Mechanical gas capture and release in a network solid via multiple single-crystalline transformations

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Metal–organic frameworks have demonstrated functionality stemming from both robustness and pliancy and as such, offer promise for a broad range of new materials. The flexible aspect of some of these solids is intriguing for so-called ‘smart’ materials in that they could structurally respond to an external stimulus. Herein, we present an open-channel metal–organic framework that, on dehydration, shifts structure to form closed pores in the solid. This occurs through multiple single-crystal-to-single-crystal transformations such that snapshots of the mechanism of solid-state conversion can be obtained. Notably, the gas composing the atmosphere during dehydration becomes trapped in the closed pores. On rehydration, the pores open to release the trapped gas. Thus, this new material represents a thermally robust and porous material that is also capable of dynamically capturing and releasing gas in a controlled manner.

Metal–organic frameworks (MOFs)1–3 represent a class of solids that, in numerous ways beyond their composition, are truly hybrid materials. Despite relying on weaker bonds than metal oxides, coordination networks have demonstrated permanent microporosity4–11. Such networks can efficiently physisorb various gases and are promising materials for storage applications12–16. Other coordination solids have shown ‘smart’ behaviour in that they can convert between different structures via some external stimulus (for example, heat, guest molecules)17–33, a property not typically observed with metal oxides. In this light, we can consider certain fundamental properties of porous networks and their respective interdependencies. For example, robustness and crystallinity are both desirable but, at the same time, are not necessarily easily reconciled. To compensate for the energetic penalty of forming a pore, a network solid must be robust and sustained by sufficiently strong interactions. Often, solids assembled by such strong interactions precipitate rapidly and lack long-range order. Thus, stability, and hence porosity, can be viewed as competing features with crystallinity49. Further to this chain of thought, dynamic motion in a network solid should be fundamentally opposed to each of these three features. Structural shifting should disfavour stability, and therefore porosity, and unquestionably, crystallinity should be diminished by movement of components in the solid50. Solids that have been observed to reconcile dynamics and crystallinity typically have components sustained by non-covalent interactions, at least partially or completely45–47, as the energetic minima in the conversion profile would be more shallow, although some exceptions do exist48.

Barium 1,3,5-benzenetrisulphonate, BaL, is a network solid that reconciles all of the above features as, via multiple crystalline transformations, it converts from open- to closed-pore solid to mechanically trap atmospheric gas molecules. This dehydrated phase is thermally stable to in excess of 550°C, but it can be rehydrated to open the pores and allow controlled release of trapped gaseous guest molecules. The use of the Ba2+ ion and sulphonate groups in this work is critical as the interaction between them is of a diffuse ionic nature. Moreover, neither the metal ions nor the ligands have strong geometrical coordinative preferences and so the interactions sustaining the network are less directional. This results in a network material that merges the stability and porosity of a strongly bonded, rigid solid with the ability of a weakly bonded solid to flex and optimize its structure. Ultimately, a thermally robust, crystalline material with controllable gas capture and release properties is obtained.

Benzene-1,3,5-trisulphonic acid, H3L, was prepared by sulphonating sodium benzene-1,3-disulphonate with oleum and HgSO4 and then metathesized to the tetrabutylammonium (TBA) salt using TBA(HSO4). Crystals of Ba3{(H3O)3(L)2(H2O)8}, compound I, were grown by diffusion of methanol into an aqueous solution of (TBA)3L and BaCl2·2H2O. Owing to their rapid desolvation, crystals were mounted under a cold stream of blowoff from liquid N2. The structure of compound I, solved as orthorhombic, Pccn with a = 21.603(2), b = 9.5042(8), c = 17.932(2) Å, shows hydrated pores down the b and c axes. Branching out from a single ligand, the structure can be described as two molecules of L forming π-stacked dimers (C···C = 3.66(1)–3.70(1) Å) that sit in a staggered conformation offset by 1.38(1) Å. Crosslinking of these dimers with Ba1 results in the formation of two-dimensional (2D) sheets in the bc plane (Fig. 1a). Each Ba1 centre is 8-coordinate with sulphonate oxygen atoms occupying six positions and water the remaining two sites. Extension in the third dimension, along the a axis, is by the
Figure 1 Single-crystal X-ray structures of fully hydrated 1, intermediates 2a and 3, and dehydrated 4. a–g. Views of 1 (a), 2a (c), 3 (e) and 4 (g) perpendicular to the plane of the aryl rings, and 1 (b), 2a (d), 3 (f) and 4 (h) in the plane of the aryl rings showing shifting, contraction and re-expansion of pores (uncoordinated water removed).

