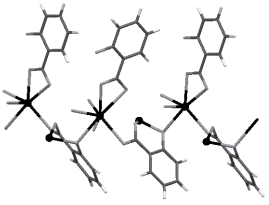
The chemistry of bismuth with salicylic acid and other carboxylic acids is an area of continuous research. Three different forms of bismuth salicylate are known, which differ in the stoichiometric ratio of bismuth and salicylic acid: the active pharmaceutical ingredient bismuth subsalicylate (**1**), 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 Bi_2O_3 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 Bi_{38} 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. Friščić, 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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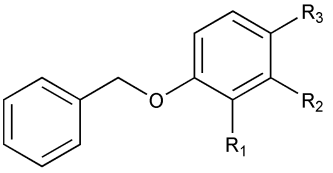
The benzyloxy-benzene derivatives form an important class of organic compounds with a wide range of analytical and biological applications. The structural characterization of five benzyloxy-benzene derivatives **[**2-benzyloxybenzoic acid (**1**), 3-benzyloxybenzoic acid (**2**), 4-benzyloxybenzoic acid (**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): R_1= -C(=O)-OH; R_2=H=R_3,
(2): R_1= H= R_3; R_2= -C(=O)-OH,
(3): R_1= H= R_2; R_3= -C(=O)-OH,
(4): R_1= -NH_2; R_2= H= R_3,
(5): R_1= H= R_3; R_2= -NH_2.

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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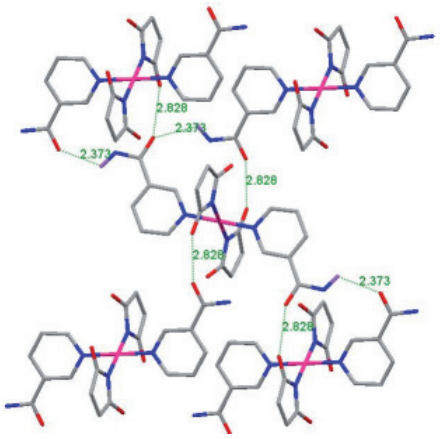
Ab initio structural elucidation of $[Pd(succ)_2(NA)_2]$ and $[Pd(sac)_2(NA)_2]$ (succ: succinimidate, sac: saccarinate, NA: nicotinamide) has been made by powder X-ray diffraction.

The new complexes were obtained by treating solutions of $[Pd(succ)_2(SMe_2)_2]$ and $[Pd(sac)_2(SMe_2)_2]$ 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 2θ-scan mode with 0.015º 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

indexing programs: ITO, TREOR90, DICVOL, KOHL, TAUP, FJZN, and LZON. The atomic coordinates obtained by Monte Carlo methods were used to initialize the Rietveld refinements, which were performed using the FULLPROF program [2].



In both cases, NA ligand "organizes" the packing by strong amide-amide hydrogen bonds forming a 3D network with four complexes around each other.

[1] T. Roisnel and J. Rodríguez-Carvajal, Mater. Sci. Forum. **2001**, *118*, 378 [2] J. Rodríguez-Carvajal, FULLPROF, V. 1.9c. LLB, CEA/Saclay, France, **2001.**

Keywords: synchrotron, rietveld, palladium

MS10.P05

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Crystal structure from X-ray powder diffraction data with Z′=2

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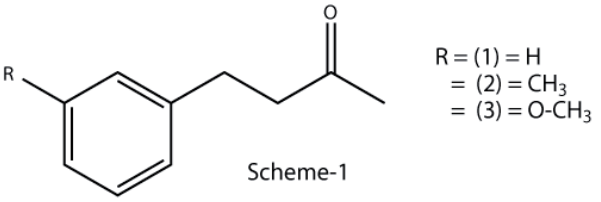
Phenylpropionic acid derivatives exhibit a strong binding ability to peroxidases, which catalyze the oxidation of a number of organic and inorganic substrates. Structural studies of phenylpropionic acid derivatives carried out by our group revealed that the crystal structures are predominantly built up by carboxylic acid dimers forming $R^2_2(8)$ synthons. In the course of our ongoing program of structural characterization of organic compounds from X-ray powder diffraction data, we came across 3-phenylpropionic acid (**1**), 3-(3-methylphenyl)propanoic acid (**2**) and 3-(3-methoxyphenyl)propanoic acid (**3**) [scheme 1]. Crystal structures of three compounds have been solved from laboratory X-ray powder diffraction data using direct-space approaches and refined by Rietveld method using the program GSAS package with an EXPGUI interface. Hirshfeld surface analysis of compounds were also performed to visualize and discriminate the features of molecular interactions in the compounds. The essential difference between the 3-phenylpropionic acid (**1**) and the compounds **2** and **3** is the presence of different substituent at the 2 positions (methyl group in **2** and methoxy in **3**). The asymmetric unit of compounds **1**-**3** contains two molecules(Z′=2). The carboxylic acid group in **1**–**3** forms O-H...O hydrogen bonded dimer with O1...O2 distances of 2.683(5) - 2.902(3) Å in an $R^2_2(8)$ graph-set motif. The interconnection of $R^2_2(8)$ rings via C-H…O hydrogen bonds generates a ladder-like one dimensional architecture based on fused $R^2_2(14)$ and $R^4_4(20)$ synthons in **1**. Pairs of molecules forming $R^2_2(8)$ rings are further connected through intermolecular C-H…O hydrogen bonds to generate three dimensional structures in compound **2**. In **3**, however, the interconnection of $R^2_2(8)$ rings via C-H…O hydrogen bonds generates a two dimensional architecture based on edge fused $R^4_4(32)R^2_2(14)$ synthon. Although crystal structures of moleculer compounds can now be accomplished from X-ray powder diffraction data, structure solution of compounds with Z′>1 is not very common.



Scheme-1

Keywords: Powder diffraction, Z prime>1, Hirshfeld surface.

MS10.P06

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TALP: A L.S. structure solution program of molecular compounds from powder data

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In recent years, global optimization methods are increasingly important in crystal structure determination of molecular compounds from powder diffraction data. Most procedures make extensive use of simulated annealing or other more or less exotic optimization algorithms [1]. Here a general easy-to-implement method based on the well-known L.S. algorithm is presented which allows solving crystal structures of a wide variety of relatively complex compounds. TALP structure solution program is based on a global optimization technique which combines a random/incremental iteration strategy for positioning the molecule with an ultra-fast Rietveld refinement. The geometry of the molecule is fixed by restraints. Unlike other structure solution programs, atom coordinates but not torsion angles are refined. Torsion angles are used only to create initial pseudo-random models.

TALP has been tested on powder diffraction data of molecular compounds of different complexity. For simple compounds with cell volumes up to 1400 $Å^3$ and 4 torsion angles, the solution is obtained straightforwardly. More complex structures with e.g. cell volumes up to 3500 $Å^3$, up to 8 torsion angles, and two independent molecules in the unit cell, have been also solved but longer time is required. Although TALP is focused on organic compounds, also coordination compounds have been successfully solved.

[1] W.I.F. David, K. Shankland, *Acta Cryst.* **2007**, *A64*, 52-64.

Keywords: Powder diffraction, molecular compounds, ab initio structure solution

MS10.P07

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Crystal structures and humidity-dependent phase transitions of Gly-L-Tyr hydrates

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Oligopeptides are one of the physiologically active substances and used as medicines, sweeteners, and food additives. They frequently crystallize as hydrates, and crystal structural transformations are induced by hydration and dehydration processes. Under such backgrounds, we aim to carry out *ab initio* crystal structure determination of oligopeptides