Flexible Yttrium Coordination Geometry Inhibits “Bare-Metal” Guest Interactions in the Metal-Organic Framework Y(btc)

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Abstract: Y(btc) (btc = 1,3,5-benzenetricarboxylate) is a metal-organic framework that exhibits significant adsorption of industrially-relevant gases such as H₂, CH₄, and O₂. Previous studies have noted a surprising lack of close interactions between the adsorbed guest molecules and Y, despite the apparent availability of a “bare-metal” binding site. We have extended our previous work in a detailed investigation of the adsorption behaviours of CO₂, CD₄, and O₂ in Y(btc) over a range of concentrations using in situ neutron powder diffraction methods. The O–Y–O bond angles enclosing the bare-metal site are found to change considerably depending on the type and quantity of guest molecules present. Multiple binding sites are found for each guest species, and the largest changes in O–Y–O angles are accompanied by changes in the filling sequences of the binding sites, pointing to an important interplay between guest-induced framework distortions and binding site accessibility. These results suggest the potential for coordinatively flexible rare-earth metal centres to promote guest-selective binding in metal-organic frameworks.

Keywords: adsorption; metal-organic framework; neutron powder diffraction

1. Introduction

The atomic-scale understanding of gas-sorption mechanisms in porous solid sorbents has become a focus of major research efforts in recent times, driven in particular by the need for efficient gas separators in many energy-related applications. Porous crystalline materials such as metal-organic frameworks (MOFs) are often targeted for these applications due to their favourable properties: good gas selectivity and capacity, ease of handling compared to liquid sorbents, as well as adequate mechanical, thermal, and chemical stabilities. Importantly, these materials are highly tuneable, and significant opportunities exist for engineering their chemistries toward particular sorbent applications. Key framework features which improve adsorption properties need to be identified and optimised for the development of better future materials. For example, many studies have shown that the presence of coordinative-unsaturated metal centres tends to enhance total uptake of gases such as hydrogen [1–3], methane [4] and ammonia [5], among others, and can also contribute to guest selectivity in the presence of gas mixtures [6]. These “bare” metal sites interact strongly with many guest molecules, yielding higher binding energies and often resulting in denser arrangements of guests.
in the pores of the sorbent material. Unfortunately, the operative stability of bare metal-containing MOFs is often compromised by their ability to readily adsorb guests from the air, such as water and gaseous species, which can lead to permanent degradation of their crystallinity and adsorptive function [7–9]. By contrast, the excellent moisture stability of the well-known Zr$_6$O$_4$(OH)$_4$(BDC)$_6$ (where BDC = benzene-1,4-dicarboxylate), also known as UiO-66(Zr) material, has been partially attributed to the absence of coordinatively unsaturated Zr in the Zr$_6$O$_4$(OH)$_4$(CO$_2$)$_{12}$ oxide cluster, preventing hydrolytic attack by water molecules [8].

Bare-metal sites are typically created in MOFs by the removal of coordinated solvent molecules from the material following its initial synthesis. In these cases, the preferred coordination geometry of the metal centre and the fixed network topology of the linker molecules both serve to maintain the overall structure of the MOF without significant changes to the framework geometry in the vicinity of the metal centre. However, MOFs containing rare-earth metals may display more flexibility in their coordination geometry upon removal of the solvent due to the greater number of satisfactory geometries adopted by these large metal ions [10–12]. One such example is Y(btc) (btc = 1,3,5-benzenetricarboxylate), a MOF which displays appreciable uptake of H$_2$ [13], CH$_4$ and O$_2$ [14]. Y(btc) is a structural analogue of Tb(btc) (also known as MOF-76 [15]) and consists of parallel 4$_1$-type helices of Y atoms linked by the bridged carboxylate groups of three btc ligands, resulting in square channels which extend along the c axis in the tetragonal space group P4$_3$22 (Figure 1). The distance between corresponding atoms on opposite walls of the square channels is ~10.3 Å, equivalent to the $a$ parameter of the unit cell. Structural studies have demonstrated significant relaxation of the linker geometry around the Y centre upon removal of the coordinated water-of-crystallisation, yielding a bare-metal site which may be less accessible to guest molecules [14]. In the same study, CD$_4$ was found to display no significant interaction with the Y centre at 1 CD$_4$:Y loading, while O$_2$ interacted weakly with Y only at the least populated of its three observed binding sites. Similarly, no interaction with the bare-metal site was reported for any of the four observed binding locations of D$_2$ in the material [13].

