resulting in high selectivity for guest inclusion or multi-step adsorption behaviors.[2-4] Dynamic effects can arise either locally from flexible ligands and/or flexibility of the coordination geometry of the metal ions, or from the global cooperative movement of the framework on a periodic scale. The mechanism of the dynamics of flexible PCPs was investigated by a coincident adsorption/X-ray powder diffraction measurement system.

In addition, we will report a new photo-responsive PCP composed of azide modules as dormant precursors. The pore surface of PCP can be activated by UV irradiation and the resulting reactive species were regularly arranged in the framework, which was observed not only by spectroscopic measurements but also crystallographic analysis using synchrotron X-ray diffraction data. The highly reactive species can react or interact with gust molecules. According to the result of adsorption measurement under photoirradiation, we found that the adsorption activity for oxygen was significantly improved by photoirradiation.[5]

[1] R. Matsuda, T. Tsujino, H. Sato, Y. Kubota, K. Morishige, M. Takata, S. Kitagawa, *Chem. Sci.* **2010**, *1*, 315-321. [2] S. Shimomura, M. Higuchi, R. Matsuda, K. Yoneda, Y. Hijikata, Y. Kubota, Y. Mita, J. Kim, M. Takata, S. Kitagawa, *Nature Chem.* **2010**, *2*, 633-637. [3] S. Bureekaew, H. Sato, R. Matsuda, Y. Kubota, R. Hirose, J. Kim, K. Kato, M. Takata, S. Kitagawa, *Angew. Chem., Int. Ed.* **2010**, *49*, 7660-7664. [4] J. Seo, R. Matsuda, H. Sakamoto, C. Bonneau, S. Kitagawa, *J. Am. Chem. Soc.* **2009**, *131*, 12792-12800. [5] H. Sato, R. Matsuda, K. Sugimoto, M. Takata, S. Kitagawa, *Nature Mater.* **2010**, *9*, 661-666.

Keywords: coordination, microporous, adsorption

MS.38.3

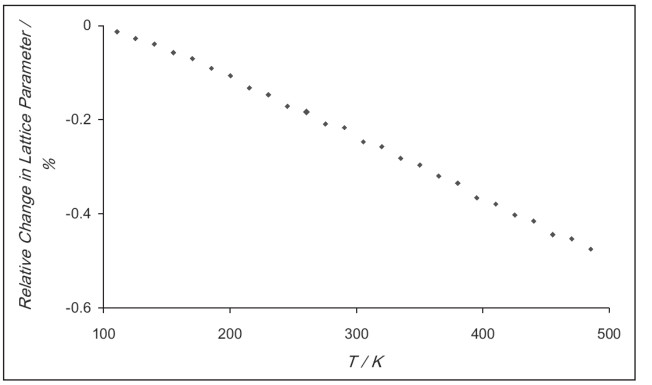
Acta Cryst. (2011) A**67,** C94

Negative thermal expansion in porous framework materials

Lisa J. Cameron, David J. Price, Cameron J. Kepert, *School of Chemistry, The University of Sydney, NSW, (Australia).* E-mail: l.cameron@chem.usyd.edu.au

The recent interest in metal-organic frameworks (MOFs) has stemmed from their wide range of potential applications, from gas storage devices to drug delivery systems [1]. Here we focus on a selection of MOFs that display the unusual property of negative thermal expansion (NTE; i.e., contraction upon warming). NTE materials have potential applications in composite materials that show zero thermal expansion over wide temperature ranges, thus being suitable for high precision instruments that are affected by thermal expansion. Through establishing mechanisms for NTE and investigating how systematic structure changes affect the size of the NTE, materials may be tailored to meet specific needs.

In this study members of the IRMOF series of compounds were investigated. These materials share a common tetranuclear metal cluster, $Zn_4O(carboxylate)_6$, bridged by varying dicarboxylate ligands. Synchrotron powder X-ray diffraction (S-PXRD) reveals the materials show linear thermal expansion from 500 – 100K, with all except one investigated here exhibiting NTE. Through comparison of the coefficients of thermal expansion (CTEs) the impact on the NTE of the variations in structure has been observed. The use of single crystal X-ray diffraction (SCXRD) to compare bond lengths at varying temperatures has also provided valuable insight into the mechanisms responsible for NTE in these multi-hinged structures.



[1] R.J. Kuppler, D.J. Timmons, Q.-R. Fang, J.-R. Li, T. A. Makal, M.D. Young, D. Yuan, D. Zhao, W. Zhuang, H.-C. Zhou, *Coordination Chemistry Reviews* **2009**, *253*, 3042.

