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The effect of pressure on Cu-btc: Framework compression vs. guest inclusion**

Alexander J. Graham,[1] Jin-Chong Tan,[2] David R. Allan[3] and Stephen A. Moggach[1],*

[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, The University of Cambridge, Cambridge, UK.

[3]Diamond Light Source, Didcot, Oxfordshire, UK.
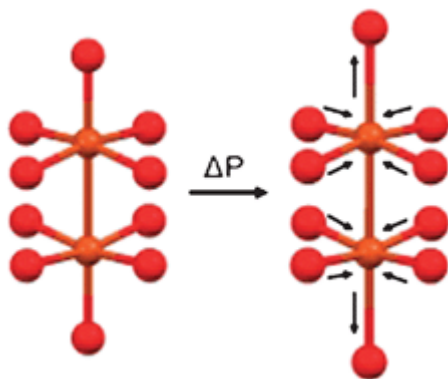
[*]Corresponding author; e-mail: smoggach@staffmail.ed.ac.uk; tel: +44 (0)1316504806; fax: +44 (0)131 650 6453

Supporting information:
Cif files for all the pressure data have been included. CCDC 846570–846577. For crystallographic data in CIF or other electronic format see http://dx.doi.org/10.1039/C1CC16045A

Graphical abstract:

Abstract

Here we present detailed structural data on the effect of high pressure on Cu-btc. Inital application of pressure (0.5 GPa), causes the pores and unit cell volume to expand as solvent is squeezed into the pores. Increasing pressure further causes more solvent to enter the pores, until at 5.0 GPa, a phase transition takes place. The transition is driven by the sudden compression and *expansion* of equatorial and axial Cu-O bonds, as we change from a pore filling to a pore emptying mechanism.

Introduction

A large body of scientific research is directed towards the design and synthesis of an ever more varied and complex variety of porous metal-organic framework (MOF) materials. MOFs have been designed for a number of different applications, including molecular sensing,[1-4] gas separation and storage,[5-8] drug transport and as high surface area catalysts.[9] Whatever the application the primary factor that makes MOFs so appealing is the ability to tune their pore size, shape and therefore selectivity. To date, there is a large body of literature where these properties have been altered via 'chemical' means, modifying the rigid organic unit, metal linker or both. More recently, the ability to tune the pore size and shape of MOFs including guest content has been achieved by applying high pressures (> 10,000 atmospheres).[10] To date, only three porous framework materials have been exposed to high-pressure, including ZIF-8 (Zn(MIm)2, MIm = 2-methylimidazole)[10], MOF-5 ($Zn_4O(BDC)_3$, BDC = 1,4-benzenedicarboxylate) and Cu-btc ($[Cu_3(TMA)_2(H_2O)_3]_n$, TMA = benzene-1,3,5-tricarboxylate).[11, 12] These studies have utilised diamond anvil cell (DAC) devices in order to apply high-hydrostatic pressure, where the sample (usually a single crystal or a polycrystalline powder) is loaded into the sample chamber and surrounded by a hydrostatic liquid. In ZIF-8 and MOF-5, initial application of pressure using a hydrostatic liquid that was small enough to enter the pores caused the framework to expand. In ZIF-8, increasing pressure further resulted in more solvent entering the pores, while the volume decreased in comparison to the initial expansion. This continued until at 1.47 GPa the sample underwent a phase transition, which resulted in both an *increase* in volume on increasing pressure and a twisting of the MIm groups. This motion in ZIF-8, often referred to as 'breathing' in MOFs has subsequently been used to model N_2 uptake in ZIF-8 under atmospheric pressure conditions.[13] The N_2 containing framework was also shown to be isostructural with that obtained at 1.47 GPa. The behaviour of MOF-5, however, is quite different. After initially expanding on increasing pressure, the sample compresses continuously, until becoming amorphous above 3.2 GPa. In MOF-5, inclusion of solvent as a function of pressure made the framework more resilient to compression and delayed the onset of amorphisation, which occurs on grinding at pressures several orders of magnitude lower.

