Investigation of the synthesis, activation, and isosteric heats of CO$_2$ adsorption of the isostructural series of metal-organic frameworks $M_3$(BTC)$_2$ ($M$ = Cr, Fe, Ni, Cu, Mo, Ru)


As Published: http://dx.doi.org/10.1039/c2dt30372h

Publisher: Royal Society of Chemistry

Persistent URL: http://hdl.handle.net/1721.1/78299

Version: Author’s final manuscript: final author’s manuscript post peer review, without publisher’s formatting or copy editing

Terms of use: Creative Commons Attribution-Noncommercial-Share Alike 3.0
Investigation of the Synthesis, Activation, and Isosteric Heats of CO₂ Adsorption of the Isostructural Series of Metal-Organic Frameworks M₃(BTC)₂ (M = Cr, Fe, Ni, Cu, Mo, Ru)

Casey R. Wade and Mircea Dincă

The synthesis, activation, and heats of CO₂ adsorption for the known members of the M₃(BTC)₂ (HKUST-1) isostructural series (M = Cr, Fe, Ni, Zn, Ni, Cu, Mo) were investigated to gain insight into the impact of CO₂-metal interactions for CO₂ storage/separation applications. With the use of modified syntheses and activation procedures, improved BET surface areas were obtained for M = Ni, Mo, and Ru. The zero coverage isosteric heats of CO₂ adsorption were measured for the Cu, Cr, Ni, Mo, and Ru analogs and gave values consistent with those reported for MOFs containing coordinatively unsaturated metal sites, but lower than for amine functionalized materials. Notably, the Ni and Ru congeners exhibited the highest CO₂ affinities in the studied series. These behaviors were attributed to the presence of residual guest molecules in the case of Ni₃(BTC)₂(Me₂NH)₂(H₂O) and the increased charge of the dimetal secondary building unit in [Ru₃(BTC)₂][BTC]₀.5.

Introduction

Owing to their microporous structures and high surface areas, metal-organic frameworks (MOFs) continue to receive significant attention as materials with potential for applications in gas storage and separation. Within this scope, more recent efforts have been devoted to developing these materials for the capture and separation of CO₂. Two common strategies for enhancing the CO₂ affinity and selectivity in MOFs include functionalization of the frameworks with amines or other basic groups and removal of terminal bound solvent molecules to expose coordinatively-unsaturated metal centers (UMCs). The former relies on chemisorptive interactions inspired by liquid amine scrubbers, while the benefit of the latter is commonly ascribed to a physisorptive process enhanced by ion-induced dipole interactions. Although the UMC approach has been exploited extensively in structurally unrelated materials, few studies exist wherein an isostructural MOF series has been explored to determine trends among various metal ions. Such studies are valuable because they can eliminate all other variables that may influence CO₂ uptake such as pore size, pore shape, and apparent surface area, thereby providing direct insight into the nature of the CO₂-metal interaction. One notable example is the family of materials known as MOF-74: M₂(DOBDC) (M = Mg, Co, Ni; DOBDC = 2,5-dioxy-1,4-benzenedicarboxylate). In this series, X-ray and neutron diffraction experiments have shown that UMCs are the initial sites of interaction of CO₂ with the framework in Mg₂(DOBDC) and Ni₂(DOBDC), while CO₂ adsorption isotherms measured at various temperatures revealed that the strength of interaction varies as Mg > Ni > Co. Studies

Figure 1. Portion of the crystal structure of M₃(BTC)₂, highlighting the dimetallic tetracarboxylate SBU. Blue, red, and grey spheres represent metal, O, and C atoms, respectively. H atoms and axial ligands on the SBU were omitted for clarity.
determined across isostructural series therefore provide important insight into the relative strength of the guest-framework interactions, which are a key to the efficient capture and release of CO₂.

