

## MS36-P08

**Copper based Bio-MOFs: Challenges and possibilities in crystal engineering**Marius Kremer<sup>1</sup>, Ulli Englert<sup>1</sup><sup>1</sup>. Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germanyemail: [Marius.Kremer@rwth-aachen.de](mailto:Marius.Kremer@rwth-aachen.de)

Metal-organic frameworks present one of the fastest growing categories of structures published in the CCD. Due to their extreme structural and chemical diversity, MOFs can be deployed in many fields of modern chemistry like gas separation, hydrogen storage or catalysis [1]. Synthesising biologically non-hazardous and medically harmless MOFs provides interesting possibilities for different medical applications like site-targeted drug delivery or medical imaging [2] and might be used to replace toxic or hazardous compounds in many other fields. This shift towards a “greener” chemistry is not only potentially beneficial for working conditions and the environmental impact of the industry, but might also lead to an economical benefit, since most reactants used are easy to store, widely available and sometimes even easily recyclable. [3]

In our experiments, we synthesised coordination complexes from non-toxic copper salts and aspartic acid. Aspartic acid, featuring two carboxylate sites, might enable bridging between multiple copper cations, leading to extended framework structures. Different copper salts were used to synthesise coordination compounds in H<sub>2</sub>O and EtOH, the products were then analysed using X-Ray diffraction, IR-spectroscopy and CHN elemental analysis. Since growing single crystals suitable for X-Ray diffraction proved challenging, several different crystallization techniques were employed during the synthesis of the substances.

## References:

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## MS36-P09

**Giant organometallic molecular containers**Alexander Virovets<sup>1</sup>, Eugenia Peresyphkina<sup>1</sup>, Manfred Scheer<sup>1</sup><sup>1</sup>. Institute of Inorganic Chemistry, Dept. of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germanyemail: [avvirovets@yahoo.com](mailto:avvirovets@yahoo.com)

One of the most outstanding and challenging areas in the modern coordination chemistry is the rational design of giant supramolecules built up from metal atoms connected to each other via polytopic organic or organometallic ligands resulting into large hollow cages. During last decade we have been investigating the chemistry of pentaphosphaferrocenes, [Cp<sup>R</sup>Fe(η<sup>5</sup>-P<sub>5</sub>)] (Cp<sup>R</sup> = η<sup>5</sup>-C<sub>5</sub>R<sub>5</sub>, R = Me (Cp\*), Me<sub>4</sub>Et (Cp<sup>x</sup>), CH<sub>2</sub>Ph (Cp<sup>bn</sup>), PhC<sub>4</sub>H<sub>9</sub> (Cp<sup>BlG</sup>)). Being stable in inert atmosphere, these organometallic compounds proved to be very attractive as versatile building blocks for the rational design of giant supramolecules with an inorganic core built up from Cu<sup>+</sup> and Ag<sup>+</sup> cations coordinated to the phosphorus atoms of the *cyclo*-P<sub>5</sub> ligands [1-3] (Fig. 1). Varying the nature of R, counterions and synthetic conditions, we obtained, in astonishingly high yields, hollow or multishell supramolecules of 2.1 – 4.6 nm in diameter alongside with the first coordination polymers with such supramolecules as nodes (Fig. 1c,f). Special crystallization techniques allow obtaining the single crystals suitable for the X-ray diffraction study using laboratory diffractometers or synchrotron radiation, which is accompanied by NMR studies in solid state and solution.

The central cavity of the hollow supramolecules (reaching 0.60 – 1.35 nm) can include various guest molecules (Fig. 1). Host supramolecule can often be adjusted to the size, shape and charge of the guest molecule. Thus, we succeeded in encapsulation of metastable molecules of white phosphorus (P<sub>4</sub>) and yellow arsenic (As<sub>4</sub>), various metallocenes (e.g., Cp<sub>2</sub>Fe, Cp<sub>2</sub>Ni, CpVC<sub>7</sub>H<sub>7</sub>) and triple-decker complexes (e.g. [(CpCr)<sub>2</sub>(η<sup>5</sup>-As<sub>5</sub>)] and [(CpMo)<sub>2</sub>(η<sup>3</sup>-P<sub>3</sub>)(η-PS)]), as well as cage molecules (C<sub>60</sub>, adamantane, o-carborane, P<sub>4</sub>S<sub>3</sub>, P<sub>4</sub>Se<sub>3</sub>) (Fig. 1a-e). The anionic and cationic species also can be encapsulated, like, e.g., the cobaltocenium cation into the negatively charged supramolecule in [CoCp<sub>2</sub>]<sup>+</sup><sub>3</sub>{[CoCp<sub>2</sub>]<sup>+</sup>@[{Cp\*FeP<sub>5</sub>}]<sub>8</sub>Cu<sub>24.25</sub>Br<sub>28.25</sub>(CH<sub>3</sub>CN)<sub>6</sub>}]<sub>4</sub> [2] (Fig. 1a).

The analysis of the host-guest interactions allowed us to reveal their novel types, namely, P<sub>5</sub>⋯P<sub>5</sub> and C<sub>5</sub>⋯P<sub>5</sub> π-π-stacking between the *cyclo*-P<sub>5</sub> ligands of the supramolecular host and Cp\*FeP<sub>5</sub> or Cp-containing guest molecules. Usually the guest molecules are disordered, statically or dynamically depending on their nature. Thus, the way of disorder of ferrocene molecule in the central cavity of supramolecular host in [FeCp<sub>2</sub>]<sup>+</sup>@[{Cp\*FeP<sub>5</sub>}]<sub>8</sub>Cu<sub>19.5</sub>Br<sub>19.5</sub>] proved to be temperature-dependent in a range between 5 and 243 K (Fig. 1e).

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