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Controlling the Adsorption of π -Acidic Gases in Iron(II)-Triazolate Metal–Organic Frameworks

By

Maria V. Paley

A dissertation submitted in partial satisfaction of the

requirements for the degree of

Doctor of Philosophy

in

Chemistry

in the

Graduate Division

of the

University of California, Berkeley

Committee in Charge:

Professor Jeffrey R. Long, Chair

Professor John Arnold

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Abstract

Controlling the Adsorption of π -Acidic Gases in Iron(II)-Triazolate Metal–Organic Frameworks

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Professor Jeffrey R. Long, Chair

The availability of coordinatively unsaturated metal sites within a rigid, extended structure has made metal–organic frameworks attractive scaffolds for the adsorption of a wide variety of gases. The work discussed in this dissertation focuses on the role of structural modification in the tuning of adsorption properties of iron-based frameworks, especially with gases of a π -acidic nature. A special emphasis is made on deconvolution of the structural and electronic factors that contribute to adsorption behavior and the insights that can be gleaned through the versatile powder X-ray diffraction technique.

Chapter 1 outlines past approaches to the synthesis of frameworks that exhibit selectivity for π -acidic gases, with a focus on carbon monoxide and hydrocarbon separations. This chapter discusses numerous mechanisms to achieve separations including size exclusion and kinetic separations but focuses on the role of unsaturated open metal sites in these separations. Works that employ structural and electronic modification techniques to enhance binding in open metal site MOFs are highlighted.

Chapter 2 discusses the synthesis of a series of novel mixed-metal MOFs that cooperatively adsorbs carbon monoxide gas through a spin transition mechanism. Control over the pressure at which the strong cooperative binding event occurs is demonstrated in $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$ ($x = 0.2, 0.5, 1$) ($\text{H}_2\text{btdd} = \text{bis}(1H\text{-}1,2,3\text{-triazolo}[4,5\text{-}b],[4',5'\text{-}i])\text{dibenzo}[1,4]\text{dioxin}$) by introducing varying quantities of chromium(III) sites into the framework lattice. A series of structural and electronic characterization techniques are employed to explain the origin of the mechanistic control. Powder X-ray diffraction shows that the mixed metal variants all undergo the same lattice contraction upon CO binding as the parent framework, but to a lesser degree with increasing Cr(III) content due to a decrease in unit cell volume of the bare framework. This is attributed to the smaller ionic radius of Cr(III) bringing the crystal lattice in its initial state closer to the volume of the lattice post-spin crossover, which decreases the barrier to transition. Infrared and Mössbauer spectroscopies confirm that the electronic contributions to gas binding amongst the variants are minor, making structural changes the dominant factor in controlling this gas adsorption mechanism.

Chapter 3 expands on the gas separation applications of mixed metal frameworks to the separation of alkynes, olefins and paraffins. The isorecticular, smaller pore analogue of the $\text{Fe}_2\text{Cl}_2(\text{btdd})$ framework discussed in *Chapter 2*, $\text{Fe}_2\text{Cl}_2(\text{bbta})$ ($\text{H}_2\text{bbta} = 1H,5H\text{-benzo}(1,2\text{-}d':4,5\text{-}d'')\text{bistriazole}$), was explored as well as a new mixed metal variant $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$. Acetylene gas adsorption isotherms showed that the frameworks have a total uptake double that expected for a ratio of one gas molecule per open metal site and that they both exhibit a selectivity for acetylene

over ethylene at room temperature. The calculated isosteric heats of adsorption for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}$ (bbta) indicated that the presence of chromium increased the binding strength of acetylene relative to the parent framework. The origin of this unexpected uptake was explored through powder X-ray diffraction which showed that the unit cell of the all-iron framework contracts upon exposure to acetylene, which is indicative of a chemisorptive interaction. Rietveld refinement of the gas dosed framework revealed a secondary binding site in the corners of the hexagonal pore channels. Infrared spectroscopy also confirmed the presence of two spectroscopically distinct binding sites, evidenced by two redshifted acetylene stretches in the gas dosed framework spectrum. It is hypothesized that the presence of terminal chloride anions on the Cr(III) sites in $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}$ (bbta) enhances acetylene binding through electrostatic interactions.

Powder X-ray diffraction plays a key role in deciphering the origin of gas adsorption phenomena in metal–organic frameworks as a whole and was a highlighted technique in *Chapter 2* and *3*. In *Chapter 4*, the versatility of powder X-ray diffraction is discussed along with some of the challenges that arise due to the nature of the technique. Contributions of powder X-ray diffraction analysis to several collaborative projects involving in frameworks exhibiting flexibility, ligand insertion and binding at open metal sites are described. Key insights in adsorption mechanisms and origins of selectivity derived from structural analysis are identified.

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Chapter 1: Structural and Electronic Considerations in the Design of Metal–Organic Frameworks for π -Acidic Gas Separations

1.1. Introduction and Background

Chemical separations are ubiquitous processes in industry, accounting for approximately half of industrial energy usage and, shockingly, 10-15% of total global energy usage each year.¹ The main cause of this excessive energy consumption is reliance on thermal separation techniques such as distillation, drying and evaporation.² Gaseous chemical separations are particularly challenging as they often contain mixtures of components with very similar chemical and physical properties.³ These separations are also critically important to the global economy, as gases such as ethylene and propylene are produced on such a massive scale that about 30 kg of the gases are produced per person annually.¹ Another valuable gas mixture known as syngas is composed of CO and H₂ which is produced through the steam reforming of methane or coal gasification.⁴ This gaseous mixture is used to produce many important commodities such as methanol or short-chain alkenes via the Fischer-Tropsch process. However, each of these applications requires a different CO:H₂ ratio, requiring recombination of the two gases after separation using cryogenic distillation.⁵ Due to the high energy demands of these separation processes, the development porous adsorbents such as activated carbons, zeolites and metal-organic frameworks for use in chemical separations is an active area of research.^{6–9}

Table 1.1. Selected physical parameters of π -acidic gases.³

Adsorbate	Boiling Point (K)	Kinetic Diameter (Å)	Dipole Moment (x10 ¹⁸ esu cm)	Polarizability (x10 ⁻²⁵ cm ³)
C ₂ H ₂	188.40	3.3	0	33.9-39.3
C ₂ H ₄	169.42	4.2	0	42.52
C ₂ H ₆	184.6	4.4	0	44.3
C ₃ H ₆	225.5	4.7	0.366	62.9
C ₃ H ₈	231.0	4.3-5.1	0.084	62.9
1-butene	266.92	4.5	79.9-85.2	0.359-0.438
<i>cis</i> -2-butene	276.87	4.23	-	0.253
<i>trans</i> -2-butene	274.03	-	84.9	0
CO	81.66	3.690	19.5	0.1098
H ₂	20.27	2.827-2.89	8.042	0
N ₂	77.35	3.64-3.80	17.403	0

Activated carbon and zeolite-based gas separations typically target differences in size and diffusion rates between the components of a gas mixture to achieve selectivity.^{6,8} These materials allow for the inclusion of heteroatoms which can impart some selectivity based on the electronic interaction of the adsorbate with the heteroatom.^{8,10} However, these atoms are often highly disordered within the material, making characterization using traditional methods such as X-ray crystallography inaccessible. Metal–organic frameworks combine the high material porosity of activated carbons and zeolites with the molecular level specificity of inorganic complexes allowing for their employment in high-performance separations. Thanks to their modular design, the material properties of MOFs can be tuned to enhance selectivity for a wide array of adsorbates and their crystalline order allows for careful characterization of the adsorbate-MOF interaction.¹¹

1.2. Physisorptive and Structure-Based Separations

Similarly to activated carbons and zeolites, many metal–organic frameworks employ size-exclusive molecular sieving mechanisms to achieve an effective separation of gaseous mixtures.¹² One mixture in particular that benefits from this separation scheme is that of acetylene from ethylene where the kinetic diameters of the components differ by almost an angstrom (Table 1.1). In the case of separations of ethylene over ethane, ethylene is adsorbed preferentially in a kinetic separation since its lower molecular weight and smaller kinetic diameter afford it with a smaller mean free path than that of ethane.¹³ A separation can be achieved if this mean free path is smaller than the pore aperture of the framework. In these separations, weak intermolecular interactions such as dispersion forces or electrostatics can also act as physisorptive binding sites, enhancing selectivity.¹⁴

One framework that employs this technique is $[\text{Cu}(\text{azpy})_2(\text{SiF}_6)]_n$ (azpy = 4,4'-azopyridine) (UTSA-200), a microporous metal–organic framework that, based on size, limits ethylene diffusion into its 3.4 Å pores and is able to retain acetylene through physisorptive interactions with the SiF_6 subunit.¹⁵ This allows for the framework to have high performance at very low concentrations of acetylene in feed streams, boasting an Ideal Adsorbed Solution Theory (IAST)¹¹ selectivity of 6000 for acetylene over ethylene at 1 bar and 1% acetylene concentration.

This same technique was employed in a separation of CO from H_2 in the framework $\text{Zn}_4\text{O}(\text{H}_2\text{O})_3(\text{adc})$ (H_2adc = 9,10-anthracenedicarboxylic acid) (PCN-13) which, in its hydrated form, has pores of 3.5 Å × 3.5 Å.¹⁶ When the aquo ligands are still in place, the framework exhibits a preference for binding H_2 since dihydrogen has a significantly smaller kinetic diameter than CO (Table 1.1). Once PCN-13 is fully activated at a higher temperature, which leads to removal of the bound water ligands, the framework has a reverse selectivity for CO over H_2 which can be attributed to the newly available binding sites within the zinc subunits.

Another type of structure-based separation mechanism that can be exploited by metal–organic frameworks is pore-gating in flexible materials. An example of this mechanism is in the material $\text{Co}(\text{MPTBDC})$ (H_2MPTBDC = 5-(3-methyl-5-(pyridin-4-yl)-4H-1,2,4-triazol-4-yl)-1,3-benzenedicarboxylic acid) (JNU-3) which exhibits a selectivity for propylene over propane.¹⁷ This selectivity is imparted by preferential electrostatic interactions of propylene with binding pockets that exist perpendicular to the one-dimensional channels of the framework. This leads to an expansion of the binding pocket for propylene at a pressure five times lower than that for propane.

1.3. Chemisorptive Mechanisms in Metal–Organic Frameworks with Open Metal Sites

The complexation of π -acidic gases with metal sites is an essential component of organometallic chemistry. For example, multitudes of carbonyl complexes exist due to the utility of carbon monoxide as a tool for spectroscopic characterization. Since carbon monoxide can act both as a σ -donating ligand and a π -accepting ligand, the C–O bond length, infrared stretching frequency or nuclear magnetic resonance chemical shift can be used as a metric for bond strength and inform on the electron donating or accepting ability of the metal site in question.¹⁸ The same can be said for π -complexes involving dihydrogen or hydrocarbon ligands in which the bond length or spectroscopic signatures play a key role in deciphering the bonding interactions with the available metal sites. These complexes also play an important role in the production of essential chemicals such as the Ziegler-Natta catalysts which are still widely used in the synthesis of polyethylene.¹⁹

A prerequisite for gas binding in molecular complexes is that the metal site must be unsaturated, containing an open coordination site. This holds true for metal–organic frameworks as well, if the interaction is to be classed as chemisorptive, where a chemical bond is formed

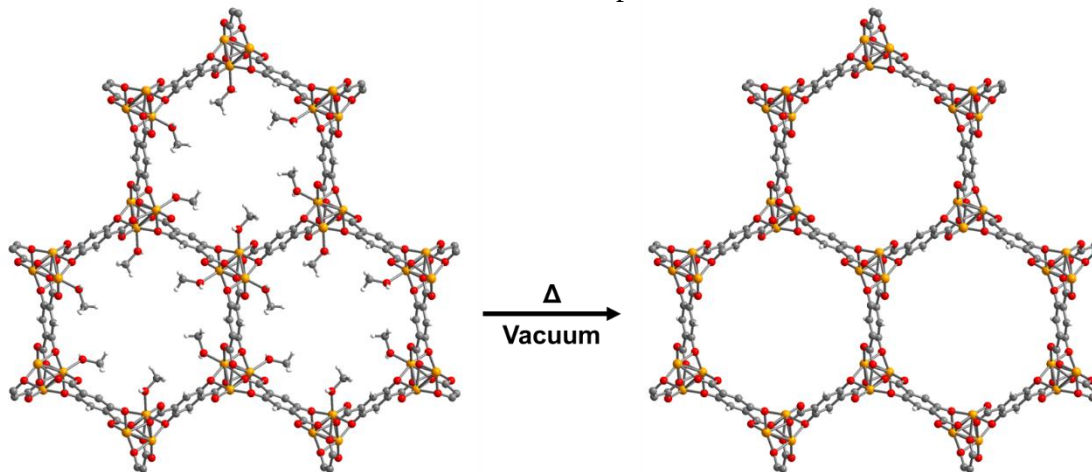


Figure 1.1. Left: Methanol solvated structure of $\text{Fe}_2(\text{dobdc})$. Upon heating under dynamic vacuum, the methanol is removed to reveal five-coordinate open metal sites (right).

between the absorbent and adsorbate.¹⁴ There has been significant interest in the synthesis of MOFs with open metal coordination sites or as they are often called “open metal sites” due to their relative geometric stability thanks to rigidity of the framework structure. In this class of MOFs, after synthesis, a solvent molecule, typically dimethylformamide, is bound to the open metal site and after exchange with a more weakly-coordinating solvent molecule, the open metal site can be accessed by heating the MOF under dynamic vacuum to remove adsorbed solvent (Figure 1.1).²⁰ Depending on the electronic characteristics of the ligand scaffold and the identity of the metal, these open metal site MOFs can be used to bind a variety of adsorbates, including π -acidic gases of interest including H_2 , N_2 , CO and hydrocarbons.^{21–24}

The first report of a framework with open metal sites was the copper-paddlewheel MOF $\text{Cu}_3(\text{btc})_2$ ($\text{H}_3(\text{btc})$ = benzene-1,3,5-tricarboxylic acid) (HKUST-1) which crystallizes with ligating water molecules that can be removed during activation.²⁵ The $\text{Cu}(\text{II})$ open metal sites of this framework generally bind adsorbates weakly because of the concentration of charge at the metal center.²⁶ It was later shown in a separate framework that the binding strength of dihydrogen and hydrocarbons could be greatly improved by introducing a $\text{Cu}(\text{I})$ open metal site into the framework $\text{Zn}_5\text{Cl}_4(\text{btdd})_3$ ($\text{H}_2(\text{btdd})$ = bis(1H-1,2,3-triazolo-[4,5-b],[4',5'-i])dibenzo-[1,4]-dioxin) (MFU-4l). This is a result of the increased diffusivity of the d-orbitals in the $\text{Cu}(\text{I})$ oxidation state which suggests that geometry, oxidation state, and metal identity are essential components in tuning interactions with π -acidic gases.²⁷

$\text{M}_2(\text{dobdc})$ (H_4dobdc = 2,5-dioxido-1,4-benzenedicarboxylate) or MOF-74 is a versatile framework containing helical chains of five-coordinate open metal sites that proceed down the c -axis of its hexagonal pores (Figure 1.1).²⁸ Each metal center is bound by two oxido and three carboxylate oxygen atoms which act as σ -donors, imparting a weak to intermediate ligand field on the metal centers which can have a variety of metal identities including, magnesium, manganese, iron, cobalt, nickel, copper and zinc.^{22,29} $\text{M}_2(\text{dobdc})$ (M = Mg , Mn , Fe , Co , Ni , Zn) was shown to exhibit reversible chemisorptive binding of carbon monoxide in which the binding strength varied

according to the electronic properties of the metal.²² As shown in Figure 1.2, variation of the metal identity leads to changes in M–CO bond strength as evidenced by the change in bond lengths in this first-row transition metal series. Additionally, the infrared spectroscopic studies of the CO dosed frameworks revealed that the Fe(II) framework had the strongest interaction with the

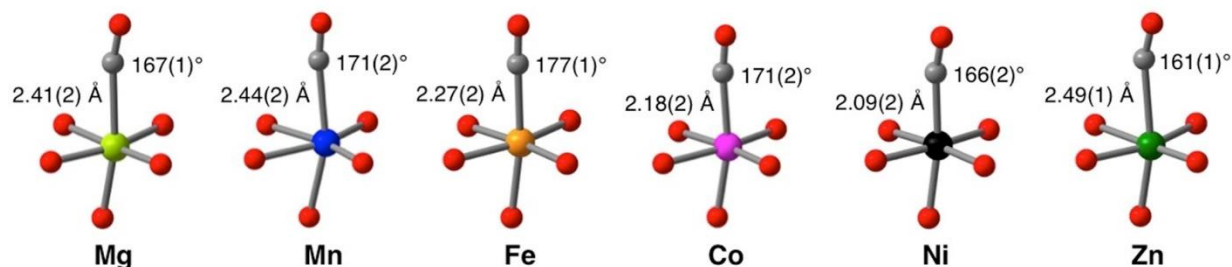


Figure 1.2. Primary coordination spheres of $M_2(\text{dobdc})$ ($M = \text{Mg, Mn, Fe, Co, Ni, Zn}$) frameworks with CO bound to the open metal site. M–CO bond lengths and M–C–O bond angles are included.²²

adsorbate, indicated by a stretching frequency centered at 2160 cm^{-1} which is equivalent to the stretch of free CO. All of the other M(II) variants exhibited stretching frequencies higher than that of free CO, which is characteristic of a non-classical interaction where CO is acting as a σ -donor ligand.³⁰ Of particular note is the absence of a spin crossover upon CO binding in the Fe(II) framework, confirmed through magnetic susceptibility measurements which show maintenance of the $S = 2$ ground state.

In another study focusing on $\text{Fe}_2(\text{dobdc})$ and its efficacy for the separations of hydrocarbon mixtures, it was found that the Fe(II) open metal sites have the ability to form π -bonding interactions with alkynes and olefins.³¹ Gas adsorption measurements revealed that the framework exhibits a selectivity for ethylene over acetylene and ethane at ambient temperatures as well as for propylene over propane which was confirmed through experimental breakthrough measurements. These selectivities were further investigated in a subsequent study which showed that $\text{Fe}_2(\text{dobdc})$ has the highest selectivity for ethylene over ethane in the $M_2(\text{dobdc})$ ($M = \text{Mg, Mn, Fe, Co, Ni, Zn}$) series, whereas $\text{Mn}_2(\text{dobdc})$ exhibits the highest selectivity for propylene over propane.³²

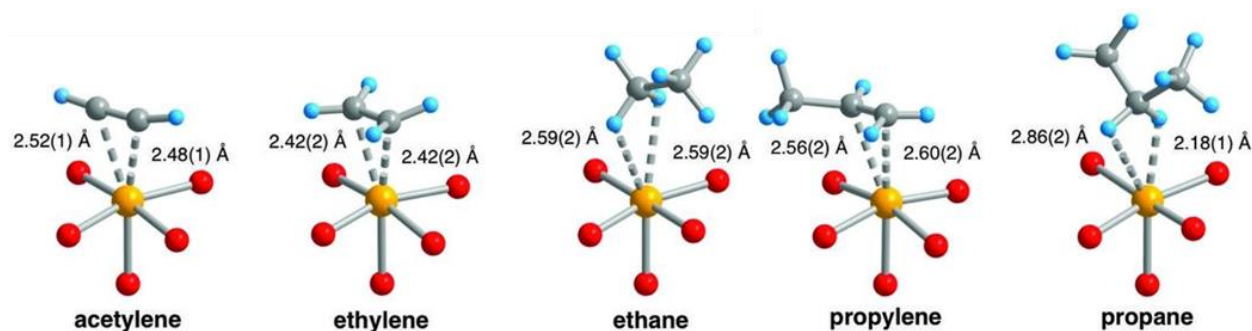


Figure 1.3. Primary coordination spheres for $\text{Fe}_2(\text{dobdc})$ bound to acetylene, ethylene, ethane, propylene and propane. Bond lengths for the closest M–C or M–H bonds with the adsorbate are shown.³¹

1.4. Tuning Structure and Electronics to Optimize π -Bonding Interactions

The tunability of the $M_2(\text{dobdc})$ series was further exploited in the synthesis of an isomeric ligand $\text{H}_4(m\text{-dobdc})$ where the oxido and carboxylate substituents are in the *meta*- positions

relative to one another, rather than *para*- as in the $H_4(dobdc)$ ligand. This affords the $H_4(m-dobdc)$ linker with a higher degree of electron donating ability as evidenced by initial studies showing exceptional hydrogen binding capabilities in the $Ni_2(m-dobdc)$ variant.³³ As a result of the efficacy of $Fe_2(dobdc)$ in hydrocarbon separations, $M_2(m-dobdc)$ ($M = Mn, Fe, Co, Ni$) frameworks were synthesized and investigated for use in olefin/paraffin separations.³⁴ IAST selectivity calculations from single-component olefin and paraffin isotherms revealed that the all $M_2(m-dobdc)$ frameworks had higher selectivities in the separation of ethylene from ethane and propylene from propane than their $M_2(dobdc)$ counterparts. The $Fe_2(m-dobdc)$ variant had the best performance of all the other metal variants which can be attributed to high enthalpy of adsorption as a result of better orbital energy matching with the adsorbate. A similar study used $M_2(dobdc)$ and $M_2(m-dobdc)$ ($M = Mn, Fe, Co, Ni$) frameworks to examine their utility in the separation of butene isomers.³⁵ It was discovered that the $Co_2(m-dobdc)$ and $Ni_2(m-dobdc)$ exhibited higher selectivities than the *para*- variants in separations of 1-butene over *cis*- and *trans*- butene. This was attributed to both electronic and structural differences in the frameworks which also crystallize in different space groups due to the symmetry of the linker.

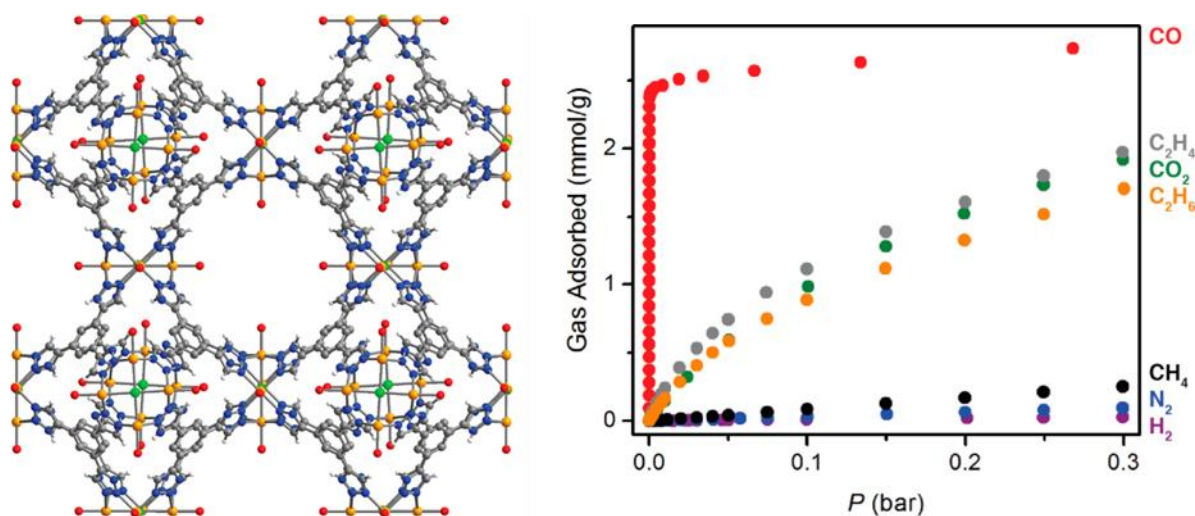


Figure 1.4. Left: Single crystal structure of dimethylformamide-solvated Fe-BTtri. Oxygen atoms of DMF molecules are in red, chloride atoms are green, iron open metal sites are orange, nitrogen atoms are blue, carbon atoms are grey and hydrogen atoms are white. Right: single component isotherms of various gases for Fe-BTtri.³⁶

Based on the weak binding of CO in the $M_2(dobdc)$ frameworks due to the ligand field afforded by the oxygen-based ligands, several new ligand scaffolds were investigated to further explore the possibilities carbon monoxide separations in open metal site MOFs. Triazolate ligands are extremely prevalent in the synthesis of molecular Fe(II) complexes that undergo spin-crossover phenomena, where the d-electrons depopulate the π^* antibonding orbitals upon some change to the external environment.³⁷ Towards that end, the framework $Fe_3[(Fe_4Cl)_3(BTtri)_8]_2 \cdot 18CH_3OH$ ($H_3BTtri = 1,3,5$ -tris(1H1,2,3-triazol-5-yl)benzene) (Fe-BTtri) was synthesized. Fe-BTtri is a cubic sodalite-type framework composed of subunits which contain four five-coordinate Fe(II) sites coordinated by four triazole ligands each and connected to the other iron sites in the subunit through a μ^4 -chloride anion.³⁶ It was found that Fe-BTtri adsorbs CO strongly with an enthalpy of adsorption of -65 kJ/mol due to a spin-crossover which occurs upon gas binding, confirmed through Mössbauer spectroscopy and magnetic susceptibility measurements. This spin crossover

only occurs upon binding of CO, leading to an extremely high IAST selectivity of 7400 for a 5% CO in a stream of hydrogen gas.

Although Fe-BTtri has a remarkable selectivity for carbon monoxide, due to its sodalite structure the framework has a low density of open metal sites leading to a relatively low overall adsorption capacity. In attempts to improve the CO adsorption capacity, a different triazole-based ligand, H₂(bbta) (H₂bbta = 1 H,5H benzo(1,2-d:4,5-d') bistriazole), was investigated.³⁸ This ligand is capable in producing two distinct framework morphologies, one being a framework isostructural with previously mentioned cubic framework MFU-4l, termed MFU-4.³⁹ Additionally a hexagonal phase, M₂X₂(bbta), is accessible which crystallizes with a morphology nearly identical to that of M₂(dobdc) with the exception of an additional bridging chloride being present in the helical c-axis chains.^{40,41} Fe₂Cl₂(bbta) was synthesized to investigate its carbon monoxide adsorption properties which revealed that this framework also undergoes a spin crossover upon CO binding, but due to the interconnectedness of the open metal in the hexagonal structure, it does so in a cooperative fashion.⁴² This leads to a step-shaped isothermal profile, shown in Figure 1.5, which is a marker of cooperative adsorption.⁴³ This mechanism was also proven to be tunable through the synthesis of Fe₂Cl₂(btdd), an isorecticular framework, which also exhibits the same CO adsorption profile, but a change in the pressure of the step-onset.

