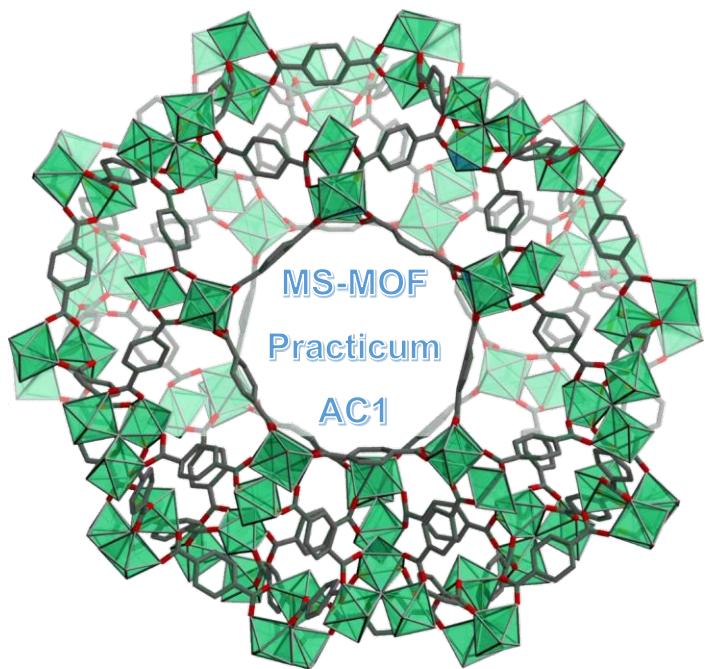


**Metal Organic Frameworks (MOFs) Practicum for  
Master Students**



HHU Düsseldorf, 2025

## Contents

Introduction .....	3
Guidelines .....	3
Laboratory work organization.....	3
Colloquiums .....	4
Protocol submission .....	5
Laboratory works descriptions (scripts) .....	8
1. [Cr <sub>3</sub> (O)(OH)(1,4-benzenedicarboxylate) <sub>3</sub> (H <sub>2</sub> O) <sub>2</sub> ], MIL-101(Cr) .....	8
2. [M <sub>2</sub> (1,4-benzenedicarboxylato) <sub>2</sub> (1,4-diazabicyclo-[2,2,2]-octane)]; DMOF-1(M), M=Cu, Zn .....	12
3. [Cu <sub>3</sub> (1,3,5-benzenetricarboxylate) <sub>2</sub> (H <sub>2</sub> O) <sub>3</sub> ]; HKUST-1(Cu) .....	16
4. [Al(OH)(fumarate)]; MIL-53(Al)-fumarate (BasoliteA520 type) .....	20

## Introduction

For completing the practicum with maximal benefits you need to complement the knowledge that you acquire on the lectures by individual work with the literature. It is important that you should not try to read all the proposed literature in depth; you should rather have a general understanding of the main ideas in MOF chemistry and be acquainted with its achievements using representative examples.

## Guidelines

The *MOF-Practicum* at the AC1 introduces the experimental aspects of modern chemistry on the example of Metal Organic Frameworks (MOFs).

The next aims are targeted:

- Stimulate the use of original scientific publications, and practice of selective reading for understanding the principles
- Give hands-on synthetic experience with basic MOF-chemistry
- Introduce you to different analytic methods and trainee to use multi-aspect analytic data to prove the identity of the target compound
- Propose a practice in cooperative data analysis (i.e. compare the results of each other).

All the basic needed information is given/referenced on this page. Every laboratory work, as given in the *Scripts*, is carried out by three people. Two such subgroups, designated as A and B, form a full  $2 \times 2$  group.

After completing the work, you shall submit one protocol for six people, under the full groupname as given in the list of works.

We encourage collective work during the preparation for the colloquiums and the writing of the protocols. That could spare time and improve your level of preparation.

## Laboratory work organization

### Preparations:

- Check the schedule of the work. **Report immediately if you cannot participate.**
- Read the description of your particular laboratory work (further *Script*). Work with the given original literature complemented by sources of your choice and prepare the answers to the control questions (they could be

asked during the laboratory work or *colloquia*; it is not obligatory to give the answers in the protocols, however, they may give you ideas about that as well).

- Prepare a *personal version of the pre-protocol* (*Vorprotokol*) preferably hand-written on ~1-2 page, with the reaction scheme, a synopsis of your activities in the lab and the main dangers (the hazard codes could be added separately in a printed form; it is a non-obligatory formality, as we demand not codes, but understanding).

Starting the work:

- Introductory formalities: lab.-work specific safety instruction (the reminder of standard rules are added to the study materials package).
- Submit the *pre-protocol* by coming at the specified time. The *preprotocol* checks are done in a form of a short conversation. If you are not ready, you cannot start.

During the work:

- Submit the prepared materials for analytics. Discuss with the assistants the time of demonstration of the analytical instruments (usually Friday).
- Reminder: do not forget to use your time efficiently during the lab. work. Read, write up your observations, prepare yourself to colloquia, etc.

After the work:

- Process the analytic data, describe your results (give detailed synthetic descriptions with photos).
- Compare the results of the two subgroups and write a common chapter to the report (if you cannot agree on how you do it, you may do it separately, but this approach is inferior).
- Submit the protocol (a single 'collective' protocol for a  $2 \times 2$  group).