Keywords: framework, NTE, porosity

MS.38.4

Acta Cryst. (2011) A**67,** C94-C95

Tuning of the structural flexibility and chemical properties of the MIL53-Al and MIL47-V

Kirill Yusenko, Olesia Kozachuk, Roland A. Fischer *Inorganic Chemistry II, Ruhr-University Bochum, (Germany).* E-mail: roland.fischer@rub.de

The Porous Coordination Polymers (PCPs) or Metal-Organic Frameworks (MOFs) are a unique class of hybrid solid-state materials with bright future due to their permanent porosity and high thermal stability. The use of these materials ranges from gas storage, separation and catalysis, to a number of diverse potential applications, including optoelectronics, sensors, smart membranes etc. To incorporate the new functions into the 1-D channel PCPs we performed detailed study of the broad series of inclusion compounds into $[Al(OH)(bdc)]_n$ (MIL53-Al) and $[V(O)(bdc)]_n$ (MIL47-V) [1], [2], [3]. $[Al(OH)(bdc)]_n$ shows a well-pronounced breathing effect on the contrary to $[V(O)(bdc)]_n$ which demonstrates neither breathing effect but has well documented catalytical and electrochemical activities. Nevertheless, both phases have the same framework topology, which makes possible to prepare mixed Al/V frameworks in a broad concentration range.

Here, we present our results obtained in the course of preparation and investigation of the mixed metal $[\{Al(OH)\}_x/\{V(O)\}_{1-x}(bdc)]_n$ and $[\{Al(OH)\}_x/\{V(O)\}_{1-x}(ndc)]_n$ ($0<x<1$, bdc = benzeneterephthalate, ndc = naphtaleneterephthalate) phases which show new structural and chemical features. Crystal structures, flexibility and inclusion phenomenon were investigated in details using PXRD, spectroscopic and electrochemical techniques. Structural characteristics (cell parameters and volume) show linear dependence on the composition in the whole range. On the other hand, structural flexibility and stability show behavior characteristic for $[V(O)(bdc)]_n$. Inclusion compounds Cobaltocene@$[\{Al(OH)\}_x/\{V(O)\}_{1-x}(bdc)]_n$andbenzene@$[\{Al(OH)\}_x/\{V(O)\}_{1-x}(bdc)]_n$ were synthesized to characterize chemical properties and flexibility of the mixed-metal phases. Crystal structures of the inclusion compounds were also solved using PXRD technique. Guests molecules are localized in the middle of the 1-D channel and their positions show flexibility of the framework induced by the framework reduction and charge transfer between cobaltocene and vanadium centers of the backbone. The phases obtained proposed as electrochemically, magnetic and catalytically active porous materials with CO_2 vs. N_2 selectivity.

[1] M. Meilikhov, K. Yusenko, R.A. Fischer, *Dalton Trans.*, **2009**, 600. [2]

M. Meilikhov, K. Yusenko, R.A. Fischer, *Dalton Trans.*, **2010,** 10990. [3] M. Meilikhov, K. Yusenko, A. Torrisi, et al., *Angew. Chem. (Int.Ed.)*, **2010**, 6212.

Keywords: coordination polymers, host-guest complexes, powder structure determination

MS.38.5

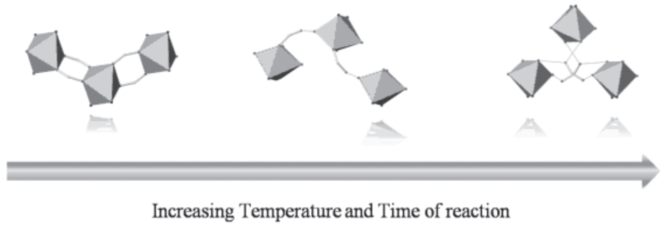
Acta Cryst. (2011) A**67,** C95

The role of synthesis conditions on SBU condensation of Mg polymeric frameworks

Ana E. Platero-Prats,[a] Víctor A. de la Peña-O'Shea,[b] Davide M. Proserpio,[c] Natalia Snejko,[a] Ángeles Monge,[a] Enrique Gutiérrez-Puebla,[a] [a]*Departamento de Nuevas Arquitecturas en Química de Materiales, Instituto de Ciencia de Materiales de Madrid, CSIC, Madrid (Spain).* [b]*Unidad de Procesos termoquímicos, Instituto Madrileño de Estudios Avanzados en Energía (IMDEA Energía), Móstoles (Spain).* [c]*Dipartimento di Chimica Strutturale e Stereochimica Inorganica, Università degli Studi di Milano, Milano (Italy).* E-mail: aplatero@icmm.csic.es

Metal-Organic Frameworks (MOFs) represent an extensive group of materials where inorganic secondary building units (SBUs) are interconnected through organic linkers with different functionalities (carboxylates, sulfonates, imidazolates, among others) [1]. Within the applications that have been described for these materials, it is worth highlighting their use in drug delivery, gas/vapour storage/separation and heterogeneous catalysis. In this sense, while the use of transition metals and rare-earth elements is widely known, alkaline-earth metals (AE) have been less considered as suitable coordination centres to obtain new MOFs. However, the advantages that would mean the obtaining of AE MOFs (especially those based on magnesium and calcium [2], [3]) are clear: their low price and the absence of environmental toxicity attributed to these elements.