Despite the vast number of MOFs synthesized, relatively few can be placed into an isostructural series, and even fewer can conceivably support UMCs. However, one of the earliest MOFs in which the presence of UMCs was evidenced, Cu₃(BTC)₂ (BTC = 1,3,5-benzentricarboxylate),⁴⁷ has become one of the most emblematic and is part of an isostructural series that currently includes Cr, Fe, Ni, Zn, Mo, and Ru analogues. The structure of Cu₃(BTC)₂, shown in Figure 1, contains dicopper paddlewheel secondary building units (SBUs) bridged by four carboxylate groups. The solvent molecules which occupy the axial sites on each Cu²⁺ ion can be readily removed by heating under vacuum to generate UMCs. Despite the popularity of Cu₃(BTC)₂ in a range of applications, including CO₂ storage, its analogues have received much less attention and none have been tested for CO₂ uptake. For instance, Cr₃(BTC)₂⁴⁸ and Mo₃(BTC)₂,⁴⁹ containing quadruply bonded dimetal units, were shown to exhibit permanent porosity and high surface areas comparable to Cu₃(BTC)₂, but gas sorption studies were limited to H₂, N₂, and O₂. The other known analogs include Zn₃(BTC)₂,⁵⁰,⁵¹ Ni₃(BTC)₂,⁵² and the mixed-valent Fe(II/III) and Ru(II/III) structures Fe₃(BTC)₂Cl⁵³ and Ru₃(BTC)₂(Cl)ₓ(OH)₁₋ₓ.⁵⁴ Although Ni₃(BTC)₂ and Ru₃(BTC)₂(Cl)ₓ(OH)₁₋ₓ were shown to exhibit permanent porosity, their reported BET surface areas were lower than those obtained for Cu₃(BTC)₂, despite the isostructural relationship, and no associated CO₂ sorption data was reported. In an effort to gain insight into the value of CO₂-UMCs interactions for CO₂ storage/separation applications, we examined the synthesis, activation, and CO₂ uptake properties of the reported members of the M₃(BTC)₂ isostructural series.

Results and discussion

Cu₃(BTC)₂ and Cr₃(BTC)₂ are both known to have fully activated SBUs, permanent porosity, and measured surface areas consistent with those predicted from the crystal structures. Accordingly, they were prepared and activated as previously described, and their powder X-ray diffraction patterns matched those expected (Figure 2).⁸,⁵⁵ The BET surface area of 1734(±1) m²/g of Cu₃(BTC)₂ measured by us falls near the upper end of the reported values for this material, which range from 692-1944 m²/g,⁵⁶-⁵⁹ and is in line with the geometric accessible surface area previously calculated from the crystal structure (2153 m²/g).⁶⁰ (Table 1, Figure 3). Likewise, an N₂ adsorption isotherm measured for Cr₃(BTC)₂ afforded a BET surface area of 2031(±6) m²/g, higher than the previously reported value of 1810 m²/g.⁴⁸ Although the synthesis of Ni₃(BTC)₂ was recently reported, the authors noted a difficulty in scaling-up the high-throughput screening conditions. We attempted to repeat this procedure on a larger scale (0.5-1.0 g) using both glass and Teflon-lined reactors and obtained mixtures of dark green crystals and brown powders in both cases. The green crystals could be mechanically separated from the brown powders by washing and decanting from DMF and gave powder X-ray diffraction patterns consistent with the M₃(BTC)₂ structure type (Figure 2). Thermogravimetric analysis (TGA) of the sample showed a gradual desorption of solvent over the 25-200 °C range, followed by the onset of rapid mass loss after 250 °C (Figure S1). In accordance with the TGA and the previously described procedure, Ni₃(BTC)₂ was activated by heating under vacuum at 150 °C for 12 hrs. After this activation procedure, the material exhibited a BET surface area of 847(±3) m²/g, only slightly lower than the reported value of 920 m²/g. In the initial report, single crystal X-ray diffraction and elemental analysis supported an empirical formula of Ni₃(BTC)₂(Me₂NH)₃(DMF)₄(H₂O)₄ in which DMF and H₂O guest molecules occupied the pores, while dimethylamine molecules produced by the in-situ decomposition of DMF were bound to the axial positions of the Ni²⁺ centers. The lower surface area in comparison to Cu₃(BTC)₂ was attributed to incomplete evacuation of the guest molecules. In an effort to improve the activation procedure and achieve a higher surface area, we carried out a solvent exchange by soaking a sample of the as-synthesized Ni₃(BTC)₂ in anhydrous methanol for 24 hrs. This approach of exchanging DMF and other high boiling solvents with more volatile ones has proven effective at facilitating evacuation and exposing UMCs in other MOFs.⁶¹ After this treatment, powder X-ray diffraction confirmed retention of sample crystallinity, and FT-IR spectroscopy showed the disappearance of the DMF ν(C=O) stretching band at 1670 cm⁻¹ (Figure S2).
Table 1. Apparent BET surface areas and isosteric heats of CO₂ adsorption measured for the porous members of the M₃(BTC)₂ series.

