Water adsorption on a copper formate paddlewheel model of CuBTC: A comparative MP2 and DFT study

J. Toda^{1,2}, M. Fischer³, M. Jorge⁴, J. R. B. Gomes^{1,*}

¹CICECO, Departamento de Química, Universidade de Aveiro, 3810-193 Aveiro, Portugal

²LSRE/LCM, Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465 Porto, Portugal

³Department of Chemistry, University College London, 20 Gordon Street, London WC1H 0AJ, United Kingdom

⁴Department of Chemical and Process Engineering, University of Strathclyde, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom

*Corresponding Author. E-mail: jrgomes@ua.pt. Phone: +351 234 401 423. Fax: +351 234 401 470

ABSTRACT Simultaneous adsorption of two water molecules on open metal sites of the HKUST-1 metal-organic framework (MOF), modeled with a $\text{Cu}_2(\text{HCOO})_4$ cluster, was studied by means of density functional theory (DFT) and second-order Moller-Plesset (MP2) approaches together with correlation consistent basis sets. Experimental geometries and MP2 energetic data extrapolated to the complete basis set limit were used as benchmarks for testing the accuracy of several different exchange-correlation functionals in the correct description of the water-MOF interaction. M06-L and some LC-DFT methods arise as the most appropriate in terms of the quality of geometrical data, energetic data and computational resources needed.

KEYWORDS Metal-Organic Framework; Density Functional Theory; Sorption; Gaussian basis sets; Moller-Plesset; Complete Basis Set Limit

HKUST-1, CuBTC or copper benzenetricarboxylate, with structural formula $\text{Cu}_3(\text{btc})_2$ ($\text{btc}=1,3,5\text{-benzenetricarboxylate}$), is one of the most studied and characterized structures in the field of metal-organic frameworks (MOF) [1]. This material was first reported in 1999 by Chui et al. [2] and its crystalline structure consists of a copper paddlewheel (PDW), with a Cu–Cu distance of 2.63 Å, where each copper atom is coordinated to four oxygen atoms of the btc linkers, and to one water molecule (solvent). The water molecules can be easily removed by heating under vacuum leaving unsaturated Cu sites available for adsorption (material activation). The benzene rings are bonded to three dimeric cupric tetracarboxylate units as shown in Figure 1.

Figure 1. The structure of the activated CuBTC MOF. Color code: Orange is copper; red is oxygen; grey is carbon; and white is hydrogen.

It has been shown that MOFs presenting coordinatively unsaturated sites (CUS), as is the case of CuBTC, have much greater potential than similar MOFs without CUS for applications in gas storage (gas-solid interaction is increased) [3], in gas separation (enhancement of the differential adsorption of certain components) [4], in catalysis (adequate redox potential) [5] and in rheology (electro-responsivity is improved) [6]. Therefore, these materials are fertile

ground for computational and experimental works with the aim of establishing consistent links between their structures and their performance in specific applications.

