## MS32-P03

# The impact of stereogenic center on the architecture of the water framework: 2-methylpyrrolidine and *sec*-butylamine hydrates

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*sec*-Butylamine and 2-methylpryrrolidine are primary aliphatic and secondary cyclic amines, respectively. They can exist in enantiopure form or as a racemic mixture. In both cases they can interact with water molecules forming hydrates of rather differentiated architecture. Their analyses shed light on the influence of stereogenic center on crystal packing and, in consequence, on the transfer of chirality to water frameworks and on their complexity.

Using the *in situ* crystallization technique [1] assisted by IR laser focused radiation we were able to obtain crystals of racemic amines, (R)-2-methylpyrrolidine and (S)-*sec*-butylamine. For each case we obtained also hydrates. As expected, racemic 2-methylpyrrolidine or *sec*-butylamine crystallize in centrosymmetric group (monoclinic $P2_1/n$ or orthorhombic *Pccn*, respectively), whereas (R)-2-methylpyrrolidine and (S)-*sec*-butylamine in non-centrosymmetric ones ($P2_1$, or $P2_12_12$, respectively). In the case of hydrates the amine molecules are incorporated to 3D water network. Racemic mixture and R isomer of 2-methylpyrrolidine lead to 7 hydrate but they differ in crystallographic systems ($P2_1/n$ or $P2_12_12_1$, respectively). The case of *sec*-butylamine is different because the presence of stereogenic center dramatically changes the symmetry. Racemic mixture of *sec*-butylamine and water leads to $7^1/_3$ hydrate ($P2_1/c$ space group) while the mixture of S isomer and water gives 6 hydrate ($P2_12_12_1$ space group).

It is worth to mention that hydrogen atoms for 2-methylpyrrolidine hydrate (both racemic and enantiopure) are ordered whereas in the case of *sec*-butylamine hydrate they are disordered.

**Acknowledgements** The work has been supported by the National Science Center grant (NCN 2011/03/B/ST4/02591)

References:

[1] Boese, R. (2014) Z. Krystallogr., 229, 595

**Keywords: chirality, hydrates, in situ crystallization**

## MS32-P04

# Porous supramolecular architectures based on π-stacking interactions between discrete metal-adenine entities and theobromine/caffeine methylxanthines

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Taking into account the great potential of MOFs, this work is focused on a relatively recent new class of analogous porous materials in which coordination bonds are released from guiding the crystal structure and supramolecular interactions play this role.[1] Herein we present the results obtained for π-π stacking interactions as the driving force to develop porous supramolecular metal-organic frameworks (SMOFs) as an alternative to more directional hydrogen bonding interactions. In particular, the use of adenine and methylxanthines has given rise to several compounds presented in this communication. The blue compound $[Cu_7(\mu\text{-ade})_6(\mu_3\text{-OH})_6(\mu\text{-}H_2O)_6](theo)_2{\cdot}28H_2O$ (**1**) (ade: adeninato, theo: theobrominato) is formed by wheel-shaped cationic units where the Cu(II) atoms are bridged by hydroxide anions, water molecules, and adeninato ligands with a m-κN3:κN9 coordination mode. The supramolecular assembly (*Figure 1*) takes place mainly through π-π stacking interactions involving the adeninato ligands of the rigid heptameric entities and theobrominate moieties. Compound **1** exhibits an open-framework with voids representing 37% of the unit cell volume, but the plasticity of the π-π interactions causes a reversible shrinkage of the porous system upon activation that precludes the adsorption of gas molecules.

Dark purple compounds $[Cu_2(\mu\text{-ade})_4(H_2O)_2]{\cdot}3H\text{-theo}{\cdot}7H_2O$ (**2**), $[Cu_2(\mu\text{-ade})_4(H_2O)_2]{\cdot}2Htheo{\cdot}18H_2O$ (**3**) and $[Cu_2(\mu\text{-ade})_4(H_2O)_2]{\cdot}(caf){\cdot}{\sim}6H_2O$ (**4**) (Htheo: theobromine, caf: caffeine) contain neutral windmill units in which two copper atoms are bridged by four m-κN3:κN9 adeninato ligands. Their crystal structures highly depend on the supramolecular interactions of the theobromine and caffeine bases. In compound **2**, two theobromine molecules are hydrogen bonded to the Hoogsteen face of two *trans*-arranged adeninato ligands, whereas a third theobromine molecule is joined to the Watson-Crick face of one of the previous adeninato ligand. In compound **3**, with a lower amount of theobromine, the Watson-Crick interaction is not present. In both compounds, the 3D crystal structure requires the additional presence of π-π stacks between the theobromine molecules.

In compound **4**, as the methyl groups of the caffeine molecule do not allow hydrogen bond interactions, the adeninato ligands are hydrogen bonded among them to generate, together with π-stacking interactions, supramolecular sheets containing rectangular windows in which the caffeine molecules are located. Only compound **4** showed permanent porosity, adsorbing a significant amount of $CO_2$ (0.88 mmol of $CO_2$/g at 5 bar and 273 K). The magnetic characterization of the compounds indicate a ferromagnetic behaviour for