**Figure 1.** The square channel of Y(btc) viewed along the $c$ axis (vanishing perspective is used). Shown are Y (light blue), C (dark grey), O (red) and H (light grey).

The linear CO$_2$ molecule has a smaller minimum diameter than CH$_4$ and is more polarisable than either H$_2$ or O$_2$, giving it the opportunity for better access to, and more favourable interactions with, the restricted Y bare-metal site in Y(btc). Furthermore, the capture of CO$_2$ by porous sorbents is of special relevance to the energy industry, due to the drive to minimise carbon dioxide emissions from the waste streams of existing fossil-fuel technologies such as coal plants [16,17], as well as ensuring
the viability of natural gas reserves. We have therefore undertaken a detailed investigation of the adsorption behaviour of CO₂ in Y(btc), extending a previous investigation of CH₄ and O₂ adsorption in the material by exploring the guest concentration effects on both the binding and the framework structure. As with the previous investigations of gas adsorption in Y(btc), neutron scattering methods were used for structural characterisation of the host-guest system, as scattering from the heavy yttrium dominates the X-ray data and inhibits the location of lighter framework and guest atoms. In the context of this new work and of results previously reported for O₂, CH₄, and H₂ [13,14], we present an analysis of the Y coordination environment in Y(btc) and its behaviour in the presence of different guest species and concentrations, with a view to understanding how MOF sorbent functionality is influenced by the use of coordinatively flexible rare-earth metal centres.

2. Results

2.1. Carbon Dioxide Adsorption

2.1.1. Adsorption Isotherms

Gas adsorption isotherms measured for Y(btc) at 298 K demonstrated good uptake of CO₂, the measured value of around 5 mmol·g⁻¹ at 10 bar being almost twice the uptake of CH₄ and four times that of O₂ or N₂ at the same pressure and temperature (Figure 2). Uptake kinetics for all gases were very rapid, with equilibration achieved within ~2 min after each dose was applied to the sample. Water adsorption in Y(btc) was found to be fully reversible and the isothermal curve was reproduced after a second adsorption cycle, highlighting the relatively-good stability of the material to moist environments (Figure S1).

![Figure 2. Adsorption isotherms for CO₂, CH₄, O₂ and N₂ at 298 K.](image)

2.1.2. Binding Site Locations

The structure of the empty Y(btc) framework was initially refined against neutron powder diffraction (NPD) data collected for the CO₂-loaded material. Three crystallographically-distinct CO₂ adsorption sites were determined, all of which were observed to be partially occupied after the first dose of 1 CO₂·Y (that is, one mole of CO₂ per mole of Y(btc)) (Table 1). Y(btc)·CO₂ refinement results can be found in the Supporting Information (Tables S1 and S2).
Table 1. Crystallographic details for CO$_2$ sites within Y(btc) at a dose of 1 CO$_2$:Y.

<table>
<thead>
<tr>
<th>Binding Site</th>
<th>Atom</th>
<th>Wyckoff Site</th>
<th>Site Symmetry</th>
<th>Fractional Coordinates</th>
<th>Fractional Occupancy</th>
<th>U$_{eq}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_{CO_2}$</td>
<td>C1a</td>
<td>8d</td>
<td>1</td>
<td>0.818(4) 0.819(8) 0.339(5)</td>
<td>0.52(2)</td>
<td>21.3(2)</td>
</tr>
<tr>
<td></td>
<td>O1a</td>
<td>8d</td>
<td>1</td>
<td>0.831(7) 0.852(7) 0.434(4)</td>
<td>0.52(2)</td>
<td>21.3(2)</td>
</tr>
<tr>
<td></td>
<td>O1b</td>
<td>8d</td>
<td>1</td>
<td>0.853(7) 0.808(6) 0.285(4)</td>
<td>0.52(2)</td>
<td>21.3(2)</td>
</tr>
<tr>
<td>B$_{CO_2}$</td>
<td>C2a</td>
<td>4a</td>
<td>2</td>
<td>0.693(1) 0.007(1) 0.167(2)</td>
<td>0.199(17)</td>
<td>17.5(3)</td>
</tr>
<tr>
<td></td>
<td>O2a</td>
<td>8d</td>
<td>1</td>
<td>0.673(8) 0.007(1) 0.167(2)</td>
<td>0.199(17)</td>
<td>17.5(3)</td>
</tr>
<tr>
<td>C$_{CO_2}$</td>
<td>C3a</td>
<td>4a</td>
<td>2</td>
<td>0 0.945(1) 0.5</td>
<td>0.11111</td>
<td>4.6(2)</td>
</tr>
<tr>
<td></td>
<td>O3a</td>
<td>8d</td>
<td>1</td>
<td>0.915(8) 0.950(8) 0.533(1)</td>
<td>0.11111</td>
<td>4.6(2)</td>
</tr>
</tbody>
</table>

