

# Gas antisolvent method (GAS method) for crystallization of metal-organic coordination complexes

Margarethe Roskosz\*, Sabine Kareth, Marcus Petermann

Ruhr-University Bochum, Chair of Particle Technology, 44801 Bochum, Germany

\* roskosz@vtp.rub.de,

## INTRODUCTION

In many industrial domains, crystallization is one of the most important steps to the formulation, purification and isolation of pharmaceutical and chemical products with desired purity and characteristics. Depending on process conditions, crystallization can be achieved by cooling, evaporation or modification of the solvent. The major drawbacks of these methods are the use of high amounts of organic solvent, high temperatures, very expensive washing steps and residual solvent in the final product. The use of a supercritical fluid technology is an alternative to these conventional methods to eliminate or reduce these disadvantages. The use of CO<sub>2</sub> as an antisolvent for the controlled precipitation of materials from conventional solvents has been widely applied to the production of a range of materials, including polymers, pharmaceutical chemicals, explosives, superconductors and catalysts.

We present the gas antisolvent method (GAS method) as a crystallization process to realize single crystal growth of metal-organic coordination complexes. The diversity of this new class allows the use of MOFs in various fields of application, in particular in the fields of gas storage and separation, catalysis and sensor technology. [1]

To study these complex structures, it is necessary to use the single crystal X-ray crystallographic analysis, in which the average arrangement of the atoms can be precisely measured and their positions in the crystal lattice can be determined. The challenge consists in the production of the required single crystals, which in addition to their monocrystalline character also have to show a minimum size of 100 µm, required for the X-ray diffractometer. Conventional crystallization methods used for the preparation of single crystals suitable for X-ray crystallography are, next to the general disadvantages of these methods, extremely time-consuming (weeks to months). [2]

With the GAS method, it was possible to produce X-ray-suitable single crystals of already known metal-organic frameworks and to compare them with crystal structures obtained from conventional crystallization methods. [3]

## MATERIALS AND METHODS

All required reagents and solvents were purchased from commercial sources used without further purification.

The metal source for the complex synthesis is copper(II) acetate. The synthesis of the linker is subject to a synthetic prescription of an already published article. [4]

**Complex Synthesis.** For the synthesis of the metal complex 0.1 g of the metal(II) acetate and the organic linker, diethyl cyanomalonate, were dissolved in a 1:2 metal:ligand molar ratio in 70 ml of ethanol and stirred at room temperature for 12 h. The resulting precipitate was filtered, dried in vacuum for 8 h and used for the crystallization without further purification.

**Gas antisolvent crystallization.** The crystallization with CO<sub>2</sub> as an antisolvent was carried out in a high-pressure view cell. The autoclave was equipped with a saturated solution of the metal complex in a chosen solvent. A crystallization time of 2 h, a pressure of 100 bar and a temperature of 40 °C were set. After the specified time, the autoclave was purged for 30 min. The precipitate was obtained as crystals.

**Conventional crystallization.** To determine an influence of the crystallization method on the structure of the complexes, the products were also crystallized by a conventional method. Different concentrations of the metal complex in various solvents were prepared. By letting these solutions evaporate at room temperature, single crystals were obtained after weeks to months.

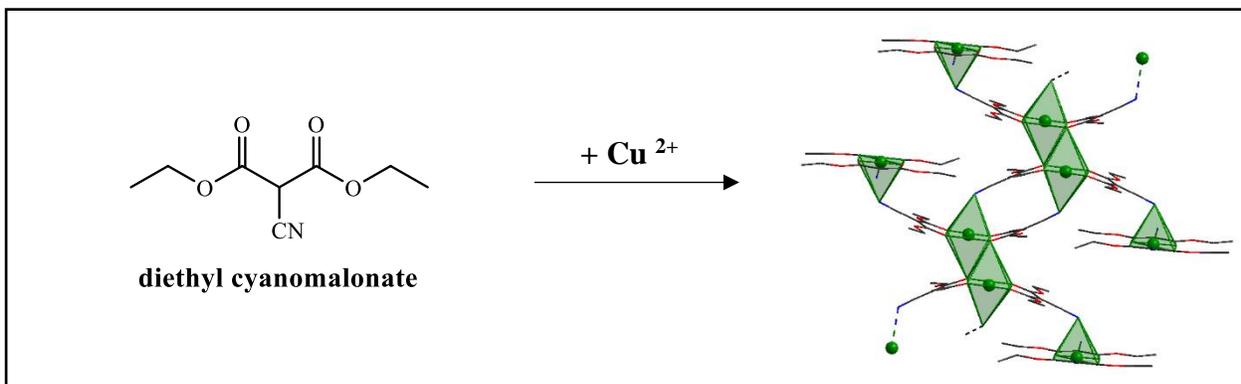


Figure 1: Formation route of the metal-organic coordination complex build of diethyl cyanomalonate as linker and copper(II) acetate as metallic component.

## RESULTS

The following results for the copper(II) complex are exemplary for the crystallization of several metal complexes.

Irrespective of the type of crystallization, the copper complex was obtained as crystals that mostly have a minimum size of 100  $\mu\text{m}$ , required for the diffractometer. Therefore, it was possible to obtain and evaluate intensity data sets by using a single-crystal X-ray diffractometer (Stoe IPDS I) with graphite monochromatic MoK $\alpha$  X-ray radiation.

Using diethyl cyanomalonate as linker and copper(II) acetate as the metallic source it was possible to design a complex of the composition  $[\text{ML}_2]_n$ . Depending on the chosen metal a one-dimensional copper(II) complex was obtained, that molecular view is shown in Figure 1.

The supramolecular arrangement of the complex is build up by self-assembly in the triclinic space group  $P\bar{1}$ . The coordinative interaction of the monomers occurs by the functional groups of the linker molecules, leading to the shape of a slightly distorted octahedral and square pyramidal coordination. The copper complex shows a stain-like arrangement with open metal sites along the strain (Figure 1).

Since both crystallization methods lead to the same structures, no influence can be observed on the molecular level.

## CONCLUSION

The use of CO<sub>2</sub> as an antisolvent opens up possibilities for the crystallization of metal-organic coordination complexes. It was possible to get X-ray suitable single crystals for structural analysis. Compared to the conventional method these crystals were obtained, instead of weeks or months, just in a few hours. In addition, no structural difference between the two methods or chosen solvents could be measured.

## REFERENCES

- [1] ZHAO D., Tuning the topology and functionality of metal-organic frameworks by ligand design, *Acc. Chem. Res.*, Vol. 44, 2011, pp. 123–133
- [2] LI L., Growth of large single MOF crystals and effective separation of organic dyes, *CrystEngComm*, Vol. 15, 2013, pp. 4094-4098
- [3] GALLAGHER P. M., Gas antisolvent recrystallization: new process to recrystallize compounds insoluble in supercritical fluids, *ACS Symp. Ser.*, Vol. 406, 1989, pp. 334-354
- [4] COOK M. C., Synthesis of the Neurotransmitter 4-Aminobutanoic Acid (GABA) from Diethyl Cyanomalonate, *Letters in Drug Design & Discovery*, Vol. 7, 2010, pp. 9-13