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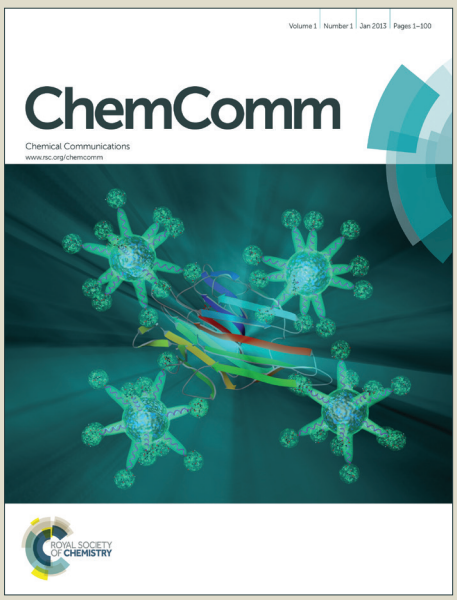

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Synthesis and structural studies of the simplest bismuth(III) oxo-salicylate complex: $[Bi_4(\mu_3\text{-}O)_2(HO\text{-}2\text{-}C_6H_4CO_2)_8]\cdot 2$ Solv (Solv = MeCN or $MeNO_2$)

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Reaction of $BiPh_3$ with salicylic acid ($HO\text{-}2\text{-}C_6H_4CO_2H$, H_2Sal) at room temperature in wet acetonitrile or nitromethane leads to the facile formation of an oxo cluster compound with formula $[Bi_4(\mu_3\text{-}O)_2(HSal)_8]$ solvated by either MeCN and $MeNO_2$ (1·2MeCN or 1·2$MeNO_2$). This simple procedure affords a convenient, high yield (>80%) synthesis of a single bismuth oxo cluster. Both adducts exhibit a nearly planar $Bi_4(\mu_3\text{-}O)_2$ core. The solvent ligands are situated in the same coordination sites in both but at long Bi---N and Bi---O distances. The ease of preparation as a pure compound makes this an ideal starting material for study of bismuth oxo-salicylate chemistry.

In the recent years there has been a growing interest in the chemistry of the carboxylato complexes of bismuth with bismuth(III) salicylate ($Bi(Hsal)_3$, $Hsal^-$ = $^-O_2CC_6H_4$-2-OH) receiving considerable attention. For centuries, bismuth compounds have been employed for treatment of syphilis, diarrhea, gastritis, and colitis among other conditions. They are well-known for their antibacterial and antiparasitic activity. Bismuth subsalicylate (BSS) has been used in the treatment of gastrointestinal disorders and is sold over the counter under the trademark names "Pepto-bismol" and "Bismatrol".[1-6] Bismuth subsalicylate, which is nominally "BiO(Hsal)," is not well defined and is probably a mixture of hydrolyzed compounds. As with other BiX_3 compounds, bismuth salicylate is sensitive to hydrolysis yielding oxide-containing materials. Model compounds have been characterized showing a bismuth-oxide core ($Bi_9O_7^{13+}$, $Bi_{38}O_{44}^{26+}$ and $Bi_{38}O_{45}^{24+}$) stabilized by carboxylate anions attached to the surface.[7-12] When normalized on Bi, the ratios in these compounds are $BiO_{0.78}(Hsal)_{1.44}$ and $BiO_{1.16}(Hsal)_{0.68}$, respectively, which vary considerably from the 1:1:1 stoichiometry of the idealized bismuth subsalicylate. A 1:1 mixture of these two compounds with ratio 1:0.97:1.06 would come much closer to the idealized value. At the same time, the number of bismuth atoms in a oxo-carboxylate molecule can range from 4 to 38, with six being the most commonly observed for hydrolysis of bismuth halides and pseudo halides, and bismuth subsalicylate might contain other bismuth oxo salicylate clusters in addition to the two referenced above. The chemistry of these oxo clusters has been reviewed.[9,11-17]

Often when reacting bismuth halides with sodium salts of alkoxides or carboxylates, oxo-compounds are obtained. We discovered that protonolysis of $BiPh_3$ using acidic organic compounds can avoid the formation of oxo ligands and have applied this methodology to the production of $[Bi(OC_6F_5)_3(toluene)]_2$, $Bi(Hsal)_3$ and various derivatives thereof.[8,18,19] This approach avoids the sodium halide salt metathesis byproducts, yielding only volatile benzene. Subsequent hydrolysis of these compounds by dissolution in wet solvents leads to a variety of bismuth-oxo alkoxides and carboxylates.[7,20] Recently, Friščić *et. al.* reported the synthesis and structure of first bismuth salicylate without any organic auxiliaries using ion- and liquid-assisted grinding (ILAG) method which has been used for mechanical synthesis of metal-organic frameworks.[21]