For better understanding of the structure of the MOFs it is advisable to use the free and simple program Mercury. You could open the provided *cif* file to work from scratch, or, sometimes use the pre-generated structure saved as an *mryx* file (the files are provided).

By combination of mouse movement with holding a button you could perform: free rotation (Left Mouse Button); 2D rotation in the plane of view (Shift + Left Mouse Button); move of the whole structure (Ctrl + Left Mouse Button); change the perspective (Shift + Right Mouse Button); change the scale (Ctrl + Right Mouse Button). We encourage you to play with the

structure further by un-ticking the "Packing" option (left-bottom of the screen), and (de)activating the Short-contact option (left-bottom of the screen). Thereby you could generate the closest neighbors by clicking on the appeared contacts. You could also change the style in the Style menu (left-top of the screen) to switch to "Ball-and-stick" representation, more usual for beginners

---

#### Protocol submission

The  $2 \times 2$  group submits one common protocol *via* E-mail. The protocol is composed of separate group-specific parts, and one common, where the results are compared (alternatively, separate protocols could also be submitted, but the results should be compared in any case. If you cannot agree to cooperate, you might do everything independently, but the comparison should be done). The common chapter for the  $2 \times 2$  group protocol is the comparison of the results. Assess the similarities and differences of the two MOFs in terms of the known structures and the experimental results, particularly the analytical data.

The group specific part consists of:

1. A short introductory part about MOFs and the part, and the exact material you are going to synthesize (the introductory part should also contain an essay on one of the physical methods of investigation, which is going to be specified). This part still could be common for the groups, if you agree on that.
2. Synthetic part with precise description of your actual actions and observations (add photos). It should include the appearance of the product and the possible time of formation, the actual purification steps, actual degassing conditions with the weight loss during degassing, and all the quantitative information (primarily the yield related ones).
3. Analytical part (a general description and, if possible, comparison with the literature should be provided for each case).
  - a. IR: find the characteristic bands for the MOF and the guest solvent molecules and show the correlations with the known structure;
  - b. PXRD: assess the compare the experimental data with the given simulated data;

- c. TGA: assess the amount of the incorporated guest solvent molecules (if applicable).
- d. Gas adsorption analysis: categorize the adsorption isotherms you have measured, according to the IUPAC recommendations included to the study materials. Calculate the BET-surface area from the given datapoints for linearized BET equation (look up the added instructions). Compare the accessible pore volume, if possible.

A note regarding **typical mistakes**:

- General:
  - o The digits of significance are given with too high precision (the synthetic yield is shown with two or three digits of significance, i.e. as xx% or xx.x%; the number of solvent molecules as xx.x given with a precision to one digit after the decimal point; IR peak values are rounded to whole numbers of  $\text{cm}^{-1}$ ; the  $2\theta$  values in the qualitative comparisons of PXRD as  $xx\theta$  for poorly defined patterns or  $xx.x\theta$  for well-defined ones; the surface area should be rounded to whole number of  $\text{m}^2 \text{ g}^{-1}$ ).
  - o There is no introduction regarding your target material with its structure and characteristics.
- Synthesis:
  - o The percentual yield is not calculated (for that you should calculate the solvent content in the as-synthesized material. It could be derived from the given weight loss during the degassing for the gas adsorption analysis, which is less precise, or TGA data. Use the one, which is actually measured and more precise).
  - o No reaction equation is given.
  - o Insufficient description of what was done (we recommend to add photos, particularly about the appearance of the product) -      IR:
  - o the bands are not assigned and compared properly (it is supposed, that you will consult with a specialized [review](#)).
- PXRD:
  - o The measured PXRD pattern(s) and the simulated one are not compared in a form of a single stacked graph (the simulated data is provided among the structural data as a file with an *xy extension*).
- TGA:

- The composition including the solvent content is not calculated (if you receive "historic/model" TGA data, you might use only the weight loss during the degassing).
- Gas adsorption analysis
  - The P/P<sub>0</sub> range is not properly chosen (the linearized BET graph should be linear for the chosen range, sufficient number of points should be used (5 is desired, but four could be enough in the case of necessity). The typical range is approx. 0-0.1, but it is almost always narrower for microporous materials than the classical 0-0.3 range).
    - The absolute and the specific (i.e. related to one gram of material) surface areas are mixed up.
- Conclusions:
  - the conclusions are too short, sometimes expressed in one sentence that everything is alright. The conclusions should not be long, though they should summarize the findings with a particular focus on comparisons between materials, namely the reported and the synthesized ones. If you have doubts, you might look through the syntheses and each of the analytical methods and shortly summarize each. However, if you could do that in a more general way, do not hesitate to do that.

#### Laboratory works descriptions (scripts)

The scripts lists a standard description and a few synthetic variants. Each group does a standard synthesis and its variant. If the second is successful, it is reported. If it is failed, the results for the "standard" synthesis is reported.

