

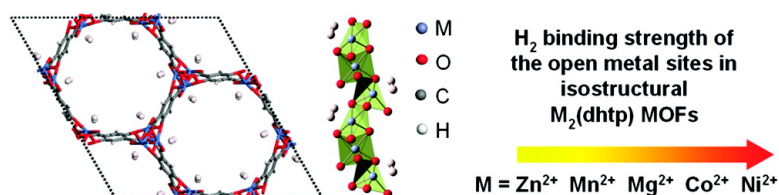
Communication

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*J. Am. Chem. Soc.*, **2008**, 130 (46), 15268-15269 • DOI: 10.1021/ja807023q • Publication Date (Web): 25 October 2008

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## Enhanced H<sub>2</sub> Adsorption in Isostructural Metal–Organic Frameworks with Open Metal Sites: Strong Dependence of the Binding Strength on Metal Ions

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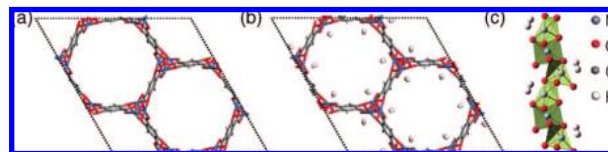
Received September 4, 2008; E-mail: wzhou@nist.gov

Porous metal–organic frameworks (MOFs) have exhibited great potential for gas storage.<sup>1</sup> The largest drawback of this class of materials for H<sub>2</sub> storage application is their weak binding strength to H<sub>2</sub>, which necessitates a cryogenic working temperature. Extensive efforts thus have been made to synthesize new MOFs with enhanced H<sub>2</sub> affinity. A successful endeavor would require a good understanding of the H<sub>2</sub> interactions with both metal clusters and organic linkers. One effective route to achieve this goal is to systematically compare isostructural MOFs with various building units. Isostructural MOFs with the same metals but different organic linkers are fairly common (e.g., the IRMOF-1 to IRMOF-16 series<sup>2</sup>), and comparison studies of the H<sub>2</sub> adsorption on such MOFs have been carried out routinely.<sup>3</sup> In contrast, isostructural MOFs with different metals are rare, mainly due to the sensitivity of the synthetic reaction to the coordination chemistry of the metal ions. For classical MOFs with fully coordinated metal ions, the direct metal–H<sub>2</sub> interaction is largely screened, and thus no dramatic effect can be expected by varying the metal species. The same is not true for MOFs with coordinately unsaturated metal sites, in which the open metal ions directly bind H<sub>2</sub>, leading to some of the largest isosteric heats of adsorption for H<sub>2</sub> ( $Q_{st}$ ) reported for physisorptive materials.<sup>4,5</sup> To our knowledge, there has been no previous report that unambiguously compares the roles of different coordinating metal ions on H<sub>2</sub> adsorption.<sup>6</sup>

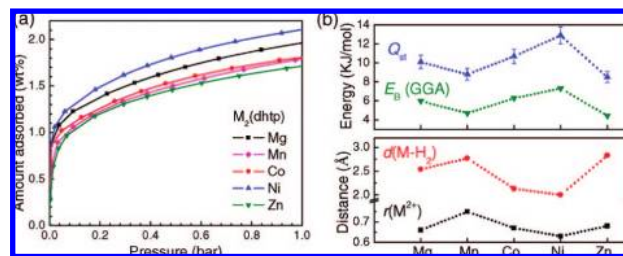
Recently, a group of isostructural MOF compounds with open metal ions [CPO-27-M (M = Mg, Co, Ni) and MOF-74 (where the metal is Zn)] were reported.<sup>7,8</sup> This MOF series [hereafter called M<sub>2</sub>(dhtp), dhtp = 2,5-dihydroxyterephthalate], with the same crystal structures (see Figure 1a), represents an ideal system to study the roles of open metals on H<sub>2</sub> binding. Importantly, the open metal sites have been confirmed to be the primary and strongest H<sub>2</sub> binding sites in these compounds by a recent neutron diffraction study on Zn<sub>2</sub>(dhtp).<sup>9</sup>

Using the methods described in the literature, we successfully synthesized M<sub>2</sub>(dhtp) (M = Mg, Co, Ni, Zn). Our further efforts to extend this series to other first-row transition metals and alkaline earth metal Ca, using similar synthesis protocol, resulted in either nonporous precipitates or porous MOFs with different crystal structures, with Mn being the only exception. This is not surprising considering the different coordination chemistry and sizes of various metal cations. In the current work, we focus on these five synthesized M<sub>2</sub>(dhtp) samples (M = Mg, Mn, Co, Ni, Zn).