CuBTC has been amply studied [7], but obtaining a proper theoretical description of the adsorbate-adsorbent interaction is not trivial due to i) the large size of the unit cell of this MOF and ii) the presence of unpaired electrons at the metal sites. Thus, the selection of the most appropriate computational approach for an accurate modeling of adsorbate-CuBTC interaction is a crucial step for understanding trends between geometric and electronic properties of MOFs and enhanced performances of these materials for specific applications. Usually, the calibration of a computational approach is made by direct comparison with accurate experimental sorption, energetic and geometric data. In the case of CuBTC, structural data is available for the hydrated and dehydrated materials. The single-crystal structural analysis of the original hydrated material synthesized by Chui et al. [2] showed Cu-O_W (Cu-O_{water}), Cu-Cu and Cu-O_{PDW} distances of 2.165 ± 0.008 Å, 2.628 ± 0.002 Å and 1.952 ± 0.003 Å, respectively. Distances of 2.19 ± 0.02 Å, 2.64 ± 0.02 Å and 1.96 ± 0.02 Å, respectively, were obtained by Prestipino et al. [1] using extended x-ray absorption fine structure (EXAFS) spectroscopy. The latter authors obtained also geometric results for the material dehydrated in vacuo at $T=453$ K. A reduction of the cell volume of the material is observed upon dehydration, with consequences in the values of the Cu-O_W, Cu-Cu and Cu-O_{PDW} distances, which shrink upon degassing to 2.17 ± 0.02 Å, 2.50 ± 0.02 Å and 1.94 ± 0.02 Å [1]. Note the ~ 0.15 Å reduction in the Cu-Cu distances reported by Prestipino et al. for the hydrated and dehydrated CuBTC samples. Wang et al. [8] used a constant-volume-variable-pressure sorption method to determine the sorption isotherm of water in CuBTC at $T=295$ K. This isotherm was considered by Castillo et al. [9] to calibrate a set of atomic charges for grand-canonical Monte Carlo (GCMC) simulations on the interaction of water with a rigid model of CuBTC. These authors found that water is preferentially adsorbed at the CUS with an enthalpy of interaction (ΔH_{int}) of -48.0 ± 6.6 kJ mol⁻¹ at $T=295$ K and at zero coverage. The ΔH_{int} was found to increase to $\sim -51.0 \pm 3.0$ kJ mol⁻¹ for larger water coverages. The enthalpic data estimated by Castillo et al. [9] is in agreement with the experimental result due to Henninger et al. [10], $\Delta H_{\text{int}} = -50.7 \pm 2.9$ kJ mol⁻¹, but at $T=313.15$ K, from combined thermogravimetry and differential scanning calorimetry measurements (TG/DSC). The TG/DSC result has to be treated with caution since the material showed signs of degradation [10]. Nevertheless, it is quite encouraging for benchmark purposes to find that two

independently determined values for the enthalpy of interaction of water with CuBTC are in very close agreement.

The interaction of water with CuBTC was also studied by means of electronic structure methods. Watanabe and Sholl [11] studied the chemisorption of several molecules, *e.g.*, H₂O, CO, NO, pyridine, and NH₃, on open Cu sites in CuBTC by DFT. In the case of water, the calculations were based on either periodic or cluster (*e.g.* Cu acetate with Cu₂(CH₃COO)₄ structural formula) models of CuBTC. The PW91 functional [12] based on the generalized-gradient approximation (GGA) was used with both models while the hybrid B3LYP approach [13,14] was also considered but only with the cluster model of CuBTC. A split-valence basis set augmented with diffuse and polarization functions was used in the cluster calculations. The calculated Cu-O_{water}, Cu-Cu and Cu-O_{PDW} distances in the case of two water molecules interacting with the PDW were 2.32 Å, 2.60 Å and 1.99 Å in the case of the periodic PW91 calculations, and 2.32 Å, 2.53 Å and 1.99 Å or 2.30 Å, 2.61 Å and 1.97 Å, in the cases of PW91 or B3LYP cluster calculations, respectively. The calculated distances were found to be in satisfactory agreement with the experimental available data for CuBTC [1,2, **Error! Bookmark not defined.**] or for Cu acetate [15]. Still, important differences are found, especially in the case of the Cu-O_{water} separation. The calculated interaction energies per water molecule were 40.5 kJ mol⁻¹, 42.9 kJ mol⁻¹ and 41.0 kJ mol⁻¹ with the periodic/PW91, cluster/PW91 and cluster/B3LYP approaches, respectively [11]. A binding energy of -47.3 kJ mol⁻¹ was computed in the case of a single molecule interacting with the periodic model.

Grajciar et al. [16] considered a different cluster model and different exchange-correlation functionals to those used by Watanabe and Sholl [11] also to obtain structural and energetic information about the H₂O-CuBTC interaction. Grajciar et al. considered a Cu-formate model (Cu₂(HCOO)₄ structural formula), the Perdew-Burke-Ernzerhof (PBE) functional [17] and the aug-cc-pVTZ basis set (triple-zeta augmented with diffuse and polarization functions) to optimize the structure of the model with two water molecules interacting with the two CUS in the model. The plane of the water molecules was aligned with the O_{PDW}-Cu-O_{PDW} vector and normal to the plane containing the four O_{PDW} atoms attached to the same Cu. The PBE/aug-cc-pVTZ optimized Cu-O_w, Cu-Cu and Cu-O_{PDW} distances were 2.286 Å, 2.533 Å and 1.996 Å, respectively. The PBE/aug-cc-pVTZ geometry was used to perform additional studies, with several DFT-based approaches (GGA, meta-GGA or hybrid functionals with and without empirical dispersion corrections), or with the coupled cluster with single, double and perturbative triple excitations at the complete basis set