<table>
<thead>
<tr>
<th></th>
<th>BET SA (m²/g)</th>
<th>BET SA (m²/mmol)</th>
<th>-ΔHads(CO₂) (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu₃(BTC)₂</td>
<td>1734±1</td>
<td>1049±1</td>
<td>29.8±0.2</td>
</tr>
<tr>
<td></td>
<td>(2153)</td>
<td>(1301)</td>
<td></td>
</tr>
<tr>
<td>Cr₃(BTC)₂</td>
<td>2031±6</td>
<td>1158±2</td>
<td>26.7±0.2</td>
</tr>
<tr>
<td>Ni₃(BTC)₂(Me₂NH)₂(H₂O)</td>
<td>1047±1</td>
<td>732±1</td>
<td>36.8±0.4</td>
</tr>
<tr>
<td>Mo₃(BTC)₂(DMF)₀.₅</td>
<td>1689±5</td>
<td>1264±3</td>
<td>25.6±0.6</td>
</tr>
<tr>
<td>[Ru₃(BTC)₂][BTC]₀.₅</td>
<td>1180±5</td>
<td>969±4</td>
<td>32.6±0.4</td>
</tr>
</tbody>
</table>

* Calculated geometric accessible surface area from ref 60.

Figure 3. Isotherms for the adsorption of N₂ in M₃(BTC)₂ (M = Cu, Cr, Mo, Ru, Ni) at 77 K.

The TGA profile for the methanol exchanged sample displayed a ~11% weight loss up to 150 °C, which was attributed to the desorption of methanol solvent, and a rapid mass loss around 300 °C that likely corresponds to framework decomposition (Figure S3). The sample was subsequently activated at 150 °C for 12 hrs. Although this treatment did not affect bulk crystallinity (Figure S4), the apparent BET surface area of this material was 1047±1 m²/g, still somewhat low in comparison to Cu₃(BTC)₂ and Cr₃(BTC)₂. Elemental analysis (C, H, N) of the activated sample matched the formula Ni₃(BTC)₂(Me₂NH)₂(H₂O), suggesting that guest molecules are instead responsible for the decreased surface area. While no clear O-H stretching (3000-3600 cm⁻¹) band is observed in the FT-IR spectrum of Ni₃(BTC)₂(Me₂NH)₂(H₂O) under N₂, the H-O-H bending mode in the 1600 cm⁻¹ region supports the presence of residual H₂O while the aliphatic C-H stretches below 3000 cm⁻¹ and weak N-H stretch at 3260 cm⁻¹ indicate the presence of residual Me₂NH in the activated sample (Figure S5).

Figure 4. FT-IR spectra of evacuated samples of Mo₃(BTC)₂(DMF)₀.₅ and [Ru₃(BTC)₂][BTC]₀.₅.

However, in line with the previous report, samples obtained under these conditions exhibited no measurable porosity after attempted activation procedures which included solvent exchange with MeOH or CH₂Cl₂ followed by heating in vacuum or supercritical CO₂ drying. Upon heating a sample of as-synthesized Fe₃(BTC)₂Cl under vacuum during attempted activation, a small amount of white residue was observed to sublime from the sample. ¹H NMR analysis of this residue showed a singlet resonance at 2.70 ppm, indicative of DABCO (Figure S6). Speculating that DABCO may block the Fe sites and/or the pores in these samples, we sought alternative pathways to access guest-free Fe₃(BTC)₂. Nevertheless, alternative synthetic procedures excluding the use of DABCO or starting from FeCl₂ failed to consistently give phase-pure material.

