

Cite this: *J. Mater. Chem. C*,  
2024, 12, 3164

## Benchmarking nitrous oxide adsorption and activation in metal–organic frameworks bearing coordinatively unsaturated metal centers†

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Anthropogenic emissions of N<sub>2</sub>O, the third most abundant greenhouse gas after CO<sub>2</sub> and CH<sub>4</sub>, are contributing to global climate change. Although metal–organic frameworks (MOFs) have been widely studied as adsorbents for CO<sub>2</sub> and CH<sub>4</sub>, less effort has focused on the use of MOFs to remove N<sub>2</sub>O from emission streams or from air. Further, N<sub>2</sub>O activation would enable its use as an inexpensive oxidant for fine chemical synthesis. Herein, we identify features that contribute to strong binding and high uptake of N<sub>2</sub>O at coordinatively unsaturated metal sites in the M<sub>2</sub>Cl<sub>2</sub>(btdd) (M = Mn, Co, Ni, Cu; btdd<sup>2-</sup> = bis(1,2,3-triazolo[4,5-*b*],[4',5'-*i*])dibenzo[1,4]dioxin) and M<sub>2</sub>(dobdc) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn; dobdc<sup>4-</sup> = 2,5-dioxido-1,4-benzenedicarboxylate) series of MOFs. Combined experimental and computational studies suggest that N<sub>2</sub>O adsorption at open-metal-sites is primarily based on electrostatic interactions, rather than  $\pi$ -backbonding, causing MOFs with more Lewis acidic metal centers to be superior N<sub>2</sub>O adsorbents. As a result, Mg<sub>2</sub>(dobdc) demonstrates strong binding and record-setting N<sub>2</sub>O uptake (8.75 mmol g<sup>-1</sup> at 1 bar and 298 K). Using density functional theory (DFT) to characterize reactive intermediates and transition states, we demonstrate that N<sub>2</sub>O activation to form a M(IV)–oxo species and N<sub>2</sub> is thermodynamically favorable in Mn<sub>2</sub>(dobdc) and Fe<sub>2</sub>(dobdc) but appears to be kinetically limited in Mn<sub>2</sub>(dobdc). Our work lays a foundation for understanding N<sub>2</sub>O adsorption and activation in MOFs, paving the way for the design of promising next-generation materials for N<sub>2</sub>O capture and utilization.

Received 7th December 2023,  
Accepted 20th January 2024

DOI: 10.1039/d3tc04492k

rsc.li/materials-c

## Introduction

N<sub>2</sub>O is the third most prevalent anthropogenic greenhouse gas after CO<sub>2</sub> and CH<sub>4</sub>, accounting for 6% of the effective radiative forcing from 1960 to 2019.<sup>1</sup> Although CO<sub>2</sub> and CH<sub>4</sub> are present in higher concentrations in the atmosphere, the global warming potential of N<sub>2</sub>O (265) is far greater (1 and 28 for CO<sub>2</sub> and CH<sub>4</sub>, respectively) and its atmospheric lifetime (116 year) is far longer (1 and 12 year for CO<sub>2</sub> and CH<sub>4</sub>, respectively).<sup>2</sup> Over the last four decades, global anthropogenic emissions of N<sub>2</sub>O have increased by 30%.<sup>3</sup> Up to 87% of this increase derives from agricultural practices such as nitrogen additions to soils.

By nature, the sources of these emissions (*i.e.*, farmlands) are diffuse, in contrast to point sources of N<sub>2</sub>O emissions such as adipic and nitric acid manufacturing.<sup>4</sup> Diffuse emissions are currently largely uncontrolled, except for preventative measures such as the use of more efficient fertilizers.<sup>5,6</sup> At point sources, N<sub>2</sub>O can be catalytically destroyed, but regulations requiring this practice have not been globally adopted.<sup>7</sup> Thus, the majority of human-caused N<sub>2</sub>O emissions are currently unabated, leading to a current estimated rate of increase in atmospheric N<sub>2</sub>O concentration of 2% per decade.<sup>3</sup> In addition to its global warming potential, N<sub>2</sub>O was found to be the dominant ozone-depleting substance emitted in the 21st century,<sup>4</sup> underscoring the urgency of curtailing N<sub>2</sub>O emissions. The environmental effects of anthropogenic N<sub>2</sub>O emissions and its long atmospheric lifetime necessitate the development of new materials for N<sub>2</sub>O capture.

Selectively capturing gases from diffuse sources such as air is a unique challenge that requires specially designed sorbents. Metal–organic frameworks (MOFs) are an emerging class of materials that have drawn significant interest for their potential applications in greenhouse gas capture,<sup>8</sup> separations,<sup>9</sup> catalysis,<sup>10</sup> and beyond.<sup>11</sup> They are crystalline, highly porous

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materials formed by connecting metal secondary building units (SBU) with multitopic organic linkers. MOFs have been designed to selectively bind CO<sub>2</sub> and CH<sub>4</sub> based on electrostatic interactions,<sup>12,13</sup> chemical reactivity,<sup>14–16</sup> hydrogen bonding,<sup>17</sup> and more. In contrast, only a small number of largely unrelated MOFs have been studied for N<sub>2</sub>O capture to date.<sup>18–25</sup> The presence of Lewis acidic open-metal-sites has been shown to enhance N<sub>2</sub>O binding;<sup>19</sup> however, a general lack of structure–property trends informing the design of new materials hinders improvements in N<sub>2</sub>O capture in porous materials.

Herein, we present a structure–activity study of N<sub>2</sub>O adsorption in MOFs, with the purpose of identifying features that lead to strong binding and high uptake. Through a combined experimental and computational analysis, we clarify the effects of the ligand field and metal identity on N<sub>2</sub>O adsorption at Lewis acidic open-metal-sites in the M<sub>2</sub>Cl<sub>2</sub>(btdd) (M = Mn, Co, Ni, Cu; btdd<sup>2-</sup> = bis(1,2,3-triazolo[4,5-b],[4',5'-i])dibenzo[1,4]-dioxin)<sup>26–28</sup> and M<sub>2</sub>(dobdc) (M = Mg, Mn, Fe, Co, Ni, Cu, Zn; dobdc<sup>4-</sup> = 2,5-dioxido-1,4-benzenedicarboxylate) series of MOFs.<sup>12,29,30</sup> From this analysis, we identify the M<sub>2</sub>(dobdc) series, particularly Mg<sub>2</sub>(dobdc) and Ni<sub>2</sub>(dobdc), as promising adsorbents that display strong binding and record-setting N<sub>2</sub>O adsorption capacities.

