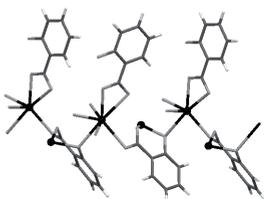


The chemistry of bismuth with salicylic acid and other carboxylic acids is an area of continuous research. Three different forms of bismuth salicylate are known, which differ in the stoichiometric ratio of bismuth and salicylic acid: the active pharmaceutical ingredient bismuth subsalicylate (**1**), the disalicylate (**2**), and the trisalicylate (**3**) involving a 1:3 stoichiometric ratio[1]. The synthesis of these from solution is complicated by the required harsh conditions and the sensitivity of the product to reaction conditions. Whereas solid-state synthetic methodologies have also been proposed,[2] their wider application is limited by issues of environmental nature and reactant toxicity. We now demonstrate the rapid, efficient and selective synthesis of into **1**, **2** and **3** by ion- and liquid-assisted grinding (ILAG)[3] directly from Bi₂O₃ and reveal the first crystal structure of a bismuth salicylate without auxiliary ligands.

Recrystallization of mechanochemically obtained **2** and **3** from N,N-dimethylformamide (DMF) yielded crystals that are isostructural with the bismuth oxo-cluster structure previously obtained from acetone by Williams *et al.*[2], with an almost identical cubooctahedral Bi₃₈ cluster, with acetone molecules coordinated to bismuth replaced by DMF. The formation of the identical bismuth core from different solvents indicates its structural robustness and supports its relevance for the activity of bismuth subsalicylate.

To further investigate this possibility, powder X-ray diffraction data was collected at the ESRF beamline ID31 for **2**. Structure solution revealed one bismuth atom and two salicylate moieties in the asymmetric unit along with a water molecule. Compound **2** is a layered material consisting of sheets held by Bi-O linkages and O-H...O hydrogen bonds. This structure is a particularly relevant addition to our understanding of the chemistry of bismuth salicylates for three reasons: a) it complements the existing model compounds based on discrete oligonuclear clusters involving auxiliary organic ligands; b) it confirms the tendency of bismuth salicylate to adopt extended structures in the absence of organic auxiliaries; c) demonstrates the absence of basic hydroxide or oxide species in bismuth disalicylate.



[1] (a) E.V. Timakova, T.A. Udalova, Yu.M. Yukhin Russ. *J. Inorg. Chem.* **2009**, *54*, 873. [2] P. C. Andrews, G.B. Deacon, C.M. Forsyth, P.C. Junk, I. Kumar, M. Maguire *Angew. Chem. Int. Ed.* **2006**, *45*, 5638. [3] T. Frišćić, D. G. Reid, I. Halasz, R.S. Stein, R.E. Dinnebier, M.J. Duer *Angew. Chem. Int. Ed.* **2010**, *49*, 712.

Keywords: Pharmaceutical, Bismuth, Salicylate

MS10.P03

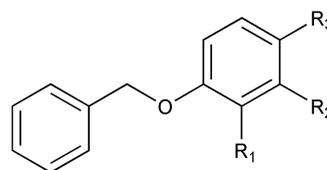
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X-ray powder diffraction study of five benzyloxy-benzene derivatives

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The benzyloxy-benzene derivatives form an important class of organic compounds with a wide range of analytical and biological applications. The structural characterization of five benzyloxy-benzene derivatives [2-benzyloxybenzoic acid (**1**), 3-benzyloxybenzoic acid (**2**), 4-benzyloxybenzoic acid (**3**), 2-benzyloxyaniline (**4**) and 3-

benzyloxyaniline (**5**)] using laboratory X-ray powder diffraction data are described, as part of our ongoing program aimed at understanding the mutual interplay between the strong and weak interactions. Crystal structures of all five compounds have been solved by direct-space approach and refined by a combination of Rietveld method and DFT based solid state geometry optimization. An investigation of close intermolecular contacts between the molecules via Hirshfeld surface analysis is also presented in order to reveal subtle differences and similarities between the five crystal structures. In the benzyloxybenzoic acids (**1-3**), the conformation of molecules depends on the position of the -C(OH)=O (carboxylic acid) group, whereas, the conformations of the two benzyloxyanilines, **4** and **5**, are quite similar. In compounds **1-3**, the carboxylic acid group with equal numbers of donors and acceptors facilitates the formation of different supramolecular assemblies. In compound **4**, the molecules are linked via C-H... π and N-H... π (arene) hydrogen bonds forming one-dimensional zig-zag chains propagating along the [100] direction. In compound **5**, aromatic π ... π stacking interactions between the phenyl rings of molecules related by inversion lead to the formation of π -stacked dimers.



- (1): R₁ = -C(=O)-OH; R₂ = H = R₃,
 (2): R₁ = H = R₃; R₂ = -C(=O)-OH,
 (3): R₁ = H = R₂; R₃ = -C(=O)-OH,
 (4): R₁ = -NH₂; R₂ = H = R₃,
 (5): R₁ = H = R₃; R₂ = -NH₂

Keywords: powder diffraction, ab-initio structure solution, Rietveld refinement

MS10.P04

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Structural elucidation by powder synchrotron diffraction of imidate palladium complexes

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Ab initio structural elucidation of [Pd(succ)₂(NA)₂] and [Pd(sac)₂(NA)₂] (succ: succinimide, sac: saccarinate, NA: nicotinamide) has been made by powder X-ray diffraction.

The new complexes were obtained by treating solutions of [Pd(succ)₂(SMe₂)₂] and [Pd(sac)₂(SMe₂)₂] in acetone with nicotinamide in excess. The resulting suspension was stirred under reflux for 1 hour. The off-white solids formed were filtered and washed with water and ether. They are insoluble and it was not possible to obtain single crystals.

High resolution X-ray powder diffraction patterns were collected at the SpLine beamline (BM25A) of the Spanish CRG at the European Synchrotron Radiation Facility (ESRF, Grenoble) with a fixed wavelength of 0.8269 Å at room temperature. Powdered samples were placed inside a 0.5 mm-diameter capillary, which was rotated during exposure. Data collection was done in a continuous 2 θ -scan mode with 0.015° step and 2 sec acquisition time per point. The incoming beam was also monitored to normalize the decay of the primary beam.

The peak positions were identified using a derivative-based algorithm that is implemented in the peak search utility of the WINPLOTR software package [1]. The indexing was carried out using the commonest