Structural and Electronic Effects on the Properties of Fe₂(dobdc) upon Oxidation with N₂O

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1. INTRODUCTION

The study of magnetic porous materials is interesting because of their many possible lightweight crystalline magnets and their potential applications. Porous materials have been used as molecular magnetic sponges to absorb water and to improve the sensitivity and efficiency of molecular sensors. Established theories and trends regarding magnetism within metal-oxide frameworks have garnered considerable attention in the field of magnetism. MOFs, which consist of metal-containing nodes connected by organic linkers, have been synthesized with structurally dependent magnetic properties, making them attractive materials for a variety of potential applications. MOFs have been synthesized with magnetically isolated nodes, magnetically coupled nodes, flexible pores, very large pore diameters, and combinations of these features. The M₂(dobdc) series, where M = Mg, Mn, Fe, Co, Ni, Cu, Zn, or Cd, and dobdc = 2,5-dioxido-1,4-benzenedicarboxylate, has been studied extensively for its gas adsorption abilities and magnetic properties. Recently, for example, it was shown that Fe₂(dobdc) can selectively adsorb olefins over paraffins. Upon adsorption of olefins, the magnetic ordering of the Fe(II) centers changes from ferromagnetic coupling down the one-dimensional chains to antiferromagnetic, which was attributed to enhanced superexchange upon olefin adsorption. Furthermore, there is experimental and computational evidence that suggests that...
Fe,(dobdc) exhibits metastable magnetic behavior that is sensitive to temperature, local coordination environment, and the type of guest molecules present in the pores of the MOF.\textsuperscript{6,18} Four derivatives of Fe,(dobdc), namely Fe,(OH),(dobdc), Fe,(O),(dobdc), Fe,(O),(Mg),(dobdc), and Fe,(O)_, were shown to be involved (in the case of the first named derivative) or postulated to be involved (in the case of the other three) in studies of the catalytic conversion of ethane to ethanol.\textsuperscript{19,20} The compound Fe,(OH),(dobdc) is a product of the reaction of ethane, N\textsubscript{2}O, and Fe,(dobdc), which proceeds through Fe,(O),(dobdc) as a theoretically calculated reactive intermediate.\textsuperscript{19,20} In particular, the high-spin (S = 2) character of the Fe(IV)–oxo species contained within this intermediate was determined to be important for facilitating the ethane oxidation reaction. In order to provide insight into the tunability of the magnetic character of these MOFs, we study here the electronic structure effects resulting from differing metal oxidation states in synthesized Fe,(dobdc) and Fe,(OH),(dobdc) compounds, as well as the highly reactive—and, therefore, fleeting—intermediate Fe,(O),(dobdc). The parent framework, Fe,(dobdc), contains Fe(II) centers with a quintet ground state,\textsuperscript{19,20} while Fe,(OH),(dobdc) contains Fe(III) centers with a sextet ground state, and Fe,(O),(dobdc) contains Fe(IV) centers with a quintet ground state.\textsuperscript{19,20}

The change in magnetic ordering upon adsorption of oxygen-containing species (e.g., H\textsubscript{2}O) has been investigated previously for many MOFs\textsuperscript{1,21} and the magnetic properties of Fe,(dobdc) with and without bound guests have previously been calculated using both cluster\textsuperscript{18} and periodic\textsuperscript{9,14,17} models. Kohn–Sham (KS) density functional calculations that employ local exchange-correlation functionals (local-spin-density approximations, generalized gradient approximations (GGAs), and meta-GGAs) have a tendency to overestimate the magnetic coupling constants between the magnetic centers within Fe,(dobdc)\textsuperscript{9,17,18}, most likely due to overdelocalization of unpaired spins. To attempt to remediate this, one can use empirical Coulomb and exchange integrals for selected subshells (the 3d subshell of Fe in the present work), which is the DFT+U method,\textsuperscript{22} or one can include a portion of Hartree–Fock exchange\textsuperscript{18,25,24} by using hybrid exchange-correlation functionals. Guidance regarding the value of the U parameter of the DFT+U method or a suitable amount of Hartree–Fock exchange for the calculation of magnetic properties can be sought from previous studies on similar materials\textsuperscript{14,25,26} or from general parametrization of exchange-correlation functionals.

Magnetic MOFs occupy an intermediate position between molecular magnets and bulk transition-metal oxide magnets. In MOFs, one can, in principle, tune the magnetic coupling constants by judicious choice of metal, linker, or both during synthesis and by post-synthetic guest molecule adsorption. Quantum mechanical computations can help to understand the underlying physics behind magnetically ordered MOFs and to predict properties that may currently be inaccessible by synthetic methods. The present work concerns magnetic exchange coupling, which is often quite small in MOFs (for example, 1–10 cm\textsuperscript{-1}), and the prediction of such small quantities is difficult. Understanding the capabilities and/or inadequacies of various methods is indispensable when assessing the accuracy of calculations, but the calculation of trends can yield insight even when absolute values show errors. When performing these calculations on MOFs, one can use either a periodic model or a cluster model. Calculations performed with cluster models can be performed with a wider array of methods, but cluster calculations can be inaccurate if the cluster is too small or must be constrained too tightly.

Here, we report structural and magnetic characteristics of Fe,(dobdc), Fe,(O),(dobdc), and Fe,(OH),(dobdc) obtained using KS density functional methods with both periodic and cluster models, together with experimental magnetic susceptibility data for Fe\textsuperscript{II}O\textsubscript{2.6}Fe\textsuperscript{II}(OH)\textsubscript{1.74}(dobdc)\textsuperscript{−} (DMF)\textsubscript{0.15}(THF)\textsubscript{0.22} (where DMF denotes dimethylformamide, and THF denotes tetrahydrofuran). Descriptions of the experimental and computational procedures can be found in section 2, while section 3 provides results and discussion, and section 4 summarizes our conclusions.