#### 1. [Cr<sub>3</sub>(O)(OH)(1,4-benzenedicarboxylate)<sub>3</sub>(H<sub>2</sub>O)<sub>2</sub>], MIL-101(Cr)

##### Materials

10 mL Teflon lined autoclave

Hot-plate magnetic stirrer,

Magnetic stirring bar

100 ml Erlenmeyer flask

Two centrifuge tubes

Glass rod

## **Chemicals**

Chromium (III) nitrate nonahydrate, Cr(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O  
1,4-Benzenedicarboxylic acid or terephthalic acid (H<sub>2</sub>BDC) C<sub>8</sub>H<sub>6</sub>O<sub>4</sub>  
Nitric acid, conc., HNO<sub>3</sub> (65-68%)  
Deionized water  
Dimethylformamide, DMF (p.a.)  
Methanol (p.a.)

## **Synthesis**

Place 401 mg Cr(NO<sub>3</sub>)<sub>3</sub> · 9H<sub>2</sub>O (1.00 mmol) and 166 mg (1.00 mmol) terephthalic acid in the Teflon insert-cup of the autoclave and add 4.8 mL of deionized water. Add 69 µL (1.00 mmol) of HNO<sub>3</sub> as an additive/modulator. Thoroughly homogenize the mixture with a glass rod. Close the Teflon cup, place it in the autoclave and seal it. Place the oven in the oven, heat it to 220°C (1 h ramp for a programmable oven) and to hold this temperature for the next 6 h. After the oven cools down (~30 K h<sup>-1</sup> rate for a programmable oven),<sup>a)</sup> open the autoclave, centrifuge off the precipitate and purify it according to the following description:

The precipitate is stirred in ~20 mL DMF at ~80 °C for 1 h and separate it by centrifugation (if there is enough time, repeat the procedure).

The precipitate is stirred in ~20 mL MeOH at 50 °C for 1 h and separate it by centrifugation. The precipitate is stirred in ~20 mL of deionized water at 60 °C for 1 h and centrifuged off again. Remove the supernatant and dry the compound at 100 °C in the oven.

## **Safety**

Methanol and dimethylformamide are moderately toxic solvents. Concentrated nitric acid is highly corrosive and could leave permanent scars; be especially accurate, when you work with it. Metal nitrates are potent oxidizers and should be handled accordingly.

## Notes:

- a) Slow cooling by using a programmable oven is slightly advantageous compared to fast cooling. Larger particles sediment easier. Alternatively, the autoclave could be cooled together with a non-programmable oven.

## **Analytics**

- Surface area and porosity measurement using the NOVA sorption analyzer. The sample should be degassed at 200 °C for 2 h.

- IR (Infrared) spectrum. The analysis should be performed in a neat sample using a KBr disk.
- PXRD (Powder X-Ray Diffraction) phase analysis
- TGA (Thermo Gravimetric Analysis). The analysis should be performed on a fresh, non-degassed sample.

#### **Variants**

<b>v1</b>	Use no modulator.
<b>v2</b>	Double the solution volume by adding deionized water (+ 5 ml).
<b>v3</b>	Double the amount of Cr(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O.
<b>v4</b>	Use double amount of HNO <sub>3</sub> .
<b>v5</b>	Use 3 mmol of NH <sub>4</sub> F instead of 1 mmol of HNO <sub>3</sub> .
<b>v6</b>	Do the synthesis at 210 °C.
<b>v7</b>	Do the synthesis for 3 h instead of 6 h.
<b>v8</b>	Use a 2:1 (mol. ratio) mixture of Cr(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O and FeCl <sub>3</sub> · 6H <sub>2</sub> O instead of Cr(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O only.
<b>v9</b>	Use CrCl <sub>3</sub> · 9H <sub>2</sub> O instead of Cr(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O.
<b>v10</b>	Perform the process on half of the scale using MW-assistance, 220 °C during 1 h.
<b>v11</b>	Use a 2:1 mol. ratio of H <sub>2</sub> BDC and 2-aminoterephthalic acid instead of H <sub>2</sub> BDC. Submit 10 mg of the degassed compound in 0.5 ml of D <sub>2</sub> O + 0.1 ml of 40% NaOD in D <sub>2</sub> O after 1 day exposure at room temperature to determine the ratio of the ligands.

#### **Control questions**

1. What is the coordination environment of the chromium atom in the MIL-101(Cr) compound? Upon which metal containing entity (coordination bonded cluster or, in the

context of MOFs, secondary building block) is it built? Explain the structural organization principles.

2. What is the role of the additive/modulator? What is the classic modulator in the synthesis of MIL-101(Cr)? Why it is not used in this work?
3. What is the rationale behind the multi-step purification procedure? Explain the meaning of each step.
4. The MIL-101(Cr) is synthesized in water medium at much higher temperatures compared to NH<sub>2</sub>-MIL-101(Al) or (NH<sub>2</sub>)-MIL-101(Cr), synthesized in DMF. The named solvents are optimal for the listed cases. Propose an explanation for the different behavior.

