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

Outline

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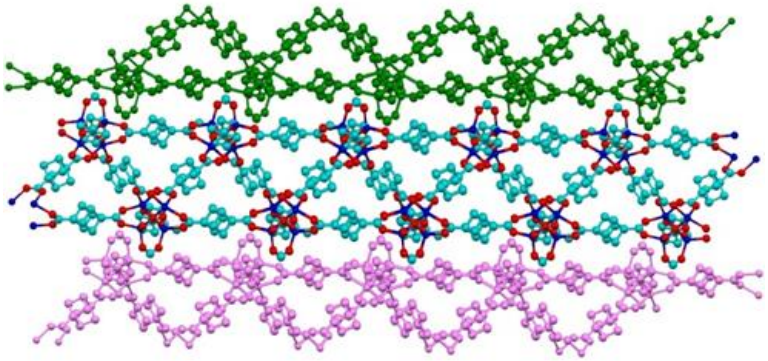
  - Metal-Organic Frameworks
  - Structure of MOF-5
- Experimental work:
  - Goal
  - Preparation and characterisation methods
  - Results of recent work, first and secoond semester’s work
- Future plans

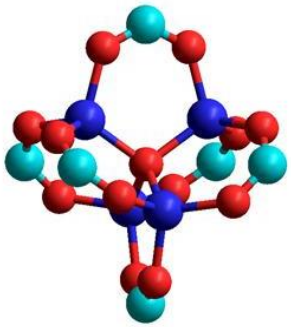


Metal-organic frameworks (MOFs)

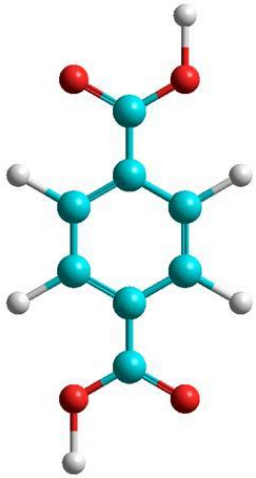
- Porous coordination polymers → high surface area
- Gas storage, heterogenous catalysis, molecular sensing, drug delivery, separation...
- Crystalline frameworks with two unique structural units:

  Rigid, inorganic metal-containing clusters at the nodes (Inorganic Secondary Building Units, SBUs)

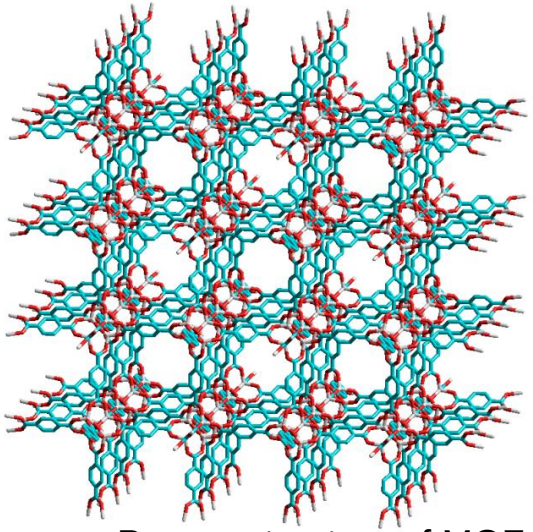
  Organic linkers join the SBUs
- Strong metal-ligand bonding → high thermal stability → easy-to-activate structures



