

Preparation and characterisation of new metal-organic frameworks

Dávid Földes

Óbuda University, Doctoral School on Materials
Sciences and Technologies

Wigner Research Centre for Physics of the H.A.S.

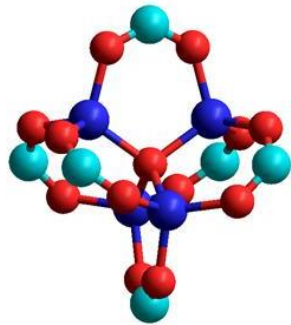
Institute for Solid State Physics and Optics

Supervisors: Éva Kováts and Sándor Pekker

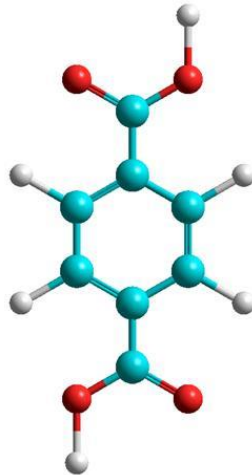


Metal-organic frameworks (MOFs)

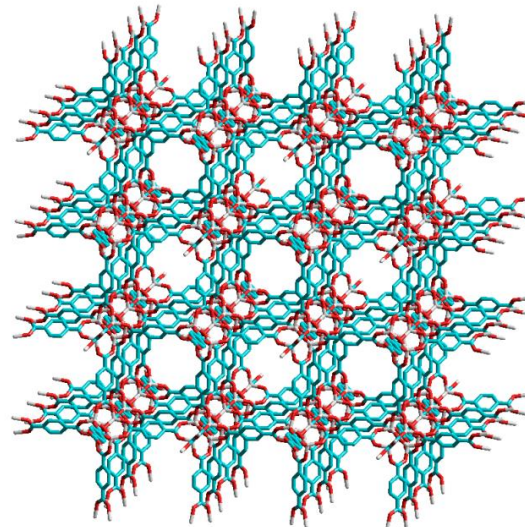
- Porous coordination polymers → high surface area
- Gas storage, heterogenous catalysis, molecular sensing, drug delivery, separation...
- Crystalline frameworks with two unique structural units:
 - Rigid, inorganic metal-containing clusters at the nodes (Inorganic Secondary Building Units, SBUs)
 - Organic linkers join the SBUs
- Strong metal-ligand bonding → high thermal stability → easy-to-activate structures