### References

1. a) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, and I. Margiolaki, "A chromium terephthalate-based solid with unusually large pore volumes and surface area", *Science* , 2005, 309, 2040–2042. b) P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle, and G. Férey, "Metal–Organic Frameworks as efficient materials for drug delivery" *Angew. Chemie Int. Ed.* 2006, **45**, 5974–5978. [The first papers on MIL-101(Cr)]
2. D.-Y. Hong, Y. K. Hwang, C. Serre, G. Férey, and J.-S. Chang, "Porous Chromium Terephthalate MIL-101 with coordinatively unsaturated sites: surface functionalization, encapsulation, sorption and catalysis" *Adv. Funct. Mater.* 2009, **19**, 1537–1552. [A good general paper on MIL-101(Cr), particularly recommended for overview]
3. T. Zhao, F. Jeremias, I. Boldog, B. Nguyen, S. K. Henninger, and C. Janiak, "High-yield, fluoride-free and large-scale synthesis of MIL-101(Cr)", *Dalt. Trans.* 2015, **44**, 16791–16801. [The use of HNO<sub>3</sub> as a modulator]

## 2. $[M_2(1,4\text{-benzenedicarboxylato})_2(1,4\text{-diazabicyclo-[2.2.2]-octane})]$ :

DMOF-1(M), M=Cu, Zn

**Commented [IB1]:** The work is too simple. It is possible to add a small addition with solvation by toluene or other comparable guest and comparison of the PXRD patterns (based on Dybtsev et al.: the framework is slightly flexible)

### Materials

2 50 ml thick wall 'Schott' glass flasks with a temperature resistant screw-caps

4 plastic centrifuge tubes

### Equipment and accessories

**Commented [IB2]:** It is worth to reinstate these entries.

Temperature controlled oven, centrifuge, spatula(s), Pasteur pipette(s) and a pipette bulb, measurement cell for the NOVA or Autosorb sorption analyzers

### Chemicals

Copper acetate monohydrate,  $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$

Zinc nitrate hexahydrate,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$

1,4 - Benzenedicarboxylic acid, terephthalic acid,  $\text{H}_2\text{BDC}$ ,  $\text{C}_8\text{H}_6\text{O}_4$

1,4-diazabicyclo-[2.2.2]-octane, DABCO,  $\text{C}_6\text{H}_{12}\text{N}_2$

*N,N*-dimethylformamide p.a., DMF

Ethanol (p.a; 96% is acceptable, but it should be without denaturing additives)

### Safety

DABCO is quite irritant and harmful for mucous membranes. Dimethylformamide is a moderately toxic solvent and its contacts with skin as well as ingestion and vapor inhalation should be avoided.

### A. Synthesis of $[\text{Cu}_2(\text{dabco})(\text{BDC})_2]$

399 mg of copper acetate (2 mmol), 332 mg of terephthalic acid (2 mmol) and 112 mg of DABCO (1 mmol) are dissolved in 25 ml of DMF in a 50 ml glass flask. The flask is sealed and its content

is heated at

120°C for 2

days.<sup>a)</sup> After cooling down the flask, the formed crystalline residue are centrifuged out. The

**Commented [IB3]:** 100% yield with 4 molecules per formula unit is 860 mg

product is washed two times by 5 ml of DMF. The washing procedure is repeated twice with ethanol and the precipitate is dried at 60 °C in air until permanent weight.

#### B. Synthesis of $[\text{Zn}_2(\text{dabco})(\text{BDC})_2]$

595 mg of  $\text{Zn}(\text{NO}_3)_2 \cdot 6 \text{ H}_2\text{O}$  (2 mmol), 332 mg  $\text{H}_2\text{bdc}$  of terephthalic acid (2 mmol) and 112 mg of DABCO (1 mmol) are dissolved in 25 ml of DMF in a 50 ml glass flask. The flask is sealed and its content is heated at 120°C for 2 days.<sup>a)</sup> After cooling down the flask, the formed crystals are centrifuged out. The product is washed by 2×5 ml of DMF. The washing procedure is repeated twice with ethanol and the precipitate is dried at 60 °C in air until permanent weight.

#### Notes:

- a) One day is permissible, however the yield will be lower.

#### Analytics

- Surface area and porosity measurement using the NOVA sorption analyzer. The sample should be degassed at 200°C for 2h.
- IR (InfraRed) spectrum. The analysis should be taken on a non-degassed sample using an ATR module.
- PXRD (Powder X-Ray Diffraction) phase analysis (preferably after the degassing of the sample). Optional: compare the PXRD of the as-synthesized products with the
- TGA (Thermo Gravimetric Analysis). The analysis should be performed on a fresh, non-degassed sample.
- **Reminder:** do not forget to document the yield (weight and percentual, relative to the theoretical yield, using the amount of DMF, found from the TGA; if the determination is not useable, assume 4 molecules of DMF per formula unit), the color and morphology of the crystals (optimally provide photos).

#### Control questions

1. What is the coordination environment of copper and zinc in the synthesized compound? Upon which metal containing entity (coordination bonded cluster or so called secondary building block) it is built? Explain how the structures are organized. Are they similar? Are the structures flexible? \*

2. Why copper acetate is used as a source of copper, but zinc nitrate as a source of zinc? Would it not be better to use zinc acetate in the latter case? Try to guess and provide the arguments, whether the synthesis would be successful if copper nitrate would be used instead of the acetate. \*

3. Explain, why the structure is thermally quite stable, despite the M-N bonds are relatively weak (there is no Coulombic interaction assistance). Compare its stability with an imagined structure sustained only by 4,4'-bipyridine linkers.