### 2. METHODS

#### 2.1. Preparation and Magnetic Susceptibility Measurements of Hydroxylated Fe,(dobdc)

The material Fe\textsubscript{2.02}Fe\textsuperscript{II}O\textsubscript{1.74}(dobdc)(DMF)\textsubscript{0.15}(THF)\textsubscript{0.22} was prepared by exposure of Fe,(dobdc) to excess N\textsubscript{2}O(g) at 60 °C. Mössbauer spectroscopy of the resultant material indicated that 87% of the Fe(II) sites had been oxidized to Fe(III). Full oxidation to the exact formula Fe\textsubscript{2}(OH)\textsubscript{2}(dobdc) could not be achieved without a loss in crystallinity. Elemental analysis of this material indicated that residual amounts of DMF and THF were present in the material. Anal. Calcd for C\textsubscript{32}H\textsubscript{28}Fe\textsubscript{2}N\textsubscript{0.15}O\textsubscript{8.11}: C, 30.94; H, 1.82; N, 0.58. Found: C, 30.90; H, 1.60; N, 0.58.

For the sake of convenience, the material Fe\textsubscript{2.02}Fe\textsuperscript{II}O\textsubscript{1.74}(dobdc)(DMF)\textsubscript{0.15}(THF)\textsubscript{0.22} will be referenced hereafter as Fe\textsubscript{2}(OH)\textsubscript{2}(dobdc). Direct current (DC) magnetic susceptibility measurements were performed on Fe\textsubscript{2}(OH)\textsubscript{2}(dobdc) under an applied magnetic field of 1000 Oe. Magnetic samples were prepared by adding powdered crystalline compounds to a 7-mm-diameter quartz tube with a raised quartz platform. Solid eicosane was added to cover the samples to prevent crystallite torqueing and provide good thermal contact between the sample and the cryogenic bath. The tubes were fitted with Teflon sealable adapters, evacuated on a Schlenk line or using a glovebox vacuum pump, and sealed under vacuum using an H\textsubscript{2}/O\textsubscript{2} flame. Following flame sealing, the solid eicosane was melted in a water bath at 40 °C. Data for Fe\textsubscript{2}(OH)\textsubscript{2}(dobdc) were corrected for diamagnetic contributions from the core diamagnetism estimated using Pascal’s constants\textsuperscript{27} to give \(\chi\) values of \(-0.00027434\) emu/mol and \(-0.00024306\) emu/mol (eicosane).

In earlier work on Fe,(dobdc),\textsuperscript{16} the temperature dependence of the magnetic susceptibility was interpreted using a two-parameter model, the Fisher model,\textsuperscript{58,29} corresponding to a chain of Fe ions interacting with nearest neighbors in the same chain and with Fe ions in z other chains. The parameters are \(J_{NN}\) and \(J_{IC}\), where \(J_{NN}\) is the magnetic coupling of nearest neighbors, and \(J_{IC}\) is the magnetic coupling of Fe atoms in different chains. We also attempted to apply this to Fe\textsubscript{2}(OH)\textsubscript{2}(dobdc), and the results of this attempt are described in section 3.3.

#### 2.2. Electronic Structure Calculations

##### 2.2.1. Exchange-Correlation Functionals

We used several exchange-correlation functionals—in particular, PBE, PBE+U, HSE06, PBE-D2, PBE+U-D2, HSE06-D2, and GAM+U for periodic calculations and PBE, M06-L, PBE0, B3LYP, M06, and HSE06 for cluster calculations. The PBE\textsuperscript{50} and GAM\textsuperscript{41,52} exchange-correlation functionals are local gradient approximations, and M06-1L\textsuperscript{33,34} is a local meta approximation. Because local approximations have a tendency to underestimate band gaps\textsuperscript{23,31,32} and overdelocalize charge distributions,\textsuperscript{30,41} we also employed hybrid approximations that replace a percentage X of local exchange by nonlocal Hartree–Fock exchange. Inclusion of some Hartree–Fock exchange also affects the atomic spin distribution\textsuperscript{42} and geometries.\textsuperscript{45,43} B3LYP,\textsuperscript{44,47} PBE0,\textsuperscript{49,48} and M06\textsuperscript{50} are global hybrids, which means that they use the same percentage X for all
interelectronic separations. PBE0 and B3LYP are global-hybrid gradient approximations with \( X = 25 \) and \( 20 \), respectively, and M06 is a global-hybrid meta approximation with \( X = 27 \).

Periodic calculations were performed with plane-wave basis sets with the Vienna Ab initio Simulation Package (VASP).\textsuperscript{31,32} Using global-hybrid functionals for plane-wave calculations can be very expensive. One way to cut the cost\textsuperscript{34,35} is to decrease \( X \) to zero at large interelectronic separations; in addition, this decrease is physically justified by the screening of nonlocal exchange by correlation effects at large interelectronic separations.\textsuperscript{36,37} This strategy is used by the HSE06,\textsuperscript{38,39} GGA+U calculations reported here, we empirically modified the +U method of ref22 that is used here is specified in VASP by using LDAU=TYPE = 1.) For all the PBE+U and GGA+U calculations reported here, we empirically modified only the s-shell of the Fe centers, for which we used literature values\textsuperscript{40,42} of 4 and 1 eV, respectively, for the Coulomb (\( U \)) and exchange (\( J \)) parameters.

In some calculations, a damped-dispersion molecular-mechanics term\textsuperscript{40} was also added, and these were labeled as PBE-D2, PBE+U-D2, and HSE06-D2 calculations. The van der Waals \( R_d \) and \( C_6 \) parameters determined by Grimme were used in the D2 terms; in particular, the global scaling parameter \( (s_8 = 0.75) \) fitted for PBE was used for PBE and PBE+U calculations, and the parameter \( (s_8 = 0.6) \) determined for the PBE0 functional was employed for the HSE06 calculations. Successful tests of these methods on extended crystalline systems are given in refs \textsuperscript{62-64}.

