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M$_2$(m-dobdc) (M = Mg, Mn, Fe, Co, Ni) Metal-Organic Frameworks Exhibiting Increased Charge Density and Enhanced H$_2$ Binding at the Open Metal Sites

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ABSTRACT: The well-known frameworks of the type M$_2$(dobdc) (dobdc$^{4-} = 2,5$-dioxido-1,4-benzenedicarboxylate) have numerous potential applications in gas storage and separations, owing to their exceptionally high concentration of coordinatively unsaturated metal surface sites, which can interact strongly with small gas molecules such as H$_2$. Employing a related meta-functionalized linker that is readily obtained from resorcinol, we now report a family of structural isomers of this framework, M$_2$(m-dobdc) (M = Mg, Mn, Fe, Co, Ni; m-dobdc$^{4-} = 4,6$-dioxido-1,3-benzenedicarboxylate), featuring exposed M$_2^+$ cation sites with a higher apparent charge density. The regioisomeric linker alters the symmetry of the ligand field at the metal sites, leading to increases of 0.4-1.5 kJ/mol in the H$_2$ binding enthalpies relative to M$_2$(dobdc). A variety of techniques, including powder x-ray and neutron diffraction, inelastic neutron scattering, infrared spectroscopy, and first-principles electronic structure calculations are applied in elucidating how these subtle structural and electronic differences give rise to such increases. Importantly, similar enhancements can be anticipated for the gas storage and separation properties of this new family of robust and potentially inexpensive metal-organic frameworks.

Introduction

Metal-organic frameworks are a well-known class of porous materials comprised of inorganic units bridged by coordinating organic linkers. In addition to possessing high internal surface areas, their physical and chemical properties can be tuned for specific applications by judicious choice of the metal center and organic ligand. These properties lead to applications in storing and separating gases, in which it is particularly important to have precise control over the strength and specificity of interactions between the pore surface and various potential adsorbates.$^1$ Indeed, strong adsorption sites are often installed on the pore surface in order to attract specific gas molecules selectively for separation applications or to increase the density of gas molecules present for storage applications.$^{3,8}$

Exposed metal cations represent an important example of strong adsorption sites that have been realized in many metal-organic frameworks. These Lewis acidic sites, which are typically formed by removing metal-coordinated solvent molecules upon heating under reduced pressure, are highly polarizing and have strong interactions with many small gas molecules.$^{3,8}$ For example, the well-established M$_4$(dobdc) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn; dobdc$^{4-} = 2,5$-dioxido-1,4-benzenedicarboxylate) structure type, also known as M-MOF-74, CPO-27-M, or M$_4$(dhmt)$^5$, contains a high density of exposed metal cations and is especially promising for the storage of a wide variety of gases. As a result of its compact, highly charged tetraanionic linker, this framework is endowed with an exceptionally high density of open metal coordination sites, which are the primary binding sites for small gas molecules such as H$_2$, CH$_4$, C$_2$H$_4$, and CO$_2$. Consequently, M$_4$(dobdc) frameworks have been investigated for numerous potential applications involving gas adsorption, including H$_2$ storage,$^{3,8,14-21}$ methane storage,$^{21,22}$ CO$_2$ capture,$^4$ and hydrocarbon separations.$^{18,23-25}$ All of these applications take

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advantage of strong interactions between gas molecules and exposed metal cations.

Discovering new frameworks with a high density of open metal coordination sites is not trivial, as it is difficult to predict what topologies will form with partial solvation of the metal nodes and will then further be amenable to desolvation. Rather, selectively tuning the most promising of the numerous existing frameworks by altering the linker, the metal, or both provides a viable strategy for developing promising new adsorbents. Since the $M_2$(dobdc) series of frameworks has high chemical and thermal stability\textsuperscript{8b,10} and has been shown to be outstanding for binding a high capacity of small gas molecules, we hoped to modify this framework by tuning the electronics of the exposed metal cations, which should subsequently tune the affinity for different gas molecules. For example, the binding of $H_2$ or CH$_4$ might be enhanced by increasing the positive charge density at the metal cation site, thus increasing its ability to polarize and bind adsorbing gas molecules more strongly. Furthermore, $M_2$(dobdc) offers the advantage of being an isostructural series of frameworks that can be formed with a variety of metals, thereby offering an additional level of control for tuning the framework for specific interactions. Based on the high density of exposed metal cations, isostructural nature of the these frameworks, and thermal stability, a combination of properties that is not paralleled by any other structure type, $M_2$(dobdc) provides an ideal platform for exploring the tunability of metal-organic frameworks to strengthen framework-gas interactions.

This work outlines the synthesis of a structural isomer of the $M_2$(dobdc) framework, which will be referred to as $M_2$(m-dobdc) \cite{Mn(m-dobdc) = 4.6-dioxido-1,3-benzenedicarboxylate}. Rather than having para carboxylic acid functionalities and para hydroxyl substituents, as in the regular $H_2$dobdc linker, $H_2$(m-dobdc) has meta carboxylic acid groups and meta hydroxyl substituents. The $H_2$(m-dobdc) linker was targeted due to its ease of synthesis and potentially low cost. Indeed, a solvent-free Kolbe-Schmitt reaction to produce $H_2$(m-dobdc) using only resorcinol, KHCO$_3$, and CO$_2$ is efficient and inexpensive. In spite of this linker isomerism, it is still possible to form a framework with a similar overall structure, replete with one-dimensional hexagonal channels and a high density of open metal coordination sites. This structural isomerism takes advantage of the fact that $M_2$(dobdc) frameworks have multiple types of coordinating functional groups in the linker, which is a rarity among most well-known metal-organic frameworks.

