The Effect of Pressure on ZIF-8: Increasing Pore Size with Pressure and the Formation of a High-Pressure Phase at 1.47 GPa.

Manuscript received: 18/05/2009; Article published: 13/08/2009

The Effect of Pressure on ZIF-8: Increasing Pore Size with Pressure and the Formation of a High-Pressure Phase at 1.47 GPa**

Stephen A. Moggach,[1,*] Thomas D. Bennett[2] and Anthony K. Cheetham[2]

[1]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

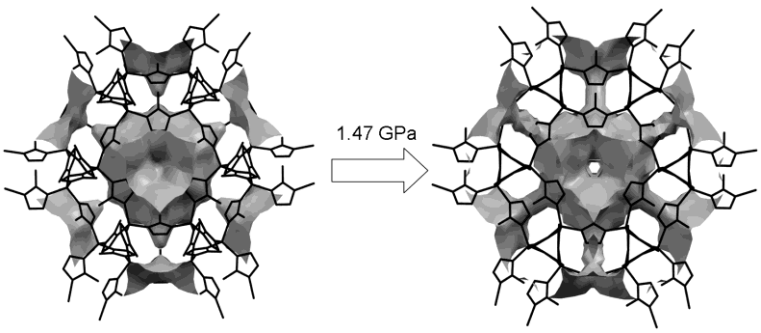
[2]Department of Materials Science and Metallurgy, University of Cambridge, UK.

[*]Corresponding author; e-mail: smoggach@staffmail.ed.ac.uk; tel: +44 (0)1316504806; fax: +44 (0)131 650 6453

[**]We thank the Royal Society of Edinburgh for a Personal Research Fellowship (to SAM), and the EPSRC and ERC for funding (to TDB and AKC, respectively).

Supporting information:
Available on the WWW under http://dx.doi.org/10.1002/anie.200902643

Graphical abstract:



Keywords:
crystal engineering; high-pressure chemistry; organic–inorganic hybrid composites; polymorphism

Abstract

On initially applying pressure to ZIF-8 to 0.18 GPa, solvent can be squeezed into the porous cavity of ZIF-8, initially increasing the pore size and unit cell volume. On increasing pressure further to 1.47 GPa, a phase transition takes place. This transition allows more solvent to not only enter the original nanopore, but increases the size of the narrow channels which connect these pores, resulting in an overall increase in porous volume and content.

Main text

Recent interest in gas storage materials has led to a plethora of papers on the synthesis of novel metal organic framework materials (MOFs).[1-4] To date, structural variation in MOFs has been achieved through chemical modification, with accompanying changes in pore size and shape (and therefore internal surface area) giving rise to an increasingly diverse array of sorption properties. Such sorption measurements are performed at pressures up to 0.01GPa, though what effect higher pressures have on the framework is relatively unknown[5], though the mechanical stability of some MOFs at high-temperatures have been discussed previously.[6] The only structural data available as a function of pressure above 0.01 GPa on any MOF is on $[Zn(C_3H_3N_2)_2]$ (ZnIm),[7] a dense zeolitic imidazolate framework (ZIF) material[8] (a subfamily of MOFs). ZIFs, related to zeolites through the 145˚ angle subtended at the bridging imidazolate ligand, are of increasing interest. Their tuneable pore size, chemical robustness and thermal stability combine the most desirable features of conventional MOF and zeolite structures, making them ideal candidates for gas storage applications.

In the previous study of ZnIm (which crystallises in the tetragonal space group $I4_1cd$), the structure was found to undergo a phase transition at 0.8 GPa to a previously unknown phase (space group $I4_1$) involving a cooperative rearrangement of the framework which was then recovered at ambient pressure. Although this material is a ZIF in terms of its topology, it contains no accessible pore volume. Here we present the first high-pressure study on a porous ZIF, ZIF-8 ($Zn(MeIM)_2$, MeIM = 2-methylimidazolate) with a sodalite (SOD) zeolite-type structure and a large accessible pore volume (>2000Å^3 per unit cell).

