

MS.73.2*Acta Cryst.* (2008). A64, C125**In-situ reactivity and selective chiral sorption in metal-organic frameworks**Matthew J Rosseinsky

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The precisely defined interior cavities of porous metal-organic frameworks with a high degree of chemical diversity are attractive for selective sorption. We describe a family of amino-acid based open frameworks (1) which display chirally selective sorption that is highly specific to the functional group disposition within the sorbed molecules. The nature of the interaction between the framework and sorbate is revealed by computational approaches used in protein-ligand docking. The cavities within metal-organic framework materials are also attractive hosts for the observation of chemical reactions with atomic-scale resolution by crystallography, permitting the observation of co-operative involvement of the surrounding solid in accommodating the changes at the reacting centre. (2)

[1] R. Vaidhyanathan et al, *Angew. Chem. Int. Ed. Engl.* 45, 6495 (2006); J. Rebilly et al *Chem. Eur. J.* in press 2008; M. Ingleson *Chem Comm* 2007, 2008

[2] D. Bradshaw et al. *Science* 315, 977 - 980, 2007.

Keywords: porous materials, reactions, amino-acid coordination compounds

MS.73.3*Acta Cryst.* (2008). A64, C125**Porosity in flexible metal-organic systems**Len J Barbour

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Over the past decade the study of porous crystalline solids has become highly topical, especially with regard to potentially important applications such as gas storage, separation and sensing. Well-known systems include zeolites and metal-organic frameworks and, to a lesser extent, organic molecular crystals. However, discrete metal complexes have received little attention as components of porous materials. One of the basic tenets of the solid state is that molecules tend to pack closely, thus affording minimal free space at the molecular scale. We are attempting to overcome this tendency by designing simple complexes that cannot pack efficiently without including solvent molecules. Indeed, we are specifically interested in forming solvent-templated complexes that do not collapse upon subsequent solvent removal. We have recently discovered several systems that behave in this manner; some of these structures can be considered to be porous in the conventional sense, but we have also noted that conventional porosity is not a prerequisite for mass transport in the solid state. These systems have now been studied using a variety of complementary techniques, including X-ray diffraction, isothermal gas sorption and molecular modeling. Non-conventional use of these techniques has enabled us to gain a deep understanding of the relationship between structure and gas sorption dynamics.

Keywords: porous materials, self assembly, crystal engineering

MS.73.4*Acta Cryst.* (2008). A64, C125**The synthesis and structure of multifunctional metal-organic frameworks**Guangshan Zhu, Fuxing Sun, Qianrong Fang, Shilun Qiu

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Metal-organic frameworks (MOFs) have received widespread attention recent years, due to the fact that they are porous with high surface areas, have tunable pores sizes and topologies.^{1,2} MOFs always exhibit amazing magnetic and optoelectronic properties at the same time as multifunctional materials. The research interests in our group are focused on the synthesis of MOFs with intriguing topologies and multifunctional properties, including: (1) MOFs with excellent hydrogen and methane storage properties. We have already synthesized a new MOF JUC-48, with the largest reported one-dimensional (1D) hexagonal nanotube-like channels of $2.4 \times 2.8 \text{ nm}^2$ and rare etb topology, which exhibits hydrogen uptakes of about 2.8 wt% at 40 bar and 77K, 1.1wt% at 100 bar and room temperature.³ (2) MOFs with large metal carboxylate clusters. The metal carboxylate clusters could expand the inorganic nodes to obtain large pores, and introduce similar physical properties to those nanosized metal oxide materials. We have successfully synthesized an open framework JUC-35, which contains the largest known undecanuclear clusters and shows optoelectronic properties.⁴ (3) Rare earth MOFs. Rare earth metals are attracting much attention to construct MOFs for their special physical characteristics. About this issue, we have synthesized a lanthanide-organic framework with 1D rhombic channels of $2.5 \times 1.7 \text{ nm}^2$.⁵

References:

(1) Ferey, G., Mellot-Draznieks, C., Serre, C., et al *Science* 2005, 309, 2040

(2) Eddaoudi, M., Kim, J., Yaghi, O. M., et al *Science* 2002, 295, 469

(3) Fang, Q. R., Zhu, G. S., Qiu, S. L., et al *Angew. Chem., Int. Ed.* 2007, 46, 6638

(4) Fang, Q. R., Zhu, G. S., Qiu, S. L., et al *Angew. Chem., Int. Ed.* 2006, 45, 6126

(5) Guo, X. D., Zhu, G. S., Qiu, S. L. et al *Inorg. Chem* 2005, 44, 3850

Keywords: metal-organic framework, multifunction, structure

MS.73.5*Acta Cryst.* (2008). A64, C125-126**Elucidating negative thermal expansion in metal-organic frameworks**Nina Lock¹, Yue Wu², Mogens Christensen³, Bo B Iversen¹, Cameron J Kepert²

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The majority of solids expand upon heating, a property known as positive thermal expansion (PTE). Considerable excitement has arisen over the past decade with the discovery of negative thermal expansion (NTE) in a number of relatively simple oxide- and cyanide-based materials [1]. The combination of NTE and PTE materials has potential applications in the preparation of zero thermal expansion materials, which are sought for a multitude of engineering purposes. NTE was recently discovered for some

metal-organic frameworks (MOFs), however, the NTE mechanism in these structurally complicated compounds still eludes in-depth understanding. Here we use X-ray diffraction techniques to elucidate the nature of the isotropic NTE mechanism in the cubic metal-organic framework $Zn_4O(BDC)_3$ (BDC = benzenedicarboxylate), also known as MOF-5 or IRMOF-1. Variable temperature synchrotron radiation powder X-ray diffraction data reveal almost linear NTE behaviour in the measured temperature range from 80-500 K with $\alpha = dL/dT = -11.2 \times 10^{-6} \text{ K}^{-1}$. Variable temperature single crystal X-ray diffraction (SCXRD) measurement over a broad temperature range has been used to probe the changes in atomic coordinates and vibrational modes causing the NTE behaviour in the framework. The results suggest population of transverse vibrations, similar to the findings in the metal cyanide frameworks [2], with preferential population of vibrational modes out-of-plane of the BDC oxygen atoms and of the BDC aromatic ring.