2.2.2. Periodic Calculations. For all periodic geometries, the nuclear positions, lattice parameters, and cell volumes of the structures were optimized in the ferromagnetic (FM) spin state, which corresponds to ferromagnetic coupling both along a chain of Fe centers and between the chains. These calculations employed a rhombohedral primitive cell (space group \( R \)) containing \( 34 \), \( 60 \), and \( 66 \) atoms for \( \text{Fe}_2(\text{dobdc}) \), \( \text{Fe}_2(\text{O})_2(\text{dobdc}) \), and \( \text{Fe}_2(\text{OH})(\text{dobdc}) \), respectively.

In these calculations, projector-augmented wave\textsuperscript{45,46} (PAW) potentials were used to describe the interaction between explicitly treated electrons and the electrons treated as core electrons, namely, the inner 10 electrons of each Fe center. Two partial waves were used for each orbital: a cutoff radius of 2.0 bohrs \( (\alpha_0) \) was used for the 3p and 4s states, and a cutoff radius of 2.2 \( \alpha_0 \) was used for the 3d states. Because of the relativistically small band gap and weak long-range magnetic interactions reported for \( \text{Fe}_3(\text{dobdc}) \),\textsuperscript{14} it is especially important to converge the MOF structures and energies, with respect to the number of \( k \)-points used for quadratures over the Brillouin zone.

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Figure 2. Cluster models with both (left) two Fe ions and (right) three Fe ions used for \( \text{Fe}_3(\text{OH})(\text{dobdc}) \). (Atom legend: blue = Fe, red = O, gray = C, and white = H.)

Our convergence tests and final choices of grids are summarized in the Supporting Information (SI).

Density functional perturbation theory (DFPT),\textsuperscript{69-72} also called linear response theory (LRT), was employed to compute the infrared spectra in the harmonic approximation. The PBE+U functional was used to compute all frequencies with an energy convergence threshold of \( 10^{-6} \text{ eV} \). Only the vibrations of Fe, carboxylate C, and O atoms were included in the DFPT calculation. The vibrational eigenmodes of each species were determined by the direct force constant approach.\textsuperscript{71}

The intensities of the infrared active modes were calculated in the dipole approximation by using Born Effective Charges (BECs).\textsuperscript{59}

2.2.3. Cluster Calculations. All cluster calculations were performed using the Gaussian 09\textsuperscript{73} software package on models similar to those used in previous research.\textsuperscript{15,18} The models contain two or three Fe ions. For the model with two Fe ions, we can compute nearest-neighbor coupling, and for the models with three Fe ions both the nearest-neighbor and the next-nearest-neighbor couplings can be computed (Figure 2). The models with two Fe ions were cut from the experimental structural model of \( \text{Fe}_3(\text{dobdc}) \), and the models with three Fe ions were cut from the periodically optimized PBE+U structures of each of the three MOFs. The cut bonds were then capped with H atoms. In the two-Fe model, the Fe–Fe distance and Fe–O–Fe angle (shown later in this work in Figure 5) were frozen to certain values, and the rest of the cluster was optimized using M06-L/def2-TZVP. This was followed by M06/def2-SV(P) single-point calculations with ferromagnetic and antiferromagnetic ordering using the def2-TZVP basis set and the PBE, PBE0, M06, and B3LYP\textsuperscript{74} exchange–correlation functionals. 2.2.4. Magnetic Coupling Parameters. Previous work has demonstrated that the Fe centers in each of the species have high-spin ground states; namely, \( \text{Fe}_3(\text{dobdc}) \) contains quintet Fe(II) centers, \( \text{Fe}_2(\text{O})_2(\text{dobdc}) \) contains quintet Fe(IV) centers, and \( \text{Fe}_2(\text{OH})(\text{dobdc}) \) contains sextet Fe(III) centers.\textsuperscript{14,15,16,17,20,21} Hence, only high-spin metal centers were considered in the magnetic coupling calculations. The periodic DFPT calculations for \( \text{Fe}_2(\text{dobdc}) \), \( \text{Fe}_3(\text{O})(\text{dobdc}) \), and \( \text{Fe}_3(\text{OH})(\text{dobdc}) \) were performed with the unit cells specified above\textsuperscript{68,69} (Figure 1). The PBE, PBE+U, PBE+U-D2, HSE06, HSE06-D2, and GAM+U geometries were each fixed to those optimized for the FM spin state, and the plane-wave coefficients were optimized for each of the three spin configurations shown in Figure 3 with an energy convergence threshold of \( 10^{-6} \text{ eV} \).

The unit cell used in this study contains two vertices of one of the hexagonal channels of \( \text{Fe}_3(\text{dobdc}) \) shown in Figure 1 with three Fe ions in each of the two vertices. The considered spin alignments of the six high-spin Fe ions are provided in Figure 3. The broken symmetry approximation\textsuperscript{26} allowed us to use the energy differences between these three spin configurations to compute the nearest-neighbor (J_{NN}) and interchain (J_{IC}) coupling values with the Heisenberg–Dirac–Van Vleck (HDV) Hamiltonian.\textsuperscript{75-77}
Figure 3. Side view of the primitive unit cell of Fe$_2$(dobdc) (atom legend: blue = Fe, red = O, gray = C, and white = H.) Red and blue circles indicate the upward or downward spin of the high-spin Fe ions, respectively. The entirely ferromagnetic (FM), intrachain antiferromagnetic (AFM1), and interchain antiferromagnetic (AFM2) spin states were considered in this work. AFM1 is actually ferromagnetic with this unit cell. Results with a doubled unit cell with strict intrachain states were considered in this work. AFM1 is actually ferrimagnetic magnetic (AFM1), and interchain antiferromagnetic (AFM2) spin