limit(CCSD(T)/CBS) method [16]. With the latter approach, a benchmark result for the energy of interaction per water molecule of $-51.2 \text{ kJ mol}^{-1}$ was obtained. The comparison of the DFT/cc-pVTZ (basis set without diffuse functions) calculations with the CCSD(T)/CBS results showed that most DFT approaches (significantly) underestimate (i.e., values are less negative) the calculated interaction energy for the H_2O -CuBTC system. The most significant underestimation was seen for the revised PBE functional (RPBE, 32.0 kJ mol^{-1}) and the lowest one was obtained for the hybrid BHLYP functional (3.6 kJ mol^{-1}), while the widely used PBE and B3LYP methods underestimated the interaction energy by $\sim 20 \text{ kJ mol}^{-1}$. The DFT results were improved considerably by the inclusion of dispersion interactions. Nevertheless, with the exception of the BHLYP functional, all the energies calculated with GGA, meta-GGA or hybrid approaches still underestimate the CCSD(T)/CBS value. Grajciar et al. developed also a density functional theory/coupled-cluster with single, double and perturbative triple excitation correction scheme (DFT/CC) approach, which was considered in additional calculations employing a periodic model. The Cu-O_w and the Cu-Cu distances are 2.21/2.23 Å and 2.55 Å, respectively, in the case of the sorption of two water molecules in the same PDW, one each side, and 2.19 Å and 2.51 Å, respectively, in the case of the sorption of a single water molecule. The interaction energies are $-55.3 \text{ kJ mol}^{-1}$ (sorption of the first molecule) and $-50.3 \text{ kJ mol}^{-1}$ (sorption of the second molecule), which yields a mean value of $-52.8 \text{ kJ mol}^{-1}$ per water molecule, not far from the CCSD(T)/CBS result. The inclusion of the zero-point vibrational energy (ZPVE) yielded a result of $-49.0 \text{ kJ mol}^{-1}$ for the interaction enthalpy of a single water molecule with CuBTC at $T=0 \text{ K}$. The uncertainties associated with each of these values are not negligible but they are consistent and show that DFT approaches have problems in describing accurately the interaction of water with the CUS of CuBTC. Despite these failures, one may think that at least one exchange-correlation functional would be able to handle accurately the water-CuBTC interaction. In fact, significant advances have been reported in the field of DFT and very difficult cases were successfully treated with these approaches, such as the adsorption of CO on MgO(001) [18] and the adsorption of CO and NO on Ni-doped MgO(001) [19].

The main objective of the present study is to check if there is any standard DFT approach that yields very good energies and structures for the water-CuBTC interaction, for which experimental and computational structural and energetic data is available. This is very important since DFT approaches, either with cluster or with periodic models, usually present a good ratio between accuracy and computational requirements, and can thus be used in optimization calculations with more realistic systems than wavefunction based methods. The

availability of a quantum mechanical method that can accurately describe adsorption in MOFs with CUS in a computationally efficient way is crucial not only for further understanding these systems at the fundamental level, but also for the development of potentials for classical simulations of sorption phenomena in such materials [20,21].

Figure 2. Structure of the fully optimized copper formate model with two adsorbed water molecules (system 6). Color code as in Fig. 1.

In this work, the post-Hartree-Fock MP2 method [22] was used to calculate the interaction energy, extrapolated to the CBS limit, of two water molecules interacting with a Cu-formate model (Figure 2). The $\text{Cu}_2(\text{HCOO})_4$ model was cut from the experimental crystallographic structure (Figure 1) [2], where the aromatic rings were replaced by H atoms, with the C-H distance fixed at 0.98 Å along the C-C_{ring} direction. Then, two water molecules were added to the model, one each side of the PDW, with the oxygen atoms at their crystallographic positions[2], i.e., Cu-O_w distances of 2.165 Å, and with their hydrogen atoms pointing outwards the cluster center. Recently, in a combined DFT and grand canonical Monte Carlo (GCMC) study of the interaction of ethylene with CuBTC, it was suggested that the $\text{Cu}_2(\text{HCOO})_4$ model is able to provide a description of the local environment of copper atoms in the CuBTC structure in a similar way to that obtained with the more realistic $\text{Cu}_2[\text{C}_6\text{H}_3(\text{COOH})_2\text{COO}]_4$, copper benzenetricarboxylate, cluster model [Error! Bookmark not defined.]. The smaller size of the former model enables the consideration of more extended basis sets and of computational approaches demanding more computing resources than those possible when using larger cluster models. The calculations performed with the