The resulting new framework has subtle differences in the electronic structure of the ligand and overall connectivity as compared to the $M_2$(dobdc) framework, which might be expected to influence interactions with small gas molecules by changing the local environment around the open metal coordination sites. Isomers of metal-organic frameworks are known and primarily derive from what are termed “framework isomers.” The structure of $M_2$(m-dobdc), however, is an example of a ligand-originated isomer.\textsuperscript{11} Relatedly, a recent $M_2$(dobdc) analogue was synthesized with thiols rather than phenols,\textsuperscript{12} but a purely structural isomer of $M_2$(dobdc) has never before been synthesized.

Here, $H_2$ adsorption is used as a probe to determine whether this new framework exhibits enhanced gas adsorption properties. The choice of $H_2$ as a probe molecule originates from its simplicity, low polarizability, and potential use as a clean, renewable fuel.\textsuperscript{2a,13} Through the use of $H_2$ adsorption isotherms, powder neutron diffraction, inelastic neutron scattering, infrared spectroscopy, and first-principles electronic structure calculations, we provide a careful comparison of the differences between $M_2$(dobdc) and $M_2$(m-dobdc) that contribute to the differences in their $H_2$ adsorption properties.

**Experimental Section**

Methanol was purchased from commercial vendors, further dried over molecular sieves, and deoxygenated by purging with N$_2$. All other reagents were purchased from commercial vendors and used without further purification, unless otherwise noted. The $H_2$(m-dobdc) ligand was synthesized according to a literature procedure.\textsuperscript{14}

**Synthesis of $M_2$(m-dobdc) ($M = Mn, Fe, Co, Ni)\textsuperscript{,}** Anhydrous MCl, (3.0 mmol) and $H_2$(m-dobdc) (240 mg, 1.2 mmol) were added to 80 mL of a mixed solvent (x% MeOH by volume in dimethylformamide (DMF), where for $M_{n} , x = 15; Fe , x = 15; Co , x = 50; Ni , x = 35) in a nitrogen-filled glove box for $M = Mn, Fe$ and in air for $M = Co, Ni$. The solution was dispensed into eight 20-mL scintillation vials, which were each sealed with a PTFE-lined cap and heated at 120 °C for 18 h. The resulting solid from each vial was combined, submerged in 20 mL of DMF, and heated at 70 °C for 24 h. The DMF was decanted and replaced with 20 mL of methanol. The resulting suspension was heated at 70 °C for 4 days, during which time the methanol was replaced every 24 h. The material was activated by heating it at 150 °C under dynamic vacuum on a Schlenk line for 12 h, followed by further activation of a small amount of the sample by heating the solid under dynamic vacuum (<30 µbar) at 180 °C (160 °C for Fe$_2$(m-dobdc) for 24 h at a ramp rate of 0.5 °C/min. It should be noted that larger scale syntheses of Co$_2$(m-dobdc) and Ni$_2$(m-dobdc) were also accomplished with no loss in crystallinity or surface area by stirring at room temperature in a round-bottom flask equipped with a reflux condenser at a concentration of 20.2 mmol $H_2$(m-dobdc) and 50.5 mmol MCl, ($M = Co, Ni$) in 1250 mL solvent. Times and temperatures were identical to the small-scale synthesis, but 200 mL of solvent was used for each exchange.

**Synthesis of Mg$_2$(m-dobdc).** This compound was synthesized in air in a round-bottom flask by adding 300 mg of Mg(NO$_3$)$_2$·6H$_2$O and 93 mg of $H_2$(m-dobdc) to 14 mL MeOH in 31 mL DMF and stirring at 120 °C for 8 h, then filtering off the resulting solid. Detailed characterization of all frameworks is contained in the Supporting Information.

**Physical Measurements.** Thermogravimetric analyses were carried out at a ramp rate of 2 °C/min under a 25 mL/min N$_2$ flow with a TA Instruments TGA Q5000. Infrared spectra were collected on a Perkin-Elmer Avance Spectrum 400 FTIR spectrometer equipped with a Pike attenuated total reflectance (ATR) accessory. Diffraction data were collected with 0.02° steps.
using a Bruker AXS D8 Advance diffractometer equipped with Cu-Kα radiation (λ = 1.5405 Å), a Göbel mirror, a Lynxeye linear position-sensitive detector, and mounting the following optics: fixed divergence slit (0.6 mm), receiving slit (3 mm), and secondary beam Soller slits (2.5°). The generator was set at 40 kV and 40 mA. Samples were then loaded on zero background sample holders or placed into air-free capillaries in a nitrogen-filled glove box and mounted using a capillary stage. Elemental analyses were obtained from the Microanalytical Laboratory of the University of California, Berkeley.

**Gas Adsorption Measurements.** Gas adsorption isotherms for pressures in the range 0–1.2 bar were measured using a volumetric method using either a Micromeritics ASAP 2020 or ASAP 2420 instrument. Samples were transferred under a dinitrogen atmosphere to preweighed analysis tubes, then capped with a Transeal. The samples were evacuated at elevated temperature until the outgas rate was less than 1 μbar/min, at which point the tube was weighed to determine the mass of the activated sample, which was typically 50–200 mg. The tube was transferred to the analysis port of the instrument and the outgas rate was again checked to ensure that it was less than 1 μbar/min. UHP-grade (99.999% purity) N₂, H₂, and He were used for all adsorption measurements. For all isotherms, warm and cold free spaces were measured using He; N₂, and H₂ isotherms at 77 K and 87 K were measured in liquid nitrogen and liquid argon baths, respectively. Oil-free vacuum pumps and oil-free pressure regulators were used for all measurements. Brunauer-Emmett-Teller (BET) and Langmuir surface areas were determined from N₂ adsorption data at 77 K using Micromeritics software.