$Zn_4O(CO_2)_6$

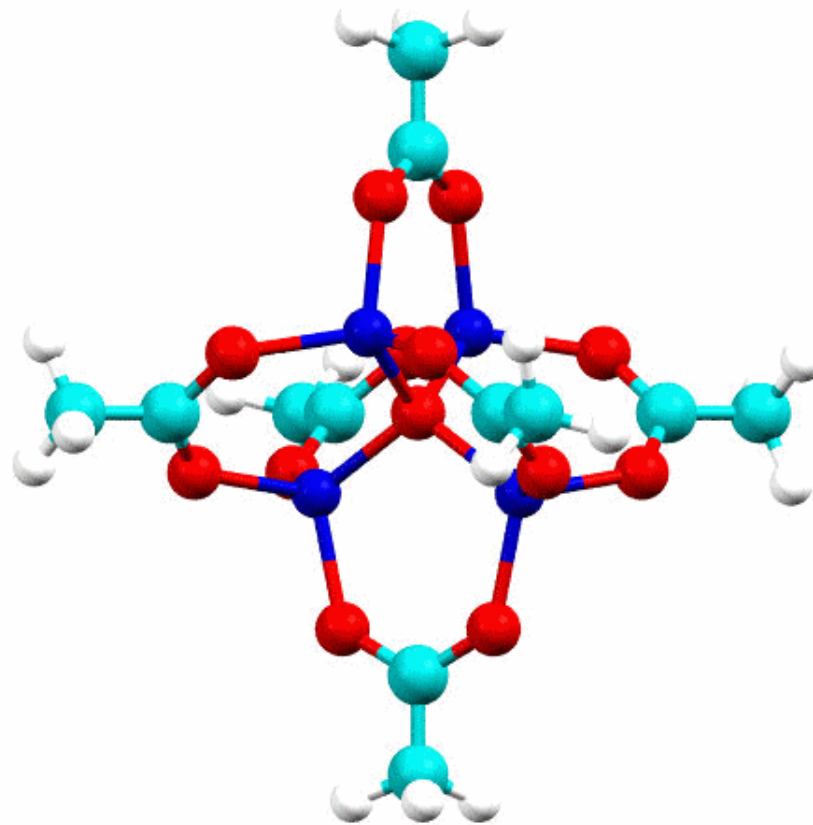


Terephthalic acid

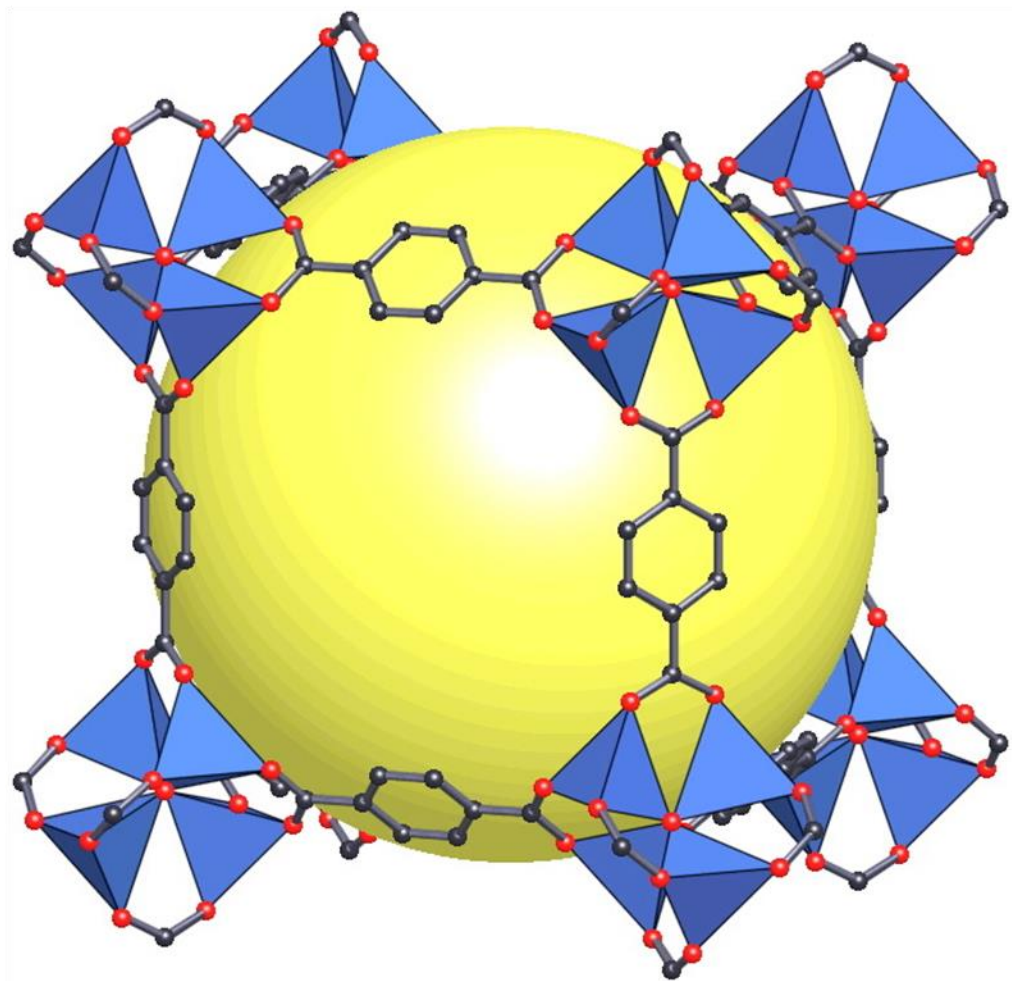


Porous structure of MOF-5

Basic zinc acetate



The structure of MOF-5

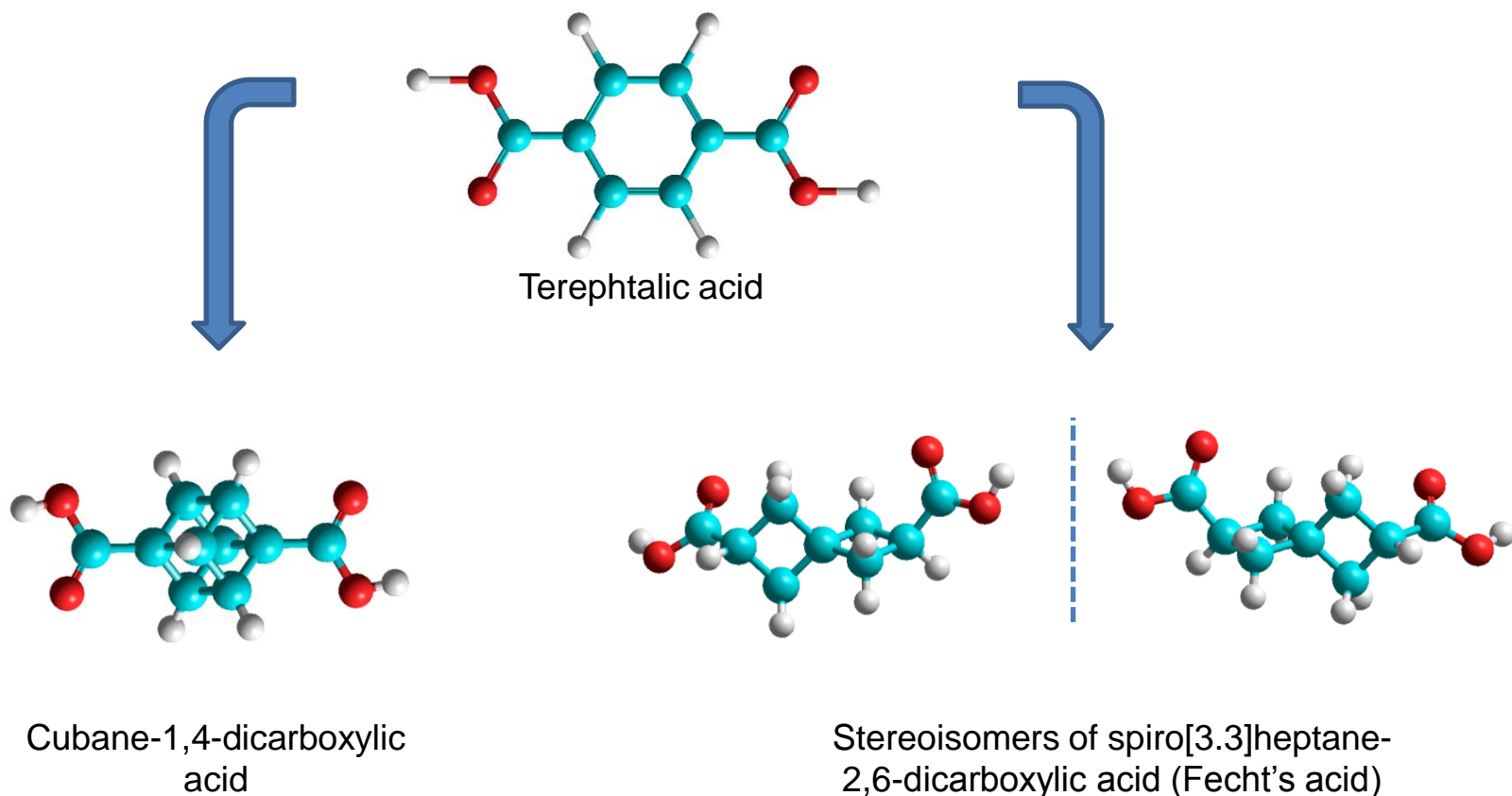


79 % void volume \rightarrow H₂ storage (10 m/m % at 100 bars and 77 K)
 $S_{BET} = 3800 \text{ m}^2 \text{ g}^{-1}$

H. Li, M. Eddaoudi, M. O'Keeffe, O.M. Yaghi, *Nature*, 402, 276-279 (1999)

Goal

- **Preparation of new MOF structures** by using various organic linkers, and zinc-containing SBUs
- Similar size → different gas adsorption?