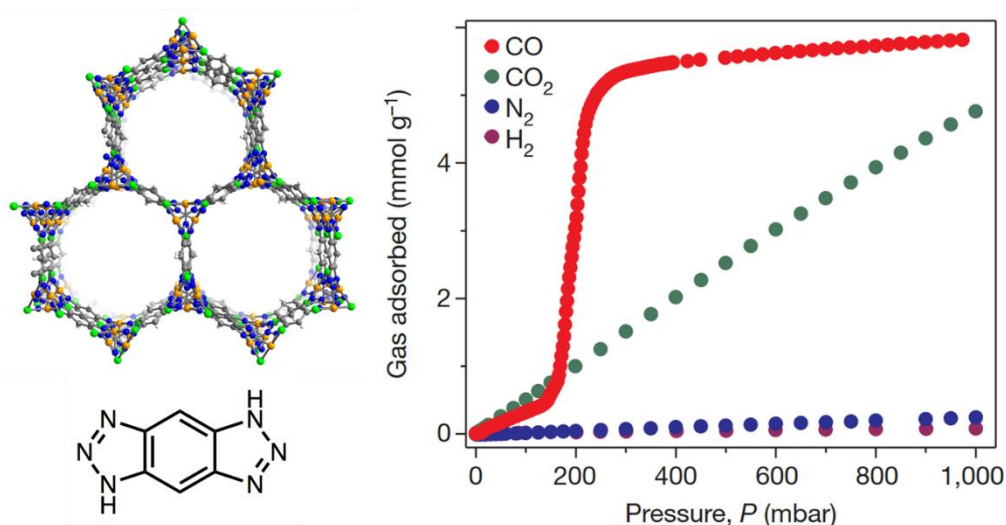


Figure 1.5. Top left is the structure of Fe₂Cl₂(bbta) shown looking down the c-axis, below which is the structure of the H₂(bbta) ligand. Right: single component isotherms for Fe₂Cl₂(bbta) which show cooperative CO adsorption (red) and weak adsorption for all other gases.⁴²

The M₂X₂(btdd) structure-type was shown to be further tunable for the adsorption of π -acidic gases through the synthesis of the framework V₂Cl_{2.8}(btdd).⁴⁴ This framework is isostructural to the Fe(II) framework with the exception of the presence terminally ligating chloride atoms that block accessibility of about 40% of the open V(II) sites due to the propensity of vanadium to exist in the V(III) oxidation state. This framework exhibits steep Langmuir-type uptake of dinitrogen at room temperature, which is rare in open metal site MOFs, thanks to the diffusivity of the V(II) d-orbitals. This framework also shows steep uptake of ethylene which affords an IAST selectivity for ethylene over ethane of 17 for a 5:95 ethylene:ethane mixture at 378 K.

1.5. Conclusions and Outlook

As described above, many frameworks exist for the capture and separation of π -acidic gases which yield a variety of separation mechanisms including, kinetic, sieving and thermodynamic. Of particular interest, due to the wealth of structural and fundamental chemistry insights that they afford, are metal–organic frameworks containing open metal sites. A myriad of structures exist which support these open metal sites, however hexagonal frameworks with helical chains of metals provide the advantage of a high density of open metal sites over other framework types. Several strategies exist for tuning adsorption properties in these frameworks, including varying the ligand and the identity of the transition metal, which can bring about significant changes in adsorption selectivity.

In general, it appears that the mid- to late transition metals iron, cobalt and nickel perform the best in terms of binding strength of alkynes, olefins and carbon monoxide indicating that the ability of the metal to π -backbond is essential to achieving selectivity in these separations. Additionally, by changing the identity of the ligand, a change in the mechanism of adsorption can be achieved, as was seen in $\text{Fe}_2\text{Cl}_2(\text{bbta})$ which undergoes a cooperative spin crossover upon binding of CO as opposed to Fe-BTtri which exhibits Langmuir-type adsorption. This present work seeks to expand on the methods by which the adsorption selectivity of π -acidic gases can be tuned and embark on a deeper mechanistic understanding of cooperative binding in Fe(II) -triazolate frameworks. Towards that end, a series of new materials were synthesized and characterized using a variety of structural and spectroscopic methods. Through these investigations, new insights were made which will hopefully be a meaningful contribution to the scientific understanding of gas adsorption in open metal site MOFs.

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Chapter 2: Cooperative Carbon Monoxide Adsorption in Mixed-Metal Metal–Organic Frameworks

2.1. Introduction

The continued rise in atmospheric CO₂ levels has now been widely recognized as a cause for grave international concern.¹ Mitigation of these rising emissions calls for the reevaluation of techniques used for well-established industrial practices such as chemical separations. Chemical separations account for over 50% of total industrial energy usage, and gaseous chemical mixtures introduce challenges during the separation process that require additional energy expenditure.² Cryogenic distillation leverages the disparate boiling points of gaseous mixture components to yield pure supplies of commodity chemicals such as alkenes and alkanes as well as to achieve streams containing appropriate CO/H₂ ratios for usage as syngas.³ Porous adsorbents have been extensively explored as replacements for cryogenic distillation because of their ability to separate gaseous mixtures at ambient temperatures and pressures.^{4,5} Composed of variable metal nodes and organic linkers, metal–organic frameworks have garnered significant interest due to the variation in gas binding sites that arises from this tunability, which often lead to unique adsorption profiles and mechanisms.

One of these profiles that is of particular interest is the Type V, or ‘step shaped’ isotherm.⁶ In nature, this isotherm shape is observed most notably in the uptake of oxygen by hemoglobin. This step shaped profile arises due to a cooperative process in which weak initial binding at vacant iron sites in the protein matrix leads to slight structural changes, making binding at subsequent sites more favorable.⁷ Type V isotherms are advantageous for applications in pressure and temperature swing adsorption processes because a larger working capacity can be achieved over a smaller pressure or temperature range, affording additional energy savings (Figure 2.1).⁸

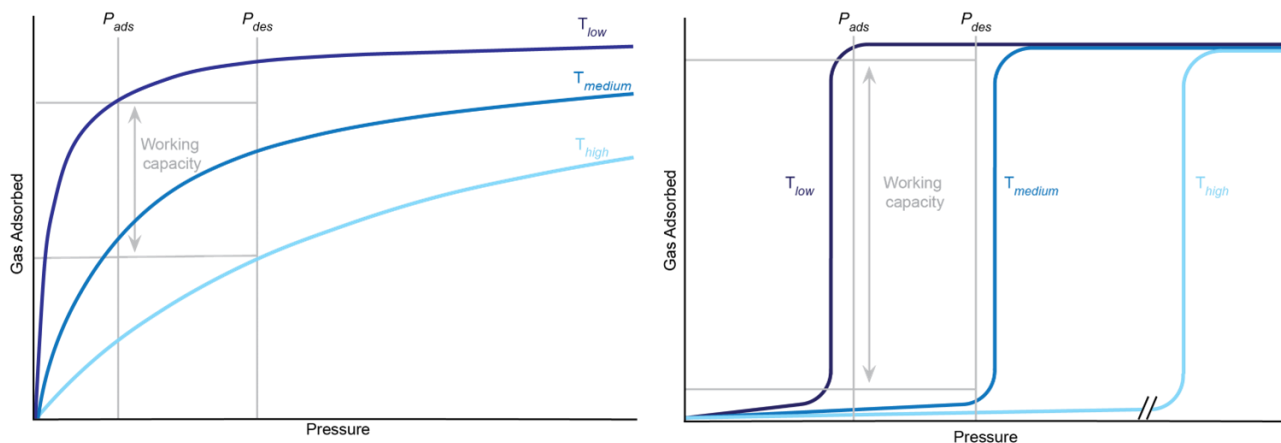


Figure 2.1 Left: Depiction of a Type I (left), or Langmuir, isotherm profile which achieves only a moderate working capacity with a large temperature swing. Right: Depiction of a Type V, or ‘step-shaped’ isotherm which has a large working capacity with a smaller temperature swing.

Several metal–organic frameworks have yielded step-shaped isotherm profiles through a variety of mechanisms.^{9–11} One mechanism is dictated by the cooperative adsorption of carbon monoxide via a spin crossover event. This mechanism was first observed in the frameworks Fe₂Cl₂(bbta) and Fe₂Cl₂(btdd) (H₂bbta = 1*H*,5*H*-benzo(1,2-*d*:4,5-*d'*)bistriazole) (H₂btdd = bis(1*H*-

1,2,3-triazolo[4,5-*b*],[4',5'-*i*]dibenzo[1,4]dioxin) which contain helical chains of five-coordinate iron(II) open metal sites that proceed down the crystallographic *c*-axis of the framework. At low pressures of CO, the Fe(II) sites interact weakly with the gas, but when a critical pressure is reached, the iron sites undergo a spin crossover which leads to a strengthening of the interaction with CO and a large uptake of gas over a narrow pressure range (Fig. 1.2).

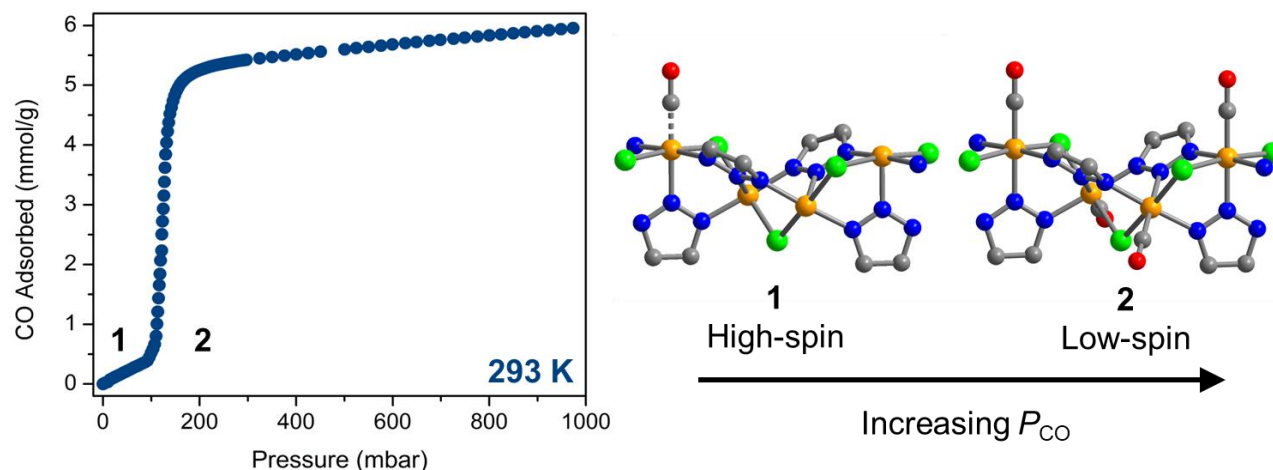


Figure 2.2. Left: a characteristic CO isotherm for $\text{Fe}_2\text{Cl}_2(\text{btdd})$, where region 1 corresponds to weakly chemisorbed CO bound to high-spin Fe(II) sites (right) and region 2 corresponds to strongly chemisorbed CO bound to low-spin Fe(II) sites.

Since the regions of strong uptake, or ‘steps’, fall into different pressure ranges for these two frameworks, it follows that the mechanism is tunable, but the structure of these frameworks provides multiple chemical handles by which the material can be modified. One of these handles is the introduction of a secondary transition metal into the helical chains of the framework. Metal dilution is a well-studied technique in molecular spin crossover complexes that is used to modify the spin crossover temperature and hysteretic behavior of the system which is a marker of the degree of cooperativity.^{12,13} Inclusion of a secondary metal also modifies the thermodynamic parameters associated with the spin crossover event including the ΔH of lattice elasticity and the ΔS of lattice vibrations due to changes in the lattice volume that arise from the difference in metal atomic radii and its impact on the crystal structure.^{14,15} This strategy provides a reliable way to modulate the spin crossover temperature in complexes that can undergo temperature induced spin transitions, but has not been employed in a metal–organic framework that experiences spin crossover due to a ligand binding event.

Here, we report the synthesis of a series of mixed-metal metal–organic frameworks of the $\text{Fe}_2\text{Cl}_2(\text{btdd})$ structure-type in which the technique of metal dilution is used to modify the gas binding properties. Carbon monoxide isotherms show that the pressure of step onset can be modulated by inclusion of a secondary metal as a result of changes in the volume of the crystal lattice. Electronic structure characterization including via infrared and Mössbauer spectroscopies reveals that the inclusion of a dilutive metal does not alter the strength of CO binding or the electron density at the Fe(II) binding sites, which suggests that the ΔH and ΔS parameters associated with the crystal lattice are being minimized as the iron fraction decreases.

2.2. Experimental

2.2.1. Materials and Methods

The $H_2(btdd)$ ligand was synthesized according to literature procedures¹⁶ with one modification: in the final triazole cyclization reaction, the $NaNO_2$ solution was cooled in an ice bath prior to addition to the reaction mixture. This yields a light tan solid, minimizing colored impurities that were observed with the literature procedure. All other reagents were purchased from commercial vendors and used without any further purification. All metal salts used for MOF synthesis were purchased in as mesh beads in ampoules sealed under inert gas at 99.999% purity. MOF syntheses and spectroscopic analyses (with the exception of STEM surface characterization) were performed air-free. Syntheses were performed in an Mbraun Unilab Pro glovebox using a nitrogen atmosphere. All gases used for adsorption, and all structural and *in-situ* spectroscopic measurements were ultra-high 5.0 (99.999%) purity. Inductively coupled plasma-optical emission spectroscopy used to determine metal ratios was performed on an Optima 7000 DV Spectrometer in the Microanalytical Facility at UC Berkeley.

$Fe_{2-x}Cr_xCl_{2+x}(btdd)$ was synthesized by combining the $H_2(btdd)$ ligand in a 1:2 molar ratio of ligand to metal salt. For $Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd)$ this translates to 1.85 mg of $CrCl_2$ (0.0150 mmol) and 17.1 mg of $FeCl_2$ (0.135 mmol). For $Fe_{1.5}Cr_{0.5}Cl_{2.5}(btdd)$ this corresponds to 4.62 mg of $CrCl_2$ (0.0375 mmol) and 14.3 mg of $FeCl_2$ (0.113 mmol). For $FeCrCl_3(btdd)$ the correct amounts of reactant are 9.23 mg of $CrCl_2$ (0.0751 mmol) and 9.52 mg of $FeCl_2$ (0.0751 mmol). 20 mg (0.0751 mmol) of the $H_2(btdd)$ ligand was weighed out into six separate 20 mL scintillation vials along with the metal salts in the desired ratio and dissolved in 10 mL of DMF. The six vials were sealed with Teflon tape and electrical tape then heated to 120 °C in an aluminum block for 4 days. If solid formed on the side of the vial over the course of the synthesis, the vial was shaken to break up the solid. After synthesis, the vials were removed from heat and vacuum filtered to remove the supernatant. The filtrate was collected and suspended in 20 mL of fresh DMF and heated to 120 °C for 24 h. The DMF was then decanted and replaced with fresh DMF. This process was repeated 5 times to reach a total of 6 washes. After the final DMF wash, the solvent was decanted and replaced with 20 mL acetonitrile (MeCN) which was heated at 60 °C for 24 h. The solvent was then decanted and replaced with 20 mL of fresh acetonitrile. This process was repeated 5 times to reach a total of 6 washes. After the final wash, the solvent was decanted, and the sample was pre-activated under vacuum at 120 °C for 2-3 h after which the sample was placed in a glass analysis tube suitable for a Micromeritics surface area and porosity analyzer (ASAP) and capped with a TranSeal, at which point it was heated under high vacuum at 150 °C, with a heating ramp rate of 2 °C/min for 3 days until an off-gassing rate of less than 3 $\mu\text{bar min}^{-1}$ had been achieved.

$Fe_{2-x}Zn_xCl_2(btdd)$ was synthesized by combining the $H_2(btdd)$ ligand in a 1:2 molar ratio of ligand to metal salt. For $Fe_{1.8}Zn_{0.2}Cl_2(btdd)$ this translates to 2.04 mg of $ZnCl_2$ (0.0150 mmol) and 17.1 mg of $FeCl_2$ (0.135 mmol). For $Fe_{1.5}Zn_{0.5}Cl_2(btdd)$ this corresponds to 5.12 mg $ZnCl_2$ (0.0375 mmol) and 14.3 mg $FeCl_2$ (0.113 mmol). For $FeZnCl_2(btdd)$ the correct amounts are 10.2 mg $ZnCl_2$ (0.0751 mmol) and 9.52 mg of $FeCl_2$ (0.0751 mmol). $Fe_{1.5}Co_{0.5}Cl_2(btdd)$ was synthesized combining 4.88 mg of $CoCl_2$ (0.0375 mmol) and 14.3 mg of $FeCl_2$ (0.113 mmol). Lastly, $Fe_{1.5}Ni_{0.5}Cl_2(btdd)$ was synthesized by combining 4.87 mg of $NiCl_2$ (0.0375 mmol) and 14.3 mg of $FeCl_2$ (0.113 mmol). The reaction mixtures were prepared via the same methods described above and the samples were washed and activated in the same manner as the chromium variants.

All mixed metal syntheses afforded about 60 mg of activated sample which corresponds to a 30% yield.

2.2.2. Powder X-ray Diffraction

High-resolution synchrotron X-ray powder diffraction data for all samples were collected at beamline 17-BM at the Advanced Photon Source at Argonne National Laboratory with a Perkin-Elmer *a*-Si flat panel detector. Diffraction patterns reported in this work were collected at a wavelength of 0.45213 Å. Samples were prepared in borosilicate glass capillaries which were dosed with 300 mbar of CO using a gas adsorption analyzer and flame sealed. The temperature was controlled during these measurements with an Oxford Cryosystems Cryostream 800. The crystal structure analyses including indexing, Pawley and Rietveld refinements were performed with the program TOPAS-Academic v4.1.16.^{17,18}

The space groups of all structures were determined by first indexing the powder patterns and performing a subsequent Pawley refinement to determine the goodness of fit for that combination of unit cell parameters. After obtaining accurate lattice parameters, the structural solution for the parent Fe₂Cl₂(btdd) framework was used as a structural model for Rietveld refinement.¹¹ All hydrogen atoms were added to the final refined structure using the CCDC program Mercury and therefore no error values are reported for these atoms in the structure information files.

2.2.3. Gas Adsorption

Gas-adsorption isotherms collected for pressures between 0 and 1 bar were measured volumetrically using a Micromeritics ASAP2020 or Micromeritics 3Flex gas adsorption analyzer. To perform these measurements, first, ~60 mg of sample was activated according to the methods previously described. To determine the mass of the sample, the analysis tube capped with a TranSeal was evacuated and weighed on an electronic balance. After activation, the tube containing the desolvated sample was then weighed and the mass of the sample was determined by subtracting the mass of the empty tube. The tube was then transferred back to the analysis port of the gas adsorption instrument. For all isotherms, warm and cold free-space correction measurements were performed using ultrahigh-purity He gas. Isotherms collected at 5–45 °C were measured in a Syltherm bath using a Julabo 200F water circulator filled with a water and ethylene glycol mixture. N₂ isotherms collected at 77 K were measured in liquid-nitrogen baths. Langmuir surface areas were determined from N₂ adsorption data collected at 77 K using Micromeritics software and BET surface areas were calculated using the BET equation.

2.2.4. Diffuse Reflectance Infrared Fourier-Transform Spectroscopy

Infrared spectra were collected using a Bruker Vertex 70 spectrometer equipped with a glowbar source, KBr beamsplitter, and a liquid nitrogen cooled mercury-cadmium-telluride detector. A custom-built diffuse reflectance system with an IR-accessible gas dosing cell was used for all measurements. Sample temperature was controlled by an Oxford Instruments OptistatDry TLEX cryostat, and sample atmosphere was controlled by a Micromeritics ASAP 2020Plus gas sorption analyzer. In a typical experiment, a sample of the desolvated framework material was dispersed in dry KBr (10 wt %) by gently mixing the two powders in an argon-filled glovebox and was subsequently evacuated at room temperature overnight. Spectra were collected in situ under UHP-grade carbon monoxide gas at 4 cm⁻¹ resolution until equilibrium was observed in both pressure

output and spectra. IRsotherms were performed by simultaneously measuring a gas adsorption isotherm on the ASAP 2020Plus and collecting IR spectra after carefully weighing out the sample mass during preparation to obtain accurate gas uptake values.

2.2.5. Mössbauer Spectroscopy

Mössbauer spectra were measured at 250 K with a constant-acceleration spectrometer, which uses a rhodium-matrix cobalt-57 source. Isomer shifts are reported relative to 27- μm α -iron foil at 295 K. *In-situ* measurements were performed in a home-built gas dosing cell composed of a copper outer casing and Teflon windows that are sealed by compressing an indium wire o-ring with a torque wrench. Stainless steel tubing leads into the copper casing using a 1/16 in. Swagelok connection, which allows the cell to be connected to a Micromeritics SmartVac activation manifold where the sample could be kept under dynamic vacuum or CO atmosphere during measurement. The sample was loaded into the cell in an Ar filled glovebox and evacuated in the cell for one hour prior to data collection. Average data collection time for samples varied from 24-96 h.

2.2.6. SQUID Magnetometry

Samples were prepared by placing the microcrystalline powder into a 5-mm-inner-diameter quartz tube. For non-gas dosed samples, the sample was mixed with eicosane which was then gently heated in a water bath to immobilize the sample and prevent crystallite torquing. The quartz tube was then flame sealed. For CO dosed measurements, the sample powders topped with a plug of compacted glass wool that prevented crystallite torquing, but enabled gas-dosing with CO. The CO-loaded samples were prepared by attaching the quartz tubes containing activated powder to a Micromeritics 3-Flex gas adsorption analyzer and dosing the sample with 300 mbar of CO. The quartz tubes were then cooled in liquid N₂ and flame sealed. Magnetic susceptibility measurements were performed using a Quantum Design MPMS2 SQUID magnetometer. Measurements of dc magnetic susceptibility were collected in the temperature range 2–300 K under applied magnetic fields of 1 T.

2.2.7. HAADF-STEM and EDS

The loose powder samples were crushed with a spatula and dispersed in dimethylformamide. A droplet was transferred onto a copper grid covered with lacey carbon and dried in air. Data was collected on an FEI TitanX microscope operated at 300 kV (Cs 1.2 mm). A Gatan HAADF detector was used for STEM. The HAADF STEM images were taken with a dwell time of 13 μs and a camera length of 130 mm (Fe₂Cl₂(btdd)) and 300 mm (Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd) and FeCrCl₃(btdd)). The scan step sizes were 10.20, 7.24, and 3.62 nm for the HAADF images of Fe₂Cl₂(btdd), Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd), and FeCrCl₃(btdd), respectively.

STEM EDS data was acquired using a Bruker windowless EDS detector (solid angle 0.7 steradians). A 40 μm condenser aperture was used for a beam convergence semi-angle of 10 mrad. The camera lengths were the same as those used for the HAADF images. The probe current was 2.09, 0.612, and 0.609 pA for the EDS scans of Fe₂Cl₂(btdd), Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd), and FeCrCl₃(btdd), respectively. EDS data was acquired with a scan step size of 20, 14, and 7 nm and pixel dwell times of 11, 28 and 28 μs for the Fe₂Cl₂(btdd), Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd), and FeCrCl₃(btdd) samples, respectively. EDS data was processed using Bruker ESPRIT software.

2.2.8. X-Ray Photoelectron Spectroscopy

The X-ray photoelectron spectroscopy (XPS) measurements were performed using the K-Alpha XPS System from Thermo Scientific. The photon source was a monochromatized Al K α line ($h\nu = 1486.6$ eV). The spectra were acquired using a spot size of 400 μm and constant pass energy. A combined low energy electron/ion flood source was used for charge neutralization. A vacuum transfer vessel was used to protect the sample from oxidation.

2.3. Results and Discussion

2.3.1. Design and Synthesis

When the parent framework $\text{Fe}_2\text{Cl}_2(\text{btdd})$ was initially reported, the synthesis and characterization of an isorecticular framework $\text{Fe}_2\text{Cl}_2(\text{bbta})$ was likewise undertaken.¹¹ Carbon monoxide gas adsorption isotherms revealed that both of these frameworks exhibited the same cooperative gas binding phenomenon that coincided with the spin-crossover event, however the pressure at which the step occurred, and in turn the spin crossover, differed for these two frameworks. Initial hypotheses attributed this occurrence to differences in the ligand field afforded by the $\text{H}_2(\text{bbta})$ and $\text{H}_2(\text{btdd})$ ligands, the former which contains just a benzene subunit, and latter containing the dibenzodioxin core.

Ligand field theory takes into account structural and electronic considerations of individual functional groups such as electron donating or withdrawing ability as well as the tendency of the moiety to engage in π -backbonding or σ -donation with the metal d-orbitals.¹⁹ Depending on these electronic characteristics, the energies of the d-orbitals are either more or less suited for mixing with the ligand bonding or anti-bonding orbitals and thus impart certain characteristics on the metal in question. According to traditional ligand field arguments, the nitrogen atoms in the triazole ligands act primarily as intermediate strength σ -donating ligands, while the halogen atoms, present in the helical chains of these frameworks, act as weak field π -donating ligands. By increasing the ligand field strength at the Fe(II) open-metal sites, the d-orbital splitting energy should also increase by allowing for increased orbital mixing with ligand-based bonding orbitals. This in turn makes it less favorable for the metal centers to adopt a high-spin configuration and brings the framework overall closer to the point of spin crossover, thereby decreasing the energy barrier to achieve this transition and lowering the step pressure. Based on resonance arguments, the dibenzodioxin core of the $\text{H}_2(\text{btdd})$ ligand affords the central triazole nitrogen with an increased σ -donating ability, whereas the two peripheral nitrogen atoms should have slightly less electron density. The same argument cannot be made for the $\text{H}_2(\text{bbta})$ ligand which should have approximately equal electronic contributions through all three triazole nitrogen atoms due to the absence of heteroatoms in the non-triazole portion of the linker.

Based on these assertions, it was speculated that a series of $\text{Fe}_2\text{X}_2(\text{btdd})$ frameworks could be synthesized where the bridging chloride atoms were replaced with other anions. This proved to be synthetically challenging, but one variant was accessible via direct synthesis from the corresponding Fe(II) salt: $\text{Fe}_2\text{Br}_2(\text{btdd})$. Attempts to synthesize a fluoride variant were unsuccessful using multiple synthetic routes including direct synthesis using FeF_2 . Attempts at

post-synthetic exchange in $\text{Fe}_2\text{Cl}_2(\text{btdd})$ using inorganic fluoride sources such as CsF and KF as well as quaternary ammonium salts such as tetramethylammonium fluoride and tetrabutylammonium fluoride led to either no change in the powder X-ray diffraction pattern or extreme loss of crystallinity. Attempts were also made to access the hydroxide variant of this framework structure type using ammonium hydroxide and potassium hydroxide; however, since these exchanges required the use of aqueous solutions, they revealed an underlying water instability in the base framework.

Due to the inaccessibility of anion substitution in the $\text{Fe}_2\text{X}_2(\text{btdd})$ -type frameworks, an alternative synthetic route was explored for probing the nature of the spin-crossover event and controlling the gas adsorption properties of these frameworks: mixed-metal framework synthesis. Metal-dilution, or inclusion of a secondary metal in a spin-crossover system, has been explored in molecular systems and coordination polymers that undergo temperature-induced and light-induced crossover phenomenon.^{12,20,21} These studies reveal that inclusion of a secondary metal change the external conditions that are required for spin-crossover to occur in these materials due to changes in the lattice cooperativity afforded by the inhomogeneity of the metals. Therefore dilution of the Fe(II) sites in the $\text{Fe}_2\text{Cl}_2(\text{btdd})$ framework was undertaken to modify the cooperative gas adsorption behavior of these materials.

