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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)$^\dagger$

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The synthesis, activation, and heats of CO$_2$ adsorption for the known members of the M$_3$(BTC)$_2$
(HKUST-1) isostructural series (M = Cr, Fe, Ni, Zn, Cu, Mo) were investigated to gain insight into
the impact of CO$_2$–metal interactions for CO$_2$ 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 CO$_2$ adsorption were measured for the Cu, Cr, Ni, Mo, and Ru
analogues 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 CO$_2$ affinities in the studied series. These behaviors were attributed to the presence
of residual guest molecules in the case of Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O) and the increased charge of the
dimetal secondary building unit in [Ru$_3$(BTC)$_2$][BTC]$_{0.5}$.

Introduction

Owing to their microporous structures and high surface areas,
metal–organic frameworks (MOFs) continue to receive signifi-
cant attention as materials with potential for applications in gas
storage and separation.$^{1–8}$ Within this scope, more recent efforts
have been devoted to developing these materials for the capture
and separation of CO$_2$.$^{7,9–14}$ Two common strategies for enhan-
cing the CO$_2$ affinity and selectivity in MOFs include functiona-
lization of the frameworks with amines or other basic
groups,$^{15–21}$ 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 com-
monly 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 CO$_2$ uptake such as pore size,
pore shape and apparent surface area, thereby providing direct
insight into the nature of the CO$_2$–metal interaction. One
notable example is the family of materials known as MOF-74:
M$_2$(DOBDC) (M = Mg, Co, Ni; DOBDC = 2,5-dioxy-1,
4-benzene dicarboxylate). In this series, X-ray and neutron dif-
fraction experiments have shown that UMCs are the initial sites
of interaction of CO$_2$ with the framework in Mg$_2$(DOBDC)$^{42,46}$
and Ni$_2$(DOBDC)$^{29}$ while CO$_2$ adsorption isotherms measured
at various temperatures revealed that the strength of initial inter-
action varies as Mg > Ni > Co.$^{28}$ Studies determined across iso-
structural 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-benzentricarboxylate),$^{47}$ has become one of the
most emblematic and is part of an isostructural series that cur-
cently includes Cr, Fe, Ni, Zn, Mo, and Ru analogues. The struc-
ture of Cu$_3$(BTC)$_2$, shown in Fig. 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$_3$ and Ru$_3$(BTC)$_2$(Cl)$_3$(OH)$_{1.5–x}$.$^{54}$
Although Ni$_3$(BTC)$_2$ and Ru$_3$(BTC)$_2$(Cl)$_3$(OH)$_{1.5–x}$ were shown

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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$_2$–UMC 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 (Fig. 2). The BET surface area of 1734(±1) m$^2$ g$^{-1}$ measured by us for Cu$_3$(BTC)$_2$ falls near the upper end of the reported values for this material, which range from 692–1944 m$^2$ g$^{-1}$, and is in line with the geometric accessible surface area previously calculated from the crystal structure (2153 m$^2$ g$^{-1}$). Likewise, an N$_2$ adsorption isotherm measured for Cr$_3$(BTC)$_2$ afforded a BET surface area of 2031(±6) m$^2$ g$^{-1}$, higher than the previously reported value of 1810 m$^2$ g$^{-1}$.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 N,N′-dimethylformamide (DMF) and gave powder X-ray diffraction patterns consistent with the M$_3$(BTC)$_2$ structure type (Fig. 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 (Fig. 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 h. After this activation procedure, the