Figure 3 shows the arrangement and orientation of all symmetry-generated locations for each of the three CO$_2$ adsorption sites within a single Y(btc) unit cell. The molecules located at sites B$_{CO_2}$ and C$_{CO_2}$ lie along the [y, 0, 1/4] and [0, y, 1/2] 2-fold axes, respectively, and therefore occur with half the multiplicity of site A$_{CO_2}$. Site occupancy restrictions arising from close interactions between these adsorption sites are discussed in Section 2.1.3.

![Figure 3](image-url)
These electron-deficient C atoms provide a favourable environment with which the electron-rich O guest atoms can interact. Similarly, O atoms from two of the nearby carboxylate groups appear to sandwich the electron-deficient C atom of CO$_2$, forming a ring of favourable electrostatic host-guest interactions below the guest molecule. Nevertheless, while site B$_{CO_2}$ appears more favourable based on the quantity of electrostatic host-guest interactions, the observed occupancy factor of 0.199(17) CO$_2$:Y at a loading of 1 CO$_2$:Y is less than half that of site A$_{CO_2}$.

The third observed adsorption site, C$_{CO_2}$, displays the longest host-guest distances and the lowest site occupancies after both CO$_2$ doses. This site is located 3.628(10) Å and 4.21(3) Å from the nearest and next-nearest btc carboxylate groups, respectively. These distances are generally considered too large to result from significant host-guest interactions, so it is proposed that this site arises from the formation of a bilayer with previously adsorbed CO$_2$ molecules. When the gas-loaded system is viewed along the c axis, it can be seen that site C$_{CO_2}$ is closest to the pore centre (Figure 3b), further supporting this hypothesis.

It should be noted that none of the three CO$_2$ adsorption sites display any significant interaction with the available Y bare-metal sites, with the closest interaction distances occurring for sites A$_{CO_2}$ and C$_{CO_2}$ at 4.16(9) and 4.640(10) Å, respectively. It is typically expected that the bare-metal sites of a coordination framework should provide guest molecules, particularly quadrupolar CO$_2$ molecules, with a favourable interaction site. This result will be discussed further below.

The total refined occupancies across the observed CO$_2$ sites after both doses of CO$_2$ equated to 80%–85% of the amount of CO$_2$ dosed, indicating that up to 20% of guests were disordered within the framework and could not be located crystallographically. The relative occupancies of each site remained largely unchanged between the first and second doses, with all occupancy factors increasing by around 100% when the total CO$_2$ dosage was doubled.

### 2.1.3. Intermolecular Interactions and Occupancy Restrictions

As seen in Figure 4, several of the possible CO$_2$ binding sites lie in close proximity to one another, and this is expected to impose some occupancy restrictions. The shortest guest-guest distance of 2.063(1) Å occurs between two symmetrically-equivalent C$_{CO_2}$ sites, restricting the maximum occupancy of this site to 50% (0.5 CO$_2$:Y). The highest observed C$_{CO_2}$ occupancy factor, ~26%, lies well within this upper bound. The nearest intermolecular distance between sites A$_{CO_2}$ and C$_{CO_2}$ (2.10(8) Å) also restricts the co-occupation of these sites to 50%. As the multiplicity of site A$_{CO_2}$ is 8, the maximum 50% occupancy of this site corresponds to 1 CO$_2$:Y. This value is approached after the second dose of CO$_2$.