$Zn_4O(CO_2)_6$

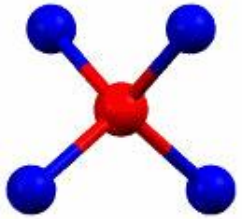


Terephtalic acid

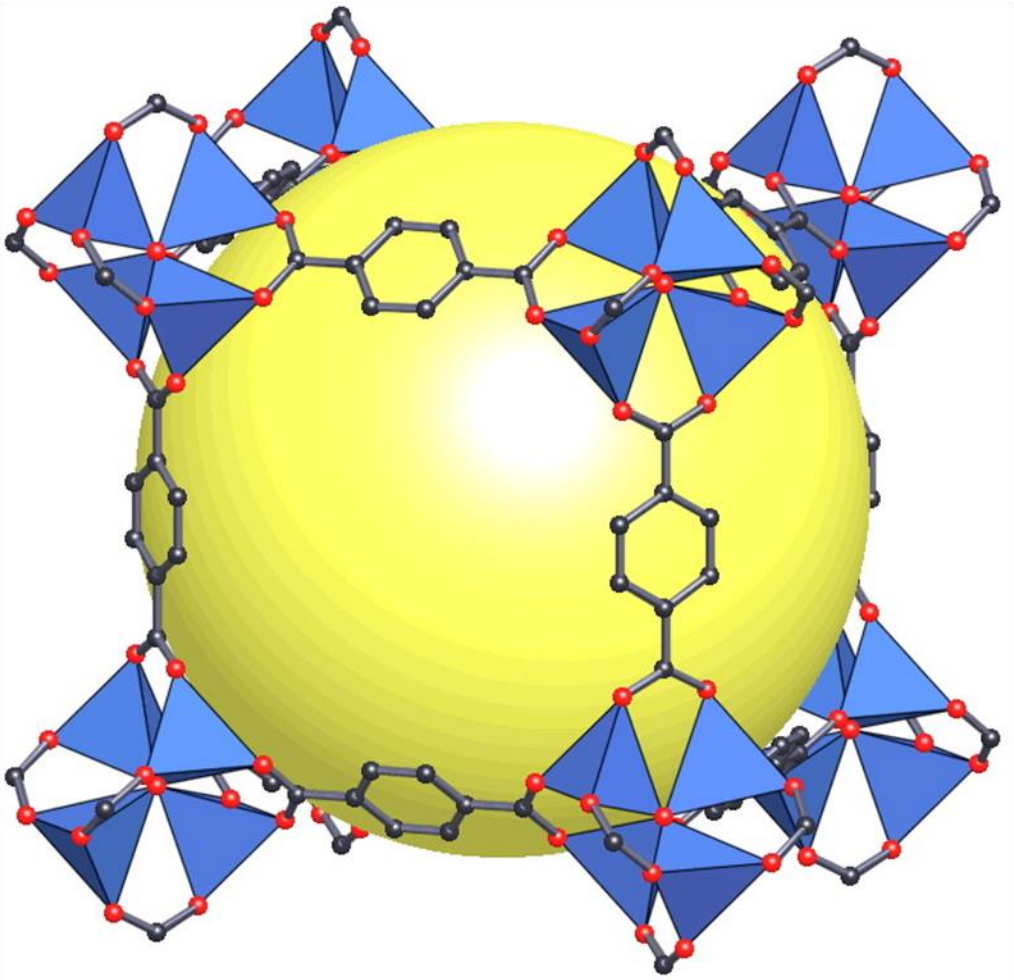


Porous structure of MOF-5

Basic zinc acetate



The structure of MOF-5

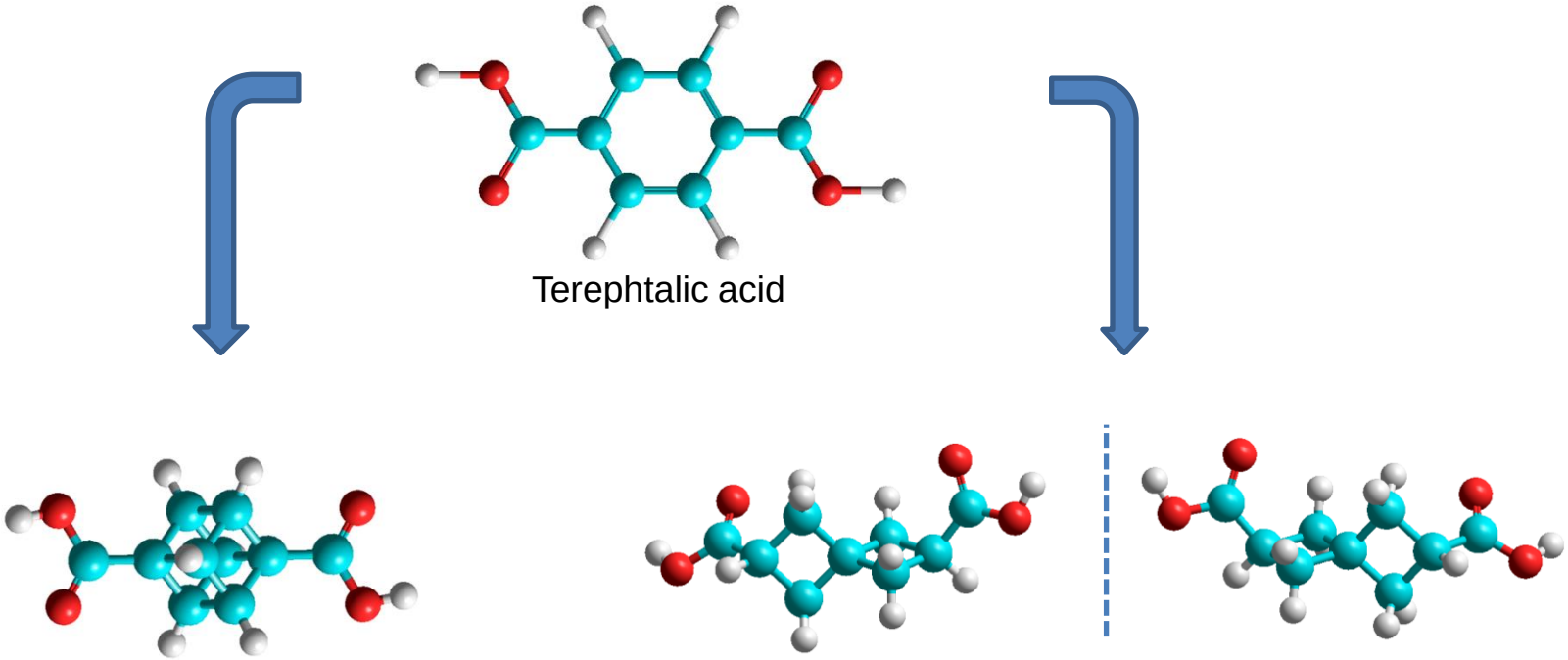


79 % void volume → H_2 storage

H. Li, M. Eddaoudi, M. O'Keeffee, 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?



Terephtalic acid

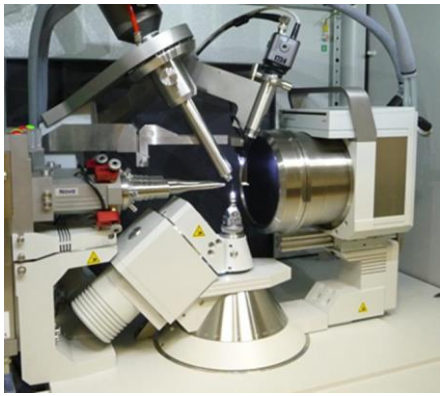
Cubane-1,4-dicarboxylic acid

Stereoisomers of spiro[3.3]heptane-2,6-dicarboxylic acid (Fecht's acid)

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 = 105-140 °C; t = 60-144 hours
- Starting materials: $Zn(NO_3)_2 \cdot 6\ H_2O$ + 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

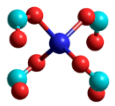
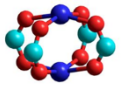
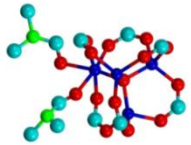