Coordination of four sulphonate oxygen atoms to the Ba2 centres, also 8-coordinate with four coordinating water molecules. This bridging of bc layers along the a axis results in the formation of pores, visible down the b (Fig. 1b) and c axes, filled by disordered water molecules. The channel width ranges from 7.60(1)–7.81(1) Å. The crystal is 17.2% water by mass and has a calculated density \( \rho_{\text{calc}} \) of 2.201 g cm\(^{-3}\).

Facile structural conversion of compound 1 occurs with dehydration. As water evacuates, the structure responds to two driving factors: (1) the network contracts to fill the void space created by desolvation; (2) the Ba centres become unsaturated on dehydration and so the structure flexes to enable further coordination of sulphonate oxygen atoms. By heating a crystal of compound 1, it was possible to form the fully dehydrated Ba\(_3\)L\(_2\) network, 4, in a single-crystal-to-single-crystal manner while also detecting two intermediate phases, 2 and 3. Unit-cell parameters are given in Fig. 1. It should be noted that diffraction patterns yielding intermediate, but statistically poor, unit cells can be
Figure 2 X-ray diffraction images of a single crystal of 1 undergoing heating while on the diffractometer. a, 192 K. b, 253 K. c, 283 K. d, 383 K. e, 333 K. f, 393 K. The image in a represents 1 and that in f represents 4 (see the Supplementary Information). Images in b-d show spots for both 2 and 3. The image in e represents a stage of rapid heating on the way to conversion to 4. The vertical lines observed in a, b, c and e represent saturation of the detector.

obtained at any point during the dehydration. This is corroborative of the continuum of intermolecular interactions enabling this transformation (see below). Thus, the snapshots provided by 2/2a and 3 are not the only transition points between 1 and 4, but simply the only ones that could be characterized. Although this presents a less precise picture of the mechanism, it is, in fact, a more accurate representation of the dynamic behaviour of this solid.

Figure 2 shows the X-ray diffraction patterns obtained by heating a crystal of 1 from −100 °C on the CCD (charge-coupled device) diffractometer from orthorhombic 1 through to trigonal 4. The structural transformations occurring in the dehydration of 1 reached pseudo-plateaux at compounds 2 and 3. At these points, it was possible to freeze the sample and collect entire crystallographic data sets. For 2, the quality of the data was poor as the crystal did not dehydrate uniformly. This resulted in domains within the crystal being at different stages of transformation and considerable structural disorder. That said, the data set of 2 enabled correlation of unit-cell parameters (monoclinic, \textit{P}2\textsubscript{1}/\textit{c}, \(a = 14.645(5)\), \(b = 17.756(5)\), \(c = 12.144(5)\) Å, \(\beta = 96.42(1)^\circ\)) to the degree of hydration. By diffusing acetone rather than methanol in the preparation of 1, good single crystals of a Ba\textsubscript{L}\textsubscript{2} phase, with unit-cell parameters and hydration levels equivalent to 2, were obtained, henceforth referred to as 2a. Calculated spot overlays for Fig. 2a,f with 1 and 4 are provided as Supplementary Information.