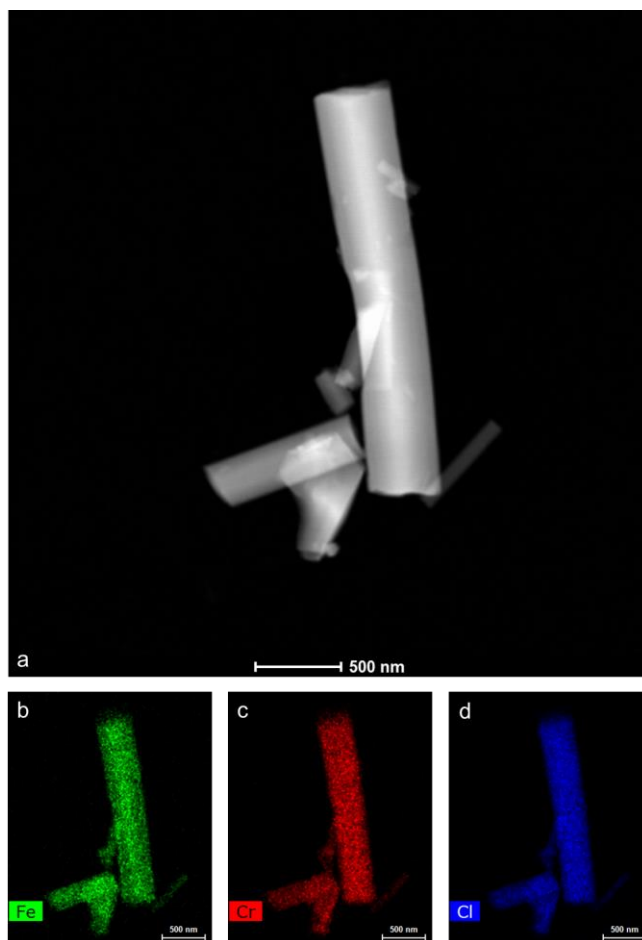
Towards that end, a series of mixed metal MOFs were synthesized according to the formulae $\text{Fe}_{2-x}\text{M}_x\text{Cl}_2(\text{btdd})$ ($\text{M} = \text{Co}, \text{Ni}$), ($x = 0.5$), $\text{Fe}_{2-x}\text{Zn}_x\text{Cl}_2(\text{btdd})$ ($x = 0.2, 0.5, 1$) and $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$ ($x = 0.2, 0.5, 1$). These frameworks were readily synthesized via solvothermal synthesis by combining the desired ratio of metal chloride salts along with the $\text{H}_2(\text{btdd})$ ligand in dimethylformamide. These frameworks were determined to be isostructural to the parent compound by powder X-ray diffraction and metal ratios were determined post-synthetically by ICP-OES. The trivalent oxidation state of the chromium present in the mixed iron-chromium system should be noted since, as stated in the Materials and Methods section, divalent chromium chloride is used in the synthesis of these frameworks. This oxidation of the metal salt during solvothermal synthesis is consistent with what was seen in the unreported synthesis of $\text{Cr}_2\text{Cl}_3(\text{btdd})$ performed by former members of the Long group. Although these frameworks were synthesized in rigorously air and water-free conditions, the affinity of DMF for water makes it difficult to fully dry. It is well understood that during syntheses that occur at high temperatures, in the presence of water, DMF decomposes in a redox reaction to form a mixture of dimethylamine, CO and formates.²² This process is also required to form many MOFs that are synthesized in the absence of acid or base modulators, as the dimethylamine acts as the base that deprotonates the organic linker. It is the current hypothesis that during redox decomposition process, the CrCl_2 metal salt is oxidized to form the Cr(III) sites that are present in the final framework. Due the challenges of weighing materials in air-free environments, occasionally the desired ratios of 10%, 25% and 50% Cr(III) or Zn(II) were not achieved as confirmed by ICP-OES and the exact ratios will be reported for experiments where the values are relevant to experimental understanding.

2.3.2. Structural Characterization via HAADF-STEM and EDS Mapping

Mixed-metal MOFs can produce several challenges when it comes to characterization in the bulk with techniques such as ICP-OES, due to the statistical heterogeneity of individual crystals. When including multiple metals in a MOF synthesis it is important to confirm that the resultant crystallites contain both metals instead of forming discrete crystals of one metal or another. Mixed-metal metal-organic frameworks can adopt multiple morphologies including those where the

metals are randomly distributed throughout the framework, as well as where a core of one metal is formed initially and a shell of a secondary metal forms around it.²⁷ To shed light on some of these outstanding questions with regards to $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$ frameworks, High-Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) and Energy Dispersive X-ray Scattering (EDS) mapping were used to characterize the chromium containing variants in this series.

Figure 2.3a shows an HAADF-STEM image of $\text{FeCrCl}_3(\text{btdd})$ which is composed of rod-shaped crystals approximately 0.5 microns in diameter and 2.5 microns in length. This crystal morphology is consistent with what is typically observed for the $\text{M}_2\text{X}_2(\text{btdd})$ framework type which should have one long axis due to its one-dimensional pore structure.²⁸ EDS mapping was performed on the same crystallite and is shown for iron (Figure 2.3b), chromium (Figure 2.3c) and chlorine (Figure 2.3d). This technique reveals that these elements are evenly distributed throughout the crystallite, however there is some variation from crystallite to crystallite in the ratio of metals observed. As another indirect measure of chromium oxidation state in this framework, chlorine mapping was performed which revealed a ratio of chloride to metal that is commensurate with the increase expected for the chromium content of the sample (Table 2.S8). Lastly, to confirm that there is no core-shell of iron or chromium forming during synthesis a HAADF-STEM line scan was performed (Figure 2.S22). This reveals that the concentration of both metals is even throughout the cross section of the crystallite, including at the edges, which would show a higher signal for one of the metals if a core shell effect was present. Additionally, XPS data probing the



metal content through the entire depth of the crystallite provided a signal for both elements at every scan point.

Figure 2.3. HAADF-STEM image of several crystals of $\text{FeCrCl}_3(\text{btdd})$ (a). The lower images show EDS mapping on the same crystals for iron (b), chromium (c), and chlorine (d).

2.3.3. Gas Adsorption

Carbon monoxide gas adsorption isotherms were performed for all materials to determine the effects of metal dilution on gas adsorption properties of these mixed metal frameworks. Figure 2.4 shows room temperature CO isotherms for $\text{Fe}_{1.5}\text{Co}_{0.5}\text{Cl}_2(\text{btdd})$ and $\text{Fe}_{1.5}\text{Ni}_{0.5}\text{Cl}_2(\text{btdd})$. These two frameworks exhibit unique isotherm shapes due to the fact that both secondary metal cations also form open metal binding sites accessible to CO, as isostructural $\text{Co}_2\text{Cl}_2(\text{btdd})$ and $\text{Ni}_2\text{Cl}_2(\text{btdd})$ frameworks have been previously reported.²³ This leads to the superposition of a Langmuir Type-I isothermal profile at low pressures with the step that occurs upon spin-crossover of the Fe(II) sites at higher pressures. As shown by the relative steepness of the pre-step region below 400 mbar in $\text{Fe}_{1.5}\text{Ni}_{0.5}\text{Cl}_2(\text{btdd})$, the Ni(II) open metal sites uptake CO more strongly than the Co(II) sites. The step onset for $\text{Fe}_{1.5}\text{Co}_{0.5}\text{Cl}_2(\text{btdd})$ occurs at 753 mbar, which is shifted to higher pressure relative to the step of the parent framework at 400 mbar, whereas the step onset for $\text{Fe}_{1.5}\text{Ni}_{0.5}\text{Cl}_2(\text{btdd})$ is located at 345 mbar. It is likely that higher pressures of CO are required to view the full step of $\text{Fe}_{1.5}\text{Co}_{0.5}\text{Cl}_2(\text{btdd})$ as at 1000 mbar the region of steep uptake has only just begun to taper.

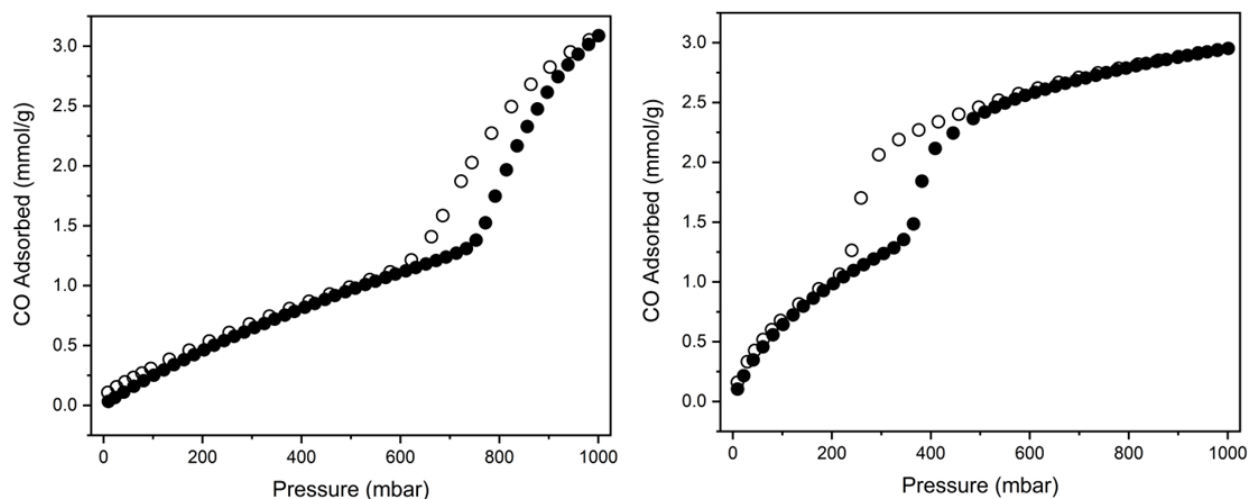


Figure 2.4. Left: Carbon monoxide isotherm for $\text{Fe}_{1.5}\text{Co}_{0.5}\text{Cl}_2(\text{btdd})$ measured at 293 K. Closed circles correspond to adsorption points and open circles correspond to desorption points. Right: Carbon monoxide isotherm for $\text{Fe}_{1.5}\text{Co}_{0.5}\text{Ni}_2(\text{btdd})$ measured at 293 K.

Variable-temperature gas adsorption isotherm measurements were undertaken for the three synthesized variants of $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$. By ICP, the materials used for these measurements were found to contain 14%, 30% and 50% Cr(III) which correspond to the chemical formulae $\text{Fe}_{1.72}\text{Cr}_{0.28}\text{Cl}_{2.28}(\text{btdd})$, $\text{Fe}_{1.4}\text{Cr}_{0.6}\text{Cl}_{2.6}(\text{btdd})$ and $\text{FeCrCl}_3(\text{btdd})$ respectively. Figure 2.5 shows room temperature CO isotherms for these three variants along with data for the all-Fe(II) parent framework. The isotherms show that the incorporation of Cr(III) into the framework lattice

maintains the cooperative adsorption behavior of the framework and that with increasing concentrations of the dilutive metal, the pressure of step onset decreases. The largest change in step pressure is between $\text{Fe}_2\text{Cl}_2(\text{btdd})$ and $\text{Fe}_{1.72}\text{Cr}_{0.28}\text{Cl}_{2.28}(\text{btdd})$, which have step onset pressures of 400 mbar and 243 mbar, respectively. The decrease in step pressure onset appears to hit an asymptote as the percentage increases with $\text{Fe}_{1.4}\text{Cr}_{0.6}\text{Cl}_{2.6}(\text{btdd})$, producing an onset of 142 mbar and 121 mbar for $\text{FeCrCl}_3(\text{btdd})$.

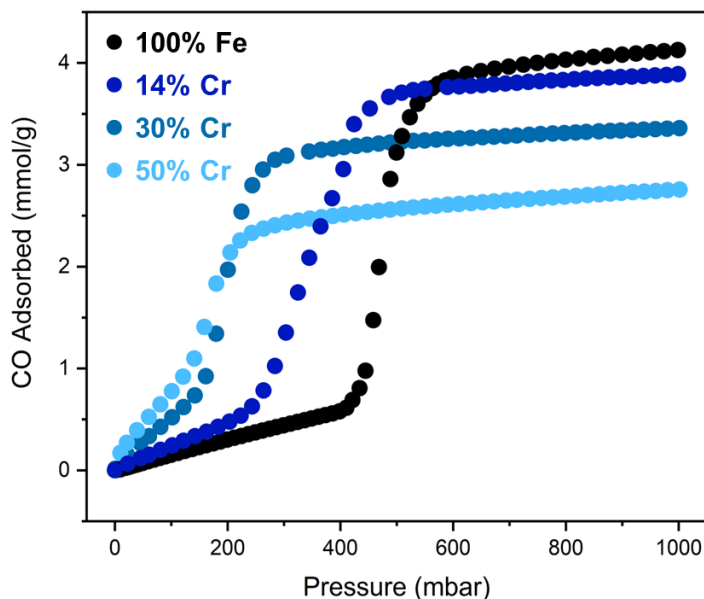


Figure 2.5. Carbon monoxide adsorption curves for $\text{Fe}_2\text{Cl}_2(\text{btdd})$ (black circles), $\text{Fe}_{1.72}\text{Cr}_{0.28}\text{Cl}_{2.28}(\text{btdd})$ (dark blue), $\text{Fe}_{1.4}\text{Cr}_{0.6}\text{Cl}_{2.6}(\text{btdd})$ (medium blue) and $\text{FeCrCl}_3(\text{btdd})$ (light blue) measured at 296 K.

Along with a decrease in step onset, the most apparent difference between the variants are their total CO capacities. The capacity change with increasing chromium content can be easily explained by the oxidation state of the metal. To provide charge balance for the trivalent chromium sites, the sixth coordination site of the metal is filled with a chloride anion, making the site inaccessible to gas binding. This assignment of oxidation state is further corroborated by normalizing the amount of CO adsorbed to the chromium and iron contents of the frameworks as determined by ICP-OES which reveals that the ratio of Fe(II) sites in these specific samples to CO adsorbed is almost exactly 1:1 (Figure 2.S29). This positive result also indicates that the frameworks are relatively free of defects and the frameworks are well activated since the capacity is near 100% for all frameworks.

Besides the change in step-onset and capacity, several other notable differences are apparent in these frameworks: increase in the slope of the pre-step region, decrease in the slope of the post-step region, and decrease in the width of hysteresis between the adsorption and desorption curves (Figure 2.S30-2.S32). These profile changes closely mimic the changes seen in the high-spin fraction vs. temperature curves that are reported for molecular spin crossover compounds.²⁴ The change in the slope of the pre-step region, hysteresis and the lowering of the slope of the isotherm post-step indicates that the energy barrier to spin-crossover is decreasing and that the entropy and enthalpy of the high-spin and low-spin states of the frameworks are converging.

These findings are consistent with studies employing metal dilution in molecular systems which likewise see a lowering of T_c , or the temperature at which 50% of the iron sites in the sample

have undergone spin crossover. These changes in the ease of crossover can be attributed to the decrease in ΔS between the initial and final states of the material. The entropy in spin crossover systems is dominated by the contribution from lattice vibrations which naturally vary due to changes in bond strength based on spin state of the iron.²⁵ As the lattice contracts with increasing amount of the secondary metal, the vibrational entropy of the initial and final states draws closer together causing a decrease in the mole fraction of CO required for spin transition. The enthalpy of the lattice elasticity also plays a role in T_c , or in the case at hand, the step pressure of the framework. The degree of compressibility, or the bulk modulus, of the material plays a key role in determining this enthalpy value. As the framework lattice contracts due to the inclusion of Cr(III) the compressibility decreases due to increasing rigidity of the metal-ligand bonds, in turn decreasing the ΔH of crossover.¹³ This can be derived from treating the inclusion of a metal with a smaller ionic radius as a source of external pressure on the system.²⁶

2.3.4. Structural Characterization via Powder X-ray Diffraction

The structural transformations that accompany spin-crossover in molecular systems are well understood and are caused by the metal-ligand bond contraction that occurs due to the depopulation of the metal-ligand antibonding orbitals upon transition from high-spin to low-spin.²⁹ This results in a unit cell contraction that can be observed via X-ray diffraction experiments that allow for varied sample environments to bring about the spin-crossover event. The $\text{Fe}_2\text{Cl}_2(\text{btdd})$ parent framework undergoes a significant unit cell contraction upon transition from high-spin to low-spin which can be observed by performing a variable temperature powder X-ray diffraction (PXRD) experiment in the presence of an intermediate pressure of carbon monoxide.¹¹ To probe the structural changes that occur in the $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$ system both upon inclusion of the secondary metal as well as in the presence of CO, variable temperature and pressure PXRD experiments were performed.

Variable temperature, isobaric experiments for $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$ are shown in Figure 2.7. The sample was dosed with 300 mbar of CO and the temperature was varied between 243 and 333 K which simulates an isothermal measurement in a closed system. This experiment reveals that at low temperatures, the low-spin phase is present, indicated by the contracted unit cell, for which exact cell volumes can be seen in Table 2.1. This unit cell contraction indicates that CO is bound, prompting a shortening of the Fe-ligand bonds. Upon heating, the material desorbs CO, which prompts a transition from the low-spin phase to the high-spin phase. As shown in the insets of Figure 2.7, the phase change occurs with no detectable intermediates, consistent with the typical first-order phase transition such as observed for spin-crossover materials.³⁰ This behavior is identical to what was seen for the all-iron parent framework and is also observed in the $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd})$ variant (Figure 2.S11).

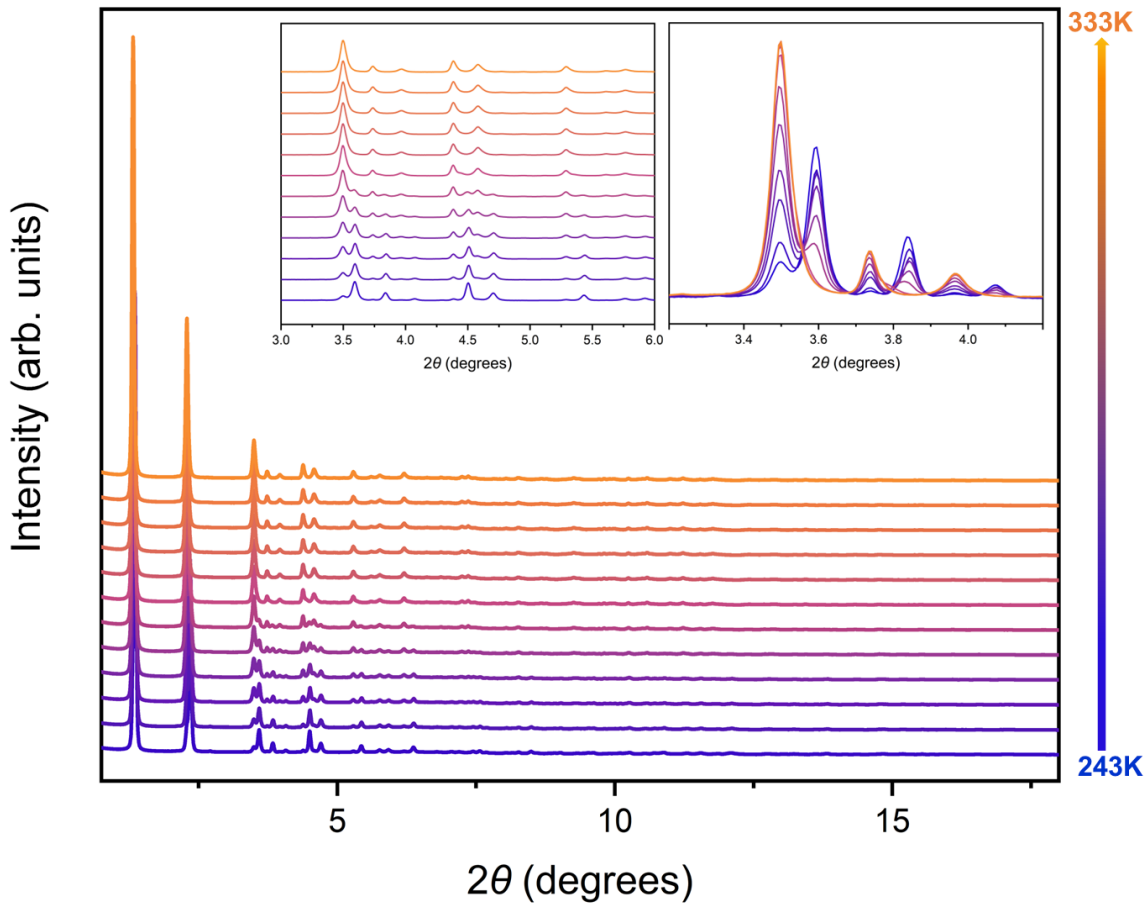


Figure 2.6. Variable temperature PXRD of $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$ collected between 243 K and 333 K under an atmosphere of 300 mbar CO, $\lambda = 0.45213 \text{ \AA}$. Insets show a closer view of the low angle region which changes significantly upon adsorption of CO at low temperatures (blue traces) and desorption of CO at high temperatures (orange traces). These changes are consistent with a phase change that occurs upon spin-crossover.

Table 2.1 shows the unit cell volumes for all variants in their high- and low-spin states. The degree of unit cell contraction has also been calculated. Several trends emerge from this data. As the concentration of chromium increases, the unit cell volume of the high-spin framework decreases, and the degree of contraction of the high-spin to low-spin transition decreases. It is apparent that the lattices of $\text{Fe}_2\text{Cl}_2(\text{btdd})$, $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$, $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd})$ undergo a significant contraction at 7.4%, 7.1% and 6.4% respectively. This unit cell contraction of the high-spin phase with increased dilution can be attributed to the smaller ionic radius of Cr(III) relative to that of high-spin Fe(II); values for selected ionic and crystallographic radii can be seen in Table 2.2. Among the chromium-containing variants, a gradual increase in the volume of the low-spin lattice volume with increasing chromium content is also observed. This is also a function of the ionic radius, as that of Cr(III) is slightly larger than that of low-spin Fe(II).

Table 2.1. Unit cell volumes and volume contraction for $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$ frameworks

	100% Fe(II)	10% Cr(III)	25% Cr(III)	50% Cr(III)
V at 333 K ($\text{\AA}^3$)	10849(6)	10064(14)	10030(14)	9790(10)
V at 235 K ($\text{\AA}^3$)	10041(3)	9352(4)	9390(3)	9480(11)
V Contraction (%)	7.4	7.1	6.4	3.2

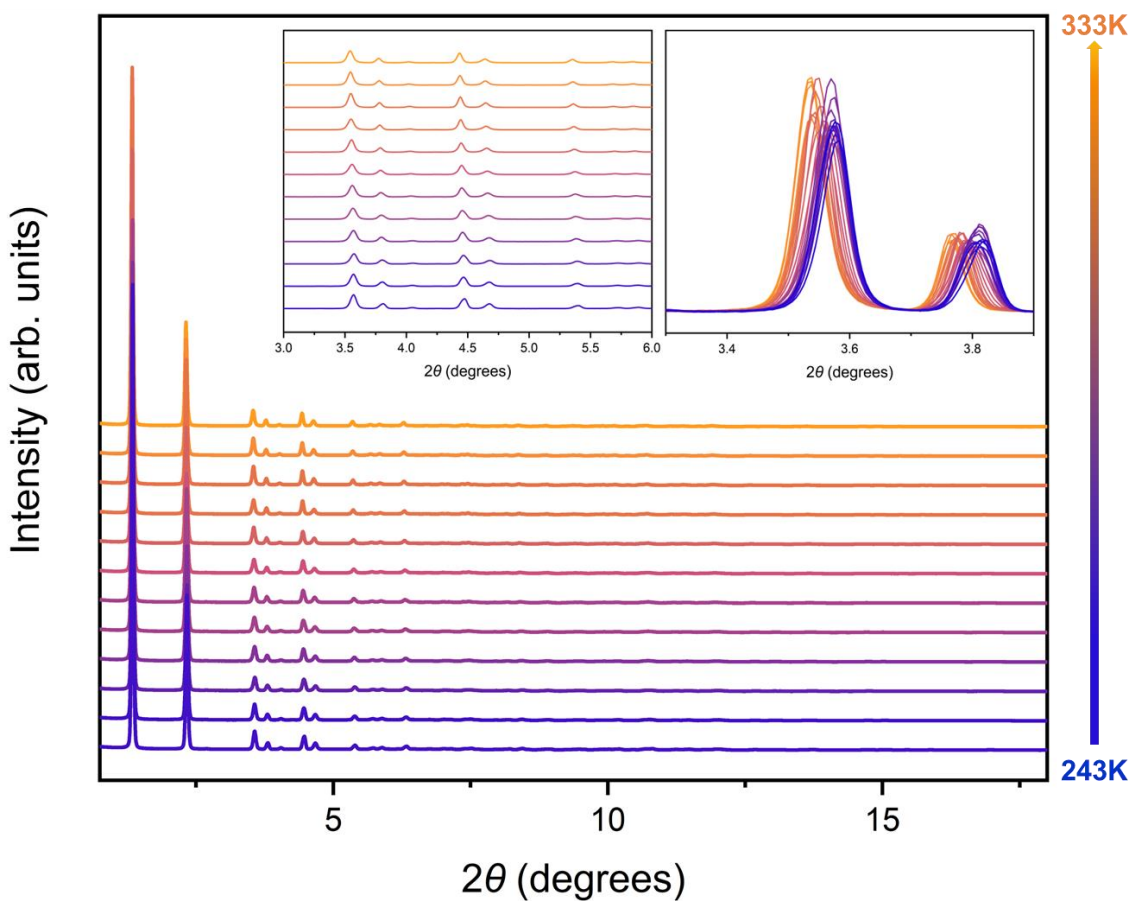


Figure 2.7. Variable temperature PXRD of data ($\lambda = 0.45213 \text{ \AA}$) for $\text{Fe}_{0.74}\text{Cr}_{1.26}\text{Cl}_{3.26}(\text{btdd})$ collected between 243 and 333 K under an atmosphere of 300 mbar of CO. Insets show a closer view of the low angle region which shows only a slight unit cell contraction upon adsorption of CO at low temperatures (blue traces) and expansion upon heating (orange traces).

Table 2.2. Ionic and crystallographic radii of selected transition metal ions.³¹

O_h Metal	Ionic Radius (Å)	Crystallographic Radius (Å)
Cr(III)	0.615	0.755
Fe(II) HS/LS	0.78/0.61	0.92/0.75
Co(II) HS/LS	0.745/0.65	0.885/0.79
Ni(II)	0.69	0.83
Zn(II)	0.74	0.88

When the chromium content reaches 63%, however, the degree of contraction decreases drastically to yield only a 3.2% change from high-spin to low-spin. A plot of the variable temperature PXRD data can be seen in Figure 2.7. This data reveals that the abrupt phase change which occurs for the other variants is absent in this framework and the lattice only undergoes a gradual contraction as shown in the inset. This suggests that at a high percentage of chromium the framework creates domains within the crystal lattice that undergo a crossover in discrete chains, disrupting the cooperativity in the material.

2.3.5. Infrared Spectroscopy

To elucidate if any electronic differences exist between the $Fe_{2-x}Cr_xCl_{2+x}(btdd)$ frameworks, *in situ* CO dosing Diffuse Reflectance Fourier Transform Infrared Spectroscopy (DRIFTS) was undertaken. First, a careful examination of the $Fe_2Cl_2(btdd)$ framework was performed to gain an in-depth understanding of the gas adsorption behavior in this system. Towards that end, a variable pressure experiment was performed at 278 K where the sample was dosed incrementally as in a typical gas adsorption isotherm while simultaneously collecting IR spectra. This yielded an isotherm with a good step shape and lower than reported capacity shown in Figure 2.8. It is likely that mass error accounts for at least part of the discrepancy. Negative adsorption observed in the desorption branch is likely a consequence of low mass amplifying accumulated error throughout the course of the experiment. Simultaneously, IR spectra were taken. Two major features were observed: a high-spin Fe(II)-CO adduct at lower pressures (2160 cm^{-1}), which disappears as a low-spin Fe(II)-CO adduct forms at higher pressures (2040 cm^{-1}) (*cf.* 2157 cm^{-1} and $2048/2039\text{ cm}^{-1}$ for $Fe_2Cl_2(bbta)$). A variety of minor features were also observed upon spin transition, which may belong to additional Fe(II)-CO species from defect sites or framework shifts. In the overtone region, high-spin Fe(II)-CO was curiously absent while a low-spin Fe(II)-CO was observed.

