

Keywords: anilinium, hydrogensulfate and hydrogen-bond

FA4-MS26-P10

16 independent molecules for an *ortho*-palladated primary amine Beatrice Braun (Calmuschi-Cula)^{a,b}, Ulli Englert^a, ^a*Institute of Inorganic Chemistry, RWTH Aachen University*, ^b*Institute of Chemistry, Humboldt University Berlin*

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During our efforts to build well-ordered binary crystals based on *ortho*-palladated primary amines [1-2], we encountered a rare and interesting example of $Z' = 16$. The complex derived from 4-methoxy-phenylethylamine crystallizes in the non-centrosymmetric space group *Pc*; the other compounds in this class are unspectacular with respect to the number of independent molecules. Only four other structures with Z' larger or equal 16 exist up to date in the CSD Database [3-7]. According to Kitaigorodskii's close packing principle [8], molecules arrange in the solid state in such a way to maximize density and minimize free volume. Void space in crystals is always unfavourable [9]. Structures with large Z' values are associated with packing conflicts [10].

In the present case, the elevated number of molecules in the asymmetric unit can be attributed to the -OMe substituent which corresponds to a soft conformational degree of freedom.

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Keywords: chemistry organometallic, crystal packing, conformational flexibility

FA4-MS26-P11

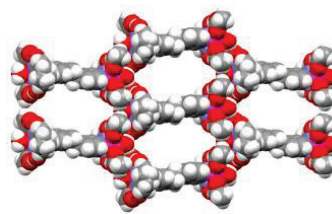
Multi-Component Crystals of DihydroErgocornine.

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Polymorphism and solvatomorphism are phenomena frequently observed in pharmaceutically active substances. The knowledge of potential crystalline forms is important particularly from the point of stability, process and final dosage form development.

Systematic research in the field of ergot alkaloids has shown, that structurally related compounds sometimes form nearly isostructural types of packing. Same structure type is shared with one or more solvent molecules, but also a mix of solvents



occupying the identical structure cavities. Number of members which fit to one structure type continually increases. In most cases a structure is quite unstable due to the solvent molecules

leaking out of its sites. According to thermal analysis, the solvent molecules tend to abandon structure in separated steps depending on time or temperature. A question arises, to what extent of partial desolvation the original structure is preserved. Is it possible to eliminate one of two molecules in the cavity? Will a single crystal survive partial desolvation? Is it possible to localize the remaining molecule(s)?

This work deals with solvatomorphism of semisynthetic ergot alkaloid dihydroergocornine mesylate, which forms interesting series of solvatomorphs. Single crystal X-ray structure data of dihydroergocornine mesylate solvated forms will be presented, sorted into structure types showing relationship among them. The desolvation process of selected phases will be described using combined TG-DTA-MS method. The new desolvated phases will be monitored with X-ray powder diffraction analysis. Hopefully a mixed solvent phase will be presented as well.

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Keywords: thermal methods, X-ray structure of ergot alkaloid, solvatomorph

FA4-MS26-P12

Crystal Structure of New Binuclear Molecule

[Cd₂(NioxH)₂(bpetha)(CH₃COO)₄(H₂O)₂] Lilia Croitor,^a Eduard B. Coropceanu,^b Mark M.

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We have further developed the strategy of 'metal dioxime building block' for construction of new generation of mixed-ligand coordination compounds with useful properties [1]. The ability of the oxime donors to form intramolecular hydrogen bonds with coordinated anion can be useful for stabilization of reactive intermediates or for enhancement of reactivity. Interaction in the system Cd(CH₃COO)₂+NioxH₂+bpetha in the molar ratio 1:2:2 resulted in binuclear molecule of the composition [Cd₂(NioxH)₂(bpetha)(CH₃COO)₄(H₂O)₂] (1), and the dioxime-free 1D coordination polymer with the monomeric unit [Cd(bpetha)(CH₃COO)₂(H₂O)] (2), where NioxH₂=1,2-cyclohexanedionedioxime, bpetha=1,2-bis(4-pyridyl)ethane. Compound 1 crystallizes in monoclinic space group *P2₁/c* with $a = 8.773(2)$, $b = 11.156(2)$, $c = 21.878(4)$ Å, $\beta = 105.41(3)^\circ$ and $Z = 2$.