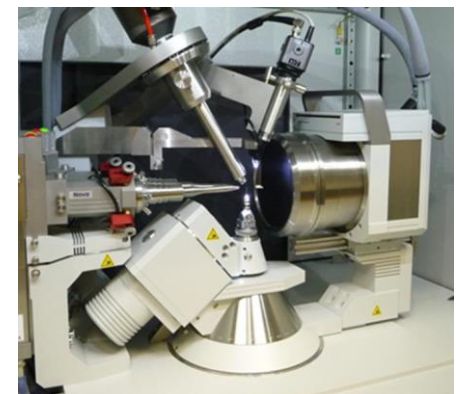


Preparation and characterisation methods

- Insoluble MOF structures → recrystallization is not possible
- Direct preparation of single crystalline MOFs:
 - Slow, room temperature diffusion syntheses
 - Solvothermal syntheses: PTFE lined pressure vessels, autogenous pressure, $T = 105\text{-}140\text{ }^{\circ}\text{C}$; $t = 60\text{-}144\text{ hours}$
- Starting materials: $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{ H}_2\text{O}$ + carboxylic acid + solvent (DMF, DEF, NMP)
- Structure determination by single crystal X-ray diffraction
- Determination of thermal stability by thermogravimetry–mass spectrometry (TG/MS)

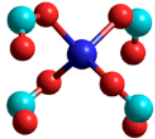
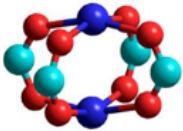
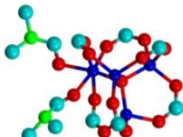
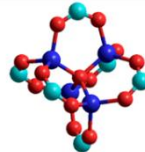
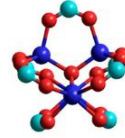
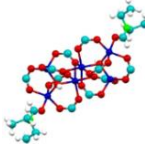


PTFE lined pressure vessel



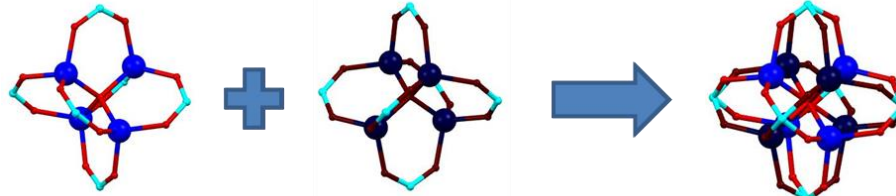
Agilent Supernova diffractometer

New MOF structures with cubane-1,4-dicarboxylic acid

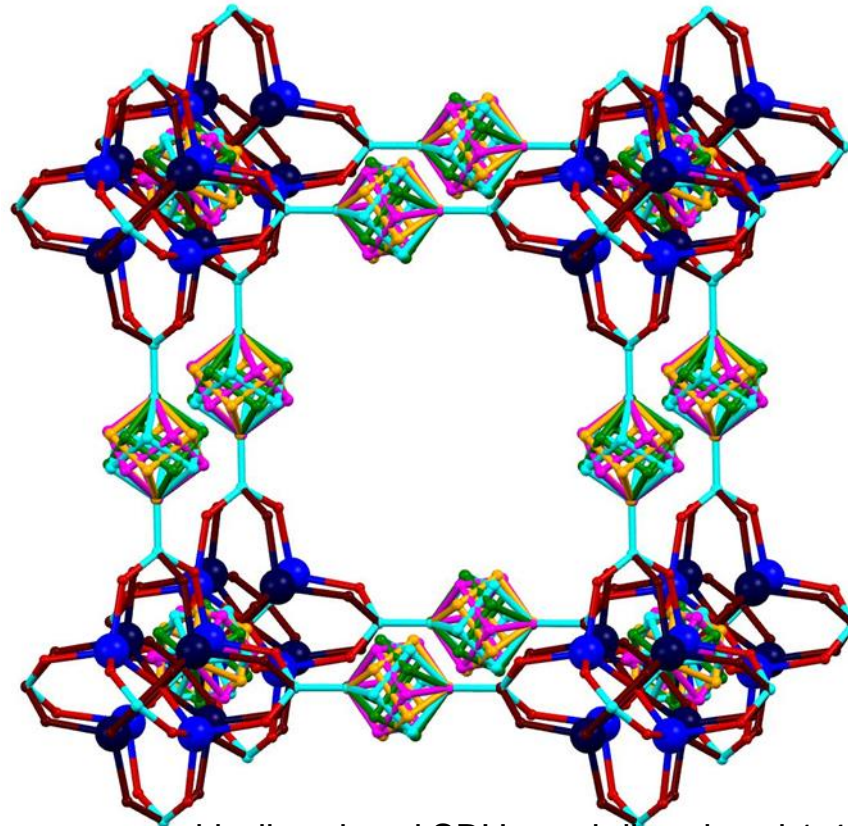
Solvent	Synthetic conditions	Result	SBU
DMF	DABCO, 120°C, 2 days	New MOF, mononuclear, interpenetrated anionic framework	
NMP	105°C, 60 ours	New crystal structure, planar MOF with paddlewheel-like binuclear SBUs	
DMF	100-140 °C, 24-60 hours	New MOF, distorted MOF-5 analogue	
DMF	100 °C, 22 hours	New MOF, high simmetry, cubic MOF-5 analogue	
DEF	105 °C, 6 days	New MOF structure, tetranuclear „double-layer” structure	
DEF	140 °C, 60 hours	New MOF structure, new hexanuclear SBU	

MOF-5 analogue with cubane

- $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + cubane-1,4-dicarboxylic acid + DMF 100 °C, 22 hours



Disordered SBUs: superposition of two perpendicular $\text{Zn}_4\text{O}(\text{CO}_2)_6$ SBUs



MOF-5 analogue structure with disordered SBUs and disordered 1,4-cubylene spacers.