We completed our survey of the M₃(BTC)₂ series containing first row transition metals by examining the synthesis and activation
of Zn₃(BTC)₂. Matzger and coworkers have recently reported the failure of Zn₃(BTC)₂ to display permanent accessible porosity. Based on positron annihilation lifetime spectroscopy experiments, they suggested that although the framework retains crystallinity and bulk porosity, surface collapse upon drying effectively blocks guest access to the framework pores. We repeated their reported synthesis of Zn₃(BTC)₂ and found that the material indeed shows no measurable N₂ uptake upon activation by heating in vacuum. Consequently, we turned our attention to the synthesis and activation of members of the M₃(BTC)₂ series containing the second row transition metals Mo and Ru. Mo₃(BTC)₂ was isolated as an air-sensitive orange-red powder by heating a mixture of Mo(CO)₆ and H₃BTC at reflux in DMF according to a literature procedure. The crystallinity of this product and its isostructural relationship to Cu₃(BTC)₂ were confirmed by powder X-ray diffraction (Figure 2). Notably, the reported activation procedure leaves a significant amount of DMF in the material (~1 DMF per Mo), which presumably binds to the Mo centers leaving few, if any, unsaturated metal sites. To minimize the amount of DMF retained in Mo₃(BTC)₂, the as-synthesized material was exchanged by soaking a sample in anhydrous methanol for 1 week and refreshing the methanol solution daily. TGA analysis of the methanol-exchanged sample showed a 12% weight loss in the 25-150 °C range, which corresponds to the loss of ~3 molecules of methanol. Gratifyingly, a sample of methanol-exchanged Mo₃(BTC)₂ heated under vacuum at 100 °C for 12 hrs and at 150 °C for 24 hrs provided a material with an apparent BET surface area of 1689(±5) m²/g, considerably higher than the previously reported value (1280 m²/g). Elemental analysis (C, H, N) of the activated sample matched an empirical formula of Mo₃(BTC)₂(DMF)₀.₅, indicating that only a small amount of DMF molecules remain trapped in the pores and a significant number of metal sites should be exposed. In fact, the remaining DMF could not be clearly assigned in the FT-IR spectrum of the sample (Figure 4). However, the symmetric ν(Mo-Mo) stretching mode is readily observable by Raman spectroscopy, and an observed shift of this band to higher energy was previously proposed to indicate desolvation of the Mo₂ SBUs in Mo₃(BTC)₂. The Raman spectrum of our methanol-exchanged sample of Mo₃(BTC)₂ shows two distinct ν(Mo-Mo) bands: an intense signal at 402 cm⁻¹ and weaker one at 417 cm⁻¹ (Figure 5). These indicate that the methanol exchange procedure followed by brief drying under vacuum at room temperature initially activates a small number of the Mo₂ SBUs. After heating in vacuum, the increase in intensity of the band at 417 cm⁻¹ indicates further activation of the material and the generation of a greater number of UMCs. The remaining shoulder at 402 cm⁻¹ in the evacuated sample agrees with the presence of a small number of coordinated DMF molecules in the structure.

