

MS31-P02

Sponge like structures assisted by hydrogen bonds

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The appearance of the metal organic frameworks (MOFs) has opened a new branch of research, the new structures are suitable for as sensing, drug delivery, heterogeneous catalysis, separation and storage etc. Following the discovery of MOFs, new covalent organic frameworks (COFs) were synthesised as metal-free analogous. Recently highly porous hydrogen-bond assisted organic frameworks (HOF) were reported. Most of the published organic frameworks are electronically neutral, but some of them are ionic metal-organic frameworks (iMOFs) or ionic covalent organic frameworks (iCOFs). Intermolecular forces and molecular inflexibility are the conditions of the formation of non-covalently bonded organic frameworks.

Three different polymorphic- and solvatomorphic iHOF frameworks of the investigated molecule (**1**: 5,5,11,11-tetrabutyl-1,3,7,9-tetraphenyl-4,5,6,10,11,12-hexahydro-5,11-diazabenzof[ef,kl]heptalene-5,11-dium-bromide) were prepared by using different crystallisation techniques and were structurally characterised using single crystal X-ray diffraction technique [1]. Crystals of **1a** were obtained by recrystallization from the saturated THF solution in the presence of the solid powder of compound **1** in a closed ampule. **1a** crystallizes in space group *Fddd* and almost the half of the unit cell (42%) was found to be filled with disordered THF solvent molecules. Br ions are placed along the channels close to the quaterner nitrogen groups. Crystals of **1b** were grown by slow evaporation of the THF solvent, the dimorphic structure has the *Pnna* space group. In this case the void volume is ~39% per unit cell. The voids are filled with disordered solvent molecule similarly to **1a**. The crystals of **1c** were received by fast evaporation of the solvent mixture of THF and pyridine to almost dryness. The molecules crystallise in the *P2₁/n* space group and contain voids of ~18% where the pyridine molecules take part in the framework construction as neutral linkers. **1a** and **1b** are polymorphs of **1**, while **1b** and **1c** are solvatomorphs.

In all reported three crystalline frameworks the structures are stabilized by C-H...Br and Br... π interactions, while pyridine is part of C-H... π interactions. The solvent THF molecules are disordered throughout the channels. The residual electron density in the channels could be taken into account by the refinement of the data with squeeze program (part of the Platon program). The necessity of molecular inflexibility in the formation of these highly porous crystals is also discussed.

References:

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MS31-P04

Synthesis, structure and chemical properties of copper(II) complexes with 2,2'-bipyridine and L-serine: porous materials and polymorphism

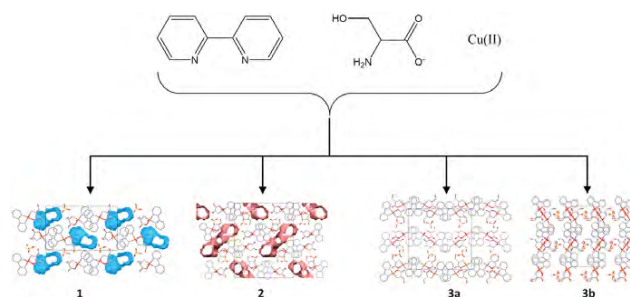
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Considering copper as an essential metal and being the key element for regular function of some proteins, copper(II) complexes with amino acids are often used as model systems for metal-protein interactions.[1] Furthermore, copper(II) complexes with heterocyclic bases and amino acids readily interact with DNA molecules through hydrogen bonds and π -interactions. These compounds showed prominent antiproliferative activity against a series of tumor cell lines.[2] Since 2,2'-bipyridine and serine are capable of forming various types of noncovalent interactions, their complexes may form predictable supramolecular motifs, thus being important in crystal engineering. In our latest research we have prepared porous complexes of copper(II) with 1,10-phenanthroline and L-serine which we were able to interconvert into each other in the solid state under controlled conditions.[3]

Herein, we present the first four crystal structures of copper(II) complexes with 2,2'-bipyridine (bpy) and L-serine (ser) obtained by fine tuning of synthetic conditions: [Cu(ser)(H₂O)(bpy)]₂SO₄·6H₂O (**1**), [Cu(ser)(bpy)(CH₃OH)]₂SO₄·3CH₂OH (**2**), and two polymorphs of the [Cu(ser)(H₂O)(bpy)]₂SO₄ (**3a** and **3b**). The two complexes with solvent of crystallization (**1** and **2**) both have porous structures, while the two polymorphs (**3a** and **3b**) do not, but all of them can be compared to the structures with phenanthroline. On the other hand, chemical properties of bipyridine complexes seem to be somewhat different than those with phenanthroline. Solution based and mechanochemical syntheses are discussed, as well as the chemical properties of these complexes.



References:

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Keywords: copper(II) complex, crystal structure, solvatomorphism