

P.11.14.2*Acta Cryst.* (2005). A61, C402**A New, Rapid 3D Tomographic Energy Dispersive Diffraction Imaging System for Materials Characterisation and Object Imaging (Rapid TEDDI)**Kern Khor, Robert Cernik, *School of Materials, Manchester, UK and Daresbury Laboratory, Warrington, UK.* E-mail: r.j.cernik@dl.ac.uk

In 1998 Hall et al [1] demonstrated that the interior features of solid objects could be very effectively and simply imaged in a non-destructive manner using synchrotron energy dispersive diffraction. They were able to demonstrate big improvements over the measurements obtained by Harding [2] who used conventional rotating anode X-ray sources. Both papers demonstrate the huge potential of (TEDDI) in materials science. Although there are many forms of tomo-graphic imaging, virtually all rely on absorptive or spectroscopic responses of a material object to invading radiation. By contrast TEDDI is unique in using both diffraction and absorption or diffraction and spectroscopic data. A white beam from a synchrotron or laboratory X-ray source is collimated to the desired spatial resolution. The small diffracting sample volume is defined by the track of the incident and scattered beams through the sample and the angle subtended by the collimator aperture. The sample is scanned in 3 dimensions in small steps. This is, however, a very time consuming process. As a consequence we are developing array solid state detectors with corresponding collimator arrays that can reduce the time for object scanning from 14 hours to a few minutes. In this way a 3D density contrast map will be obtained with full structural and chemical information at each voxel point. This development will be explained in more detail in the context of a wide range of diverse applications.

[1] Hall C., Barnes P., et al, *Nuclear Instruments & Methods in Physics Research Section B-beam interactions with materials and atoms*, 1998, **140**, 253-257. [2] Harding G, et al, *Physics in Medicine and Biology*, 1990, **35**, 33-41.

Keywords: synchrotron, materials, tomography**P.11.15.1***Acta Cryst.* (2005). A61, C402**Synthesis and Structural Characterization of Novel Metal-Organic Frameworks**Hyunsoo Park^a, David M. Moureau^a, John B. Parise^{a,b}, ^a*Department of Chemistry, SUNY Stony Brook.* ^b*Department of Geosciences, SUNY Stony Brook, NY, USA.* E-mail: hypark@notes.cc.sunysb.edu

Studies of structurally and chemically diverse open framework solids have been flourishing in the recent years in an attempt to increase and improve applications of such materials in areas such as catalysis, sorption and ion-exchange. Our research is aimed at finding new 3-dimensional porous frameworks, which may possess interesting physical properties. We report the hydrothermal synthesis and structural characterization of several new metal-organic hybrid frameworks constructed from various metal cations and organic ligands of different functionalities.

For example, $Zn_2(C_2H_2N_3)_2(C_8H_4O_4) \cdot H_2O$, synthesized using 1,2,4-triazole and 1,4-benzenedicarboxylic acid as organic linkers, possesses a structure (P4/ncc, $a = 13.521(2) \text{ \AA}$, $c = 27.221(5) \text{ \AA}$, $Z = 8$) based on the sheets containing 8-membered rings of $ZnON_3$ tetrahedra and triazole molecules along the (001) direction. The sheets are connected by benzenedicarboxylates through Zn – O – C links to produce channels which are occupied by water molecules. Its thermal behavior has also been characterized by thermogravimetric analysis. It is stable up to 300°C before the organic molecules start to decompose, leading to the framework collapse.

Keywords: materials structure and characterization, porous materials, X-ray crystallography**P.11.15.2***Acta Cryst.* (2005). A61, C402**Spin-Crossover and Nanoporosity: Magnetic, Structural and Guest-Exchange Studies**Natasha F. Sciortino, Cameron J. Kepert, *Department of Chemistry,**University of Sydney.* E-mail: sciort_n@chem.usyd.edu.au

Spin-crossover and permanent nanoporosity describe two highly desirable and traditionally independent properties concerning the design, synthesis and characterisation of functional coordination framework materials. By integrating these properties, we are developing a new series of *smart* materials capable of a physical response to their environment. Such capabilities include guest-induced electronic, magnetic and optical switching with applications towards chemical sensors, molecular switches and data storage materials.

The new network $[Fe(dps)_2Ag(CN)_2ClO_4] \cdot 3(C_2H_6O)$ (**1**) ($dps = 4,4'$ -dipyridylsulfide) is the first three-dimensional framework to display a synergy of spin-crossover and nanoporosity (~46% void volume). Variable-temperature single-crystal X-ray diffraction (SCXRD) techniques were employed over the range 90 K-300 K to elucidate the structural consequences of a reversible low-spin to high-spin transition. Modified *in-situ* SCXRD techniques were used to observe the implications of guest-exchange on structural integrity and spin-crossover functionality.