Our attempts to synthesize Ru₃(BTC)₂ starting from RuCl₃·xH₂O or Ru₂Cl(µ-OAc)₄ according to literature procedures yielded either amorphous products or poorly crystalline materials. Increasing the reaction temperature above that reported in the literature produced significant amounts of Ru metal. However, employing Ru₂Cl(µ-OPiv)₄ (OPiv = O₂C─C(CH₃)₃) as the ruthenium source afforded material with a higher degree of crystallinity (Figure S8). TGA analysis showed steady weight loss from room temperature to around 300 °C (Figure S9), prompting us to attempt activation of the as-synthesized...
Ru$_3$(BTC)$_2$ by heating at 150 °C under vacuum for 48 hrs. An N$_2$
adsorption isotherm on the activated material revealed an
apparent BET surface area of 1180±5 m$^2$/g, significantly higher
than that measured in the earlier report (704 m$^2$/g). Although the
reported material has been formulated as Ru$_3$(BTC)$_2$(Cl)$_x$(OH)$_y$,
elemental analysis of our activated sample showed only trace
amounts of chlorine, suggesting that Cl$^-$ does not provide the
charge balance for the {Ru$_3$}$_2$ paddlewheel units. While pivalate
or acetate counteranions cannot be ruled out, their presence is
unlikely based on the absence of aliphatic C-H stretching bands
in the 2800-3000 cm$^{-1}$ region of the IR spectrum of the activated
sample (Figure 4). In fact, elemental analysis (C, H) of the
activated sample matches well with the charge balanced formula
[Ru$_3$(BTC)$_2$][BTC]$_{0.5}$, which suggests that BTC$^{3-}$ anions residing
in the pores provide charge balance for the {Ru$_3$}$_2$ units and are
likely responsible for the slightly decreased BET surface area
versus the Cu, Cr, and Mo congeners.

While the measured BET surface areas of Cu$_3$(BTC)$_2$ and
Cr$_3$(BTC)$_2$ compare well with the literature values, the
synthetic and activation protocols adopted for Ni$_3$(BTC)$_2$,
Mo$_3$(BTC)$_2$, and Ru$_3$(BTC)$_2$ resulted in higher BET surface areas
than those previously reported. A better comparison of these
values is provided by expressing them in m$^2$/mmol of
M$_x$(BTC)$_y$(guest)$_z$ to account for the greater bulk density of
Mo$_3$(BTC)$_2$ and Ru$_3$(BTC)$_2$ and the presence of guest molecules.
As shown in Table 1, values of the surface areas expressed in
these units are similar for the Cu, Cr, and Mo analogs, while that
of [Ru$_3$(BTC)$_2$][BTC]$_{0.5}$ shows it is slightly less porous, as
expected based on the presence of guest BTC$^{3-}$ anions. The
apparent molar surface area of 716 m$^2$/mmol for
Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O) activated after methanol exchange is
appreciably lower than the other members of the series, presumably
due to the Me$_2$NH$_2$ and H$_2$O guest molecules. Given the
high surface areas exhibited by the Cu, Cr, Mo, and Ru
samples, it is reasonable to assume that UMCs are being
generated during the activation procedures, and therefore we set
out to probe the effects of the identity of these open metal sites on
CO$_2$ affinity.

CO$_2$ adsorption isotherms were measured for the activated MOFs
from 0-800 torr at three temperatures over the 313-334 K range.
The isotherms, shown in Figure 6, were fitted to virial equations
similar to those previously used to describe gas-solid adsorption. The
isosteric heats of adsorption were then calculated using the virial coefficients from the fitting procedure
and a modified Clausius-Clapeyron equation.