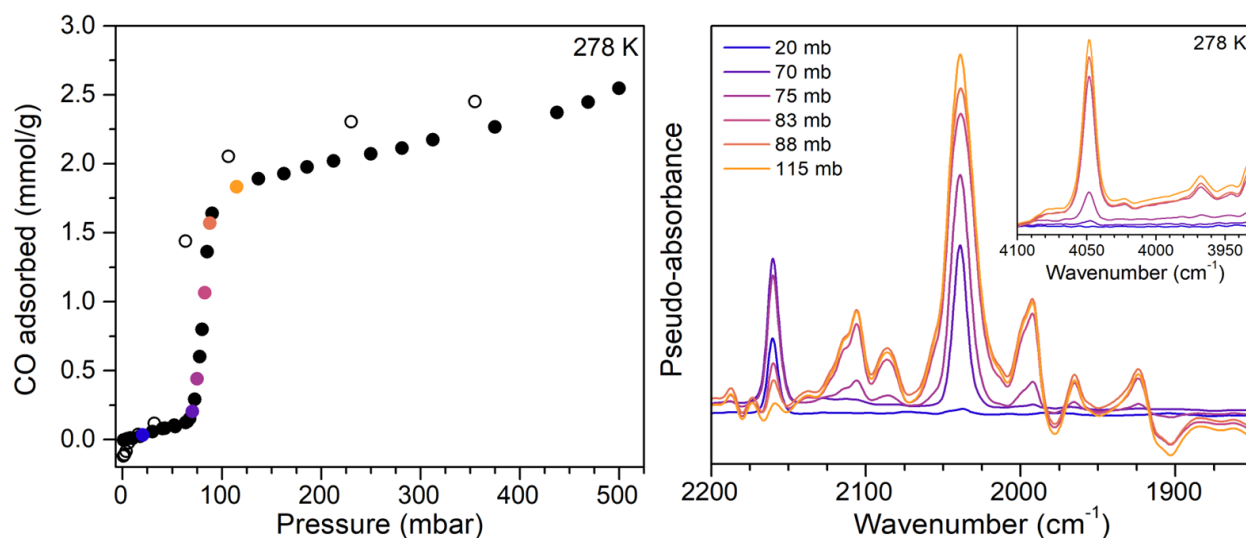


Figure 2.8. Left: CO isotherm for $\text{Fe}_2\text{Cl}_2(\text{btdd})$ at 278 K. Colored points correspond to IR spectra shown (right). The inset in the plot on the right shows the first vibrational overtone of the fundamental associated with the C–O stretch.

Figure 2.9 shows IR spectra for $\text{Fe}_2\text{Cl}_2(\text{btdd})$ derivatives dosed below and above the step pressure. This allows for identification a blue-shifted CO stretch at low pressures, which results from a non-classical CO-metal interaction where the CO acts primarily as a σ -donor due to the relative Lewis-acidity of the high-spin Fe(II) open metal sites. This non-classical interaction is typical of high-spin Fe(II)-CO complexes that form due to weak ligand fields at the iron center.³² At higher pressures, a red-shifted CO stretch emerges once the framework undergoes the spin-crossover event, indicating that the Fe(II) center is now able to engage in π -back bonding.

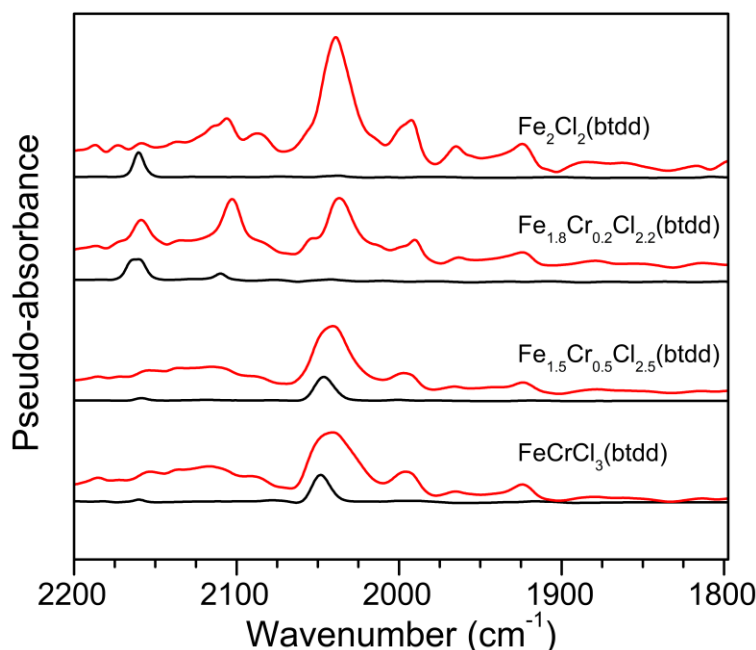


Figure 2.9. Comparison of $\text{Fe}_2\text{Cl}_2(\text{btdd})$ and derivatives when dosed with CO before (black) and after (red) the step. From top: $\text{Fe}_2\text{Cl}_2(\text{btdd})$ prestep (20 mb CO, 278 K) and poststep (500 mb CO, 278 K); $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$ prestep

(127 mb CO, 298 K) and poststep (1 bar CO, 273 K); Fe_{1.5}Cr_{0.5}Cl_{2.5}(btdd) prestep (13 mb CO, 298 K) and poststep (1 bar CO, 273 K); FeCrCl₃(btdd) prestep (6.8 mb CO, 298 K) and poststep (1 bar CO, 273 K)

The trend in pressures which bring about the low-spin phase mirrors that of the bulk isotherms but sheds additional light on the facileness of transition in each framework. Notably, dosing low pressures of CO into Fe_{1.5}Cr_{0.5}Cl_{2.5}(btdd) and FeCrCl₃(btdd) yielded low-spin CO species immediately at 2046 cm⁻¹, unlike the pure iron frameworks where initially only high-spin CO was observed. High-spin CO species at 2158 cm⁻¹ was observed for both mixed-metal frameworks, which depletes sooner in the FeCrCl₃(btdd) framework than the Fe_{1.5}Cr_{0.5}Cl_{2.5}(btdd) framework, ostensibly converting to the low-spin CO species as higher CO coverages are reached. Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd) displays three main features when dosed with CO – a high-spin species at 2161 cm⁻¹, a species at 2109 cm⁻¹ and a low-spin species at 2037 cm⁻¹. Again, the high-spin species saturates first then depletes at higher coverages, while the low-spin species is only observed at higher coverages.

Table 2.3. Pressures and stretching frequencies for Fe₂Cl₂(btdd) derivatives.

	Pre-step pressure (mbar)	Post-step pressure (mbar)	$\nu(\text{CO})$ High-Spin (cm ⁻¹)	$\nu(\text{CO})$ Low-Spin (cm ⁻¹)
Fe ₂ Cl ₂ (btdd)	20	500	2160	2040
Fe _{1.8} Cr _{0.2} Cl _{2.2} (btdd)	127	1000	2161	2037
Fe _{1.5} Cr _{0.5} Cl _{2.5} (btdd)	13	1000	2158	2046
FeCrCl ₃ (btdd)	6.8	1000	2158	2046

Table 2.3 shows an overview of pressures and the resultant stretching frequency for Fe_{2-x}Cr_xCl_{2+x}(btdd) samples. It should be emphasized that the stretching frequencies of all materials are very similar, which suggests that the electronic differences between the variants are negligible. Although no clear trend in stretching frequencies emerges, examination of the CO stretches shows that as chromium is introduced into the system, a widening of the full-width half maximum (FWHM) of the peak can be observed. This phenomenon is attributed to the formation of distinct secondary and tertiary Fe(II) sites with the addition a secondary metal. These sites arise from the assumed random distribution of metal atoms within the crystal lattice which is corroborated by EDS mapping. This random distribution yields three crystallographically distinct Fe(II) sites depicted in Figure 2.10. These sites should also have slightly different bonding interactions with the CO, which can account for the broadening of the FWHM in the mixed-metal systems.

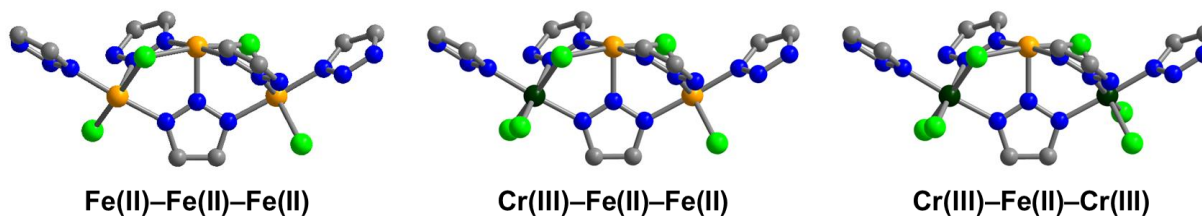


Figure 2.10. Three electronically and structurally distinct Fe(II) sites exist within this framework and are assumed to be randomly distributed.

2.3.6. Mössbauer Spectroscopy and Magnetic Susceptibility Measurements

Mössbauer spectroscopy can be used to assess the electronic characteristics of iron-containing materials and was used as a complement to IR spectroscopy to elucidate electronic structure differences between the $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$ frameworks. Measurements of all four variants were performed both under vacuum and under 1 bar of CO, to observe the relevant parameters of each framework's high-spin and low-spin state. All frameworks are unambiguously assigned to high-spin Fe(II) while under vacuum and exhibit a complete conversion to low-spin Fe(II) when exposed to 1 bar of CO at 250 K. There is no detectable presence of the low-spin Fe(II) state for any of the frameworks in the absence of gas. Tables 2.S10-2.S12 show the parameters for all variants both before and after spin crossover.

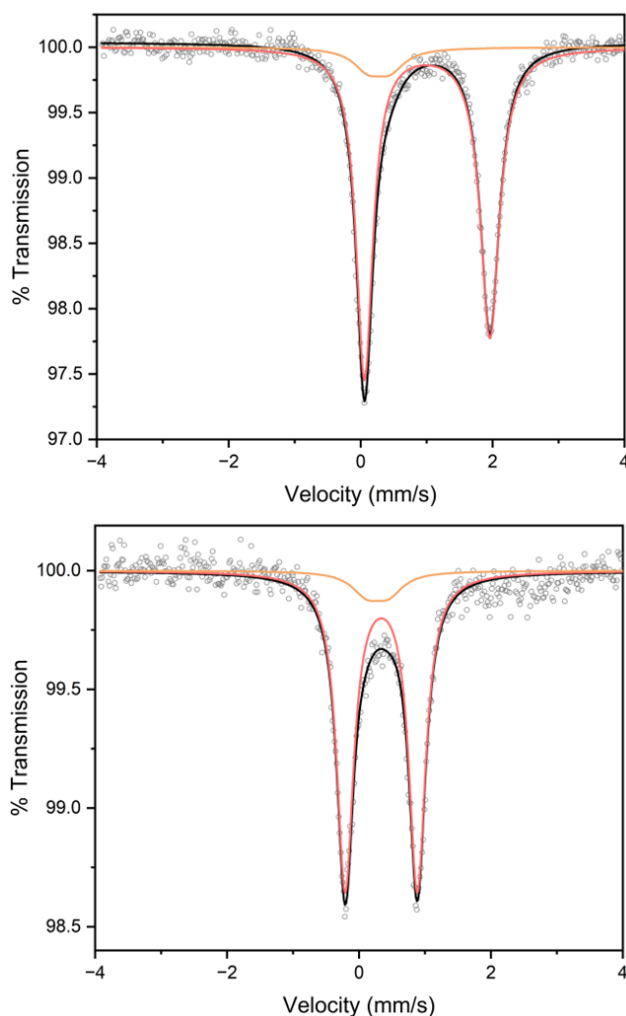


Figure 2.11. Top: Mössbauer spectrum $\text{FeCrCl}_3(\text{btdd})$ under vacuum. Bottom: Mössbauer spectrum $\text{FeCrCl}_3(\text{btdd})$ under 1 bar of carbon monoxide. Both spectra were collected at 250 K.

In the absence of CO, the spectra for $\text{Fe}_2\text{Cl}_2(\text{btdd})$, as well as the $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$ and $\text{FeCrCl}_3(\text{btdd})$ variants were fit to three sites. Two of these sites are assigned to high-spin Fe(II). The presence of two sites can be explained by the statistical variation in the repeating units of the framework, which yields structurally distinct Fe(II) sites as shown in Figure 2.11. The third site in these materials is assigned to high-spin Fe(III) which appears in low concentrations due to the extreme oxygen sensitivity of these samples which leads to oxidation during transfer and loading. $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd})$ was fit to two sites, one of which is assigned to high-spin Fe(II) and the second to high-spin Fe(III). The absence of a second high-spin Fe(II) site is attributable to low sample concentration for this particular sample during measurement.

When exposed to 1 bar of CO, all samples undergo a spin crossover, and the major sites are assigned to low-spin Fe(II). These major low-spin features are only fit to one site, unlike in the high-spin spectra due to the convolution of the two sites, indicating that upon bond contraction they become electronically indistinguishable based on the resolution of the instrument. It is clear that the isomer shifts and quadrupole splittings for all variants are the same within the error of the technique, which unambiguously shows that the d-orbital manifolds of the Fe(II) sites in these frameworks have similarly distributed electron density. This is a notable result in light of the large changes in the gas adsorption behavior which can therefore be attributed solely to the structural changes brought about by the inclusion of Cr(III) metal centers.

An additional experiment was undertaken with $\text{FeCrCl}_3(\text{btdd})$, in which the sample was dosed with 5 mbar CO and the temperature was raised as high as possible while maintaining a reasonable signal to noise ratio for the measurement. This corresponded to a temperature of 278 K. The resultant spectrum reveals a convolution of the high- and low-spin species, which are fit to slightly different parameters which is due to the change in measurement temperature. This suggests, much like the IR and PXRD measurements, that the high-spin and low-spin species can co-exist in this material and there are no intermediates that are detectible on the Mössbauer time scale.

An interesting qualitative observation during Mössbauer measurements was that collection time for each sample was dependent on temperature and Cr(III) concentration. For example, under vacuum, $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$ took approximately 72 h of collection time to generate a spectrum with adequate signal to noise. Once dosed with 1 bar of CO, the collection time was just one third of that for the evacuated spectrum. Similarly, the evacuated spectrum for $\text{FeCrCl}_3(\text{btdd})$ was collected in 36 h, significantly less time than the other variants. This can be attributed to an increase in the recoil free fraction of the absorber due to the drastic unit cell contraction that is seen upon spin crossover as a result of metal-ligand bond contraction. This effect is mimicked by the unit cell contraction observed with increasing amounts of Cr(III). Reducing energy lost to vibrations within the crystal lattice increases the efficiency of the Mössbauer effect, decreasing collection time.³³

Magnetic susceptibility measurements were performed on $\text{Fe}_2\text{Cl}_2(\text{btdd})$ and $\text{FeCrCl}_3(\text{btdd})$. Dc magnetic susceptibility were collected which reveals that the magnetic behavior is similar to that observed for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ which shows values consistent with high-spin Fe(II) ($S = 2$) in the absence of CO and low-spin Fe(II) ($S = 0$).¹¹ Based on molecular precedents where systems undergo temperature based spin crossover, when the barrier to spin crossover is lowered, the T_c should decrease. As the data for $\text{Fe}_2\text{Cl}_2(\text{btdd})$ indicates, the ligand field of these frameworks is insufficient to prompt a spin crossover even at low temperatures. If the lowering of the isothermal step-pressure of $\text{FeCrCl}_3(\text{btdd})$ and the other Cr(III) containing variants were an indication of a lowering in the electronic barrier to spin transition, it could be speculated that temperature alone might bring about a spin crossover in $\text{FeCrCl}_3(\text{btdd})$. Instead, as the $\chi_M T$ plot in Fig. 2.12 shows, the high-spin state of $\text{FeCrCl}_3(\text{btdd})$ persists to the temperature limit of the measurement. $\chi_M T$ values of 4.95 emuK/mol at 1000 Oe, 4.8044 emuK/mol at 10000 Oe are observed, which align well with the expected value of 4.878 emuK/mol for a 50:50 mixture of high-spin Fe(III) and Cr(III). This small disparity reflects a small contribution from temperature independent paramagnetism, which is suppressed at higher fields. Because of this, the higher field data is a better representation of the actual system. Additionally, the $\chi_M T$ values oscillate by a nontrivial amount, reflecting spin-orbit contributions and the downward slope with temperature likely represents the presence of antiferromagnetic coupling.

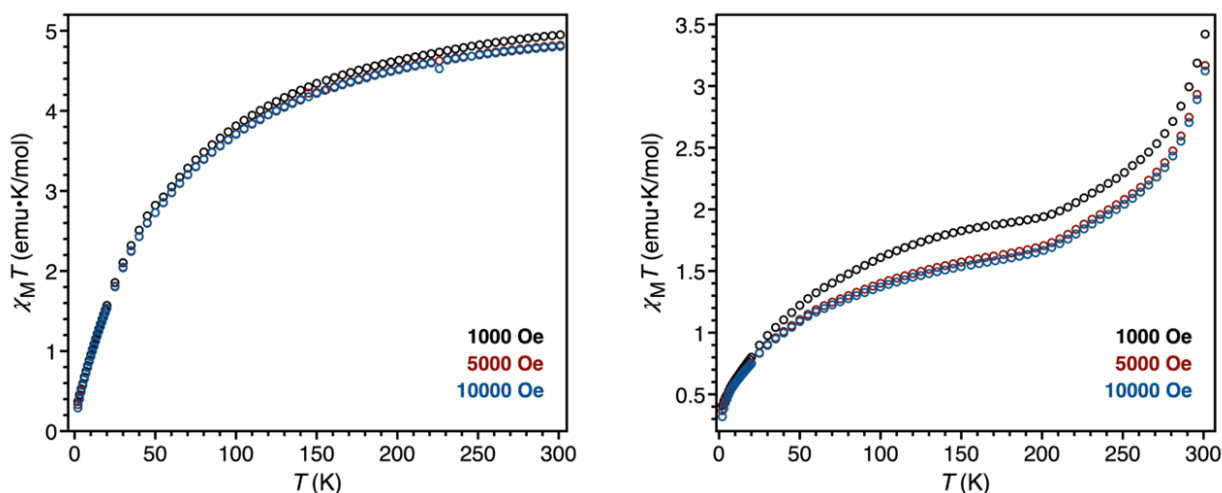


Figure 2.12. Magnetic susceptibility times temperature data collected for $\text{FeCrCl}_3(\text{btdd})$ (left) and $\text{FeCrCl}_3(\text{btdd})$ dosed with 300 mbar CO (right).

Magnetic susceptibility measurements were also collected on $\text{FeCrCl}_3(\text{btdd})$ dosed with 300 mbar CO. The steep descent from 300 to 200 K indicates that an appreciable amount of the sample remained high-spin until cooling. At 200 K, the curve levels out, which indicates that the Fe(II) centers have fully transitioned to the low-spin $S = 0$ state, which results in an overall $\chi_M T$ value at 1000 Oe of 1.94 emuK/mol, and a value at 10000 Oe of 1.66 emuK/mol. For a sample containing 1:1 diamagnetic, low-spin Fe(II) and Cr(III), the expected $\chi_M T$ value is 1.876 emuK/mol, which is also within the expected range for the Cr(III)-only moment.

2.4. Conclusions and Future Work

The design of Fe(II)-based mixed-metal metal–organic frameworks was undertaken to deduce the driving force behind the spin crossover adsorption event and demonstrate control over gas adsorption behavior in $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$ -type materials. Carbon monoxide gas adsorption measurements showed that increasing concentration of Cr(III) within the crystal lattice leads to a decrease in the pressure of step onset in the cooperative adsorption mechanism characteristic of this framework type. HAADF-STEM imaging with EDS mapping confirmed the even distribution of metals throughout each crystallite. Powder X-ray diffraction measurements revealed that the unit cell volume of the frameworks decrease with increasing Cr(III) content due to the smaller ionic radius of Cr(III) relative to that of high-spin Fe(II). PXRD also shows that at a high enough concentration of chromium, the distinctive phase change that accompanies this cooperative spin crossover event upon CO adsorption is not observed, rather a gradual unit cell contraction is seen, representing a disruption in the cooperativity of the system.

Infrared spectra collected with *in situ* dosing of CO show similar $\nu(\text{CO})$ values for all variants during both high-spin and low-spin interactions. This indicates that the bonding interaction between the Fe(II) metal center and CO is invariant of Cr(III) content despite the drastic change in isothermal profile. Similarly, Mössbauer spectra for all variants have comparable parameters, illustrating that the metal-ligand bonding interactions are largely the same for all framework variants. These spectra also confirm that the same spin crossover phenomenon is observed under CO atmosphere for all frameworks despite the decrease in degree of cooperativity observed in the structural data. Magnetic susceptibility data shows that although the step onset of the framework can be modulated, even at high concentrations of Cr(III), the energetic barrier to spin crossover remains too high for the material to undergo a temperature induced spin crossover.

Since control over the spin crossover event in this material has been found to be structural in nature but still highly dependent on a binding event involving a strong-field ligand, applicability of this material to separations involving gases other than CO remains a challenge. Weaker π -acid gases such as hydrogen and acetylene prove to still have too weak of an electronic interaction with the Fe(II) sites to prompt a spin crossover and produce a step-shaped isothermal profile (see Figure 2.S33). Isotherm measurements involving these gases show that even the high percentage Cr(III) materials with the lowest step pressures have a Type-I isotherm shape, which is not notable. Therefore, it is likely that only gases that can strongly interact with the Fe(II) sites such as PF_3 would prompt a step-shaped adsorption profile.

2.5. Supplementary Information

2.5.1. Improved Synthesis, Structural and Isothermal Characterization of $\text{Fe}_2\text{Cl}_2(\text{btdd})$

Attempts at synthesizing the parent framework $\text{Fe}_2\text{Cl}_2(\text{btdd})$ using previously established synthetic procedures yielded a material that had poor CO uptake, lacked crystallinity and had a low surface area. Experiments undertaken to isolate the cause of these issues revealed that the synthesis of this material is sensitive to the presence of methanol. In the previously reported procedure, methanol was used both as a co-solvent with DMF during the solvothermal synthesis and as the solvent used for solvent exchange with DMF during washes. To combat these issues, a new synthetic procedure, outlined below, was developed which eliminates the need for methanol.

$\text{Fe}_2\text{Cl}_2(\text{btdd})$ was synthesized by combining 20.0 mg of $\text{H}_2(\text{btdd})$ (0.075 mmol), 19.0 mg of FeCl_2 (0.150 mmol) and 10 mL of DMF in a 20 mL scintillation vial. The reaction mixture was heated to 120 °C inside a N_2 filled glovebox for four days. The filtrate was collected and suspended in 20 mL of fresh DMF and heated to 120 °C for 24 h. The DMF was then decanted and replaced with fresh DMF. This process was repeated a total of 6 times. After the final DMF wash, the solvent was decanted and replaced with 20 mL acetonitrile (MeCN) which was heated at 60 °C for 24 h. The solvent was then decanted and replaced with 20 mL of fresh acetonitrile. This process was repeated a total of six times. After the final wash, the solvent was decanted, and the sample was preactivated under vacuum at 120 °C for 2-3 h after which the sample was placed in a glass analysis tube suitable for a Micromeritics surface area and porosity analyzer (ASAP) capped with a TranSeal, at which point it was heated under high vacuum at 150 °C, with a heating ramp rate of 2 °C/min for 3 days until an offgassing rate of less than 3 $\mu\text{bar min}^{-1}$ had been achieved.

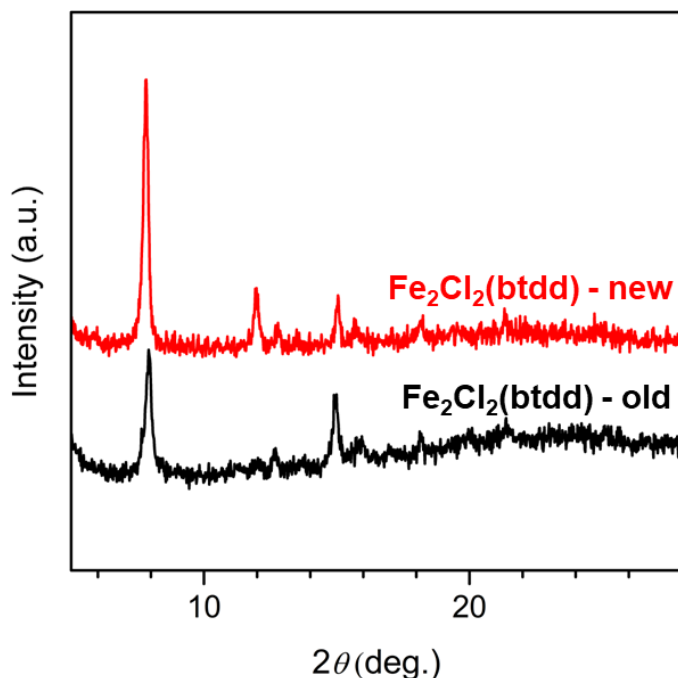


Figure 2.S1. PXRD patterns of the materials synthesized via the previously reported procedure (black trace) and the procedure eliminating the use of methanol (red trace), $\lambda = 1.54 \text{ \AA}$.

Figure 2.S1 shows powder X-ray diffraction patterns of materials synthesized using the old and new procedures and confirm that the new synthetic procedure yields an isostructural, crystalline material. Figure 2.S2 shows CO isothermal data which reveals that the material synthesized by the new procedure has a higher capacity and a lower step pressure than those previously reported, suggesting that more of the open metal sites are accessible for gas binding and less defect sites are present.

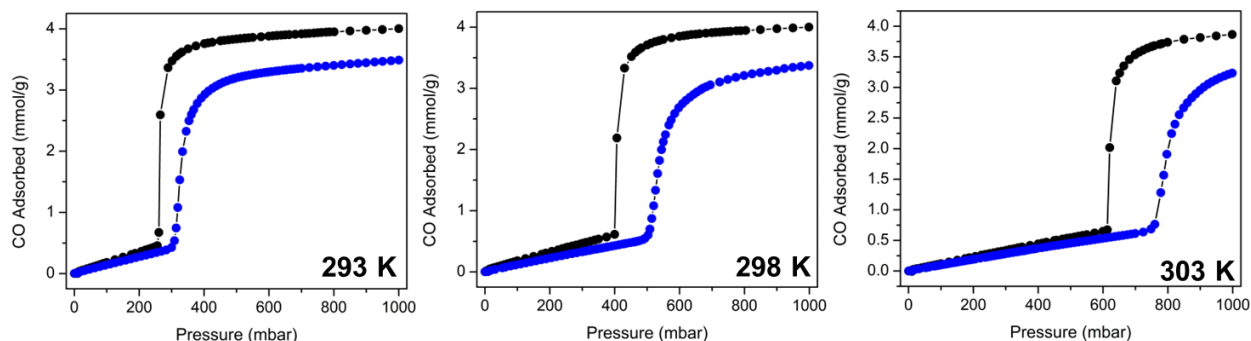


Figure 2.S2. Carbon Monoxide isotherms of material synthesized by the new procedure (black traces) and the previously reported procedure (blue traces) at 293, 298 and 303K.