![Figure 4. Intermolecular interactions of CO$_2$ molecules at a dose of 1 CO$_2$:Y, as viewed along the a axis. Shown are CO$_2$ adsorption-site A$_{CO_2}$ (green), site B$_{CO_2}$ (orange) and site C$_{CO_2}$ (blue), and framework atoms Y (light blue), C (dark grey), and O (red). Framework H atoms are omitted for clarity.](image-url)
The nearest interactions between sites $A_{CO_2}$ and $B_{CO_2}$ occur at a distance of 2.35(2) Å. These two sites are aligned in an offset-parallel orientation relative to one another that takes advantage of the electrostatic interactions between the slightly positively-charged C and slightly negatively-charged O atoms. Although an end-to-side interaction (similar to that observed in solid CO$_2$) would more effectively exploit the quadrupolar nature of the CO$_2$ molecule, the observed arrangement appears to represent an optimal guest-guest configuration given the space constraints inside the Y(btc) pore and the presence of additional host-guest electrostatic interactions.

2.2. Methane and Oxygen Adsorption at High Dosage

Each NPD measurement described in [14] for CD$_4$ and O$_2$ at 1 guest:Y dosing was immediately followed by a second dose of 1 guest:Y applied to the same sample, for a total dose amount of 2 guest:Y. NPD data were also collected after the second dose of each gas. The fractional occupancies at all binding sites previously identified for CD$_4$ and O$_2$ increased after the second dose, but no new binding sites were identified for either gas (Table 2). Full refinement results for the guest-loaded systems with 2 guest:Y loading can be found in the Supporting Information (Tables S3 and S4).

Table 2. Unit-cell parameters and site-occupancy factors determined using Rietveld analysis of NPD data for empty and guest-loaded Y(btc).

<table>
<thead>
<tr>
<th>Guest:Y</th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>Fractional Occupancy</th>
<th>$R_{wp}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>None$^1$</td>
<td>10.2998(1)</td>
<td>13.8635(2)</td>
<td>- - - - 3.46</td>
<td></td>
</tr>
<tr>
<td>1 CD$_4$</td>
<td>10.2970(2)</td>
<td>13.8581(3)</td>
<td>0.39(4) 0.274(8) - 0.67(5) 4.85</td>
<td></td>
</tr>
<tr>
<td>2 CD$_4$</td>
<td>10.2949(3)</td>
<td>13.8432(4)</td>
<td>0.740(5) 1.006(12) - 1.75(6) 5.81</td>
<td></td>
</tr>
<tr>
<td>1 O$_2$</td>
<td>10.2974(3)</td>
<td>13.8600(5)</td>
<td>0.722(16) 0.220(14) 0.198(10) 1.14(4) 5.58</td>
<td></td>
</tr>
<tr>
<td>2 O$_2$</td>
<td>10.29363(15)</td>
<td>13.8522(2)</td>
<td>1.32(2) 0.337(14) 0.440(12) 2.09(5) 3.97</td>
<td></td>
</tr>
<tr>
<td>1 CO$_2$</td>
<td>10.2976(2)</td>
<td>13.8639(3)</td>
<td>0.52(2) 0.199(17) 0.111(11) 0.86(5) 4.85</td>
<td></td>
</tr>
<tr>
<td>2 CO$_2$</td>
<td>10.2709(7)</td>
<td>13.8579(6)</td>
<td>0.966(12) 0.37(2) 0.260(11) 1.59(4) 7.04</td>
<td></td>
</tr>
</tbody>
</table>

$^1$ From [14].

A reversal of binding site preference upon increased loading was observed for CD$_4$, with site $B_{CD_4}$ (interacting with the carboxylate groups and first aryl carbon atom) displaying a higher occupancy than site $A_{CD_4}$ (interacting with carboxylate only) after the second dose. Similarly, the preference for guest binding at sites $B_{O_2}$ (near carboxyl and aryl carbons) and $C_{O_2}$ (Y bare metal site) was reversed after the second O$_2$ dose, though site $A_{O_2}$ (carboxylate groups and first aryl carbon) remained the dominant binding site, containing more than half of the adsorbed O$_2$.

Adsorption of all guests results in a slight contraction of the unit cell of Y(btc) (Table 2). The $a$ parameter decreases slowly and uniformly with increased loading of CO$_2$, CD$_4$ and O$_2$, except for a sharp decrease of ~0.25% between the first and second CO$_2$ dose. The $c$ parameter also decreases uniformly by a similar magnitude, with the largest overall change occurring for O$_2$ (~0.15% decrease after the second dose).

