharutina, O. K.; Pushilin, M. A.; Gerasimenko, A. V.; Adonin, N. A.; Starichenko, V. F. *Russ. J. Coord. Chem.* **2004**, 30, 309.
- (21) Andrews, P. C.; Blair, V. L.; Ferrero, R. L.; Junk, P. C.; Kumar, I. *Chem Commun.* **2013**, 49, 2870.
- (22) Rae, A. D.; Gainsford, G. J.; Kemmitt, T. *Acta Cryst.* **1998**, B54, 438.
- (23) Stavila, V.; Davidovich, R. L.; Gulea, A.; Whitmire, K. H. *Coord. Chem. Rev.* **2006**, 250, 2782.

- (24) Halime, Z.; Lachkar, M.; Furet, E.; Halet, J.-F.; B. Boitrel *Inorg. Chem.* **2006**, *45*, 10661.
- (25) Massiani, M., -C.; Papiernik, R.; Hubert-Pfalzgraf, L. G.; Daran, J.-C. *Polyhedron* **1991**, *10*, 437.
- (26) Sheldrick, G. M. *SADABS 5.1, Göttingen* **1997**.

Keywords: bismuth, salicylate, carboxylate, hydrate, hydrolysis,

Table of Contents Entry

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