We have proceeded with the assumption that solubility of the growing oxo-species controls the ultimate product nuclearity and that simple changes in solvent polarity could result in the

observation of different nuclearity products. Consequently, we have explored the effect of solvent on the protonolysis of $BiPh_3$ in a variety of solvents. Herein we report the facile synthesis of the tetranuclear oxo cluster $Bi_4O_2(Hsal)_8$, which is found to be solvated by two molecules of either MeCN and $MeNO_2$ in the solid state. This core is the simplest and the smallest oxo salicylate core among the known complexes of this class. In 2008 Timakova *et. al.* produced an oxo cluster with same formula "$Bi_2O(Hsal)_4$" but its structure was not determined.[22]

Pale brown crystals of **1**·2 MeCN and colourless crystals of **1**·2 $MeNO_2$ grew over a period of 2-3 days upon dissolution of $BiPh_3$ and H_2Sal in acetonitrile (MeCN) or nitromethane ($MeNO_2$) that were used as received (details are provided in the Electronic Supplementary Information). All manipulations were done in air, and the yields were good (>80%). It should be noted that very little water (2.2 mg per 110 mg $BiPh_3$) is required to achieve this stoichiometric transformation and sufficient water is available in undried solvents. Even if the solvents are pre-dried, however, sufficient water is available from the atmosphere as the reactions are done in air to achieve the desired outcome, although crystallization may be slower if starting with dry solvents. The crystals of the two compounds, which are isomorphous, were identified by single crystal X-ray diffraction as the bismuth-oxo cluster **1** containing a $Bi_4(\mu_3\text{-}O)_2$ core (**Figure 1**) bound with eight salicylate ligands and two weakly interacting solvent molecules.

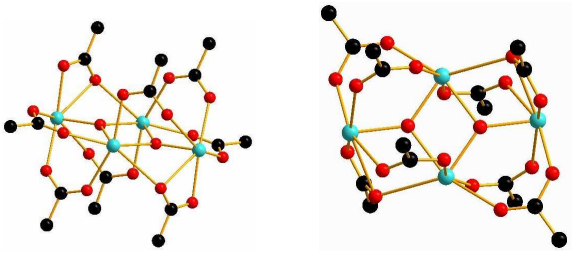


Figure 1: The core Bi_4O_2 core present in compounds **1**·2MeCN and **1**·2$MeNO_2$ shown (**A**) from the side of the Bi_4O_2 plane and (**B**) perpendicular to the Bi_4O_2 plane. The carbon atoms are black, the oxygen atoms are red and the bismuth atoms are blue. The weakly coordinated solvents and all atoms but the carboxylate and the ipso carbons of the salicylate ligands have been omitted for clarity.

Even with an excess of salicylic acid (H_2sal) the same product is formed. The formation of bismuth oxo cluster is presumably due to the hydrolysis of the intermediate $Bi(Hsal)_3$ species and the products are likely kinetically prevented from further hydrolysis by their limited solubility in the chosen solvents. Several solvent parameters were considered to explain the difference in observed nuclearities from different solvents. The similarity in products formed in MeCN and $MeNO_2$ could be in part due to the similarity of the dielectric constants of these two solvents (37.5 vs 34.8, respectively). The dielectric constant of acetone and dmso, from which Bi_9 and Bi_{38} oxo compounds have been obtained, have both smaller and larger dielectric constants (20.7, 46.7, respectively). Solvent dipole moments also do not give an obvious trend, with that of MeCN being similar to dmso (3.92 vs 3.96) while $MeNO_2$ is similar to acetone (3.1 vs 2.9). What does seem safe to conclude, however, is that acetone and dmso more strongly solvate the bismuth oxo clusters as the Bi-O distances for those solvents are much shorter (2.73 to 2.81 Å) when compared to the two compounds reported here, where the Bi-O or Bi-N distances are > 3.0 Å.

The $Bi_4(\mu_3\text{-}O)_2$ core is composed of two edge-sharing $Bi_3(\mu_3\text{-}O)$ triangles in a typical butterfly arrangement. The carboxylates of the salicylate anion bridge between bismuth atoms, stabilizing the Bi_4O_2 core, which is the central fragment of both the compounds (**Figure 1**). **Figure 2** shows the full molecular structure of **1**·2MeCN. The bismuth oxide core is surrounded by eight mono-deprotonated salicylate ligands and two weakly interacting solvent molecules. The two molecules have crystallographically-imposed inversion symmetry. There are two unique environments for the bismuth atoms, those occupying the "hinge" of the butterfly and those occupying the "wingtips." Each wingtip bismuth atom has a coordination number of six and central bismuth atom has coordination number of 5, or six, if the weakly-bound solvent molecules are included).