MP2 method considered different degrees of geometry optimization (systems 0 to 6), Figure 3. In system 0, the hydrogen atoms of the two water molecules were fully relaxed while the rest of the atoms remained fixed, Figure 3a. The other molecular systems were obtained from system 0 and differ by the number of atomic coordinates that were fully relaxed. Relaxation was considered just for the water molecules in system 1, Figure 3b, for water molecules and O_{PDW} positions in system 2, Figure 3c, for water molecules and Cu in system 3, Figure 3d, for water molecules, Cu and O_{PDW} positions in system 4, Figure 3e, for all the positions except Cu atoms in system 5, Figure 3f, and full-optimization (water and paddle-wheel positions) was considered in the case of system 6 (not shown). The shape of the different systems is identical to that shown in Figure 2 and the most significant differences between them are the Cu-Cu and Cu- O_W distances.

Figure 3. Optimized (red) and fixed (black) atoms in the MP2 calculations for systems 0 to 5 (panels a to f, respectively). All the atoms were optimized in the case of system 6 (not shown).

The correlation-consistent valence X- ζ basis sets with polarization functions by Peterson et al. [23] (cc-pVXZ with X=2, 3 or 4) were used to describe the electronic configurations of O, C and H atoms and the valence electrons of Cu. The inner electrons of Cu were described with the pseudopotential of Figgen et al. [24] resulting in the corresponding cc-pVXZ-PP basis sets. The X=2 (double zeta) basis sets were used for geometry optimizations while X=3 (triple zeta) basis sets were used to calculate single point energies. The CBS limit was obtained using the Truhlar et al. [25] extrapolation scheme based on the energies calculated with the X=2 and X=3 basis sets. All calculations were performed with the Gaussian 09 code [26]. The calculations considered the water-PDW and the PDW systems in the triplet state and the isolated water molecule in the singlet state.

For the systems considering different degrees of optimization, the interaction energies and the interaction enthalpies extrapolated to the CBS limit together with selected distances are given in Table 1.

Table 1. MP2 interaction energy and enthalpy, per water molecule and in kJ mol^{-1} , extrapolated to the CBS limit and Cu-water and Cu-Cu distances in Å for systems 0-6.

System	Relaxation ^a	E_{int}	H_{int} ^b	d(Cu-O _w)	d(Cu-Cu) ^c
0	H _w	-62.4	-55.8	2.165	2.628 (2.628)
1	O _w , H _w	-64.5	-57.9 ^d	2.210	2.628 (2.628)
2	O _w , H _w , O _{PDW}	-64.2	-57.6 ^d	2.210	2.628 (2.628)
3	O _w , H _w , Cu	-62.2	-55.6 ^d	2.214	2.592 (2.497)
4	O _w , H _w , Cu, O _{PDW}	-62.0	-55.4 ^d	2.210	2.626 (2.525)
5	O _w , H _w , O _{PDW} , C, H _{PDW}	-61.3	-54.7 ^d	2.204	2.628 (2.628)
6	Full optimization	-57.5	-49.4 ^e	2.208	2.581 (2.501)
			-50.9 ^f		
Exptl.	—	—	-50.7±2.9 ^{f,g}	2.165±0.008 ^h	2.628±0.002 ^h
				2.19±0.02 ⁱ	2.64±0.02 ⁱ

^aFor labels and degrees of optimization, please refer to Figs. 2 and 3. ^bThe corrections for calculating the interaction enthalpy were obtained from the vibrational frequency calculations, with the cc-pVDZ(-PP) basis sets, performed for the fully optimized system (i.e., system 6). ^cIn parenthesis is given the Cu-Cu distance for the bare cluster model. ^dEnthalpy at $T = 0$ K (ZPE from full-optimization run). ^eEnthalpy at $T = 0$ K. ^fEnthalpy at $T = 313.5$ K. ^gRef. [10]. ^hRef. [2]. ⁱRef. [1].