2.5.2. Synthesis, Structural and Isothermal Characterization of $\text{Fe}_2\text{Br}_2(\text{btdd})$

$\text{Fe}_2\text{Br}_2(\text{btdd})$ was synthesized by combining 20.0 mg of $\text{H}_2(\text{btdd})$ (0.075 mmol), 32.4 mg of FeBr_2 (0.150 mmol) and 10 mL of DMF in a 20 mL scintillation vial. The reaction mixture was heated to 120 °C inside a N_2 filled glovebox for four days. The filtrate was collected and suspended in 20 mL of fresh DMF and heated to 120 °C for 24 h. The DMF was then decanted and replaced with fresh DMF. This process was repeated a total of 6 times. After the final DMF wash, the solvent was decanted and replaced with 20 mL acetonitrile (MeCN) which was heated at 60 °C for 24 h. The solvent was then decanted and replaced with 20 mL of fresh acetonitrile. This process was repeated a total of six times. After the final wash, the solvent was decanted, and the sample was preactivated under vacuum at 120 °C for 2-3 h after which the sample was placed in a glass analysis tube suitable for a Micromeritics surface area and porosity analyzer (ASAP) capped with a TranSeal, at which point it was heated under high vacuum at 100 °C, with a heating ramp rate of 0.2 °C/min for 3 days until an offgassing rate of less than $3 \mu\text{bar min}^{-1}$ had been achieved. This framework, like the chloride analogue is likewise sensitive to the solvent used for synthesis and washing. As shown in Figure 2.S3, the framework loses crystallinity after six washes are performed in methanol to remove the DMF from the open metal site prior to activation like was used in previous syntheses of these frameworks. If acetonitrile is used instead, the framework retains crystallinity and exhibits an improved capacity.

Powder X-ray diffraction patterns of $\text{Fe}_2\text{Br}_2(\text{btdd})$ shown in Figure 2.S4 confirm that it is isostructural with the chloride analogue, with a slightly expanded unit cell volume due to the presence of the larger anion (Table 2.S1). This mainly results from an expansion along the *c*-axis of the unit cell which corresponds to the helical chain of iron (II) atoms and halogen atoms. This expansion along *c* corresponds with a contraction along the *ab* plane due to a decrease in the M–X–M bond angle, which protrudes into the pore more as the size of the bridging anion increases.

This phenomenon has been observed with other frameworks structure-type upon anion exchange.^{16,34}

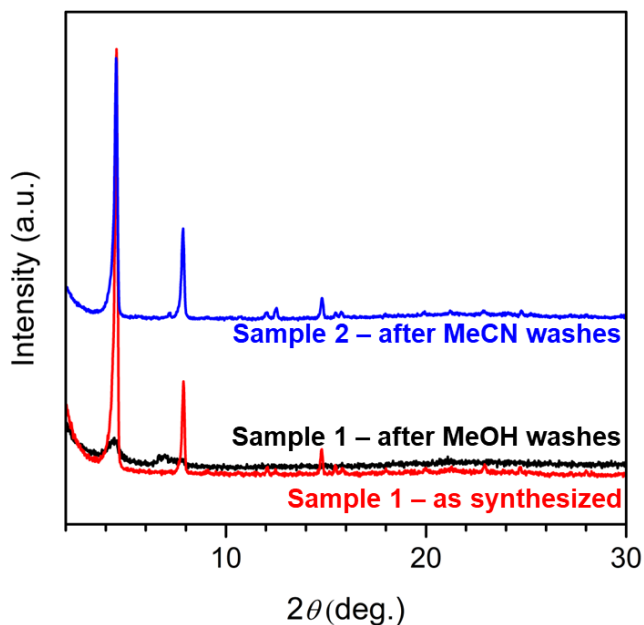


Figure 2.S3. PXRD patterns of $\text{Fe}_2\text{Br}_2(\text{btdd})$ depicting the degradation in crystallinity that occurs when Fe(II) frameworks of this structure-type are exposed to methanol. A powder pattern for one batch of sample, Sample 1, is shown both before (red) and after (black) washes with methanol. A second batch of sample is shown, Sample 2, after acetonitrile is used for washing (blue) where the framework retains crystallinity, $\lambda = 1.54 \text{ \AA}$.

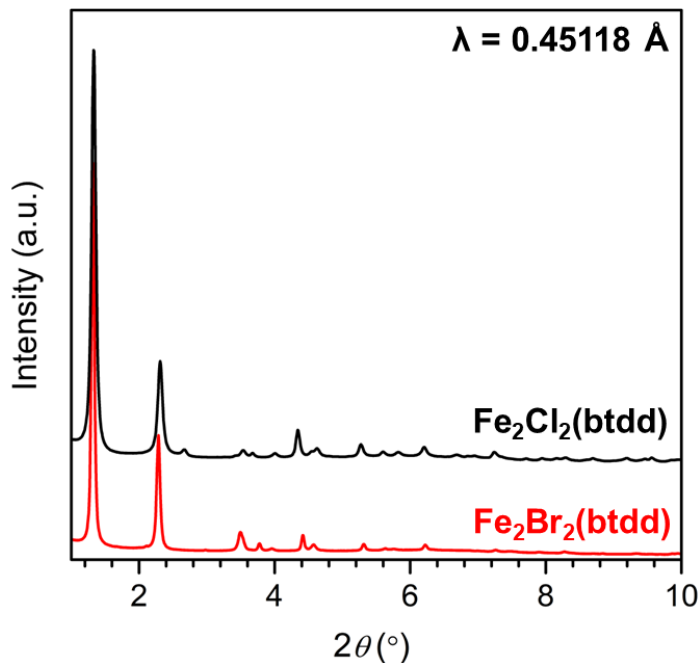
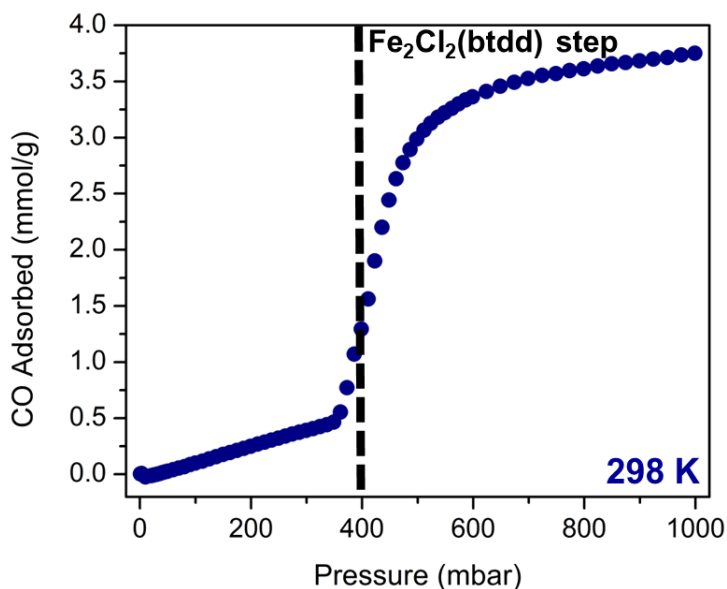


Figure 2.S4. Powder X-ray diffraction patterns of $\text{Fe}_2\text{Cl}_2(\text{btdd})$ (black trace) and $\text{Fe}_2\text{Br}_2(\text{btdd})$ (red trace), $\lambda = 0.45118 \text{ \AA}$.

Table 2.S1. Unit cell parameters for Fe₂Cl₂(btdd) and Fe₂Br₂(btdd)

	Fe ₂ Cl ₂ (btdd)	Fe ₂ Br ₂ (btdd)
Space Group	<i>R-3m</i>	<i>R-3m</i>
<i>a</i> (Å)	39.166(9)	39.065(2)
<i>c</i> (Å)	8.1664(19)	8.3687(5)
vol. (Å³)	10849(6)	11061(1)

Carbon monoxide isotherms were collected for Fe₂Br₂(btdd) which show that it exhibits a total uptake of 3.7 mmol/g (Figure 2.S5) which corresponds to 100% of the expected uptake similarly to the chloride analogue. The decrease in the expected capacity from 4.0 mmol/g with the chloride analogue to 3.7 mmol/g is due to the increase in the molecular weight due to the addition of the heavier bromide anion. Based on traditional ligand field theory, it is expected that the bromide analogue would have a weaker ligand field than the chloride analogue due to the larger energy mismatch between the diffuse high-energy orbitals of the bromine and those of the iron. Based on this assumption it was expected that the bromide would have a higher step pressure than the chloride framework since it should take a higher pressure and concentration of the strong field CO ligand to undergo a spin crossover. Contrary to this supposition, the bromide framework has a step pressure onset of 50 mbar lower than its chloride counterpart. With the additional information provided by the mixed-metal analogues which suggest the barrier to transition is structurally dictated, it follows that the contraction of the *ab* plane closer to that of the low-spin structural state is the factor that most contributes to this change in gas adsorption behavior.

**Figure 2.S5.** Carbon monoxide isotherm for Fe₂Br₂(btdd) collected at 298 K. The dashed black line indicates the pressure at which the step onset of Fe₂Cl₂(btdd) occurs.

2.5.3. Synthesis of $\text{Fe}_5\text{Br}_4(\text{btdd})_3$ and $\text{Co}_5\text{Br}_4(\text{btdd})_3$

As was discussed in Chapter 1, an additional framework morphology is accessible using the $\text{H}_2(\text{btdd})$ ligand, termed MFU-4l. This framework crystallizes in the cubic space group $Fm-3m$ and is composed of pentanuclear Kuratowski-like clusters where a central octahedral metal atom is surrounded by four tetrahedrally coordinated metal atoms capped with a terminal halogen atom.³⁵ Previously, this framework was only reported as being synthesized using ZnCl_2 and other metals could be incorporated through post-synthetic metal substitution. During explorations into the synthesis of $\text{Fe}_2\text{Br}_2(\text{btdd})$ it was found that all-iron and all-cobalt variants of the MFU-4l framework were accessible by using MBr_2 salts and the following procedure: $\text{H}_2(\text{btdd})$ (20 mg, 0.0751 mmol) was combined with FeBr_2 (32.4 mg, 0.150 mmol, 2 eq.) or CoBr_2 (32.8 mg, 0.150 mmol, 2 eq.) and dimethylformamidium trifluoromethanesulfonate (100.6 mg, 0.451 mmol, 6 eq) in a solution of 10% MeOH/DMF (10 mL) for four days. The filtrate was collected and suspended in 20 mL of fresh DMF and heated to 120 °C for 24 h. The DMF was then decanted and replaced with fresh DMF. This process was repeated 5 times to reach a total of 6 washes. After the final DMF wash, the solvent was decanted and replaced with 20 mL of methanol which was heated at 60 °C for 24 h. The solvent was then decanted and replaced with 20 mL of fresh methanol. This process was repeated 5 times to reach a total of 6 washes. After the final wash, the solvent was decanted, and the sample was pre-activated under vacuum at 120 °C for 2-3 h after which the sample was placed in a glass analysis tube suitable for a Micromeritics surface area and porosity analyzer (ASAP) and capped with a TranSeal, at which point it was heated under high vacuum at 150 °C, with a heating ramp rate of 2 °C/min for 3 days until an off-gassing rate of less than 3 $\mu\text{bar min}^{-1}$ had been achieved.

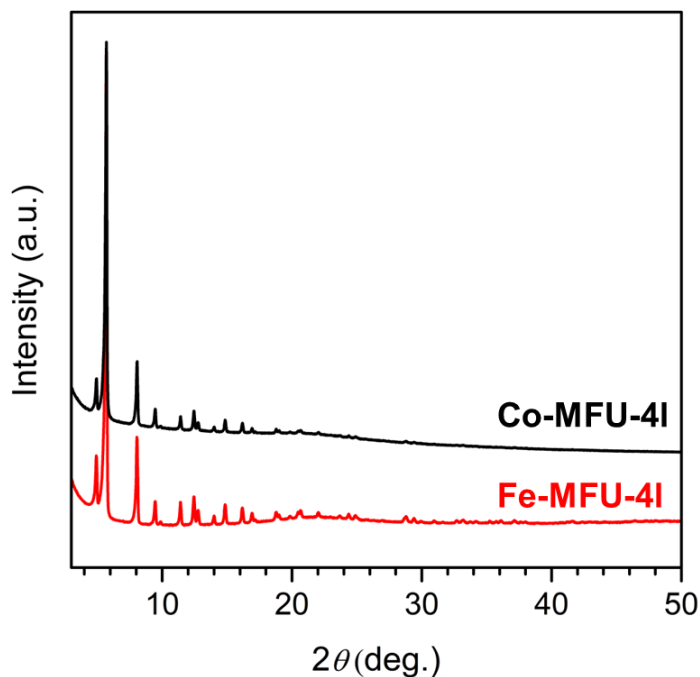


Figure 2.S6. Powder X-ray diffraction patterns of Co-MFU-4l (black trace) and Fe-MFU-4l (red trace), $\lambda = 1.54 \text{ \AA}$ (Cu $K\alpha$).

Table 2.S2. Selected crystallographic parameters and Langmuir surface areas for Fe-MFU-4l and Co-MFU-4l

	Fe₅Br₄(btdd)₃	Co₅Br₄(btdd)₃
Space group	<i>Fm-3m</i>	<i>Fm-3m</i>
<i>a</i> (Å)	31.0117(7)	30.89(3)
<i>Vol.</i> (Å³)	29824(2)	29500(9)
SA_{Lang} (m²/g)	2770	2800

2.5.4. Diffuse Reflectance Infrared Fourier Transform Spectroscopy of Fe₂X₂(btdd)

Variable pressure IRsotherms for Fe₂Cl₂(btdd) are shown in Figure 2.S6. Two major features were observed, a high-spin Fe(II)-CO adduct at lower pressures (2160 cm⁻¹), which disappears and forms a low-spin Fe(II)-CO adduct at higher pressures (2040 cm⁻¹) (*cf.* 2157 cm⁻¹ and 2048/2039 cm⁻¹ for Fe₂Cl₂(bbta)). A variety of minor features were observed upon spin transition, which may belong to additional Fe(II)-CO species from defect sites or framework shifts. In the overtone region, HS Fe(II)-CO was curiously absent while a LS Fe(II)-CO was observed.

In order to elucidate these minor peaks, ¹³CO was dosed into the system and subtracted from ¹²CO spectra (Figure 2.S6). This series of experiments were performed at lower pressures and the spin transition was induced *via* cooling in order to conserve ¹³CO usage. From these spectra it is clear that additional HS and LS Fe(II)-CO species are formed after the step. It is also notable that the SHO approximation holds unusually well for calculating the effect of the isotopic shift on ν , corroborating with the lack of peaks in the overtone region. The only peak observed in the overtone region is not coincident with the main LS Fe(II)-CO species – in the VT series the overtone appears at 260 K and below only, whereas CO on LS Fe(II) is already significantly populated at 263 K; furthermore, while it appears coincident with the minor LS Fe(II)-CO species, it is more than twice the energy of the fundamental, thus is cannot be the corresponding overtone. Thus, a satisfactory assignment of all Fe(II)-CO species cannot be completed at this time.

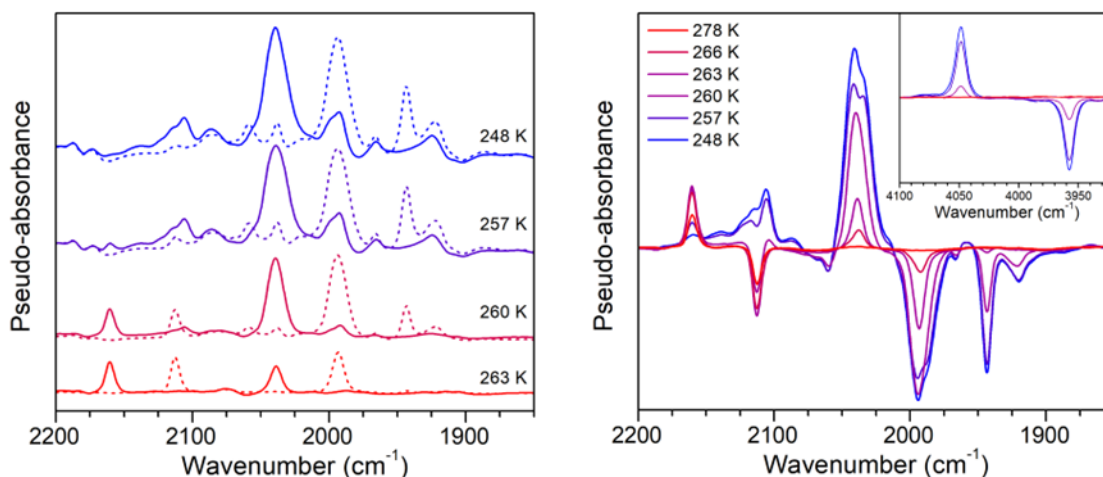


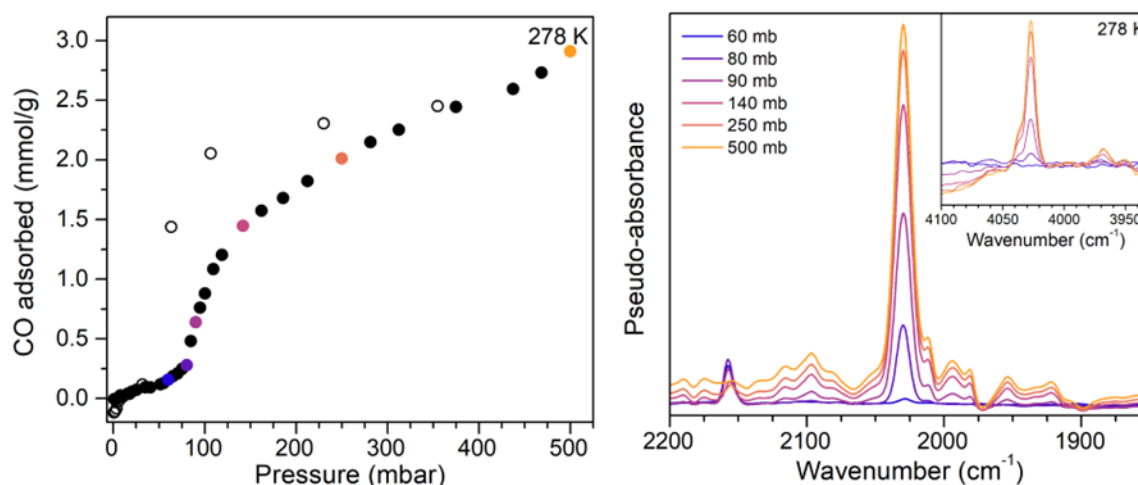
Figure 2.S7. Fe₂Cl₂(btdd) dosed with ¹²CO (solid) and ¹³CO (dashed) at temperatures surrounding the spin transition. Right: isotopic subtraction spectra for Fe₂Cl₂(btdd) dosed with ¹²CO and ¹³CO, eliminating peaks arising from framework shifts.

Table 2.S3. Peak positions for CO and ^{13}CO for high-spin and low-spin $\text{Fe}_2\text{Cl}_2(\text{btdd})$.

	$\nu\text{CO} (\text{cm}^{-1})$	$\nu^{13}\text{CO} (\text{SHO}) (\text{cm}^{-1})$
High-spin Fe(II)–CO	2160	2113 (2112)
Low-spin Fe(II)–CO	2040	1994 (1995)
High-spin Fe(II)–CO (minor)	2106	2059 (2059)
Low-spin Fe(II)–CO (minor)	1996	1944 (1952)
Overtone	4049	3958 (3959)

An analogous series of experiments were performed on the bromide analogue. 15.7 mg of framework was mixed with KBr up to a total mass of 215.7 mg, of which 57 mg was loaded into the cell for a total of 4.14 mg framework.

An IRsotherm was performed at 278 K, yielding an isotherm which was not as definitive as the chloride analogue (Fig. 1.S7). Given that the step shape and position of this material has varied in the past based on preparation and analysis conditions, it is likely that process of dispersion in KBr coupled with the small amount of material measured impacted upon appearance of the isotherm. Nevertheless, analogous signals to the chloride variant were observed in the framework, suggesting that the abnormal uptake is due to differences in measurement method rather than fundamental changes in the chemistry of the material. Signals corresponding to the HS Fe(II)–CO adduct was observed at low pressures (2158 cm^{-1}) which converts to LS Fe(II)–CO at higher pressures (2030 cm^{-1}). Both features are observed at lower energies than the analogous $(\text{CO})_x\text{Fe}_2\text{Cl}_2(\text{btdd})$ species (2160 cm^{-1} and 2040 cm^{-1} respectively), indicating a larger degree of electron transfer to the CO from the brominated framework.

**Figure 2.S8.** CO isotherm for $\text{Fe}_2\text{Br}_2(\text{btdd})$ at 278 K (left). Colored points correspond to IR spectra shown (right).

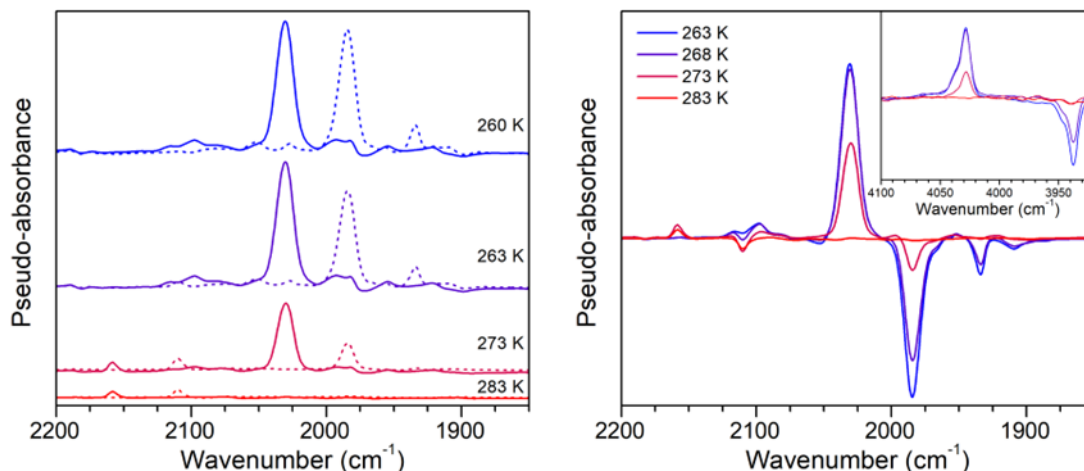


Figure 2.S9. $\text{Fe}_2\text{Br}_2(\text{btdd})$ dosed with ^{12}CO (solid) and ^{13}CO (dashed) at temperatures surrounding the spin transition (left). Isotopic subtraction spectra for $\text{Fe}_2\text{Br}_2(\text{btdd})$ dosed with ^{12}CO and ^{13}CO , eliminating peaks arising from framework shifts (right).

Table 2.S4. Peak positions for CO and ^{13}CO for high-spin and low-spin $\text{Fe}_2\text{Br}_2(\text{btdd})$

	$\nu\text{CO} (\text{cm}^{-1})$	$\nu^{13}\text{CO} (\text{SHO}) (\text{cm}^{-1})$
High-spin Fe(II)–CO	2158	2110 (2110)
Low-spin Fe(II)–CO	2030	1985 (1985)
High-spin Fe(II)–CO (minor)	2097	2051 (2050)
Low-spin Fe(II)–CO (minor)	(1978)	1934
Overtone	4028	3938 (3938)

2.5.5. DRIFT Spectroscopy of $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$

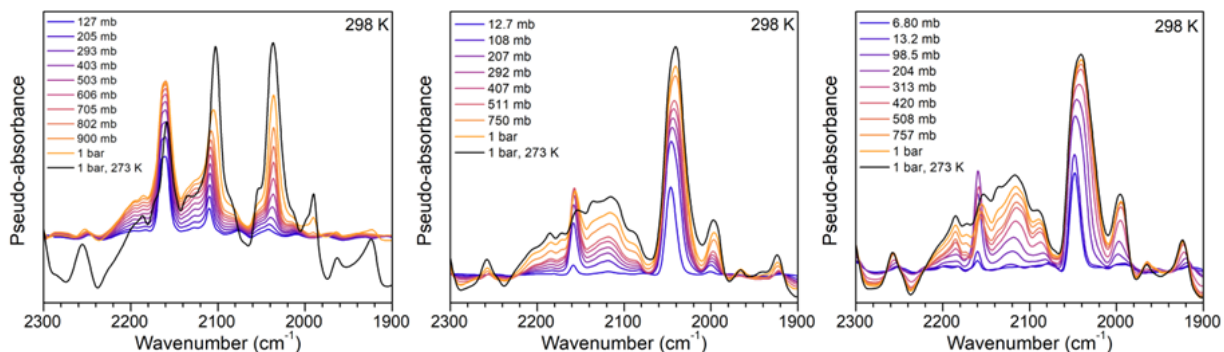


Figure 2.S10. *In situ* FTIR spectra of mixed $\text{Fe}_x\text{Cr}_{2-x}\text{Cl}_{2+x}(\text{btdd})$ under various pressures of CO at 298 K. After dosing at 1 bar, every sample was cooled to 273 K in an attempt to saturate the sites. 10%, 25% and 50% chromium substitutions are shown from left to right.

2.5.6. Powder X-Ray Diffraction

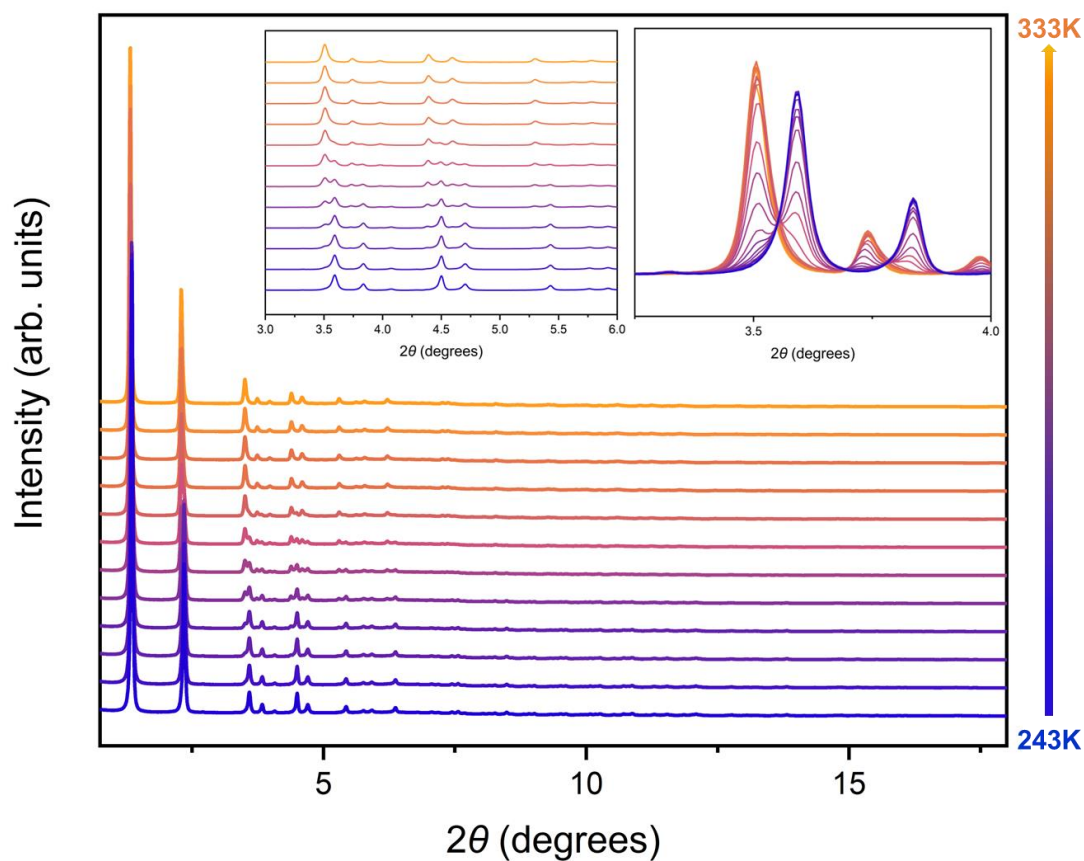


Figure 2.S11. Variable temperature PXRD of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btd})$ collected between 243K and 333K under an atmosphere of 300 mbar CO, $\lambda = 0.45213 \text{ \AA}$. Insets show a closer view of the low angle region which shows only a slight unit cell contraction upon adsorption of CO at low temperatures (blue traces) and expansion upon heating (orange traces).