Several unique properties of **1** have been demonstrated: 1) complete spin transition, incurring a 7.7% crystal volume change; 2) robustness to desorption at 375 K, with complete retention of structural integrity; and 3) sensitivity of spin-crossover to the presence of guest species. Additional guest-exchange studies also establish **1** to be a highly nanoporous framework that exhibits rapid, reversible and complete sorption/desorption of a range of small molecules.

Keywords: spin-crossover, nanoporosity, *in situ* SCXRD**P.11.15.3***Acta Cryst.* (2005). A61, C402**In situ Control of Guest Exchange in Single Crystal X-ray Diffraction**Joseph J. Bevitt, Cameron J. Kepert, *School of Chemistry, The University of Sydney.* E-mail: bevitt_j@chem.usyd.edu.au

By variation of template, with novel *in-situ* variable temperature Single Crystal X-ray Diffraction techniques we demonstrate the reversible nature of guest uptake by a coordination polymer, confirming their analogy with zeolites. Our work also demonstrates the subtle changes imposed on the host framework due to various guests (including 1-propanol, carbon dioxide, dinitrogen and argon) and their occupancies, quantifying the extent of host-guest interactions. Host distortions include asymmetric layer shifts of up to 0.7 Å, framework 'scissoring', ligand torsion angle changes, changes in nitrate binding and host symmetry. We present our techniques and demonstrate their applicability to the study of dynamic structures.

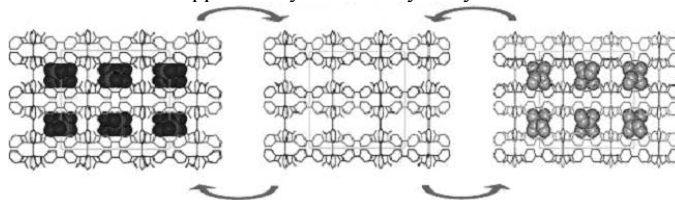


Figure: Reversible exchange of guests into the evacuated framework is achieved through repeated heating and cooling of sample under guest atmospheres.

Keywords: guest exchange, *in-situ* experiments, gas sorption**P.11.15.4***Acta Cryst.* (2005). A61, C402-C403**Two new Inorganic-organic Hybrids with Framework Gallium 1,2-ethylenediphosphonates Containing Pyridine**Zhanhui Yuan^a, William Clegg^a, Martin Attfield^b, ^a*School of Natural Sciences - Chemistry, University of Newcastle upon Tyne, UK.* ^b*Centre for Microporous Materials, University of Manchester, UK.* E-mail: zhanhui.yuan@ncl.ac.uk

This paper reports the synthesis of two new open framework gallium 1,2-ethylenediphosphonate materials which contain open zeolite like structure linked to form a completely novel type of open framework architecture with interconnecting channels. The new materials are templated by pyridine. As far as we know, the new

structure $[\text{Ga}_3\text{F}(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_2](\text{C}_5\text{H}_5\text{N})$ (**I**) is not currently known, and the nitrogen atom from the pyridine molecular has coordinated with metal gallium to form strong N-Ga bonds in an octahedral GaO_4FN unit, and pyridine molecules sit in the channels which are formed by building unit, connected by diphosphonate. The structure $[\text{Ga}_4\text{F}_2(\text{O}_3\text{PC}_2\text{H}_4\text{PO}_3)_3]^{2-} 2[\text{C}_5\text{H}_5\text{N}]^+$ (**II**) contains pyridine cations within the channels formed by building unit, connected by diphosphonate and has a stronger hydrogen contact between oxygen from diphosphonate and nitrogen from pyridine. The new structures (**I**) and (**II**) are good examples to present three dimensional structures with channels constructed by two novel building units connecting diphosphonate groups, and two kinds of pyridine moieties. One pyridine has linked through Ga-N bond and another is free as cation, which has been found in channels as a template. The two materials exhibit microporous frame-work materials with pyridine template within the pores.

Keywords: gallium 1,2-ethylenediphosphonate, framework, pyridine

P.11.15.5

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Mechanism of Phase Transition Caused by Water Absorption in FAPO-34

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It was made clear that the phase transition mechanism caused by the water absorption in FAPO-34 using the single-crystal X-ray (SCX) analysis and EXAFS Fourier transform spectra analysis.