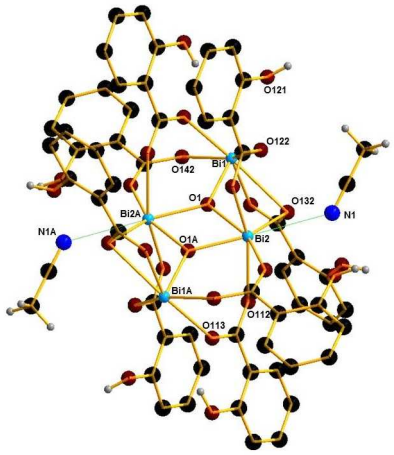


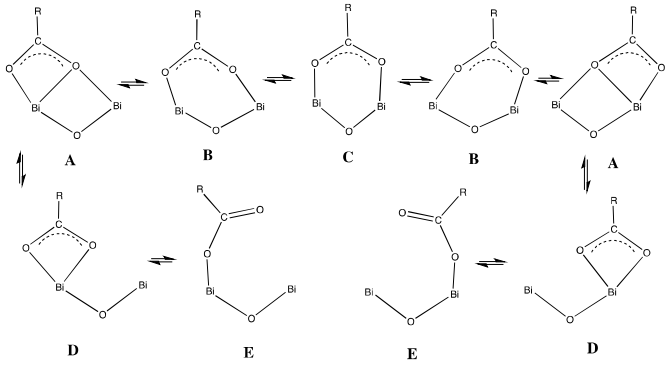
Figure 2: Molecular structure of **1**·2MeCN. Anisotropic displacement parameters are shown at the 30% level. Hydrogen atoms on the salicylate ligands have been omitted for clarity. The structure of **1**·2$MeNO_2$ is found in the Electronic Supplementary Information.

The presence of the inversion symmetry requires that there are four unique salicylate environments. Three of these are similar in that the ligands are bridging between the wingtip and hinge bismuth atoms with one oxygen atom of the carboxylate attached in a terminal fashion to each bismuth. Two of these ligands lie essentially perpendicular to and above the Bi_4O_2 plane while the other lies roughly in that plane. The other $Hsal^-$ environment shows the carboxylate to be chelating a wingtip bismuth atom very asymmetrically. The weaker bound oxygen atom of that unit is also involved in a bridging interaction to the hinge bismuth atom. Similarly, the other bismuth carboxylates reported earlier have planar four-membered Bi_2O_2 ring structures and tend to undergo polymerization. The core structure is similar to those found in $[Bi_4O_2(OSiEt_3)_8]$[14] and $Bi_4O_2(O_2CC_6H_2F_3\text{-}3,4,5)_8{\cdot}2Ar$ [Ar = C_6H_6, C_6H_4-1,4-Me_2].[23] Due to the crystallographic symmetry, the four Bi atoms lie rigorously in a plane. In the MeCN compound the μ_3-O atom lies 0.1933(5) Å out of this plane and the corresponding distance in the nitromethane derivative is 0.1834(29) Å.