Prior to our pressure experiment, an ambient pressure and temperature X-ray data set was collected on a crystal of ZIF-8 (0.1 x 0.2 x 0.2 mm) in order to provide data for comparison with the high pressure studies (which were also performed at ambient temperature, see below). The same crystal was then loaded into a modified Merrill-Bassett diamond anvil cell (DAC) equipped with 600μm culet diamonds and a tungsten gasket (Figure 1a).[9] The sample and a chip of ruby (as a pressure calibrant) were loaded into the DAC with a 4:1 (v/v) mixture of methanol and ethanol as a hydrostatic medium.

The ruby fluorescence method was utilised to measure the pressure.[10] High pressure diffraction data were then collected at 0.18, 0.52, 0.96 and 1.47 GPa. Data were also collected on decreasing pressure at 0.82 and 0.39 GPa. The sample was then downloaded from the pressure cell and an ambient temperature and pressure data collection was obtained following the pressure experiments. The pore volume and solvent content were calculated using the SQUEEZE algorithm within PLATON.[11] Void analysis was carried out using the program MERCURY[12] using a probe radius and grid spacing of 1.2 and 1.0 Å respectively.

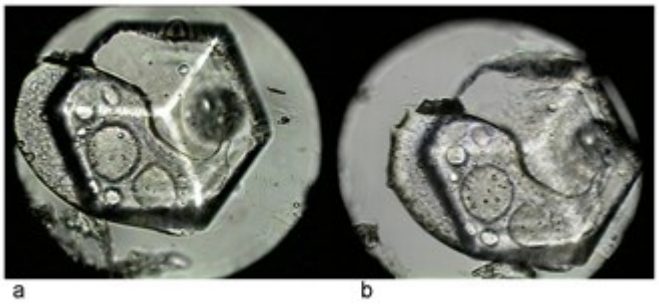


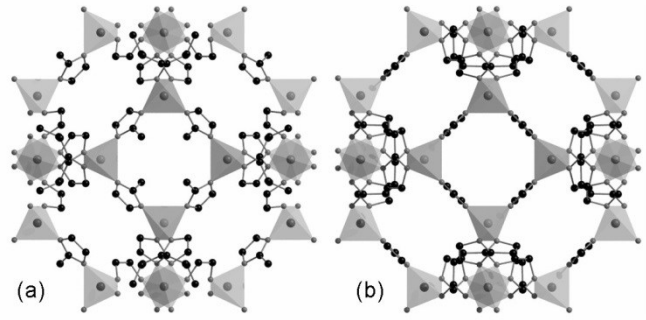
Figure 1. Optical image of single crystal of ZIF-8 at (a) ambient pressure and (b) ZIF-8-II at 1.47 GPa in a diamond-anvil cell.

ZIF-8 (phase-I) crystallises in the cubic space group *I*-43*m* (a = 16.9856(16) Å, Vol. = 4900.5(8) Å^3, Figure 2a). Under ambient pressure and temperature conditions, ZIF-8 contains one nano-sized pore per unit cell located at the centre of the cell with a volume of 2465 Å^3. Connecting these large nanopores are eight smaller channels (Figure 3a). From our ambient pressure single crystal data, it was clear that some solvent was still in the pore, with the electron count within the pore (calculated using the SQUEEZE algorithm within PLATON) measuring 219 e^-/cell equating to 12 molecules of methanol per unit cell (Table 1). On increasing pressure initially to 0.18 GPa, the sample actually increased in volume (from 4900.5(8) to 4999.6(2) Å^3), with an associated increase in pore volume (2465 to 2556 Å^3). This result is counterintuitive, as an increase in pressure usually results in a decrease in volume. Interestingly, the electron density within the pore also increased to 283 e^-/cell, indicating that the hydrostatic media surrounding the sample (used to apply pressure evenly) was being squeezed into the large nanopore, increasing the pore content and size, as well as the cell volume. A broadly similar effect has been seen in zeolite-rho,[13] though less dramatically than in the present case. On increasing the pressure further to 0.96 GPa, the cell and pore volume began to decrease, with the cell volume at 0.96 GPa remarkably being just below that measured at ambient pressure. The electron density within the pore however continued to rise, measuring 421 e^-/cell at 0.96

GPa. On increasing the pressure further to 1.47 GPa the sample underwent a single crystal to single crystal phase transition.