Even at the lowest measurement temperature, the maximum CO$_2$
loading did not exceed 0.7 molecules of CO$_2$ per metal at 800 torr
for any of the studied MOFs, ensuring that the enthalpy values are
representative of the interaction between CO$_2$ molecules with
the strongest binding sites in each material. However, at these
measurement temperatures (313-334 K), the adsorbed CO$_2$
molecules should be expected to sample a number of strong
binding sites, both at the UMCs and framework ligand sites. This
is reflected in a plot of the adsorption enthalpies versus CO$_2$
adsorbed (Figure 7) which shows only slight decreases in the
enthalpies from zero-coverage to the maximum CO$_2$ adsorbed.
The zero-coverage isosteric heats of CO$_2$ adsorption measured for
this series (25.6-32.6 kJ/mol) are in line with those observed for
MOFs containing UMCs (21-47 kJ/mol), but considerably lower
than values reported for amine functionalized materials (38-96
kJ/mol) measured using adsorption isotherms. Moreover, the
CO$_2$ adsorption enthalpy measured for Cu$_3$(BTC)$_2$ (29.8 kJ/mol)
is close to the values obtained by Wang (-35 kJ/mol) and Xiang
(-28.0 kJ/mol). Both Cr$_3$(BTC)$_2$ and Mo$_3$(BTC)$_2$(DMF)$_{0.5}$ showed
slightly lower zero coverage heats of CO$_2$ adsorption of 26.7
kJ/mol and 25.6 kJ/mol, respectively. Neutron scattering and
spectroscopic studies of H$_2$ adsorption in Cr$_3$(BTC)$_2$ have
suggested that the exposed Cr$^{5+}$ sites are not occupied at low H$_2$
loading. Indeed, the same scenario may hold for CO$_2$ adsorption
by Cr$_3$(BTC)$_2$ and Mo$_3$(BTC)$_2$(DMF)$_{0.5}$ in this study. This would
explain their similar enthalpies and lower affinity versus
Cu$_3$(BTC)$_2$, where the Cu$^{2+}$ center has been shown to be the
initial site of interaction with CO$_2$ at low loading (1-1.5
CO$_2$/Cu). In contrast, both [Ru$_3$(BTC)$_2$][BTC]$_{0.5}$ and
Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O) exhibited higher CO$_2$ adsorption
enthalpies of 32.6 and 36.8 kJ/mol, respectively. In the case of the Ru
analogue, this higher affinity may be assigned to the
greater positive charge of the diruthenium units (5+) versus the
other dimetal units (4+) in the series, but could also be due to
CO$_2$ interaction with the extraframework BTC$^{3-}$ anions, which act
as Lewis bases. The higher CO$_2$ affinity exhibited by the
Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O) sample seemed surprising since few,
if any open Ni$^{2+}$ centers should be exposed given the presence of
coordinating guest molecules. However, experiments carried out
by Snurr and coworkers have shown that slightly hydrated
Cu$_3$(BTC)$_2$ exhibits increased and steeper CO$_2$ uptake versus
fully evacuated samples. This behavior agreed with grand
canonical Monte Carlo simulations which indicated increased
interaction energy due to Coulombic interactions between the
coordinated water molecules and CO$_2$. In the present case, similar
effects could be responsible for the higher heat of CO$_2$
adsorption displayed by Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O), despite a diminished
apparent surface area and overall CO$_2$ uptake due to guest
molecules.
Conclusions

Increased BET surface areas (on a molar basis) have been obtained for the members of the \(M_3(\text{BTC})_2\) isostructural series \(M = \text{Ni}, \text{Mo}, \text{Ru}\) using improved activation procedures and syntheses. In the case of \(M = \text{Mo}\), a solvent exchange procedure with methanol provided a material with only a small amount of residual DMF guest molecules. Likewise, methanol exchange carried out on a sample of \(\text{Ni}_3(\text{BTC})_2\) prior to evacuation resulted in an increased apparent BET surface area, but elemental analysis supported the presence of guest solvent molecules and an empirical formula of \(\text{Ni}_3(\text{BTC})_2(\text{Me}_2\text{NH})_2(\text{H}_2\text{O})\). An alternative procedure adopted for the synthesis of the Ru analog afforded a crystalline product formulated as \([\text{Ru}_3(\text{BTC})_2][\text{BTC}]_{0.5}\). Despite the presence of \(\text{BTC}^{2-}\) guest anions in this structure, the material exhibited only a moderately decreased surface area versus the Cu, Cr, and Mo analogues. Samples of \(\text{Fe}_3(\text{BTC})_2\text{Cl}\) and \(\text{Zn}_3(\text{BTC})_2\) could be prepared according to literature procedures, but the resulting materials showed no indication of \(\text{N}_2\) accessible microporosity.

