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

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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*

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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.1-4 Within this scope, more recent efforts have been devoted to developing these materials for the capture and separation of CO2.7-10 Two common strategies for enhancing the CO2 affinity and selectivity in MOFs include functionalization of the frameworks with amines or other basic groups,15-23 and removal of terminal bound solvent molecules to expose coordinatively-unsaturated metal centers (UMCs).24-39 The former relies on chemisorptive interactions inspired by liquid amine scrubbers,40,41 while the benefit of the latter is commonly ascribed to a physisorptive process enhanced by ion-induced dipole interactions.42 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.42-45 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(DOBCD) (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(DOBCD)42,43 and Ni2(DOBCD),29 while CO2 adsorption isotherms measured at various temperatures revealed that the strength of interaction varies as Mg > Ni > Co.28 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 CO$_2$.

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, Cu$_3$(BTC)$_2$ (BTC = 1,3,5-benzenetricarboxylate),$^{47}$ 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 Cu$_3$(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 Cu$^{2+}$ ion can be readily removed by heating under vacuum to generate UMCs. Despite the popularity of Cu$_3$(BTC)$_2$ in a range of applications, including CO$_2$ storage, its analogues have received much less attention and none have been tested for CO$_2$ uptake. For instance, Cr$_3$(BTC)$_2$,$^{48}$ and Mo$_3$(BTC)$_2$, $^{49}$ containing quadruply bonded dimetal units, were shown to exhibit permanent porosity and high surface areas comparable to Cu$_3$(BTC)$_2$, but gas sorption studies were limited to H$_2$, N$_2$, and O$_2$. The other known analogs include Zn$_3$(BTC)$_2$, $^{50,51}$ Ni$_3$(BTC)$_2$, $^{52}$ and the mixed-valent Fe(II/III) and Ru(II/III) structures Fe$_3$(BTC)$_2$Cl,$^{53}$ and Ru$_3$(BTC)$_2$(Cl)$_3$(OH)$_1.5$,$^{54}$ Although Ni$_3$(BTC)$_2$ and Ru$_3$(BTC)$_2$(Cl)$_3$(OH)$_1.5$,$^{54}$ were shown to exhibit permanent porosity, their reported BET surface areas were lower than those obtained for Cu$_3$(BTC)$_2$, despite the isostructural relationship, and no associated CO$_2$ sorption data was reported. In an effort to gain insight into the value of CO$_2$-UMCs interactions for CO$_2$ storage/separation applications, we examined the synthesis, activation, and CO$_2$ uptake properties of the reported members of the M$_3$(BTC)$_2$ isostructural series.

Results and discussion  

Cu$_3$(BTC)$_2$ and Cr$_3$(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).$^{48,55}$ The BET surface area of 1734(±1) m$^2$/g of Cu$_3$(BTC)$_2$ measured by us falls near the upper end of the reported values for this material, which range from 692-1944 m$^2$/g, $^{56-59}$ and is in line with the geometric accessible surface area previously calculated from the crystal structure (2153 m$^2$/g).$^{60}$

Likewise, an N$_2$ adsorption isotherm measured for Cr$_3$(BTC)$_2$ afforded a BET surface area of 2031(±6) m$^2$/g, higher than the previously reported value of 1810 m$^2$/g.$^{48}$ Although the synthesis of Ni$_3$(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 M$_3$(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, Ni$_3$(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) m$^2$/g, only slightly lower than the reported value of 920 m$^2$/g. In the initial report, single crystal X-ray diffraction and elemental analysis supported an empirical formula of Ni$_3$(BTC)$_2$(Me$_2$NH)$_3$(DMF)$_4$(H$_2$O)$_4$ in which DMF and H$_2$O guest molecules occupied the pores, while dimethylamine molecules produced by the in-situ decomposition of DMF were bound to the axial positions of the Ni$^{2+}$ centers. The lower surface area in comparison to Cu$_3$(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 Ni$_3$(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).

Figure 2. Experimental powder X-ray diffraction patterns showing the isostructural relationship among the M$_3$(BTC)$_2$ series (M = Cu, Cr, Fe, Ni, Zn, Mo, Ru).
Table 1. Apparent BET surface areas and isosteric heats of CO$_2$ adsorption measured for the porous members of the M$_3$(BTC)$_2$ series.

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<td>(m$^2$/g)</td>
<td>(m$^2$/mmol)</td>
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<td>Cu$_3$(BTC)$_2$</td>
<td>1734±1</td>
<td>1049±1</td>
<td>29.8±0.2</td>
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<td>Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O)</td>
<td>1047±1</td>
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<td>36.8±0.4</td>
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<td>Mo$_3$(BTC)$<em>2$(DMF)$</em>{0.5}$</td>
<td>1689±5</td>
<td>1264±3</td>
<td>25.6±0.6</td>
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<tr>
<td>[Ru$_3$(BTC)$<em>2$][BTC]$</em>{0.5}$</td>
<td>1180±5</td>
<td>969±4</td>
<td>32.6±0.4</td>
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$^a$ Calculated geometric accessible surface area from ref 60.

