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Neutron diffraction structural study of CO₂ binding in mixed-metal CPM-200 metal–organic frameworks†

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Metal–organic frameworks featuring open metal coordination sites have been widely studied for the separation of gas mixtures. For CO₂/N₂ separations, these materials have shown considerable promise. Herein, we report the characterization of a subset of the well-known PCN-250 class of frameworks upon CO₂ adsorption via powder neutron diffraction methods. Notably, in contrast to previously reported data, they display only moderate CO₂ adsorption enthalpies, based on metal cation–CO₂ interactions. Further, we show charge balance in these materials is likely achieved via ligand vacancies rather than the presence of μ₃-OH groups in the trimetallic cluster that comprises them.

In addition to the broad interest they draw as a result of their structural diversity and tunability,^{1,2} metal–organic frameworks (MOFs) have been thoroughly investigated over the past two decades as a result of their potential utility in gas storage³ and separation applications.⁴ Particularly in the case of the latter, they have been studied for hydrocarbon,⁵ noble gas,⁶ H₂/D₂,⁷ halogen,⁸ O₂/N₂,⁹ and CO₂/N₂ separations.¹⁰ MOFs containing metal cations with accessible coordination sites have shown promise here as these typically endow MOFs with high enthalpy and/or selective binding sites.¹¹ Although recent work has largely shown that MOFs featuring coordinatively-unsaturated metal cation sites may not be compatible with certain separation processes,¹² they have continued to receive considerable attention in this regard.¹³ For example, although many open metal site MOFs display incredibly high CO₂/N₂ selectivities,¹⁴ the presence of

H₂O in high concentrations in flue gas likely prevents their implementation in large-scale separation applications.¹⁵

In a more fundamental manner, the fact that many of these framework types are isolable for a range of transition metal cations makes them prime candidates to study spectroscopically¹⁶ and crystallographically.¹⁷ Although MOF-74 and HKUST-1 analogues are recognizable here, many other framework families offer this advantage.¹⁸ Members of the so-called soc-MOF (MIL-127, PCN-250, or CPM-200) frameworks are similarly isolable across a series of metals.¹⁹ The indium(III) version of this framework was first isolated over 10 years ago (Fig. 1).²⁰ The structure, M₃O(abtc)_{1.5} (abtc = 3,3',5,5'-azobenzene tetracarboxylate) has since been isolated for Fe(III), Mn(II), Ga(III), Al(III), and others.^{21–24}

These materials have shown high selectivities and uptake capacities for hydrocarbon separations,²⁵ methane and hydrogen storage,²⁶ and CO₂/N₂ separations.²⁷ Mixed-metal analogues are

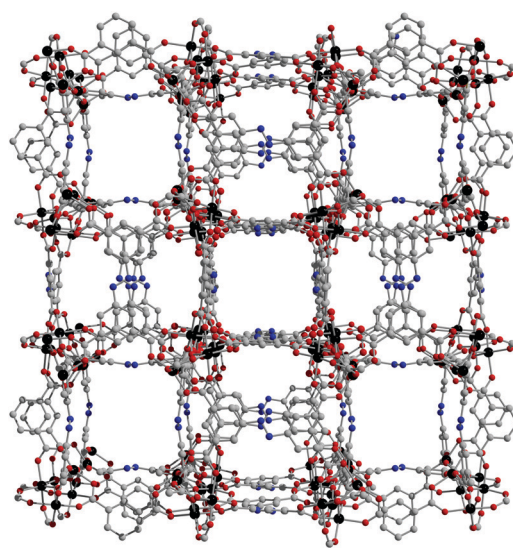


Fig. 1 A portion of the structure of CPM-200 (also known as MIL-127, TMBB, SNUU-61, and PCN-250). The square pores in the structure are based on M₃O(RCO₂) clusters and azobenzene tetracarboxylate ligands.

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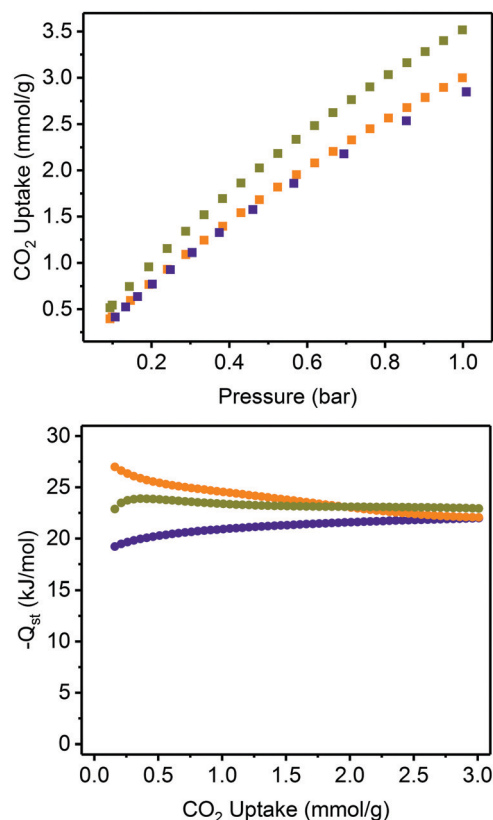