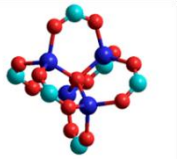
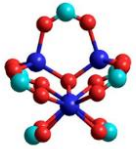
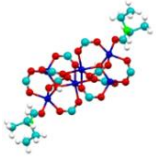


Agilent Supernova diffractometer

Results

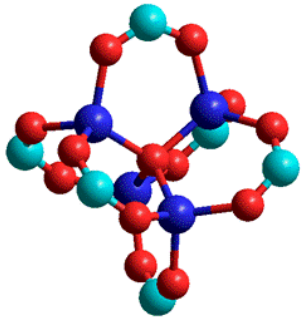
- Recent work:
  - preparation of 6 new MOF structures with Zn-containing nodes (mononuclear, binuclear, tetranuclear, hexanuclear) and cubane-1,4-dicarboxylic acid linkers
  - synthesis of a new compound with tetranuclear zinc-containing nodes and (*RS*)-spiro[3.3]heptane-2,6-dicarboxylic acid linkers
- First semester:
  - characterisation of thermal properties
  - detailed characterisation of hexanuclear MOF with cubane
  - storing water-sensitive MOFs
  - detailed planning of spiro[3.3]heptane-2,6-dicarboxylic acid synthesis
- Second semester and ongoing:
  - preparation of spiro[3.3]heptane-2,6-dicarboxylic acid

