Density Functional Theory Meta-GGA+U Study of Water Incorporation in the Metal Organic Framework Material Cu-BTC

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Water absorption in the metal-organic framework (MOF) material Cu-BTC, up to a concentration of 3.5 \( \text{H}_2\text{O} \) per Cu ion, is studied via density functional theory at the meta-GGA+U level. The stable arrangements of water molecules show chains of hydrogen-bonded water molecules and a tendency to form closed cages at high concentration. As expected, Cu-water oxygen interactions and water-water hydrogen bonding dominate the energetics. Stability is further enhanced by van der Waals interactions, electric field enhancement of water-water bonding, and hydrogen bonding of water to framework oxygens. We hypothesize that the tendency to form such stable clusters explains the particularly strong affinity of water to Cu-BTC and related MOFs with exposed metal sites.

Introduction

The need to reduce greenhouse gas emissions has driven the search for materials to capture and sequester carbon dioxide at a low-enough cost to be economically viable. Metal-organic framework (MOF) materials offer great promise for the capture of \( \text{CO}_2 \)[1, 2]. Absorption and desorption from MOF materials via swings of temperature and pressure in principle requires less energy than do current aqueous capture technologies[2]. In addition, MOF materials can be created with a wide variety of pore sizes, shapes, connectivities, and topologies. These attributes, as well as the effects of cation substitution on metal sites, can in principle be used to tailor both the physical and chemical interactions of the MOF with gas molecules to optimize desirable properties such as \( \text{CO}_2 \) selectivity, capture rates, and costs of absorption/desorption cycles[1].

A particularly interesting and well-studied example of a MOF material is Cu-BTC, also known as HKUST-1 (Ref. 3). This material (Fig. 1) consists of copper dimers linked by 1,3,5-benzenetricarboxylate \( \text{C}_6\text{O}_9\text{H}_3 \) (BTC) units. The structure has a three-dimension cubic framework with channels of alternating 13.3 Å and 11.1 Å cuboctahedral pores connected by 6.4 Å square windows along 100-type directions, and 5.5 Å tetrahedral side pockets connected to the 13.3 Å pores via 3.7 Å triangular windows[4, 5].

As formed in atmospheric conditions, Cu-BTC contains a significant degree of water. This water can be removed via heat-treatment under near vacuum[3, 6, 7], leaving a structure with partially “exposed” Cu ions[8] facing the large cuboctahedral pores, allowing for particularly strong interactions with adsorbates at these Cu sites. These exposed ions lead to several potential applications in addition to carbon capture, including catalysis[6], hydrogen storage[9], storage of other gases such as NO[10], and gas separation[11].

Dry Cu-BTC has a \( \text{CO}_2 \) uptake of as much as 19.8 weight % at atmospheric pressure[12], and a high selectivity of \( \text{CO}_2 \) over \( \text{N}_2 \)[2, 12]. The situation of hydrated Cu-BTC is interesting. Up to about one \( \text{H}_2\text{O} \) per Cu site, there is theoretical and experimental evidence for a slight increase in \( \text{CO}_2 \) uptake[13–15]. For water concentrations greater than about one \( \text{H}_2\text{O} \) per Cu, a situation which we call here “highly-hydrated Cu-BTC”, the \( \text{CO}_2 \) uptake is reduced[14, 16, 17]. At high-enough concentrations of \( \text{H}_2\text{O} \), Cu-BTC loses almost all of its \( \text{CO}_2 \) capacity[14]. The last fact likely prevents the use of Cu-BTC as a material for post-combustion carbon capture, as flue gases in coal-burning plants contain significant water vapor[15]. In some MOFs, water can even break down the structure completely[19].

In spite of the importance of the highly-hydrated state of Cu-BTC for its performance, little is known about the structure of water in this state. Absorption isotherm measurements[14, 19] show that as much as 32 to 40 mol kg\(^{-1}\) of water can be absorbed into Cu-BTC. Assuming an ideal pore structure, this corresponds to 6.5 to 8.0 \( \text{H}_2\text{O} \) per Cu. An NMR study[20] suggests that the state of highly-hydrated Cu-BTC has one water molecule bound to each Cu in equilibrium with fluid water in the

FIG. 1: Cu-BTC viewed along (a) 100 and (b) 110 directions.