Fig. 2 (top) CO_2 adsorption PCN-250 at 298 K where the tan, orange and violet symbols represent uptake in the In/Mg, Fe/Mg, and V/Mg materials, respectively. (bottom) Isothermic heats of CO_2 adsorption in these frameworks.

also isolable for a wide variety of metal ions to afford CPM-200 frameworks,¹⁹ $\text{M}_1\text{M}_2\text{M}_2\text{O}(\text{abtc})_{1.5}$ where $\text{M}_1/\text{M}_2 = \text{V/Mg, Fe/Mg, In/Mg, In/Ni, In/Mn, In/Co, Ga/Mg, and Sc/Mg}$. It is notable that although the V/Mg and In frameworks were shown to display incredible CO_2 adsorption enthalpies in excess of -65 kJ mol^{-1} at low coverage, PCN-250 typically displays enthalpies more in line with those previously reported for MOFs with open M^{2+} or M^{3+} sites.²⁷

To further investigate the mechanism of CO_2 adsorption in these materials, we targeted the synthesis of a representative subset of these frameworks with the V/Mg, Fe/Mg, and In/Mg analogues. Their syntheses are relatively straightforward and involve the solvothermal reaction of mixed salt starting materials to afford mixed metal MOFs. The reported solvent exchange and activation procedures afforded Langmuir surface areas of 1492, 1577, and $1377 \text{ m}^2 \text{ g}^{-1}$ for V/Mg, Fe/Mg, and In/Mg, respectively. Although these values are slightly lower than those previously reported for frameworks of this composition, they are in good agreement with other reported PCN-250 and MIL-127 surface areas.^{21–24} Accordingly, 298 K CO_2 uptake at 1.0 bar is slightly lower than the reported values, although the shape of the isotherms are similar. Consistent with the shallow nature of the isotherms and by using a more reliable methodology to calculate adsorption enthalpies,³¹ the low coverage isosteric heats of adsorption are low and range from approximately -20 to -27 kJ mol^{-1} for all three frameworks (Fig. 2).

In order to more thoroughly understand the mechanism of CO_2 adsorption in these frameworks, we turned to powder neutron diffraction. Initially, powder diffraction patterns of activated materials were collected at $\sim 10 \text{ K}$ and Pawley fits were performed to obtain initial lattice parameters, peak shapes, background function, and to confirm that no impurity phases were present. Although a number of crystal structures have been reported for this framework type, they are in the solvated state. For the activated frameworks, the crystal structures were solved by the global optimization method of using simulated annealing in real space, using half of the abtc^{4-} linker as a rigid body, while allowing for rotation of the carboxylic acid groups and some deviation of nitrogen bond angles. High quality refinements were obtained once additional parameters were incorporated, including the addition of partially occupied H_2O molecule on the open metal site and allowing for fractional linker occupancies of less than unity, with the resulting Rietveld refinements displayed in Fig. S1–S9 (ESI[†]). VMg₂ and Fe₂Mg refinements included $\sim 2/3$ and $\sim 1/3$ metal equivalents of water respectively, the presence of which was confirmed with 99% certainty by Hamilton *R*-ratio tests.²⁸ Metal ratios were fixed at experimentally obtained values from inductively coupled plasma-optical emission spectroscopy (ICP-OES). Occupancies which refined within 1% of unity were fixed and thermal parameters were constrained to be identical for all atoms in the abtc^{4-} linker.

The charge counting in these mixed metal materials is particularly interesting and previously reported as $\text{M}_1^{3+}\text{M}_2^{2+}_2(\text{OH})(\text{abtc})_{1.5}$. In contrast to the previous single crystal X-ray measurements, neutron measurements are more sensitive to lighter Z elements, and did not indicate the presence of hydrogen atoms near the central metal-polyhedra oxygen, nor did the oxygen appear to be significantly off-center. Fits which split the position of the oxygen atom to off-center in both directions were also not preferred. This suggests a formula of $\text{M}_1^{3+}\text{M}_2^{2+}_2\text{O}(\text{abtc})_{1.5}$ which is charge imbalanced. Refinements were significantly worse when the central metal-polyhedra oxygen had an occupancy less than one, the metal occupancies were determined from ICP-OES, thus either abtc^- vacancies must exist or the material is charge imbalanced.

