

Determination of the hydrogen absorption sites in $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})$ by single crystal neutron diffraction

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A variable temperature (5–300 K) single crystal Laue neutron diffraction study has been conducted, and the gas absorption sites within hydrogen-loaded $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})$ have been located.

The technology already exists in the form of fuel cells to convert stored chemical energy, in the form of hydrogen gas, directly into electrical energy with high efficiency.¹ The crucial factor that is hindering progress towards the commercial implementation of these devices is the safe and efficient storage of the hydrogen fuel gas, and the development of storage media designed to overcome this difficulty is at the forefront of current research.² Of the various materials under consideration, ordered porous materials such as metal–organic frameworks are considered to be capable of fulfilling this role.³

It is the ability to adapt the surface chemistry of the framework cavities that makes metal–organic frameworks attractive contenders for hydrogen storage applications. It is hoped that by optimising the chemical and electronic nature of the framework architecture the gas uptake, at a given pressure and temperature, can be maximised. To allow for a systematic approach to the modification of a particular framework, with an aim to improve its gas absorption properties, it is imperative to understand which sections of the structure interact strongly with the physisorbed hydrogen gas, namely, to locate the gas absorption sites. Once this is known these aspects of the structure can be enhanced to increase the absorption characteristics of the framework.

Although there have been reported examples of the use of single crystal and powder X-ray diffraction for determining the location of absorption sites for a variety of gases (CO_2 , Ar, and O_2) within porous coordination polymer complexes,⁴ in terms of the advancement of these materials for hydrogen storage purposes, this information is of limited use. It is of greater benefit to determine accurately the location of hydrogen gas molecules themselves included within a framework structure, as this knowledge is of direct relevance. Although there have been reports of the use of X-ray diffraction for locating physisorbed hydrogen gas within the cavities of coordination polymer complexes, the

accuracy of the results obtained by this method is limited by the low X-ray scattering ability of hydrogen.⁵ Herein we report on the first example of the use of single crystal neutron diffraction for the elucidation of the hydrogen gas absorption sites within a metal–organic framework. The model framework material chosen for this study was $\text{Zn}_4\text{O}(1,4\text{-benzenedicarboxylate})$ ($\text{Zn}_4\text{O}(\text{BDC})_3$)⁶ (Fig. 1) for which the gas absorption properties have been well documented.⁷

At 300 K, 150 K, and 120 K the neutron Laue data showed an absence of hydrogen gas within the $\text{Zn}_4\text{O}(\text{BDC})_3$ framework cavities; the following discussion will be confined to a consideration of the data collected at 120 K, 50 K, 30 K and 5 K.† Table 1 provides pertinent structure refinement details. From our previous X-ray diffraction study of nitrogen-loaded $\text{Zn}_4\text{O}(\text{BDC})_3$, in which nitrogen gas was found to 62% occupy the α -site at 120 K, it may be expected that hydrogen gas would also partially occupy the α -site at this temperature.⁸ However no significant nuclear density was observed at this site at 120 K. This may be due to an absence of hydrogen in the cavity at this temperature, or to extremely large disorder of any hydrogen molecules present.

All Laue patterns exhibited the expected face centred cubic symmetry (space group $Fm\bar{3}m$). The $\text{Zn}_4\text{O}(\text{BDC})_3$ framework is

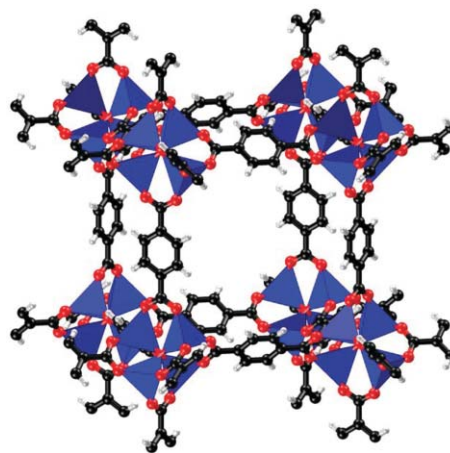


Fig. 1 A single unit cell of the $\text{Zn}_4\text{O}(\text{BDC})_3$ structure. The framework nodes comprise four Zn_4O tetrahedra that share a common vertex. These nodal metal clusters are linked via 1,4-benzenedicarboxylate (BDC) molecules to give a three-dimensional net congruent with the α -polonium structure. The distance between the centres of adjacent metal clusters is 12.94 Å. After accounting for the van der Waals radii of the framework atoms, hypothetically, a sphere with a diameter of ~ 8 Å could diffuse freely through the framework structure. Blue: zinc; red: oxygen; black: carbon; grey: hydrogen.