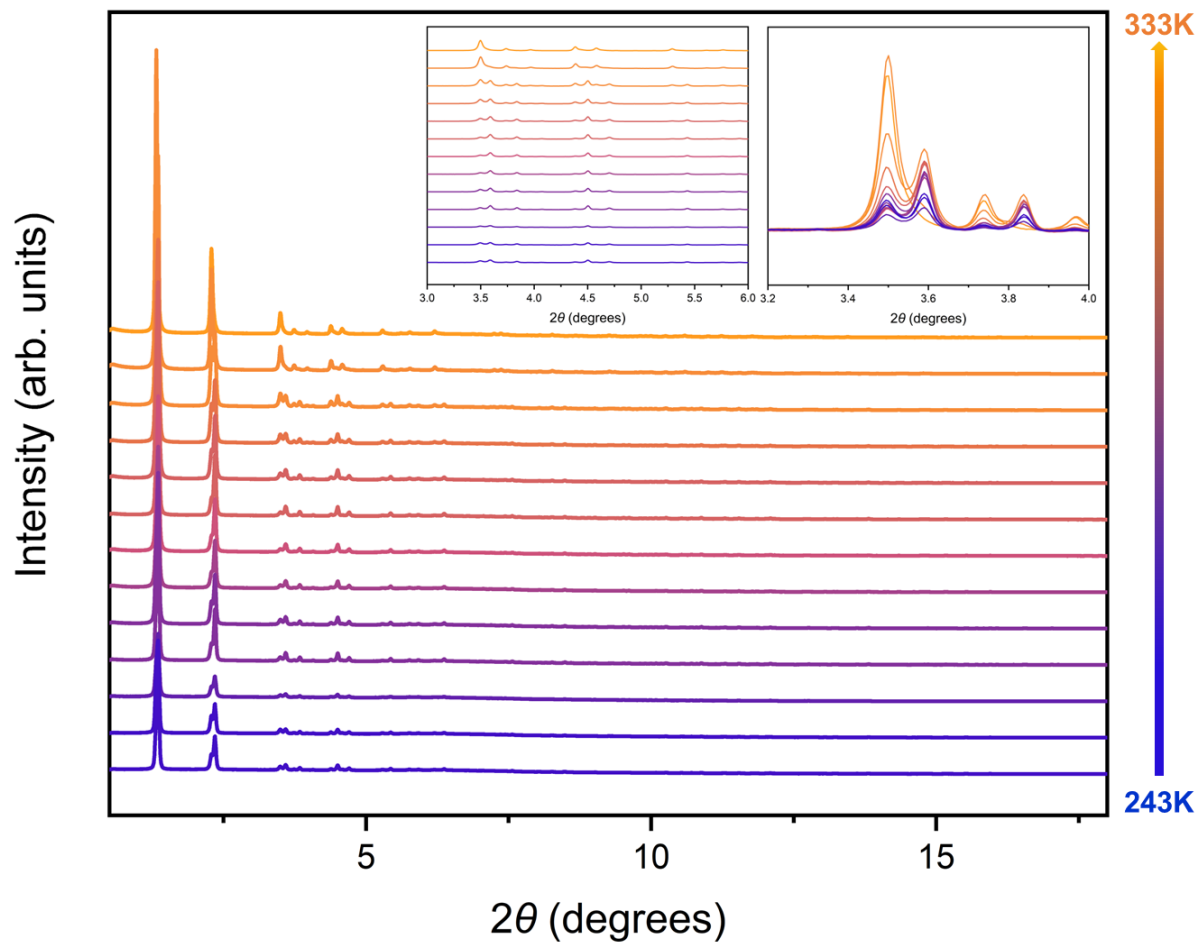


Figure 2.S12. Variable temperature PXRD of FeCrCl₃(btdd) collected between 243K and 333K under an atmosphere of 300 mbar CO, $\lambda = 0.45171 \text{ \AA}$. Insets show a closer view of the low angle region which shows only a slight unit cell contraction upon adsorption of CO at low temperatures (blue traces) and expansion upon heating (orange traces).

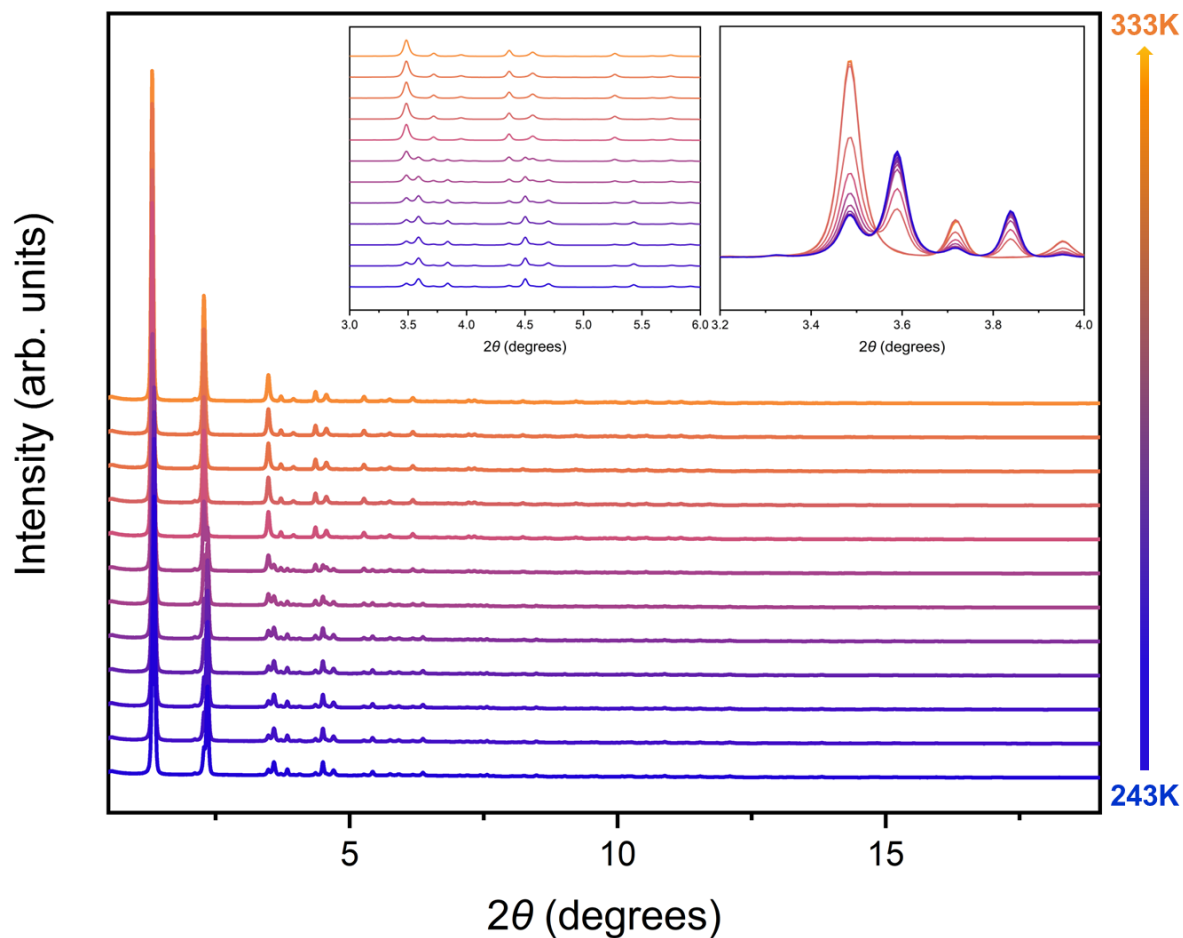


Figure 2.S13. Variable temperature PXRD of $\text{Fe}_{1.8}\text{Zn}_{0.2}\text{Cl}_2(\text{btdd})$ collected between 243K and 333K under an atmosphere of 300 mbar CO, $\lambda = 0.45171 \text{ \AA}$. Insets show a closer view of the low angle region which shows only a slight unit cell contraction upon adsorption of CO at low temperatures (blue traces) and expansion upon heating (orange traces).

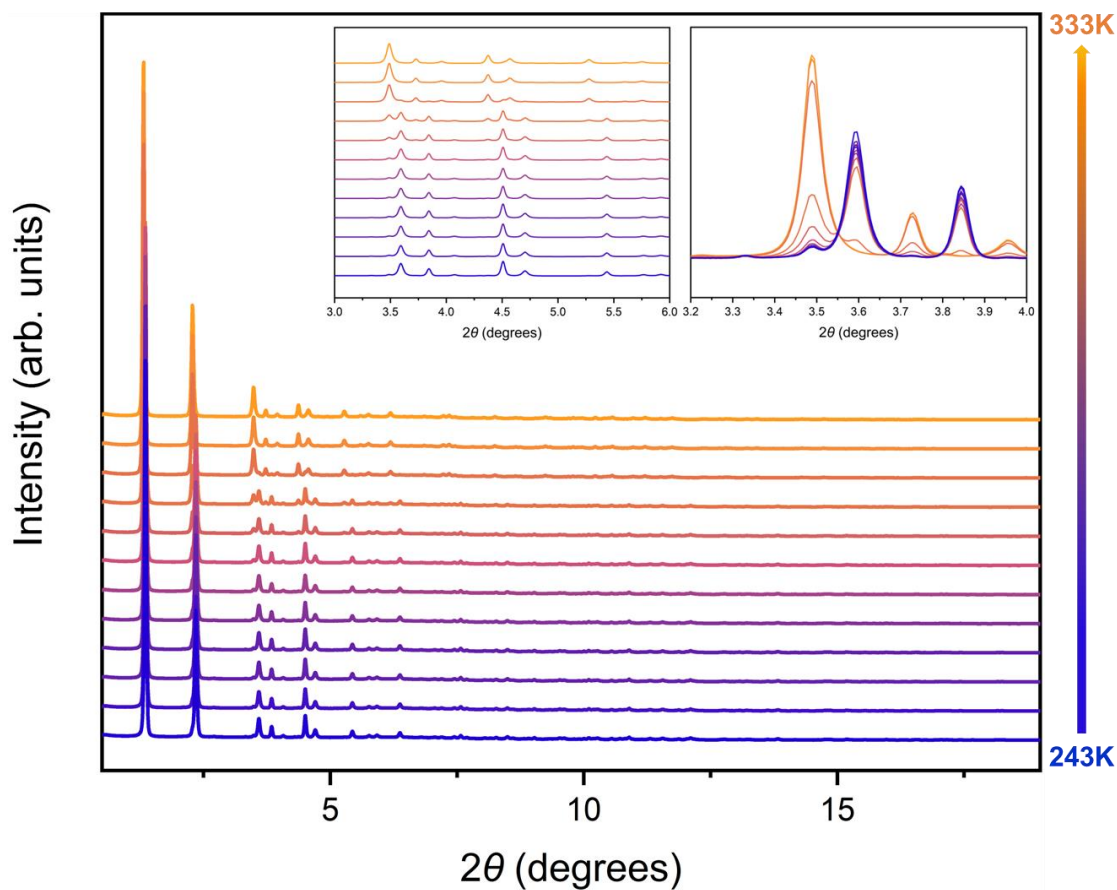


Figure 2.S14. Variable temperature PXRD of $\text{Fe}_{1.5}\text{Zn}_{0.5}\text{Cl}_2(\text{btdd})$ collected between 243K and 333K under an atmosphere of 300 mbar CO, $\lambda = 0.45171 \text{ \AA}$. Insets show a closer view of the low angle region which shows only a slight unit cell contraction upon adsorption of CO at low temperatures (blue traces) and expansion upon heating (orange traces).

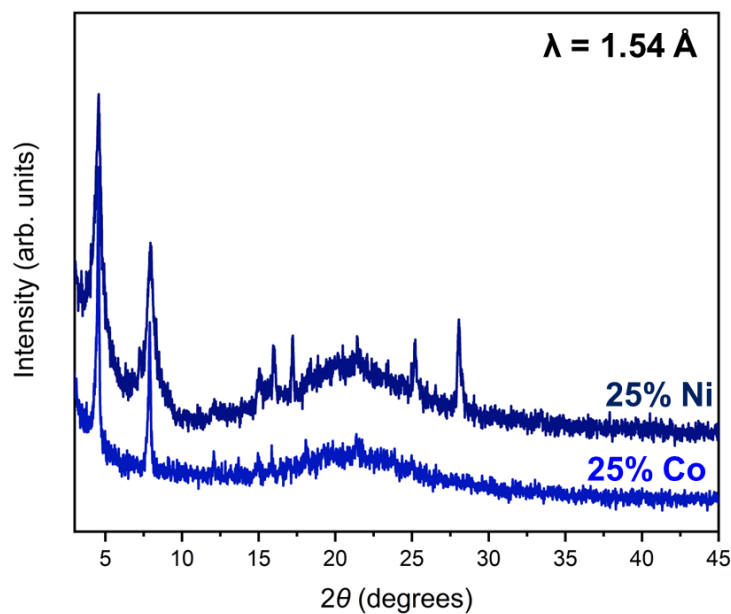


Figure 2.S15. PXRD of as synthesized $\text{Fe}_{1.5}\text{Co}_{0.5}\text{Cl}_2(\text{btdd})$ (lighter blue trace) and $\text{Fe}_{1.5}\text{Ni}_{0.5}\text{Cl}_2(\text{btdd})$ (dark blue trace) collected at room temperature, $\lambda = 1.54 \text{ \AA}$.

2.5.7. X-Ray Photoelectron Spectroscopy

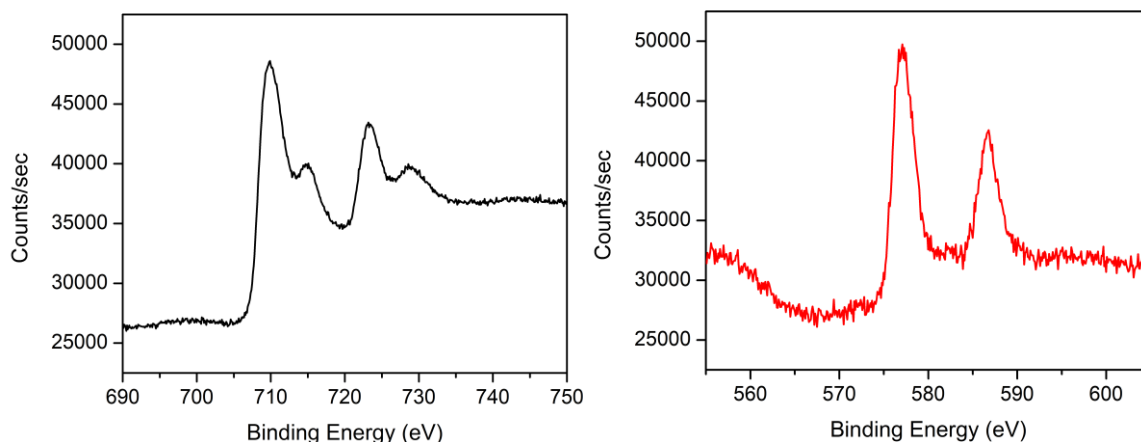


Figure 2.S16. X-ray photoelectron spectrum for $\text{Fe}_{1.72}\text{Cr}_{0.27}\text{Cl}_{2.27}(\text{btdd})$ for iron 2p (left) and chromium 2p (right), peak positions are shown in Table 2.S5.

Table 2.S5. Iron 2p and chromium 2p binding energies for $\text{Fe}_{1.72}\text{Cr}_{0.27}\text{Cl}_{2.27}(\text{btdd})$

Fe binding energy (eV)	Cr binding energy (eV)
729.08	586.98
723.18	576.78
714.78	
709.98	

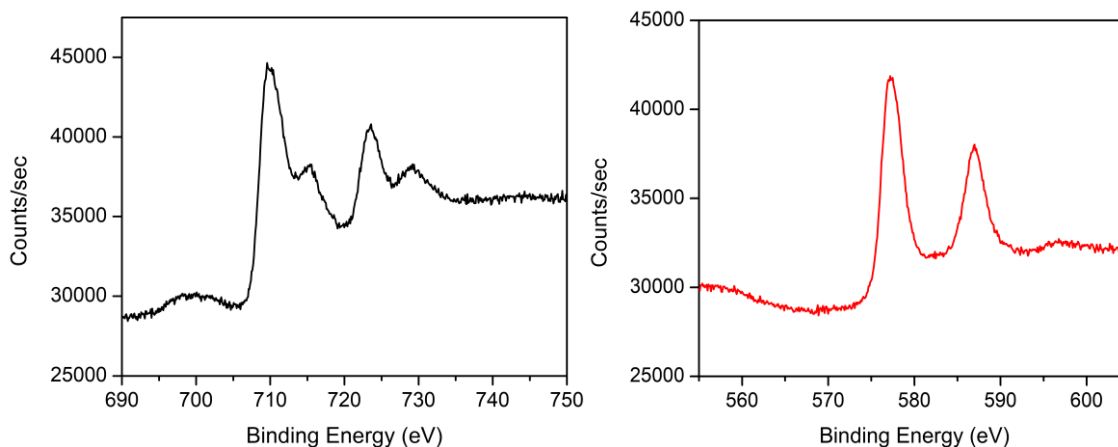
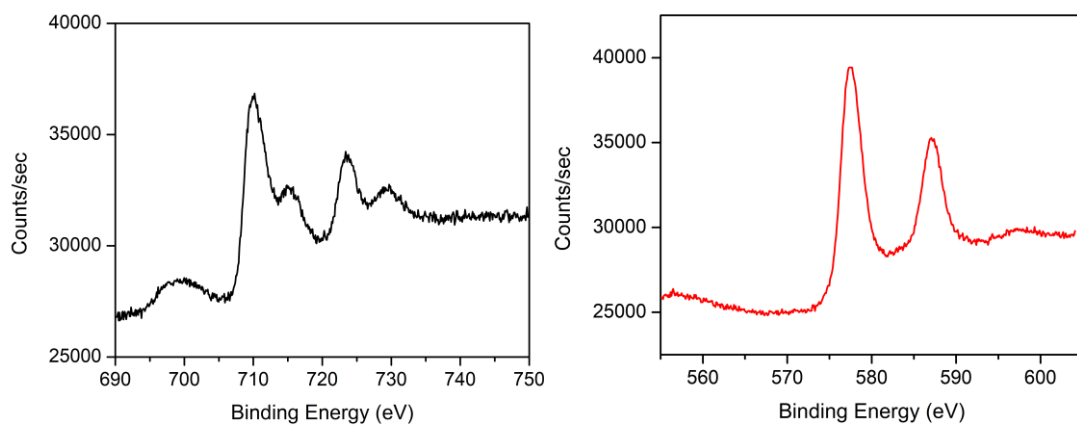


Figure 2.S17. X-ray photoelectron spectrum for $\text{Fe}_{1.40}\text{Cr}_{0.60}\text{Cl}_{2.60}(\text{btdd})$ for iron 2p (left) and chromium 2p (right), peak positions are shown in Table 2.S6.

Table 2.S6. Iron 2p and chromium 2p binding energies for Fe_{1.40}Cr_{0.60}Cl_{2.60}(btdd)

Fe binding energy (eV)	Cr binding energy (eV)
729.38	586.88
723.58	577.08
715.08	
709.88	

**Figure 2.S18.** X-ray photoelectron spectrum for Fe_{1.11}Cr_{0.89}Cl_{2.89}(btdd) for iron 2p (left) and chromium 2p (right), peak positions are shown in table 2.S7.**Table 2.S7.** Iron 2p and chromium 2p binding energies for Fe_{1.11}Cr_{0.89}Cl_{2.89}(btdd)

Fe binding energy (eV)	Cr binding energy (eV)
729.68	586.98
723.78	577.38
714.88	
709.88	

2.5.8. HAADF-STEM and EDS

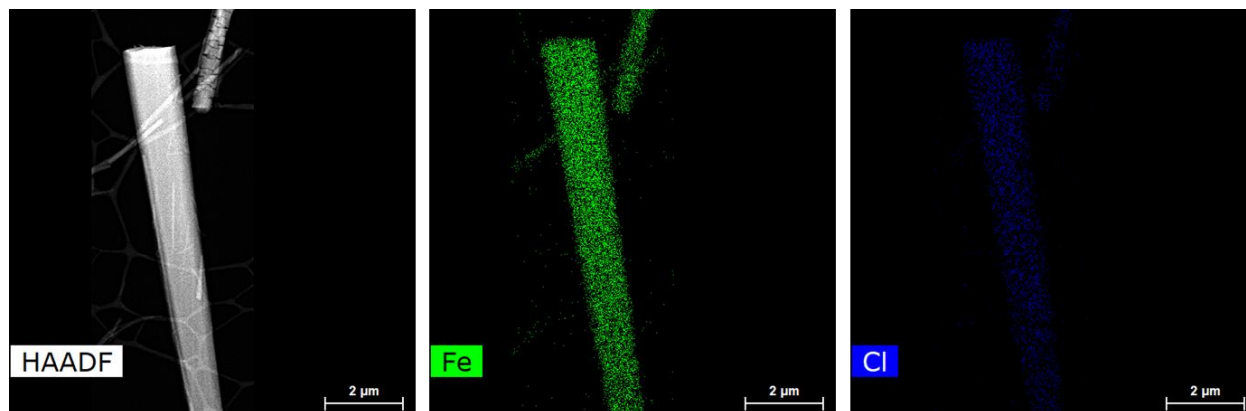


Figure 2.S19. HAADF-STEM image of $\text{Fe}_2\text{Cl}_2(\text{btdd})$ (left) and EDS mapping of iron (middle) and chlorine (right) contents in the rod-shaped crystallites. No additional metals were identified in the EDS spectrum.

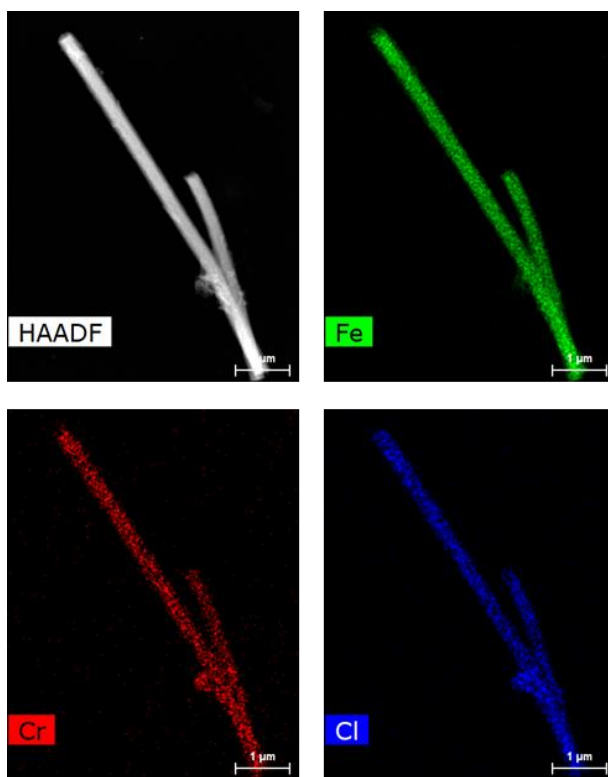


Figure 2.S20. HAADF-STEM image of $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$ (top left) and EDX mapping of iron (top right), chromium (bottom left), and chlorine (bottom right). Molecular formula determined from EDS mapping: $\text{Fe}_{1.85}\text{Cr}_{0.15}\text{Cl}_{2.15}(\text{btdd})$

Table 2.S8. Fe, Cr and Cl mass ratios as determined by EDS mapping for FeCrCl₃(btd).

Element	Expected Mass Ratio (%)	Experimental Mass Ratio (%)
Fe	26	29(6)
Cr	24	29(3)
Cl	50	42(3)

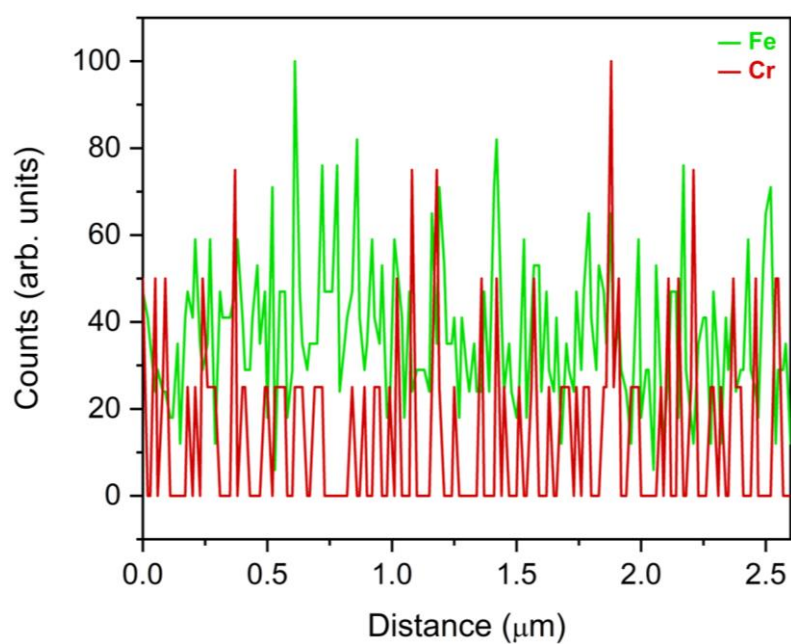


Figure 2.S21. EDS line scan of the crystallite shown in Figure 2.S20, the counts associated with chromium content (red) and iron content (green) are displayed. Randomness of the lines indicates the metals are randomly distributed throughout the crystallite.