Beyond reducing its environmental impact, N<sub>2</sub>O capture is incentivized by the opportunity to utilize it as a cheap, abundant, and potent oxidant in organic synthesis.<sup>31–33</sup> As a kinetically inert molecule, transition metal catalysts and/or high temperatures and pressures are required to facilitate N<sub>2</sub>O activation. Thus, MOFs and zeolites containing Fe(II) sites have been explored as catalysts for N<sub>2</sub>O utilization.<sup>34–39</sup> In particular, Fe<sub>2</sub>(dobdc) has been demonstrated to catalyze C–H oxidation of hydrocarbons using N<sub>2</sub>O as an oxidant.<sup>37,40–42</sup> Bearing strong similarities to enzymatic iron-based catalysts,<sup>43–45</sup> this occurs through a 2 e<sup>-</sup> transfer from high spin Fe(II) to the oxygen of N<sub>2</sub>O, cleaving the N–O bond and forming a high spin Fe(IV)–oxo intermediate. This process is calculated to be followed by  $\sigma$ -attack and H atom abstraction by the Fe(IV)–oxo and radical rebound to generate the oxidized product.<sup>40</sup> Herein, DFT calculations support that N<sub>2</sub>O activation is also thermodynamically favorable in Mn<sub>2</sub>(dobdc), and we map out an approximate reaction coordinate for this process using the climbing-image nudged elastic band method (CI-NEB). While combined analysis of computation and experiment suggests that this reaction is kinetically limited in Mn<sub>2</sub>(dobdc), our work motivates further study of N<sub>2</sub>O activation in related Mn-based MOFs. Overall, our findings stimulate the development of new framework materials for selective N<sub>2</sub>O capture and conversion to mitigate its environmentally destructive impact.

## Results and discussion

### N<sub>2</sub>O adsorption analysis

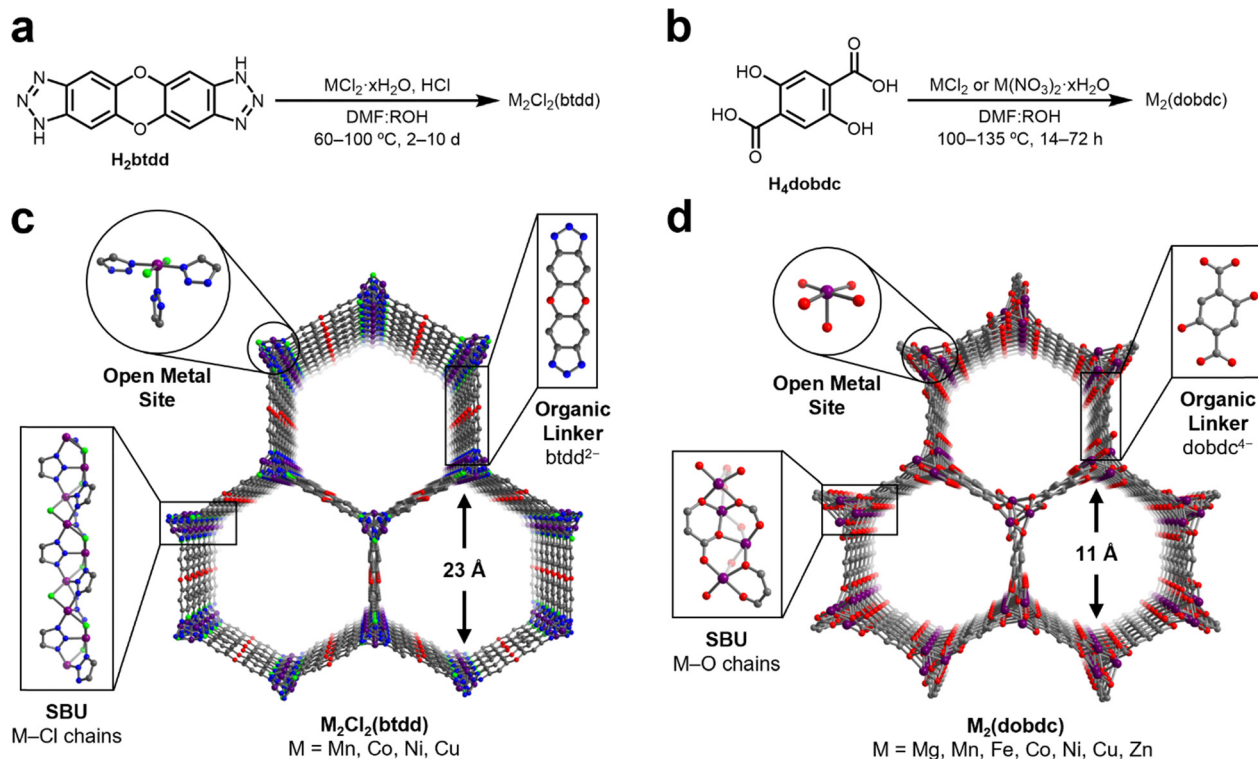
N<sub>2</sub>O is a weakly  $\sigma$ -donating and  $\pi$ -accepting ligand, which has limited the number of well-characterized transition metal adducts of N<sub>2</sub>O to only a small handful, typically bound as

$\eta^1$ -N or  $\eta^2$ -N<sub>2</sub> coordinated N<sub>2</sub>O through  $\pi$ -backbonding interactions.<sup>46–52</sup> Although N<sub>2</sub>O has a relatively weak dipole moment (0.161 D),<sup>53</sup> sorbents could compensate by incorporating Lewis acidic sites to strengthen electrostatic interactions between N<sub>2</sub>O and the sorbent material. MOFs containing highly Lewis acidic coordinatively unsaturated metal centers are effective adsorbents for a wide variety of gases through strong electrostatic interactions.<sup>54</sup> To identify robust structure–property trends regarding N<sub>2</sub>O binding at open-metal-sites, we targeted isostructural frameworks accommodating a range of metal ions in similar ligand fields. These criteria should effectively yield insights into the interplay of the metal identity and ligand field on the binding strength of N<sub>2</sub>O at open-metal-sites in MOFs.

Two groups of MOFs that fulfil these requirements are the M<sub>2</sub>Cl<sub>2</sub>(btdd) and M<sub>2</sub>(dobdc) series. These MOFs are composed of hexagonal-pored structures formed by connecting one-dimensional, rod-like metal SBUs with ditopic organic linkers (Fig. 1). Porous channels extend through the materials and, after activation, become lined with a high density of coordinatively unsaturated metal sites confined in square pyramidal geometries. While the overall structures of the M<sub>2</sub>Cl<sub>2</sub>(btdd) and M<sub>2</sub>(dobdc) series are similar, their SBUs lead to distinctive ligation of the metal sites. In M<sub>2</sub>Cl<sub>2</sub>(btdd), metal ions are coordinated to three individual triazolate groups through one nitrogen atom per triazolate. Each triazolate coordinates to three distinct metal ions, and two chlorides ( $\mu_2$ ) bridge neighboring metals, forming M–Cl chains. For this study, the isostructural Mn, Co, Ni, and Cu MOFs of this series were synthesized according to reported procedures (Fig. 1a and Sections S3–S6, ESI<sup>†</sup>).<sup>26,28,55</sup> In the M<sub>2</sub>(dobdc) series, the secondary building units are composed of metal-salicylate chains, forming an oxygen-based ligand field. The Mg, Mn, Fe, Co, Ni, Cu, and Zn variants of M<sub>2</sub>(dobdc) were synthesized in accordance with the literature (Fig. 1b and Sections S7–S13, ESI<sup>†</sup>).<sup>12,30,56–59</sup> All MOFs analyzed in this study were confirmed to be highly crystalline and match the expected structures *via* powder X-ray diffraction (PXRD). The porosity of all MOFs was confirmed using 77 K N<sub>2</sub> adsorption/desorption measurements. The calculated surface areas are similar to those reported in the literature in every case.

