

FA4-MS31-P01

Supramolecular coordination networks of metal polycarboxylate complexes. William Clegg, Rachel Gill, Ross W. Harrington and James M. Holcroft, *School of Chemistry, Newcastle University, U.K.*
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In the last few years we have been investigating structural and physical properties of complexes of a wide range of polycarboxylic acids with many main-group, transition and lanthanide metals. Ligands have 2–6 carboxylate groups and some have other functional groups that can coordinate to metal centres. Since most of the structures are polymeric coordination networks, solubilities are generally low and it has been necessary to develop synthetic methods that generate the products slowly, including solvothermal and ionothermal synthesis and slow diffusion through solid, liquid and gel media. While some crystals can be satisfactorily studied by single-crystal diffraction with standard laboratory equipment, many are very small and require synchrotron facilities, with which we have had considerable success. Structures include 1D (chain), 2D (sheet) and 3D assemblies, some of them with pores or channels containing counterions and/or solvent molecules. The metal-organic frameworks may be charged or neutral. Along with structural characterization by single-crystal diffraction, we have also carried out powder diffraction, thermal and adsorption experiments, and some spectroscopic studies. A selection of results will be presented, illustrating the range of structures and properties found, and trends and relationships that have emerged.

Keywords: supramolecular chemistry, metal-organic frameworks, coordination chemistry

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Oriented supercrystals of anisotropic iron oxide nanoparticles. Sabrina Disch^a, Erik Wetterskog^b, German Salazar-Alvarez^b, Raphaël P. Hermann^{a,c}, Lennart Bergström^b, Thomas Brückel^a, ^a*Institut für Festkörperforschung, JCN S and JARA-FIT, Forschungszentrum Jülich, Germany*, ^b*Department of Materials and Environmental Chemistry, Arrhenius Laboratory, Stockholm University, Sweden*, ^c*Faculty of Science, University of Liège, Belgium*
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Intensive research has been dedicated to magnetic nanostructures, both because of their possible applications, e.g. in medical imaging, catalysis, information storage, and owing to the interest in fundamental understanding of their magnetic properties. Magnetic nanoparticles, compared to bulk materials, show unique physical properties such as superparamagnetism or enhanced anisotropy constants. Self-assembly of nanocrystals into highly ordered superlattices is a widely investigated phenomenon, and its understanding promises new routes for the formation of large-scale ordered structures for nanotechnology. For magnetic nanostructures, assembly techniques involving an external magnetic field have been applied successfully for formation of large and highly ordered nanostructures [1].

In this contribution, the self-orientation of anisotropic iron oxide nanocrystals into long range ordered superstructures will

be presented. We will show that a slight variation of the nanocrystal shape induces a structural phase transition. Detailed structural analysis as performed by grazing incidence small-angle X-ray scattering reveals a superstructure that marks the transition between structures formed by nanospheres and nanocubes.

[1] Ahniyaz, A.; Sakamoto, Y. Bergström, L., *Proc. Natl. Acad. Soc.*, 2007, 104, 17570.

Keywords: self-assembly, nanocrystalline arrays, GISAXS

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A Supramolecular Compound Mimicking the Cu-Containing Active Site of pMMO enzyme. Maciej Grzywa^a, Björn Bredenkötter^a, Dirk Volkmer^a, Wojciech Nitek^b, Jan Sonntag^c, Elias Klemm^c, ^a*Institute of Inorganic Chemistry II, Ulm University, Germany*, ^b*Faculty of Chemistry, Jagiellonian University, Poland*, ^c*Institute of Chemical Technology, Faculty of Chemistry, University of Stuttgart, Germany*
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Porous metal complexes are extensively investigated for their intriguing architectures as well as for the wide range of potential applications in gas storage, separation, purification and heterogeneous catalysis [1], [2].

Structural and functional investigations on transition metal complexes, especially copper species are of great interest due to the fact that multicopper active sites in many natural enzymes take part in catalytic oxidation reactions. For example, particulate methane monooxygenase (pMMO), a membrane-bound metallo-enzyme in methanotrophs catalyzes the conversion of methane to methanol at ambient temperature [3], [4]. Multicopper active sites have been identified in other oxidases, such as laccase [5].

The aim of our research is to synthesize and characterize model compounds which mimic the structure and function of pMMO. We have therefore solvothermally synthesized a new supramolecular complex assembled from 1,2-bis(3,5-dimethyl-1H-pyrazol-4-yl)benzene ligands and four triangular trinuclear copper(I) cores. In the presentation, details about the synthesis, structural characterization, as well as thermal, spectroscopic and gas sorption properties of the title compound will be given.

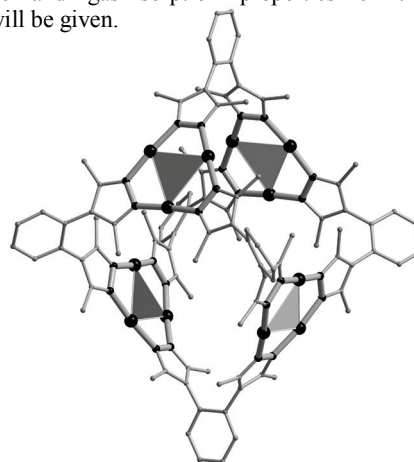


Fig. 1. Coordination unit of a Cu-containing supramolecular compound featuring four fused trinuclear Cu(I) centres. Cu, large black bolls, N small black bolls. For clarity H atoms and solvent molecules were omitted.