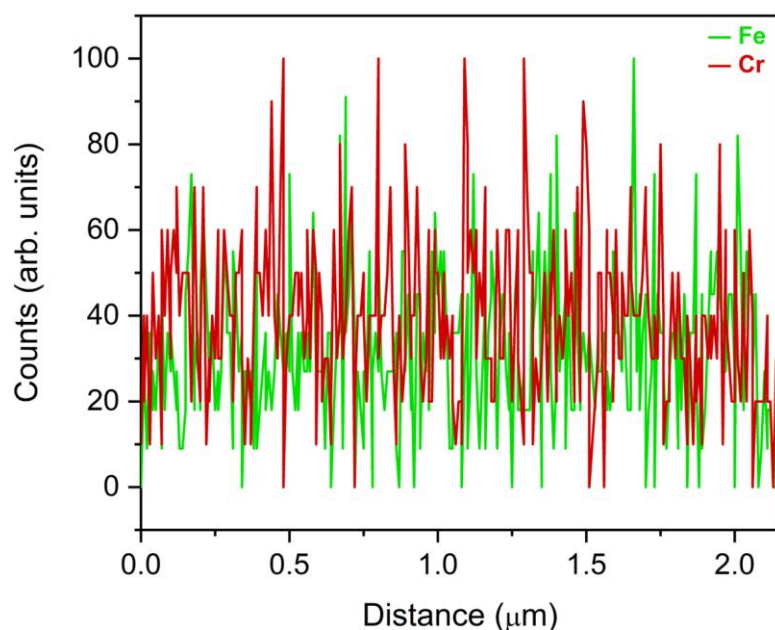


Figure 2.S22. EDS line scan of the $\text{FeCrCl}_3(\text{btdd})$ crystallite shown in Figure 2.3 in the main text, the counts associated with chromium content (red) and iron content (green) are displayed. Randomness of the lines indicates the metals are randomly distributed throughout the crystallite. As compared to the line scan in Figure 2.S19, the counts for chromium are noticeably higher, which is consistent with the higher chromium percentage expected in this sample. Molecular formula determined from EDS mapping: $\text{Fe}_{0.92}\text{Cr}_{1.08}\text{Cl}_{3.08}(\text{btdd})$

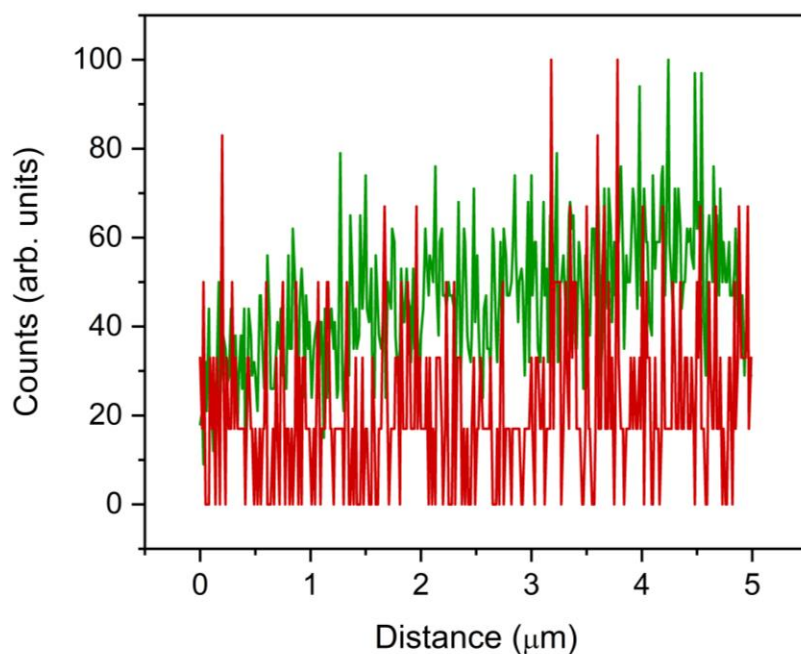


Figure 2.S23. EDS line scan of the $\text{FeCrCl}_3(\text{btdd})$ crystallite shown in Figure 2.3.

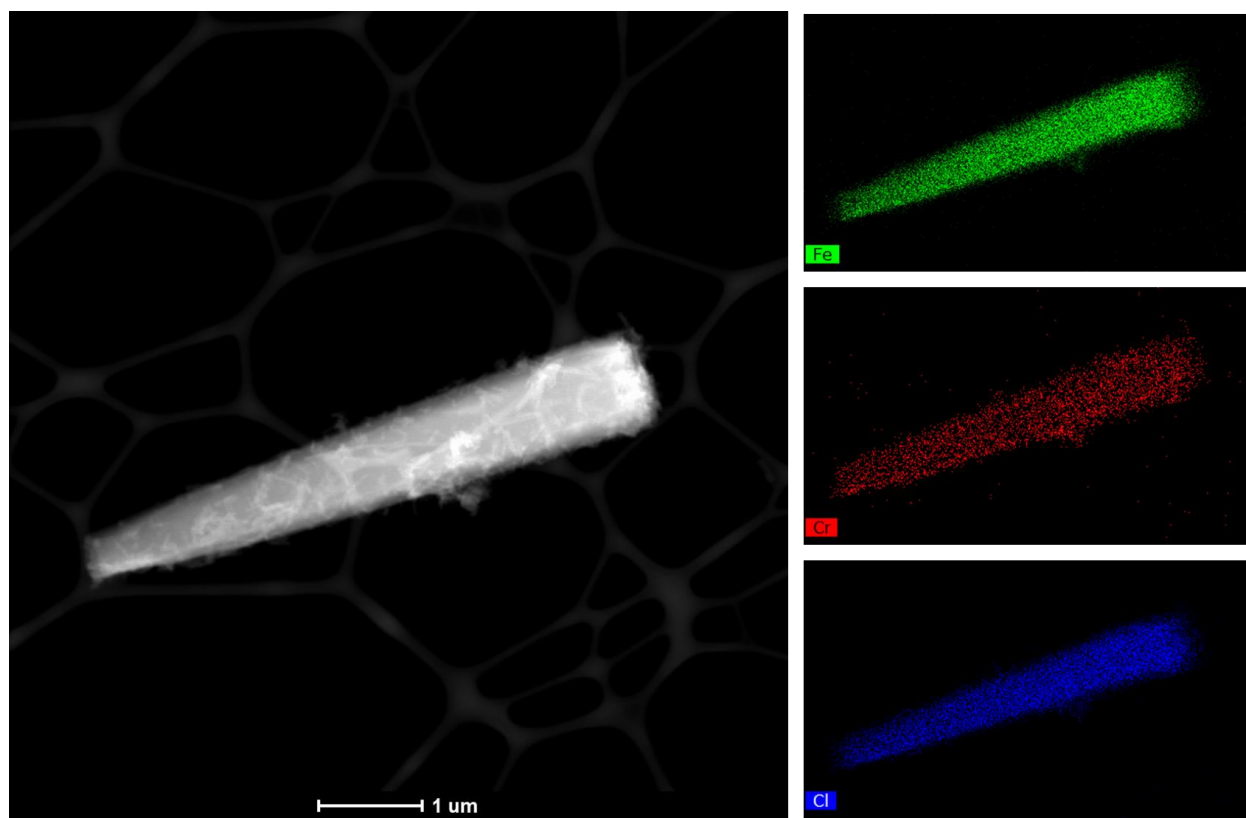


Figure 2.S24. HAADF-STEM image of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btd})$ (top left) and EDX mapping of iron (top right), chromium (bottom left), and chlorine (bottom right). Molecular formula determined from EDS mapping: $\text{Fe}_{1.85}\text{Cr}_{0.15}\text{Cl}_{2.15}(\text{btd})$

2.5.9. Mössbauer Spectroscopy



Figure 2.S25. Disassembled *in situ* gas dosing cell (top), closeup of the copper sample holder with Teflon window and indium gasket shown after compression (bottom left), gas line connections and insertion into the instrument (bottom right).

Mössbauer spectroscopy of iron and chromium mixed metal frameworks as well as $\text{Fe}_2\text{Cl}_2(\text{btdd})$ was performed in a home-built *in situ* gas dosing cell depicted in Figure 2.SX. To perform these measurements, the cell was disassembled as shown in the top picture and brought into a glovebox where the sample was loaded. The sample was then sealed with a 1.5 mm indium gasket (fashioned from wire purchased from VWR Scientific, part number AA38517-G1) which was compressed against the 1/32 inch thickness Teflon window with a torque of 80 ounces. The sample was then connected to the gas line which leads to the Micromeritics SmartVac Prep via the Swagelok quick-connect seal and the line was evacuated to 0.0013 mbar prior to opening the three-way valve to evacuate the sample. Measurements were collected first under vacuum and later under 1 bar of CO gas dosed through the SmartVac manifold. Measurements were collected at 250 K as initial runs were performed using a slightly thinner indium gasket that afforded a poorer seal which failed at temperatures below 200 K. Measurements performed on all other frameworks were performed by placing the sample into the void space of a plastic o-ring on Scotch brand packing tape in an inert atmosphere glovebox. The sample was sealed in 3-4 layers of packing tape and loaded onto the Mössbauer rod with Kapton tape.

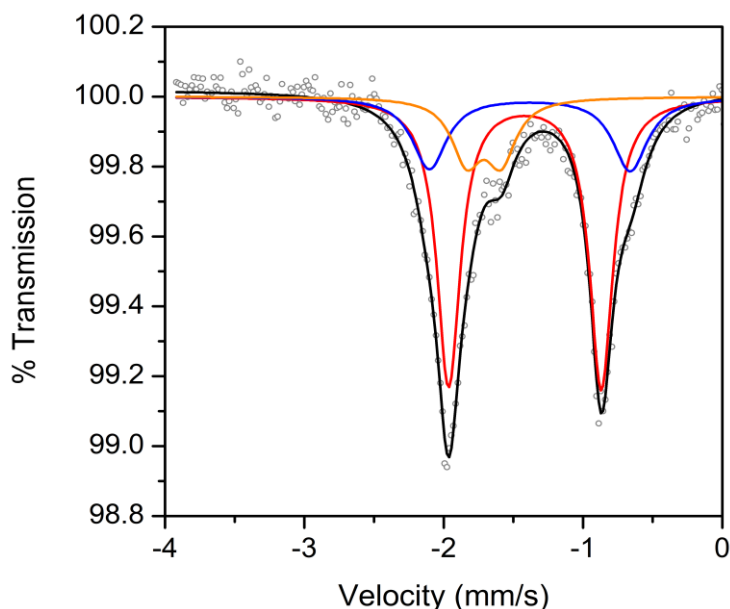


Figure 2.S26. Mössbauer spectrum of $\text{Fe}_2\text{Br}_2(\text{btdd})$ collected at 100 K. The fit parameters shown in Table 2.S9 indicate that site 1 (blue trace) and site 2 (red trace) can be assigned to high-spin Fe(II) and constitute a majority of the sample. Site 3 (orange trace) can be assigned to high-spin Fe(III) which is attributed to oxidation during sample transfer to the instrument.

Table 2.S9. Mössbauer fit parameters for $\text{Fe}_2\text{Br}_2(\text{btdd})$.

	Site 1	Site 2	Site 3
δ (mm/s)	1.092	1.162	0.501
ΔE_Q (mm/s)	2.191	2.881	0.493
Γ (mm/s)	0.407	0.602	0.515

Area (%)

61.5

22.3

16.2

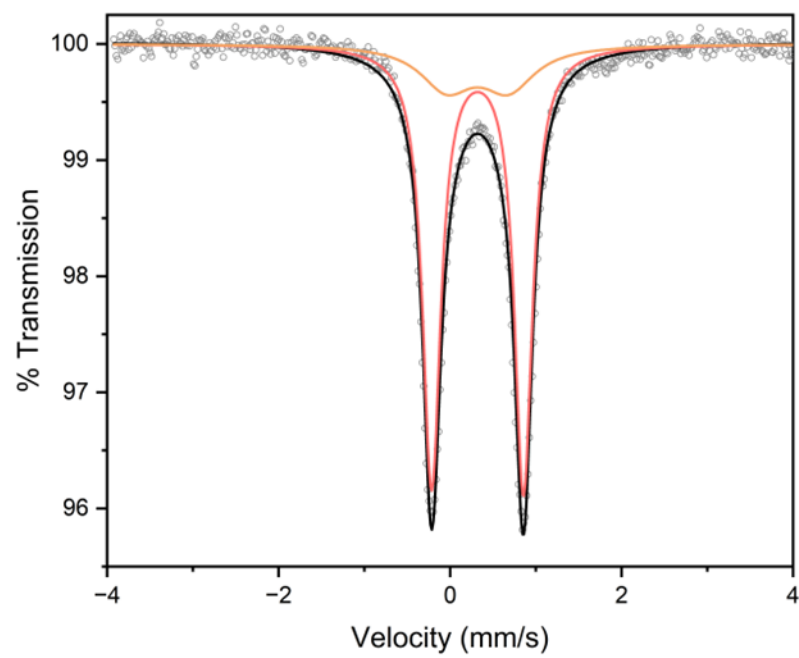
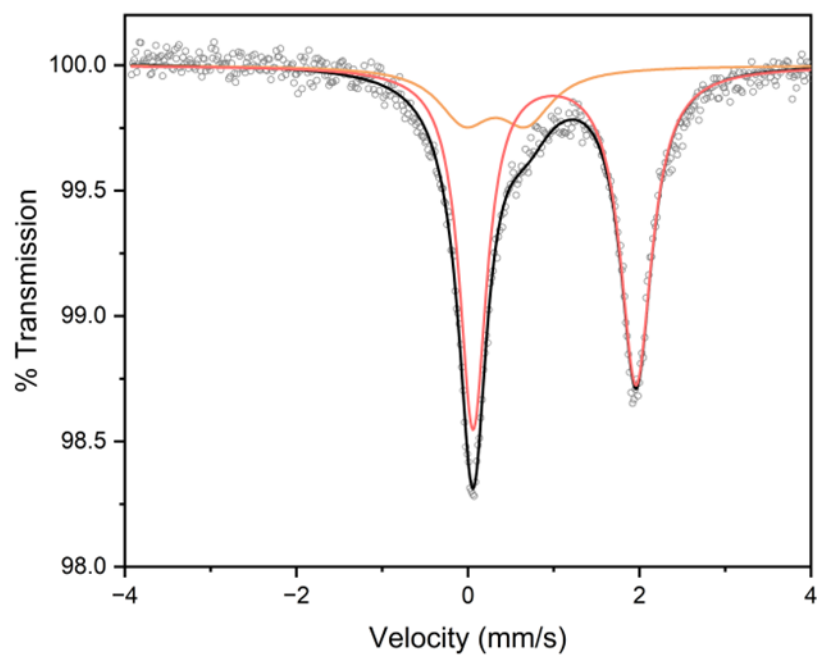


Figure 2.S27. Top: Mössbauer spectrum of $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$ under vacuum collected at 250 K. Bottom: Mössbauer spectrum of $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$ at 1 bar of CO collected at 250 K

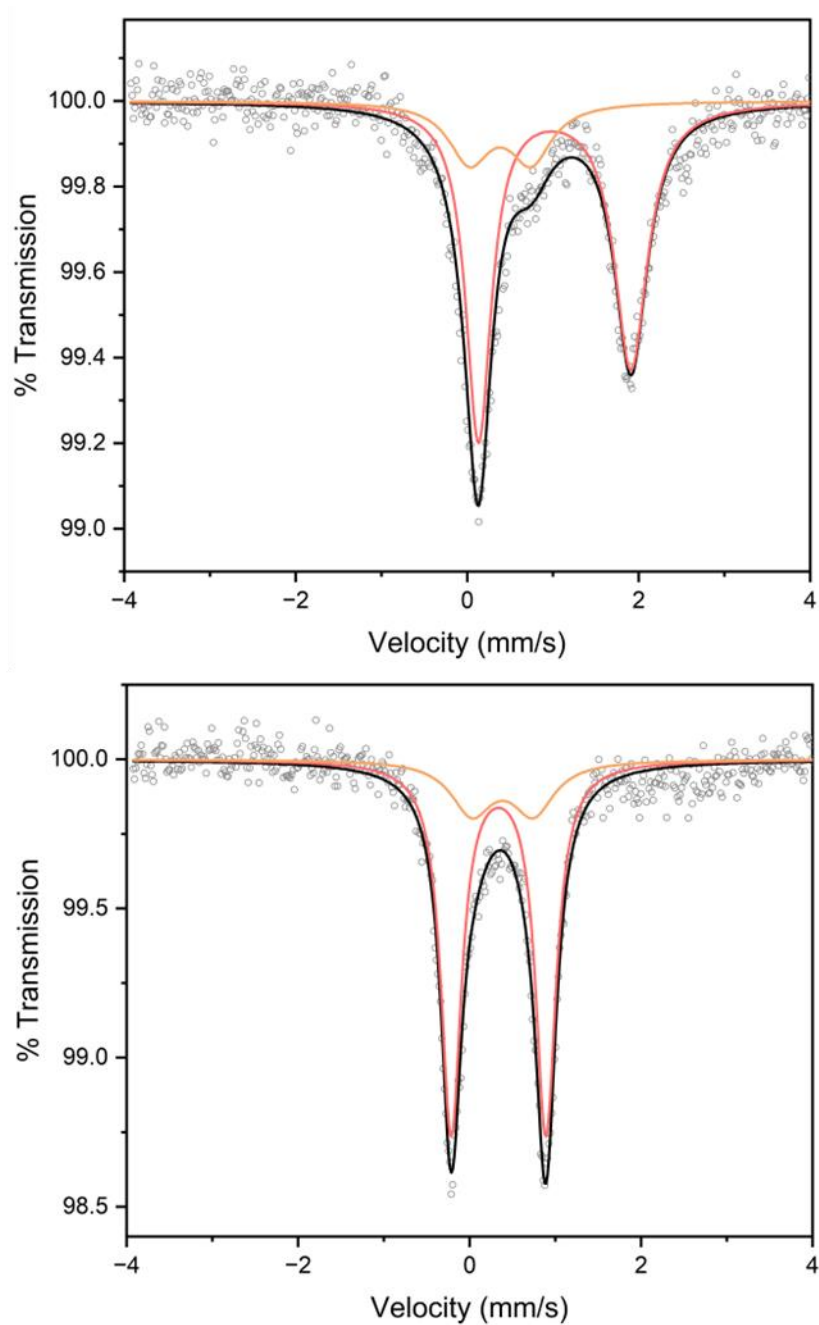


Figure 2.S28. Top: Mössbauer spectrum of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd})$ under vacuum collected at 250 K. Bottom: Mössbauer spectrum of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd})$ at 1 bar of CO collected at 250 K

Table 2.S10. Mössbauer fit parameters for $\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$.

	$\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$		$\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd}) \bullet 1.8\text{CO}$	
	Site 1	Site 2	Site 1	Site 2
δ (mm/s)	1.010	0.321	0.320	0.321
ΔE_Q (mm/s)	1.900	0.721	1.071	0.721
Γ_L (mm/s)	0.386	0.744	0.258	0.744
Γ_R (mm/s)	0.445	0.744	0.255	0.744
Area (%)	79.1	20.9	79.1	20.9

Table 2.S11. Mössbauer fit parameters for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd})$.

	$\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd})$		$\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd}) \bullet 1.5\text{CO}$	
	Site 1	Site 2	Site 1	Site 2
δ (mm/s)	1.021	0.385	0.338	0.385
ΔE_Q (mm/s)	1.776	0.718	1.104	0.718
Γ_L (mm/s)	0.358	0.590	0.292	0.590
Γ_R (mm/s)	0.470	0.590	0.292	0.590
Area (%)	78.5	21.5	78.5	21.5

Table 2.S12. Mössbauer fit parameters for $\text{FeCrCl}_3(\text{btdd})$.

	$\text{FeCrCl}_3(\text{btdd})$		$\text{FeCrCl}_3(\text{btdd}) \bullet \text{CO}$	
	Site 1	Site 2	Site 1	Site 2
δ (mm/s)	1.009	0.279	0.338	0.279
ΔE_Q (mm/s)	1.902	0.331	1.093	0.331
Γ_L (mm/s)	0.306	0.545	0.312	0.545

Γ_R (mm/s)	0.354	0.545	0.312	0.545
Area (%)	90.5	9.5	90.5	9.5

2.5.10. Gas Adsorption Measurements

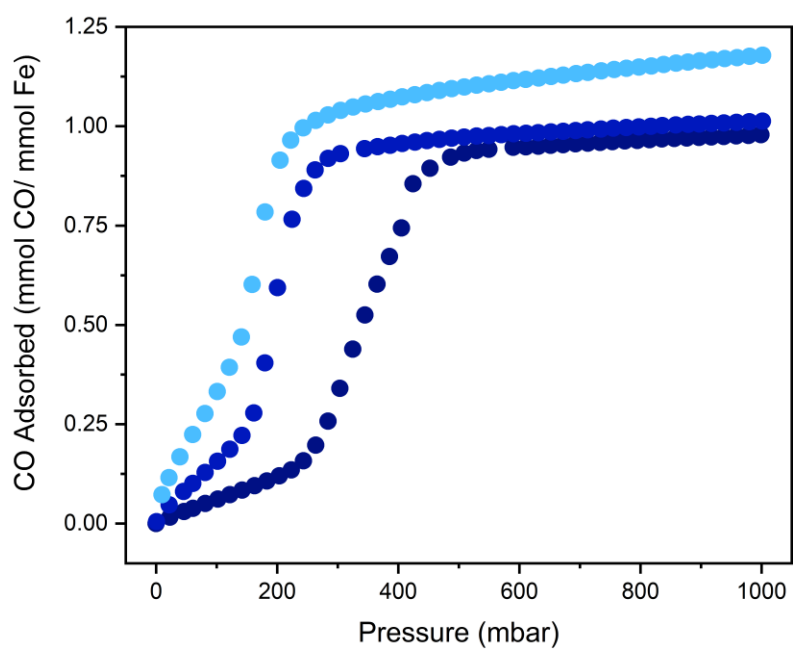


Figure 2.S29. CO isotherms for $\text{Fe}_{1.72}\text{Cr}_{0.28}\text{Cl}_{2.28}(\text{btdd})$ (dark blue), $\text{Fe}_{1.4}\text{Cr}_{0.6}\text{Cl}_{2.6}(\text{btdd})$ (medium blue) and $\text{FeCrCl}_3(\text{btdd})$ (light blue) measured at 296 K where the y-axis represents mmol of CO adsorbed per mmol of Fe(II) present in the sample. Molecular formulae were determined using ICP ratios.

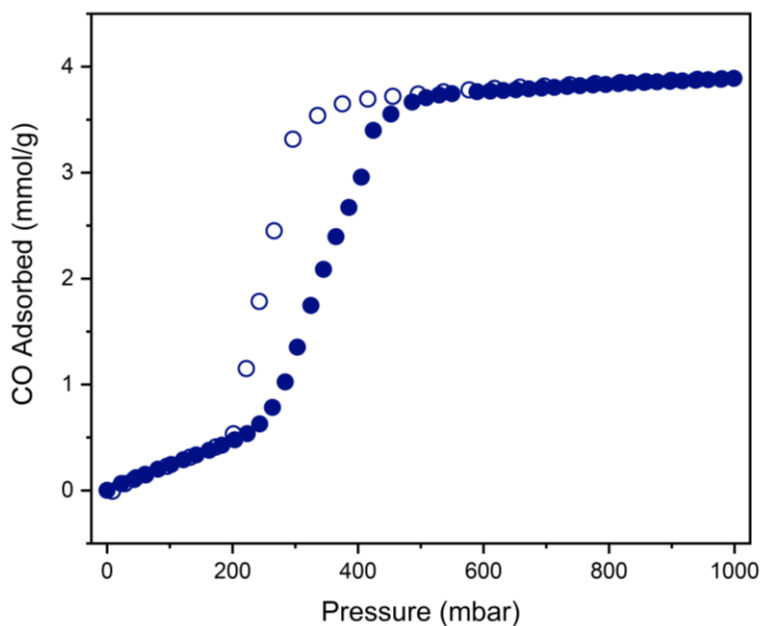


Figure 2.S30. CO isotherm for $\text{Fe}_{1.72}\text{Cr}_{0.28}\text{Cl}_{2.28}(\text{btdd})$ collected at 296 K where adsorption points are denoted by filled circles and desorption points are denoted by open circles. The hysteresis between adsorption and desorption curves decreases with increasing chromium content.

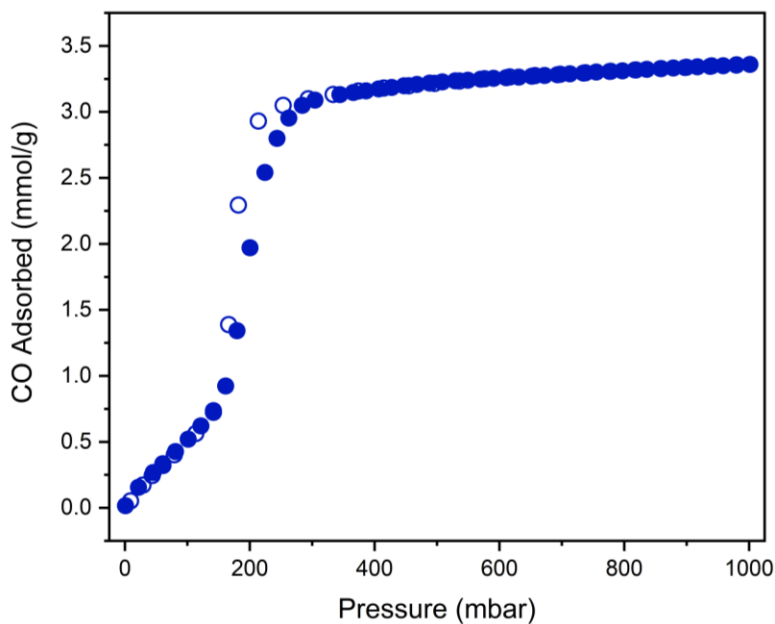


Figure 2.S31. CO isotherm for $\text{Fe}_{1.4}\text{Cr}_{0.6}\text{Cl}_{2.6}(\text{btdd})$ collected at 296 K where adsorption points are denoted by filled circles and desorption points are denoted by open circles. The hysteresis between adsorption and desorption curves decreases with increasing chromium content.

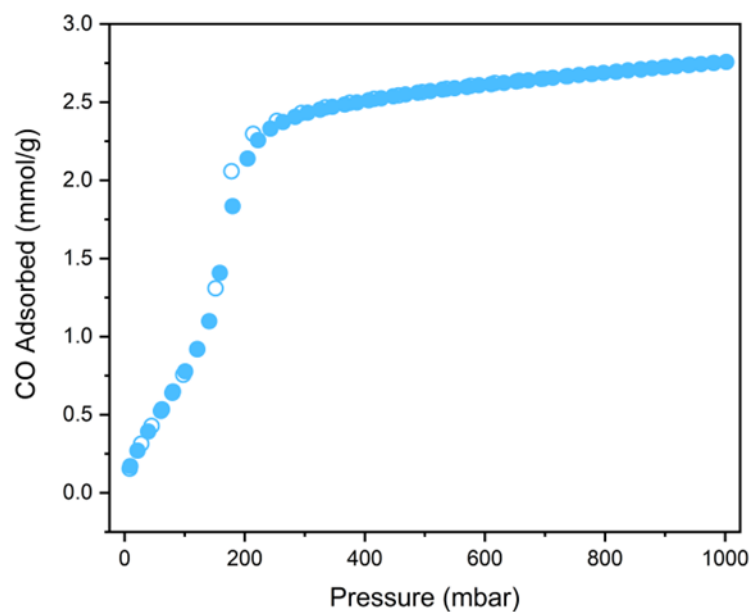


Figure 2.S32. C_2H_2 isotherm for $\text{FeCrCl}_3(\text{btdd})$ collected at 296 K where adsorption points are denoted by filled circles and desorption points are denoted by open circles. The hysteresis between adsorption and desorption curves decreases with increasing chromium content.

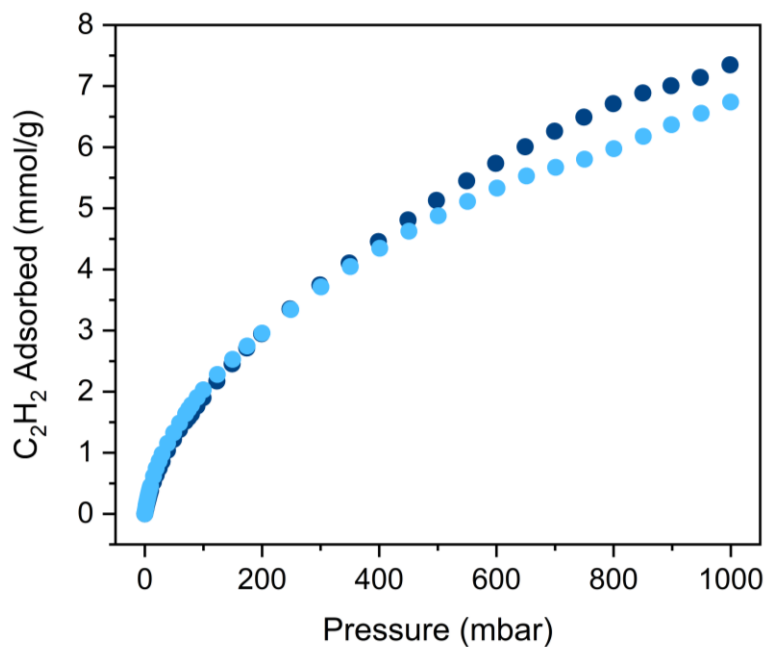


Figure 2.S33. C_2H_2 isotherms for $Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd)$ and $Fe_{1.5}Cr_{0.5}Cl_{2.5}(btdd)$ collected at 298 K.