On loss of ∼5% of the water from the structure of 1 (non-coordinated water) to give 2/2a, two major structural changes occur. The Ba\textsuperscript{2+} ions, which had been aligned into ribbons in 1, begin translation towards a hexagonal pattern about the L molecules (Fig. 1c). This is accompanied by a redistribution of the pores in the network. The pores between aryl groups contract, forming \pi-stacked tetramers of L (C···C = 3.667(3)–3.935(3) Å) as opposed to dimers in 1. These tetramers are then separated from each other by 6.69(3)–6.73(3) Å (Fig. 1d). The columns of tetramers are crosslinked, through sulphonate groups by Ba\textsuperscript{2+}, into a network of 1D pores, as opposed to 2D pores in 1. The net effect is still a denser phase (\(\rho_{\text{calc}} = 2.519 \text{ g cm}^{-3}\)). Notably, all Ba centres retain coordinated water, enabling the coordinated RSO\textsubscript{3}- groups to arrange themselves about the metal in a manner that permits the aryl groups to stack and obtain an energetic minimum. Ba1 and Ba3 are both 7-coordinate with two coordinated water molecules and five sulphonate oxygen atoms. Ba2 is 7-coordinate with four coordinated water molecules and three sulphonate oxygen atoms.

The loss of the next 9–10% of water from the structure is accompanied by the gradual progression of the structure towards a hexagonal pattern as shown by the structure of compound 3 (∼3% water, crystallized as orthorhombic, \textit{P}ccn with \(a = 9.461(2)\), \(b = 17.943(4)\), \(c = 15.453(4)\) Å) (Fig. 1e). The most significant change from 2 to 3, however, occurs perpendicular to the plane of the L molecules as shown in Fig. 1f. Rather than an alternating structure of stacked L tetramers and ∼6.7 Å pores observed in 2a, compound 3 shows no prominent pores. Rather, a further contracted structure is observed (\(\rho_{\text{calc}} = 2.791 \text{ g cm}^{-3}\)) with two sets of aryl–aryl distances (3.68(1)–3.74(1) Å and 3.99(1)–4.11(1) Å). Two two-fold disordered pairs of Ba\textsuperscript{2+} ions exist in 3: Ba1/Ba2 is 6-coordinate with five ligated sulphonate oxygen atoms and one water molecule; Ba3/Ba4 is 7-coordinate with homoleptic sulphonate coordination.

Compound 4, the fully dehydrated phase with trigonal symmetry, crystallized in \textit{P}3\textsubscript{1} with \(a = 9.607(2)\), \(b = c = 16.354(3)\) Å. This is demonstrated by the perfect alignment of the Ba\textsuperscript{2+} ions into hexagonal arrays about L molecules. The Ba centres in the hexagonal pattern are bridged into columns by the perpendicular crosslinking of SO\textsubscript{3} groups of L, (Fig. 1g). Compound 4 contains two crystallographically unique Ba centres, each 8-coordinate with homoleptic sulphonate coordination. With no water coordinated to the Ba ions, the ligated sulphonate groups distribute as spherically as possible about the sizable Ba ions (Ba\textsuperscript{2+} \(r_{\text{calc}} = 2.14 \) Å); this requires the aryl groups of L to
adopt an inefficient packing mode. Two sets of inter-aryl C–C distances are observed in 4; molecules of L form cofacial dimers (3.86(1)–3.96(1) Å and 4.09(1)–4.19(1) Å) generating small but not insignificant voids. Therefore, a key point with respect to the transformation is that the pores between aryl rings initially contract on loss of channel water but then, at the lowest degrees of hydration, they re-expand to enable sulphonate ligation to Ba\(^{2+}\) and achieve the minimum energy structure. This is corroborated by the fact that compound 4 (\(\rho_{\text{calc}} = 2.689\) g cm\(^{-3}\)) is actually less dense than 3. This forms the closed pores defined by the aryl rings and the Ba ions. With the size of Ba\(^{2+}\), six cations are able to bridge sulphonate groups and effectively form a continuous belt about two cofacial L molecules. The L molecules and six Ba ions then frame a cavity in which gases may be trapped.