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

Sample	Solvent	Synthetic conditions	Result	SBU
FD90	DMF	DABCO, 120°C, 2 days	New MOF, mononuclear, interpenetrated anionic framework	
FD80	NMP	105°C, 60 ours	New crystal structure, planar MOF with paddlewheel-like binuclear SBUs	
FD130	DMF	100 °C 60 hours	New MOF, distorted MOF-5 analogue	
FD138	DMF	140 °C, 60 hours		
FD98	DMF	100 °C, 24 hours	New MOF, high simmetry, cubic MOF-5 analogue	
FD137	NMP	105 °C, 60 hours		
FD84	DEF	105 °C, 6 days	New MOF structure, tetranuclear „double-layer” structure	
FD143	DEF	140 °C, 60 hours	New MOF structure, new hexanuclear SBU	

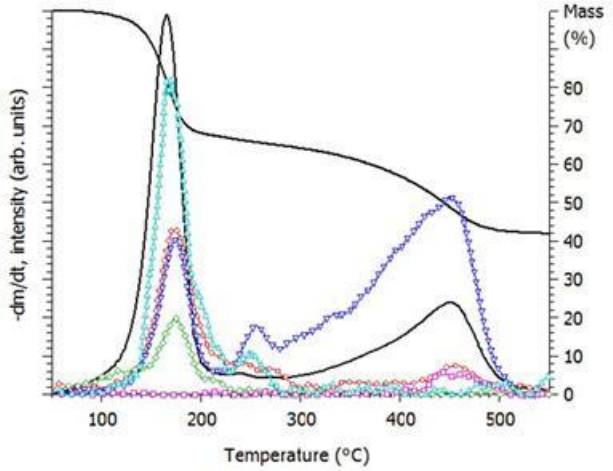
MOF-5 analogue with cubane

- $Zn(NO_3)_2 \cdot 6H_2O$ + cubane-1,4-dicarboxylic acid + DMF or NMP, 105 °C, 60 hours

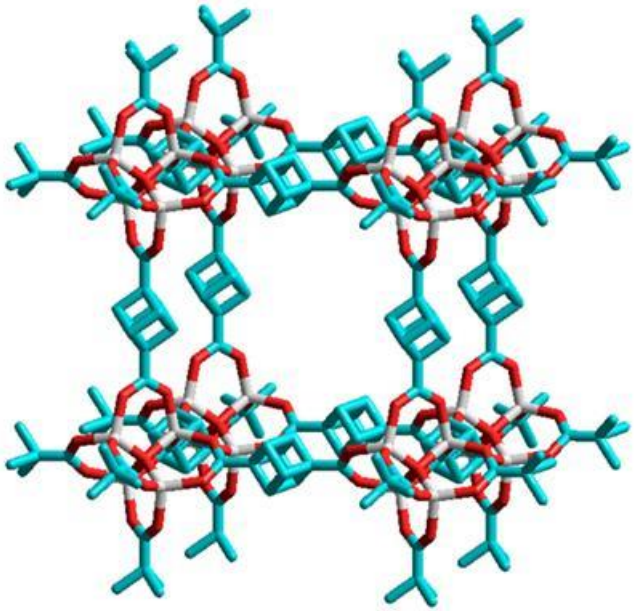


$Zn_4O(CO_2)_6$

Cell parameters:
$Pm\bar{3}m$, $a = b = c = 12.9591$ Å,
$\alpha = \beta = \gamma = 90°$,
$V = 2176.33$ Å^3.