For the related siloxide compound, the μ_3-O atom is farther from the plane (0.6087(4) and 0.593(14) Å for two independent molecules).[14] The Bi-O bond (hinge) distances Bi(2)-μ_3-O(1) and Bi(2)-μ_3-O(1A) in **1**·2MeCN are 2.284(6) Å and 2.133(5) Å whereas the analogous distances in **1**·2 $MeNO_2$ are 2.274(3) Å and 2.117(3) Å. The Bi(1)-μ_3-O(1)) distances in **1**·2 MeCN and **1**·2 $MeNO_2$ are 2.078(5) Å and 2.092(5) Å, respectively. These Bi-O bond distances are similar to those found in $[Bi_4O_2(OSiEt_3)_8]$[14] and $Bi_4O_2(O_2CC_6H_2F_3\text{-}3,4,5)_8{\cdot}2Ar$ [Ar = C_6H_6, C_6H_4-1,4-Me_2].[23] The corresponding Bi-O (hinge/wingtip) bond distances in $Bi_4O_2(O_2CC_6H_2F_3\text{-}3,4,5)_8{\cdot}2C_6H_6$ are 2.115(2) and 2.275(2)/2.089(3) Å whereas in $Bi_4O_2(O_2CC_6H_2F_3\text{-}3,4,5)_8{\cdot}2C_6H_4$-1,4-$Me_2$ they are 2.124(3) and 2.276(3)/2.083(2) Å. As expected the Bi-O distances in Bi_4O_2 core (hinge) are longer than wingtip Bi-O distances. The bismuth-carboxylate oxygen bond lengths in **1**·2 MeCN range from 2.285(3) Å to 2.631(3) Å, whereas in **1**·2 $MeNO_2$ the range is from 2.216(6) Å to 2.641(7) Å. These distances are similar to the other known bismuth carboxylates.[24-26] The solvent to Bi distances are long (3.06(2) Å) for MeCN and 3.103(4) for $MeNO_2$) but the solvents are clearly oriented so that they interact, albeit weakly, with the metal center. We expect the Bi_4O_2 core will prove to be the simplest bismuth oxo salicylate. The only other possible compound with a lower nuclearity would be the corresponding mononuclear formulation $Bi_2O(Hsal)_4$, but such a formulation is unlikely as it would be difficult for bismuth to satisfy its coordination requirements with such a simple formulation without addition of additional donor ligands. In contrast to the salicylic acid system, using substituted salicylic acids ($Hsal^R$) such as 4-methyl salicylic acid[19] has not yet led to isolation of a crystalline oxo-cluster. This difference could arise from the different acidities of the aromatic acids, with the less acidic compounds being unable to solvolyze all of the phenyl groups, or the differences in solubility between the various substituted $PhBi(Hsal^R)_2$ compounds.

Interestingly, the dissolution of **1**.2 MeCN in wet acetone leads to the formation of pure Bi_{38} oxo-cluster only which was previously reported by Andrews *et.al*.[5] Repeating the reaction several times lead to the formation of well-formed prismatic crystals and the percentage yield was found to be 34%. These crystals showed unit cell parameters consistent with $Bi_{38}O_{44}$ oxo-cluster (a = 31.26 Å, b = 31.34 Å, c = 31.47 Å; $\alpha = \beta = \gamma = 90°$). The bismuth analysis was done by the acid digestion of the Bi_{38} oxo- cluster and titration against EDTA using xylenol orange as an indicator and hexamethylenetetramine as a buffer. The percentage of bismuth was found to be 57.5% which is in good agreement with the theoretical value of 59.2%. An image of the crystals has been provided in the Electronic Supplementary Information.

The title compounds **1**·2 MeCN and **1**·2 $MeNO_2$ are soluble in DMSO, and the NMR data indicate that there is a single salicylate environment. Since there are clearly four different environments for salicylate ligands in the solid state structure, a dynamic process must equilibrate the NMR signals. This is most likely due to migration of the salicylate ligands about the Bi_4O_2 core, which can be readily accommodated by the ability of the bridging ligands to switch between terminal and bridging configurations in a concerted process with other salicylate ligands. This can be easily envisioned by examining **Figures 1A** and **Scheme 1** where the three $Hsal^-$ ligands lying above and below the Bi_4O_2 plane show different degrees of bridging (**A** – **C**) between the bismuth atoms, poising them for moving around the oxo core. The η^1 (**D**) and η^2 (**E**) configurations have been observed in other bismuth salicylate structures. This is analogous to the now classical example of terminal ↔ semibridging ↔ bridging exchange mechanism of CO ligands in metal carbonyl clusters.[27] We cannot completely rule out dissociation into a symmetrical $Bi_2O(Hsal)_4(solvent)_x$ as a mechanism for exchange, but this seems less likely.



Scheme 1. The different bridging modes of the salicylate ligand (R = HO-2-C_6H_4) in the title compounds that can explain the fluxionality observed in the ^{1}H NMR spectrum.

Conclusions

The reaction of $BiPh_3$ with salicylic acid in wet acetonitrile and nitromethane leads to the formation of tetranuclear oxo cluster with a planar Bi_4O_2 core. The products from reactions in different solvents have been crystallographically authenticated. These compounds represent the simplest bismuth oxo cluster compounds containing salicylate. The synthesis is convenient and proceeds in very good yields to produce a single oxo cluster species that should prove useful as a starting reagent for further bismuth-oxo salicylate reactions. A facile method for producing only $Bi_{38}O_{44}$ cluster was established as well.

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Notes and references

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Electronic supplementary information (ESI) available: Full experimental and analytical details, including crystallographic data and tables. Full labelled figures and tables of selected bond lengths and angles. Crystallographic Information Files are on file with the Cambridge Crystallographic Data Centre: CCDC 979170 and 979171. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/XXXX

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