An interesting variation of the interaction energy (and also of the enthalpy) with the degree of optimization is found. The energy (per H₂O molecule) calculated for system 0 is -62.4 kJ mol^{-1} , it increases to -64.5 kJ mol^{-1} for system 1 and then diminishes to -57.5 kJ mol^{-1} for system 6. The difference between the largest and the smallest interaction energy is 7.0 kJ mol^{-1} , and in the case of systems 0 (experimental geometry) and 6 (MP2 geometry) the difference amounts to 4.9 kJ mol^{-1} . The variation in the calculated interaction energies has no correlation with the variation in the calculated Cu-water and Cu-Cu distances. As it can be seen in Table 1, the Cu-water (Cu-O_w) distance is approximately 2.21 Å for systems 1-6, i.e.

0.045 Å or 0.02 Å larger than the experimental counterparts from refs. 2 and 1, respectively. For the fully optimized structure (MP2 level), the Cu-H₂O distance is 2.208 Å, while a slightly more prominent variation is seen in the Cu-Cu distance, which is 0.047 Å or 0.059 Å smaller than the experimental values. A comparison of the Cu-Cu distances for the bare and for the water-containing paddle-wheel models in the case of systems 3, 4, and 6 shows that the shortening of the Cu-Cu distance is already present in the bare model. The differences between the Cu-Cu distances for the bare and for the water-containing paddle-wheels are 0.080 Å, 0.095 Å and 0.101 Å, in systems 6, 3 and 4, respectively.

The atomic charges taken from Natural Population Analysis (NPA) show that the charges of the copper atoms change more than the other atoms in the PDW on going from the bare PDW (values between approximately +1.10 a.u. and +1.14 a.u.) to the water-PDW (values between approximately +1.01 a.u. and +1.04 a.u.) systems. The NPA charges of the H_{PDW} and C atoms of the bare PDW systems are always more positive than the charges of the same atoms of the water-PDW systems. In case of the NPA charges calculated for the O_{PDW} atoms, it is found that the charges of these atoms in the bare models are more negative for systems 0 to 4 and less negative for systems 5 and 6 than in the corresponding water-PDW models. The maximum differences found for H_{PDW}, C and O_{PDW} atoms are one order of magnitude smaller than in the case of copper atoms, which is understandable since the latter are those directly interacting with water molecules. Note that due to the tilting of the H_W over the O_{PDW} atoms, the NPA charges for the O_{PDW} closer to the H_W atoms are more negative than those not interacting with the H_W atoms. The changes in the NPA charges on the bare or water PDW systems with different degrees of relaxation are found to never exceed 0.034 a.u.. In the case of the fully relaxed systems, the NPA charges of the H_{PDW}, C, O_{PDW}, and Cu atoms are, respectively, 0.14 a.u., 0.71 a.u., -0.70 a.u. and 1.08 a.u. in the bare model and are, respectively, 0.14 a.u., 0.71 a.u., -0.70 a.u. and 1.01 a.u. in the water-PDW system. The charges of the O_W and H_W atoms of water-PDW system 6 are, respectively, -0.88 a.u. and 0.49 a.u., which are not far from the NPA charges of the atoms in a water molecule in the gas phase, respectively, -0.88 a.u. and 0.44 a.u.. The total charge in each water molecule is +0.10 a.u.. The comparison of the natural orbital atomic occupancies in water-PDW and bare-PDW Cu atoms show identical occupancies except in the cases of the 4s, 4p, 3d_z² and 3d_{x²-y²} orbitals, which suggests that despite different atom types are being compared, tetra- or pentacoordinated copper atoms, their influence on the orbital analysis is minimal. The atomic occupancies of the 4s and 3d_{x²-y²} orbitals are smaller in the case of the water-PDW than in the case of the bare-PDW model while the occupancies of the 4p and 3d_z² are larger in the former than in the latter model. The

larger difference of the natural atomic occupancies of the Cu atoms in the two models is found for the $4p_z$ orbital which is more populated in the water-PDW system by ~ 0.08 a.u., which is approximately the value of the charge donated by the water molecules to the substrate.