**Powder Neutron and X-ray Diffraction Experiments.** Neutron powder diffraction (NPD) experiments were carried out on 0.8358, 0.9567, and 0.9702 g activated Co₃(m-dobdc), Ni₃(m-dobdc), and Co₉(dobdc) samples respectively, using the high-resolution neutron powder diffractometer, BT1, at the National Institute of Standards and Technology Center for Neutron Research (NCNR). The samples were placed in a He purged glove box and loaded into a vanadium sample can equipped with a valve for gas loading, and sealed using an indium O-ring. NPD data were collected using a Ge(311) monochromator with an in-pile 60° collimator corresponding to a wavelength of 2.078 Å. The samples were loaded onto bottom-loading closed cycle refrigerators and initial data collected on the activated Co₃(m-dobdc) and Ni₃(m-dobdc) frameworks at 10 K. As part of the initial structure solution, x-ray diffraction (XRD) measurements were carried out on 12.8 mg of Co₇(m-dobdc) at the Advanced Photon Source (APS) on the 17-BM materials diffractometer (λ=0.7291 Å) at 298 K. The activated Co₇(m-dobdc) sample was transferred into quartz capillary in a He purged glovebox and wax sealed for the X-ray measurements. For comparison of the D₃ structural dependence on ligand connectivity, Co₉(dobdc) and Co₉(m-dobdc) were each individually connected to a gas manifold of known volume and exposed to a known dose, approximately 0.75 and 2.25 D, per Co²⁺, at 100 K (refined composition given in Tables S12−S24, S9). Both samples were slow cooled from 100 K to 10 K to ensure full equilibration and complete adsorption, as evidenced by a zero pressure reading on the barometer by 25 K, for data collection. Further D₃ structural data was collected on Co₇(m-dobdc) and Ni₇(m-dobdc) as a function of dose with final loadings of 0.75, 1.25, 1.5, 1.75, 2.0, 2.25, and 3.0 D, per Co²⁺ and 1.0, 2.0, and 3.0 D, per Ni²⁺. Structural data for H₂ was measured on Co₇(m-dobdc) at a loading of 0.7 H₂ per Co²⁺. Refined compositions are given in Tables S12 and S15−S20 (Co) and Tables S21−S23 (Ni). Details on the structure solutions are available in the Supporting Information.

**Inelastic Neutron Scattering.** Inelastic neutron scattering (INS) spectra were collected using the Filter Analyzer Neutron Spectrometer (FANS) at the NCNR on the same samples used for the NPD experiments. Spectra were obtained at 7 K using the pyrolytic graphite (002) monochromator and 20−20° collimation options. Data were first collected for the bare framework, followed by data collection for the sample loaded with normal-H₂ (n-H₂), which contains a 3:1 mixture of ortho (o-H₂) to para (p-H₂), respectively. For Co₇(m-dobdc), data were collected at loadings of 0.33, 0.5, 1.0, 2.0, 3.0, and 4.0 n-H₂ molecules per Co atom, while for Ni₇(m-dobdc) data were collected at loadings of 0.67, 1.0, 2.0, 3.0, and 4.0 n-H₂ molecules per Ni atom. Gas was loaded into the sample using the same methodology as described in the NPD experiments. The spectra of the bare frameworks were subtracted from the spectra obtained from the H₂ loaded samples and Gaussian peaks were fit to the rotational transitions using the DAVE suite of programs. Further measurements of the framework vibrational densities of states for the activated Co₃(m-dobdc) material were made to higher energies (35 meV to 160 meV) using the Cu(220) monochromator with 20−20° collimation.

**Infrared Spectroscopy.** Infrared spectra were acquired using a Bomem DA3 Michelson interferometer equipped with a globar source, CaF₂ beamsplitter and a liquid nitrogen cooled mercury-cadmium-telluride detector. A cutoff filter above 9000 cm⁻¹ was used to prevent unwanted sample heating from the IR source. A custom-built diffuse reflectance system with a sample chamber that allows both the temperature and atmosphere of the material to be controlled was used for all experiments. Powder samples of the framework (~10 mg) were transferred under inert atmosphere to a cup affixed to a copper slab providing thermal contact to a cold-finger cryostat (Janis ST-300T). The sample temperature was monitored by a Si-diode thermometer. Known quantities of H₂ gas were dispensed from a calibrated gas manifold by monitoring the change in pressure.

**DFT Calculations.** Due to the extended nature of the M₉(dobdc) and M₈(m-dobdc) structures, cluster modeling was completed on the linker of interest coordinated to a pair of Co atoms bound to either end of the organic linker. To truncate the system, the ligating oxygen atoms that are not part of the included linker were added as formaldehyde molecules in order to conserve charge. The experimentally determined crystal structures were truncated as described and frozen. The geometry of a hydrogen molecule bound to the frozen system based on neutron diffraction data was then optimized. The range-separated, dispersion corrected functional oB97X-D implemented in the electronic structure software Q-Chem was used with an ultra fine (99, 590) grid and a triple split-valence basis set with polarization (6-31G**) for the core electrons of the Co. A small core Stuttgart-Born (SRSC) effective core potential is employed to model the core electrons of the Co. Binding is further analyzed using the ALMO EDA. Charge transfer is accounted for using the perturbative Roothaan step approach, which allows for assignment of forward and backward energies as well as generation of complementary occupied-virtual orbital pairs (COVPs) to visualize charge transfer.

