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The aim of the study of optical resolution processes is to achieve a more efficient and less time consuming way of enantiomer separation. Supercritical fluid extraction as an alternative green technology for optical isomer separation was applied for the resolution of ibuprofen. Ibuprofen is widely used as non-steroidal anti-inflammatory drug. The resolution of ibuprofen (**1**) with the mixture of (+)-(*R*)-phenylethylamine (**2**) and benzylamine (**3**) was compared to the results obtained without the achiral additive [1]. Single crystal X-ray studies were performed on the salts of (+)-(*R*)-phenylethylamine crystallized with (-)-(*R*)-ibuprofen (**4**) and (+)-(*S*)-ibuprofen (**5**) as well as on the co-crystal resulted from the crystallisation of the racemic ibuprofen with the achiral benzylamine (**6**) in order to study the influence of the structurally similar achiral additive. (+)-(*R*)-phenylethylamine crystallises with (-)-(*R*)-ibuprofen and (+)-(*S*)-ibuprofen, respectively with 1:1 stoichiometry. Unexpectedly, the crystal of the benzylamine – ibuprofen salt contains an additional neutral ibuprofen molecule thus having 1:2 stoichiometry obtaining both from solution crystallisation and by mass balance calculation of the supercritical fluid CO₂ extraction. The lack of the methyl moiety in the benzylamine in structure (**6**) compared to the (+)-(*R*)-phenylethylamine molecule in structures (**4**) and (**5**) results a sterically favourable closer packing, higher crystal density. There is enough space in crystal (**6**) close to the ladder like hydrogen bond column to bond a neutral ibuprofen molecule as end group in the low acidity medium.

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Keywords: co-crystal, crystal packing, chiral separation

FA4-MS26-P08

p-Toluidinium nitrate. Houda Boussekine, Nourredine Benali-Cherif, *Laboratoire des Structures, Propriétés et Interactions Inter Atomiques (LASPI²A). Centre Universitaire de Khenchela, Algérie.*
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p-toluidine is an organic benzene derivative with a methyl substituent and an amino group, the name is derived from toluene and aniline. p-toluidine can cause anoxia due to formation of methemoglobin and hematuria in man [1].

The crystal structure of p-methylanilinium nitrate was determined as part of our investigations on the structural characteristics of organic-inorganic layered compounds and an ongoing study on D—H...A hydrogen-bonding in systems of hybrid materials including anilinium derivatives such as, 3-hydroxyanilinium hydrogensulfate [2], o-methylanilinium nitrate [3], 2-carboxyanilinium dihydrogenphosphite [4] and 2-carboxyanilinium nitrate [5].

The asymmetric unit of the title compound, p-toluidinium nitrate or p-methylanilinium nitrate, C₇H₁₀N⁺. NO₃⁻ contains a monoprotonated p-methylanilinium cation and nitrated anion. The crystal of the title compound, C₇H₁₀N⁺. NO₃⁻ consists of anionic- cationic layers linked by a complex three-dimensional hydrogen-bond network. The structure is stabilized by anion-cation N—H...O hydrogen-bonding.

The structure of (C₇H₁₀N⁺. NO₃⁻) is composed of cationic(C₇H₁₀N⁺) and anionic (NO₃⁻) linked through N-H...O hydrogen bonds and building up a corrugated layers parallel to the (001) plane

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FA4-MS26-P09

Hydrogen bonding in Anilinium hydrogensulfate.
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The main purpose of this structural study was a determination of the arrangement of the cations and anions which are held together by two-dimensional hydrogen-bond networks.

Hydrogen bonding is one of the most versatile noncovalent forces in supramolecular chemistry and crystal engineering [1]. Therefore, in the past decades assessment of discrete hydrogen bonding patterns had received great attention [2] because of its widespread occurrence in biological systems.

The aim of this paper is to discuss hydrogen patterns assuring the connection between anilinium and hydrogensulfate entities and to establish their different graph-set motifs [3].

Bis (anilinium hydrogensulfate) is one of the hybrid compounds, rich in H-bonds [4-5], which could have potential importance in constructing sophisticated assemblies from discrete ionic or molecular building blocks due to the strength and the directionality of hydrogen bonds [6].

Recently, similar structures containing anilinium cations have been reported. Among examples, can be named the following ones: anilinium nitrate [7], , anilinium hydrogenphosphite and anilinium hydrogenoxalate [8].

The structure of may be described as formed by alternating sheets of cations and anions which are held together with four five centered N-H...O bonds to form $C_4^4(10)$ infinite chains running through the c direction. Moreover, strong O-H...O hydrogen bonds observed between bisulfate anions generate $C_2^2(8)$ chains in the a axis direction. The infinite chains resulting from anion-anion and anion-cation interactions can be described as zigzag layers parallel (ac) plans. The crossing of these chains builds up different rings with $R_3^3(10)$ and $R_5^4(16)$ graph set motifs [9].

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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

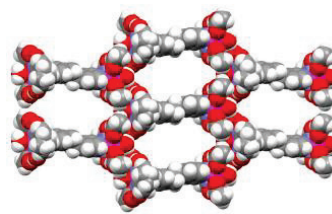
FA4-MS26-P11

Multi-Component Crystals of DihydroErgocornine. Jan Čejka^a, Blanka Klepetářová^b, Radka Zajíčková^a, Bohumil Kratochvíl^a and Alexandr Jęgorov^c. ^a*Institute of Chemical Technology Prague, Czech Republic*, ^b*Institute of Organic Chemistry and Biochemistry AS CR, Prague, Czech Republic*, ^c*Teva Czech Industries, Research and Development, České Budějovice, Czech Republic*

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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

leaving 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

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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 $Z = 2$.