The comparison of the MP2 results in Table 1 with available computational and experimental data is very good. The enthalpy computed for system 6, $H_{\text{int}, T=0\text{K}} = -49.4 \text{ kJ mol}^{-1}$, compares very well with the DFT/CC value due to Grajciar et al. [16], i.e., $H_{\text{int}, T=0\text{K}} = -49.0 \text{ kJ mol}^{-1}$, that was calculated using a periodic model approach. The MP2 enthalpy is also in close agreement with the TG/DSC value due to Henninger et al. [10]. Calculated and experimental results at $T=313.15 \text{ K}$ are $-50.9 \text{ kJ mol}^{-1}$ and $-50.7 \pm 2.9 \text{ kJ mol}^{-1}$, respectively, i.e., they differ by only 0.2 kJ mol^{-1} . The calculated value for the interaction energy, $E_{\text{int}} = -57.5 \text{ kJ mol}^{-1}$, is also not far from the CCSD(T)//CBS value, $E_{\text{int}} = -51.2 \text{ kJ mol}^{-1}$, calculated by Grajciar et al. [16]. Additionally, the Cu-O_w and the Cu-Cu distances calculated with MP2 for system 6 are slightly in better agreement with the experimental values than those calculated with the periodic DFT/CC approach. Nevertheless, the differences between the MP2 and DFT/CC values, calculated with cluster and periodic approaches, respectively, are smaller than $0.03 \text{ \AA}$. This finding suggests that the $\text{Cu}_2(\text{HCOO})_4$ cluster is adequate to model the CuBTC framework and supports recent findings [Error! Bookmark not defined.].

The performance of several different exchange-correlation functionals will be analyzed below from comparison of the DFT results with the MP2/CBS and with the experimental results compiled in Table 1. The functionals considered in this work were the hybrid M06 [27], M06-2X [27], M05-2X [28] and B3LYP [13,14] and the double-hybrid B2PLYP [29], mPW2PLYP [30] and B2PLYP-D (including dispersion) [31] approaches, the pure M06-L [32] and B97-D (including dispersion) [33] functionals, the long-range corrected versions of the hybrid B3LYP and wPBE and of the pure BP86, PBE and BLYP methods, namely, CAM-B3LYP [34], LC-wPBE [35], LC-BP86 [36-38], LC-PBE [36,39] and LC-BLYP [36,37,40] functionals, and also the long-range hybrid wB97XD functional [41]. Note that the calculation of the MP2-like correlation in the double hybrid methods requires much more computational resources in the latter than in the other DFT approaches listed above. The same basis sets used for the MP2 calculations were considered in the DFT calculations. The non-extrapolated interaction energies and enthalpies, together with Cu-O_w and Cu-Cu distances for the fully optimized water-PDW complexes, are compiled in Table 2.

Table 2. Non-extrapolated DFT interaction energy and enthalpy at $T=0$ K, per water molecule and in kJ mol^{-1} , and Cu-water and Cu-Cu distances in Å for system 6.^a

Method	cc-pVDZ(-PP)				cc-pVTZ(-PP)			
	E_{int}	H_{int}	d(Cu-O _w)	d(Cu-Cu)	E_{int}	H_{int}	d(Cu-O _w)	d(Cu-Cu)
M06-L	-76.3	-67.9	2.246	2.546	-61.2	-53.8	2.258	2.551
M06	-83.4	-75.3	2.211	2.567	-62.5	-54.8	2.234	2.560
M06-2X	-100.3	-91.3	2.194	2.695	-78.6	-70.0	2.207	2.699
M05-2X	-96.6	-87.7	2.186	2.642	-73.3	-64.9	2.203	2.650
B3LYP	-75.6	-67.8	2.247	2.607	-51.6	-44.4	2.274	2.613
B2PLYP	-80.7	-72.3	2.228	2.601	-58.1	-49.6 ^b	2.248	2.600
B2PLYP-D	-88.1	-78.9	2.228	2.604	-65.4	-56.2 ^b	2.245	2.605
mPW2PLYP	-85.9	-77.3	2.217	2.613	-62.9	-54.3 ^b	2.235	2.612
LC-wPBE	-77.8	-69.2	2.214	2.574	-53.4	-44.4	2.242	2.578
LC-BP86	-98.1	-88.7	2.148	2.551	-71.5	-63.1	2.162	2.555
LC-PBE	-90.5	-81.3	2.157	2.548	-64.1	-55.8	2.174	2.552
LC-BLYP	-99.6	-90.3	2.166	2.593	-70.7	-62.3	2.185	2.600
CAM-B3LYP	-86.3	-77.4	2.208	2.608	-60.7	-52.5	2.229	2.614
B97-D	-73.3	-64.0	2.317	2.568	-51.6	-42.5	2.349	2.573
wB97XD	-82.5	-74.0	2.224	2.620	-61.6	-53.6	2.247	2.621