Figure 3. Isotherms for the adsorption of N$_2$ in M$_3$(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) m$^2$/g, still somewhat low in comparison to Cu$_3$(BTC)$_2$ and Cr$_3$(BTC)$_2$. Elemental analysis (C, H, N) of the activated sample matched the formula Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O), 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 Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O) under N$_2$, the H-O-H bending mode in the 1600 cm$^{-1}$ region supports the presence of residual H$_2$O while the aliphatic C-H stretches below 3000 cm$^{-1}$ and weak N-H stretch at 3260 cm$^{-1}$ indicate the presence of residual Me$_2$NH in the activated sample (Figure S5).$^{52-65}$

Dark orange-red crystals of Fe$_3$(BTC)$_2$Cl could easily be obtained according to the reported procedure by heating a mixture of FeCl$_3$, 1,4-diazabicyclo-[2.2.2]-octane (DABCO), and H$_3$BTC in N,N-dimethylformamide (DMF) in a sealed Teflon bomb at 150 °C.

Figure 4. FT-IR spectra of evacuated samples of Mo$_3$(BTC)$_2$(DMF)$_{0.5}$ and [Ru$_3$(BTC)$_2$][BTC]$_{0.5}$.

Figure 5. Raman spectra of Mo$_3$(BTC)$_2$ recorded after solvent exchange with methanol (- - -) and after activation of the methanol-exchanged sample by heating under vacuum (—). 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 CH$_2$Cl$_2$ followed by heating in vacuum or supercritical CO$_2$ drying. Upon heating a sample of as-synthesized Fe$_3$(BTC)$_2$Cl under vacuum during attempted activation, a small amount of white residue was observed to sublime from the sample. $^1$H 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 Fe$_3$(BTC)$_2$. Nevertheless, alternative synthetic procedures excluding the use of DABCO or starting from FeCl$_3$ failed to consistently give phase-pure material.

We completed our survey of the M$_3$(BTC)$_2$ series containing first row transition metals by examining the synthesis and activation.
of Zn$_3$(BTC)$_2$. Matzger and coworkers have recently reported the failure of Zn$_3$(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 Zn$_3$(BTC)$_2$ and found that the material indeed shows no measurable N$_2$ uptake upon activation by heating in vacuum. Consequently, we turned our attention to the synthesis and activation of members of the M$_3$(BTC)$_2$ series containing the second row transition metals Mo and Ru.

Mo$_3$(BTC)$_2$ was isolated as an air-sensitive orange-red powder by heating a mixture of Mo(CO)$_6$ and H$_3$BTC at reflux in DMF according to a literature procedure. The crystallinity of this product and its isostructural relationship to Cu$_3$(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 Mo$_3$(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 (Figure S7). Gratifyingly, a sample of methanol-exchanged Mo$_3$(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) m$^2$/g, considerably higher than the previously reported value (1280 m$^2$/g). Elemental analysis (C, H, N) of the activated sample matched an empirical formula of Mo$_3$(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 Mo$_2$ SBUs in Mo$_3$(BTC)$_2$. The Raman spectrum of our methanol-exchanged sample of Mo$_3$(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 Mo$_2$ 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 Ru$_3$(BTC)$_2$ starting from RuCl$_3$·xH$_2$O or Ru$_2$Cl(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 Ru$_2$Cl(µ-OPiv)$_4$ (OPiv = O$_2$C─C(CH$_3$)$_3$) 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 sample.
Ru(BTC)$_2$; by heating at 150 ºC 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$_2$(BTC)$_2$(Cl)$_x$(OH)$_{1-x}$, 5, elemental analysis of our activated sample showed only trace amounts of chlorine, suggesting that Cl$^-$ does not provide the charge balance for the [Ru$_2$]$_{5^-}$ 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$_2$(BTC)$_2$][BTC]$_{0.5}$, which suggests that BTC$^{3-}$ anions residing in the pores provide charge balance for the [Ru$_2$]$_{5^-}$ 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, 48,56-59 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$_3$(BTC)$_2$(guest)$_x$ to account for the greater bulk density of M$_3$(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. 66 The isosteric heats of adsorption were then calculated using the virial coefficients from the fitting procedure and a modified Clausius-Clapeyron equation. 61 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. 7 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) 24 and Xiang (-28.0 kJ/mol). 38 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$^{2+}$ sites are not occupied at low H$_2$ loading. 57 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). 42 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. 59 This behavior agrees 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 M₃(BTC)₂ isostructural series M = Ni, Mo, Ru using improved activation procedures and syntheses. In the case of M = 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 Ni₃(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 Ni₃(BTC)₂(Me₂NH)₂(H₂O). An alternative procedure adopted for the synthesis of the Ru analog afforded a crystalline product formulated as [Ru₃(BTC)₂][BTC]₀.₅. Despite the presence of BTC⁻⁻⁻ guest anions in this structure, the material exhibited only a moderately decreased surface area versus the Cu, Cr, and Mo analogues. Samples of Fe₃(BTC)₂Cl and Zn₃(BTC)₂ could be prepared according to literature procedures, but the resulting materials showed no indication of N₂ accessible microporosity.