2.3. The Yttrium Coordination Sphere

The possible region for guest binding between the Y atom and the guest-accessible pore space is enclosed by carboxylate O atoms belonging to four different btc ligands. The opposite pairs of these O atoms are crystallographically equivalent and correspond to sites designated O1 and O3. The angles formed by these atom pairs and the Y centre change considerably upon removal of the water of crystallisation from the as-synthesised framework, with the btc ligands closing in around the vacated binding site (Table 3). The subsequent addition of other guest molecules causes a partial re-opening of the O1–Y–O1 angle, even though the direct interactions between the guests and Y at this location are minimal [14]. Interestingly, the angle opening becomes more pronounced at higher loadings of CD$_4$ and O$_2$, but does not change significantly with increased CO$_2$ loading. The O3–Y–O3
angle, by contrast, contracts further upon the addition of guests to the empty framework. The only exception occurs at the 2O$_2$:Y loading where the angle becomes slightly larger than that of the empty framework, probably due to the small amount of O$_2$ binding to the bare Y site at high loadings [14]. A graphical representation of the changing YO$_6$ coordination environment is shown in Figure 5.

Table 3. Opposing O–Y–O angles which enclose the bare-metal Y site in the hydrated, dehydrated and guest-loaded Y(btc) materials. O1 and O3 refer to the relevant framework O atoms [13,14].

<table>
<thead>
<tr>
<th>Guest:Y</th>
<th>O1–Y–O1 (°)</th>
<th>Change from Dehydrated (%)</th>
<th>O3–Y–O3 (°)</th>
<th>Change from Dehydrated (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrated</td>
<td>167.9(3)</td>
<td>-</td>
<td>137.6(3)</td>
<td>-</td>
</tr>
<tr>
<td>Dehydrated</td>
<td>139.3(5)</td>
<td>-</td>
<td>120.8(5)</td>
<td>-</td>
</tr>
<tr>
<td>1 CO$_2$</td>
<td>143.1(11)</td>
<td>3.8</td>
<td>115.9(8)</td>
<td>-4.9</td>
</tr>
<tr>
<td>2 CO$_2$</td>
<td>143(3)</td>
<td>3.7</td>
<td>115.7(19)</td>
<td>-5.1</td>
</tr>
<tr>
<td>1 CD$_4$</td>
<td>141.9(10)</td>
<td>2.6</td>
<td>114.3(8)</td>
<td>-6.5</td>
</tr>
<tr>
<td>2 CD$_4$</td>
<td>147.2(11)</td>
<td>7.9</td>
<td>114.6(9)</td>
<td>-6.2</td>
</tr>
<tr>
<td>1 O$_2$</td>
<td>141.9(7)</td>
<td>2.6</td>
<td>117.3(6)</td>
<td>-3.5</td>
</tr>
<tr>
<td>2 O$_2$</td>
<td>147.5(8)</td>
<td>8.2</td>
<td>121.4(6)</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Figure 5. Graphical representation of the YO$_6$ coordination geometry site in Y(btc) under various guest loading conditions. Y is represented by light blue spheres. The O1, O2 and O3 positions are depicted for the hydrated structure (light grey), empty structure (red), and guest-dosed structures at 1 guest:Y (dark blue) and 2 guest:Y (orange) loading concentrations.

3. Discussion

The four guest species D$_2$, CO$_2$, CD$_4$, and O$_2$ display markedly different adsorption behaviour in Y(btc). In the absence of direct binding to the bare-metal site, the polar carboxylate groups tend to offer the most favourable adsorption sites and dominate guest occupation at low dosage amounts. However, the precise locations and orientations of these binding sites are unique to each guest, and the order of subsequent site filling also varies among the different species.

D$_2$ occupies four distinct binding sites, and is the only guest for which these sites are filled in a sequential fashion. Luo et al. [13] found that Site A, which lies near the carboxylate C atoms, is more than 65% occupied before any significant population is observed at Site B, which is closer to the aryl rings. Following the addition of further D$_2$, Site A saturates and Site C near the carboxylate O atoms populates almost to the level of Site B; B and C then co-fill to saturation. Site D appears to interact primarily with the carboxylate O atoms and other bound D$_2$ molecules, and is only slightly populated at loadings higher than 4 D$_2$:Y.
By contrast, CO$_2$ partially occupies three different binding sites after a single dose of 1 CO$_2$:Y, though Site A$_{CO_2}$ (near the carboxylate groups) is dominant. All three site populations increase proportionally when the total loading is increased to 2 CO$_2$:Y. The very similar O–Y–O angles observed after the first and second doses of CO$_2$ (Table 3) indicate that the framework geometry is not greatly affected by the overall increase in CO$_2$ loading, which may explain the unchanging relative favourability of the three binding sites.

