

MS36-P08

Copper based Bio-MOFs: Challenges and possibilities in crystal engineeringMarius Kremer¹, Ulli Englert¹¹. Institute of Inorganic Chemistry, RWTH Aachen University, Aachen, Germanyemail: 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 H₂O 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.

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MS36-P09

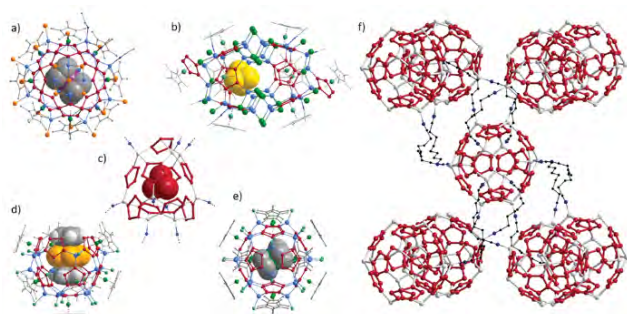
Giant organometallic molecular containersAlexander Virovets¹, Eugenia Peresyphkina¹, Manfred Scheer¹¹. Institute of Inorganic Chemistry, Dept. of Chemistry and Pharmacy, University of Regensburg, Regensburg, Germanyemail: avvirovets@yahoo.com

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^RFe(η⁵-P₅)] (Cp^R = η⁵-C₅R₅, R = Me (Cp*), Me₄Et (Cp^x), CH₂Ph (Cp^{bn}), PhC₄H₉ (Cp^{BlG})). 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⁺ and Ag⁺ cations coordinated to the phosphorus atoms of the *cyclo*-P₅ 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 (P₄) and yellow arsenic (As₄), various metallocenes (e.g., Cp₂Fe, Cp₂Ni, CpVC₇H₇) and triple-decker complexes (e.g. [(CpCr)₂(η⁵-As₅)] and [(CpMo)₂(η³-P₃)(η-PS)]), as well as cage molecules (C₆₀, adamantane, o-carborane, P₄S₃, P₄Se₃) (Fig. 1a-e). The anionic and cationic species also can be encapsulated, like, e.g., the cobaltocenium cation into the negatively charged supramolecule in [CoCp₂]⁺₃{[CoCp₂]⁺@[{Cp*FeP₅}]₈Cu_{24.25}Br_{28.25}(CH₃CN)₆]₄} [2] (Fig. 1a).

The analysis of the host-guest interactions allowed us to reveal their novel types, namely, P₅⋯P₅ and C₅⋯P₅ π-π-stacking between the *cyclo*-P₅ ligands of the supramolecular host and Cp*FeP₅ 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 [FeCp₂]⁺@[{Cp*FeP₅}]₈Cu_{19.5}Br_{19.5}] proved to be temperature-dependent in a range between 5 and 243 K (Fig. 1e).

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MS36-P10

Modifying the RheManTec Triad – a small molecule meanders into the macromolecular world

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Drug development can be approached from numerous angles especially when including the use of transition metal complexes. The utilisation of structural analysis in small molecules can provide a valuable platform whereby additional functionalization of the model pharmaceutical can be evaluated. Particularly when considering the possible bio-activity and receptor binding of the small molecule. Kinetic and mechanistic studies can further describe the coordination tendencies of the small molecule and is critical for understanding reactivity and stability which may be associated to the structural effects. Furthermore to expand the library of information into a system which realistically mimics a biological environment, structural analysis can be conducted by the combination of the small molecules with proteins in a methodology similar to fragment based drug development.

Our research interest is in the modification of bifunctional chelators coordinated to the tricarbonyl complexes of the group 7 Manganese Triad. Particular interest is focused on the radionuclides of ^{99m}technetium(I) and ^{186/188}rhenium(I) for their application in diagnostic or therapeutic nuclear medicine. To this end we have meandered our way from a small molecule study, involving the kinetic and crystallographic properties of the *fac*-[M(CO)₃]⁺ core (M = Re, Tc) and crossed over into the world of macromolecular crystallography. The coordination possibilities of multiple amino acid residues to the *fac*-[Re(CO)₃]⁺ complex in a protein is described. Furthermore, the formation of mono-nuclear versus multi-nuclear complexes can be observed in both small molecule and macromolecular studies.

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