The X-ray powder diffraction patterns from the five M<sub>2</sub>(dhtp) samples [see Supporting Information (SI)] all can be indexed and fitted using the reported crystal structure,<sup>7,8</sup> confirming that they



**Figure 1.** (a) [001] view of the unit cell of M<sub>2</sub>(dhtp). The crystal structure has a trigonal lattice and space group  $R\bar{3}$ . The one-dimensional (1-D) pore geometry is apparent. (b) The unit cell with H<sub>2</sub> molecules on the open metal sites. Note that each metal ion can directly bind to one H<sub>2</sub>, which corresponds to  $\sim 1.2$  wt% adsorption capacity. (c) A close view of the metal oxide polyhedron, which form 1-D chains along the crystal  $c$ -axis. The metal ions are coordinately unsaturated, resulting in a distorted pyramid configuration. The H<sub>2</sub> molecule strongly adsorbed on the metal site partially serves the role of the missing ligand in a stable octahedral coordination.



**Figure 2.** (a) Excess H<sub>2</sub> adsorption isotherms of M<sub>2</sub>(dhtp) at 77 K, 0–1 bar. (b) The empirical transition metal ion radius, the calculated M–H<sub>2</sub> distance, the experimental  $Q_{st}$  (along with error bar), and the calculated  $E_B(\text{GGA})$  of M<sub>2</sub>(dhtp). A strong correlation between them is apparent.

are indeed isostructural. In such structures, M<sup>2+</sup> cations are bonded with five oxygen atoms in a square-pyramid coordination environment, leaving the M<sup>2+</sup> in the center of the square plane open and accessible to the adsorbed gas molecule (see Figure 1b and 1c). Interestingly, the Mg, Co, Ni, and Zn compounds have very close lattice parameters  $a$  and  $c$ , while the unit cell of the Mn compound is notably larger (see Table S1 in SI). The variation of the lattice parameters can be rationalized by the different ionic radii of these divalent cations with a coordination number of 5. The ionic radii for Mg<sup>2+</sup>(V), Co<sup>2+</sup>(V), Ni<sup>2+</sup>(V), and Zn<sup>2+</sup>(V) are 0.66, 0.67, 0.63, and 0.68 Å, respectively,<sup>10</sup> quite close to each other. In contrast, Mn<sup>2+</sup>(V) has a larger size of 0.75 Å, resulting in the largest lattice parameters in this series.

H<sub>2</sub> adsorption isotherms (at 77, 100, and 150 K) were measured using a Sieverts-type apparatus.<sup>11</sup> The samples were fully activated at 200 °C in a dynamic vacuum before the adsorption measurements (see SI). The data at 77 K, in the low pressure region, are shown in Figure 2a. The initial heats of H<sub>2</sub> adsorption ( $Q_{st}$ ), derived using the modified Clausius–Clapeyron equation,<sup>12</sup> are shown in Table 1. As expected, the H<sub>2</sub> adsorption behaviors of the M<sub>2</sub>(dhtp) depend strongly on the metal species. Although the adsorption at high

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**Table 1.** Summary of Data Obtained for  $M_2(\text{dhtp})$ , including the Initial Isothermic Heat of Adsorption ( $Q_{\text{st}}$ ) for  $\text{H}_2$ , the Calculated Metal– $\text{H}_2$  Distance (from GGA), the Total  $\text{H}_2$  Binding Energy ( $E_{\text{B}}$ ), and the Pure Coulomb Contribution ( $E_{\text{C}}$ )<sup>a</sup>

M	$d(\text{M}-\text{H}_2)$ (Å)	$Q_{\text{st}}$ (kJ/mol)	$E_{\text{B}}$ , GGA (kJ/mol)	$E_{\text{C}}$ , GGA (kJ/mol)	$E_{\text{B}}$ , LDA (kJ/mol)
Mg	2.54	10.1	5.99	12.44	24.77
Mn	2.77	8.8	4.70	11.05	22.41
Co	2.13	10.7	6.28	12.80	35.62
Ni	2.00	12.9 (13.5)	7.33	14.98	39.03
Zn	2.83	8.5 (8.8)	4.43	10.46	21.97

<sup>a</sup> Note that our initial  $Q_{\text{st}}$  was obtained at a low  $\text{H}_2$  loading of  $\sim 0.1$  wt %. The error bar of  $Q_{\text{st}}$  is  $\pm 3\%$ . Previously reported  $Q_{\text{st}}$  values for Ni and Zn (from refs 4 and 9, respectively) are also shown (in parentheses).

pressure (see SI) may be complicated by several factors, the adsorption at very low pressure and corresponding initial  $Q_{\text{st}}$  should directly reflect how strongly the metal ion binds  $\text{H}_2$ , since the primary  $\text{H}_2$  binding is right on the open metal site. Overall, the  $Q_{\text{st}}$ 's of these compounds are significantly larger than those of classical MOFs ( $\sim 4\text{--}5$  kJ/mol<sup>11</sup>). Within this series,  $\text{Zn}_2(\text{dhtp})$  has the lowest  $Q_{\text{st}}$  ( $\sim 8.5$  kJ/mol), while the  $Q_{\text{st}}$  of  $\text{Ni}_2(\text{dhtp})$  is  $\sim 50\%$  higher ( $\sim 12.9$  kJ/mol, being the highest).