FAPO-34 is known as the one of the Chabazite type zeolite. [1] The crystals of FAPO-34 including organic template in the framework (**as-made**) were obtained by hydrothermal synthesis method. To utilize as the water absorption material, the **as-made** crystals were baked in some temperature conditions to remove the organic template. The **as-made** crystals baked at high temperature (**HT**) caused phase transition, but the one baked at low temperature (**LT**) kept the structure after the water absorption.

As the results of SCX and EXAFS analysis, it was made clear that the specific water coordination to Fe on the framework causes the phase transition of **HT**. SCX analysis showed the direct coordination of the water to Al and Fe on the framework and the structural skew of the framework caused by the specific water coordination to Fe of **HT**. EXAFS analysis showed that Fe of **LT** is covered by something else other than water.

[1] Ristic A., Tusar N.N., Arcon I., Thibault-Starzyk F., Hanzel D., Czyniewska J., Kaucic V., *Micropor. Mesopor. Mater.*, 2002, **56**, 303-315.

Keywords: absorption material, phase transitions, structure analysis

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Direct Observation of Hydrogen Molecules adsorbed in a Coordination Polymer

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Hydrogen is a very important material for the development of a clean energy system. The use of physisorption in microporous coordination polymers is one of the most promising candidates for the hydrogen gas storage. The fundamental structural information of adsorbed H_2 molecules is indispensable for the rational synthetic strategy of these materials. Although the weakest X-ray scattering amplitude of hydrogen has made it difficult to determine the structure of H_2 molecules, we have succeeded in direct observation of H_2 molecules adsorbed in the nanochannels of the coordination polymer

by the *in-situ* synchrotron powder diffraction experiment of gas adsorption and the MEM/Rietveld charge density analysis [1].

The H_2 molecules were found to be adsorbed without any chemical bonding to the host framework, in the condition that they can be easily adsorbed and released. The position of H_2 molecule was displaced from the center of the nanochannel. It was located near the metal-oxygen unit near one corner of the rectangular nanochannel. The size of the H_2 molecule is suited to the size of the pocket of the cavity. The structural information of H_2 molecule at the beginning stage of gas adsorption was obtained. That gives us the guideline for the design of high performance hydrogen gas storage materials.

[1] Y. Kubota, et al., *Angew. Chem. Int. Ed.*, 2005, **44**, 290-293.

Keywords: gas storage materials, microporous coordination polymer, synchrotron powder diffraction

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Magnetic and Structural Properties of Rare Earth Hybrid Frameworks

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Aliphatic dicarboxylates (**AD**), $-\text{O}_2\text{C}(\text{CH}_2)_n\text{CO}_2-$, have shown to be excellent ligands for crystal engineering transition metal molecular magnets [1]. With the aim of extending these studies to rare earth systems we have synthesized a series of organic inorganic hybrids of Ln(III) and **AD** anions, with $1 \leq n \leq 4$, from solutions under ambient conditions. Their single crystal x ray structural analysis show the formation of inorganic polymeric arrangements of different dimensionalities. AC susceptibility, χ' , measurements performed within the temperature range $13 < T < 330\text{K}$ show noticeable changes in the $\chi'T$ curve slope at different T values. To investigate the potential structural contribution to those magnetic ordering variations, we performed single crystal x-ray analysis in the temperature ranges of interest in steps of 2K. We discuss possible links between modifications in superexchange paths connecting cations —and eventually in hydrogen bonds networks— and magnetic response.

[1] Rodríguez-Martín Y., et al., *Cryst Eng Comm*, 2002, **87**, 522.

Keywords: organic inorganic hybrid materials, framework structures, molecular magnets

P.11.15.8

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Novel Modular Coordination Frameworks

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Crystal Engineering of Coordination Frameworks has been experiencing a great growth in recent years. Despite the majority of the compounds reported in the literature could only be usually isolated in small amounts due to inherent limitations of the synthetic techniques employed, we have optimised the hydrothermal synthetic approach for the synthesis of large and phase-pure quantities of such materials [1]. N-(phosphonomethyl)iminodiacetic and etidronic acids are precursors of multidentate organic ligands which not only exhibit unusual and flexible coordination properties, but also contain a number of potentially interesting nuclei to study using, e.g., solid-state NMR techniques. We have focused our research in the *in situ* synthesis of rigid building blocks (*i.e.*, Secondary Building Units, SBUs) formed by these ligands and V^{4+} which, along with various metal centres (e.g., Co^{2+} , Mn^{2+} and Ce^{3+}) and rod-like bridging organic molecules (such as 4,4'-bipyridine and pyrazine), self-assemble into peculiar frameworks of various topologies and dimensionalities [2], [3].