^aThenon-extrapolated MP2/cc-pVDZ(-PP) energy and MP2 enthalpy are $-86.4 \text{ kJ mol}^{-1}$ and $-78.3 \text{ kJ mol}^{-1}$, respectively.

^bTheenthalpic corrections were taken from calculations using cc-pVDZ(-PP) basis sets.

The analysis of the results calculated with the double-zeta basis set shows that all the functionals considered in this work overestimate the MP2 benchmark enthalpy of interaction ($-49.4 \text{ kJ mol}^{-1}$, cf. Table 1) by more than 14 kJ mol^{-1} . The smallest and largest deviations are found for the B97-D (14.6 kJ mol^{-1}) and M06-2X approaches (41.9 kJ mol^{-1}), respectively. In terms of geometrical parameters, the comparison with the available experimental single-crystal results [2] reproduced in Table 1 shows that LC-BP86, LC-PBE and LC-BLYP give the best Cu-O_w lengths while M05-2X, mPW2PLYP and wB97XD give the best Cu-Cu distances. The comparison with the EXAFS data [1], also reproduced in Table 1, shows that the M05-2X and M06-2X approaches yield the best Cu-O_w distances and that the M05-2X provides the best Cu-Cu distance. The Cu-Cu distances obtained with the M06-L, LC-BP86 and LC-PBE approaches are too short and the Cu-O_w length optimized with the B97-D is too large when compared with the experimental results. Interestingly, the LC-wPBE distances are very close to the corresponding MP2 results.

The consideration of the triple-zeta basis sets improves the quality of the enthalpic data and most functionals provide results that are less than 10 kJ mol^{-1} away from the benchmark MP2 value. The exceptions are the values calculated with the M06-2X, M05-2X, LC-BP86 and LC-BLYP approaches which are significantly more negative than the MP2 result. The B2PLYP approach is the one giving the best comparison with the MP2 extrapolated enthalpy and five other approaches (M06-L, B3LYP, LC-wPBE, wB97XD and

CAM-B3LYP) give results within ± 5 kJ mol⁻¹ from the MP2 value. In terms of geometrical parameters, the consideration of triple basis instead of double basis sets brings small changes to the global picture described above when analyzing the data obtained with the cc-pVDZ(-PP) basis set.

The DFT/cc-pVDZ(-PP) and DFT/cc-pVTZ(-PP) geometries were considered in single-point calculations with the cc-pVDZ(-PP) and cc-pVTZ(-PP) basis sets for extrapolating the energies and the enthalpies to the CBS limit using an identical procedure to that considered for MP2 (Table 1), i.e., using the Truhlar et al. scheme [25]. This procedure eliminates the problems arising from the basis set superposition errors (BSSE).

Table 3. DFT interaction energy and enthalpy at $T=0$ K extrapolated to the CBS limit, per water molecule and in kJ mol⁻¹, for system 6.^a

Method	cc-pVDZ(-PP) geometry		cc-pVTZ(-PP) geometry	
	E_{int}	H_{int}	E_{int}	H_{int}
M06-L	-55.6	-47.2 ^b	-56.3	-48.9 ^c
M06	-55.0	-46.8 ^b	-55.6	-47.8 ^c
M06-2X	-70.6	-61.6 ^b	-71.4	-62.8 ^c
M05-2X	-65.0	-56.1 ^b	-65.5	-57.1 ^c
B3LYP	-42.8	-35.1 ^b	-43.6	-36.4 ^c
B2PLYP	-50.1	-41.6 ^b	-50.4	-41.9 ^b
B2PLYP-D	-57.5	-48.3 ^b	-57.7	-48.5 ^b
mPW2PLYP	-55.0	-46.3 ^b	-55.1	-46.5 ^b
LC-wPBE	-44.5	-35.9 ^b	-45.4	-36.4 ^c
LC-BP86	-62.0	-52.6 ^b	-62.8	-54.3 ^c
LC-PBE	-54.6	-45.4 ^b	-55.3	-47.0 ^c
LC-BLYP	-60.3	-51.0 ^b	-61.1	-52.8 ^c
CAM-B3LYP	-51.5	-42.6 ^b	-52.2	-44.1 ^c
B97-D	-43.5	-34.6 ^b	-44.4	-35.3 ^c
wB97XD	-53.9	-45.4 ^b	-54.7	-46.6 ^c