This observation prompted Hamilton *R*-ratio tests on both VMg₂ and InMg₂, both confirming with 99% certainty that the linker occupancy is reduced by $\sim 1/6$. This led to compositions of $\text{V}_{0.88(4)}\text{Mg}_{2.21(11)}\text{O}(\text{abtc})_{1.25(5)}(\text{H}_2\text{O})_{2.46(18)} (7.06(11)^+/7.00(18)^-)$ and $\text{In}_{0.90(5)}\text{Mg}_{2.10(11)}\text{O}(\text{abtc})_{1.26(6)} (6.90(12)^+/7.0(2)^-)$, both within error of charge balance. Similar linker vacancies have been previously observed and are even tunable for some MOFs.²⁹ In the case of UiO-66, however, the linker vacancy is occupied by a defect-compensating ligand from synthesis. It is likely then that these heterometallic MOFs also include a charge neutral defect-compensating ligand, such as MeOH or H_2O . To observe these reduced occupancy molecules requires further experimental analyses, such as IR/UV-vis and either EXAFS or total structure analysis, and hence we were not able to observe them here. The lack of such molecules in our model contributes to the imperfect refinement to the data.

Curiously, the heterometallic ratio of Fe₂Mg was not previously observed, rather it was reported as FeMg₂, similar to the

other materials presented herein and in contrast to the previously reported mixed Fe/Co framework which is nominally considered $\text{Fe}_2\text{CoO}(\text{abtc})_{1.5}$. Given this, our material is more accurately $\text{Fe}_{2.04(10)}\text{Mg}_{0.96(5)}\text{O}(\text{abtc})_{1.5}(\text{H}_2\text{O})_{1.17(13)}$ ($8.04(11)^+/8^-$), again within the error of being charge balanced. This balancing, along with observing a 2 : 1 rather than a 1 : 2 ratio, explains why the linkers for Fe_2Mg refined to unity rather than observing ligand vacancies.

For both VMg_2 and Fe_2Mg , it was observed that the carboxylic acid groups rotated to be in line with the metal atoms in the metal polyhedra. For InMg_2 however, the carboxylic acid groups rotated the opposite way, leading to significantly distorted polyhedra, which is common behavior for indium oxides.³⁰ No metal adsorbed water was observed for InMg_2 , though because indium scatters incoherently and introduces considerable structural disorder with distorted indium polyhedra, no peaks were observed beyond $Q = 2.2 \text{ \AA}^{-1}$. Hence it may be possible water is present, though it is unlikely due to the sensitivity that neutron diffraction has for low Z elements.

For CO_2 doses on Fe_2Mg , a water position was first determined in the bare structure, the occupancy of which (0.39) was uniformly similar at all three CO_2 loadings. As previously mentioned, there was no metal-bound water apparent in the InMg_2 structure. Upon dosing a single CO_2 molecule per metal cluster, a single adsorption site in each MOF sample is apparent (Fig. 3). For Fe_2Mg ,

the CO_2 molecule is O-bound and coordinated to the metal cation at a distance of $2.28(5) \text{ \AA}$ with an M–O–C angle of 115.7° and an occupancy of 0.42. The M–O distance is consistent with those previously reported for Mg-MOF-74 (2.36 \AA), Fe-MOF-74 (2.29 \AA), and Fe-BTT (2.36 \AA), while the M–O–C angle is approximately halfway between the values observed in Mg-MOF-74 and Fe-MOF-74 , 106° and 131° , respectively.^{31,32} At a loading of one CO_2 /cluster, the InMg_2 framework similarly displays a single adsorption site. Here, CO_2 is disordered over the three metal cations and adopts an η^2 configuration with M–O and M–C distances of $2.58(2) \text{ \AA}$ and $2.83(2) \text{ \AA}$, respectively. This geometry enforces a significantly diminished M–O–C angle of 89.5° with an occupancy of 0.35. Though the M–O distance appears long for InMg_2 , when the distance is corrected by the larger cationic radius of In^{3+} vs. Fe^{3+} ($\Delta 0.25 \text{ \AA}$) the M–O distance is in excellent agreement with CO_2 adsorption on open metal sites (2.33 vs. $\approx 2.3 \text{ \AA}$). The diminished CO_2 – InMg_2 angle is likely induced by the distortions in octahedral In^{3+} oxides. The origin of these distortions may be similar in nature to octahedral In^{3+} , which allow the HOMO and LUMO bands to split further due to differing symmetries.³³