Cell parameters: $P\bar{m}3m$, $a = b = c = 12.74 \text{ \AA}$, $\alpha = \beta = \gamma = 90^\circ$, $V = 2068.4 \text{ \AA}^3$.

Chemical reactions of MOF-5 and MOF-5 analogue

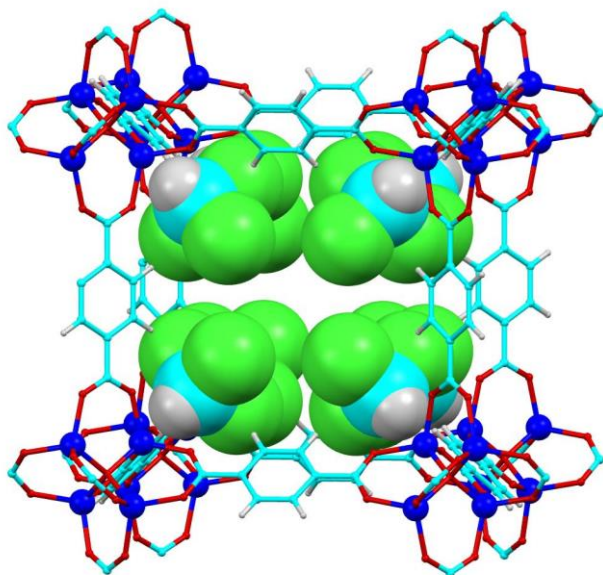
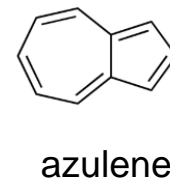
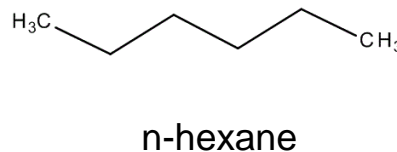
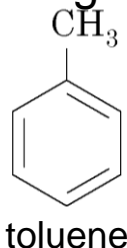
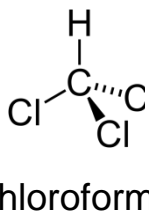
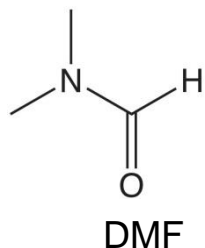
- Solvent exchange: DMF to CHCl_3 , toluene, n-hexane, cyclohexane



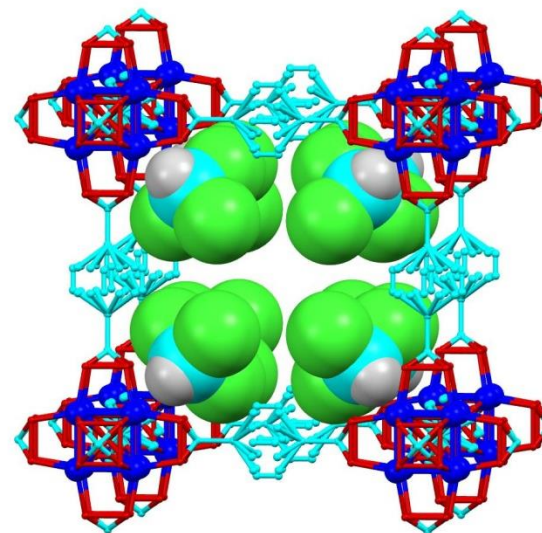
→ storing water sensitive samples

→ better structure determination

- Inclusion of azulene (soaking in 1 mg/ml azulene-toluene solution)



MOF-5 – chloroform solvate

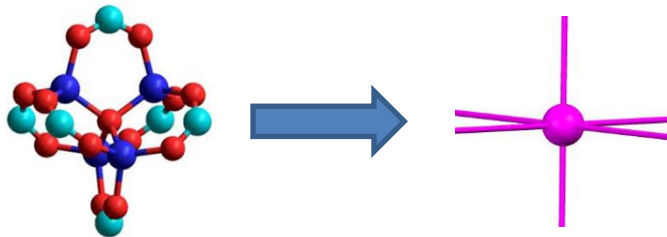


Chloroform solvate of MOF-5 analogue structure

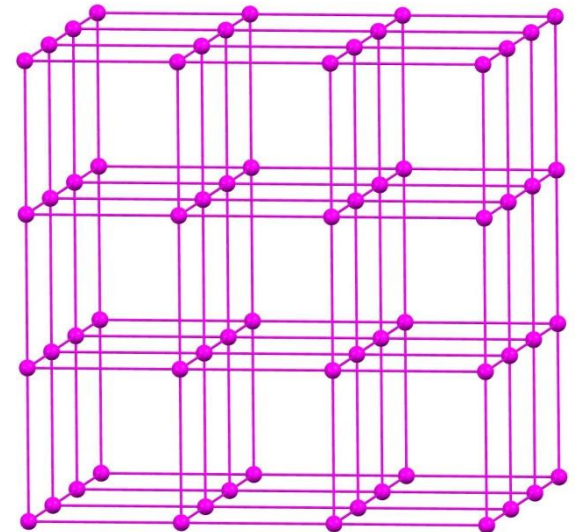
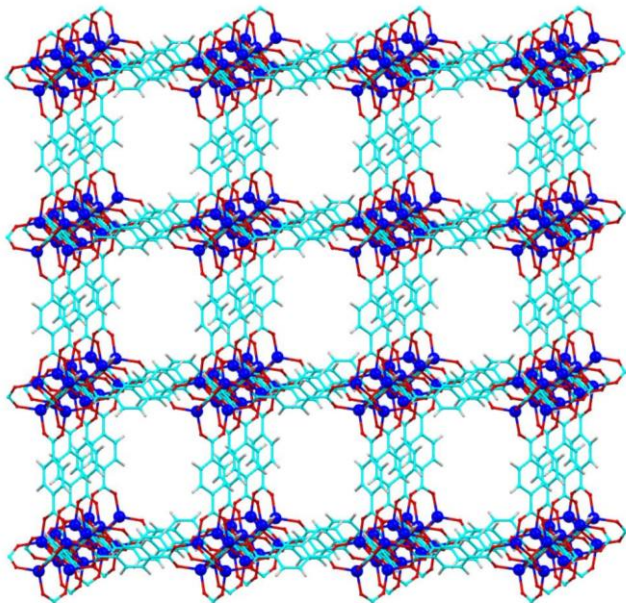
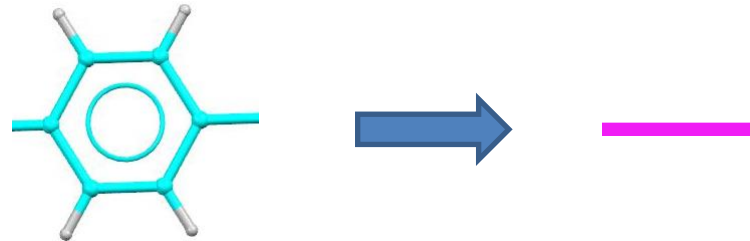
Topology analysis of new MOF structures