During the transition, the crystal appeared to 'jump' in the pressure cell. This can be seen in Figure 1a&b, where the crystal has re-orientated itself in a different location within the gasket chamber on undergoing the transition. There have been occasional reports of crystals that jump on undergoing phase transitions on application of temperature (referred to as the thermosalient effect); however, we could not find any reference to examples on application of pressure (barosalient). Further study, however, is required in order to truly establish if this barosalient transition occurs here.

The transition was also accompanied by a change in appearance of the crystal (note the rippled effect in Figure 1b). The new high-pressure phase (ZIF-8-II) still maintains the *I*-43m space group symmetry, but the imidazolate ligands twist, re-orientating in order to increase the accessible pore volume (Figures 2a&b). In particular, this re-orientation increases the size of the eight narrow channels which link the nanopores throughout the framework (Figures 3a&b). Although the volume of the nanopore decreases in size on undergoing the transition (from 2485 to 2439 $Å^3$ at 0.96 and 1.47 GPa respectively), the overall effect is to increase the pore volume due to the increase in size of the linking channels. Remarkably, the cell volume increases on undergoing the transition and has a larger volume than that measured under ambient pressure conditions. The total solvent in the pores at 1.47 GPa measures 738e^-/cell, equating to 41 methanol molecules per unit cell, which is significantly higher than at ambient pressure (12 per unit cell). On decreasing the pressure, the transition was found to be reversible, reverting back to phase-I at 0.82 GPa. On removing the sample from the DAC, the cell volume reverted back to its ambient pressure value; however, the pore volume and contents were found to decrease compared to the same sample measured prior to the pressure experiment (Table 1).



← ***Figure 2.*** Packing arrangement of ZIF-8 at (a) ambient pressure and (b) ZIF-8-II at 1.47 GPa. ZnN_4 tetrahedron are drawn as rigid polyhedra. H-atoms have been excluded for clarity. Note the change in orientation of the imidazolate groups on undergoing the transition from (a) to (b).

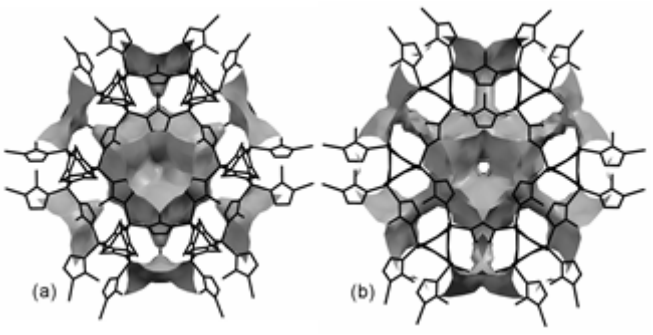


Figure 3. Packing arrangement of ZIF-8 at (a) ambient pressure and (b) ZIF-8-II at 1.47 GPa. ZnN4 tetrahedron are drawn as rigid polyhedra. H-atoms have been excluded for clarity. Note the change in orientation of the imidazolate groups on undergoing the transition from (a) to (b).

Pressure (GPa)	***a* (Å)**	**Cell Volume (Å^3)**	**Total Pore Volume (Å^3)**	**Electron Count**	**MeOH Molecules**
0	16.9856(16)	4900.5(8)	2465	219	12
0.18	17.0993(4)	4999.6(2)	2556	283	16
0.52	17.0630(4)	4967.8(2)	2529	381	21
0.96	16.9775(4)	4893.5(2)	2485	421	23
1.47$^{\#}$	17.0710(17)	4974.8(9)	2439	636	41
0.82*	17.042(5)	4950(3)	2525	425	24
0.39*	17.093(5)	4994(3)	2541	337	19
0*	16.9920(8)	4906.1(4)	2447	41	2

Table 1. Crystallographic and pore data for ZIF-8 as a function of pressure. Phase-II is indicated with a $^{\#}$ at 1.47 GPa. Pore volume, electron count, and number of MeOH molecules are calculated per unit cell. * refers to those values on decreasing pressure.