Figure 4. Schematic representation of the nearest-neighbor coupling constant ($J_{NN}$) and the interchain coupling constant ($J_{IC}$) of the primitive unit cell of Fe$_2$(dobdc). (Atom legend: blue = Fe, red = O, gray = C, and white = H.)

magnetic sites $i$ and $j$, and $\mathbf{S}_i$ is the spin vector on center $i$. A positive $J_{ij}$ in eq 1 denotes ferromagnetic (FM) coupling between centers $i$ and $j$, and a negative value indicates antiferromagnetic (AFM) coupling. Note that only matrix elements that contain high-spin Fe sites (i.e., diagonal matrix elements) are eigenfunctions of the HDV Hamiltonian. Also note that the diagonal matrix elements in the HDV Hamiltonian are equivalent to those of the Ising model, which is commonly used for magnetic systems.6,76 We considered one FM state and two AFM states (AFM1 and AFM2) to be the ones that allow the most direct calculation of the magnetic couplings; note that AFM2 is the ground-state configuration of Fe$_2$(dobdc).

Since all Fe sites in Fe$_2$(dobdc) and its derivatives Fe$_2$(O)$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc) are equivalent, the four nearest-neighbor interactions represented by $J_{NN}$ in Figure 4 are all equivalent. For the atoms at the edge of the unit cell, additional nearest-neighbor interactions arise due to interaction with the periodic image of the unit cell. This accounts for two more $J_{NN}$ values, resulting in a total of six $J_{NN}$ for the primitive cell.

While the treatment described above for nearest-neighbor interactions is unambiguous, the treatment of interchain coupling requires more consideration. Each chain of Fe ions is surrounded by three other chains of Fe ions. Although the three neighboring chains are equally distant, the Fe ions are staggered, so that the smallest interchain Fe-Fe distance is not the same for all three neighboring chains of a given Fe ion; in particular, the distance to the nearest Fe ion in each of the three surrounding chains in Fe$_2$(dobdc) is 7.4, 8.1, and 9.0 Å. If the data were sufficient to accommodate a multi-parameter analysis, one would recognize at least three different interchain couplings and also include next-nearest neighbors within a given chain. However, the interchain coupling was found to be small, and the theory might not be good enough to distinguish several different small couplings. Even more significantly, the experiment (as explained in section 2.1) was interpreted in terms of only two parameters, one intrachain parameter $J_{NN}$ and one interchain parameter $zJ_{IC}$. Therefore, we took the same approach computationally. However, we obtained slightly different results if we assumed that the interchain coupling was caused only by the nearest interchain interaction ($z = 1$) or was caused by equal interactions with the nearest neighbors in each of the three surrounding chains ($z = 3$). We will report the equations and the resulting magnetic coupling for the approach in which we computed the magnetic coupling values, assuming that each metal center would interact with only the closest metal center of the three neighboring chains, which was reasonable, because one of the interchain Fe-Fe distances was smaller than the other two. This limited interchain coupling model, corresponding to $z = 1$, leads to a total of six interactions per unit cell. The model with $z = 3$ would lead to 18. We note that the two treatments yield identical values of $zJ_{IC}$ but slightly different values of $J_{NN}$ (Table S5).

Using the energies calculated for the three spin states (FM, AFM1, and AFM2) shown in Figure 3, the $J_{NN}$ and $J_{IC}$ values can be extracted for Fe$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc) (which have total spin magnitudes (I)$M_z$) of 2 on every Fe site) by solving the following three equations:

\[ \sum_{i,j} J_{NN} S_i S_j = -2 \sum_j \sum_i J_{NN} S_i S_j \]  
where the subscripts $i$ and $j$ represent the Fe sites of the unit cell shown in Figure 4, $J_{NN}$ is the isotropic magnetic coupling between

\[ J_{IC} = \frac{1}{96} [E_{222,333} - E_{222,222}] \]

\[ J_{NN} = \frac{1}{64} [E_{222,222} - E_{222,222}] \]

For the unit cell of Fe$_2$(OH)$_2$(dobdc), where each Fe ion has a spin of $S/2$, the $J_{NN}$ and $J_{IC}$ values can be extracted by solving the following three equations:
distance in Fe2(dobdc), the density functional calculations ignore PBE, because of its underestimation of the Fe···0.25 center in Fe2(OH)2(dobdc) and the organic linker. Table S2 in the SI shows that, after oxidation to Fe(III), the due to Fe···0.25 experiment, with the exception of PBE, which significantly underestimates the Fe···0.25 distances and angles computed with all the methods and the theoretical model. Calculations with the actual experimental composition (Fe2(OH)2(dobdc)) may yield more accurate frequencies. Molecular DFT calculations are known to systematically overestimate experimental fundamental stretching frequencies, but usually by only 2%–5%.82

3. RESULTS AND DISCUSSION
3.1. Equilibrium Structures and Infrared Spectra. The SI compares equilibrium structures computed by PBE, PBE+U, PBE+U-D2, HSE06, HSE06-D2, and GAM+U. In the case of Fe2(dobdc), there is good agreement between the bond distances and angles computed with all the methods and the experiment, with the exception of PBE, which significantly underestimates the Fe···Fe distances and the Fe···O···Fe angle. Table S2 in the SI shows that, after oxidation to Fe(III), the experimental Fe···Fe distance increases by 0.15–0.16 Å. If we ignore PBE, because of its underestimation of the Fe···Fe distance in Fe2(dobdc), the density functional calculations predict that there is an increase in the Fe···Fe distance by 0.25–0.28 Å. Figure 5 shows the local environment of a metal center in Fe2(OH)2(dobdc) and the organic linker.