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

<table>
<thead>
<tr>
<th></th>
<th>BET SA/m$^2$ g$^{-1}$</th>
<th>BET SA/m$^2$ mmol$^{-1}$</th>
<th>$\Delta$H$_{ads}$(CO$_2$)/kJ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$_3$(BTC)$_2$</td>
<td>1734 ± 1</td>
<td>1049 ± 1</td>
<td>29.8 ± 0.2</td>
</tr>
<tr>
<td>Cr$_3$(BTC)$_2$</td>
<td>2031 ± 6</td>
<td>1158 ± 2</td>
<td>26.7 ± 0.2</td>
</tr>
<tr>
<td>Ni$_3$(BTC)$_2$(Me$_2$NH)$_2$(H$_2$O)</td>
<td>1047 ± 1</td>
<td>732 ± 1</td>
<td>36.8 ± 0.4</td>
</tr>
<tr>
<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>
</tr>
<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>
</tr>
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$^a$ Calculated geometric accessible surface area from ref. 60.
material exhibited a BET surface area of 847 (±3) m² g⁻¹, only slightly lower than the reported value of 920 m² g⁻¹. In the initial report, single crystal X-ray diffraction and elemental analysis supported an empirical formula of Ni₃(BTC)₂×(Me₂NH)₁×(DMF)₁×(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 with MeOH or CH₂Cl₂ followed by heating in vacuum, this product and its isostructural relationship to Cu₃(BTC)₂ were readily observable by Raman spectroscopy, and an observed shift of this band to higher energy was previously proposed to indicate a higher surface area, we carried out a solvent exchange with MeOH or CH₂Cl₂ followed by heating in vacuum. Consequently, 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 (Fig. 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 (Fig. S7†). Gratifyingly, a sample of methanol-exchanged Mo₃(BTC)₂ heated under vacuum at 100 °C for 12 h and at 150 °C for 24 h provided a material with an apparent BET surface area of 1689 (±5) m² g⁻¹, considerably higher than the previously reported value (1280 m² g⁻¹). Elemental analysis (C, H, N) of the activated sample matched the formula Mo₃(BTC)₂×(Me₂NH)₇×(H₂O)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 (Fig. 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...
reported in the literature (160 °C) produced significant amounts of Ru metal. However, employing Ru\textsubscript{2}Cl(μ-OPiv)\textsubscript{4} (OPiv = \textasciitilde O\textsubscript{2}C-C(CH\textsubscript{3})\textsubscript{3}) as the ruthenium source under the reported reaction conditions afforded material with a higher degree of crystallinity (Fig. S8†). TGA analysis showed steady weight loss from room temperature to around 300 °C (Fig. S9†), prompting us to attempt activation of the as-synthesized Ru\textsubscript{3}(BTC)\textsubscript{2} by heating at 150 °C under vacuum for 48 h. An N\textsubscript{2} adsorption isotherm on the activated material revealed an apparent BET surface area of 1180(±5) m\textsuperscript{2} g\textsuperscript{-1}, significantly higher than that measured in the earlier report (704 m\textsuperscript{2} g\textsuperscript{-1}). Although the reported material has been formulated as Ru\textsubscript{3}(BTC)\textsubscript{2}(Cl)(OH)\textsubscript{1.5}... elemental analysis of our activated sample showed only trace amounts of chlorine, suggesting that Cl\textsuperscript{−} does not provide the charge balance for the \{Ru\textsubscript{2}\}\textsuperscript{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\textsuperscript{-1} region of the IR spectrum of the activated sample (Fig. 4). In fact, elemental analysis (C, H) of the activated sample matches well with the charge balanced formula [Ru\textsubscript{3}(BTC)\textsubscript{2}]\textsubscript{0.5}, which suggests that BTC\textsuperscript{3−} anions residing in the pores provide charge balance for the \{Ru\textsubscript{2}\}\textsuperscript{5+} units and are likely responsible for the slightly decreased BET surface area \textit{versus} the Cu, Cr, and Mo congeners.

While the measured BET surface areas of Cu\textsubscript{3}(BTC)\textsubscript{2} and Cr\textsubscript{3}(BTC)\textsubscript{2} compare well with the literature values,\textsuperscript{48,56–59} the synthetic and activation protocols adopted for Ni\textsubscript{3}(BTC)\textsubscript{2}, Mo\textsubscript{3}(BTC)\textsubscript{2}, and Ru\textsubscript{3}(BTC)\textsubscript{2} resulted in higher BET surface areas than those previously reported. A better comparison of these values is provided by expressing them in m\textsuperscript{2} mmol\textsuperscript{-1} of M\textsubscript{3}(BTC)\textsubscript{2(guest)}\textsubscript{x} to account for the greater bulk density of Mo\textsubscript{3}(BTC)\textsubscript{2} and Ru\textsubscript{3}(BTC)\textsubscript{2} and the presence of guest molecules. As shown in Table 1, the values of the surface areas expressed in these units are similar for the Cu, Cr, and Mo analogs, while that of [Ru\textsubscript{3}(BTC)\textsubscript{2}]\textsubscript{0.5} shows it is slightly less porous, as expected based on the presence of guest BTC\textsuperscript{3−} anions. The apparent molar surface area of 716 m\textsuperscript{2} mmol\textsuperscript{-1} of Ni\textsubscript{3}(BTC)\textsubscript{2}(Me\textsubscript{2}NH)\textsubscript{2}(H\textsubscript{2}O) activated after methanol exchange is appreciably lower than the other members of the series, presumably due to the Me\textsubscript{2}NH\textsubscript{2} and H\textsubscript{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\textsubscript{2} affinity.

CO\textsubscript{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 Fig. 6, were fitted to virial equations similar to those previously used to describe gas–solid adsorption.\textsuperscript{66} The isosteric heats of adsorption were then calculated using the virial coefficients from the fitting procedure and a modified Clausius–Clapeyron equation.\textsuperscript{61}

Even at the lowest measurement temperature, the maximum CO\textsubscript{2} loading did not exceed 0.7 molecules of CO\textsubscript{2} per metal at 800 Torr for any of the studied MOFs, ensuring that the enthalpy values are representative of the interaction between CO\textsubscript{2} molecules with the strongest binding sites in each material. However, at these measurement temperatures (313–334 K), the adsorbed CO\textsubscript{2} molecules should be expected to sample a number of strong binding sites, both at the UMCs and framework ligand sites.

Fig. 4 FT-IR spectra of evacuated samples of Mo\textsubscript{3}(BTC)\textsubscript{2}(DMF)\textsubscript{0.5} and [Ru\textsubscript{3}(BTC)\textsubscript{2}]\textsubscript{0.5}.