Completely de-solvating porous materials can often be difficult and may require heating the sample under high or low vacuum. Here, by applying pressure we have removed the guest material from the compound, providing a new route by which to remove guest solvent from porous MOFs.

In summary, we have shown that by applying pressure to ZIF-8 we can force the hydrostatic medium to enter the pore, initially increasing the volume of both the nanopore and unit cell. On increasing pressure further, more solvent can be forced into the nanopore even though the nanopore volume decreases, until the sample undergoes a phase transition. This transition allows more solvent to enter not only the original nanopore, but increases the size of the narrow channels which connect these

pores, resulting in an overall increase in porous volume and content. Modification of the pore volume, size, shape and therefore selectivity has therefore been achieved on application of pressure. Pressure could therefore be used as a means of inserting larger molecules into the pores which would otherwise not fit.

This could be used to increase the accessible surface area for gas storage materials. MOF-177 for example has a pore large enough to include a C_{60} molecule which may provide additional sites for sorption of H_2 or other gases.[14]

The hydrostatic media that are used for pressure experiments are selected so as to apply pressure evenly to the sample. They are chosen based on a number of factors, including the solubility and reactivity of the sample, but they also limit the highest pressures obtainable during the experiment (hydrostatic media become non-hydrostatic at elevated pressures and crush the sample). Here, the hydrostatic medium (a 4:1 mixture of methanol and ethanol) is interacting dynamically with the large accessible pore volume in ZIF-8. The compressibility of MOFs has been shown to be hydrostatic media selective;[15] however, this is the first detailed example showing what happens to the structure of a porous MOF on increasing pressure. Effects include an unprecedented increase in volume on increasing pressure, a pressure induced phase transition (modifying the pore size, shape and volume), and an unexpected removal of guest solvent molecules from the framework, without structural degradation.

Experimental Section

A solid mixture of zinc nitrate hexahydrate Zn(NO3)2.6H2O (0.525g, 1.76 x 10^{-4} mol) and 2-methylimidazole (m-IM) (0.015g, 1.83 x 10^{-4} mol) was dissolved in 9ml DMF in a 12ml Teflon-capped vial. The vial was heated at a rate of 200˚C/hr to 130˚C, held at this temperature for 24hrs then cooled at a rate of 5˚C/hr to room temperature. Colourless polyhedral crystals were filtered from the reaction mixture, washed with chloroform (5ml x 3) and dried in air (30 min). The yield obtained was 0.0064g, 11% based on 2-methylimidazole. The product was formulated using elemental analysis as $Zn(MeIM)_2$,(DMF)(H_2O) ($C_{11}H_{19}N_5O_2Zn$; Calcd. C, 41.51; H, 5.97; N, 22.01. Found. C, 42.04; H, 5.46; N, 21.83). The sample was immersed in methanol for 48hrs at ambient temperature to effect solvent exchange, this being confirmed by TGA.

X-ray diffraction data were collected with Mo-Kα radiation (λ = 0.71073 Å) at room temperature and pressure on a Bruker Smart Apex diffractometer. Refinement was carried out against $|F|^2$ in CRYSTALS[16] starting from the low temperature coordinates of Wu *et al*., 2007.[17] High pressure diffraction data were collected on the same sample (0.2 × 0.2 × 0.1 mm^3) on a Bruker APEX II

diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data were collected in ω-scans in twelve settings of 2θ and ϕ with a frame and step size of 40 seconds and 0.3° respectively. This data collection strategy was based on that described by Dawson *et al*., 2004.[18] The data were integrated using the program SAINT[19] using 'dynamic masks' to avoid integration of regions of the detector shaded by the body of the pressure cell.[18] Absorption corrections for the DAC and sample were carried out with the programs SHADE[20] and SADABS[21] respectively. High pressure refinements of ZIF-8 were carried out against $|F|^2$ using the program CRYSTALS.[16] All 1,2 and 1,3 distances of the 2-methylimidazolate ligand were restrained to the values observed from our ambient pressure structure. All torsion angles and metal to ligand distances were refined freely. Hydrogen atoms attached to carbon were placed geometrically based on the neutron data from ref [17].

