The effect of pressure on Cu-btc: framework compression vs. guest inclusion† ‡

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Here we present detailed structural data on the effect of high pressure on Cu-btc. Application of pressure causes solvent to be squeezed into the pores until a phase transition occurs, driven by the sudden compression and expansion of equatorial and axial Cu–O bonds.

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 (> 10000 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 (ZnO(BDC)3, BDC = 1,4-benzenedicarboxylate)11 and Cu-btc ([Cu3(TMA)2(H2O)3], TMA = benzene-1,3,5-tricarboxylate).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 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 N2 uptake in ZIF-8 under atmospheric pressure conditions.13 The N2 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 (Flourinert),

![Fig. 1](image-url) A representation of the three distinct but interconnected pore volumes in Cu-btc. Guest accessible cavities at (0,0,0) (pink), (111) (yellow) and (111) (blue) are shown.
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.

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).

Cu-btc crystallises in the cubic space group \textit{Fm}-3m (a = 26.434(6) \text{ Å}, Vol. = 18471(12) \text{ Å}^3). Pairs of Cu(II) ions, bridged by four carboxylate (\text{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).

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 \(\approx 11.500 \text{ Å}^3\) (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 \textit{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 \textit{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). Pore volume and solvent content were calculated using the \textit{SQUEEZE} algorithm within the program \textit{PLATON}.\textsuperscript{14} The unit cell volume difference between data collected at 3.0 and 5.0 GPa, however, amounts to only 632 \text{ Å}^3. 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.\textsuperscript{15} 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.\textsuperscript{16} In contrast metal–ligand bond distances are relatively more flexible and compliant in nature,\textsuperscript{17} for example, pressure induced co-ordination changes have been observed.\textsuperscript{18} 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 \textit{increases} in length (Fig. 3). This coincides nicely with the increase in unit cell volume observed on increasing pressure to 0.5 GPa, which suggests that the swelling phenomena observed here is driven by the elongation of the Cu–O2 bonds. 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. It is striking to see that, upon increasing pressure further to 3.9 GPa, the axial Cu–O2 bond 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.

\begin{table}[h]
\centering
\caption{Crystallographic and pore data for Cu-btc as a function of pressure. Pore volume and electron count are calculated per unit cell}
\begin{tabular}{|c|c|c|c|c|}
\hline
Pressure (GPa) & \(d\) (Å) & Cell volume (Å\(^3\)) & Total pore volume (Å\(^3\)) & Electron count \\
\hline
0.0 & 26.3015(4) & 18194.6(5) & 11597 & 1858 \\
0.5 & 26.3867(12) & 18371.9(14) & 11741 & 2441 \\
1.3 & 26.3368(12) & 18267.9(14) & 11656 & 2897 \\
1.8 & 26.3081(12) & 18208.3(14) & 11586 & 2689 \\
2.2 & 26.2896(15) & 18169.9(18) & 11573 & 3035 \\
3.0 & 26.2564(15) & 18101.1(18) & 11519 & 3337 \\
3.9 & 26.1823(18) & 17948.3(30) & 11445 & 3897 \\
5.0 & 25.9467(17) & 17468.1(20) & 10996 & 3278 \\
\hline
\end{tabular}
\end{table}
On increasing pressure to 5.0 GPa (and on entering the pore emptying region), the axial Cu–O2 bond actually increases in length again while the volume and equatorial Cu–O1 bonds (which until now remained relatively unchanged), suddenly decrease (Fig. 3). Interestingly, our results therefore demonstrate that the transition at higher pressure is driven not by a decrease in pore content, but by the sudden compression of the significantly stiffer equatorial Cu–O1 bonds. We postulate that the sudden shortening of the Cu–O1 bonds causes the axial Cu-O2 bond to increase in length on undergoing the transition, and the transition here is driven by the need to minimise the volume of the system at 5.0 GPa.

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 caused the relatively compliant axial Cu–O bond (Cu–O2), to increase in length (Fig. 1). On increasing pressure further to 3.9 GPa, the unit cell volume and the 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, with which the high pressure squeezes the solvent out of the pores; this is accommodated by the extension of the compliant (axial) Cu–O2 bond. Conversely, the volume decreases quite dramatically here. Importantly, we discover that the transition from a pore filling to a pore emptying mechanism is in fact associated with the sudden compressibility of the stiffer 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.

Notes and references