After synthesis, the MOFs were each evaluated as N<sub>2</sub>O sorbents by measuring N<sub>2</sub>O adsorption and desorption isotherms at 25 °C, 35 °C, and 45 °C (Sections S3–S13, ESI<sup>†</sup>). Adsorption data were fit using dual-site Langmuir–Freundlich models (eqn (S1), ESI<sup>†</sup>). These fits were subsequently used to calculate enthalpies of N<sub>2</sub>O adsorption ( $-\Delta H_{\text{ads}}$ ) in each MOF using the Clausius–Clapeyron equation (eqn (S2), ESI<sup>†</sup>). The resulting  $-\Delta H_{\text{ads}}$  values as a function of N<sub>2</sub>O uptake in both series of MOFs are summarized in Fig. 2 and Table 1. Critically, PXRD and surface area measurements confirm the stability of every MOF towards N<sub>2</sub>O except for Fe<sub>2</sub>(dobdc), which has been previously shown to react irreversibly with this gas.<sup>37,40–42</sup> As a result, the adsorption data for this MOF were excluded from the analysis below.

The M<sub>2</sub>Cl<sub>2</sub>(btdd) series were first evaluated as N<sub>2</sub>O sorbents. Despite their high density of open-metal-sites, all MOFs of this



**Fig. 1** General synthesis conditions of (a)  $\text{M}_2\text{Cl}_2(\text{btdd})$  (M = Mn, Co, Ni, Cu) and (b)  $\text{M}_2(\text{dobdc})$  (M = Mg, Mn, Fe, Co, Ni, Cu, Zn) MOFs (R = Et, Me, *i*Pr, H). Structures of (c)  $\text{M}_2\text{Cl}_2(\text{btdd})$  and (d)  $\text{M}_2(\text{dobdc})$ . Purple, light green, blue, grey, and red spheres represent metal, chlorine, nitrogen, carbon, and oxygen atoms, respectively. Hydrogen atoms are omitted for clarity.

series only weakly interact with  $\text{N}_2\text{O}$  ( $-\Delta H_{\text{ads}} < 25 \text{ kJ mol}^{-1}$ ). The difference in binding strength between the variants is minor: Mn, Co, and Ni analogues exhibit similar binding strengths, followed by Cu (Table 1). MOFs bearing coordinatively unsaturated Cu sites are commonly poor adsorbents due to Jahn–Teller axial distortion at the Cu sites.<sup>12,60</sup> Lacking substantial differences in binding strength between variants, the influence of the metal identity appears to be overshadowed by that of the ligand field in the  $\text{M}_2\text{Cl}_2(\text{btdd})$  series. The Lewis acidities of the metals are likely tempered by the electron-donating coordination environment of triazolate and chloride ligands. These ligands produce electron-rich metal centers that are less Lewis acidic than those found in other materials. Although these MOFs are capable of binding polar gases such as  $\text{NH}_3$ ,<sup>26</sup> the absence of a significant dipole moment on  $\text{N}_2\text{O}$  makes the  $\text{M}_2\text{Cl}_2(\text{btdd})$  MOFs ineffective  $\text{N}_2\text{O}$  adsorbents. Lacking suitable binding sites, the  $\text{M}_2\text{Cl}_2(\text{btdd})$  series show very limited uptakes; the quantity of  $\text{N}_2\text{O}$  adsorbed under equilibrium conditions, even at 1000 mbar  $\text{N}_2\text{O}$  and 298 K (Table 1), does not come close to saturating the available open-metal-sites.

Decreasing the ligand field strength surrounding the open-metal-sites should produce more Lewis acidic metal centers and thus lead to stronger electrostatic interactions with  $\text{N}_2\text{O}$ . Switching from  $\text{M}_2\text{Cl}_2(\text{btdd})$  to  $\text{M}_2(\text{dobdc})$  preserves the coordination geometry of the metal centers, but the oxygen-based SBU provides a weaker ligand field overall. Indeed, every

member of the  $\text{M}_2(\text{dobdc})$  series binds  $\text{N}_2\text{O}$  more strongly at low pressures than the  $\text{M}_2\text{Cl}_2(\text{btdd})$  MOFs (Fig. 2b). Moreover, the comparatively electron-deficient coordination environments in this series emphasize the influence of the metal identity on  $\text{N}_2\text{O}$  binding strengths; enthalpies of adsorption vary by as much as  $20 \text{ kJ mol}^{-1}$  among  $\text{M}_2(\text{dobdc})$  variants (Table 1).  $\text{N}_2\text{O}$  binding strengths in these series mirror the empirical Irving–Williams series:  $\text{Cu} < \text{Zn} < \text{Mn} < \text{Co} < \text{Mg} < \text{Ni}$ .<sup>61</sup> Like  $\text{Cu}_2\text{Cl}_2(\text{btdd})$ ,  $\text{Cu}_2(\text{dobdc})$  likely exhibits weak  $\text{N}_2\text{O}$  adsorption because of axial distortion.<sup>12</sup> In contrast,  $\text{Mg}_2(\text{dobdc})$  is an especially effective  $\text{N}_2\text{O}$  adsorbent due to the hard nature of its Lewis acidic  $\text{Mg}(\text{II})$  cations. As the effective charge of the transition metal centers increases from Mn to Ni,<sup>62</sup> the  $\text{N}_2\text{O}$  binding strengths increase as well. As a result,  $\text{Ni}_2(\text{dobdc})$  is the strongest  $\text{N}_2\text{O}$  adsorbent assessed in this study ( $-\Delta H_{\text{ads}} = 43.8 \pm 0.6 \text{ kJ mol}^{-1}$ ). Compared to other commonly studied gases ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$ ),  $\text{N}_2\text{O}$  is generally more strongly bound by the  $\text{M}_2(\text{dobdc})$  series, which is likely due to its modest dipole moment. In particular,  $\text{N}_2\text{O}$  binding is approximately  $2\text{--}6 \text{ kJ mol}^{-1}$  stronger than  $\text{CO}_2$  in all cases except for in  $\text{Mg}_2(\text{dobdc})$ , in which  $\text{CO}_2$  binds more strongly by approximately  $3 \text{ kJ mol}^{-1}$ .<sup>12</sup>  $\text{O}_2$  and  $\text{N}_2$  binding enthalpies are consistently  $10\text{--}20 \text{ kJ}$  lower than those of  $\text{N}_2\text{O}$  as well.<sup>63</sup> These findings highlight the discrepancy between the comparatively strong binding of  $\text{N}_2\text{O}$  at metal centers compared to  $\text{CO}_2$ ,  $\text{O}_2$ , and  $\text{N}_2$  and the lack of well-characterized  $\text{N}_2\text{O}$ -bound metal complexes.<sup>46–50</sup>