The structure of phase II at 1.47 GPa was solved by SIR92.[22] The numbering scheme used is the same as CSD refcode OFERUN. Data from the downloaded sample (after the pressure experiment) were collected at room temperature. The same experimental procedure was carried out as for the room temperature collection above. Detailed crystallographic data are summarised in Electronic Supplementary Information (ESI), and are also available from the CSD quoting deposition numbers CCDC 739161 – 739168.

References

[1] R. Banerjee, A. Phan, B. Wang, C. Knobler, H. Furukawa, M. O'Keeffe, O. M. Yaghi, *Science* 2008, *319*, **939.**

[2] R. Kitaura, G. Onoyama, H. Sakamoto, R. Matsuda, S.-i. Noro, S. Kitagawa, *Angew. Chem., Int. Ed.* 2004, *43*, **2684.**

[3] A. K. Cheetham, C. N. R. Rao, R. K. Feller, *Chem. Commun.* 2006, **4780.**

[4] G. Ferey, *Chem. Soc. Rev.* 2008, *37*, **191.**

[5] S. A. Moggach, S. Parsons, *Specialist Periodic Reports* 2009, In Press.

[6] J. Hafizovic Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga, K. P. Lillerud, *J. Am. Chem. Soc.* 2008, *130*, **13850.**

[7] E. C. Spencer, R. J. Angel, N. L. Ross, B. E. Hanson, J. A. K. Howard, *J. Am. Chem. Soc. FIELD Full Journal Title:Journal of the American Chemical Society* 2009, *131*, **4022.**

[8] R. Lehnert, F. Seel, *Z. Anorg. Allg. Chem.* 1980, *464*, **187.**

[9] S. A. Moggach, D. R. Allan, S. Parsons, J. E. Warren, *J. Appl. Cryst.* 2008, *41*, **249.**

[10] G. J. Piermarini, S. Block, J. D. Barnett, R. A. Forman, *Journal of Applied Physics* 1975, *46*, **2774.**

[11] A. L. Spek, Utrecht University, Utrecht, The Netherlands, 2004.

[12] I. J. Bruno, J. C. Cole, P. R. Edgington, M. Kessler, C. F. Macrae, P. McCabe, J. Pearson, R. Taylor, *Acta Crystallographica, Section B* 2002, *58*, **389.**

[13] Y. Lee, J. A. Hriljac, T. Vogt, J. B. Parise, M. J. Edmondson, P. A. Anderson, D. R. Corbin, T. Nagai, *J. Am. Chem. Soc.* 2001, *123*, **8418.**

[14] J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem., Int. Ed.* 2005, *44*, **4670.**

[15] K. W. Chapman, G. J. Halder, P. J. Chupas, *J. Am. Chem. Soc.* 2008, *130*, **10524.**

[16] P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout, D. J. Watkin, *Journal of Applied Crystallography* 2003, *36*, **1487.**

[17] H. Wu, W. Zhou, T. Yildirim, *J. Am. Chem. Soc.* 2007, *129*, **5314.**

[18] A. Dawson, D. R. Allan, S. Parsons, M. Ruf, *Journal of Applied Crystallography* 2004, *37*, **410.**

[19] Bruker-Nonius, Bruker-AXS, Madison, Wisconsin, USA, 2006.

[20] S. Parsons, The University of Edinburgh, Edinburgh, United Kingdom, 2004.

[21] G. M. Sheldrick, Bruker-AXS, Madison, WIsconsin, USA, 2004.

[22] M. C. Burla, R. Caliandro, M. Camalli, B. Carrozzini, G. L. Cascarano, L. De Caro, C. Giacovazzo, G. Polidori, R. Spagna, *Journal of Applied Crystallography* 2005, *38*, **381.**