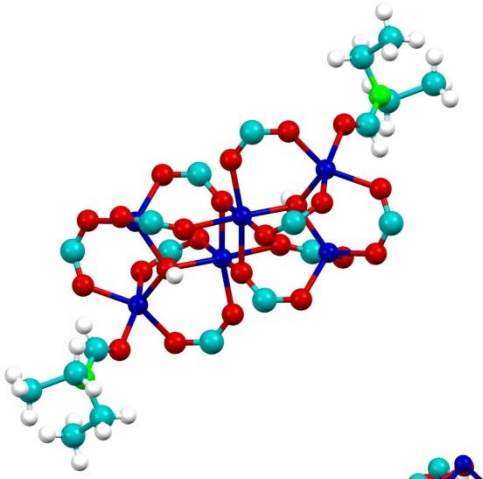


TG/MS of MOF-5 analogue



Hexanuclear structure

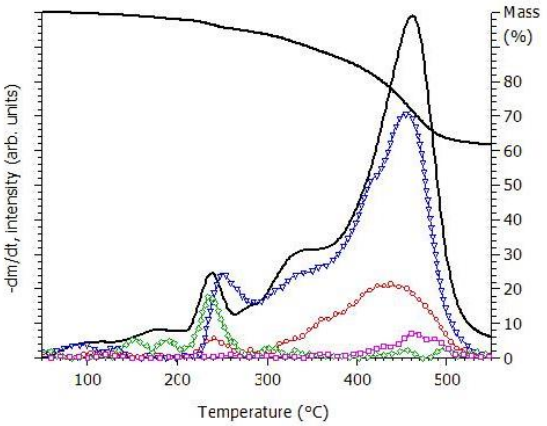
- $Zn(NO_3)_2 \cdot 6H_2O$ + cubane-1,4-dicarboxylic acid + DEF, 140 °C, 60 hours



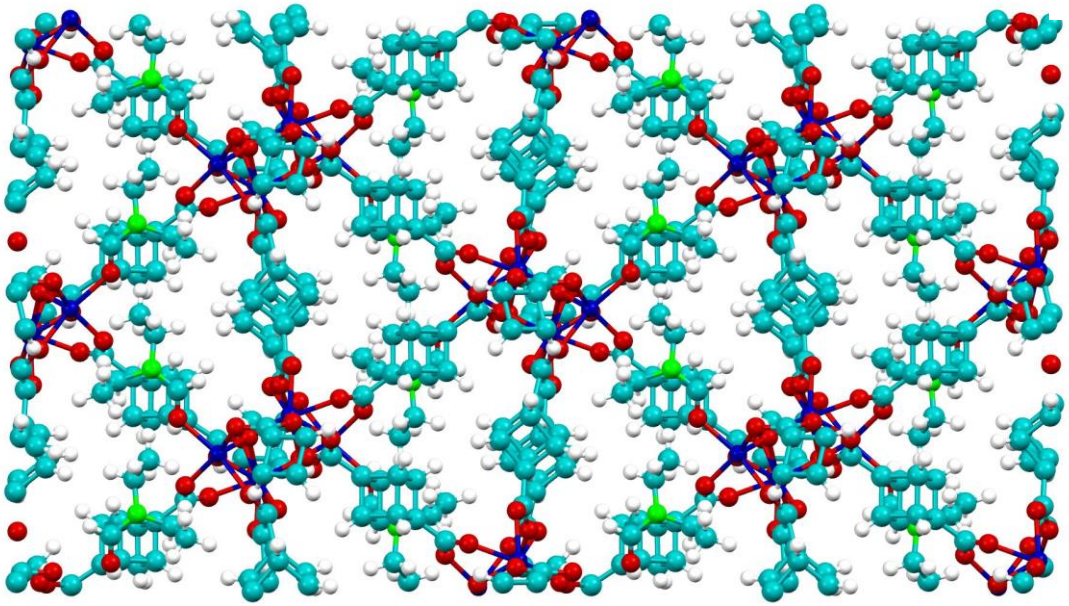
$Zn_6(OH)_2(CO_2)_{10}(DEF)_2$

Cell parameters:
$P2_1/c$, a = 16.8011 Å,
b = 20.2238 Å,
c = 12.0017 Å,
α = 90.00°,
β = 110.036°,
γ = 90.00°,
V = 3831 Å^3.

Stochiometry:
$Zn_6(OH)_2[C_8H_6(CO_2)_2]_5(DEF)_2$

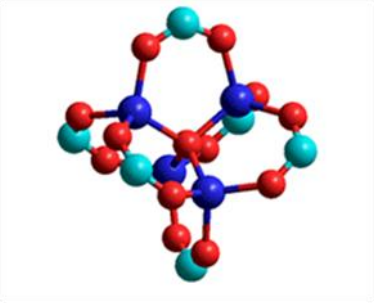


TG/MS inert



MOF-5 structure with Fecht's acid

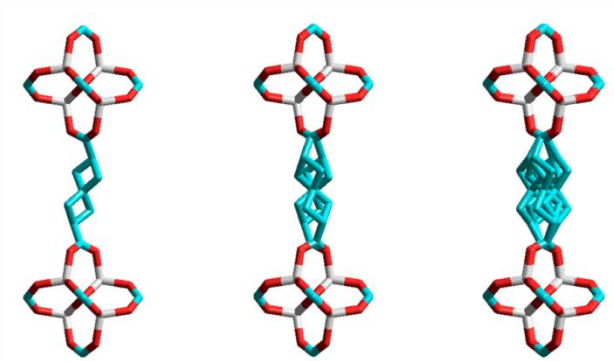
- $Zn(NO_3)_2 \cdot 6H_2O$ + (*RS)*spiro[3.3]heptane-*2,6-dicarboxylic* acid + DMF/toluene (1:1) + TEA/toluene (vapour diffusion), R.T.