**Results and Discussion**

**Structural Characterization of M₈(m-dobdc).** A less expensive regioisomer of H₂dobdc was selected in order to form a framework with the same overall topology and a high density of open sites as in M₈(dobdc), but with potentially different local geometry and electronic properties. After the synthesis of H₈(m-dobdc) from
resorcinol, it was possible to synthesize an isostructural series of $M_2$(m-dobdc) ($M = Mg$, Mn, Fe, Co, or Ni) frameworks (Figure 1) exhibiting powder x-ray diffraction patterns (Figures S1–S5) analogous to the respective $M_4$(m-dobdc) frameworks, indicating that the two series adopt similar structures. Thermogravimetric analyses of the $Co_2$(m-dobdc) and $Ni_2$(m-dobdc) frameworks show initial mass losses of 33% and 14%, respectively, indicative of volatilization of trapped solvent molecules and thus porosity (Figure S6a). After repeatedly washing each compound with methanol to replace the metal-bound DMF, the frameworks were activated by heating under dynamic vacuum at 180 °C. Thermogravimetric analysis of the activated frameworks indicated that $Mn_2$(m-dobdc) and $Co_2$(m-dobdc) are stable to 250 °C and the $Ni_2$(m-dobdc) is stable to 350 °C.

To confirm that the $M_2$(m-dobdc) frameworks are indeed structurally analogous to $M_4$(m-dobdc), powder x-ray and neutron diffraction experiments were used to solve the crystal structure of $Co_2$(m-dobdc) (Figure 2). Similar to $Co_4$(m-dobdc), $Co_2$(m-dobdc) possesses helical chains of Co$^{2+}$ centers running parallel to the crystallographic c axis. Upon activation and removal of a bound DMF molecule, each metal center is ligated by a combination of oxido and carboxylate donors in a square pyramidal geometry, with open coordination sites directed into the one-dimensional hexagonal channels of the framework. Based on the change in point group symmetry of the linker from $C_2v$ in $H_4$(m-dobdc) to $C_s$ in $H_2$(m-dobdc), a change in the space group from $R\bar{3}$ in $Co_2$(m-dobdc) to $R3m$ in $Co_4$(m-dobdc) is observed. Additional structural differences between the two compounds are apparent. For instance, the orientation of the carboxylate groups of the linker is changed, with the CO$_2^-$ unit twisting out of the plane of the aromatic ring by approximately 12.5° in $Co_2$(m-dobdc), as compared to just 3.5° in $Co_4$(m-dobdc). Furthermore, metal centers in $Co_2$(m-dobdc) that face into the same pore align directly along the crystallographic b axis, resulting in a $Co...Co$ separation of 14.9(1) Å across the channels. In $Co_4$(m-dobdc), the metals are offset from each other by one third of a twist in the chain, leading to a $Co...Co$ separation of 15.24(8) Å across the channels. A structureless Le Bail refinement of the other $M_2$(m-dobdc) ($M = Mg$, Mn, Fe, Ni) compounds afforded related unit cells, confirming that the entire series is isostructural.

With such similar crystal structures, the surface areas would be expected to be similar for the two types of frameworks. Indeed, a geometric approximation of the surface areas for $Co_2$(m-dobdc) and $Co_4$(m-dobdc) predicts them to both be 1297 m$^2$/g. Low-pressure $N_2$ adsorption isotherms collected at 77 K reveal type I isotherms characteristic of microporous solids for the $M_2$(m-dobdc) ($M = Mn$, Fe, Co, Ni) compounds (Figure S1i). Langmuir and BET surface areas were calculated (Table 1) and in each case the results are comparable to those reported for $M_4$(m-dobdc). Based on the similar framework structure, this indicates full evacuation of the pores and complete desolvation of the framework. Furthermore, the $Co_4$(m-dobdc) BET surface area of 1264 m$^2$/g is very close to the predicted surface area of 1297 m$^2$/g from the geometric calculations. Achieving complete activation of the Mg analogue has proven challenging and all efforts have thus far resulted in materials with lower than expected surface areas. As a result, the remaining data will focus only on the other four $M_2$(m-dobdc) compounds.

**H$_2$ Adsorption Isotherms.** To probe the potentially modified electronic structures at the open metal coordination sites, low-pressure $H_2$ adsorption isotherms were measured for the four $M_4$(m-dobdc) ($M = Mn$, Fe, Co, Ni) frameworks at 77 K and 87 K (Figures S20–S23). As for the $M_4$(m-dobdc) series, $Ni_2$(m-dobdc) has the greatest

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**Table 1.** Langmuir and BET surface areas of the $M_4$(m-dobdc) and $M_2$(m-dobdc) frameworks. The values for $M_4$(m-dobdc) are from literature sources.

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<th>$Mn$</th>
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<th>$Co$</th>
<th>$Ni$</th>
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<td>1432</td>
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<tr>
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<th>$Mn$</th>
<th>$Fe$</th>
<th>$Co$</th>
<th>$Ni$</th>
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<tr>
<td>Langmuir (m$^2$/g)</td>
<td></td>
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<td></td>
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<tr>
<td>$M_2$(m-dobdc)</td>
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<td>1624</td>
<td>1504</td>
<td>1502</td>
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values are comparable to previously observed values for the M₂(dobdc) series.\textsuperscript{24}

Increasing the binding enthalpy of H₂ in metal-organic frameworks is important for practical applications, as a binding enthalpy of \(-15\) to \(-20\) kJ/mol is predicted to be optimal for the on-board storage of H₂ at ambient temperatures.\textsuperscript{25} The low-coverage isosteric heats of adsorption of Mn₂(dobdc), Fe₂(dobdc), Co₂(dobdc), and Ni₂(dobdc) are \(-10.3\), \(-11.1\), \(-11.6\), and \(-12.3\) kJ/mol, respectively. This trend in binding enthalpies for H₂ is consistent with the Irving-Williams series, which predicts that high-spin complexes increase in stability moving from Group 7 to 10.\textsuperscript{26} The trend further mirrors that observed for H₂ binding within M₂(dobdc) frameworks (Table 2). Calculated isosteric heat of adsorption values are highly sensitive to the fitting equation used, the temperatures at which data is collected and the quality of the fits. Given this, the values for the M₂(dobdc) series were calculated from isotherms collected in this work (except Fe₂(dobdc), which was previously reported by our group and fit using the same method\textsuperscript{45}) in order to maintain consistency in the collected isotherms and the manner in which they are fit. These values all agree with the literature values for the M₂(dobdc) series except for Ni₂(dobdc), which we found to be \(-1\) kJ/mol less than the literature value of \(-12.9\) kJ/mol.\textsuperscript{24} This discrepancy most likely arises from a difference in data collection, isotherm temperatures, and equation used to fit the data. Consequently, our data that was collected and fit in the same manner as the M₂(dobdc) data presented here is used for comparison. Importantly, the isosteric heats of adsorption for the M₂(dobdc) compounds are, on average, \(-10.0\) kJ/mol stronger than in the corresponding M₂(dobdc) frameworks (Table 2) and are as much as \(-1.5\) kJ/mol stronger in the case of Mn, which also has the largest percent increase (17\%) in binding enthalpy.