Variable temperature CO₂ adsorption studies on the porous members of the M₃(BTC)₂ isostructural series revealed zero coverage isosteric heats of CO₂ adsorption consistent with those reported for MOFs containing UMCs. We found that in this series the heat of adsorption varied as Ni > Ru > Cu > Mo ≈ Cr. Due to the presence of donor guest molecules, it seems unlikely that the high enthalpy of adsorption observed for Ni₃(BTC)₂(Me₂NH)₂(H₂O) is due to metal-CO₂ 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-CO₂ interaction. Notably, [Ru₃(BTC)₂][BTC]₀.₅, which bears a higher formal charge on the dimetal unit than the other isostructural MOFs, exhibited a slightly higher CO₂ adsorption enthalpy than the Cr, Cu, and Mo analogues. We attributed this behavior to the formation of stronger electrostatic interactions between CO₂ and the [Ru₂]⁵⁺ sites. This interpretation is in agreement with the higher enthalpy reported for the more ionic Mg₂(DOBDC) (39-47 kJ/mol) versus the isostructural and softer Co (37 kJ/mol) and Ni (37-42 kJ/mol) derivatives. However, a potential interaction between CO₂ and the Lewis basic BTC⁻⁻⁻ 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 Mg²⁺, or incorporation of more highly charged dimetal units could lead to M₃(BTC)₂ analogues with increased CO₂ affinity at low coverage.

Experimental

General Considerations

Trimesic acid (Aldrich), Cr(CO)₆ (Strem), Ni(NO₃)₂·6H₂O (Strem), Cu(NO₃)₂·2.5H₂O (Strem), Mo(CO)₆ (Strem), RuCl₃·xH₂O (Pressure Chemical), N,N-dimethylformamide (99.8%, VWR), and ethanol (ACS grade, Mallinckrodt) were used as received unless otherwise noted. Fe₆(BTC)₂Cl₅, Zn₃(BTC)₂, Cu₉(BTC)₂, Cr₃(BTC)₂, and Ru₃(OPV)₂Cl₆ were prepared according to literature procedures. Powder X-ray diffraction patterns were collected on a Bruker Advance D8 diffractometer using Nickel-filtered Cu-Kα radiation (λ = 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 N₂-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 N₂ and CO₂ adsorption isotherms. Oven-dried sample tubes equipped with TranSeal™ (Micrometrics) were evacuated and tared. Samples (100-200 mg) were transferred to the sample tube, which was then capped by a TranSeal™. Samples were heated to the appropriate temperatures and held at those temperatures until the outgas 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. N₂ 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 ≤ P/P₀ ≤ 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. CO₂ isotherms were measured between 313 and 324 K using a Micrometrics thermocouple-controlled heating mantle. Ultra high purity grade (99.999% purity) N₂, CO₂, and He, oil-free valves and gas regulators were used for all free space corrections and measurements. Isotheric heats of adsorption were calculated by fitting the adsorption isotherms to a virial equation.

Synthesis of [Mo₃(BTC)₂][DMF]₁₄

A dry 100 mL Schlenk flask was charged with Mo(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 x 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 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 Mo₃(C₃H₆O₆)₃(C₂H₆NO), C: 31.71; H: 1.30; N: 0.95. Found: C, 32.06; H, 1.47; N 1.05.

Synthesis of [Ru₃(BTC)₂][BTC]₁₄

A 23 mL teflon-lined acid digestion bomb was charged with Ru₃(OPV)₂Cl (0.54 g, 0.84 mmol), trimesic acid (0.24 g, 1.14 mmol), acetic acid (161 μL, 2.8 mmol), and H₂O (12 mL). The
This procedure could be carried out in either a 23 mL teflon-lined acid digestion bomb or a 75 mL thick-walled glass bomb with a teflon screw cap (Synthware). In a representative procedure, the glass reactor was charged with Ni(NO$_3$)$_2$·6H$_2$O (0.76 g, 2.6 mmol), trimesic acid (0.41 g, 1.9 mmol), 2-methylimidazole (0.11 g, 1.3 mmol), and dry, degassed DMF (30 mL). The vessel was sealed and heated in an oven to 170 °C for 2 days. After allowing to cool to room temperature, a mixture of the solvent and brown powder was decanted from the green crystals which had separated on the inside of the glass. The green crystals were then washed with DMF (5 × 10 mL) to remove any of the remaining powder and dried in vacuo at room temperature to afford 0.160 g (17 %) of product. The product was soaked in methanol for 24 h at ambient temperature, and the solvent was refreshed once after 12 h. The resulting material was filtered, dried in vacuum for 12 h at room temperature, and further activated by heating under vacuum at 150 °C for 24 h. Elemental analysis calc. for Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O): C, 37.83; H, 3.17; N, 4.01. Found: C, 37.96; H, 3.25; N 4.77.

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Notes and references