[1] Evans, J. Chem. Soc., Dalton Trans. (1999) 3317

[2] Chapman et al., J. Am. Chem. Soc. (2005) 127, 15630

Keywords: negative thermal expansion, structure and property, metal-organic frameworks

MS.74.1

Acta Cryst. (2008). A64, C126

Magnetic and crystal structure in connection with ferroelectric properties of multiferroic RMn_2O_5

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RMn_2O_5 (R=Y and rare earth) are well known multi-ferroic compounds. A colossal magnetoelectric effect is reported such that magnetic field induces an electric polarization. We found successive phase transitions of magnetic and dielectric ordering occurring simultaneously, using neutron and x-ray scattering as well as electrical measurements. The character of magnetic ordering is essentially incommensurate - commensurate and again to incommensurate phase transitions. From the magnetic and dielectric phase diagram in magnetic-field and temperature, we can easily say that the origin of colossal magnetoelectric effect is the phase transition from the magnetic incommensurate and weak ferroelectric phase to the commensurate and ferroelectric phase. We will show the magnetic structure to discuss the mechanism to introduce ferroelectric polarization. For all the compounds, the spin configuration for Mn^{4+} and Mn^{3+} ions in the commensurate magnetic phase, where spontaneous electric polarization occurs, was determined to be a transverse spiral spin structure propagating along the c -axis. By contrast, the alignment of the induced $4f$ -moment of R^{3+} ions has a variety depending on the character of each element. The lattice modulation wavevector q_L was carefully measured, and we found the lattice modulation vector q_L is exactly twice of the magnetic propagation vector q_M , $q_L = 2q_M$, in all phases. The precise structure giving the spontaneous polarization is still unclear at the moment. The structure analysis of modulation (magnetostriction pattern) in ferroelectric and magnetically commensurate phase of YMn_2O_5 was successfully carried out.

Keywords: magnetic structures, ferroelastics, physical properties

MS.74.2

Acta Cryst. (2008). A64, C126

Ferroelectricity from magnetic order

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Magnetic insulators with competing exchange interactions can give rise to strong fluctuations and qualitatively new ground states. The proximity of such systems to quantum critical points can lead to strong cross-coupling between magnetic long-range order and the nuclear lattice. Case in point is a class of multiferroic materials in which the magnetic and ferroelectric order parameters are directly coupled, and a magnetic field can suppress or switch the electric polarization [1]. Our neutron measurements reveal that ferroelectricity is induced by magnetic order and emerges only if the magnetic structure creates a polar axis [2-5]. The spin dynamics and the field-temperature phase diagram of the ordered phases provide evidence that competing ground states are essential for ferroelectricity. The origin of the magneto-electric coupling most probably arises from strain derivatives of the isotropic exchange interactions and anisotropic exchange couplings such as Dzyaloshinskii-Moriya interactions.

References

[1] T. Kimura et al, Nature 426, 6962 (2003).

[2] G. Lawes et al, Phys. Rev. Lett. 95, 087205 (2005).

[3] M. Kenzelmann et al, Phys. Rev. Lett. 95, 087206 (2005).

[4] M. Kenzelmann et al, Phys. Rev. B 74, 014429 (2006).

[5] M. Kenzelmann et al, Phys. Rev. Lett. 98, 267205 (2007).

Keywords: multiferroic, frustration, ferroelectricity

MS.74.3

Acta Cryst. (2008). A64, C126-127

Function from frustration in modern multiferroics

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Although in conventional ferroelectrics the requirements of magnetism and ferroelectricity are chemically incompatible[1], recent investigations of spin frustrated manganite perovskites $RMnO_3$ (where R is a rare earth ion) have shown that this chemical incompatibility can be overcome by frustration[2]. In particular spin frustrated perovskite manganites for appropriate size R-ions show a peculiar transverse spiral magnetic ordering that breaks inversion symmetry[3]. What is novel about these materials is that the direction of the ferroelectric polarization can be controlled via magnetic field. In this talk I will discuss the mechanism by which ferroelectricity can be coupled to magnetism in $RMnO_3$ perovskites and describe the changes in the magnetic structure associated with changes in the ferroelectric polarization. The magnetic excitation spectrum that we have recently measured using cold neutron spectroscopy supports evidence that the fundamental driving mechanism behind these multiferroics is the coupling of a magnon to polar phonons, or electromagnon[4]. I will further show how the ordering of the rare earth spins couples to the Mn-spins[5] and in the case of R=Dy can enhance the ferroelectric polarization by as much as a factor of 3[6]. In collaboration with N. Aliouane, S. Landsgessel, O. Prokhenko, E. Dudzik, Ralf Feyerherm, J. Strempfer and I. Zekinoglou, M. Mostovoy and D. Senff and M. Braden.

[1] N. A. Hill, J.Phys. Chem. B104, 6694(2000).