**Powder Neutron Diffraction.** In an effort to understand further why the M₂(dobdc) frameworks show higher H₂ binding enthalpies than the structurally similar M₁(dobdc), neutron diffraction experiments were performed on microcrystalline powder samples dosed with precise quantities of D₂. Data were collected upon successively dosing the evacuated Co₂(dobdc) and Ni₂(dobdc) samples with loadings ranging from 0.75 to 3.0 D₂ molecules per metal center and cooling to 10 K. Based on previous results for M₁(dobdc) frameworks,\textsuperscript{46} as well as the isosteric heats of adsorption for M₂(dobdc) that begin to decrease at loadings near 1 H₂/metal, it was anticipated that the open metal coordination site would provide the primary hydrogen binding site. Indeed, this site, designated site I, was found to be the only D₂ binding site in Co₂(dobdc) at the lowest loading of 0.75 D₂ per Co²⁺ (Figure 4a). The center of the D₂ electron density was observed to be at a separation of 2.23(5) Å from the metal center, closer than the 2.32(2) Å found for Co₁(dobdc) at the same loading (Tables S12-S13), which is further confirmation that the hydrogen binds more strongly to the open metal sites within the meta framework. The
same binding site is apparent in Ni$_2$(m-dobdc), with a comparable M···D$_2$ distance of 2.18(4) Å at a loading of 1.0 D$_2$ per Ni$^{2+}$, which is within error of the distance of 2.20(1) Å observed for Ni$_2$(dobdc) at 4 K.\(^{37}\)

Increasing the D$_2$ loading in Co$_2$(m-dobdc) revealed several secondary binding sites. At a loading of 1.25 D$_2$ per metal, a second binding site (site II) adjacent to the primary site becomes populated (Figure 4b). This can be attributed to a D$_2$···D$_2$ interaction based on a short D$_2$···D$_2$ separation of 2.88(4) Å, combined with a D$_2$···O interaction occurring at a separation of 3.28(6) Å from the nearest framework oxygen atom. Site II is in a similar location to the secondary binding sites observed in Co$_2$(dobdc) and Mg$_2$(dobdc),\(^{56}\) whereby the second bound D$_2$ appears to rely on D$_2$···D$_2$ interactions in all cases. The site I to site II D$_2$···D$_2$ separation, however, of 3.05(2) Å in Co$_2$(m-dobdc) at a loading of 2.25 D$_2$ per metal is significantly shorter than the 3.16(2) Å observed at the same loading in Co$_2$(dobdc) or the 3.16(8) Å arising for a similar loading of 1.2 D$_2$ per metal in Mg$_2$(dobdc). This closer site I to site II separation in Co$_2$(m-dobdc) is most likely a polarization effect, as the more strongly bound D$_2$ residing at site I has a larger induced dipole, leading to a stronger interaction with a D$_2$ molecule adsorbed at site II.

A third binding site (site III) located approximately 3.08 Å above the mean plane of the aromatic ring of the m-dobdc$^-$ linker becomes populated at higher loadings of D$_2$. This site is equidistant (3.25(6) Å) to two D$_2$ molecules at neighboring site I positions in Co$_2$(m-dobdc), whereas in Co$_2$(dobdc), the different symmetry leads to two distinct site I···site III interactions at distances of 3.06(3) and 3.24(3) Å. Importantly, for Co$_2$(m-dobdc) there are only half as many D$_2$ molecules situated at site III as in Co$_2$(dobdc) at high loadings, which leads to the observation of a fourth binding site (site IV) not seen in the M$_2$(dobdc) series. We note that a fourth site was identified in Zn$_2$(dobdc),\(^{66}\) but this is not the same site seen in the Co$_2$(m-dobdc) case. The differing symmetry of the meta framework contributes to this additional binding site, as the two framework oxygen atoms interacting with the D$_2$ molecule in site IV are equivalent in Co$_2$(m-dobdc), but not in Co$_2$(dobdc). Relative to site I, larger atomic displacement parameters for the refined D$_2$ molecules at binding sites II, III, and IV are also indicative of weaker interactions. Neutron diffraction measurements of Ni$_2$(m-dobdc) with different loadings of D$_2$ resulted in the identification of the same binding sites as those found for Co$_2$(m-dobdc) (Tables S21–S23).

Neutron diffraction experiments intended to elucidate binding sites are generally performed using D$_2$ instead of H$_2$ because the large incoherent scattering cross-section of H atoms contributes strongly to the background and reduces data quality. In addition, the coherent scattering cross-section of a D atom is approximately four times larger than that of an H atom. While it has been shown through gas adsorption measurements that metal-organic frameworks tend to adsorb D$_2$ slightly more strongly than H$_2$,\(^{24}\) it has been assumed that both molecules behave similarly when binding, only displaying extremely minor differences in interaction distances. In order to test this assumption, we measured and successfully refined the
structure of Co$_2$(m-dobdc) dosed with a low loading of H$_2$. We believe this is the first structural data from powder neutron diffraction reported for H$_2$ in a metal-organic framework. As expected from the D$_2$ data, a dose below 1.0 H$_2$ per metal site resulted in binding exclusively at site I. Interestingly, the center of the H$_2$ density was found to be 2.26(4) Å from the Co atom, perhaps slightly longer than the Co...D$_2$ distance of 2.23(5) Å, although still within the associated error. Whether this is indicative of a slightly stronger interaction with D$_2$ is somewhat unclear due to the resolution of the data; however, it does confirm that H$_2$ and D$_2$ can be expected to behave similarly for the purposes of structural determination.