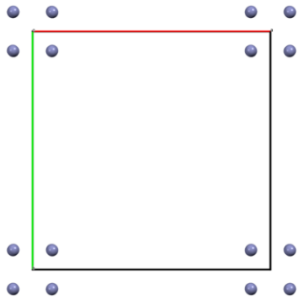
$Zn_4O(CO_2)_6$

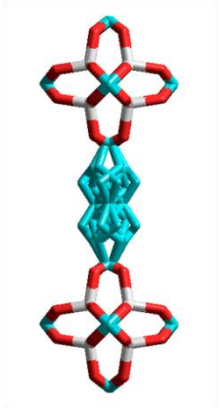
a = b = c = 13.8 Å

α = β = γ = 90.00°



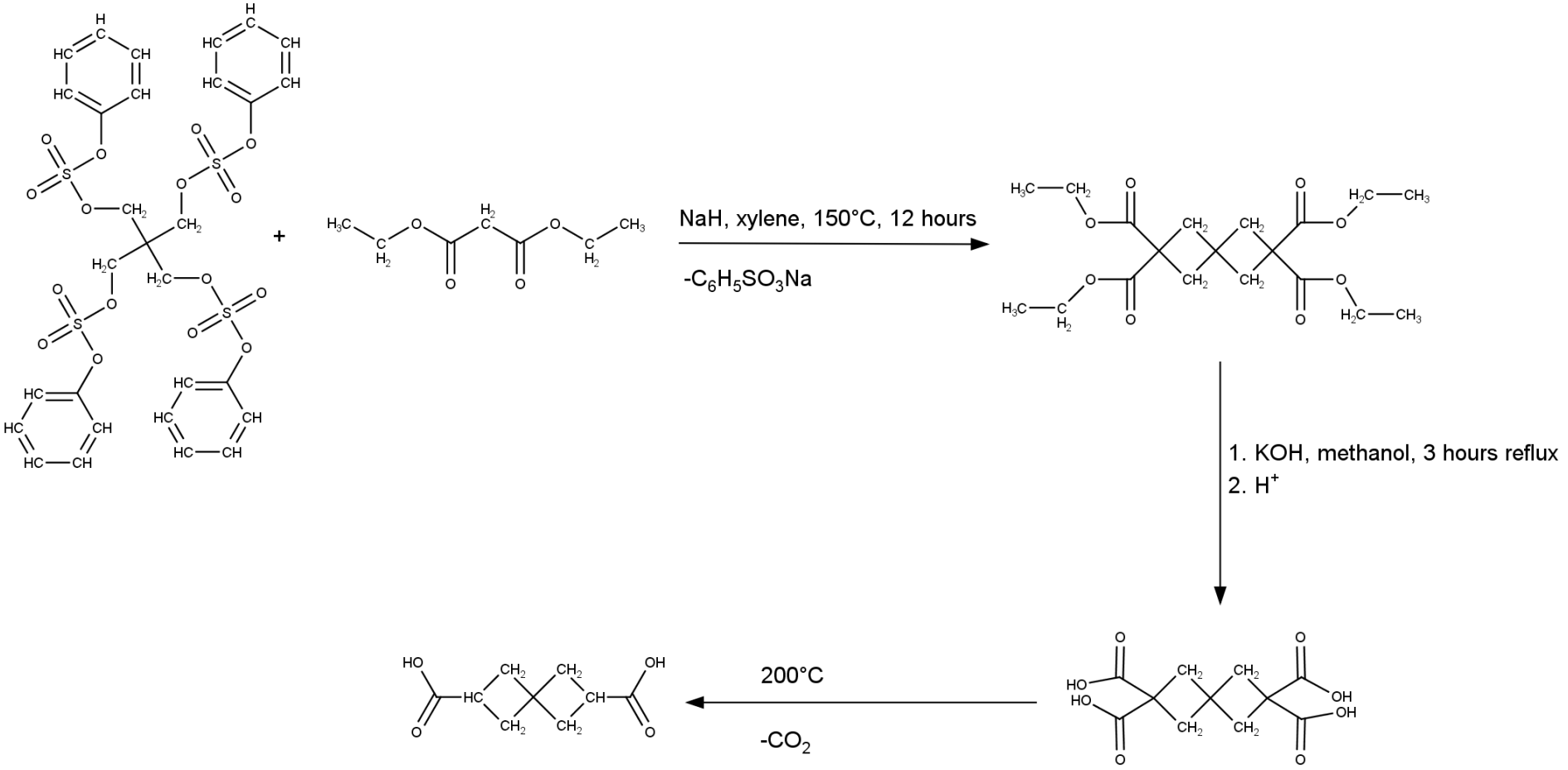
Possible incorporation of racemic spiro[3.3]heptane-2,6-dicarboxylic acid