4. What is the known surface area of this MOF? If 4,4'-bipyridine is used instead of DABCO in this synthesis, a similar precipitate could be obtained, however its porosity is significantly less. Explain that fact and try to predict, what kind of building block should give the highest porosity.

5. Suppose that 1,2-ethylenediamine is taken instead of DABCO. What kind of compounds as a result of this change one could anticipate? \*

\* - An optional question of elevated complexity

**Variants (applicable for both syntheses, like v1A or v1B)**

v1	Use 1/5-th of the DMF amount
v2	Use 4,4'-bipyridine instead of DABCO
v3	Use 1/5-th of the DMF amount and perform an MW-synthesis
v4	Mix the solid components together, add 100 mL-1000 mL of DMF (more ethanol makes it closer to the “conventional synthesis”; use the amount chosen by the assistant) and perform a mechanochemical synthesis (30 min, 30 Hz).
v5	Use metal acetate hydrate instead of metal nitrate hydrate.
v6	Use ethanol instead of DMF, and add 4 mmol of NEt <sub>3</sub> as a base. Reflux the mixture upon stirring for 1 h.

v7	Dissolve the metal salt in 10 ml of water, while the DABCO and the ligand together with a double molar amount of NaOH in water. Quickly combine the solutions under vigorous stirring, stir 1 minute, centrifuge the product out and wash it two times by 10 mol of EtOH using centrifugation. It is better, if you leave the product under ethanol overnight for solvent exchange and preventing the hydrolytic degradation of the MOF and, after the last centrifugation, quickly dry it in vacuum oven at 90 °C and 20-30 mbar (30 min is sufficient). Alternatively, the product could be dried in air after two washings by EtOH.
v9	Use a 1:1 mixture of copper and zinc nitrate hydrates. Optimally, submit the MOF to EDX or AAS analyses to find the metal ratio in the product.
v10	Two mixtures are prepared: a slurry of the zinc nitrate hydrate and H <sub>2</sub> BDC in 20 ml of methanol and a solution of DABCO (0.140 g, 1.25 mmol) and 500 µL of triethylamine in 20 ml of methanol. The two solutions are combined at room temperature and stirred for 2h. The product is processed further as described in the standard version (the washing with DMF is desirable to remove the rests of the ligand). Note that if you use DMF instead of methanol, you should end up with pillared Kagome network, with an isomeric structure to DMOF (based upon <a href="#">Inorg. Chem. 2019, 58, 12, 7690</a> )
v11	Use aminoterephthalic acid instead of terephthalic acid (the rapid version, as in v10 is possible, and rather preferable).

### References:

1. K. Seki, "Design of an adsorbent with an ideal pore structure for methane adsorption using metal complexes.", *Chem. Commun.* **2001**, (16), 1496-1497. [The original paper on [Cu<sub>2</sub>(dabco)(BDC)<sub>2</sub>]. It is concise and still worth reading]
2. D. N. Dybtsev, H. Chun and K. Kim, "Rigid and flexible: A highly porous metal-organic framework with unusual guest-dependent dynamic behavior.", *Angew. Chem.-Int. Ed.* **2004**, 43 (38), 5033-5036. [The original paper on [Zn<sub>2</sub>(dabco)(BDC)<sub>2</sub>] and its flexibility. Primary reading.]
3. H. Chun, D. N. Dybtsev, H. Kim and K. Kim, "Synthesis, X-ray crystal structures, and gas sorption properties of pillared square grid nets based on paddle-wheel motifs:

- implications for hydrogen storage in porous materials", *Chemistry* **2005**, 11, 3521-3529.  
[Report on a family of  $[M_2(L^N)][R_xBDC]_2$  materials]
4. S. Kitagawa, et. al., Functional porous coordination polymers. *Angew. Chem.-Int. Ed.* **2004**, 43 (18), 2334-2375. [A review on MOFs; selective reading is advised]
  5. A. Schneemann, V. Bon, I. Schwedler, I. Senkovska, S. Kaskel and R. A. Fischer, "Flexible metal-organic frameworks", *Chem. Soc. Rev.* **2014**, 43, 6062-6096. [A review on flexible MOFs; do not read everything, but skim selectively]

### 3. $[Cu_3(1,3,5\text{-benzenetricarboxylate})_2(H_2O)_3]$ ; HKUST-1(Cu)

#### Materials

50 mL round bottom flask

Air condenser

Hot-plate magnetic stirrer

Magnetic stirring bar

2 or 30 ml PTFE lined autoclaves

100 ml beaker

4 or 25 ml centrifuge tubes

#### Chemicals

Copper nitrate trihydrate,  $Cu(NO_3)_2 \cdot 3H_2O$

Nickel (II) nitrate hexahydrate,  $Ni(NO_3)_2 \cdot 6H_2O$  (optional)

1,3,5-benzenetricarboxylic acid (H<sub>3</sub>BTC),  $C_9H_6O_6$

Ethanol (p.a.)

Deionized water

#### Safety

$Ni(NO_3)_2 \cdot 6H_2O$  and DMF are moderately toxic. The general rules of work in the laboratory should be followed; ingestion, inhalation and skin contact with the substances should be avoided. Metal nitrates are potent oxidizers and should be handled accordingly.