[1] Tonigold, M., Lu, Y., Breidenkötter, B., Rieger, B., Bahnmüller, S., Hitzbleck, J., Langstein, G., Volkmer, D., *Angew. Chem. Int. Ed. Engl.* 2009, 48, 7546. [2] Czaja A., et al., *Chem. Soc. Rev.*, 2009, 38, 1284. [3] Que, L., Tolman, W. B., *Nature*, 2008, 455, 333. [4] Lieberman, R., Rosenzweig, A., *Nature* 2005, 434, 177. [5] Chan, S., Yu, S., *Acc. Chem. Res.* 41, 8, 969.

Keywords: copper compounds-1, biomimetics-2, catalyst structure -3

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Defect Engineering in Colloidal Photonic Crystals.

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Imaging of lattice defects in crystalline materials has captured the attention of the scientific community for many decades. Because the size of typical defects is of the order of the lattice period of a crystal, techniques to image stacking faults, dislocations and vacancies have never been able to resolve their structure down to the core level. By crystallizing micron-sized colloidal particles into close-packed structures, we are now able to study crystal structures and defects in real and reciprocal space. We use synchrotron microradian X-ray diffraction to image the average crystal structure over large crystalline areas. Through confocal microscopy, we also have access to the local crystal structure on a single particle level. The combination of these techniques enables us to identify the global crystal structure and explain it through the presence of local defects. Using this approach, we have identified a large concentration of intrinsic stacking faults in colloidal crystals that were previously thought to be pure face-centred cubic in structure. Through confocal microscopy we found Lomer-Cottrell dislocations to be responsible for the nucleation of these stacking faults. Exploiting this growth mechanism, we were able to selectively grow stacking faults into colloidal crystals by sedimentation onto a structured template containing a 2D projection of a Lomer-Cottrell dislocation. This is of interest for the applicability of colloidal crystals as photonic materials.

Keywords: defects, colloids, photonic crystals

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Magnetic Exchange Interactions through H-bonds in Copper(II) Carboxylates.

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Hydrogen bonds and coordination bonds are used as interesting tools for inorganic crystal engineering to build up building blocks that possess their application in supramolecular structures [1]. Some copper(II) complexes, as examples, have shown that the intermolecular hydrogen bonds can modified their magnetic properties [2]. Similar system of hydrogen bonds have been found in some supramolecular isomers [3] of the other copper(II) carboxylate complexes.

We have recently published dinuclear complex $[\text{Cu}(\mu\text{-nia})(5\text{-MeSal})_2(\text{H}_2\text{O})_2]_2$ (nia = nicotinamide, 5-MeSal = 5-methoxysalicylate anions) [4] and mononuclear complex $[\text{Cu}(\text{nia})(3\text{-NO}_2\text{Bz})_2(\text{H}_2\text{O})_2]$ (3-NO₂Bz = 3-nitrobenzoate anion) [5], which exhibit similar magnetic properties. Very similar magnetic properties of mononuclear and binuclear complexes could be explained by the presence of very similar supramolecular synthons that are pathway for the magnetic exchange interactions. The hydrogen bonds, described by supramolecular synthons, formed by coordinated water molecule and two carboxylatogroups on each copper atom could create supramolecular dimers of two mononuclear complex molecules [4] and supramolecular chains of dinuclear complex molecules [5]. In this report we present series of 1-D coordination polymers of general formula $[\text{Cu}(\mu\text{-dena})(\text{RCO}_2)_2(\text{H}_2\text{O})_n]$ (RCO₂ are substituted benzoate or salicylate anions, dena = N,N-diethylnicotinamide) with similar magnetic properties, that are explained as a consequence of the supramolecular synthons allowing to create two dimensional layer structures based on the 1-D coordination polymers bonded by hydrogen bonds. This could be given as the proof, that the hydrogen bonds described above are the main path for observed magnetic exchange and for that reason the similarity in magnetic properties (maximum of susceptibility at similar temperature and the value of antiferromagnetic interactions $2J$) are observed in all complexes, despite they are of different crystal structures, and different dimensionality (monomeric, dimeric, or polymeric).

[1] Beatty A.M., *Coord. Chem. Rev.*, 2003, 246, 131. [2] Yamada Y., Ueyama N., Okamura T., Mori W., Nakamura A., *Inorg. Chim. Acta*, 1998, 275-276, 43. [3] Abourahma H., Moulton B., Kratsov V., Zaworotko M.J., *J. Am. Chem. Soc.*, 2002, 124, 9990. [4] Valigura D., Moncol J., Korabik M., Púčková Z., Lis T., Mroziński J., Melnik M., *Eur. J. Inorg. Chem.*, 2006, 3813. [5] Vasková Z., Moncol J., Korabik M., Valigura D., Svorec J., Lis T., Valko M., Melnik M., *Polyhedron*, 2010, 29, 154.

Keywords: crystal structure, hydrogen bonds, magnetic exchange interactions

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Cocrystals of flucytosine: Models for drug-receptor interactions.

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Flucytosine (5-fluorocytosine) is a systemic antifungal drug. It is intrafungally converted into 5-fluorouracil and inhibits RNA and DNA synthesis [1]. Furthermore, it has a novel application as a prodrug active against liver tumours [2]. The interaction between flucytosine and its receptor, as well as the base pairing, can be imitated by hydrogen-bonded complexes [3]. In order to examine these interactions we cocrystallized flucytosine together with several model compounds containing complementary functional groups and studied the preferred conformations adopted by the model compounds.

Since the cocrystallization of supramolecular complexes is not a straightforward procedure, we have developed a concept for designing these structures. After selection of model compounds, we calculate the structures and energies of a multitude of alignments ("constellations") by our force-field program MOMO [4]. Various analytical tools (especially IR spectroscopy and powder diffraction) are used to identify the