The experimental infrared (IR) spectra of Fe2(dobdc) and Fe2(OH)2(dobdc) in Figure 6 provide a good test of the PBE+U computations, which are depicted in Figure 7. The theoretical spectra were normalized to match the intensities of the experimental Fe···O stretches that occur at ~820 cm−1. The peaks occurring below 500 cm−1 are likely due to Fe···O bending modes, while those between 600 and 1000 cm−1 are due to Fe···O stretches. The PBE+U Fe(III)···O stretches frequencies in Fe2(OH)2(dobdc) occur between 619 and 630 cm−1, which is ~40 cm−1 less than the experimental value of 667 cm−1.19

The PBE+U O···H stretching frequency in Fe2(OH)2(dobdc) is 3773 cm−1, and the experimental value is 3683 cm−1. The Fe(IV)···oxo stretch is known, in other cases, to occur between 776 cm−1 and 843 cm−1.31 We find that the PBE+U Fe(IV)···oxo stretches occur here between 888 cm−1 and 899 cm−1. Thus, the theory underestimates the Fe(III)···O···H stretching frequency and may overestimate the Fe(IV)···oxo stretching frequency. However, the experimental Fe(IV)···oxo-containing material is quite different than the theoretical model. Calculations with the actual experimental composition (Fe2(O)10Mg10(dobdc)) may yield more accurate frequencies. Molecular DFT calculations are known to systematically overestimate experimental fundamental stretching frequencies, but usually by only 2%–5%.82

3.2. Electronic Structure and Density of States. To gain insight into the electronic structures, the orbital projected density of states (OP-DOS) is provided for each MOF in the SI. The OP-DOS plots were extracted using the default settings for atomic radii in VASP. The atomic radii could be considered tunable parameters that can be improved by computing and comparing to reasonable atomic charges,33 but the default parameters yielded decent results, when compared to the experiment. Figures S3 and S4 show the OP-DOS obtained using PBE+U and HSE06, respectively, for each MOF in its
contains Fe(IV), but predicts a larger gap of 1.8 eV for Fe$_2$(OH)$_2$(dobdc), the
from 619 cm$^{-1}$ to 630 cm$^{-1}$ were multiplied by a factor of 10 for more visible comparison to the experiment. The main consideration in these plots is the band gap, i.e., the difference in energy between the highest occupied orbital and the lowest unoccupied one. PBE+U and HSE06 both predict a sizable band gap, in particular 1.3 and 2.1 eV, respectively, which are substantially larger than the gap of 0.3 eV reported by Zhang et al. ref 14. We investigated the reason for this discrepancy and found that the band gap decreased as the volume increased, but even with a 15% volume fluctuation, it was not feasible to extract the interchain and intrachain magnetic couplings as antiferromagnetic. The $\chi_M T$ value at 300 K and 1000 Oe is 6.85 emu K/mol, which is much lower than both the expected value for two isotropic $S = 1/2$ spins (8.75 emu K/mol) and the expected value assuming 0.26 mol (13% of iron sites) of $S = 2$ Fe(II) per formula unit (8.39 emu K/mol). The low magnetic moment is attributed to the presence of 13% Fe(II), which, in addition to simply having a lower magnetic moment than that of Fe(III), may also display enhanced antiferromagnetic coupling with its nearest-neighbor spins. The magnetic susceptibility of Fe$_2$(dobdc) was measured in ref 16, where the fitting procedure used to compute the experimental coupling values for Fe$_2$(dobdc) is also described. The fitting procedure is briefly summarized in section 2.1.

3.3. Magnetic Susceptibility Measurements. The magnetic susceptibility of Fe(II)$_{0.26}$Fe(III)(OH)$_{1.74}$(dobdc) (DMF)$_{0.15}$(THF)$_{0.22}$ (Fe$_2$(OH)$_2$(dobdc)) was measured in the present work. DC magnetic susceptibility measurements were performed under an applied magnetic field of 1000 Oe across the temperature range of 2−300 K. The measurements of Fe$_2$(OH)$_2$(dobdc) revealed a decreasing $\chi_M T$ product with decreasing temperature across the full temperature range measured (Figure 8). This trend supports the assignment of both intrachain and interchain magnetic coupling parameters with the Fisher model, as was done for Fe$_2$(dobdc). The results in Figure 8 indicate that Fe$_2$(dobdc) has ferromagnetic intrachain coupling and antiferromagnetic interchain coupling. The precise coupling parameters for Fe$_2$(OH)$_2$(dobdc) could not be readily derived because of the fact that the synthesized MOF was only partially oxidized, with $\sim 13\%$ of the Fe sites remaining in the Fe(II) state. However, a Curie−Weiss fit to the expression $1/\chi = (T − \theta)/C$ for the high-temperature regime (50−300 K) of the inverse magnetic susceptibility data for both Fe$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc) (Figure S18) permitted some assessment of the differences in magnetic coupling behaviors for the two frameworks. For Fe$_2$(dobdc), the Curie−Weiss analysis resulted in a positive Weiss temperature of $\theta = 11$ K, which is consistent with ferromagnetic interactions being dominant, and a Curie constant of $C = 6.3$ emu K/mol. In contrast, the Curie−Weiss analysis for Fe$_2$(OH)$_2$(dobdc) resulted in $\theta = −139$ K and $C = 10.0$ emu K/mol. The negative sign of the Weiss temperature ($\theta$) for Fe$_2$(OH)$_2$(dobdc) indicates that antiferromagnetic

Figure 7. Experimental and theoretical (PBE+U) infrared spectra of (top) Fe$_2$(dobdc) and (bottom) Fe$_2$(OH)$_2$(dobdc). All spectra were normalized based on the highest peak. The experimental spectra for Fe$_2$(dobdc) were taken from ref 19. The Fe−OH stretch theoretical peak intensities (those that are indicated by the red arrow in the range from 619 cm$^{-1}$ to 630 cm$^{-1}$) were multiplied by a factor of 10 for more visible comparison to the experiment.