- IUPAC recommendation
- ToposPro
- Simplified underlying network:

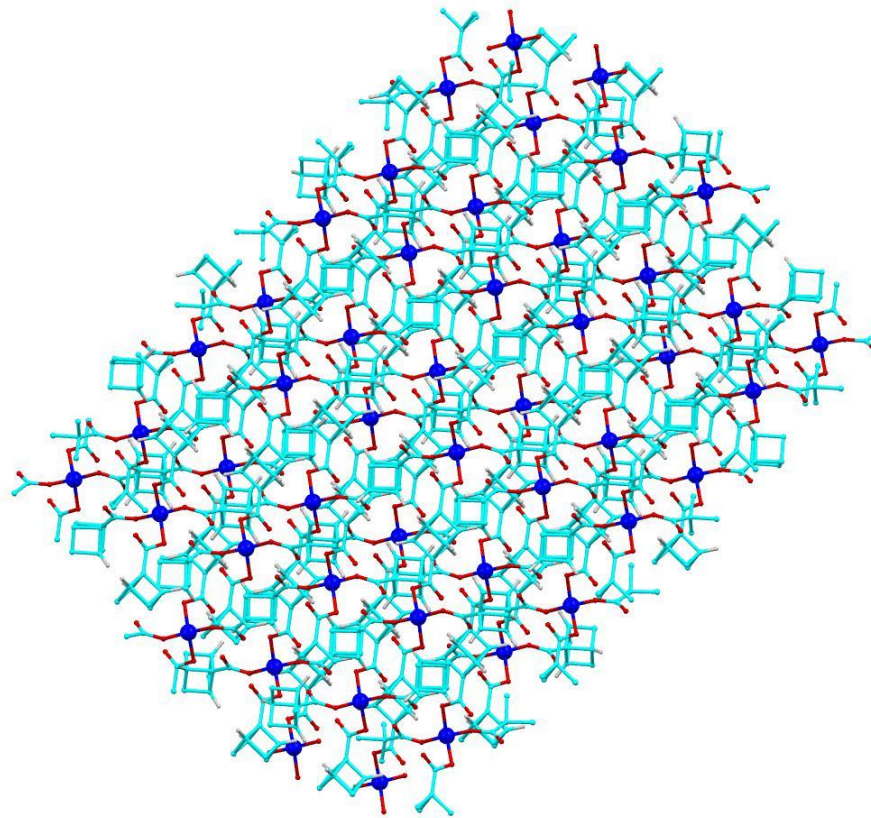
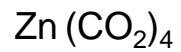
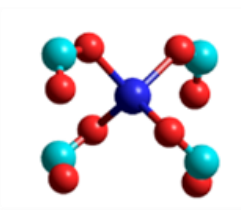
SBUs → simple points



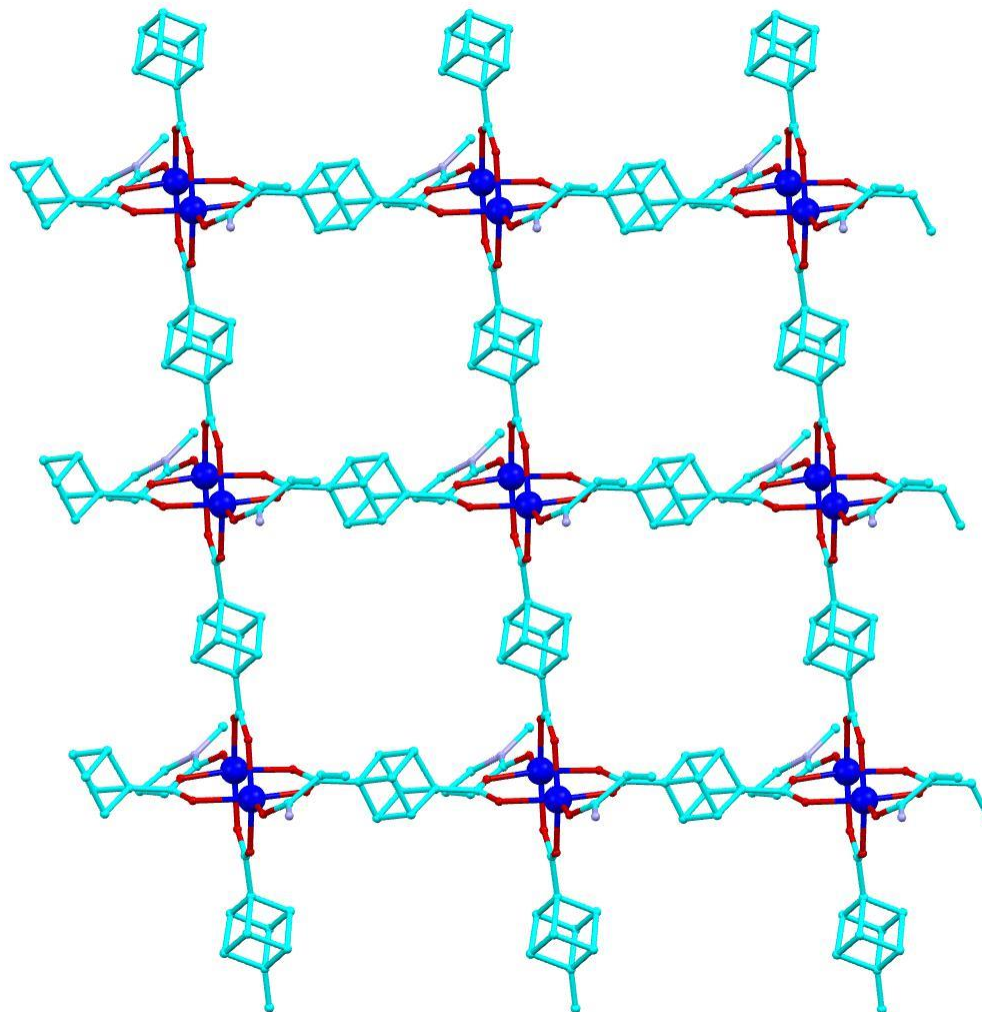
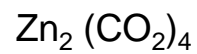
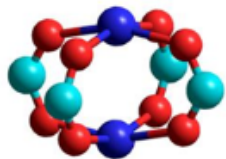
organic spacers → single bonds