^aThe MP2/CBS energy and MP2/CBS enthalpy are -57.5 kJ mol⁻¹ and -49.4 kJ mol⁻¹, respectively. ^bThe enthalpic corrections were taken from calculations using cc-pVDZ(-PP) basis sets. ^cThe enthalpic corrections were taken from calculations using the cc-pVTZ(-PP) basis set.

As it can be seen in Table 3, several DFT approaches yield energies and enthalpies that are within 5 kJ mol⁻¹ of the MP2 benchmark data reported in Table 1 for system 6, namely, M06-L, M06, B2PLYP-D, mPW2PLYP, LC-BP86, LC-PBE, LC-BLYP, and wB97XD, and only four approaches give results that differ by more than 10 kJ mol⁻¹, namely, the M06-2X, B3LYP, LC-wPBE and B97-D methods. The best agreement with MP2 energetic and enthalpic data is found for B2PLYP-D, with differences of 1.1 and 0.9 kJ mol⁻¹ for calculations with the double or the triple basis sets, respectively, but the M06-L, M06, mPW2PLYP and LC-PBE results are also very close to the MP2 values. The M06-L enthalpy based on geometries optimized with the triple basis sets is the one in closest agreement with the MP2

benchmark. The local version of the M06 family of functionals was found recently to provide very good results for other difficult systems, such as the interaction of CO with the (111) surfaces of Rh, Pt, Cu, Ag and Pd [42] or the interaction of benzene, pyridine, thymine and cytosine with the Au(111) surface [43] modelled with a periodic cell approach. Therefore, M06L seems to be a very convenient DFT approach for studying weak interactions between molecules and materials. This conclusion is based on the consistency of very good results obtained with the M06-L approach for different difficult systems dominated by weak interactions, and is also due to its easier implementation on computational codes and to its smaller need for computational resources than, for instance, the B2PLYP-D approach.

From the discussion above, the M05-2X and M06-L functionals seem to be among the most interesting for geometry optimization and for calculating the enthalpy of interaction, respectively. Thus, we have combined the two approaches, i.e., the M05-2X geometries were used to perform single-point energy calculations with the M06-L functional, to obtain M06-L//M05-2X extrapolated interaction energies and enthalpies (Table 4).

Table 4. M06-L//M05-2X interaction energy and enthalpy at $T=0$ K extrapolated to the CBS limit, per water molecule and in kJ mol^{-1} , for system 6.^a

Method	cc-pVDZ(-PP) geometry		cc-pVTZ(-PP) geometry	
	E_{int}	H_{int}	E_{int}	H_{int}
M06-L//M05-2X	-55.0	-46.0	-55.3	-46.9

^aThe enthalpic corrections were taken from M05-2X calculations using cc-pVXZ(-PP), X=2 or 3, basis sets.

From the data in Table 4, it is clear that the combination of the two Minnesota functionals is providing very good results (differences to the MP2 benchmark results are smaller than 3.5 kJ mol^{-1}) for the water-CuBTC system but, in order to understand the quality of the combined approach, additional calculations for other gas-CuBTC systems are required, which are now in progress in our laboratories.

In summary, B2PLYP-D and M05-2X approaches yielded the best energetic and geometric data for the water-CuBTC system, respectively. However, the combined M06-L//M05-2X approach, the pure M06-L functional and the long-range corrected LC-BLYP method seem to provide the best compromise between the quality of calculated geometrical data, energetic data and computational resources needed. The latter are suggested for future studies involving interaction of molecules with MOFs presenting CUS, which is important to obtain fundamental insight but also to develop potentials for classical simulations of gas sorption in those materials [20,21].

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