Two enantiomers, 8 position

Preparation of spiro[3.3]heptane-2,6-dicarboxylic acid



Emil Buchta, Wolfgang Merk, Liebigs Ann. Chem. Bd., 694, 1-8 (1965)
H. J. Backer, and H. J. B. Schurink, Rec. trav. chim, 50, 921 (1931)
Hans Wynberg, and J. P. M. Houbiers, J. Org. Chem, 36, 834-842 (1971)

Summary

- Recent work:

- preparation of 6 new MOF structures with Zn-containing nodes (mononuclear, binuclear, tetranuclear, hexanuclear) and cubane-1,4-dicarboxylic acid linkers
- Synthesis of a new compound with tetranuclear zinc-containing nodes and (*RS*)-spiro[3.3]heptane-2,6-dicarboxylic acid linkers

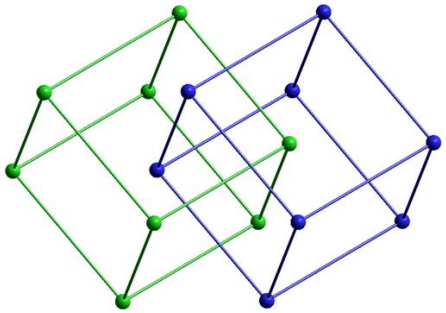
- First semester: detailed characterisation of hexanuclear MOF with cubane, characterisation of thermal properities (all samples are stable up to 200 °C, easy-to-activate frameworks), storing water sensitive MOFs
- Second semester: preparation of 0.8 g (*RS*)-spiro[3.3]heptane-2,6-dicarboxylic acid

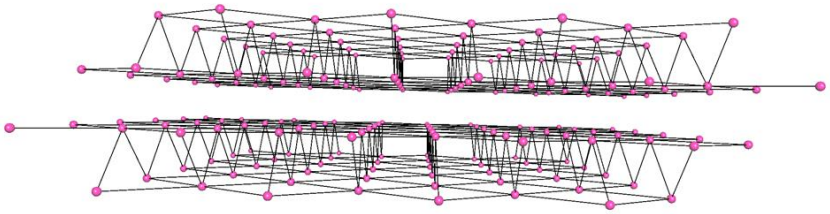
Courses, conferences

- Courses:
  - Polimerek kémiája és fizikája (5)
  - Természetes- és nem természetes alapú polimerek (5)
  - Korszerű elválasztási módszerek az anyagkutatásban (5)
  - Nanotechnológia (in process)
- Conference contributions:
  - International Joint Conference on Enviromental and Light Industry Technologies, International Symposium on Design and Innovative Technologies, Budapest, 19th November, 2015, poster presentation, „New metal-organic frameworks with the incorporation of cubane”
  - Fiatal Diplomások Fóruma, 24th November, 2015, oral presentation, „Új kubántartalmú fémorganikus vázszerkezetek”
  - Debreceni Röntgendiffrakciós Kerekasztal, Debrecen, 20th January, 2016, oral presentation , „Új kubántartalmú fémorganikus vázszerkezetek”
  - Műszaki Kémiai Napok 2016, Veszprém, 28th April, 2016, oral presentation, „Új kubántartalmú fémorganikus vázszerkezetek”

Future plans

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





Acknowledgement

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Thank you for attention!