## Synthesis

Copper nitrate trihydrate (0.85 g, 3.5 mmol), 1,3,5-benzenetricarboxylic acid (0.42 g, 2.0 mmol) and 25 mL of ethanol are placed in a 50 mL round-bottom flask equipped with a magnetic stirring bar and an air condenser. The mixture is refluxed under mild stirring during 48 h using an oil bath. <sup>a)</sup> The flask is cooled down and the formed precipitate is separated by centrifugation. The product is washed with water (2×10 mL) and ethanol (2×10 mL). The solid is dried at 60 °C in air until permanent weight.

### Notes:

- a) Use preferably a set-up with passive cooling (air condenser), due to administrative regulations regarding overnight syntheses that employ active cooling by flowing water.
- b) The only reason for using two batches is that the reaction is not very well reproducible, particularly on larger scales. You should work up only the batch(es), where the green crystals of the product are present (normally along with a large quantity of brown impurities).
- c) Two days of heating time are better, but normally there is not enough time available (consult with your assistant). If a programmable oven is available, it is advisable to apply a linear-gradient cool down during the last 5 h of the heating to obtain larger crystals. Obtaining the latter is an aesthetic point only, but rapid cooling might influence somewhat the yield and purity.
- d) Short ~1h drying at 60 °C. Note the weight.
- e) Avoid prolonged grinding, particularly avoid the use of excessive force. Intensive grinding decreases the crystallinity of the material. It is enough to do a ~1 min mild grinding (10 µm particles are well suiting the need; you cannot control the size, hence the number is given just as a general indication).
- f) Separate ~30 mg of the ground material for all the analyses, except the gas adsorption analysis.
- g) Use a shaker. If not available, use magnetic stirring and a stoppered Erlenmeyer flask as a container.
- h) Separate the solid by centrifugation and add the fresh portion (~15 ml) of methanol

## Analytics

- Surface area and porosity measurement using the NOVA sorption analyzer. The samples should be degassed at 150 °C for 2 h.

- IR (Infrared) spectra, neat on the as-synthesized sample (optionally the IR spectrum after the MeOH exchange of the HKUST-1(Ni) could also be asked).
- PXRD (Powder X-Ray Diffraction) phase analysis of the as-synthesized samples.
- TGA (Thermo Gravimetric Analysis) of the as-synthesized samples.
- **Reminder:** to document the color and morphology of the obtained crystals (making photos are highly encouraged). Do not forget to give the yields of the as-synthesized product. For that it is necessary to know the molecular weight share of the framework, which is calculated from the TGA, or, less precisely, estimated from the weight change during the degassing. Therefore, give the weight of the as-synthesized product, the corresponding yield of the guest-free product, and the yield as a part of the theoretical.

### Variants

v1	Double the amount of Cu(NO <sub>3</sub> ) <sub>2</sub> ·3H <sub>2</sub> O.
v2	Use 2:1 molar ratio of copper and nickel nitrate hydrates instead of using copper nitrate hydrate only (observe the difference in colours between the product obtained in the course of a standard synthesis and this modification . Upon agreement with the assistants, submit the sample for EDX to determine the ratio of Cu and Ni).
v3	Use 1:2 molar ratio of copper and nickel nitrate hydrates instead of using copper nitrate hydrate only (observe the difference in colours between the product obtained in the course of a standard synthesis and this modification . Upon agreement with the assistants, submit the sample for EDX to determine the ratio of Cu and Ni).
v4	Use 9:1 mixture of EtOH:H <sub>2</sub> O by volume instead of absolute ethanol as a solvent (a minor amount of non-dissolved trimesic acid is not a problem at the beginning).
v5	Use copper chloride hydrate instead of copper nitrate hydrate.
v6	Add 2 mmol of NEt <sub>3</sub> as the last component after 5 min of stirring of the prepared reaction mixture and perform the synthesis as described.

v7	Add 2 mmol of NaOH as the last component after 5 min of stirring of the prepared reaction mixture and perform the synthesis as described.
v8	Mix the solid components together, add 50-500 mL of ethanol (more ethanol makes it closer to the "conventional synthesis"; use the amount chosen by the assistant) and perform a mechanochemical synthesis (20 min, 30 Hz).
v9	Use copper hydroxy carbonate or copper acetate instead of copper nitrate, mix the solid components together, add 50-500 mL of ethanol (more ethanol makes it closer to the "conventional synthesis"; use the amount chosen by the assistant) and perform a mechanochemical synthesis (20 min, 30 Hz).
v10	Perform the process using 4 ml of EtOH instead of 25 ml using MWassistance, 100 °C during 10 min.
v11	Perform a synthesis using 2 mmol of NEt <sub>3</sub> and 2 ml of EtOH using MWassistance, 100 °C during 10 min.
v12	465 mg Cu(NO <sub>3</sub> ) <sub>2</sub> ·2.5 H <sub>2</sub> O in 10 mL of water is quickly added under vigorous stirring to a solution of 280 mg of H <sub>3</sub> BTC and 0.16 g NaOH in 10 mL water. The stirring is continued for 1 min and the mixtures were centrifuged out immediately and immediately washed two times by 10 ml of ethanol using centrifugation. It is better, if you leave the product under ethanol overnight for solvent exchange and preventing the hydrolytic degradation of the MOF and, after the last centrifugation, quickly dry it in vacuum oven at 90 °C and 20-30 mbar (30 min is sufficient). Alternatively, the product could be dried in air after two washings by EtOH (based on <i>Cryst. Growth Des.</i> 2020, 20, 10, 6787)

### Control questions

- What are the coordination environments of copper? What is the secondary building unit, upon which the structure is built? Outline the structural organization principles and note the differences between the two MOFs.
- What other metal ions could be used for the synthesis of HKUST-1 type MOFs? What could their relative stability be?