The relative  $\text{H}_2$  binding strength of different metals can be qualitatively understood on the basis of coordination preference of these divalent cations. Previous analyses of various Mg-containing structures show that  $\text{Mg}^{2+}$  has a firm coordination number of 6 with an overwhelming preference for oxygen-containing ligands.<sup>13</sup> This explains well both the exceptional  $Q_{\text{st}}$  of  $\text{CO}_2$  for  $\text{Mg}_2(\text{dhtp})$  reported in a recent work<sup>8</sup> and the good  $Q_{\text{st}}$  for  $\text{H}_2$  found by us. The coordination number of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  can readily vary between 4 and 6. For high spin octahedral transition metal complexes, their stability for the replacement of water by other ligands often follows the empirical, Irving–Williams sequence<sup>14</sup> (i.e., “ $\text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} > \text{Zn}^{2+}$ ”). The  $Q_{\text{st}}$  for  $\text{H}_2$  that we observed for the four transition metal  $M_2(\text{dhtp})$  matches this order reasonably well.

To more directly relate the  $\text{H}_2$  affinity of different metal ions to their electronic structures, we performed first-principles calculations based on density-functional theory (DFT), using the PWSCF package.<sup>15</sup> For  $\text{H}_2$  binding on these exposed metal sites, our previous study on  $\text{Mn}_4\text{Cl-MOF}$  has clearly shown that the electrostatic Coulomb interaction is the most important contribution.<sup>16</sup> Therefore, despite the fact that the dispersive interactions are not well-treated in standard DFT, a qualitative comparison of various open metals is possible. Here we adopted the generalized gradient approximation (GGA) of DFT, which typically underestimates the binding but gives accurate results for charge transfer, Coulomb interaction, etc. For comparison, we also performed calculations using the local density approximation (LDA) of DFT, which typically overestimates the binding.

The calculated metal– $\text{H}_2$  distance, the binding strength, and the electrostatic contributions to the overall binding are summarized in Table 1. Interestingly, the general trend of the binding energy and electrostatic interaction variation on different metals agree well with the experimental trend, although GGA and LDA underestimate and overestimate the binding strength, respectively. This confirms that the major interaction between the open metal center and the  $\text{H}_2$  molecule is indeed Coulomb attraction, successfully captured by standard DFT calculations. For transition metal ions, the spin states may also have an important impact on the  $\text{H}_2$  binding.<sup>16</sup> We found that there exists only one possible spin state for each metal in these MOFs, which is  $5/2$ ,  $3/2$ , and  $2/2$  for  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Ni}^{2+}$ , respectively. Adsorption of  $\text{H}_2$  was found not to alter the spin states. Thus, we can easily

understand why the empirical Irving–Williams sequence describes well the relative  $\text{H}_2$  binding strength in these MOFs: (a) The metal complex is indeed in the high spin octahedral configuration, and (b) the electrostatic interaction plays a major role in the  $\text{M}-\text{H}_2$  interaction, a primary basis for the “Irving–Williams series”.

From our calculations, it is clear that a strong correlation exists between the empirical transition metal ion radius, the calculated  $\text{M}-\text{H}_2$  distance, and the experimental  $Q_{\text{st}}$  (as well as the calculated  $E_{\text{B}}$ ), as shown in Figure 2b. Among the five metals,  $\text{Ni}^{2+}$  has the smallest ion radius (0.63 Å), the shortest  $\text{M}-\text{H}_2$  distance (2.00 Å), and thus the highest  $Q_{\text{st}}$  in this MOF series. It would be interesting to see how  $\text{Cu}^{2+}$  fits in this picture if  $\text{Cu}_2(\text{dhtp})$  can be synthesized. It is not obvious whether  $\text{Cu}^{2+}$  would bind to  $\text{H}_2$  more strongly than  $\text{Ni}^{2+}$ , since although  $\text{Cu}^{2+}$  has an ion radius (0.65 Å) slightly larger than  $\text{Ni}^{2+}$ , it often forms distorted octahedral complexes, due to the Jahn–Teller effect.

In summary, by combining experimental efforts with theoretical calculations, we directly compared the role of metals in a representative, isostructural MOF system,  $M_2(\text{dhtp})$ . In this series, we found the  $\text{H}_2$  binding following the trend of “ $\text{Zn}^{2+} < \text{Mn}^{2+} < \text{Mg}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+}$ ”. Our results suggest that the relative strength of interaction of  $\text{M}^{2+}-\text{H}_2$  may be empirically predicted by the ionic radius of the cations in same coordination environment. This may provide a convenient guideline for the future development of MOFs with unsaturated metal sites.

**Acknowledgment.** This work was partially supported by DOE BES Grant No. DE-FG02-08ER46522 (T.Y.).

**Supporting Information Available:** Synthetic procedure, X-ray powder diffraction data,  $\text{H}_2$  adsorption isotherms, description of our DFT calculations. This materials is available free of charge via the Internet at <http://pubs.acs.org>.

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JA807023Q