Compound **2** crystallizes in monoclinic space group $C2/c$ with $a=11.697(3)$, $b=18.756(4)$, $c=8.549(4)\text{\AA}$, $\beta=94.50(1)^\circ$ and $Z=4$. In the binuclear molecule **1** (Figure) each Cd(II) cation is hexacoordinated in the N_3O_3 -environment in the shape of square bipyramid. Its basal plane is defined by a bidentate $NiOxH_2$ molecule and two monodentate acetate anions; water molecule and bidentate bpetha ligand occupy the apical sites, bpetha being coordinated to a symmetry-related metal atom in a bridge function and provides Cd–Cd separation of 13.86 Å. The water molecule in the apical position of the metal polyhedron demonstrates its cross-linking function being involved in hydrogen bonding with oxygen atoms of acetate anions via two $R_2^2(16)$ H-bonded cycles giving rise to the ordered layer where each binuclear unit is involved in 8 $OH\cdots O$ hydrogen bonds and is linked with four symmetry-related neighbors. The assembling of four molecules generates voids with the linear dimensions of ca. 11.16 x 22.24 Å, thus demonstrating the gradual increase in comparison with $[Cd_2(NiOxH_2)(bpy)(CH_3COO)_4(H_2O)_2]$ (where $bpy=4,4'$ -bipyridine) [1], where the voids have dimensions of ca. 11.12 x 20.47 Å.

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Keywords: cadmium compounds, coordination compounds, single-crystal X-ray crystallography

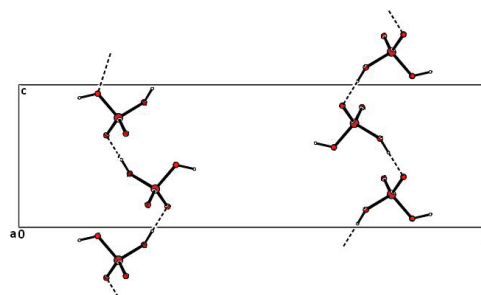
FA4-MS26-P13

Hydrogen-Bonding Graph-Set Motifs in p-Aminobenzoic Acid Derivatives. Amani Direm, Nourredine Benali-Cherif, *Laboratoire des Structures, Propriétés et Interactions Inter Atomiques (LASPPA). Centre Universitaire de Khenchela, Algérie*
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The present work is devoted to the analysis and the comparison of hydrogen-bonding graphs in crystal structures of six previously studied p-aminobenzoic acid salts : p-Carboxyanilinium dihydrogenphosphate (I) [1], p-Carboxyanilinium hydrogensulfate (II) [2], p-carboxyphenylammonium dihydrogenmonophosphate monohydrate (III) [3], bis (p-carboxyphenylammonium) sulfate (IV), p-carboxyphenylammonium perchlorate monohydrate (V) and p-carboxyphenylammonium nitrate (VI) [4].

These structures are dominated by N–H...O and O–H...O hydrogen bonding networks between the p-carboxyphenylammonium cations and the ionic molecules. O–H...O interactions between anions are present in the dihydrogenphosphate derivatives (I) and (III) giving rise to a $C_2^2(8)$ infinite chains. While intermolecular cation-cation H-bonds are only observed in the three compounds (IV), (V) and (VI).

The first-level graph set [5] of these compounds contains only D descriptors. Furthermore, the dihydrogenphosphate anions in (I) self-assemble to form supramolecular C(4) chains along the c direction (see Figure below). While, the high-level graph sets of all six structures comprise essentially ring and chain motifs.



The C(4) chain motifs running parallel to the [001] direction.

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Keywords: p-Aminobenzoic acid salts, H-bonds, Graph sets

FA4-MS26-P14

Polymorphic salts of the antibiotic 4-aminosalicylic acid. M. Teresa Duarte,^{a*} Vânia André,^a Dario Braga,^b Fabrizia Grepioni,^c *Centro de Química Estrutural, DEQB, Instituto Superior Técnico, Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal,* ^b*Dipartimento di Chimica "G. Ciamician", Università di Bologna, Via Selmi 2, 40126 Bologna, Italy*
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4-aminosalicylic acid (ASA) is an antibiotic used in the treatment of tuberculosis. ASA has also shown to be safe and effective in the treatment of inflammatory bowel diseases [1]. Solvates, molecular salts and cocrystals of ASA have recently been disclosed and fully characterized by our group, using 6-membered non-aromatic rings, such as dioxane, morpholine and piperazin [2] or bigger cyclic compounds, such as 4,4'-bipyridine and DABCO [3] as crystal cofomers. Furthermore, studies on salt formation were conducted and three polymorphic ammonia salts of ASA have been synthesized and characterized. Different synthetic routes and methods lead to different final forms: liquid-assisted grinding and gas-solid diffusion yield pure polymorphic form II while the forms obtained by solution techniques are highly dependent on solvent and solution preparation conditions. These crystal forms are also obtained using slurry technique. The crystal structures of the three forms were determined and further characterization has been performed by XRPD, DSC, TGA and HSM.