At present, we are engaged in the obtaining of new Alkaline Earth Polymeric Frameworks (AEPF) based on flexible ligands, which have been yet proved to provoke interesting polymorphism phenomena in MOFs. We present here a peculiar case where the use of a flexible fluoride dicarboxylate ligand (4,4'-hexafluoroisopropylidene) and an additional aromatic nitrogenated ligand (1,10-phenantroline) has given rise to four new phases, for which the inorganic SBUs present different degrees of condensation. Herein, we show the role that play the synthesis conditions on the obtaining of different structural properties, allow us to successfully tackle the synthesis of new AEPFs. Thus, four different Mg-PF materials, which exhibit three- and two- dimensional supramolecular frameworks, were obtained by controlling the synthesis conditions: **i)** a molecular Mg(II) material with polymorphism (**AEPF-6**, α- and β- phases), **ii)** a 1-D Mg(II) MOF (**AEPF-7**) and **iii)** a 1-D helical Mg(II) MOF (**AEPF-8**). A combination of structural and topological comparative analyses with computational studies was performed to depict the structural an energetically processes involved in the synthesis mechanism of these networks.



[1] Metal-Organic Frameworks themed issue, *Chem. Soc. Rev.* **2009**, *38*. [2] A.E. Platero Prats, V.A. de la Peña-O'Shea, N. Snejko, A. Monge, E. Gutiérrez-Puebla, *Chem. Eur. J.* **2010**, *16,* 11632 [3] A.E. Platero Prats, V.A. de la Peña-O'Shea, M. Iglesias, N. Snejko, A. Monge, E. Gutiérrez-Puebla, *Chem. Cat. Chem*. **2010**, *2,* 147.

Keywords: alkaline-earth metals, topology, theoretical calculations

MS.39.1

Acta Cryst. (2011) A**67,** C95

The structure and dynamics of hydrogen storage materials based on boron and nitrogen

Mark Bowden,[a] Bill David,[b,c] Kate Ryan,[c] Martin Jones,[c,b] Gregory Schenter,[a] Tom Autrey,[a] [a]*Pacific Northwest National Laboratory, Richland WA, (USA).* [b]*Rutherford Appleton Laboratory, Oxford (UK)* [c]*Inorganic Chemistry Laboratory, University of Oxford, Oxford (UK).* E-mail: mark.bowden@pnl.gov

Compounds based on boron, nitrogen and hydrogen are promising candidates for chemical storage of hydrogen. They possess high volumetric and gravimetric storage capacities, and can release hydrogen at relatively low temperatures (less than 200 °C). The crystal structures of these materials are characterised by a high degree of mobility, especially in the positions of hydrogen atoms. The temperature dependence of this mobility results in a number of phase transitions which we have investigated through neutron and X-ray powder diffraction studies, coupled with molecular dynamics simulations and ^{2}H NMR lineshape analysis.

The orthorhombic-tetragonal phase transition of ammonia borane (NH_3BH_3) takes place because of a dynamic reorientation of the NH_3BH_3 molecules about a 4-fold axis at temperatures greater than 225 K. Above ca. 335 K the reorientation becomes more facile and the structure is akin to the "rotator phases" observed for n-alkanes. This high temperature transition is a key step in the thermal release of hydrogen from ammonia borane.

Ammonium borohydride ($[NH_4]^+[BH_4]^-$) has N and B atoms arranged in a rock salt configuration, but the overall symmetry is dictated by the arrangement and dynamics of hydrogen. We have observed a series of phase transitions as ammonium borohydride is cooled and the hydrogen atoms become fixed in a fewer number of positions. Related ionic structures investigated include the diammoniate of diborane ($[NH_3BH_2NH_3]^+[BH_4]^-$) and methylammonium borohydride. The former compound has relatively little hydrogen dynamics, limited to reorientation of the BH_4^-groups, but is subtly different from the related chloride. The latter compound exhibits considerable rotational hydrogen disorder and bears a strong resemblance to the analogous halides. X-ray Rietveld refinements of these ionic light element compounds are improved by correct distribution of electron density away from the positively charged amine groups toward the negatively charged borohydride.

.

Keywords: hydrogen storage, dynamics, phase transitions

MS.39.2

Acta Cryst. (2011) A**67,** C95-C96

Synchrotron x-rays and neutrons as essential tools in Li battery research: new structures and new properties of LiFePO4-based cathodes

C. Masquelier,[a] C. Masquelier, S. Hamelet,[a] M. Casas Cabanas,[a,b] J.M. Tarascon,[a] [a]*Université de Picardie Jules Verne, Amiens, (France).* [b]*University of Antwerp, (Belgium).* E-mail: Christian.masquelier@u-picardie.fr