Fig. 5 Raman spectra of Mo\textsubscript{3}(BTC)\textsubscript{2} recorded after solvent exchange with methanol (−−) and after activation of the methanol-exchanged sample by heating under vacuum (—).
The low CO2 coverage in the measurements is reflected in a plot of the adsorption enthalpies versus CO2 adsorbed (Fig. 7) which shows only slight decreases in the enthalpies from zero-coverage to the maximum CO2 adsorbed. The zero-coverage isosteric heats of CO2 adsorption measured for this series (25.6–32.6 kJ mol\(^{-1}\)) are in line with those observed for MOFs containing UMCs (21–47 kJ mol\(^{-1}\)), but considerably lower than values reported for amine functionalized materials (38–96 kJ mol\(^{-1}\)) measured using adsorption isotherms. Moreover, the CO2 adsorption enthalpy measured for Cu3(BTC)2 (29.8 kJ mol\(^{-1}\)) is close to the values obtained by Wang (−35 kJ mol\(^{-1}\))\(^{24}\) and Xiang (−28.0 kJ mol\(^{-1}\))\(^{38}\). Both Cr2BTC3 and Mo3(BTC)2(DMF)\(_{0.5}\) showed slightly lower zero coverage heats of CO2 adsorption of 26.7 kJ mol\(^{-1}\) and 25.6 kJ mol\(^{-1}\), respectively. Neutron scattering and spectroscopic studies of H2 adsorption in Cr3(BTC)2 have suggested that the exposed Cr\(^{2+}\) sites are not occupied at low H2 loading.\(^{67}\) Indeed, the same scenario may hold for CO2 adsorption by Cr3(BTC)2 and Mo3(BTC)2(DMF)\(_{0.5}\) in this study. This would explain their similar enthalpies and lower affinity versus Cu3(BTC)2, where the Cu\(^{2+}\) center has been shown to be the initial site of interaction with CO2 at low loading (1–1.5 CO2–Cu).\(^{42}\) In contrast, both [Ru3(BTC)2][BTC]\(_{0.5}\) and Ni3(BTC)2(Me2NH)\(_2\)(H2O) exhibited higher CO2 adsorption enthalpies of 32.6 and 36.8 kJ mol\(^{-1}\), 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 CO2 interaction with the Lewis basic, extra-framework BTC3\(^–\) anions. The higher CO2 affinity exhibited by the Ni3(BTC)2(Me2NH)\(_2\)(H2O) 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 Cu3(BTC)2 exhibits increased and steeper CO2 uptake versus fully evacuated samples.\(^{59}\) This behavior agreed with grand canonical Monte Carlo simulations which indicated increased interaction energy due to Coulombic interactions between the coordinated water molecules and CO2. In the present case, similar effects could be responsible for the higher heat of CO2 adsorption displayed by Ni3(BTC)2(Me2NH)\(_2\)(H2O), despite a
diminished apparent surface area and overall CO2 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 BTC3– 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 attribute this behavior to the formation of stronger electrostatic interactions between CO2 and the {Ru2}+ sites. This interpretation is in agreement with the higher enthalpy reported for the more ionic Mg2+(DOBDC) (39–47 kJ mol–1 versus the isostructural and softer Co (37 kJ mol–1) and Ni (37–42 kJ mol–1) derivatives.26,28,31 However, a potential interaction between CO2 and the Lewis basic BTC3– 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. Fe3(BTC)2Cl,53 Zn3(BTC)2,51 Cu3(BTC)2,55 Cr3(BTC)2,48 and Ru3(OPv)4Cl68 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–1 under a nitrogen gas flow of 90 mL min–1. 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 TranSeals™ (Microelectronics) 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 min–1. 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.69,70 The reported errors in the BET surface area values are based on the fitting to the BET equation. CO2 isotherms were measured between 313 and 334 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. Isosteric heats of adsorption were calculated by fitting the adsorption isotherms to a virial equation.66

Synthesis of [Mo4(BTC)4][DMF]0.5

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 × 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 at 100 °C for 12 h and at 150 °C for 24 h. Elemental analysis carried for Mo4(C6H3O6)2(C7H7NO)0.5: C, 31.71; H, 1.30; N, 0.95. Found: C, 32.06; H, 1.47; N 1.05.
Synthesis of [Ru(μ-BtC)2][BtC]$_e$$_s$

A 23 mL Teflon-lined acid digestion bomb was charged with Ru$_2$(OPv)$_4$Cl (0.54 g, 0.84 mmol), trimesic acid (0.24 g, 1.14 mmol), acetic acid (161 μL, 2.8 mmol), and H$_2$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 x 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 150 °C for 48 h. Elemental analysis calcd for Ru$_3$(C$_9$H$_3$O$_6$)$_2$(C$_9$H$_3$O$_6$)$_0.5$: C, 32.91; H, 0.92; Cl 0.0. Found: C, 32.79; H, 1.46; Cl, trace.

Synthesis of Ni$_3$(BtC)$_2$(Me$_2$NH)$_2$(H$_2$O)

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 (0.54 g, 0.84 mmol), trimesic acid (0.24 g, 1.14 mmol), acetic acid (161 μL, 2.8 mmol), and H$_2$O (12 mL). The reaction 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 x 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 calcd 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