Figure 8. Experimental magnetic susceptibility times temperature curves of Fe$_2$(dobdc)$^{16}$ (blue) and Fe$_2$(OH)$_2$(dobdc) (green). The applied magnetic field strength during the susceptibility measurement of each material was 1000 Oe.
interactions are prevalent. Concurrently, the large increase in the magnitude of $\theta$ which is dependent on the spin states present and the number and strength of the magnetic coupling pathways,$^{84}$ suggests that the magnetic interactions are stronger within Fe$_2$(OH)$_2$(dobdc), since the Fe spins involved only increase from quintet to sextet states, while the number of magnetic coupling pathways presumably remains unchanged. Thus, we can state qualitatively that adding a hydroxide anion and oxidizing the metal sites of Fe$_2$(dobdc) switches the nearest-neighbor magnetic coupling behavior from ferromagnetic to antiferromagnetic and increases the magnetic coupling strength.

### 3.4. Magnetic Coupling Parameters

The calculated magnetic coupling parameters for Fe$_2$(dobdc), Fe$_2$(O)$_2$(dobdc), and Fe$_2$(OH)$_2$(dobdc) are provided in Tables 1 and 2. As mentioned above, the PBE+U calculations were run with both primitive unit cells (54, 60, or 66 atoms) and doubled cells (108, 120, or 132 atoms), as indicated in the second column of Table 1. This table shows that there is no significant difference between the PBE+U calculations with 54 and 108 atoms in the unit cell, which indicates that the primitive cell is adequate for these computations. The same is true for couplings in Fe$_2$(O)$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc).

The PBE nearest-neighbor couplings in Fe$_2$(dobdc) are two orders of magnitude larger than both the experimental ones and those computed with the other methods tested in Table 1. The PBE values are calculated for the PBE geometry, which has short Fe···Fe distances. The overestimation of magnetic properties by GGA functionals is well-established.$^{85}$ A previous study$^{93}$ of magnetic interactions in Fe$_2$(dobdc) employed the PBE exchange-correlation functional with experimental geometries and obtained a $J_{\text{NN}}$ value of 28 cm$^{-1}$, which is smaller but still a significant overestimation. They concluded$^{94}$ that there is fairly strong ferromagnetic coupling in Fe$_2$(dobdc). It now appears that such large calculated $J_{\text{NN}}$ values are an artifact of the simple gradient approximation used in the PBE functional. This was shown in previous work,$^{18}$ where a calculation with a hybrid meta-GGA gave a value of 3.6 cm$^{-1}$, in good agreement with the experimental value of 4.1 cm$^{-1}$.

It was pointed out in section 2.2.4 that the magnetic coupling constants are slightly dependent on whether we perform the analysis with $z = 1$ or $z = 3$. The nearest-neighbor Fe···Fe distance is 3.0 Å, and the next-nearest neighbor Fe···Fe distance within a chain is 5.0 Å. Thus, the next-nearest-neighbor distance is significantly shorter than the shortest interchain Fe···Fe separation, which suggests that the next-nearest-neighbor intrachain coupling should be calculated. The next-nearest-neighbor coupling results are shown in Table 1, where we report the results with $z = 1$. (Note that the value computed for $J_{\text{IC}}$ is independent of whether or not $J_{\text{NN}}$ is computed and is also independent of whether we use $z = 1$ or $z = 3$.) Excluding PBE, the nearest-neighbor couplings ($J_{\text{NN}}$) obtained with $z = 3$ are very similar for Fe$_2$(dobdc), Fe$_2$(OH)$_2$(dobdc), and Fe$_2$(O)$_2$(dobdc), whereas the results for $J_{\text{IC}}$ are unchanged.

Table 1 shows that the PBE+U and HSE06 calculated values of $J_{\text{NN}}$ are smaller than the PBE values and are in more reasonable agreement with the experimental measurements.
agreement with the experiment. For Fe$_2$(dobdc), the coupling values obtained by HSEO6 and HSEO6-D2 are similar to each
other and are larger than those predicted by PBE+U, whereas for the Fe$_2$(OH)$_2$(dobdc) and Fe$_2$(O)(dobdc) cases, HSEO6
and HSEO6-D2 yield magnetic couplings that are smaller than the values computed with PBE+U and PBE. PBE+U and
HSEO6 predict the same signs of the magnetic couplings.

Table 1 shows that the periodic calculations of $J_{\text{NN}}$ using PBE+U yield values of 0.3, −1.1, and −0.9 cm$^{-1}$ for Fe$_2$(dobdc), Fe$_2$(OH)$_2$(dobdc), and Fe$_2$(O)(dobdc), respectively. These $J_{\text{NN}}$ values may be compared to the respective $J_{\text{IC}}$
values of $-0.6$, $-2.1$, and 0.4 cm$^{-1}$. The magnitude of the
PBE+U $J_{\text{IC}}$ coupling values for Fe$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc) are larger than the $J_{\text{NN}}$ values, whereas the
PBE+U $J_{\text{IC}}$ value of Fe$_2$(O)(dobdc) is smaller than the $J_{\text{NN}}$
value. Note that the $J_{\text{IC}}$ coupling values for Fe$_2$(OH)$_2$(dobdc) are notably larger than the other two cases with all
functionals. This may indicate that, separate from the oxidation of the metal centers, addition of the (OH)$^-$ groups enhances interchain magnetic coupling.

Table 2 provides the results of cluster model calculations that may be compared to the periodic calculations in Table 1.