**Inelastic Neutron Scattering.** Inelastic neutron scattering (INS) experiments were carried out to probe the site-specific binding properties of H$_2$. Data for various loadings of H$_2$ after subtraction of the spectra for the evacuated materials are shown in Figure 5. At loadings up to and including 1.0 n-H$_2$ (corresponding to a 3:1 ortho-H$_2$:para-H$_2$ ratio) molecule per metal atom, two low-energy rotational lines are apparent at 7.8(1) and 9.5(1) meV for Co$_2$(m-dobdc) and 7.5(1) and 9.3(1) meV for Ni$_2$(m-dobdc). These features are similar to those observed in INS spectra for several compounds in the M$_x$(dobdc) series at low loadings, and have been assigned to transitions occurring from the J = 0 state to sublevels of the split J = 1 rotational state for initial H$_2$ molecules adsorbed at the metal centers. This assignment has been confirmed through correlation with neutron diffraction and DFT calculations. Presumably, there is also a higher-energy transition, not collected within this current data range, as seen in the M$_x$(dobdc) series. The splitting between the low energy peaks of approximately 1.6 meV for both Co$_2$(m-dobdc) and Ni$_2$(m-dobdc) is smaller than that observed for any of the M$_x$(dobdc) materials. The position of the first peak is at higher energies than that of the first peak of the M$_x$(dobdc) frameworks (except for the Zn analogue), and the position of the second peak is at lower energies than is observed for all the M$_x$(dobdc) compounds. The energy splitting of these peaks has been previously shown to have no correlation with the binding strength of H$_2$ at the open metal site.

At loadings above 0.75 H$_2$ molecules per metal, as sites II-IV begin to populate, the additional H$_2$ molecules affect the rotational potential for H$_2$ molecules at site I. This adjusts the rotational energy level, resulting in a shift of the first peak to lower energies and the second peak to higher energies. These peak shifts are similar to those observed for the M$_x$(dobdc) frameworks, with magnitudes of approximately 0.7 meV for Co$_2$(m-dobdc) and 0.5 meV for Ni$_2$(m-dobdc), though much less than the 1.4 meV shift observed for Fe$_2$(dobdc). Adsorption of H$_2$ at the secondary sites also results in a significant increase in the area of the peak at 9 meV and appearance of features near 12 and 15 meV as a new subset of rotational levels associated with the rotationally hindered second adsorption site. Transitions in this energy range are also observed in spectra reported for higher loadings of the M$_x$(dobdc) materials, indicating the similarity in adsorption potentials at these secondary sites.40,46

**Infrared Spectra.** Since the higher binding enthalpies and low-coverage H$_2$ uptake cannot reasonably be attributed to a significant change in the macrostructure of the framework, infrared spectroscopy was used to further probe the binding of H$_2$ at the open metal coordination sites. The vibrational frequency of adsorbed H$_2$ is almost always lower than that of the molecule in the gas phase (4161 cm$^{-1}$), and it is now well established that for metal-organic frameworks, there is a strong correlation between the magnitude of the frequency shift and the binding energy at a particular site. A comparison of the H$_2$ vibrational frequencies is shown at two different H$_2$ loadings for Ni$_2$(m-dobdc), Ni$_2$(dobdc), Co$_2$(m-dobdc), and Co$_2$(dobdc) (Figure 6) and for Mn$_2$(m-dobdc) and Mn$_2$(dobdc) (Figure S45). At this temperature, the pure vibrational part of the spectrum consists of an ortho-para pair that is separated by just 6 cm$^{-1}$ in the gas phase. The

![Figure 5](image1.png)

Figure 5. INS data for Co$_2$(m-dobdc) (left) and Ni$_2$(m-dobdc) (right) at loadings of 0.33 (black), 0.50 (dark green), 0.67 (light green), 1.0 (red), 2.0 (blue), 3.0 (yellow), and 4.0 (purple) n-H$_2$ molecules per metal atom. Data are shown after subtraction of the spectrum of the evacuated framework and offset for clarity.

![Figure 6](image2.png)

Figure 6. Comparison of the IR spectra of Ni$_2$(m-dobdc), Ni$_2$(dobdc), Co$_2$(m-dobdc), and Co$_2$(dobdc) at two different concentrations. The right peak shows the H$_2$ bound to the open metal site and the left peak shows the H$_2$ bound to the secondary adsorption sites. Spectra are offset for clarity.
peak near $4025 \text{ cm}^{-1}$ in each spectrum corresponds to the H$_2$ bound to the open metal site.