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We compared various exchange-correlation (XC) functionals to see if the correct binding energies of small molecules correct. We then need to hydrate the Cu-BTC structure. We begin with the positions of the water molecule oxygens (O_W) determined by Wong-Ng et al. (Fig. 2). In this study, each crystallographically distinct O_W site (shown by a different color) is only partially occupied. Indeed, many of the potential sites are too close together to be simultaneously occupied. In Fig. 2(b) and Fig. 2(c), we show two different choices for placing O_W that avoid unphysically close pairs of water molecules. The first has an arrangement of 28 water molecules with the O_W forming a polyhedra, and the second consists of 6 independent water molecules. A recent X-ray powder diffraction refinement of Cu-BTC, on the other hand, shows evidence for 2.3 bound water molecules per Cu atom, in three different partially occupied binding sites, although it was not possible to determine the hydrogen positions for these water molecules.

### Computational Methods

First principles density functional theory calculations, as encoded in the VASP software, were used to calculate the relaxed configurations investigated here and their electronic structures. All calculations were performed for a primitive cell of Cu-BTC containing 156 framework atoms plus any H_2O adsorbates. Because of the large cell, only a single k-point at the origin was used. The plane wave cutoff was 500 eV for all calculations. Van der Waals forces were treated using the “DFT-D2” approximation of Grimme, and were included in all calculations.

To study water absorption in Cu-BTC, it is crucial to get the interactions between H_2O molecules correct. We compared various exchange-correlation (XC) functionals to see if the correct binding energies of small water clusters could be obtained. The results for two such XC, the PBEsol generalized gradient approximation (GGA), and the PBEsol plus RTPSS meta-GGA functional (one that also uses the second derivative of the charge density), are shown in Table I and compared with benchmark calculations of water binding energies that were performed using the DFT code GAUSSIAN with highly-converged basis sets. The results show 30\% to 40\% water-water overbonding for the case of the GGA calculations, but excellent agreement with the GAUSSIAN results for the meta-GGA approximation. The meta-GGA approximation was therefore used for the rest of this work, despite being several times more computationally expensive than the GGA approximation.

As noted in previous DFT works, improvement in the agreement between DFT results and experiments for systems containing magnetic ions can generally be achieved if on-site Coulomb terms are included in what is commonly termed the "GGA + U" approach. To determine the onsite Coulomb parameters to use for Cu-BTC, we began with the experimental structure of Cu_2CO_3(OH)_2 (malachite). Malachite has numerous structural features analogous to those in Cu-BTC, including the same species (Cu,O,C,H), Cu in the Cu^{2+} valence state, Cu coordinated to a square of oxygen, and OH units which are analogous to the H_2O admolecules in hydrated Cu-BTC, but malachite is simpler to investigate because of its smaller unit cell.

Our aim was to adjust the U parameter for both Cu and O so as to fit the bandgap and experimental crystallographic structure of malachite as well as possible, and, assuming transferability, to use the same values to study Cu-BTC. We were unable to find any value of the malachite bandgap in the literature. Our calculations, however, suggested that a bandgap of 1.75 eV leads to a minimum of absorption at around 2.3 eV, at the characteristic green color of malachite, and we thus fit to this value. We used the malachite coordinates given by Zigan et al. (Ref. 33 cited in Ref. 35), because hydrogen positions were given. To quantify the structural agreement with experiment, we fixed ions at their experimental positions and calculated the root mean square residual forces on the ions. For a calculated bandgap of 1.75 eV, the residual forces were minimized for Cu U = 3.08 eV and oxygen U = 7.05 eV. The magnitude of the U value for Cu largely controls the calculated bandgap, by (controlling the splitting in the Cu d levels), while including a nonzero U for oxygen greatly reduces the residual forces. Magnetism of Cu^{2+} ions with their d^9 electronic configurations was treated using spin-polarized DFT calculations. The antiferromagnetic arrangement of the 2 Cu on the Cu-Cu dimer was found to be lower in energy than the ferromagnetic one, in agreement with previous studies. We then need to hydrate the Cu-BTC structure. We begin with the positions of the water molecule oxygens (O_W) determined by Wong-Ng et al. (Fig. 2). In this study, each crystallographically distinct O_W site (shown by a different color) is only partially occupied. Indeed, many of the potential sites are too close together to be simultaneously occupied. In Fig. 2(b) and Fig. 2(c), we show two different choices for placing O_W that avoid unphysically close pairs of water molecules. The first has an arrangement of 28 water molecules with the O_W forming a polyhedra, and the second consists of 6 indepen-