At this stage, it is prudent to discuss the nature of intermolecular interactions in this material and how they contrast those in other (dynamic) MOF solids. Generally, structural transformations in MOFs could be classified as arising from either reorientations of macroscopic components (for example, shifting of layers) or as due to changes to the metal ion’s coordination sphere. Most MOFs, to maintain pores, rely on strong and directional metal–ligand bonding with metal ions of regular coordinative preferences. Thus, any changes in coordination resulting from a macroscopic structural shift are clearly defined and bond cleavage and formation is unambiguous. An excellent illustration is the recent paper by Rosseinsky and co-workers\(^{18}\). In this work, a network incorporates an aquated Co(II) centre that H-bonds to an included, non-ligated, 4,4′-bipyridine molecule. On heating, the primary-water sphere molecule is lost and replaced by the formerly second-sphere bipyridine molecule. Surprisingly, on rehydration, the bipyridine molecule is replaced by water and resumes its second-sphere role. Here, we have specifically chosen the Ba\(^{2+}\)/organosulphonate couple owing to the diffuse ionic nature of the intermolecular interactions and the adaptable coordination preferences of both metal and ligand components. This contrast can be illustrated by considering that, in 2, Ba2 is ligated, including ligands closer than 2.813(3) Å, by three water molecules and four sulphonate oxygen atoms. However, three further sulphonate donors lie from 2.884(3)–3.063(3) Å away from the Ba centre and four others from 4.467(3)–4.701(3) Å. Factoring the irregular geometry of Ba\(^{2+}\) (ranges from 7–9 coordinate typically) with the spherical ligation offered by RSO\(^{-}\) groups (a 180° rotation translates an O atom ∼2.9 Å), loss of coordinated water would enable even slight macroscopic shifts to maintain oxygen ligation to the metal ion. Thus, rather than an ‘all or nothing’ ligand-bonding scenario, for which the structural shifts require a specific orientation of components, the dynamics in this material are based more on the availability of a continuum of donor atoms. This illustration is meant to both affirm the exceptional behaviour of systems such as the Rosseinsky example above (as well as others cited) but also emphasize that, for networks from adaptable components, dynamic crystalline behaviour should be viewed more as the rule and less the exception\(^{34}\). Thus, 2/2a and 3 represent two of numerous stages in a continual structural transformation between 1 and 4. Powder X-ray diffraction of 1 (see Supplementary Information, Fig. S13) shows conversion to other crystalline phases on dehydration, still including compounds 2 and 3, and finally to 4 with heating.

Compound 4 is tremendously thermally robust. Differential scanning calorimetry/thermogravimetric analysis revealed, after dehydration to 225 °C, a stable plateau to 574 °C (see the Supplementary Information). Decomposition at this point was abrupt (∼30% loss in 3–5 °C) and inconsistent with an equilibrium process. The temperature of the mass loss varied with the particular gaseous atmosphere. For example, heating 1 in Ar(g) gave decomposition at 567 °C. These observations infer confinement of a finite and different number of gas molecules within each closed pore with different gases. This results in pressure differences ultimately manifested as variations in decomposition temperature.

During the selection of single crystals of 4, as the crystals were immersed in Paratone oil, bubbles of gas emerged from the solid (Fig. 3). Repeating this with various solvent combinations revealed that water, even in small amounts as present in Paratone, was being absorbed by crystals of 4. This served to rehydrate the Ba ions and open the ‘Ba-belted’ closed-pore cavities described previously. The clear implication of this result was that gas comprising the atmosphere could be taken up by the network and actually trapped within the pores of 4. A video that shows the real-time release of gas from a pellet of 4 is provided as Supplementary Information. Such regulated gas release has been observed for calixarene-based van der Waals crystals\(^{33,46}\) but, to our knowledge, never for a coordination network or any more strongly bonded system.