At higher loadings (1.0 and 2.0 CO_2 /cluster) these sites show minimal changes. However, two additional crystallographically distinct adsorption sites are apparent. Of the two pore types in

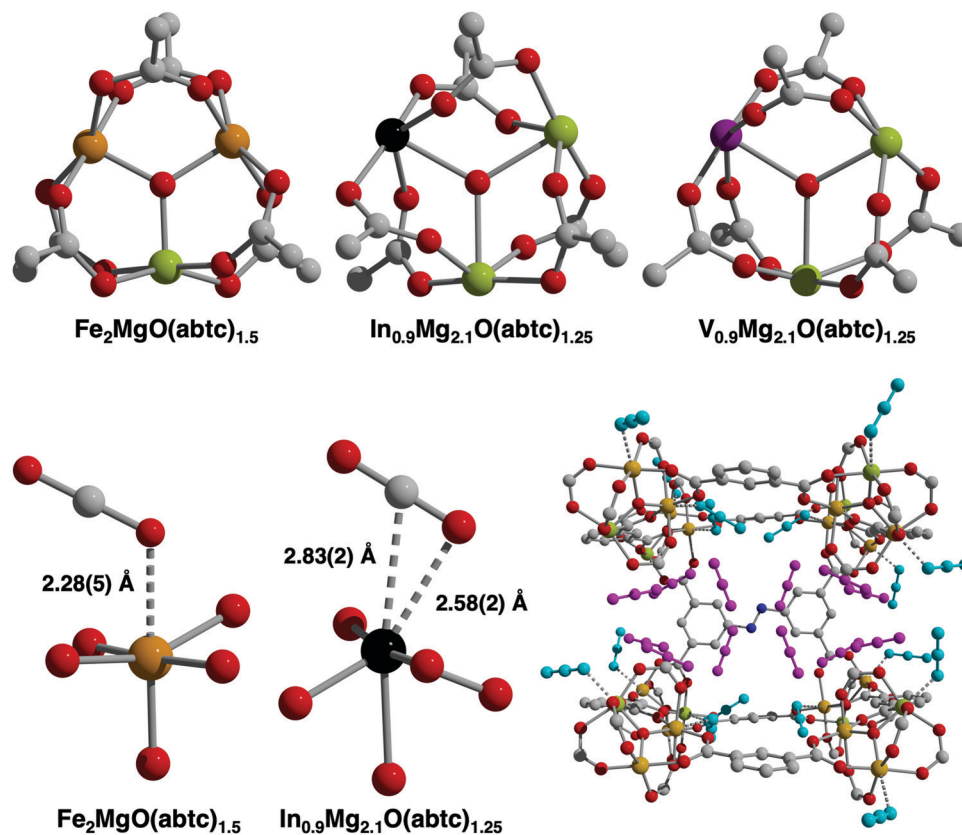


Fig. 3 Portions of the structures of CPM-200 as determined by neutron powder diffraction. (top) The M_3O SBUs in the activated materials where orange, green, black, violet, grey, and red represent iron, magnesium, indium, vanadium, carbon, and oxygen, respectively. Metal-coordinated water molecules have been omitted for clarity. (bottom) CO_2 in the Fe_2Mg and InMg_2 materials bind at the metal cation sites in the geometries shown. At higher loadings, additional CO_2 binding sites are apparent and are similar across both structures (bottom right).

the structure, all of the CO₂ molecules are found in the pore into which the metal cation sites are pointing. Here, CO₂ interacts with the corner and surface of the cubic pore at distances of 2.3–3.5 Å. These types of sites are similar to those observed in previously reported crystallographic studies.^{17,31,32}

The foregoing results shed light on both the mechanism of charge balancing in a family of mixed-metal MOFs and the nature of CO₂ adsorption in these materials. Although the mixed-metal variants of the PCN-250 (CPM-200) have been referred to as M₁M₂OH(abtc)_{1.5} their structures are more likely M₁M₂O-(abtc)_{1.5-x}. This interpretation of the neutron diffraction data is in line with previous M₃X (X = OH⁻ or O²⁻) structures which are most typically assigned as μ₃-O units. Additionally, the potential presence of linker defectiveness in these framework types may provide a means to tune their porosity, stability, and gas uptake properties going forward.

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Conflicts of interest

There are no conflicts to declare.

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