In a previous high-pressure powder diffraction study on the Cu-framework Cu-btc (Fig. 1), high-pressure experiments were carried out in the presence of methanol-ethanol-water (MEW, 16:3:1 by volume), isopropyl alcohol (IPA) and Flourinert (FC-70, perfluorotri-*N*-pentylamine) as the hydrostatic liquids.[12] In this study, Chapman *et al.* illustrated that with MEW and IPA, the Cu-btc framework exhibits a clear transition between two distinct regions of near linear compressibility. The change in compressibility here was ascribed to a change from a pore filling, to a pore emptying transition, where the transition pressure was affected by the size of the hydrostatic liquid entering the pores (molecules in MEW are smaller than IPA, and therefore delaying the onset of the transition from ~0.8 to ~2.2 GPa). When a non-penetrating hydrostatic liquid was used (Fluorinert), direct compression of the framework occurred. The pore filling mechanism observed on initially applying pressure made Cu-btc much more resilient to compression, and corresponds well with our previous studies of MOF-5. However, no detailed structural data was reported. Guest content and framework flexibility was hypothesized from a detailed analysis of the unit cell volume as a function of pressure alone.
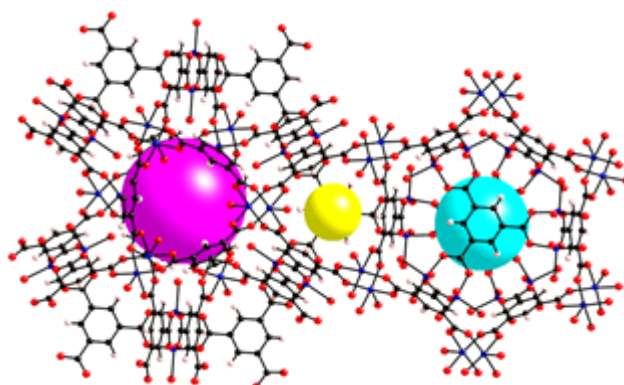
Fig. 1. A representation of the three distinct but interconnected pore volumes of the Cu-btc framework.

Here we present a single crystal X-ray diffraction study on the porous framework Cu-btc. Prior to our pressure experiment, an ambient pressure and temperature X-ray data set was collected on a crystal of Cu-btc in order to provide data for comparison with the high pressure studies (which were also performed at ambient temperature). The same crystal was then loaded into a Merrill-Bassett Diamond Anvil Cell (DAC) equipped with 600 µm culets and a tungsten gasket using MEW as the hydrostatic liquid. High-pressure data were collected at station I19 at the DIAMOND Light Source in approximately 0.5 GPa steps between ambient pressure and 5.0 GPa (Table 1.)

Pressure (GPa)	$a(\text{Å})$	Cell Volume (Å^3)	Total Pore Volume (Å^3)	Electron Count
0.0	26.3015(4)	18194.54	11597	1858
0.5	26.3867(12)	18371.96	11741	2441
1.3	26.3368(12)	18267.98	11656	2689
1.8	26.3081(12)	18208.28	11586	2897
2.2	26.2896(15)	18169.87	11575	3035
3.0	26.2564(15)	18101.08	11519	3337
3.9	26.1823(18)	17948.32	11445	3897
5.0	25.9467(17)	17468.1	10996	3278

Table 1. Crystallographic and pore data for Cu-btc as a function of pressure. Pore volume and electron count are calculated per unit cell.

Cu-btc crystallises in the cubic space group *Fm*-3*m* (a = 26.434 (6) Å, Vol. = 18471(12) Å³). Pairs of Cu(II) ions, bridged by four carboxylate (μ_2-OCO) groups on discrete 1,3,5-benzenetricarboxylate (btc) ligands, form Cu(II) dimers (square planar connectivity) which are linked via the trigonal btc molecules to form an extended three-dimensional network. The Cu(II) dimers coordinate to water molecules to form a Jahn-Teller distorted axis creating a distorted octahedral environment around the Cu(II) centres, forming the well known Cu-paddlewheel building unit (Fig. 2).

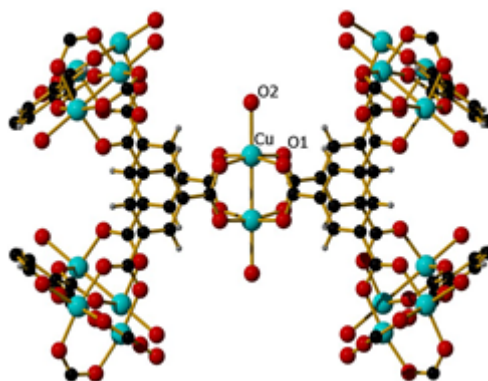**Fig. 2.** Representation of the Cu paddlewheel units present in Cu-btc showing the equatorial and axial Cu-O bonds, Cu-O1 and Cu-O2 respectively.

Cu-btc contains three distinct guest accessible pores which are linked together along the body diagonal ([111] direction) of the cubic structure with a total pore volume of ≈ 11,500 Å³ (Fig. 1). From our ambient pressure single crystal data, it was clear that there were some residual water

molecules in the pores equating to 186 water molecules per unit cell. On initially increasing pressure to 0.5 GPa, a sudden and marked increase in pore content was observed, equating to a volume *increase* on increasing pressure. This coincides well with our previous studies on MOF-5 and ZIF-8 and equates to the uptake of the hydrostatic media within the pores. On increasing pressure further to 3.9 GPa, a gradual and steady increase in pore content was observed, while the volume decreased continuously. The data collected here quite nicely coincides with the previous powder diffraction study by Chapman *et al*., and confirms their hypothesis of a pore filling mechanism within this pressure regime. On increasing pressure further to 5.0 GPa, a sudden and marked decrease in volume occurs, and corresponds to the pore emptying mechanism described previously. However, although a decrease in pore content is observed on increasing pressure from 3.9 to 5.0 GPa, the pore content is not reduced substantially ($\approx$16% decrease), and equates to approximately the same pore content as observed at 3.0 GPa on increasing pressure (Table 1). The unit cell volume difference between data collected at 3.0 and 5.0 GPa, however is 632 Å³. It would therefore appear that some other effect, rather than just pore content is responsible for the sudden unit cell volume decrease above 3.9 GPa.