Table 2. Isotropic Magnetic Coupling Constants of the Fe Centers for Each Studied MOF, As Obtained by Cluster Calculations"a

<table>
<thead>
<tr>
<th>Method</th>
<th>$J_{\text{NN}}$ (cm$^{-1}$)</th>
<th>$J_{\text{IC}}$ (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBE+/PBE</td>
<td>64.6</td>
<td>18.2</td>
</tr>
<tr>
<td>PBE+/PBE+U</td>
<td>14.3</td>
<td>18.7</td>
</tr>
<tr>
<td>HSEO6/PBE+U</td>
<td>2.4 (0.4)</td>
<td>-3.2 (-0.1)</td>
</tr>
<tr>
<td>M06/PBE+U</td>
<td>4.3</td>
<td>-3.9</td>
</tr>
<tr>
<td>PBE0/PBE+U</td>
<td>2.5</td>
<td>-3.1</td>
</tr>
<tr>
<td>B3LYP/PBE+U</td>
<td>2.7</td>
<td>-4.1</td>
</tr>
<tr>
<td>expt</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

"X/Y indicates a cluster calculation with method X employing a fragment of a MOF optimized by periodic calculations with method Y. Only nearest- and next-nearest-inchain coupling values ($J_{\text{NN}}$ and $J_{\text{IC}}$) were computed, and they may be compared with Table 1. Values shown in parentheses represent the $J_{\text{NN}}$ value (in cm$^{-1}$). Data taken from ref 16.

Because they are very similar to the experimental geometries (Table S2), the PBE+U optimized periodic structures were used to make the clusters in all cases except one. The PBE+/PBE $J_{\text{NN}}$ Value is much larger than the PBE+/PBE+U value, in part because the periodic PBE metal–metal bond distances are too small for Fe$_2$(dobdc) (as noted above in the discussion of Table S2). The PBE+/PBE cluster calculation predicts $J_{\text{NN}}$ values for Fe$_2$(dobdc) that are significantly larger than experiment. However, the cluster $J_{\text{NN}}$ values obtained by HSEO6, M06, PBE0, and B3LYP are all quite reasonable, when compared to both the periodic and experimental magnetic coupling parameters.

The results with PBE+U structures in Table 2 show that Hartree–Fock exchange in HSEO6, PBE0, M06, and B3LYP decreases the predicted intrachain coupling values. If one assumes that one effect of the U parameter is to mimic Hartree–Fock exchange, this is consistent with the periodic results.

The cluster values of $J_{\text{NN}}$ in Table 2 are considerably smaller than the periodic calculations of $J_{\text{NN}}$ in Table 1. However, they
do correctly predict the experimentally determined magnetic ordering of Fe$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc). In the case of Fe$_2$(O)(dobdc), the magnetic coupling values are likely extremely weak, which is why GAM+U and HSEO6/PBE+U in Table 2 predict different magnetic orderings than the other functionals. This demonstrates the difficulty of accurately calculating the small energies of these interactions.

It was suggested by Park et al. that the changes in magnetism within Fe$_2$(dobdc) upon guest adsorption are due to structural changes within the MOF. When the intrachain Fe--Fe distances were less than ~3.12 Å, the magnetic interactions were interpreted as being dominated by direct exchange between the metal centers and were ferromagnetic; at longer Fe--Fe separations, the magnetic interactions were interpreted as dominated by superexchange through the bridging O atoms. In our work, Fe$_2$(OH)$_2$(dobdc) has intrachain Fe--Fe distances of ~3.12 Å (Table S2) and the nearest-neighbor AFM coupling is calculated to be very weak (Tables 1 and 2). For comparison, Fe$_2$(OH)$_2$(dobdc) has intrachain Fe--Fe distances of ~3.22 Å and shows a larger AFM coupling. But the Fe--Fe separation is not the only geometrical parameter that changes. The Fe--O--Fe bond angles increase from Fe$_2$(dobdc) to Fe$_2$(OH)$_2$(dobdc) to Fe$_2$(OH)$_2$(dobdc) (see Table S2). Table 1 shows that these structural changes are associated with a switch from positive $J_{\text{NN}}$ values to negative $J_{\text{NN}}$ values—i.e., a switch from FM to AFM coupling of the nearest-neighbor metal centers. However, many factors besides geometry may contribute to the changes in magnetic coupling. These factors include electronic effects resulting from (1) the presence of the (OH)$^-$ and O$^2-$ ligands, (2) the change in oxidation state Fe(III) for (OH)$^-$ and to Fe(IV) for O$^2-$, and (3) the change in spin state of the metal centers from quintet to sextet, resulting from the inclusion of the (OH)$^-$ ligands. The magnetic coupling equations for Fe$_2$(OH)$_2$(dobdc) (eq 5) take into account the effect of the spin state change (3), but completely separating all three of these electronic contributions from the geometric contributions required a separate set of calculations, as discussed in the next two paragraphs.

To compute the aforementioned electronic contributions, two approaches were considered. In the first approach, the three-Fe cluster model of Fe$_2$(OH)$_2$(dobdc) carified from the PBE+U periodic structure was used. The three (OH)$^-$ groups were removed from this cluster, which changed the Fe(III) centers to Fe(II) centers. While keeping the positions of all atoms in the cluster fixed, magnetic coupling constants were calculated using M06/def2-TZVP. This was done to separate the electronic and geometric contributions to the magnetic coupling. The coupling constant of this new cluster (~1.1 cm$^{-1}$) should be compared to the M06 magnetic coupling results for Fe$_2$(dobdc) (4.3 cm$^{-1}$) and Fe$_2$(OH)$_2$(dobdc) (3.9 cm$^{-1}$) in Table 2. We can see that both electronic and geometric effects play important roles in the magnetic couplings studied here.