In each case, the spectra for loadings of 0.5 H$_2$ molecules per metal, which are known to arise purely from H$_2$ bound to the open metal site, show a greater frequency shift for the Co$_2$(m-dobdc) and Ni$_2$(m-dobdc) than for Co$_2$(dobdc) or Ni$_2$(dobdc). This shift is consistent with the stronger H$_2$ binding observed in the M$_2$(m-dobdc) frameworks based on equilibrium adsorption isotherms and neutron diffraction studies. Upon further loading, the secondary adsorption sites begin to be populated, which is evidenced by a second peak that grows in around $4125 \text{ cm}^{-1}$. The energy of the peaks associated with the secondary sites is very similar to those seen for M$_2$(dobdc), consistent with the INS transitions for H$_2$ bound to the secondary sites, which were also similar between M$_2$(m-dobdc) and M$_2$(dobdc) compounds. This supports our hypothesis that the electronic structure at the metal center is significantly altered with the m-dobdc$^+$ linker, leading to a higher initial isosteric heat of adsorption, while the secondary sites in M$_2$(m-dobdc) and M$_2$(dobdc) are similar in binding potential due to structural similarities between the two frameworks. Furthermore, a consistent shift in the frequency for the metal-adsorbed H$_2$ molecules as a function of concentration is seen for both the Co$_2$(m-dobdc) and Ni$_2$(m-dobdc) samples, although not to the same degree in the Mn$_2$(m-dobdc) sample. These concentration shifts have previously been attributed to H$_2$...H$_2$ interactions, and it is interesting to note that the shifts seem largely unaffected by the change in linker. Furthermore, these shifts correlate well with the shifts seen in rotational potential as the secondary binding sites are populated in the INS data shown in Figure 5.

Variable-temperature infrared spectroscopy is a standard technique for establishing the enthalpy of adsorption at a particular site. Figure 7 shows the spectra obtained for H$_2$ in Co$_2$(m-dobdc) while lowering the sample temperature from 142 to 75 K. In each case, the initial H$_2$ pressure for the system was set such that only the open metal site was occupied over the full temperature range. The fractional occupancy is then determined by the ratio of the area under the infrared band to that observed at complete saturation. The inset in Figure 7 shows the van’t Hoff relationship plot used to extract both the enthalpy and entropy change upon adsorption. The data obtained in this way for the different materials are summarized in Table 3. The slopes extracted from the van’t Hoff plots are sensitive to small variations in the maximum saturation area; as such, an error on the order of 0.5 kJ/mol is estimated. Even with these limitations, the data is consistent with the calculated isosteric heats of adsorption from the H$_2$ adsorption isotherms, showing an enthalpy increase from Mn to Co to Ni. More importantly, these infrared spectroscopy-based heat of adsorption values are about 1.4 kJ/mol larger than those calculated for their respective M$_2$(m-dobdc) counterparts from similar infrared experiments. The binding enthalpy of $-13.7 \text{ kJ/mol}$ in Ni$_2$(m-dobdc) is among the highest reported H$_2$ binding enthalpies in a metal-organic framework to date. This is consistent with the trends observed using values calculated from H$_2$ adsorption isotherms. We further note that the measured large entropy changes are consistent with previous studies, in which a strong correlation between the enthalpy and entropy change of the bound hydrogen in different metal-organic frameworks was observed. Overall, the redshift seen in the infrared spectra for the adsorbed H$_2$ in M$_2$(m-dobdc) as compared to M$_2$(dobdc) indicates that the H$_2$ is more strongly bound and the variable-temperature data confirms the increased binding enthalpies seen from the H$_2$ adsorption data.

### Electronic Structure Calculations

Density functional theory (DFT) was used to examine the differences in the electronic structures at the open metal sites by using representative complexes to model the M$_2$(dobdc) and M$_2$(m-dobdc) frameworks. DFT has shown itself to be a fairly robust method for modeling chemical systems; its major failings, self-interaction error and lack of dispersion interactions, are well-known and can be corrected for by using appropriate functionals that account for these failings, namely range-separation and explicit dispersion correction. Previously, the ΩB97X-D functional was used...
Table 4. ALMO energy decomposition analysis of H₂ binding to the dobdc⁺ and m-dobdc⁺ complexes.

<table>
<thead>
<tr>
<th>Component</th>
<th>dobdc⁺</th>
<th>m-dobdc⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>frozen</td>
<td>1.3</td>
<td>7.9</td>
</tr>
<tr>
<td>polarization</td>
<td>-4.8</td>
<td>-9.5</td>
</tr>
<tr>
<td>charge transfer</td>
<td>-12.2</td>
<td>-17.1</td>
</tr>
<tr>
<td>total</td>
<td>-16.0</td>
<td>-18.6</td>
</tr>
</tbody>
</table>

Table 5. Forward and backbonding contributions to the charge transfer term for the dobdc⁺ and m-dobdc⁺ complexes.

<table>
<thead>
<tr>
<th>Bonding/Backbonding</th>
<th>dobdc⁺</th>
<th>m-dobdc⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂ → Co bonding</td>
<td>-9.4</td>
<td>-11.8</td>
</tr>
<tr>
<td>Co → H₂ backbonding</td>
<td>-3.4</td>
<td>-5.3</td>
</tr>
</tbody>
</table>

Modeling M₄(dobdc)-type frameworks accurately with electronic structure theory is challenging because fragmenting the structure at any point will lead to the neglect of important interactions from the chains formed by the M⁺⁺ ions. In an attempt to understand the nature of the differences in hydrogen binding between M₄(dobdc) and M₄(m-dobdc), some accuracy in the calculated energetics is sacrificed in order to learn relevant information about the differences between the two systems. In this vein, our modeling focused on the linker of interest coordinated to two Co⁺⁺ centers; the remaining ligands on each Co⁺⁺ ion were truncated as formaldehyde molecules in order to maintain charge balance. Since the key open coordination site for each Co⁺⁺ center in the framework is enforced by constraints on the ligands imposed by the macrostructure of the framework, which could not be explicitly included in our model, an unconstrained optimized geometry of the model would not actually reflect the structural properties of the framework in question. Thus, the geometry of the linker complex was taken from the experimentally determined crystal structure of the framework and subsequently frozen before the interaction with H₂ was optimized. Furthermore, the Co···H₂ distance was taken from the neutron diffraction spectra and used as a constraint to ensure an accurate depiction of this interaction in the model system.

