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Synthesis and Crystal Structure of Layered Zinc Phosphates: Accurate Hydrogen bonding in $(NH_4)Zn_2(PO_4)(HPO_4)$

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In the family of metal phosphates, zinc phosphates occupy a relevant position. The design and synthesis of these structures have become the focus of much interest due to their vast structural and compositional diversities. The crystal structure of a new layered ammonium zinc phosphate, $(NH_4)Zn_2(PO_4)(HPO_4)$, has been reported by Bircsak and Harrison in 1998, obtained as a sub-product from hydrothermal synthesis. Recently, $(NH_4)Zn_2(PO_4)(HPO_4)$ has been synthesized from hydrothermal conditions as a unique product in the system H_3PO_4-$(NH_2)CO$-$ZnCl_2$-H_2O and the hydrogen atoms positions have been determined by X-ray single crystal diffraction, allowing us to accurately determine the hydrogen bonding network. The chemical and structural features of this material make it potentially interesting in fields such proton conduction, ion exchange and intercalation. It is especially interesting to highlight the reaction of $(NH_4)Zn_2(PO_4)(HPO_4)$ when placed in an ammonia vapor atmosphere at room temperature. Ammonia molecules are inserted into the interlayer space and a new layered zinc phosphate is formed containing $N_2H_7^+$ units beetwen the layers. Although several ammonium ions with varying degrees of clustering can be described in the gas phase, at the moment, only a crystalline stable compound containing this unit-type has been partially resolved, N_2H_7I.

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Molecular Complexes of Homologous Alkanedicarboxylic Acids and D-Tartaric acid with Isoniazid

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Concepts of *crystal engineering* and *supramolecular synthons* represent a new paradigm toward the design of novel pharmaceutical multiple component crystalline phases with desired composition, physical and mechanical properties [1]. Supramolecular synthesis may be explored to obtain novel and improved pharmaceuticals from known active pharmaceutical ingredients and pharmaceutically accessible additives [2]. The directional nature of hydrogen bonds is the master key today in the desirable self-assembly of molecules in the solid state. Carboxylic acid-pyridine synthon has emerged as a reliable tool in design of molecular complexes of homologous alkanedicarboxylic acids with isonicatine amide [3]. We have utilize this approach as recurring design strategy in supramolecular synthesis of composition of pharmaceutical phases involving isoniazid. Isoniazid or isonicotinic acid hydrazide (**INH**) is used as a first-line treatment for tuberculosis, in combination with other drugs for the treatment of active disease and also used for prevention of tuberculosis in people who have been exposed to active disease. The supramolecular reaction of **INH** with dicarboxylic acids resulted in both genuine co-crystals and organic salts depending on the nature of the dicarboxylic acid. As the some of the used dicarboxylic acid are pharmaceutically acceptable additives this result may be considered novel potential pharmaceutical phases. X-ray diffraction study of five representatives of this supramolecular system reveals that crystallization isoniazid with adipic, succinic and malonic acids is carried out in co-crystals of 2:1 stoichiometry, while the crystalisation of **INH** with oxalic or D-tartaric acids is resulted in organic salts of 1:1 stoichiometry. In the structure of co-crystals adipic and succinic acids reside inversion center and malonic acid sits on the two-fold rotation axis and invariably form acid - pyridine O-H•••N hydrogen bond synthons with two neighboring **INH** molecules. In the case of malonic acid these hydrogen bonds are very hard (O•••N=2.527Å, O-H=1.217Å, H•••N=1.316Å and O-H ...N=171.81deg) and hydrogen atom weakly connected with acid and closely approach to aromatic nitrogen of isaniazid. In the structure of organic salt of oxalic acid the **INH** molecule is twice protonated on aromatic nitrogen and terminal amino-group and alternate in the charge assisted N-H•••O-bonded zigzag chain with oxalate di-anion. The aromatic nitrogen-oxalate and secondary amino-group-oxalate NH•••O bonds equal 2.527 and 2.683 Å, respectively. Carboxylic acid-pyridine synthon has not been found in the structure of organic salt of D-Tartaric acid with **INH.** Bifurcated NH•••O and NH•••N bonds unite monoprotonated on aromatic moieties **INH** in head-to-tail fashion into the chain.

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