CD$_4$ occupies only two binding sites in Y(btc). The population at Site A$_{CD_4}$ is only slightly higher than at Site B$_{CD_4}$ for 1 CD$_4$:Y, but at higher loadings there is a reversal of preference and Site B$_{CD_4}$ saturates before Site A$_{CD_4}$. The more rapid increase in the occupancy of B$_{CD_4}$ may indicate that this site is the more energetically favourable adsorption site, but is sterically hindered due to its location in the acute angle between the btc ligands. As additional CD$_4$ is introduced, the energetic barrier associated with this steric deterrent could be exceeded by guest-guest repulsions, allowing higher occupancy to be achieved. The considerable change in the O1–Y–O1 angle between the first and second doses of CD$_4$ tends to support the theory that ligand repositioning on increased loading alters the local CD$_4$ binding environment.

O$_2$, like CO$_2$, binds at three different sites which are all partially occupied at 1 O$_2$:Y loading, with one site dominating strongly. However, the dominant adsorption site A$_{O_2}$ is associated more closely with the carboxylate C and adjoining aryl C atoms than with the carboxylate O atoms favoured by A$_{CO_2}$. Furthermore, the two less favourable sites (B$_{O_2}$ and C$_{O_2}$) show a reversal of preference at high loading which is not observed for B$_{CO_2}$ and C$_{CO_2}$. This is probably due to the very different local environments of the respective sites: C$_{O_2}$ is a bare-metal binding site, whereas the CO$_2$ molecules at all sites show significant interactions with the ligands only. It is notable that the greatest “opening” of the O–Y–O angles (especially O3–Y–O3) is observed for the second O$_2$ dose, and this increase in the steric accessibility of the bare Y site is almost certainly linked to the increased favourability of this site at the higher dosing level. A slight decrease of the distance between CO$_2$ and the Y centre from 3.77(6) Å at 1 O$_2$ to 3.72(4) Å at 2 O$_2$ is also observed, signifying stronger metal-guest interactions.

Finally, the water adsorption isotherm measured at 298 K (Figure S1) shows a large step, which is also consistent with the initial inaccessibility of the bare Y site. Up to a partial pressure ($P_0$) of 0.08 the water uptake is comparatively low, and attributed to adsorption only on exterior surface sites. The steep adsorption step, equivalent to approximately 4 water molecules per formula unit, probably occurs when the chemical pressure is sufficient to overcome the energetic barrier to opening the structure.

It is clear that the opening of the O–Y–O angles is important for promoting the accessibility of binding sites which are energetically favourable for otherwise sterically-hindered guest molecules. Whilst O$_2$ is able to induce this opening at higher concentrations, allowing the guest to interact with the Y, CO$_2$ is not able to force access to the bare-metal site. Similarly, CD$_4$ does not interact closely with Y even at high guest loadings, but remains preferentially sandwiched between btc units in a corner position, likely as a consequence of its tetrahedral shape as shown for other MOFs [18].

The demonstrated ability of the btc ligands around Y to undergo guest-specific rearrangement leading to changes in site binding enthalpy has important implications for tailoring sorbent selectivity in MOFs. Guest-induced structural changes are generally common in flexible MOFs [19,20] and can extend even to extreme modifications such as topotactic switching of interpenetration schemes [21], leading to fundamental changes in pore size and shape. Although the effects of the guest-induced site opening in Y(btc) observed in our work are relatively subtle, they represent an avenue for the tuning of adsorptive behaviour which has been largely unexplored so far. The utilisation of these coordinatively flexible metal centres may offer new strategies in MOF design, especially when combined with existing guest-responsive structural features, potentially leading to important applications in carbon capture and fuel storage.
4. Materials and Methods

4.1. Sample Preparation

A mixture of Y(NO$_3$)$_3$·6H$_2$O (5.22 g, 13.6 mmol) and 1,3,5-benzenetricarboxylic acid (1.06 g, 5.04 mmol) was dissolved at room temperature in a 1:1:1 (by volume) mixture of N,N-dimethylformamide, ethanol and water (240 mL). This solution was divided equally into four 100 mL Parr Teflon-lined vessels which were heated at a rate of 1.1 K·min$^{-1}$ to 363 K and maintained at this temperature for 18 h. The resulting clear, needle-shaped crystals were allowed to cool to room temperature before being isolated by vacuum filtration and washed with ethanol (100 mL). The combined sample was ground to a fine white powder and desolvated by heating in a glass sample tube at 573 K under high vacuum (~10$^{-5}$ mbar).