Several experiments were undertaken to ascertain the nature of the gas capture. N\(_2\) and CO\(_2\) sorption measurements on 4 showed no porosity. However, none would be expected for a closed-pore system. Sample 1 was then probed for porosity with continuous-flow hyperpolarized \(^{129}\)Xe NMR (Fig. 4). The signal at ∼130 p.p.m.
is consistent with Xe in channels of 0.6–0.8 nm diameter, but, with drying, the volume of Xe in the material diminished until a signal for confined Xe is barely detectable. However, the observed bubbling could be reconciled by modelling the accessibility of the pores in 4 to gases of different radii (Fig. 5). The pores in 4 can contain gases with a radius of 1.4 Å (N₂) and, expectedly, gases with a radius of 2.1 Å (Xe) to a much smaller extent. Allowing for one disordered water molecule makes the pores virtually inaccessible to a sphere of even 1.2 Å radius. Thus, for the larger Xe atom, it is likely even trace moisture renders it an ineffective probe of this material. Characterization of atmospheric gases as trapped in the pores was difficult owing to their thermal motion and the fact that the same gases surround the crystals. To ultimately show that gases comprising the external atmosphere could be included in closed pores of 4, a colourimetric experiment was carried out (see Fig. 6 for details). Crystals of 1 were dehydrated to 4 in an atmosphere of NH₃(g) then heated under vacuum to liberate externally adsorbed NH₃. The dried crystals were then placed in an aqueous Co(NO₃)₂ solution. The Co²⁺ ions readily adsorbed to the crystal's surface to give a pink colour. This coincided with release of gas from the crystal as water rehydrated the Ba ions and opened the closed pores. Addition of water, as in the Supplementary Information video, does also cause dissolution. In this case, dissolution is apparently slowed by adsorption of Co(11). However, in ~2 min, the crystals changed colour from pink to a deep green characteristic of hexamine Co(11). As any externally sorbed gases would have been removed in the desorption cycle, the only source for NH₃(g) would be the interior of the solid, confirming that the external atmosphere was trapped during dehydration. Figure 6b shows spots of green visible indicating where NH₃ is escaping the crystal. Given the 'pore re-opening' mechanism of the gas uptake, little selectivity in the process was expected. All gases (CO₂, O₂, N₂, CH₄, He, Ar, Xe, NH₃) examined as the external atmosphere were taken up.

With respect to gas release from the crystal, two processes are in operation. On rehydrating 4 by addition of drops of 25% water in methanol, powder X-ray diffraction (see Supplementary Information, Fig. S14) confirms the solid reverts to hydrated crystalline forms that require re-opening of the pores. Dissolution of the solid does occur at moderate to high degrees of hydration, rapidly releasing gas as shown in the Supplementary Information video. At controlled low degrees of hydration, it is expected that gas could be released exclusively by pore opening, as observed with Paratone (Fig. 3). The fact that release is controllable by rehydration though is independent of mechanism. Regarding visualization of gas release, there are several pertinent variables. More gas trapping, and hence more bubbling, is enhanced by: higher water content in the rehydrating solvent, higher heating rates in the dehydration cycle, longer heating cycles and smaller particles of 4. The actual visualization is enhanced by a more viscous medium as the bubbles merge on the solid surface.

The mechanical properties of a solid are inherently linked to the strength and directionality of the interactions that sustain its connectivity. In attempts to generate porous materials, efforts have focused on strong bonding and regimented interactions. However,
the natural world is replete with examples where weak interactions function cooperatively to form stable assemblies. The culmination of this approach is not simply the ability to optimize the assembly process but to enable dynamics and, ultimately, to derive function cooperatively to form stable assemblies. The reconciliation is enabled by the cooperative use of weaker, less-directional interactions and properties of network solids (robustness, porosity, crystallinity and dynamics) in a single compound. This transformation process continued until the crystals were at room temperature, at which point they were heated to 380 K for a period of 3 h and a full data set was collected giving 4.

**METHODS**

**PREPARATION OF L**

Sodium benzene-1,3-disulphonate (20.0 g, 70.94 mmol) was added to 20% aqueous oleum (50.0 ml) and HgSO₄ (800 mg, 2.68 mmol, 4 wt%). The reaction mixture was heated at 290 °C for 24 h, and then cooled to room temperature. The brown mixture was poured into water (600 ml) and quenched with 30% NaOHaq until the solution pH was > 10, and then diluted to 1,200 ml with water. This solution was filtered using a 5 μm sintered glass frit to remove Hg(OH)₂, leaving a clear yellow solution. An aqueous solution (20 ml) of (TBA)HSO₄ (38.9 g, 114.57 mmol) was added to this solution and stirred for 10 min. The TBA salt of L was extracted from the basic mixture using dichloromethane extractions (6 × 125 ml). The extracts were combined, dried (MgSO₄) and filtered, giving a clear solution. The solvent was removed to give tri-tetrabutylammonium benzene-1,3,5-trisulphonate, TBA,L. Yield: 24.05 g, 32%. Found: C, 61.89; H, 10.92; N, 4.09. Calculated for TBA,L: C, 62.20; H, 10.73; N, 4.03. 1H NMR (300 MHz D₂O) 0.916–0.965 (t, 36H, J = 0.247 Hz), 1.281–1.404 (m, 24H, J = 0.0239), 1.539–1.679 (m, 24H, J = 0.0256), 3.136–3.193 (t, 24H, J = 0.0274), 8.294 (s, 3H). 13C NMR (300 MHz dimethysulphoxide) 147.18 (C–SO₃), 122.93 (C–H), 57.28 (α-CH₃), 22.99 (β-CH₂), 18.99 (γ-CH₃), 13.27 (CH₃).