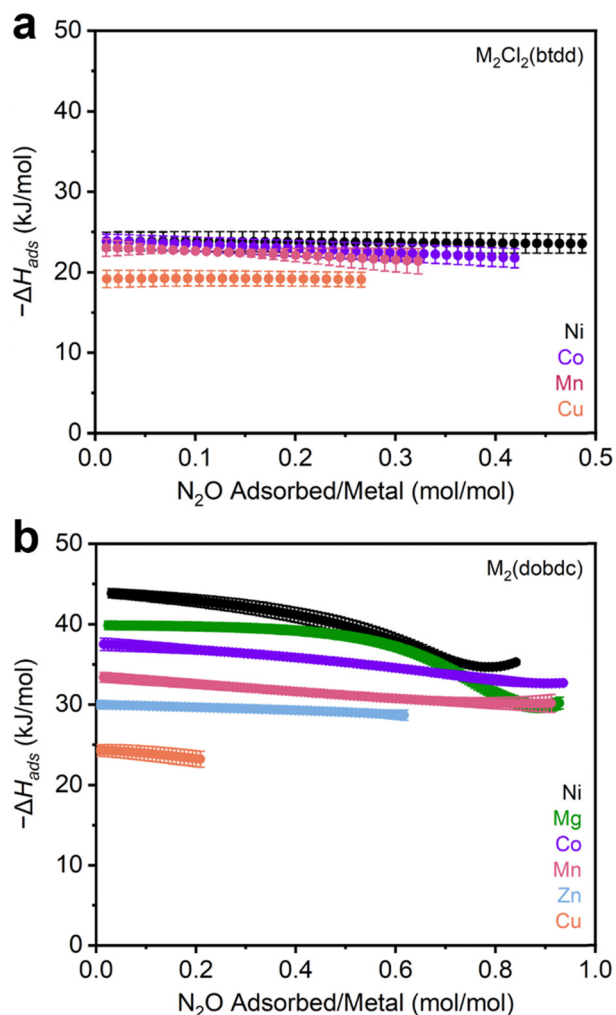


Fig. 2 (a)  $-\Delta H_{\text{ads}}$  vs.  $\text{N}_2\text{O}$  uptake calculated from  $\text{N}_2\text{O}$  adsorption isotherms in (a)  $\text{M}_2\text{Cl}_2(\text{btdd})$  ( $M = \text{Ni}, \text{Co}, \text{Cu}, \text{Mn}$ ) and (b)  $\text{M}_2(\text{dobdc})$  ( $M = \text{Ni}, \text{Mg}, \text{Co}, \text{Mn}, \text{Zn}, \text{Cu}$ ) MOFs.

Table 1  $\text{N}_2\text{O}$  adsorption enthalpies and maximum uptake values at 298 K in  $\text{M}_2\text{Cl}_2(\text{btdd})$  and  $\text{M}_2(\text{dobdc})$  MOFs

MOF	$-\Delta H_{\text{ads}} \text{N}_2\text{O}$ ( $\text{kJ mol}^{-1}$ )	Maximum uptake at 298 K ( $\text{mmol g}^{-1}$ )
$\text{Mn}_2\text{Cl}_2(\text{btdd})$	$23.0 \pm 1.1$	2.37
$\text{Co}_2\text{Cl}_2(\text{btdd})$	$23.9 \pm 0.8$	3.10
$\text{Ni}_2\text{Cl}_2(\text{btdd})$	$23.8 \pm 1.1$	3.49
$\text{Cu}_2\text{Cl}_2(\text{btdd})$	$19.2 \pm 1.1$	1.86
$\text{Mg}_2(\text{dobdc})$	$39.9 \pm 0.5$	8.75
$\text{Mn}_2(\text{dobdc})$	$33.4 \pm 0.6$	7.77
$\text{Co}_2(\text{dobdc})$	$37.5 \pm 0.8$	7.26
$\text{Ni}_2(\text{dobdc})$	$43.8 \pm 0.6$	6.44
$\text{Cu}_2(\text{dobdc})$	$24.3 \pm 0.7$	2.21
$\text{Zn}_2(\text{dobdc})$	$30.0 \pm 0.5$	5.37

Strong  $\text{N}_2\text{O}$  binding is accompanied by relatively high  $\text{N}_2\text{O}$  capacities in the  $\text{M}_2(\text{dobdc})$  series of frameworks. In particular, the second-strongest adsorbent of  $\text{N}_2\text{O}$  identified in this work,  $\text{Mg}_2(\text{dobdc})$ , adsorbs  $8.75 \text{ mmol g}^{-1}$  at 1000 mbar of  $\text{N}_2\text{O}$  and 298 K, surpassing the previous record-holder, MIL-100 (Cr)

( $5.78 \text{ mmol g}^{-1}$ , MIL = Materials Institute Lavoisier), by a significant margin.<sup>20</sup> The Mn, Co, and Ni  $\text{M}_2(\text{dobdc})$  variants also exceed the previous record for  $\text{N}_2\text{O}$  uptake in a MOF. Overall, this comparison underlines the  $\text{M}_2(\text{dobdc})$  series, especially  $\text{Mg}_2(\text{dobdc})$ , as promising adsorbents that exhibit high gravimetric  $\text{N}_2\text{O}$  capacities coupled with strong and tunable binding strengths.

### Computational survey of $\text{N}_2\text{O}$ adsorption.

After establishing the  $\text{M}_2(\text{dobdc})$  series as effective  $\text{N}_2\text{O}$  adsorbents, we further evaluated  $\text{N}_2\text{O}$  binding in this series using DFT calculations (Section S14, ESI†). For these calculations, trimetallic cluster models were generated to approximately study the one-dimensional chain SBU (Fig. 3a). Similar cluster models have been used to evaluate  $\text{N}_2\text{O}$  reduction in  $\text{Fe}_2(\text{dobdc})$ .<sup>40,41</sup> For each member of the  $\text{M}_2(\text{dobdc})$  series, excluding  $\text{Mg}_2(\text{dobdc})$  for redundancy, two types of cluster models were simulated: a trimetallic system and a Mg-diluted system. In the Mg-diluted models, both edge metal ions were replaced with  $\text{Mg}(\text{II})$  ions. The purpose of including the Mg-diluted systems is to simulate only one open-shell metal center and decouple adsorption energetics from the potential influence of metal-metal coupling on  $\text{N}_2\text{O}$  adsorption. All systems are neutral with all  $\text{M}(\text{II})$  ions in the high-spin state where applicable (Table S13, ESI†).

The energies of adsorption ( $-\Delta E_{\text{ads}}$ ) for both  $\eta^1\text{-N}$  and  $\eta^1\text{-O}$  coordinated  $\text{N}_2\text{O}$  adducts in the model clusters were first calculated (Fig. 3b–c and Table S11, ESI†). In both the trimetallic and Mg-diluted models,  $\eta^1\text{-O}$  coordinated  $\text{N}_2\text{O}$  is slightly more stabilized ( $2\text{--}10 \text{ kJ mol}^{-1}$ ) than  $\eta^1\text{-N}$  coordinated  $\text{N}_2\text{O}$ . This aligns with the approximately 60%/40%  $\eta^1\text{-O}/\eta^1\text{-N}$  population split determined from neutron diffraction data collected on  $\text{N}_2\text{O}$ -dosed  $\text{Fe}_2(\text{dobdc})$ .<sup>37</sup> The calculated formation energies of  $\text{N}_2\text{O}$  adducts in the Mg-diluted series (Fig. 3b) approximately match the trend observed experimentally:  $\text{Cu} \approx \text{Mn} < \text{Fe} \approx \text{Zn} < \text{Co} < \text{Ni} \approx \text{Mg}$ . However, some divergence is noted in the trimetallic systems (Fig. 3c): the Mn-based trimetallic system binds  $\text{N}_2\text{O}$  considerably more strongly than the equivalent Mg-diluted model, suggesting multiple metal effects that require consideration of metal-metal coupling (see below). Additionally,  $\eta^1\text{-N}$  coordination to  $\text{Mn}_2(\text{dobdc})$  is slightly more favorable than  $\eta^1\text{-O}$  in the trimetallic model.

