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Keywords: Bioinorganic, Copper, Complex

MS24.P87

Discrete and Polymeric Metal-Organic Systems Based on the Methanetriacetic Acid

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The construction of multidimensional frameworks and the design of infinite MOF'S with transition metal ions and lanthanides is a field of great interest due to the applications that can be developed from these new materials. Carboxylic acids with specific geometries can be used to generate topological networks by design. In this work we have focused on the methanetriacetic acid, a tricarboxylate with a C_3-symmetry whose arms can coordinate to different number of metal nuclei as it has been recently reported in a series of gadolinium(III) complexes [1]. However, now we have turned our attention not only to the design of polymeric systems based on the methanetriacetic acid, but also to discrete systems taking into account the tritopic nature of the ligand to coordinate with three elements and using blocking ligands.

Here we present a series of copper(II) complexes of different dimensionalities that show the coordination chemistry that can be done with the methanetriacetate ligand. The conditions of the synthesis, mainly the stoichiometry of the reaction, afforded Cu(II) compounds whose crystal structure and magnetic properties have been investigated.
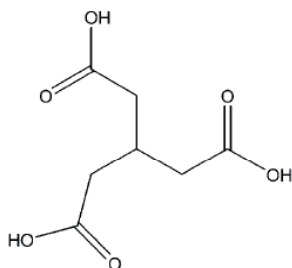
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Keywords: copper, crystal structure, carboxylic acids.

MS25.P01

Creating nothing out of something: thermolabile groups in metal-organic frameworks (MOFs)

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We are interested in the 'reverse' post-synthetic modification of MOFs, *viz* the expulsion of functional groups whilst conserving framework crystallinity and enhancing porosity [1, 2]. This can be accomplished using specifially designed thermolabile and photolabile ligand side-arms. In this talk I will outline our recent results in this area. We have found that when thermo/photolabile groups are tethered to various biphenyl-4,4'-dicarboxylate ligands, we observe several interesting and useful outcomes, for example (i) the suppression of network interpenetration (catenation), (ii) the expansion of cavities and apertures within the framework, (iii) the unmasking of useful functional groups that are located on the surface of this void space, and (iv) the synthesis of MOFs that cannot be prepared directly. This methodology has been extended to the preparation of chiral, catalytically-active MOFs.
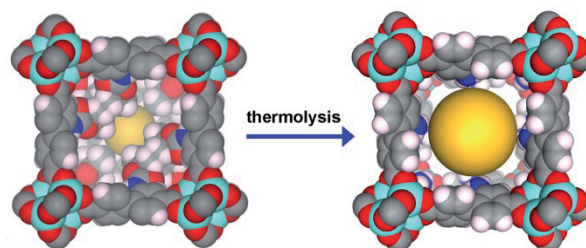
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Keywords: metal-organic frameworks, porous materials, catalysis

MS25.P02

The structural chemistry of nano-crystalline ferrihydrite

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Nano-crystalline oxyhyroxides are implicated in a variety of processes, including toxic metal sequestration, sorption, acid-mine drainage, and the global iron and sulfur cycles [1,2]. The composition, single-phase nature and atomic arrangements in nano-crystalline ferrihydrite have been controversial for at least 50 years [3-6]. Contrary to previous reports [5], the scattering data from nano-crystalline ferrihydrite is consistent with a single-phase model [6], greatly simplifying modeling of local and global cycles. Considerable debate still surrounds the atomic arrangement in ferrihydrite [5-8]. A growing body of evidence, gleaned from a combination of structural and thermal probes, confirms the composition of ferrihydrite is close to $Fe_{10}O_{14}(OH)_2$ and that a single-phase model suffices for explanation of the atomic arrangement in inorganically and biologically derived 2- and 6-line varieties.

The kernel of the debate over appropriate structural models for ferrihydrite boils down to the presence [4,6,7], or not [5,8], of iron(III) in the tetrahedral environment. Real space modeling of the pair distribution function (PDF) derived from analysis of the total high-energy elastic x-ray and neutron scattering has been particularly instructive in this regard. While muti-phase models [5,8] have been used in the past, there are features in the PDF of ferrihydrite, that are inconsistent with both single and multiphase models that do not include a component of tetrahedral coordination for Fe(III). In particular a 3.44Å peak in the X-ray PDF is observed in ferrihydrite. Only the x-ray PDFs for minerals containing tetrahedral Fe(III), maghemite and magnetite, contain peaks close to this value of *r*. Multi-phase models containing only octahedral Fe(III) cannot produce a strong 3.44Å