**PREPARATION OF 1 AND 2a**

TBA,L (230 mg, 0.239 mmol) and BaCl₂·2H₂O (87.71 mg, 0.359 mmol) were dissolved in water (2 ml). Single crystals of 1 were grown by vapour diffusion of methanol into this solution. In 4–5 days, large (0.5 mm × 0.5 mm) transparent crystalline blocks of Ba₃(H₂O)₆(L₁)(H₂O)ₙ, 1, that were suitable for X-ray analysis had grown. Using acetone as the diffusing solvent yielded single crystals of 2a.

**TRANSFORMATION OF 1 TO 2 AND 3 WITH DEHYDRATION**

Crystals of 1 were left at ambient conditions. After a day, the crystals had transformed to compound 2 (monoclinic, P2₁/n, a = 14.6451, b = 17.7557, c = 12.1443 Å, β = 95.96°). The crystal was continually dehydrating at this point and a high-quality X-ray data set was not attainable even at low temperature. Slight variations in the cell parameters were observed on the crystals standing for more or less time. On standing for 7–14 days, the dehydration reached a more defined plateau and a solvable data set was obtained for compound 3 (orthorhombic, P2₁/c, a = 9.5625, b = 17.6670, c = 15.6630 Å).

**VARIABLE-TEMPERATURE SINGLE-CRYSTAL X-RAY DIFFRACTION AND TRANSFORMATION TO 4**

Single crystals of 1 were flash frozen (173 K) using a liquid nitrogen stream, and glued onto a Pyrex glass fibre using a two-component epoxy. The crystals were indexed, collected and underwent a heating program of 10°C steps using the Oxford Cryostream on the diffractometer. At each step, the crystals were re-indexed. The process continued until the crystals were at room temperature, at which point they were heated to 380 K for a period of 3 h and a full data set was collected giving 4.

**¹²⁹Xe NMR MEASUREMENTS**

Crystals of 1 were gravity filtered from their water/alcohol solution and dabbed dry on filter paper. The crystals were transferred to the NMR probe, and left overnight under a stream of argon at 80°C before any experiments were carried out. Hyperpolarized ¹²⁹Xe gas was produced under continuous-flow conditions using an optical pumping set-up similar to that previously reported. The polarizer was located within the fringe field of the spectrometer’s superconducting magnet and a 30 W continuous-wave diode laser from OptoPower, operating at a wavelength of 785 nm, was used as the source of optical excitation. The gas mixture of xenon, helium and nitrogen with a volume composition of 1%-96%-3% respectively, and flow rates of 110–160 cm3 min⁻¹ (gas flow normalized to standard conditions), was delivered through 1.5-mm-inner-diameter plastic tubing from the polarizer directly to the sample contained in a modified Morris Instruments NMR probe equipped with a 5 mm coil. The continuous-flow hyperpolarized ¹²⁹Xe NMR experiments were carried out on a Bruker AMX-300 spectrometer operating at 83.03 MHz (magnetic field of 7.04 T). For all single-pulse experiments, 1,024 scans were acquired with a pulse recycle time of 1 s. Variable-temperature experiments were carried out over the range of 173–368 K at 15° intervals regulated by a Bruker BVT3000 temperature controller unit. The chemical shifts of ¹²⁹Xe were referenced to xenon gas extrapolated to zero pressure. Before experiments were repeated the next day, the sample was left in the probe under a room-temperature flow of argon gas. A week later, the sample was probed again, at which point it was heated in a 120°C oven for 6 h before NMR experiments were carried out.

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