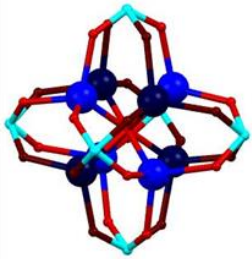
Mononuclear structure with 3-fold interpenetrated diamond topology



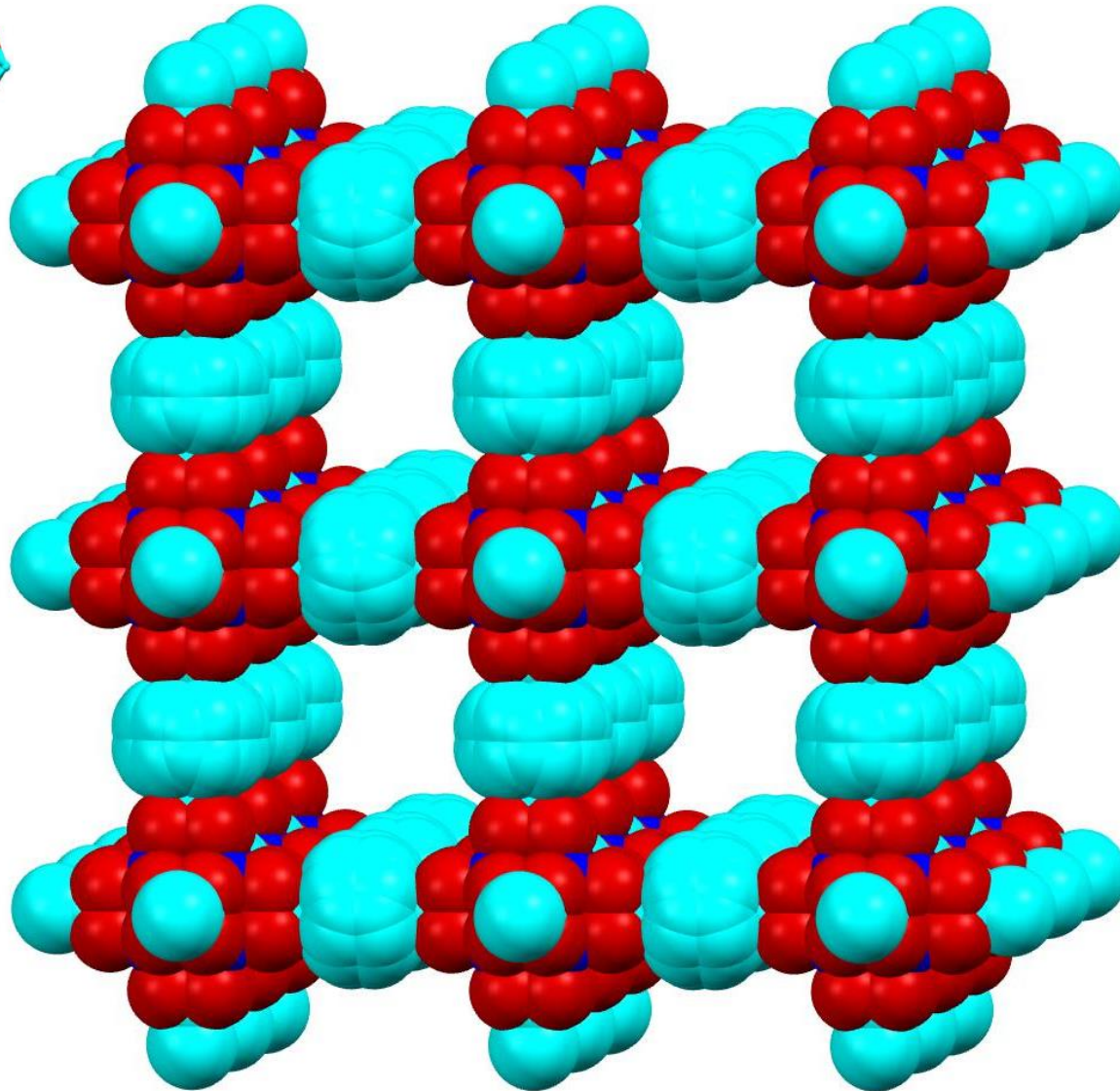
Binuclear planar structure with sql topology