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Table 1 Structure refinement details

	120 K	50 K	30 K	5 K
Collected reflections	5693	4701	6281	12468
Unique reflections	417	411	416	434
No. parameters	17	19	22	24
$R(\text{int})$	0.4189	0.3606	0.3826	0.3922
$R(\sigma)$	0.2161	0.2033	0.1722	0.1345
Goof (S)	2.272	1.996	2.130	3.117
$R_1 [I > 3\sigma(I)]$	0.2721	0.2154	0.2304	0.2444
$wR_2 [I > 3\sigma(I)]$	0.2585	0.2228	0.2834	0.2476

ordered at all temperatures and no phase transitions were observed.

At 50 K, a single hydrogen absorption site (α -site) in the framework cavity is occupied, and is located on a site of $3m$ symmetry (Wyckoff site $32f$). As the individual atoms of this molecule could not be resolved, a single hydrogen 'atom' was positioned at this site (H1) and after careful refinement the occupancy of H1 was found to be 100%. This site was also shown to be 100% occupied at 30 K, but at this lower temperature the individual atoms of the physisorbed hydrogen gas could be resolved. The second atom of this molecule, H2, is disordered over three positions due to the 3-fold axis on which atom H1 is located. The H1–H2 bond length is 0.72(4) Å, a value that is close to the expected distance of 0.74130(6) Å.⁹ Therefore at 50 K and 30 K the formula for the hydrogen-loaded framework is $\text{Zn}_4\text{O}(\text{BDC})_3 \cdot 4\text{H}_2$.

At 5 K, the α -site is again 100% occupied, and the H1–H2 bond length is calculated as 0.70(4) Å. An additional gas absorption site (β -site), can be identified at this temperature, denoted H4 in Fig. 2. Unfortunately, the individual atoms of this second molecule cannot be resolved, therefore a single atom model (H4) has been used to represent the 'molecule'. H4 is located on a site of $3m$ symmetry ($32f$), over the face of a ZnO_4 tetrahedron, and after cautious refinement this 'molecule' was found to have a total occupancy value of 98%, although the isotropic temperature factor for this 'molecule' is rather high ($U_{\text{iso}} = 0.18(3) \text{ \AA}^2$), so care must be taken not to place too much reliance on the occupancy value. The formula for the hydrogen-loaded framework at 5 K is $\text{Zn}_4\text{O}(\text{BDC})_3 \cdot 8\text{H}_2$.

The shortest framework–gas distances are listed in Table 2. For comparison, the sum of the van der Waals radii for oxygen and

Table 2 Shortest framework–gas distances at 5 K

Contact	Distance/Å
H1...C1	3.39(2)
H1...O1	3.75(6)
H1...O2	3.37(3)
H1...Zn1	3.61(5)
H2...C1	3.12(5)
H2...C2	3.73(6)
H2...O2	3.23(5)
H2...Zn1	3.84(5)
H4...O2	3.45(5)
H4...Zn1	3.64(6)

hydrogen is 2.72 Å, for zinc and hydrogen it is 2.59 Å, and for carbon and hydrogen it is 2.90 Å.¹⁰ It is evident that the interaction of the hydrogen gas with the electronic potential of the framework is very weak, as would be expected for physical absorption. However, it should be borne in mind that the hydrogen molecules are likely to be oscillating or tumbling about their centres of mass, which systematically increases the calculated intermolecular hydrogen gas–framework distances, and increases their estimated standard deviations.