Across the series, the model systems reveal that  $\eta^1\text{-O}$  and  $\eta^1\text{-N}$  adducts of  $\text{N}_2\text{O}$  are bent, with bond angles and  $\text{M}\text{--}\text{N}_2\text{O}$  distances in agreement with those solved from the neutron diffraction data in  $\text{N}_2\text{O}\text{--}\text{Fe}_2(\text{dobdc})$  (Table S12, ESI†), the only definitively characterized structure of  $\text{N}_2\text{O}$  bound to a metal center within a MOF reported to date.<sup>37</sup> In the DFT-calculated structure,  $\eta^1\text{-N}$  coordinated  $\text{N}_2\text{O}$  exhibits a typical bond angle of  $115\text{--}123^\circ$  ( $122^\circ$  in  $\text{N}_2\text{O}\text{--}\text{Fe}_2(\text{dobdc})$ ), whereas  $\eta^1\text{-O}$  coordinated  $\text{N}_2\text{O}$  exhibits slightly smaller bond angles ranging from  $105\text{--}120^\circ$  ( $117^\circ$  in  $\text{N}_2\text{O}\text{--}\text{Fe}_2(\text{dobdc})$ ). Bond lengths of  $\eta^1\text{-N}$  and  $\eta^1\text{-O}$  coordinated  $\text{N}_2\text{O}$  ( $2.25\text{--}2.57 \text{ \AA}$  and  $2.27\text{--}2.54 \text{ \AA}$ , respectively) vary over only a narrow range. These models reinforce that  $\text{N}_2\text{O}$  binding across the  $\text{M}_2(\text{dobdc})$  series is primarily based on electrostatic interactions rather than  $\pi$ -backbonding, which

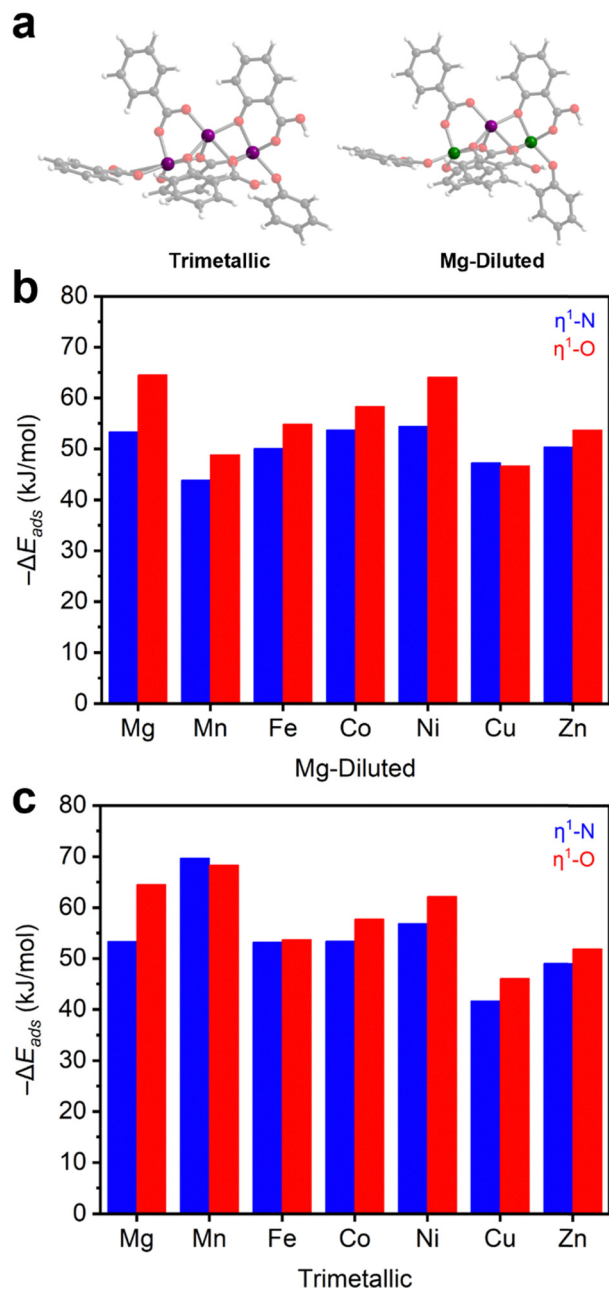


Fig. 3 (a) Trimetallic (left) and Mg-diluted (right) cluster models of  $\text{Mn}_2(\text{dobdc})$ . Purple, green, grey, red, and white spheres represent metal, magnesium, carbon, oxygen, and hydrogen atoms, respectively. DFT-calculated negative adsorption energies ( $-\Delta E_{\text{ads}}$ ) of  $\eta^1\text{-N}$  (blue) and  $\eta^1\text{-O}$  (red) coordinated  $\text{N}_2\text{O}$  in the (b) Mg-diluted and (c) trimetallic systems.

would be expected to lead to linear  $\eta^1\text{-N}$  (V, Cu, Ru, Rh) or side-on  $\eta^2\text{-N,N}$  (Co, Ni) interactions with  $\text{N}_2\text{O}$ .<sup>46–52</sup>

It should be noted that  $\text{N}_2\text{O}$  adsorption has been modelled previously in a small variety of other open-metal-site MOFs. The  $\text{Fe}(\text{II})$ - and  $\text{Cu}(\text{II})$ -based paddlewheel nodes in  $\text{M}_3(\text{btc})_2$  ( $\text{btc}^{3-}$  = benzene-1,3,5-tricarboxylate) MOFs show bent  $\eta^1\text{-N}$  and  $\eta^1\text{-O}$  coordination modes for  $\text{N}_2\text{O}$ .<sup>54</sup> Likewise,  $\text{N}_2\text{O}$  adducts have been modelled for the trinuclear carboxylate-bridged, oxygen-centered nodes ( $\text{M}_3(\mu_3\text{-O})(\text{RCOO})_6$ ,  $\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$ )

common among MOFs such as MIL-100, MIL-101, and MIL-127.<sup>64</sup> The calculated binding of  $\eta^1\text{-N}$  coordinated  $\text{N}_2\text{O}$  at V centers is linear, but other adducts are bent, with similar bond angles and bond lengths as calculated in the  $\text{M}_2(\text{dobdc})$  series herein. In the Kuratowski-type SBU of Cu-MFU-4l (MFU = Metal–Organic Framework Ulm–University), DFT calculations support an approximately linear  $\eta^1\text{-N}$  coordinated  $\text{N}_2\text{O}$  molecule, indicating possible  $\pi$ -backbonding from the Cu(I) centers.<sup>19</sup> Overall, these findings support that  $\text{N}_2\text{O}$  is predicted to bind in a bent fashion at most metal centers in MOFs.