While comparing absolute energy differences gives a single number to describe H₂ binding, energy decomposition analysis (EDA) breaks down that number into physically interpretable components. An EDA based on absolutely localized molecular orbitals (ALMOs) breaks down total binding energies into frozen energy, polarization, and charge transfer components. The frozen term is due to permanent electrostatics and Pauli repulsions, since the H₂ electron density is being brought within the van der Waals radius of the Co atom. The polarization term corresponds to the favorable interaction of electrons in the H₂ and complex fragments relaxing in the presence of the other fragment without electron transfer. Charge transfer stems from energy lowering when electrons are allowed to flow from one fragment to the other. A recent generalization of the ALMO EDA to open-shell molecules allows for the application of this method to general metal-containing systems.

The binding energy decomposition analysis clarifies the differences in these two species (Table 4). Specifically, there is more charge transfer and polarization in the m-dobdc⁺ containing complex, which is accompanied by a partially offsetting increase in the energetically unfavorable frozen term. This larger frozen term is the result of the increased steric repulsion that stems from a shorter Co···H₂ distance in the m-dobdc⁺ complex. The increased charge transfer energy of H₂ binding in this species is key, as that is the largest term in the total calculated binding energy. A breakdown of the charge transfer term can be seen in Table 5; in both cases, the largest portion of the charge transfer comes from the H₂ σ orbital to the unoccupied orbitals of the Co complex. The increased H₂ to Co forward donation is indicative of more positive charge at the metal cation in the m-dobdc⁺ complex as compared with the dobdc⁺ complex. This explains the experimentally determined increase in binding enthalpy of H₂ in the M₄(dobdc) frameworks as compared with their M₄(m-dobdc) analogues, as increased positive charge at the metal center leads to stronger polarization of the bound H₂. Additionally, a difference is seen in the location of the bound H₂ relative to the linker in the two complexes. In the dobdc⁺ linker complex, the H₂ binds to create a nearly octahedral geometry around the Co⁺⁺ ion, with a distance of 3.30 Å from the H₂ to the aromatic carbon bonded to the carboxylate group (the

Figure 8. The calculated binding modes of H₂ in a) the dobdc complex and b) the m-dobdc complex in both of which the Co⁺⁺ is purple and the H₂ is above the Co⁺⁺. The corresponding COVPs are shown for c) the dobdc complex and d) the m-dobdc complex, with occupied and virtual orbitals shown as solid and mesh, respectively, at a 0.05 Å⁻¹ isodensity.
alpha carbon). Conversely, in the m-dobdc complex, the 
H₂ is reoriented toward the linker at a distance of 2.64 Å 
from the alpha carbon (Figure 8a-b). This difference 
suggests that a change in the charge at the alpha carbon 
due to the different symmetry of the m-dobdc linker 
possibly facilitates a change in the binding geometry for 
H₂. While this significant change may be an artifact 
associated with the small cluster models, it is the same 
trend seen experimentally for the H₂-alpha carbon 
distance, which is 3.48(3) Å in Co₂(m-dobdc) and 3.59(2) Å in Co₂(dobdc).

The orbital interactions between H₂ and the Co 
complexes provide further insight into the stronger H₂ 
binding in Co₂(m-dobdc). While increased forward 
backbonding is a product of increased charge density at 
the metal, the nature of the backbonding from the complex to 
H₂ is quite different. This can be seen by looking at the 
complementary occupied virtual orbital pairs (COVPs) 
that contribute most to backbonding (Figure 8c-d). In the 
dobdc complex, the occupied orbital is primarily 
localized on the metal center, while in the m-dobdc species, 
the donating orbital includes contributions from the 
π system of the linker. This increased backbonding for 
m-dobdc agrees with the redshift seen in the H₂ infrared 
spectra for the M₅(m-dobdc) frameworks, as increased 
backbonding will weaken the H–H bond. This possible 
extra interaction with the linker in the m-dobdc complex, 
coupled with the larger forward donation of the 
H₂ to the more positively charged metal center, are the 
key differences between these two systems that help to 
explain the stronger H₂ binding seen in M₅(m-dobdc) 
versus M₅(dobdc).

Conclusions
The foregoing results demonstrate the synthesis of a 
new family of metal-organic frameworks, M₅(m-dobdc) 
(M = Mg, Mn, Fe, Co, Ni), representing a potentially less 
expensive version of their well-known structural isomers 
M₅(dobdc). Hydrogen was used as an initial probe to 
determine how electronic and structural differences in 
the new frameworks modified the interactions of the 
open metal coordination sites with adsorbates. The Mn, 
Fe, Co, and Ni variants exhibited greater isosteric heats of 
H₂ adsorption by approximately 1 kJ/mol compared to the 
M₅(dobdc) compounds. The results from powder neutron 
diffraction, inelastic neutron scattering, and infrared 
spectroscopy experiments performed on hydrogen-loaded 
samples of Co₅(m-dobdc) all support this as arising from 
stronger interactions between the metal centers and the 
H₂ molecules. Future efforts will focus on the larger-scale 
production of M₅(m-dobdc) compounds, and determining 
whether the enhanced charge density at the metal sites 
leads to improvements compared to their M₅(dobdc) 
aalogues in the efficacy of key gas separations, including 
O₂ from air,^{39} CO₂/N₂,^{40,39} CO₂/H₂,^{41} CO/H₂,^{41} ethylene/ethane,^{42} propylene/propane,^{41} and methane 
purification.^{43}

ASSOCIATED CONTENT

Supporting Information. Additional framework 
characterization, powder diffraction patterns, 
thermogravimetric analyses, infrared spectra, BET isotherm 
fits, adsorption isotherms, details on isotherm fitting, 
neutron diffraction atomic parameters, Rietveld refinement 
plots, additional VTIR spectra, COVPs, and additional 
experimental details. This material is available free of charge 
via the Internet at http://pubs.acs.org.

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Notes
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