It is immediately apparent from a space-filling diagram of one of the framework cavities at 5 K (Fig. 2) that the hydrogen gas congregates in the vicinity of the framework nodes. At 120 K, the evacuated framework contains $\sim 77\%$ of void space that is accessible to the hydrogen gas, and at 5 K the physisorbed hydrogen gas occupies approximately 12% of this volume.

Using second-order Møller–Plesset perturbation theory, Sagara *et al.* calculated a binding energy of 6.86 kJ mol⁻¹ for the interaction between the physisorbed hydrogen gas and the nodal regions of the $\text{Zn}_4\text{O}(\text{BDC})_3$ architecture.¹¹ A lower binding energy of approximately 5.27 kJ mol⁻¹ was estimated for the interaction between hydrogen gas and a fully protonated 1,4-benzenedicarboxylic acid molecule, a model which can be considered as a simple representation of the linker sections of the $\text{Zn}_4\text{O}(\text{BDC})_3$ framework. The grand canonical Monte Carlo simulations executed by the same authors indicated that the absorption sites surrounding the metal clusters become saturated at 78 K and 4800 kPa; at 300 K the hydrogen gas was predicted to reside not only on sites located adjacent to nodes, but also near the BDC links.

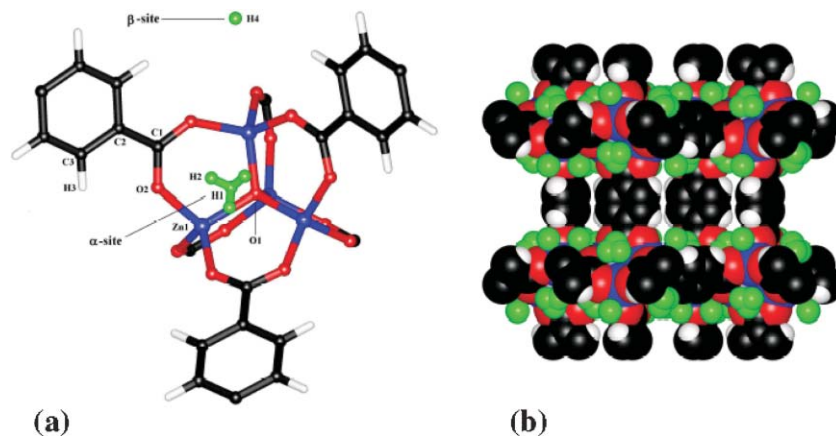


Fig. 2 (a) The location of the hydrogen absorption sites at 5 K relative to the framework atoms. The α -site is 100% occupied at 50 K, 30 K and 5 K. The β -site is 98% occupied at 5 K. Only one of the H2 atoms is labelled for clarity. (b) Space-filling diagram of one of the framework cavities at 5 K; the orientation of the diagram is the same as in Fig. 1. Blue: zinc; red: oxygen; black: carbon; grey: framework hydrogen atoms; green: absorbed hydrogen gas.

The neutron diffraction results are in partial agreement with these theoretical findings. As predicted, the relatively high-energy absorption sites situated near to the metal clusters were found to be fully occupied at low temperature (5 K). However, no evidence of hydrogen gas residing in the framework channels was seen at 300 K, and at none of the temperatures investigated was there any hydrogen gas located in the vicinity of the BDC linker molecules. That said, we do acknowledge that the neutron data are weak especially at higher temperatures. Additionally, the neutron data were collected with a $\text{Zn}_4\text{O}(\text{BDC})_3$ single crystal which had been loaded at room temperature with hydrogen gas at a pressure of ~ 1 atm, and as such the amount of gas loaded into the framework will be reduced with respect to the Monte Carlo simulations. Both these factors may account for our inability to observe nuclear density at the lower energy sites that are theoretically predicted to be occupied at higher temperatures.

A variable temperature (30–293 K) X-ray diffraction analysis of argon- and nitrogen-loaded $\text{Zn}_4\text{O}(\text{BDC})_3$, also indicated that the nodal regions of the framework are the principal sites for gas absorption.⁸ The two key sites (those most frequently occupied) identified from the X-ray study correspond to the α - and β -sites determined from these current neutron data for the hydrogen-loaded material (Fig. 2).