A notable exception to the trends outlined above is the trimetallic Mn cluster, in which  $\eta^1\text{-N}$  coordinated  $\text{N}_2\text{O}$  is nearly linear ( $172^\circ$ ), suggesting that  $\pi$ -backbonding occurs from the Mn  $d$  orbitals into the  $\pi^*$  orbital of  $\text{N}_2\text{O}$ , which has previously been invoked in linear  $\eta^1\text{-N}$  V, Cu, Ru, and Rh adducts of  $\text{N}_2\text{O}$  to justify the stability of those complexes.<sup>46,48–50,52</sup> Consistently, the Mn–N bond length (1.95 Å) is considerably shorter than in other models (Fig. S68, ESI†). These characteristics are distinct from the equivalent Mg-diluted cluster, suggesting that metal–metal coupling may affect the binding mode of  $\text{N}_2\text{O}$  in these calculations. We thus evaluated  $\text{N}_2\text{O}$  binding in the open-shell trimetallic systems (Mn through Cu) using broken-symmetry density functional theory (BS-DFT) with two spin flip configurations (*i.e.*, in the central metal or in one edge metal) to quantify the metal–metal coupling and to extract coupling constants (Fig. S69 and Section S14, ESI†). To ensure that the BS-DFT calculations converged to the desired states, the spin density was visually inspected (Fig. S70, ESI†). In particular, the energetic difference in the trimetallic Mn system in comparison to the dilute case indicates especially strong metal–metal coupling (Table S14, ESI†). From this data, we calculated strong magnetic coupling along the SBU chains in the trimetallic Mn system ( $J = 314.27 \text{ cm}^{-1}$ ), which becomes even stronger after  $\text{N}_2\text{O}$  binding regardless of the coordination mode ( $J = 857.47 \text{ cm}^{-1}$  for  $\eta^1\text{-N}$ ,  $J = 857.47 \text{ cm}^{-1}$  for  $\eta^1\text{-O}$ ). Consistently, magnetic susceptibility measurements (Fig. S77, ESI†) and prior first principles studies support that  $\text{Mn}_2(\text{dobdc})$  exhibits antiferromagnetic coupling below approximately 27 K.<sup>62,65</sup> Adsorbate-induced changes in magnetic coupling are also predated in the  $\text{M}_2(\text{dobdc})$  series; for example, in  $\text{Fe}_2(\text{dobdc})$ , the ferromagnetic exchange strength along the SBU chains is attenuated by interaction with weak adsorbates (*e.g.*,  $\text{CH}_4$ ,  $-\Delta H_{\text{ads}} = 20 \text{ kJ mol}^{-1}$ ), and the coupling becomes antiferromagnetic upon interaction with strong adsorbates (*e.g.*,  $\text{C}_2\text{H}_2$ ,  $-\Delta H_{\text{ads}} = 47 \text{ kJ mol}^{-1}$ ).<sup>66</sup> Our results point to an additional stabilization of the  $\text{N}_2\text{O}$  adducts of  $\text{Mn}_2(\text{dobdc})$  related to enhanced metal coupling, possibly leading to greater  $\pi$ -backbonding from Mn to  $\text{N}_2\text{O}$  and favoring linear  $\eta^1\text{-N}$  coordination. Above 27 K, however, this effect is no longer expected to significantly contribute to the adsorption interactions as the spins become randomly oriented. Consistently, the experimental binding enthalpies do not show enhanced adsorption in  $\text{Mn}_2(\text{dobdc})$  relative to other MOFs in the series. Nevertheless, if a suitable Mn-based open-metal-site MOF with a higher Néel temperature were to be identified, this feature could potentially be leveraged to enhance  $\text{N}_2\text{O}$  binding.

Evaluating N<sub>2</sub>O activation in the M<sub>2</sub>(dobdc) series

N<sub>2</sub>O activation to form M(IV)-oxo species and N<sub>2</sub> in MOFs has been principally studied in Fe<sub>2</sub>(dobdc) and other Fe(II)-based frameworks.<sup>37–41,67,68</sup> Unfortunately, Fe(II)-based systems are prohibitively air sensitive for practical applications. Identifying more air-stable materials capable of N<sub>2</sub>O activation would be a significant step towards utilizing N<sub>2</sub>O as a green oxidant. In order to determine whether this reactivity is unique to Fe<sub>2</sub>(dobdc), the same cluster models were used to calculate the favorability of M(IV)-oxo formation in the remainder of the M<sub>2</sub>(dobdc) series (Table S15 and Section 14, ESI†). DFT calculations with both the trimetallic and Mg-diluted cluster model series show that, in addition to Fe<sub>2</sub>(dobdc), M(IV)-oxo formation is thermodynamically favorable ( $\Delta E_f < 0$  kJ mol<sup>-1</sup>) in Mn<sub>2</sub>(dobdc) (Fig. 4a and Section 14, ESI†). Indeed, M(IV)-oxo formation is calculated to be significantly more thermodynamically favorable in Mn<sub>2</sub>(dobdc) (−183.1 and −176.1 kJ mol<sup>-1</sup> for trimetallic and Mg-diluted systems, respectively) than in Fe<sub>2</sub>(dobdc) (−55.5 and −52.7 kJ mol<sup>-1</sup> for trimetallic and Mg-diluted systems, respectively). In contrast, M(IV)-oxo formation is endothermic in the Mg, Co, Ni, Cu, and Zn analogues, ruling out these materials as potential catalysts for N<sub>2</sub>O activation. This is fairly expected due to the electronic instability of terminal M(IV)-oxo complexes of octahedral symmetry possessing greater than five d electrons.<sup>69</sup> Precedent for N<sub>2</sub>O activation in Mn-based systems is found in manganese oxides, which catalyze the decomposition of N<sub>2</sub>O<sup>70</sup> and the oxidation of 1-butene at high temperatures.<sup>71</sup> Likewise, Mn-substituted polyoxometalates have been shown to activate N<sub>2</sub>O and catalyze the epoxidation of alkenes,<sup>72,73</sup> and Mn-substituted zeolites catalyze N<sub>2</sub>O decomposition as well.<sup>74,75</sup>

To determine the potential viability of N<sub>2</sub>O activation by Mn<sub>2</sub>(dobdc), an approximate reaction coordinate for this process was modelled using the CI-NEB method (Fig. 4b and Text S1, ESI†). The η<sup>1</sup>-O coordinated N<sub>2</sub>O adduct of the Mg-diluted Mn<sub>2</sub>(dobdc) cluster model was used as the initial state, and the Mn(IV)-oxo-containing Mg-diluted cluster was used as the final state (Section S14, ESI†). During N<sub>2</sub>O activation, the Mn(IV)-oxo bond is formed and the O–N bond is broken, forming N<sub>2</sub>. From the initial state, the M–O bond length shrinks significantly and is matched by a substantial lengthening of the O–N bond. During this transition, the energy of the system rises sharply early on, after which it falls to roughly the energy of the final state. Likewise, a constant M–O bond length, consistent with Mn(IV)-oxo formation, was observed in the second half of the reaction coordinate, as the rest of the pathway is characterized by O–N bond elongation as unbound N<sub>2</sub> moves away from the cluster. The approximate transition state of the reaction is rather early, with Mn–O and N–O bond lengths of 2.00 Å and 1.39 Å, respectively (Fig. 4c). From the difference in energy between the initial state and this approximate transition state, the kinetic barrier to N<sub>2</sub>O activation in this model cluster was calculated to be approximately 113 kJ mol<sup>-1</sup>. This barrier is comparable to the calculated activation barriers of 167 kJ mol<sup>-1</sup> in the Mn-based trinuclear MOF nodes and 109 kJ mol<sup>-1</sup> in the Mn-substituted polyoxometalate discussed above.<sup>64,73</sup>