### Table I: Total binding energies of water dimers and hexamers (in eV).

| DFT code    | water dimer   | water hexamer |
|-------------|---------------|---------------|
| VASP GGA    | -0.30         | -2.92         |
| VASP meta-GGA | -0.23         | -2.13         |
| GAUSSIAN    | -0.23(1)      | -2.07(12)     |
(b) Model-42, a fullerene-like arrangement of 42 O\(_W\) molecules. We refer to models with these starting configurations of O\(_W\) as “Model-28” and “Model-30”, respectively, where the number refers to how many water molecules per primitive Cu-BTC cell, or, equivalently, per large 13 Å pore.

The choice in Fig. 2(c) has the same topology as the C\(_{28}\) fullerene of T\(_d\) symmetry. We show the topology in Fig. 3(a). In fullerenes, each carbon has three carbon neighbors. In the equivalent water structure, a highly hydrogen-bonded structure is produced in an analogous way to the ice rules for three-dimensional ice: each O\(_W\) is covalently bonded to two hydrogens, and each O\(_W\)-O\(_W\) neighbor link has one hydrogen atom that is bonded to one O\(_W\) and forms a hydrogen bond to the other. These observations inspired us to look for other fullerene-like arrangements of O\(_W\) molecules that might be accommodated in Cu-BTC. We looked at all low-energy fullerene geometries in the online Atlas of Fullerenes Structures from N = 20 to N = 60 at various orientations and scalings within the Cu-BTC large pore to see what structure would best accommodate one O\(_W\)-O\(_W\) distances of 2.9 Å, while having one O\(_W\) near each exposed Cu. The best candidate structure is a 42-molecule structure equivalent to the “C\(_{12}\) #45” fullerene, where the O\(_W\) have the topology shown in Fig. 3(b). We call this “Model-42”. For each model, as well as a model “Model-12”, with one H\(_2\)O per Cu, we initially randomized the hydrogen positions, then performed a full relaxation until all forces were converged within 0.03 eV Å\(^{-1}\).

Results and Discussion

The calculated structure of dry Cu-BTC is shown in Table I and compared with a recent experimental X-ray powder diffraction refinement. Extremely good agreement (within 0.02 Å) is obtained for all atomic positions except for H, which are 0.14 Å from the experimental positions. We note, however, that the experimental refinement treated the organic ligand as a rigid body; and did not further refine the average hydrogen positions, which have little effect on the X-ray powder diffraction pattern in any case.

The relaxed structures for all the hydrated Cu-BTC models are shown in Fig. 4. Hydrogen bonds are shown as thin lines. The key structural parameters and energetics results are shown in Table III. As the number of water molecules increases, the structure changes from individual water molecules bound to Cu to clusters of water molecules bound to one or more Cu, to a closed cage encompassing all of the water molecules. The trend in key interatomic distances with increasing numbers of water molecules agrees with experiment.
FIG. 4: Structures of model water clusters inside large pore of Cu-BTC, relaxed via density functional theory. (a) Model-12; (b) Model-28; (c) Model-30; (d) Model-42, where the number refers to the number of water molecules inside the large pore. Hydrogen bonds shown in red.

Although Model-28 and Model-30 begin with atoms at positions suggested by experimental structure refinement, certain water oxygen positions relax as much as 1.6 Å, suggesting a significant (quasi)static contribution to the large experimental displacement factors found for water oxygens[21]. A common feature of the relaxed DFT positions and the experimental ones is that all of the waters are within and near the inner surface of the large 13 Å pore. The results show that 3.5 molecules per Cu are easily accommodated in this region. If water also occupies the interior of the large pore as well as the 11 Å and 5.5 Å pores, then Cu-BTC can accommodate the 6.5 to 8.0 H₂O molecules per Cu ion suggested by experiment without requiring larger (defect) pores.