Rosi *et al.* identified two distinct hydrogen absorption sites within the $\text{Zn}_4\text{O}(\text{BDC})_3$ cavities using inelastic neutron scattering spectroscopy (INS) at 10 K.⁷ The authors concluded that one site was associated with the hydrogen gas interacting with the zinc atoms of the framework nodes, and the second site with the BDC linker molecules. Later, Rowsell *et al.* re-analysed these INS data and postulated that both the hydrogen gas absorption sites are connected with the ZnO_4 nodal clusters.¹² The first of these sites was said to be located over the shared vertex of the ZnO_4 units that is situated at the centre of the node, and the neutron results presented herein concur with this assignment (α -site). However, in the more recent paper the authors speculated that the second site is located over an edge of the ZnO_4 tetrahedra; this is at odds with the model derived from our neutron diffraction data in which the second site is positioned over the face of the ZnO_4 tetrahedra (β -site) (Fig. 2).[‡]

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Notes and references

† CCDC 282407–282412. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b511941c

‡ Colourless cubic crystals of $\text{Zn}_4\text{O}(\text{BDC})_3$ were obtained by heating a solution of N,N' -diethylformamide, zinc nitrate tetrahydrate, and 1,4-benzenedicarboxylic acid in a tightly capped vial at 100 °C for 12 h. A crystal suitable for diffraction analysis, with dimensions $0.4 \times 0.4 \times 0.6$ mm³, was immersed in chloroform before being affixed with grease to the wall of a glass Lindemann capillary. This capillary was attached to a gas manifold and placed under vacuum ($<10^{-3}$ Torr) to evacuate all solvent and air, before being back-filled with hydrogen gas at ~ 1 atm and sealed. All neutron data were collected with the *Very Intense Vertical Axis Laue Diffractometer (VIVALDI)*¹³ at the Institut Laue-Langevin (Grenoble, France). A beam of thermal neutrons covering a wavelength range of 0.8–5.2 Å was utilised. Neutron-sensitive image plates, covering a

total of 63% of the full solid angle, were employed to record the Laue patterns. A standard ILL Orange cryostat was used to control the sample temperature.¹⁴ Data were recorded at the following temperatures: 300 K, 150 K, 120 K, 50 K, 30 K and 5 K. At each temperature three or four Laue patterns were recorded, each at a different setting of ϕ , the rotation about an axis perpendicular to the incident beam, within the range of $-120 < \phi < -20^\circ$ ($\Delta\phi = 20^\circ$). The exceptions were the 5 K data collection, for which eight patterns were recorded ($-120 < \phi < 20^\circ$ [$\Delta\phi = 20^\circ$]), and the 300 K data collection, for which five Laue patterns were recorded ($-120 < \phi < -20^\circ$ [$\Delta\phi = 20^\circ$]). The exposure time for each pattern was approximately 4.5 h. The diffraction patterns were indexed with the program LAUEGEN,¹⁵ and the reflections were integrated with a modified two-dimensional version of the algorithm formulated by Wilkinson *et al.* and Prince *et al.*¹⁶ The data were normalised, to account for the incident wavelength spectrum, by comparison of recurring and equivalent reflections; this was performed with the program LAUENORM.¹⁷ Only data that were within the wavelength band 0.95–3.0 Å with $d \geq 0.95$ Å (the resolution limit of the Laue patterns), and had $I > 3\sigma I$ were included in this procedure. The absorption by the capillary, the cryostat heat shields, and the sample was estimated to be approximately 0.7–1.0%. This negligible degree of absorption would have been mostly accounted for during the empirical normalisation procedure, and as such no additional absorption correction was deemed necessary. Full-matrix least-squares structure refinement was carried out with SHELXTL.¹⁸ Since the unit-cell length cannot be ascertained from white-beam neutron Laue data collected at a steady-state source we assumed a value at each temperature extrapolated from the published monochromatic X-ray values of 25.8821(5) Å at 30 K, 25.8878(4) Å at 90 K, and 25.856(3) Å at 120 K.⁸ All six structures were refined in the cubic space group $Fm\bar{3}m$. Graphics have been generated with OLEX version 2.55.¹⁹

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