4.2. Isothermal Adsorption Measurements

Gas adsorption isotherms for N$_2$ (supplied at 99.99% purity) and water vapour were measured using the IGA-002 gravimetric system (Hiden-Isochema, Warrington, UK). The freshly-synthesised sample was loaded into a stainless steel basket and heated to 523 K under high vacuum (<10$^{-6}$ mbar) for 7 h, after which the mass (~67 mg) remained stable. Adsorption isotherms were measured at 298 K with the system temperature maintained within 0.1 K. At each data point the pressure in the sample chamber was set and the mass allowed to equilibrate before moving to the next data point. In the case of water isotherms, the maximum equilibration time allowed per pressure point was 5 h, at which point the measurement was continued. The equilibrium mass was corrected for the buoyancy of the sample and balance components.

4.3. Neutron Diffraction

Neutron powder diffraction (NPD) data were collected using the high-resolution neutron powder diffractometer ECHIDNA [22] at the Australian Nuclear Science and Technology Organisation (ANSTO). The desolvated sample (1.376 g) was transferred to a 6 mm-diameter cylindrical vanadium can inside a helium-filled glovebox and loaded onto a custom-designed gas-delivery centrestick, which has been described elsewhere [23,24]. At all times, the sample was maintained in vacuo or in a helium atmosphere to prevent unwanted adsorption of gaseous species from the air. The sample stick was inserted into a top-loading cryofurnace for the duration of the experiment, and the sample was repeatedly dosed and reactivated in situ via a thermally-isolated capillary line.

Each dose of a known amount of gas was introduced to the sample at 250 K and slowly cooled to below the condensation/deposition point, at which point the pressure in the system decreased to almost zero. The sample was then cooled over 1 h to the measurement temperature of 10–15 K. No evidence was found any of in the diffraction patterns for the presence of frozen gases, implying that all of the gas was adsorbed by the sample. Diffraction data were acquired over the angular range 17° < 2θ < 137° with an incident neutron wavelength of 2.4425(1) Å, determined using a LaB$_6$ (NIST SRM 660b) standard reference material. A correction for the Debye-Scherrer ring curvature was applied before data reduction. The sample was re-activated prior to the introduction of new guest species by heating at 350 K under vacuum (~10$^{-5}$ mbar) for approximately 1 h.

4.4. Structural Analysis

Rietveld structural refinements were performed using the program GSAS [25] with the EXPGUI [26] interface. A pseudo-Voigt peak profile function incorporating axial divergence asymmetry (CW neutron Type III, as defined in GSAS) was used, and a 12-term shifted Chebyshev background function was refined. Fractional coordinates and isotropic atomic displacement parameters (ADPs) were refined for all framework atoms. Fourier difference maps were generated in GSAS after initial refinement of the empty framework structure and visualised using VESTA [27] in order to identify...
the CO₂ adsorption sites. The CO₂ guests were modelled as complete molecules with variable site occupancies in subsequent refinement cycles.

**Supplementary Materials:** The following are available online at www.mdpi.com/1996-1073/9/10/836/s1. Figure S1: Water vapour adsorption isotherm for the Y(btc) framework at 298 K. Table S1: Rietveld refinement results for the Y(btc) framework dosed with 1 CO₂:Y. Table S2: Rietveld refinement results for the Y(btc) framework dosed with 2 CO₂:Y. Table S3: Rietveld refinement results for the Y(btc) framework dosed with 2 CD₄:Y. Table S4: Rietveld refinement results for the Y(btc) framework dosed with 2 O₂:Y.

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**Conflicts of Interest:** The authors declare no conflict of interest.

**References**

10. Duyker, S.G.; Halder, G.J.; Southon, P.D.; Price, D.J.; Edwards, A.J.; Peterson, V.K.; Kepert, C.J. Topotactic structural conversion and hydration-dependent thermal expansion in robust LnMIII(CN)₆·nH₂O and flexible ALnFeII(CN)₆·nH₂O frameworks (A = Li, Na, K; Ln = La–Lu, Y; M = Co, Fe; 0 ≤ n ≤ 5). *Chem. Sci.* 2014, 5, 3409–3417. [CrossRef]


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