Variable temperature \(\text{CO}_2\) adsorption studies on the porous members of the \(M_3(\text{BTC})_2\) isostructural series revealed zero coverage isosteric heats of \(\text{CO}_2\) adsorption consistent with those reported for MOFs containing UMCs. We found that in this series the heat of adsorption varied as \(\text{Ni} > \text{Ru} > \text{Cu} > \text{Mo} \approx \text{Cr}\). Due to the presence of donor guest molecules, it seems unlikely that the high enthalpy of adsorption observed for \(\text{Ni}_3(\text{BTC})_2(\text{Me}_2\text{NH})_2(\text{H}_2\text{O})\) is due to metal-\(\text{CO}_2\) interactions, and we speculate that the guests may play a role in the increased affinity. The differences observed among the remainder of the series support the notion that metal identity affects the strength of the initial framework-\(\text{CO}_2\) interaction. Notably, \([\text{Ru}_3(\text{BTC})_2][\text{BTC}]_{0.5}\) which bears a higher formal charge on the \(\text{Ru}, \text{Cu}, \text{and Mo}\) analogues. We attributed this behavior to the formation of \(\text{Ru}^2\) high enthalpy of adsorption for \(\text{Ni}_3(\text{BTC})_2(\text{Me}_2\text{NH})_2(\text{H}_2\text{O})\) due to metal-\(\text{CO}_2\) interactions, and we speculate that the guests may play a role in the increased affinity. The differences observed among the remainder of the series support the notion that metal identity affects the strength of the initial framework-\(\text{CO}_2\) interaction. Notably, \([\text{Ru}_3(\text{BTC})_2][\text{BTC}]_{0.5}\) which bears a higher formal charge on the \(\text{Ru}, \text{Cu}, \text{and Mo}\) analogues. We attributed this behavior to the formation of stronger electrostatic interactions between \(\text{CO}_2\) and the \([\text{Ru}_3\]^{2+}\) sites. This interpretation is in agreement with the higher enthalpy reported for the more ionic \(\text{Mg}_4(\text{DOBDC})\) (39-47 kJ/mol) versus the isostructural and softer \(\text{Co}\) (37 kJ/mol) and \(\text{Ni}\) (37-42 kJ/mol) derivatives. However, a potential interaction between \(\text{CO}_2\) and the Lewis basic \(\text{BTC}^{2-}\) anions residing in the Ru material may contribute to the observed increase in adsorption enthalpy here. Overall, these results suggest that the use of more electropositive divalent metals, such as \(\text{Mg}^{2+}\), or incorporation of more highly charged dimetal units could lead to \(M_3(\text{BTC})_2\) analogues with increased \(\text{CO}_2\) affinity at low coverage.

Experimental

General Considerations

Trimesic acid (Aldrich), \(\text{Cr}(\text{CO})_6\) (Strem), \(\text{Ni(NO}_3)_2\cdot6\text{H}_2\text{O}\) (Strem), \(\text{Cu(NO}_3)_2\cdot2.5\text{H}_2\text{O}\) (Strem), \(\text{Mo}(\text{CO})_6\) (Strem), \(\text{RuCl}_3\cdot\text{H}_2\text{O}\) (Pressure Chemical), \(\text{N}_2\text{N}-\text{dimethylformamide}\) (99.8%, VWR), and ethanol (ACS grade, Mallinckrodt) were used as received unless otherwise noted. \(\text{Fe}_3(\text{BTC})_2\text{Cl}\), \(\text{Zn}_3(\text{BTC})_2\), \(\text{Cu}_3(\text{BTC})_2\), \(\text{Cr}_3(\text{BTC})_2\), and \(\text{Ru}_2(\text{OPv})_4\) were prepared according to literature procedures. Powder X-ray diffraction patterns were collected on a Bruker Advance D8 diffractometer using Nickel-filtered Cu-K\(_\alpha\) radiation (\(\lambda = 1.5418\) Å). Powder X-ray diffraction samples were prepared by placing a thin layer of sample on a glass slide inside a polyurethane domed sample holder. IR spectra were collected using either a Bruker Tensor 37 or Bruker Alpha (contained in a N\(_2\)-filled glovebox) FTIR spectrometer, both equipped with a diamond crystal Bruker Platinum ATR accessory. Raman spectra were collected using a Horiba Raman Microscope with a 633 nm laser.

Thermogravimetric analysis (TGA) was performed on a TA Instruments Q500 Thermogravimetric Analyzer at a heating rate of 1 °C/min under a nitrogen gas flow of 90 mL/min. Elemental analyses were performed at Midwest Microlabs (Indianapolis, IN).