correlation, without producing even stronger 1.99Å (Fe-O) or 3.0Å (Fe-Fe vector from edge-sharing octahedra) correlations. The strong 3.44Å correlation is key since it suggests not only the presence of tetrahedrally coordinated Fe(III) but the presence of a Keggin cluster-like configuration with ^{IV}Fe(III) apex-sharing with the surrounding 12 ^{VI}Fe(III). Such a configuration maximize the intensity of the 3.44Å peak while keeping the edge-sharing Fe-Fe pair numbers, contributing to the peak at 3Å, low. Structural models containing phases with only Fe in 6-fold coordination, regardless of the number of phases added to the model, fit the XN data poorly.

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MS25.P03

### Modular assembly of porous organic materials

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The possibility of applications in areas such as catalysis, gas storage and separation has fuelled intensive research into the development of porous materials, in particular molecular and hybrid frameworks [1-3]. Much progress has been made with framework materials in terms of controlling properties such as pore size [2], but programmed placement of accessible functionality has proved more challenging [4], due in part to the 'one pot' synthetic methods employed.

An alternative strategy is the use of prefabricated porous components to assemble an array of specifically functionalised pores. Our work on organic cages has shown that these metal-free covalent molecules crystallise to form solids with permanent porosity. This results from the inherent cage voids and inefficiency in cage packing [5]. A wide synthetic diversity is available to tune both the internal pore size and the packing of the cage molecules by exploiting steric and non-covalent interactions of groups at the cage apices. These materials also exhibit solid state structural diversity, with a number of solvates and polymorphs being observed. For example, 'on-off porosity' switching [6] results from the capacity of these materials to undergo solid state transformations in response to the presence of chemical triggers.

Recent work has realised the potential to combine cages with different functionalities to achieve the modular assembly of porous materials from discrete cage components [7]. Simple mixing of the constituent prefabricated cages in solvent results in self-assembly of highly porous cocrystals, driven by chiral recognition. This highlights a promising new modular strategy for the design and synthesis of porous functional materials.

Crystal structures of porous organic crystals of (from left) quasiracemic cage cocrystal, (**1**-*S*, **3**-*R*), racemic cage, (**3**-*S*, **3**-*R*), and chiral cage, **5**-*R*.
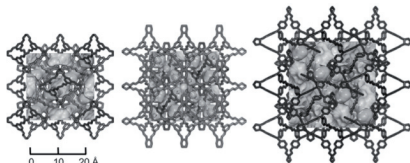
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## MS25.P04

Zeolitic tetrazolate framework (ZTF) with high capacity storage of carbondioxide

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Selective carbon dioxide capture from coal-fired power plant is critical issues as these plants produce post-combustion flue gases with ~15% CO_2 concentration [1]. At present, the separation of CO_2 from such a low pressure stream of gases is performed by amine sorbents through chemisorptions [2]. We describe herein, for the first time, the isolation of a three dimensional amino functionalized Zeolitic Tetrazolate Framework (ZTF-1) where N1 and N4 are coordinated to metal centers (M–TET–M angle is close to 145°, coincident with the Si–O–Si angle) and adopt a tetrahedral framework reminiscent of those found in zeolites. This is the first report of a –NH_2 functionalized MOF among different metal imidazolates/triazolates/tetrazolates where only N1 and N4 are coordinated to tetrahedral metal centers with M–L–M angle is close to 145°. The framework adopts a dia topology. ZTF-1 shows high CO_2 (273K) and H_2 (77K) uptake due to the presence of free –NH_2 group and uncoordinated tetrazolate nitrogen [3].
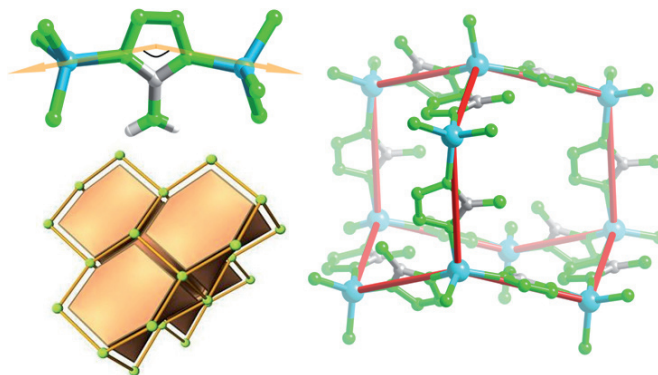
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