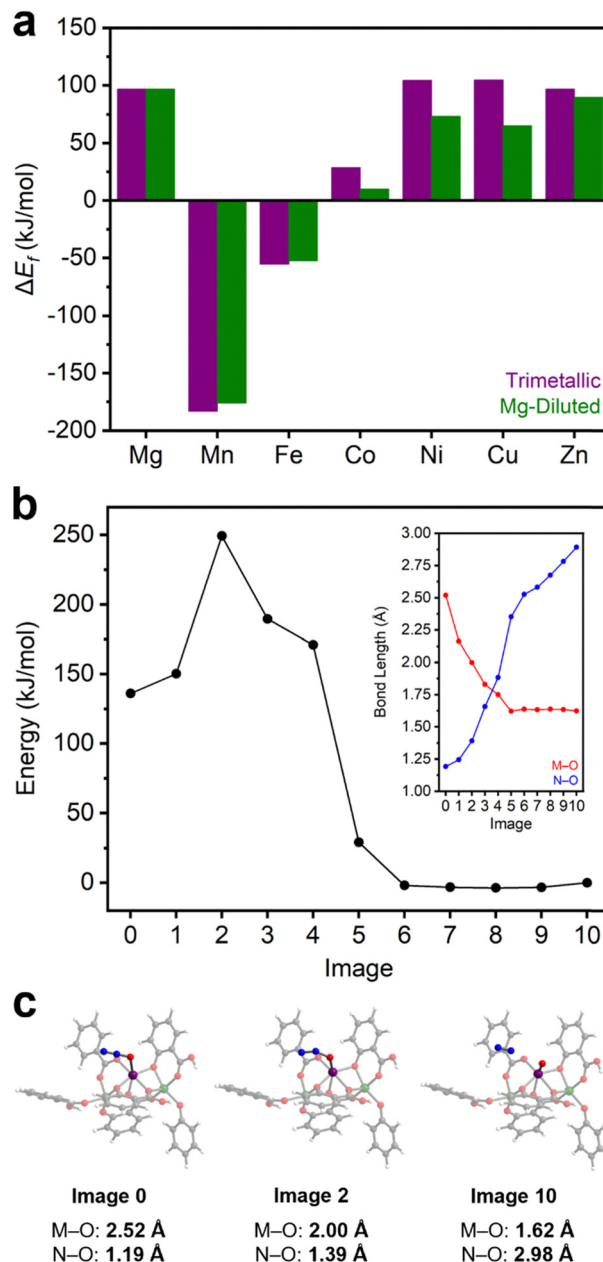


Fig. 4 (a) DFT-calculated energies of M-oxo formation ( $\Delta E_f$ ) in the trimetallic (purple) and Mg-diluted (green) models of M<sub>2</sub>(dobdc). (b) CI-NEB-calculated approximate reaction coordinate of Mn-oxo formation from η<sup>1</sup>-O coordinated N<sub>2</sub>O in the Mg-diluted system. Inset: M–O (red) and N–O (blue) bond lengths vs. image number. (c) Structures of the initial (left), transition (center), and final (right) states. Purple, green, blue, grey, red, and white spheres represent manganese, magnesium, nitrogen, carbon, oxygen, and hydrogen atoms, respectively.

In previous studies, heating N<sub>2</sub>O-dosed Fe<sub>2</sub>(dobdc) at only 35 °C was sufficient to partially oxidize the material, and its complete oxidation was accomplished at 60 °C after prolonged heating.<sup>37</sup> The activation barrier for Fe(IV)-oxo formation in N<sub>2</sub>O-bound Fe<sub>2</sub>(dobdc) was calculated to be 94 kJ mol<sup>-1</sup> (enthalpy of activation = 82 kJ mol<sup>-1</sup>).<sup>40</sup> While we note that the method used to calculate the barrier in Fe<sub>2</sub>(dobdc) differs

from this work, it is nonetheless a useful comparison. Although the calculated activation barrier for Mn(IV)-oxo formation in Mn<sub>2</sub>(dobdc) is notably larger, the conditions that lead to Fe(IV)-oxo formation in Fe<sub>2</sub>(dobdc) are mild. As such, we evaluated whether more forceful conditions (*i.e.*, higher temperatures) could enable Mn(IV)-oxo formation in Mn<sub>2</sub>(dobdc). To probe this possibility, N<sub>2</sub>O adsorption measurements in Mn<sub>2</sub>(dobdc) at 180 °C, 250 °C, and 300 °C were collected to identify potential N<sub>2</sub>O activation through changes in the adsorption properties of the material (Fig. S72, ESI†). Fully reversible N<sub>2</sub>O adsorption was measured at 180 °C; however, measurements at 250 °C and 300 °C consistently yielded anomalous negative adsorption, possibly indicating reactivity with the MOF. For further analysis, a bulk sample of Mn<sub>2</sub>(dobdc) was prepared by dosing the MOF with N<sub>2</sub>O at 300 °C (Section S15, ESI†). The BET surface area of Mn<sub>2</sub>(dobdc) after heating at 300 °C (1285 ± 3 m<sup>2</sup> g<sup>-1</sup>) under vacuum for 24 h is comparable to that of the pristine MOF (1344 ± 3 m<sup>2</sup> g<sup>-1</sup>), supporting that this MOF is stable at elevated temperatures. Notably, the BET surface area is significantly attenuated after N<sub>2</sub>O dosing at 300 °C (896 ± 2 m<sup>2</sup> g<sup>-1</sup>) (Fig. S73, ESI†). The reduction in surface area is accompanied by a color change from orange to brown. PXRD measurements confirm that Mn<sub>2</sub>(dobdc) retains its crystallinity after this process, although some peak-broadening was observed, indicative of partial decomposition (Fig. S74, ESI†).

Magnetic susceptibility measurements were used to characterize the product(s) resulting from high-temperature treatment of Mn<sub>2</sub>(dobdc) with N<sub>2</sub>O. The magnetic moments in Mn<sub>2</sub>(dobdc) calculated from susceptibility measurements before ( $\mu_{\text{eff}} = 5.94\mu_{\text{B}}$ ) and after ( $\mu_{\text{eff}} = 5.89\mu_{\text{B}}$ ) (Fig. S80 and S81, ESI†) N<sub>2</sub>O treatment at 300 °C closely match the value expected for Mn(II) with a spin of 5/2 (5.92 $\mu_{\text{B}}$ ), indicating a lack of oxidation at the metal center after N<sub>2</sub>O treatment (Fig. 5). Despite this, increased magnetic susceptibility relative to unreacted Mn<sub>2</sub>(dobdc) was consistently noted in

