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**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 methanetricarboxylic acid, a tricarboxylate with a C3-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 methanetricarboxylic 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 methanetricarboxylate 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.

**Keywords:** Bioinorganic, Copper, Complex

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**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 specifically 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.

**Keywords:** metal-organic frameworks, porous materials, catalysis

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**The structural chemistry of nano-crystalline ferricydrhyde**

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Nano-crystalline oxyhydroxides are implicated in a variety of processes, including toxic metal sequestration, sorption, acidine drainage, and the global iron and sulfur cycles [1,2]. The composition, single-phase nature and atomic arrangements in nano-crystalline ferricydrhyde have been controversial for at least 50 years [3-6]. Contrary to previous reports [5], the scattering data from nano-crystalline ferricydrhyde is consistent with a single-phase model [6], greatly simplifying modeling of local and global cycles. Considerable debate still surrounds the atomic arrangement in ferricydrhyde [5-8]. A growing body of evidence, gleaned from a combination of structural and thermal probes, confirms the composition of ferricydrhyde is close to Fe3O4(OH), 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 ferricydrhyde 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 multi-phase models [5,8] have been used in the past, there are features in the PDF of ferricydrhyde, that are inconsistent with both single and multiphase models that do not include a component of tetrahedral coordination for Fe(III). In particular a 3.44 Å peak in the X-ray PDF is observed in ferricydrhyde. 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 3.44 Å peak in the X-ray PDF.

**Keywords:** metal-organic frameworks, porous materials, catalysis

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