The binding energy per water molecule for one H₂O attached to each Cu site is -0.53 eV. In the highly-hydrated state, the magnitude of the binding energy per water molecule is even larger. Where does this enhanced stability come from? To determine this, we broke down the binding energy of each model into three parts: intracluster energy; cluster-framework van der Waals energy (vDW), and the excess part, due to chemical and nondispersive electrostatic interaction of the cluster with the framework. The intracluster binding energy was calculated by removing the framework and performing a DFT energy calculation on just the cluster. The vDW (dispersion) energy was calculated using the approximation of Grimme, only counting vDW interactions between the H₂O cluster and the framework. The chemical component of the cluster-framework binding energy was obtained by simply subtracting the vDW and intracluster parts from the total. As a control, we also took a 28-molecule water cluster, moved it to the medium 11 Å pore, naming this model “Model-28MP”, fully relaxed the system (Fig. 5), and broke down its energy into components. The results are shown in Table IV.

All of the larger clusters in the large pore had greater chemical/electrostatic binding energy than the single H₂O per Cu case. This results from two sources: enhancement of H₂O-H₂O binding under an electric field[38–40] (generated by the exposed Cu ions), and additional H-bonding of H₂O H to O in the framework itself, seen in Fig. 4(b) and (d). A water cluster in the medium

### TABLE IV: Breakdown of interactions of water clusters in Cu-BTC. Total cluster binding energy ΔE is broken down into three components: intracluster (intra), cluster-framework Van der Waals (vdW), and cluster-framework chemical interactions (chem). All energies in eV.

| Model          | N_W | ΔE  | intra | vdW   | chem |
|----------------|-----|-----|-------|-------|------|
| DFT Model-12   | 12  | 6.30| -0.22 | -1.49 | -4.59|
| DFT Model-28   | 28  | 16.66| -8.13 | -2.66 | -5.86|
| DFT Model-30   | 30  | 17.49| -9.96 | -2.60 | -4.93|
| DFT Model-42   | 42  | 26.81| -16.64| -3.91 | -6.25|
| DFT Model-28MP | 28  | 14.81| -12.72|  0.01 |  0.01|

FIG. 5: Structure of a 28-water cluster inside a medium pore of Cu-BTC, relaxed via density functional theory. (a) 100 view (b) 110 view.
11 Å pore with no exposed Cu can not take advantage of electric field enhancement of bonding nor hydrogen bonding with the framework, and, indeed the excess chemical energy for this case is found to be essentially zero (Table IV). Although the configuration of 28 water molecules inside the medium pore has a nearly ideal polyhedral structure (Fig. 5a), compare with Fig. 5(a), and lower intrachannel energy than for 28 water molecules inside a large pore (Table IV), the overall binding energy of 28 water molecules is about 1.8 eV more stable inside the large pore.

All calculations were performed at zero temperature, and do not include thermal motion. Given that water is a liquid at room temperature, what can we say about the nature of the water in highly-hydrated Cu-BTC at room temperature? Here, we refer to a recent molecular dynamics simulation[41] on “MIL-53”, a Cr-based MOF with a smaller unit cell than Cu-BTC. They found, at room temperature, dynamic hydrogen bonds, one $O-W$ distance of 5.8 Å, is near a minimum of the $O-O$ pair distribution function of water ice[42]. On the other hand, an $O-O$ distance with the third-neighbor peak in the $O-O$ pair distribution function for both ice and liquid water[42, 43].

Conclusions

Meta-GGA+U density functional theory calculations are shown to reproduce the experimental structure of dry Cu-BTC and also to accurately give the interaction energies of small water clusters. Applying these calculations to models for hydrated Cu-BTC, we find that hydrogen-bonded water clusters have their stability enhanced by interactions with the exposed metal ions, van der Waals interactions, electric field enhancement of water-water bonding, and hydrogen bonding of water to framework oxygens. This explains the great affinity of water for Cu-BTC and related metal-organic frameworks.

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