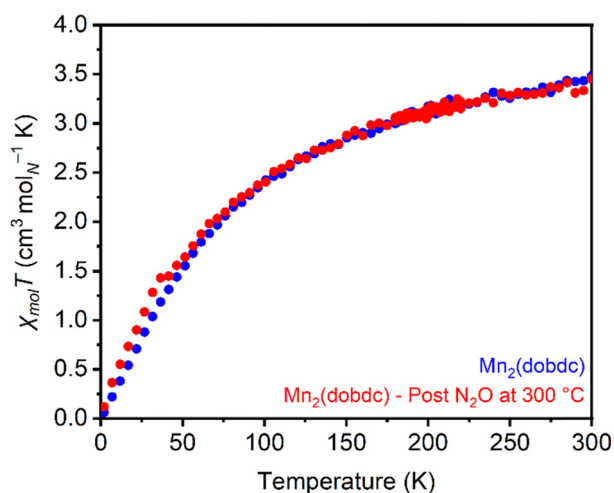


Fig. 5 Variable-temperature magnetic susceptibility ( $\chi_{\text{mol}}T$ ) measurements of Mn<sub>2</sub>(dobdc) under an applied field of 1000 Oe before (blue) and after (red) N<sub>2</sub>O treatment at 300 °C. The minor increase in  $\chi_{\text{mol}}T$  of the N<sub>2</sub>O-treated sample from approximately 2–40 K is attributed to slight O<sub>2</sub> contamination.

moment *vs.* field measurements collected at 5 K after N<sub>2</sub>O treatment at 300 °C (Fig. S82, ESI†). This finding may point to reactivity between N<sub>2</sub>O and the redox-active linker instead,<sup>76</sup> as oxidation of the high-spin Mn(II) sites to Mn(IV) should result in a decrease in the magnetic susceptibility.

To further characterize the reaction of Mn<sub>2</sub>(dobdc) with N<sub>2</sub>O, we utilized variable-temperature diffuse reflectance Fourier transform (DRIFTS) spectroscopy (Fig. S75 and S76, ESI†). A sample of Mn<sub>2</sub>(dobdc) was heated under an atmosphere of N<sub>2</sub>O (approx. 1 bar) from 25 °C to 300 °C and held at 300 °C for 15 h. Spectra were collected periodically throughout the duration of the measurement. New Mn–O stretches corresponding to Mn(IV)-oxo (approx. 845 cm<sup>-1</sup>)<sup>77</sup> or Mn(III)-OH species (600–700 cm<sup>-1</sup>)<sup>78</sup> were not observed (Fig. S76, ESI†). Likewise, stretches corresponding to quinone formation due to linker oxidation were not observed (1657 cm<sup>-1</sup>).<sup>76</sup> However, a weak O–H stretching frequency at 3673 cm<sup>-1</sup> emerged over time, and the prominent stretch at 1406 cm<sup>-1</sup> reduced in intensity after prolonged treatment with N<sub>2</sub>O (Fig. S75, ESI†). Overall, while the MOF appears to react with N<sub>2</sub>O at high temperatures, the DRIFTS and magnetic data indicate a lack of oxidation at the metal centers. This finding suggests that the high kinetic barrier to Mn(IV)-oxo formation in Mn<sub>2</sub>(dobdc) is likely prohibitive, despite its thermodynamic favorability. Elucidating the products of this MOF's reaction with N<sub>2</sub>O is the focus of ongoing work.

## Conclusions

Herein, we identify features that contribute to strong binding and high uptake of N<sub>2</sub>O at Lewis acidic, coordinatively unsaturated metal sites in MOFs. We utilize the M<sub>2</sub>Cl<sub>2</sub>(btdd) and M<sub>2</sub>(dobdc) series as model systems to facilitate comparisons, as their general structures are related but distinguished by the ligation of the open-metal-sites. In the M<sub>2</sub>Cl<sub>2</sub>(btdd) series, the binding enthalpies of N<sub>2</sub>O are generally low (<25 kJ mol<sup>-1</sup>) and within error, despite variations in the metal identity. In contrast, the salicylate-based SBU in the M<sub>2</sub>(dobdc) series provides a weaker, oxygen-based ligand field. N<sub>2</sub>O binding strengths in these MOFs mostly mirror the Irving–Williams series, with Ni<sub>2</sub>(dobdc) exhibiting the strongest adsorption of N<sub>2</sub>O among all tested MOFs ( $-\Delta H_{\text{ads}} = 43.8 \pm 0.6$ ). Notably, Mg<sub>2</sub>(dobdc) exhibits a record-breaking N<sub>2</sub>O gravimetric capacity (8.75 mmol g<sup>-1</sup> at 1000 mbar of N<sub>2</sub>O and 298 K) among MOFs. While these Lewis acidic sites are effective for N<sub>2</sub>O capture, they are not necessarily selective for N<sub>2</sub>O among other polar(izable) gases, such as H<sub>2</sub>O.<sup>79</sup> Achieving selective adsorption of N<sub>2</sub>O at open-metal-sites will be the focus of future work.

Using the cluster systems to computationally model the oxidation of the M<sub>2</sub>(dobdc) series by N<sub>2</sub>O, forming M(IV)-oxo species, we find that M-oxo formation is also thermodynamically favorable in Mn<sub>2</sub>(dobdc) according to DFT calculations. We thus used the CI-NEB method to map a reaction coordinate for this process and determined an approximate activation barrier of 113 kJ mol<sup>-1</sup>, which is higher than that calculated

for Fe<sub>2</sub>(dobdc) (94 kJ mol<sup>-1</sup>). Although experiments indicate that this kinetic barrier is too high to be overcome in Mn<sub>2</sub>(dobdc), these findings suggest that Mn-based MOFs may be promising alternatives to traditionally studied Fe-based materials for N<sub>2</sub>O activation.

Overall, this work adds to the growing body of research seeking to utilize N<sub>2</sub>O as a green oxidant, in which Mn-based solid-state catalysts remain relatively understudied. The results reported herein will help to drive the identification and development of other effective MOF-based sorbents to mitigate environmentally destructive N<sub>2</sub>O emissions.

## Author contributions

P. J. M and H. J. K. conceived the project. T. A. P. carried out the synthesis, characterization, and gas sorption measurements of MOF samples under the supervision of P. J. M. P. J. M. and M. E. Z. also synthesized MOF samples. H. J. and A. N. carried out computational studies under the supervision of H. J. K. T. J. A. carried out magnetic measurements. T. A. P. and H. J. prepared the first draft of the manuscript, which was edited and approved by all co-authors.

## Conflicts of interest

P. J. M. is listed as a co-inventor on several patents related to metal-organic frameworks.

## Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Award Number DE-SC0021000 (T. A. P., T. J. A., M. E. Z., P. J. M.). Computational modeling was supported by the National Science Foundation under Award Number CBET-1846426 (H. J., A. N., H. J. K.) as well as a National Science Foundation Graduate Research Fellowship under Grant 1122374 (to A. N.). T. J. A. thanks Cornell University for financial support through a recruiting fellowship. We acknowledge the support of a Camille Dreyfus Teacher-Scholar Award to P. J. M. (TC-23-048). This work made use of a Bruker 500 MHz spectrometer, the purchase of which was supported by the National Science Foundation (CHE-1531632). This work made use of the Cornell Center for Materials Research Shared Facilities, which are supported through the NSF MRSEC program (DMR-1719875). This work used Expanse at the San Diego Supercomputing Center through allocation CHE140073 from the Advanced Cyberinfrastructure Coordination Ecosystem: Services & Support (ACCESS) program, which is supported by National Science Foundation grants 2138259, 2138286, 2138307, 2137603, and 2138296. We thank Prof. Joseph Zadrozny (the Ohio State University) for helpful discussions.

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