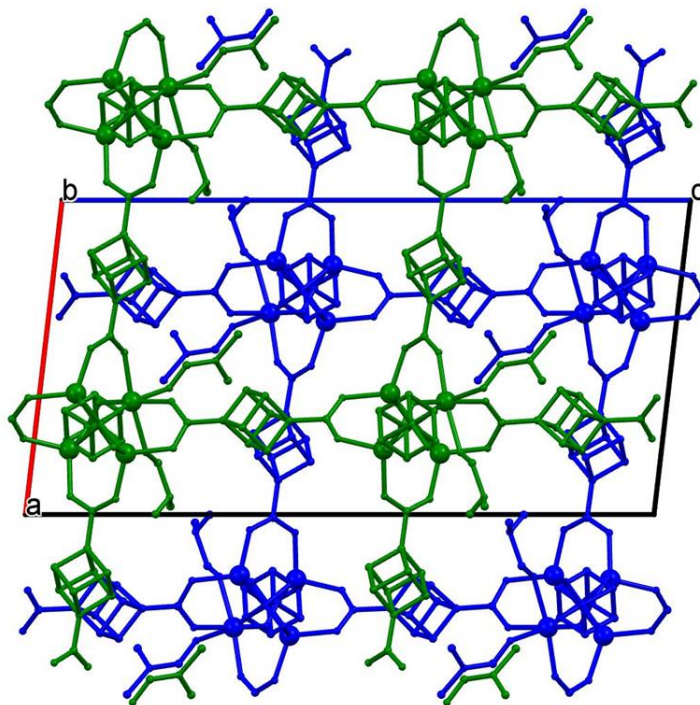
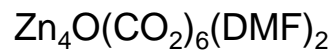
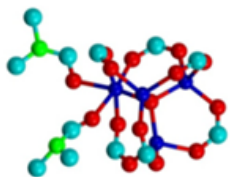
MOF-5 analogue with pcu topology



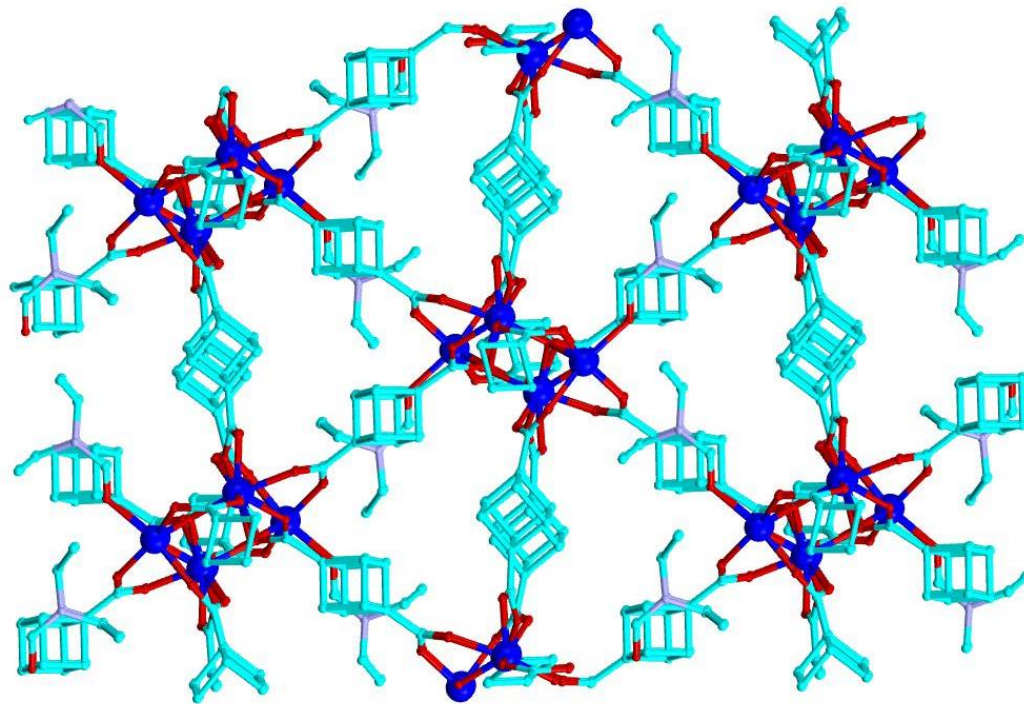
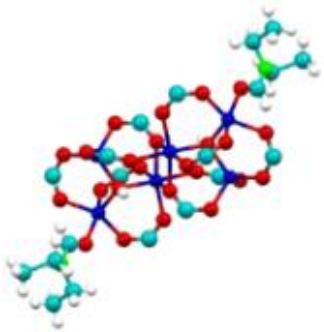
Disordered
 $\text{Zn}_4\text{O}(\text{CO}_2)_6$



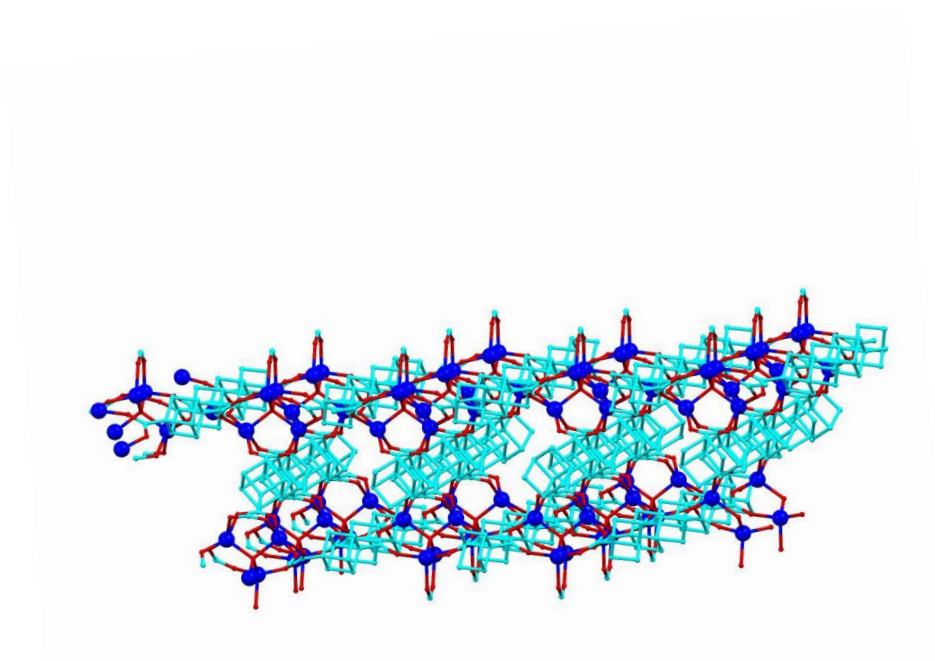
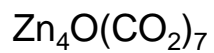
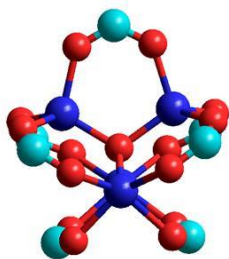
Interpenetrated MOF-5 analogue with 2-fold interpenetrated pcu topology