The second approach was to go in the reverse direction, meaning that we started with the Fe$_2$(dobdc) cluster and then added (OH)$^-$ groups. Three (OH)$^-$ groups were added to the cluster model of Fe$_2$(dobdc) carified from the PBE+U periodic structure, and only these added groups were optimized using M06/def2-TZVP, while the remainder of the cluster was kept fixed. The oxidation state and spin state of the metal centers were thus the same as for Fe$_2$(OH)$_2$(dobdc), while the metal coordination geometry was the same as in Fe$_2$(dobdc). The
magnetic coupling of Fe$_2$(dobdc) (4.3 cm$^{-1}$) (Table 2) changed to 0.2 cm$^{-1}$ when (OH)$^-$ was added, which is an effect of 4.1 cm$^{-1}$. The value of 0.2 cm$^{-1}$ can be compared to the M06 magnetic coupling result in Table 2 for Fe$_2$(OH)$_2$(dobdc) of $-3.9$ cm$^{-1}$, which also has an effect of 4.1 cm$^{-1}$. This means that the metal oxidation and addition of (OH)$^-$ and the change in geometry had impacts of similar magnitude. These results show that the presence of the (OH)$^-$ groups (1), the change in oxidation state (2), and the change in spin state (3) all contribute considerably to the magnetic ordering of Fe$_2$(OH)$_2$(dobdc). We also found that the geometry has an important effect on the magnetic coupling.

To examine the overall effect of the geometry, we examined the OP-DOS results from the periodic calculations of each structure. However, we also wanted to understand how distinct geometrical parameters, such as Fe···Fe distance and Fe−O−Fe angle, contribute to the magnetic coupling. We thus designed cluster models to separate the contributions of these parameters.

The periodic calculations on Fe$_2$(dobdc) (Table 1) are in general agreement with previous work. The results for the hydroxylated case in Table 1 are consistent with the qualitative inference from the experiment in section 3.3 that oxidation of the metal sites of Fe$_2$(dobdc) and concurrent addition of hydroxide anions to these sites switches the nearest-neighbor magnetic coupling behavior from ferromagnetic to antiferromagnetic and increases its strength. The interactions between the bridging O atoms and the Fe atoms can strongly influence the type and magnitude of the magnetic exchange within a material. The OP-DOS calculations of the Fe 3d and the bridging O 2p orbitals show that overlap between these orbitals is larger for Fe$_2$(O)$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc) than for Fe$_2$(dobdc). This may indicate that there is more interaction between the metal electrons through the bridging oxygens in Fe$_2$(O)$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc). The increasing Fe−O−Fe bond angle leads to an increase in the magnitude of the AFM coupling, because the electrons in the Fe 3d interact more strongly through the bridging oxygen electrons via superexchange (Figure 9). The superexchange interaction was developed into a set of semiempirical rules by Goodenough and Kanamori. These rules predict an AFM interaction if the metal−ligand−metal angle is close to 180°, and a weak FM interaction if the angle is close to 90°. The computations performed in this work align reasonably well with these rules, although the actual situation is complicated by the fact that the Fe−O distances and Fe−Fe distances change, along with the change in bond angle. Similar interaction trends have been observed previously within Fe$_2$(dobdc) when olefins were bound to the metal centers.

In order to somewhat separate changes in intrachain Fe···Fe distances and Fe−O−Fe angles, we performed cluster calculations using the two-Fe model, where two degrees of freedom, Fe···Fe distance and Fe−O−Fe angle, were set to (2.9 Å, 85°), (2.9 Å, 105°), (3.1 Å, 95°), (3.3 Å, 85°), and (3.3 Å, 105°) to see how the change in either the Fe···Fe distance or the Fe−O−Fe angle affects the magnetic coupling. With these two internal coordinates frozen, all other coordinates were optimized. The $J_{\text{NN}}$ values were found to be 10, $-6.3$, 1.5, 5.0, and $-1.2$ cm$^{-1}$, respectively. This shows that if the Fe···Fe distance is kept fixed to 2.9 or 3.3 Å and the Fe−O−Fe angle is increased from 85° to 105°, $J_{\text{NN}}$ decreases and becomes negative. On the other hand, if the Fe−O−Fe angle is fixed to 85° or 105°, and the Fe···Fe distance is increased from 2.9 Å to 3.3 Å, the $J_{\text{NN}}$ value again decreases. Hence, changing either the Fe···Fe distance or the Fe−O−Fe angle has an effect on the magnetic coupling.

4. CONCLUSIONS

In contrast to Fe$_2$(dobdc), Fe$_2$(O)$_2$(dobdc) and Fe$_2$(OH)$_2$(dobdc) feature antiferromagnetic (AFM) coupling down each metal chain (Figure 10). Previous work by Bloch et al. and calculations performed by Park et al. suggest that the shift from ferromagnetic (FM) to AFM coupling is the result of ligands changing the intrachain Fe···Fe distances and Fe−O−Fe angles. Here, we find that the effect can also be partially accounted for by the electronic effect of the ligands, the oxidation state of the metal centers, and/or the spin state of the metal centers, even in the absence of geometry changes. This indicates that structural and electronic changes upon framework oxidation likely act in concert to effect magnetic coupling.

The computationally efficient PBE+U and GAM+U approaches predict structural properties that agree quite well with the values obtained using more expensive hybrid functionals. Inclusion of damped dispersion effects by molecular mechanics does alter equilibrium volumes; however, the effect is minor when compared to the inclusion of Hartree–Fock exchange. Thus, rescaling PBE+U or GAM+U unit cells...
and correcting for the electronic structure with single-point hybrid functional calculations appears to be an efficient approach to calculate magnetic properties of MOFs. Cluster models can be used to compute $J_{NN}$ coupling values quite accurately, and can be used conveniently with a wider array of computational methods at a lower cost. However, capturing accurately, and can be used conveniently with a wider array of periodic and cluster-based modeling. Ongoing research is provided one is aware of the strengths and limitations of both properties and their structural dependences for these materials, theory can correctly describe the magnetic and electronic MOF structure does require periodic calculations. Overall, computing Alliance in Berlin and Hannover) and JUROPA approach to calculate magnetic properties of MOFs. Cluster and comments on the manuscript. This work was supported by We thank Professor Joachim Sauer for insightful discussions.

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