3. Conjecture, which solvents – for example in the row of hexane, dimethylformamide, diethylether, chloroform, dimethylsulfoxide, water, benzene -- might also be suitable for the synthesis and explain your logic.

5. How do the compounds change their colors upon degassing and why?

### Literature

1. S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. Guy. Orpen, I. D. Williams, "A chemically functionalizable nanoporous material  $[\text{Cu}_3(\text{TMA})_2(\text{H}_2\text{O})_3]_n$ ", *Science*, **1999**, 283, 1148–1150 [The original paper on HKUST-1(Cu)]
2. P. Maniam and N. Stock, "Investigation of porous ni-based metal-organic frameworks containing paddle-wheel type inorganic building units via high-throughput methods" *Inorg. Chem.*, **2011**, 50, 5085–5097 [The original paper on HKUST-1(Ni)]
3. C. R. Wade and M. Dincă, "Investigation of the synthesis, activation, and isosteric heats of CO<sub>2</sub> adsorption of the isostructural series of metal–organic frameworks M<sub>3</sub>(BTC)<sub>2</sub> (M = Cr, Fe, Ni, Cu, Mo, Ru)", *Dalt. Trans.*, **2012**, 41, 7931–7938 [A source on different HKUST-1(M) materials].
4. C. Prestipino, L. Regli, J. G. Vitillo, F. Bonino, A. Damin, C. Lamberti, A. Zecchina, P. L. Solari, K. O. Kongshaug, S. Bordiga, "Local Structure of Framework Cu(II) in HKUST-1 Metallorganic Framework: Spectroscopic Characterization upon Activation and Interaction with Adsorbates", *Chem. Mater.* 2006, **18**, 1337–1346 [Additional read: the interaction of adsorbate with the activated MOF-material]
5. M. Hartmann, S. Kunz, D. Himsel, O. Tangermann, S. Ernst, A. Wagener, „Adsorptive Separation of Isobutene and Isobutane on Cu<sub>3</sub>(BTC)<sub>2</sub>”, *Langmuir*, **2008**, 24, 8634–8642. [Additional read: an model use of Cu<sub>3</sub>(BTC)<sub>2</sub> as in adsorptive separation]

### 4. [Al(OH)(fumarate)]; MIL-53(Al)-fumarate (BasoliteA520 type)

### Materials

20 mL beaker

50 mL round bottom flask (broad neck is advised, e.g. 29/42)

Dropping funnel (with an optional adapter to fit the 50 ml flask)

Petri dish (small, ~20 mm diameter)

Two magnetic stirring bars (one small for the beaker and one larger for the round bottom flask)

2□25 ml centrifuge tubes

## **Chemicals**

Aluminium sulfate octadecahydrate;  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$

Fumaric acid;  $\text{C}_4\text{H}_4\text{O}_4$

Sodium hydroxide; NaOH

Deionized water

## **Safety**

There are no highly toxic compounds used in this work, but adherence to accurate laboratory work practices is expected. Sodium hydroxide is corrosive; the contact of the solid or its solutions with the eye's cornea could cause blindness.

## **Synthesis**

480 mg of NaOH (12 mmol) followed by 0.387 g fumaric acid (4 mmol) are dissolved in 7 ml water<sup>a)</sup> and transferred to a dropping funnel. 1.33 g  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  (2 mmol) is dissolved in 7.5 ml of water in a round bottom flask at room temperature. The solution was heated up to

60 °C, and the first solution is dropwise added during 15 minutes (Al:Fumaric acid:NaOH:H<sub>2</sub>O ~1:1:3:200 molar ratio).<sup>b)</sup> The stirring is continued for further 1 h, maintaining the temperature constant. After cooling, the precipitate is separated by centrifugation and washed two times with water.

The product is dried in a vacuum drying oven at 200 °C for at least 1 h.<sup>c)</sup> A small amount of the product is hydrated for the TGA analysis (see the respective part in the Analytics section).

## Notes:

- a) Use a small beaker for preparation of the solution. Here and further the use of deionized water is implied.
- b) Use a bath. The relatively slow addition is performed in order to maintain the temperature of the mixture constant. The original preparation is done on a much larger scale and both solutions are pre-heated to 60 °C. The quality of the material might potential depend on the speed of addition, but in this case a simple.
- c) The heating-up time of the oven should not be counted. <30 Torr is sufficient for this purpose, i.e. membrane pump could be used. Do not forget to cover the opening of

the vial with a piece of aluminium foil, perforated at a few points, in order to prevent sample loss and accidental contamination of the oven during evacuation.