In our previous work on amino acids, compression of covalent bond lengths is not expected within this pressure regime, rather compression of much weaker intermolecular interactions takes place.[14] This effect has also been modelled computationally by Brand, where a study on pentaerythritol tetranitrate (PETN) showed no significant compression of covalent bond lengths to 6.54 GPa.[15] In contrast metal-ligand bond distances are much more flexible, for example, pressure induced co-ordination changes have been observed.[16] The unit cell compression of Cu-btc is therefore likely to be mediated through the Cu-O bonding interactions within the Cu-paddlewheel. In Cu-btc, there are two symmetry independent Cu-O bonding interactions, the axial Cu-O bond (Cu-O2) which points into the pores of the guest-accessible cavities at (0,0,0) and the equatorial Cu-O bond (Cu-O1, Fig. 2) All four Cu-O1 bonds are symmetry equivalent. On initially increasing pressure to 0.5 GPa, no reduction in the equatorial Cu-O1 bonds occurs, while the axial Cu-O2 bond actually *increases* in length (Fig. 3). This coincides nicely with the increase in unit cell volume observed on increasing pressure to 0.5 GPa, and the swelling phenomena observed here appears to be driven by the elongation of the Cu-O2 bond. We postulate that increasing the pore content with MEW at 0.5 GPa increases H-bonding interactions with the O2 water ligand that points into the large central pore volume at (0,0,0), weakening the Cu-O2 bond causing it to increase in length. On increasing pressure further to 3.9 GPa, the axial Cu-O2 bond then continuously decreases in length, even though the pore content increases, while the equatorial Cu-O1 bonds remain unchanged (Fig. 3). It would therefore appear that after the initial swelling, the overriding drive to smaller volume on applying pressures higher than 0.5 GPa appears to override any energy penalty for compressing the axial Cu-O2 bond.

On increasing pressure to 5.0 GPa (and on entering the pore emptying region), the axial Cu-O2 bond actually *increases* in length agaon while the equatorial Cu-O1 bonds, which until now remained relatively unchanged, suddenly decrease (Fig. 3). On initial application of pressure to 0.5 GPa, elongation of the axial Cu-O2 bond actilly resultsed in the volume *increasing* on increasing pressure. Conversely, on entering the pore-emptying region on increasing pressure between 3.9 to 5.0 GPa, the volume actually decreases. It would therefore appear that the transition at higher pressure is driven not by a decrease in pore content, but by the sudden compression of the very stiff equatorial Cu-O1 bonds. We postulate that the sudden shortening of the Cu-O1 bonds also causes the axial Cu-O2 bond to increase in length on undergoing the transition.
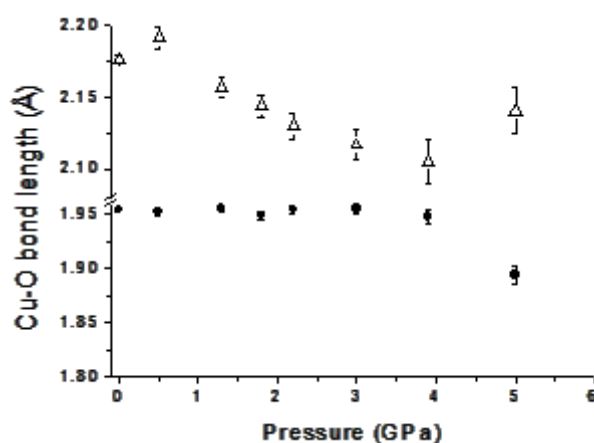

Fig. 3. Equatorial Cu-O1 bonds (circles) and axial Cu-O2 bond length as a function of pressure.

In summary, we have shown that by applying pressure to Cu-btc we can force the hydrostatic medium to enter the pore, initially causing the sample to expand. Expansion of the pore here is driven by the elongation of the axial Cu-O bond (Cu-O2) which points into the largest pore volume. On increasing pressure further to 3.9 GPa, the unit cell volume and axial Cu-O bond contract, even though more solvent enters the pore, showing that the overall drive to smaller volume overcomes any energy penalty for the swelling phenomena observed on initial application of pressure. On increasing pressure further to 5.0 GPa, we enter a pore emptying region, where increasing pressure causes the solvent to be pushed out of the pores, and the axial Cu-O bond to increase in length. Conversely, the volume decreases quite suddenly here, and we find that the transition from a pore filling to pore emptying transition is driven by the sudden compressibility of the equatorial Cu-O1 bonds. The Cu-O1 bonds are actually very resilient to any compression to 3.9 GPa, and only contract on increasing pressure to 5.0 GPa.

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