Gas sorption measurements

A Micromeritics ASAP 2020 Surface Area and Porosity Analyzer was used to measure \(\text{N}_2\) and \(\text{CO}_2\) adsorption isotherms. Oven-dried sample tubes equipped with TranSeals\textsuperscript{TM} (Micrometrics) were evacuated and tared. Samples (100-200 mg) were transferred to the sample tube, which was then capped by a TranSeal\textsuperscript{TM}. Samples were heated to the appropriate temperatures and held at those temperatures until the outgass rate was less than 2 mTorr/minute. The evacuated sample tubes were weighed again and the sample mass was determined by subtracting the mass of the previously tared tubes. \(\text{N}_2\) adsorption isotherms were measured volumetrically at 77 K. Surface areas were calculated by fitting the isotherm data to the BET equation with the appropriate pressure range (0.0001 \(\leq P/P_0 \leq 0.1\)) determined by the consistency criteria of Rouquerol. Reported error in the BET surface area values are based on the fitting to the BET equation. \(\text{CO}_2\) isotherms were measured between 313 and 324 K using a Micrometrics thermocouple-controlled heating mantle. Ultra high purity grade (99.999% purity) \(\text{N}_2\), \(\text{CO}_2\), and He, oil-free valves and gas regulators were used for all free space corrections and measurements. Isosteric heats of adsorption were calculated by fitting the adsorption isotherms to a virial equation.

Synthesis of \([\text{Mo}_3(\text{BTC})_2][\text{DMF}]_{0.5}\)

A dry 100 mL Schlenk flask was charged with \(\text{Mo}(\text{CO})_6\) (1.13 g, 4.28 mmol), trimesic acid (0.75 g, 3.57 mmol), and degassed DMF (60 mL) under a nitrogen atmosphere. The reaction mixture was heated to reflux with rapid stirring for 1 week after which a fine orange/red solid separated. The flask was cooled to room temperature and the solids were separated by filtration and washed with dry, degassed DMF (3 \(\times\) 20 mL). The product was soaked in methanol for 1 week at ambient temperature, and the solvent was refreshed daily to facilitate DMF exchange. After 1 week, the solid was filtered and dried in \textit{vacuo} at room temperature to afford 0.38 g (36%) of light orange powder. The material was further activated by heating in vacuum at 100 °C for 12 hrs and at 150 °C for 24 hrs. Elemental analysis calcd. for \(\text{Mo}_9(\text{C}_9\text{H}_3\text{O}_3)_2(\text{C}_2\text{H}_4\text{NO}_3)_{6.5}\) C, 31.71; H, 1.30; N, 0.95. Found: C, 32.06; H, 1.47; N 1.05.

Synthesis of \([\text{Ru}_3(\text{BTC})_2][\text{BTC}]_{0.5}\)

A 23 mL teflon-lined acid digestion bomb was charged with \(\text{Ru}_2(\text{OPv})_4\)Cl (0.54 g, 0.84 mmol), trimesic acid (0.24 g, 1.14 mmol), acetic acid (161 \(\mu\)L, 2.8 mmol), and \(\text{H}_2\text{O}\) (12 mL). The
reaction vessel was sealed and heated in an oven to 160 °C for 4 days. After allowing to cool to room temperature, the product was collected by filtration as a dark brown powder, washed with ethanol (3 × 10 mL), and dried in vacuo at room temperature to afford 0.27 g (72 %) of product. The sample was activated by heating under vacuum at 100 °C for 48 h. Elemental analysis calcd. for Ru2(C4H2O9)3(C4H4O4)0.5·C, 32.79; H, 1.46; Cl 0.1.

Acknowledgements

This work was supported by the MIT Energy Initiative through a Seed Fund to MD. We thank Prof. Yang Shao-Horn for use of the Raman spectrometer.

Notes and references

a Department of Chemistry, Massachusetts Institute of Technology, 77 Massachusetts Avenue, Cambridge, Massachusetts 02139, United States. Fax: XX XXXX XXXX; Tel: XX XXXX XXXX; E-mail: xxxx@aaa.bbb.ccc

† Electronic Supplementary Information (ESI) available: additional spectral data. See DOI: 10.1039/b000000x/