### Analytics

- Surface area and porosity measurement using the Nova or the Autosorb gas adsorption analyzer. The sample should be degassed at 200-250 °C for 2 h (note the chosen temperature).
- IR (Infrared) spectrum, neat. PXRD (Powder X-Ray Diffraction) phase analysis.
- PXRD (Powder X-Ray Diffraction) phase analysis. If you did not store the sample in a hermetic container, submit the hydrated sample (see the description of the TGA analysis)/
- TGA (Thermo Gravimetric Analysis). A small amount of the sample, dried in vacuum, should be re-hydrated for this analysis. Mix ~20 mg of the material on a Petri dish with a small amount water until formation of a paste. Let the sample dry in air at room temperature overnight (you might submit the still wet sample, which is going to dry until the analysis will be taken).

### Variants

v1	Perform the reactions in saturated solutions (note the amount of water needed).
v2	Halve the amount of NaOH used.
v3	Double the amount of NaOH used.
v4	Double the amount of water used.
v5	Use 90 °C instead of 60 °C (prevent the evaporation of the solvent by using watch glasses).
v6	Combine the solutions at room temperature, but then apply the step with heating.
v7	Do not use heating.
v8	Use Al(NO <sub>3</sub> ) <sub>3</sub> · 9H <sub>2</sub> O instead of Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 18H <sub>2</sub> O.
v9	Use AlCl <sub>3</sub> · 6H <sub>2</sub> O instead of Al <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> · 18H <sub>2</sub> O.

v10

Use a 1:1 molar ratio mixture of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$  and indium sulfate or nitrate hydrate.

### Control questions

1. What is the coordination environment of the aluminium atoms in the aluminium fumarate MOF? Upon which metal containing entity (coordination bonded cluster or, in the context of MOFs, secondary building block) is it built? Explain the structure organization principle.
2. Compare the structure of aluminium fumarate with the structure of MIL-160 (the work of the parallel group)? Are they similar? What are the differences?
3. What is the role of NaOH? What outcome one would expect, if the 1:1 fumaric acid to NaOH ratio would be used? The same question for the case when no NaOH is used at all?
4. Why is the drying temperature so high? What could be the difference, if the drying would be performed in air at 60 °C?
5. It is proposed to store the dried sample in a hermetic container. What will happen, if the sample is stored in the ambient air? What differences could be observed by the analytical methods, used in this work?
6. The BasoliteA520 is a trademark of BASF company (slightly other versions of the material exists, but the structure is generally the same). The preparation of BasoliteA520 was patented, as it was viewed as a candidate for potential industrial usage. Could you explain or at least conjecture, why the material is considered promising? (Optional) one special case is water adsorption; explain, what are the possible advantages compared with other MOFs?
7. (Optional) Explain, what could one expect, if the activated aluminium fumarate is soaked in a dichloromethane solution of a) HBr b) p-toluenesulfonic acid,  $p\text{-MeC}_6\text{H}_4\text{SO}_3\text{H}$  c)  $\text{Br}_2$  c) peroxybenzoic acid,  $m\text{-CIC}_6\text{H}_4\text{CO}_3\text{H}$ , with possible heating d) *tert*-butylhydroperoxide,  $t\text{BuOOH}$ , with possible heating.

### Literature

1. E. Alvarez, N. Guillou, C. Martineau, B. Bueken, B. Van de Voorde, C. Le Guillouzer, P. Fabry, F. Nouar, F. Taulelle, D. de Vos, J.-S. Chang, K. H. Cho, N. Ramsahye, T. Devic, M. Daturi, G. Maurin and C. Serre, "The structure of the aluminum fumarate MetalOrganic Framework A520", *Angew. Chemie* **2015**, 127, 3735–3739. [The paper

- devoted to the proof of the structure of the aluminium fumarate and proper characterization]
- 2. Gaab, N. Trukhan, S. Maurer, R. Gummaraju and U. Müller, "The progression of Albased metal-organic frameworks – From academic research to industrial production and applications", *Microporous Mesoporous Mater.* **2012**, 157, 131–136. [Review on aluminium MOFs.]
  - 3. Jeremias, D. Fröhlich, C. Janiak and S. K. Henninger, "Advancement of sorption-based heat transformation by a metal coating of highly-stable, hydrophilic aluminium fumarate MOF", *RSC Adv.* **2014**, 4, 24073–24082. [Potential use aluminium fumarate in water adsorption; in part an output of the HHU.]
  - 4. P. G. Yot, L. Vanduyfhuys, E. Alvarez, J. Rodriguez, J.-P. Itié, P. Fabry, N. Guillou, T. Devic, I. Beurroies, P. L. Llewellyn, V. Van Speybroeck, C. Serre and G. Maurin, "Mechanical energy storage performance of an aluminum fumarate metal-organic framework", *Chem. Sci.* **2016**, 7, 446–450. [Optional: a possibility of mechanical storage using a MOF on the example of aluminium fumarate with the intrinsic capability of its framework for "wine-rack"-type deformation.]
  - 5. C. Kiener, U. Müller and M. Schubert, Germany Pat. WO 2007/118841 A2, 2007. E. Leung, U. Müller, N. Trukhan, H. Mattenheimer, G. Cox, S. Blei; WO 2012/042410 patent, application number 10183283.2, 2012 [The BASF patents on the Basolite A520 material. Not for reading, just for general information and maybe for learning how a patent on MOFs might look like. The second patent describes the preparation, which is used in this work with minor modifications.]