Hexanuclear structure with hex topology

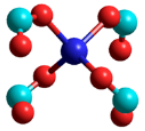
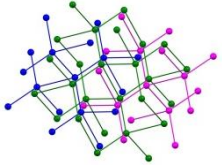
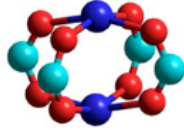
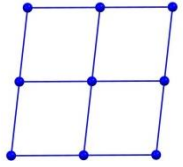
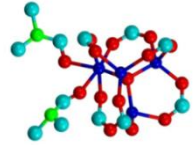
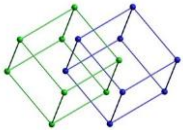
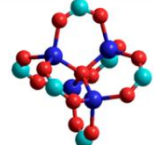
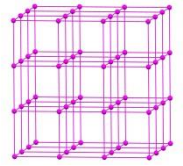
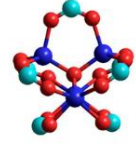
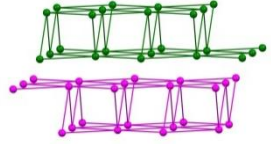

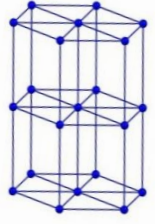


Double-layer structure with new underlying network topology



Double-layer structure with new underlying network topology

Topology analysis of new MOF structures with cubane

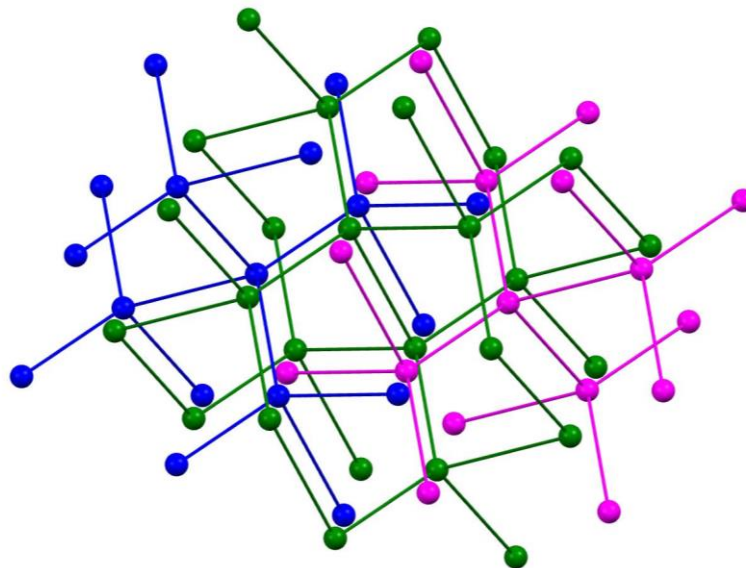
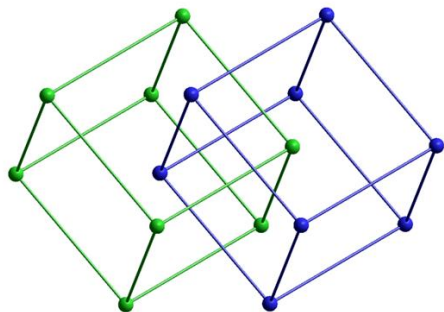
Sample	SBU	Simplified underlying network topology
Mononuclear, interpenetrated anionic framework		dia 3-fold interpenetrated 
Planar MOF with paddlewheel-like binuclear SBUs		sql 
Distorted MOF-5 analogue		pcu 2-fold interpenetrated 
High symmetry, cubic MOF-5 analogue		pcu 
„Double-layer” structure		New topology! 
Hexanuclear MOF structure		hex 

Summary

- Recent work:
 - preparation of 6 new MOF structures with Zn-containing nodes (mononuclear, binuclear, tetranuclear, hexanuclear) and cubane-1,4-dicarboxylic acid linkers
 - Preparation of (*RS*)-spiro[3.3]heptane-2,6-dicarboxylic acid
 - Synthesis of a new compound with tetranuclear zinc-containing nodes and (*RS*)-spiro[3.3]heptane-2,6-dicarboxylic acid
- First semester of 2016/2017 : preparation of **MOF-5 analogue structure** with high yield and good reproductivity, **solvent exchange** of MOF-5 and the novel MOF-5 analogue structure with cubane-1,4-dicarboxylic acid, **topology analysis** of our new MOF structures
- Courses: Pórusos anyagok (5), Válogatott fejezetek az anyagvizsgálati módszerekből I. (5)
- Conference contribution: SIWAN-7, October 12-15, Szeged, poster presentation

Future plans

- Publication of the new MOF structures
- Activation, gas adsorption
- Resolution of (*RS*)-spiro[3.3]heptane-2,6-dicarboxylic acid
- Preparation of chiral MOFs
- Host-guest interactions with small organic molecules
- Preparing more MOF structures with other transition metals (e.g. Cu)



Acknowledgement

- Éva Kováts, Wigner Research Centre for Physics of the H.A.S., Institute for Solidstate Physics and Optics
- Sándor Pekker, Wigner Research Centre for Physics of the H.A.S., Institute for Solidstate Physics and Optics
- Emma Jakab, Research Centre for Natural Sciences of the H.A.S., Institute of Materials and Environmental Chemistry
- Gábor Bortel, Wigner Research Centre for Physics of the H.A.S., Institute for Solidstate Physics and Optics
- Gábor Oszlányi, Wigner Research Centre for Physics of the H.A.S., Institute for Solidstate Physics and Optics



Thank you for attention!