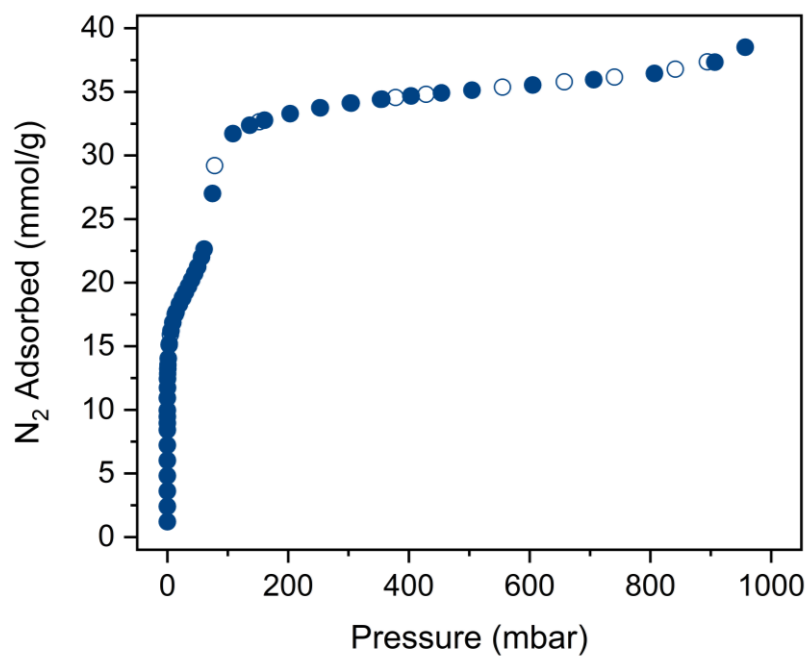


Figure 2.S34. N_2 isotherm of $Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd)$ collected at 77K.

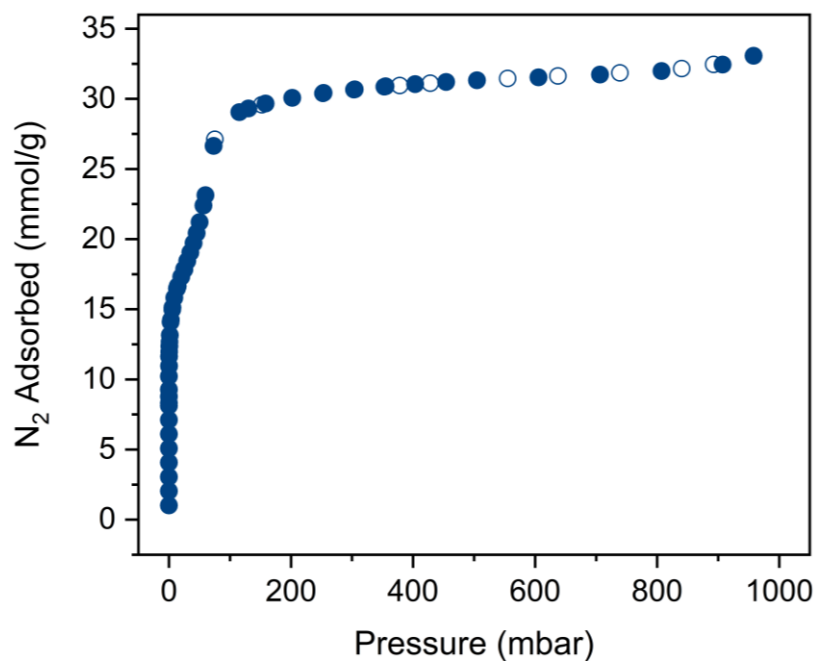


Figure 2.S35. N_2 isotherm of $Fe_{1.8}Cr_{0.2}Cl_{2.2}(btdd)$ collected at 77K

Table 2.S13. Langmuir and BET surface areas for $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{btdd})$. BET surface areas of $\text{Fe}_2\text{Cl}_2(\text{btdd})$ and $\text{FeCrCl}_3(\text{btdd})$ are in progress.

Compound	$\text{SA}_{\text{Langmuir}}$ (m^2/g)	SA_{BET} (m^2/g)	slope	y-int	P_{low} (bar)	P_{high} (bar)	q_{sat} (mmol/g)	C
$\text{Fe}_2\text{Cl}_2(\text{btdd})$	3970	-	-	-	-	-	-	-
$\text{Fe}_{1.8}\text{Cr}_{0.2}\text{Cl}_{2.2}(\text{btdd})$	3580	1850	0.0527	3.73E-5	1.92E-4	3.49E-2	19.0	1414
$\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{btdd})$	3500	1650	0.0590	2.41E-5	1.91E-4	2.00E-2	17.0	2443
$\text{FeCrCl}_3(\text{btdd})$	3090	-	-	-	-	-	-	-

Additional variable temperature carbon monoxide isotherms are being performed for all mixed metal iron-chromium and iron-zinc MOFs. These isotherms will be fit to a piecewise Langmuir-Freundlich equation to extract meaningful thermodynamic parameters to describe the gas adsorption event as was done in Reference 11.

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2.7. Acknowledgements

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Chapter 3: Modifying Acetylene Adsorption Strength Through Metal Dilution in Iron-Triazolate Metal–Organic Frameworks

3.1. Introduction

Hydrocarbon gases are essential petrochemically-derived commodity chemicals that have many industrial applications, including use as fuels and as precursors for chemical synthesis.¹ Due to the source of their derivation, these gases are typically extracted as a complex mixture which requires several steps to separate. These separation steps rely on energy intensive techniques, such as cryogenic distillation or extractive separation which require heating or cooling of the feed stream.² These techniques also rely on minute differences in the chemical and physical properties of the mixture components, such as boiling point, kinetic diameter, dipole moment and polarizability.³ Due to the similarities in the physical properties of these gases, designing energy efficient adsorbents that can exploit these differences is a challenge.

Table 3.1. Physical parameters of selected gases.⁴

Adsorbate	Boiling Point (K)	Kinetic Diameter (Å)	Dipole Moment (x10 ¹⁸ esu cm)	Polarizability (x10 ⁻²⁵ cm ³)
C ₂ H ₂	188.40	3.3	0	33.9-39.3
C ₂ H ₄	169.42	4.2	0	42.52
C ₂ H ₆	184.6	4.4	0	44.3
CO ₂	216.6	3.3	0	29.11

Metal–organic frameworks have been extensively studied for use in hydrocarbon separations which often employ techniques such as chemical sieving or kinetics effects to achieve the desired separation.^{3,5} One of the most effective strategies that has emerged among this class of materials is the targeting of the ability of olefins and paraffins to form π -bonds with various chemical moieties.⁶ Frameworks containing open metal sites are particularly suited for this strategy due to the excess electron density afforded by the unsaturated coordination geometries available for gas binding. A canonical example of this technique is in the separation of acetylene from ethylene using Fe₂(dobdc), which boasts coordinatively-unsaturated Fe(II) metal sites.⁷ It was later shown with longer chain hydrocarbons that by modifying the ligand scaffold and thereby the structural properties of the framework, the thermodynamics of the adsorptive separation could be adjusted.⁸

With the successes in tuning carbon monoxide adsorption in Fe₂Cl₂(btdd) by introducing a secondary metal into the framework lattice shown in Chapter 2, employment of this technique towards separation of other gases capable of π -bonding was a research area of interest. Here, we report the synthesis of a new framework Fe_{1.5}Cr_{0.5}Cl_{2.5}(bbta) and assess its propensity for use in light hydrocarbon separations. We use Fe₂Cl₂(bbta) as control to determine the changes in adsorption resulting from the structural modification of this framework. Powder X-ray diffraction was used to elucidate the gas binding motifs in these frameworks and infrared spectroscopy was used to determine the electronic differences between the two materials.

3.2. Experimental Section

3.2.1. Materials and Methods

Two sources of the $H_2(bbta)$ ligand were used in this work. Some of the ligand was synthesized according to literature procedures⁹ but due to the synthetic challenges of procedure and the price of the reagents, the ligand was also purchased from Chemsoon (CAS: 7221-63-8). The literature procedure yields a light tan solid with long needle-like crystals, while the ligand purchased from the commercial vendor was a pale-yellow microcrystalline powder. Both linkers had identical NMR spectra and produced materials with identical powder diffraction patterns and surface areas. All other reagents were purchased from commercial vendors and used without any further purification. All metal salts used for MOF synthesis were purchased in as mesh beads in ampoules sealed under inert gas at 99.999% purity. MOF syntheses and spectroscopic analyses were performed air-free. Syntheses were performed in an Mbraun Unilab Pro glovebox using a nitrogen atmosphere. All gases used for adsorption, and all structural and *in-situ* spectroscopic measurements were ultra-high 5.0 (99.999%) purity. Inductively coupled plasma-optical emission spectroscopy used to determine metal ratios was performed on an Optima 7000 DV Spectrometer in the Microanalytical Facility at UC Berkeley.

Due to the discovery of the methanol sensitivity of the $Fe_2X_2(btdd)$ frameworks, the synthesis of $Fe_2Cl_2(bbta)$ was also modified to eliminate methanol. $Fe_2Cl_2(bbta)$ was synthesized by combining the $H_2(bbta)$ ligand in a 1:2.5 molar ratio of ligand to metal salt. This corresponds to 39.6 mg of $FeCl_2$ (0.312 mmol) and 20.0 mg of $H_2(bbta)$ (0.125 mmol). For $Fe_{1.5}Cr_{0.5}Cl_{2.5}(bbta)$, it was found that a 1:1 ratio of metal salt to ligand yielded a more crystalline and higher capacity material, a ratio which corresponds to 3.84 mg $CrCl_2$ (0.0312 mmol) and 11.9 mg $FeCl_2$ (0.0934 mmol). The $H_2(bbta)$ ligand was weighed out into six separate 20 mL scintillation vials. Six times the value of the desired metal salt was weighed out and dissolved in 12 mL of dimethylformamide (DMF) measured using a micropipette. 2 mL of each metal salt solution was placed into each of the six vials and diluted with an additional 6 mL of DMF, for a total reaction volume of 10 mL. The six vials were sealed with Teflon tape and electrical tape then heated to 120 °C in an aluminum block for 4 days. If solid formed on the side of the vial over the course of the synthesis, the vial was shaken to break up the solid. After synthesis, the vials were removed from heat and vacuum filtered to remove the supernatant. The filtrate was collected and suspended in 20 mL of fresh DMF and heated to 120 °C for 24 hours. The DMF was then decanted and replaced with fresh DMF. This process was repeated 5 times to reach a total of 6 washes. After the final DMF wash, the solvent was decanted and replaced with 20 mL acetonitrile (MeCN) which was heated at 60 °C for 24 hours. The solvent was then decanted and replaced with 20 mL of fresh acetonitrile. This process was repeated 5 times to reach a total of 6 washes. After the final wash, the solvent was decanted, and the sample was pre-activated under vacuum at 120 °C for 2-3 hours after which the sample was placed in a glass analysis tube suitable for a Micromeritics surface area and porosity analyzer (ASAP) and capped with a TranSeal, at which point it was heated under high vacuum at

200 °C, with a heating ramp rate of 2 °C/min for 3 days until an off-gassing rate of less than 3 $\mu\text{bar min}^{-1}$ had been achieved.

3.2.2. Powder X-ray Diffraction

High-resolution synchrotron X-ray powder diffraction data for all samples were collected at beamline 17-BM at the Advanced Photon Source at Argonne National Laboratory with a Perkin-Elmer *a*-Si flat panel detector. Diffraction patterns reported in this work were collected at a wavelength of 0.45192 Å. Samples were prepared in borosilicate glass capillaries which were dosed with 500 mbar of CO, ethylene or ethane using a gas adsorption analyzer and flame sealed. The temperature was controlled during these measurements with an Oxford Cryosystems Cryostream 800. The crystal structure analyses including indexing, Pawley and Rietveld refinements were performed with the program TOPAS-Academic v4.1.16.^{10,11}

The space groups of all structures were determined by first indexing the powder patterns and performing a subsequent Pawley refinement to determine the goodness of fit for that combination of unit cell parameters. After obtaining accurate lattice parameters, the structural solution for the parent $\text{Fe}_2\text{Cl}_2(\text{bbta})$ framework was used as a structural model for Rietveld refinement.¹² All hydrogen atoms were added to the final refined structure using the CCDC program Mercury and therefore no error values are reported for these atoms in the structure information files and figures.

3.2.3. Gas Adsorption

Gas-adsorption isotherms collected for pressures between 0 and 1 bar were measured volumetrically using a Micromeritics ASAP2020 or Micromeritics 3Flex gas adsorption analyzer. To perform these measurements, first, ~60 mg of sample was activated according to the methods previously described. To determine the mass of the sample, the analysis tube capped with a TranSeal was evacuated and weighed on an electronic balance. After activation, the tube containing the desolvated sample was then weighed and the mass of the sample was determined by subtracting the mass of the empty tube. The tube was then transferred back to the analysis port of the gas adsorption instrument. For all isotherms, warm and cold free-space correction measurements were performed using ultrahigh-purity He gas. Isotherms collected in the range 5–45 °C were measured in a Syltherm bath using a Julabo 200F water circulator filled with a water and ethylene glycol mixture. N_2 isotherms collected at 77 K were measured in liquid-nitrogen baths. Langmuir surface areas were determined from N_2 adsorption data collected at 77 K using Micromeritics software and BET surface areas were calculated using the BET equation.

3.2.4. Diffuse Reflectance Infrared Fourier-Transform Spectroscopy

Infrared spectra were collected using a Bruker Vertex 70 spectrometer equipped with a glowbar source, KBr beamsplitter, and a liquid nitrogen cooled mercury-cadmium-telluride detector. A custom-built diffuse reflectance system with an IR-accessible gas dosing cell was used for all measurements. Sample temperature was controlled by an Oxford Instruments OptistatDry TLEX cryostat, and sample atmosphere was controlled by a Micromeritics ASAP 2020Plus gas sorption analyzer. In a typical experiment, a sample of the desolvated framework material was dispersed in dry KBr (10 wt %) by gently mixing the two powders in an argon-filled glovebox and was subsequently evacuated at room temperature overnight. Spectra were collected in situ under UHP-grade carbon monoxide gas at 4 cm^{-1} resolution until equilibrium was observed in both pressure

output and spectra. IRsotherms were performed by simultaneously measuring a gas adsorption isotherm on the ASAP 2020Plus and collecting IR spectra after carefully weighing out the sample mass during preparation to obtain accurate gas uptake values.

3.3. Results and Discussion

3.3.1. Design and Synthesis

As was established in Chapter 2, due to the smaller size of the H₂(bbta) ligand, the pressure of step onset in Fe₂Cl₂(bbta) is 200 mbar lower than that of Fe₂Cl₂(btdd). This makes Fe₂Cl₂(bbta) a good candidate for implementation of metal dilution to target other π -acidic gases such as acetylene and ethylene and determine if these gases can prompt a spin crossover. Towards that end, Fe_{1.5}Cr_{0.5}Cl_{2.5}(bbta) was synthesized through solvothermal methods using FeCl₂ and the H₂(bbta) in dimethylformamide. The framework was determined to be isostructural to Fe₂Cl₂(bbta) using powder X-ray diffraction and a structural solution, shown in Figure 3.1, was obtained via Rietveld refinement. The chromium percentage was confirmed using ICP-OES.

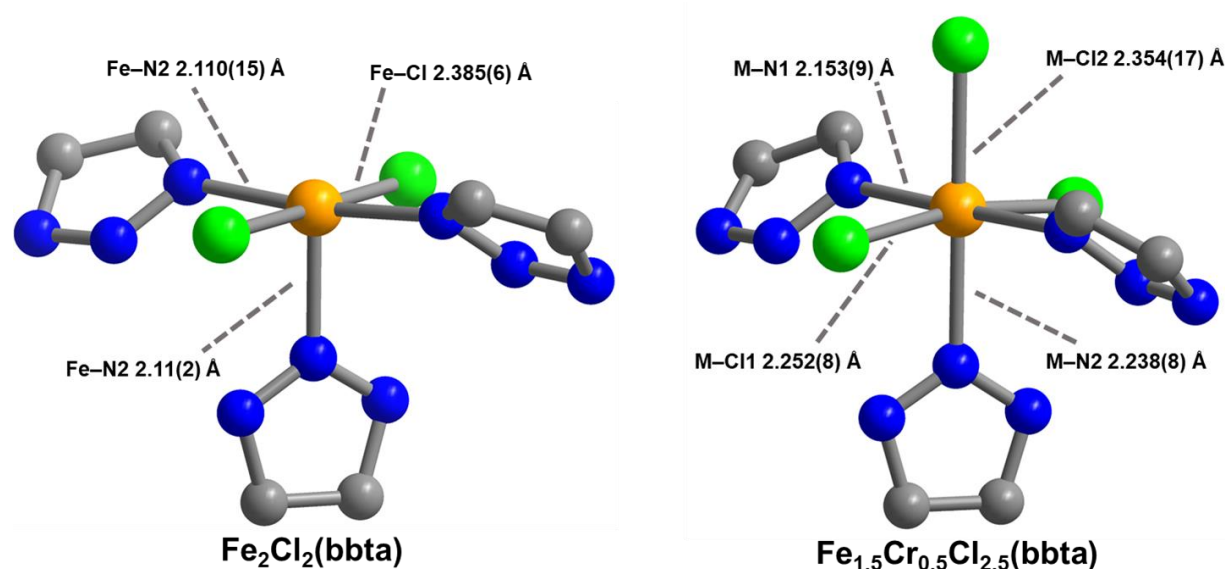


Figure 3.1. Left: Depiction of the coordination geometry at the open metal site of Fe₂Cl₂(bbta) including selected bond distances. Iron, chlorine, nitrogen and carbon are represented by orange, green, blue and grey spheres respectively. Right: Coordination geometry and selected bond distances of Fe_{1.5}Cr_{0.5}Cl_{2.5}(bbta) derived from Rietveld refinement of powder X-ray diffraction data.

Fe₂Cl₂(bbta) was synthesized using a new methanol-free reaction pathway outlined in the Experimental Section. Despite a myriad of efforts, the full capacity and surface area of this

framework both using the literature synthesis¹² or the modified synthesis never reached the reported/theoretical value of 5.87 mmol of CO gas per gram of material, equal to one gas molecule per open metal site. The average surface area for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ that is regularly achievable is around $900 \text{ m}^2/\text{g}$ which corresponds to a CO capacity is 4.0 mmol/g (Fig. 2.2). $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ exhibits a CO capacity of 3.0 mmol/g (Fig. 2.3), which is consistent with the capacity of the Fe(II) framework where 25% of the metal sites are occupied by terminal chloride anions.

3.3.3. Gas Adsorption

To investigate the utility and tunability of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ for use in hydrocarbon separations a variety of gas adsorption isotherms were performed. A typical carbon monoxide isotherm for this framework is shown in Figure 3.2, which displays the expected cooperative adsorption behavior with a step onset centered at 200 mbar. This step onset is slightly higher than that previously reported, which occurs at 180 mbar. As previously mentioned, the capacity of this framework is also about 2 mmol/g lower than the theoretical and reported capacity. This is likely due to defect sites, as the microcrystalline powder that forms during the reaction is extremely fine which is typically a sign of the formation of atypical morphologies as a result of rapid crystallization.¹³ This is observed for both the literature and the modified synthetic procedures. The presence of defect sites is also supported by the decrease in the slope of the step region of the isotherm relative to that of $\text{Fe}_2\text{Cl}_2(\text{btdd})$, which exhibits near full capacity CO uptake, suggesting a paucity of defect sites. A decrease in the slope of cooperative processes is an indicator of a decrease in degree of cooperativity of a system, which can be explained by the presence of defect sites such as linker and metal absences which would disrupt the spin crossover which requires metal site coupling to proceed unimpeded.¹⁴

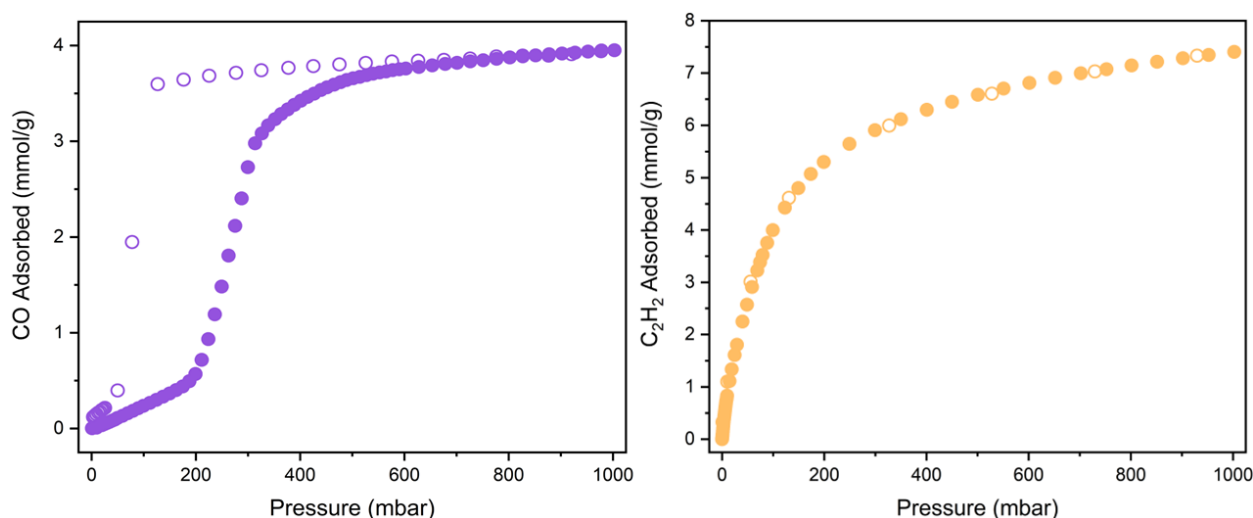


Figure 3.2. Left: Carbon monoxide isotherm, Right: acetylene isotherm for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ collected at 298 K. Closed circles denote adsorption, open circles denote desorption.

Also shown in Figure 3.2 is an acetylene isotherm for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ collected at 298 K which shows Langmuir-Type I behavior with relatively steep uptake at low pressures, indicative of chemisorption with physisorption apparent at higher pressures.¹⁵ Most notably, the total uptake of this material at 1 bar is 7.4 mmol/g, nearly double that of the CO uptake which can be taken as a proxy for the number of accessible open metal sites. This suggests that there is an additional strong adsorption site present in the framework that can accommodate an additional acetylene molecule.

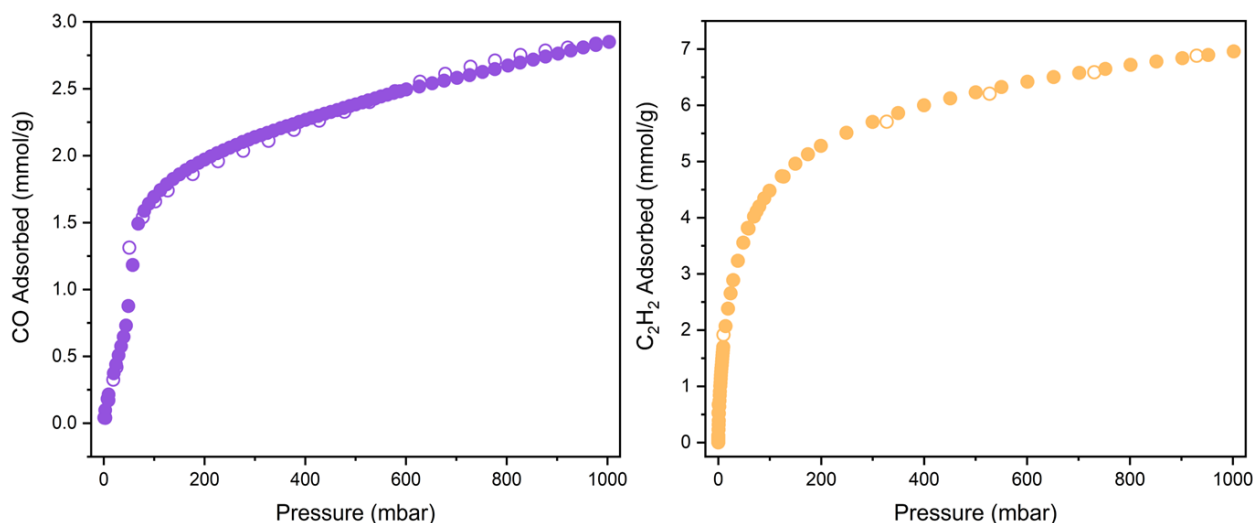


Figure 3.3. Left: Carbon monoxide isotherm, Right: acetylene isotherm for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ collected at 298 K. Closed circles denote adsorption, open circles denote desorption.

Figure 3.3 shows a carbon monoxide isotherm of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ with a step pressure onset at 30 mbar, which is significantly lower than that of $\text{Fe}_2\text{Cl}_2(\text{btdd})$ at 200 mbar. This is consistent with the experiments performed for the $\text{M}_2\text{X}_2(\text{btdd})$ analogues and can be attributed to lattice contraction of the framework from inclusion of Cr(III) reducing ΔH and ΔS of lattice vibration and bond contraction during the spin crossover event.^{16,17} As previously stated, the capacity of this framework drops by 25% relative to that of the all-Fe(II) framework, consistent with the inclusion of non-gas binding, chloride-terminated Cr(III) metal centers. Room temperature acetylene isotherms for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ show the same increase in uptake, in this case about a 2.3-fold increase in overall capacity, which implies there are several binding sites available akin to $\text{Fe}_2\text{Cl}_2(\text{bbta})$.

This result, however, disproves the hypothesis that lowering the barrier to spin crossover makes cooperative gas binding behavior accessible with weaker π -acidic gases since acetylene also has empty π -antibonding orbitals available for back-bonding with the Fe(II) open metal site like CO. This could be due to the fact that, unlike CO, acetylene is not capable of σ -donation to the high-spin Fe(II) sites before the metal undergoes spin crossover and engages in backbonding. This σ -donation from the adsorbate increases the electron density at the high spin metal site, facilitating crossover, a phenomenon which is evidenced by infrared experiments with $\text{Fe}_2\text{X}_2(\text{btdd})$ frameworks, which show non-classical metal-carbonyl interactions characterized by blue shifted CO stretches.^{18,19}

Despite the lack of cooperativity and because of the unexpected acetylene uptake capacity in $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{bbta})$ frameworks, ethylene, ethane and CO_2 isotherms were measured to evaluate

the utility of these frameworks for use in hydrocarbon separations. Acetylene, ethylene, ethane and CO₂ isotherms for Fe₂Cl₂(bbta) collected at 298 K are shown in Figure 3.4. Isotherms were also collected at 308 and 318 K (Fig. 2.S1) to calculate thermodynamic parameters and selectivity values derived from fits using the Langmuir-Freundlich equation. The isosteric heat of adsorption for all gases was calculated using the Clausius-Clapeyron relation which resulted in a value of –52 kJ/mol for acetylene at 1 mmol/g, indicating that this material has a strong chemisorptive interaction with the gas.²⁰ This value is only slightly lower than that of CO which was reported to be –62 kJ/mol.¹² Interestingly the isosteric heat of adsorption for CO₂ is the next highest after acetylene with a value of –34 kJ/mol at 1 mmol/g loading followed by ethylene at –30 kJ/mol and ethane at –13 kJ/mol. Ideal Adsorption Solution Theory (IAST)²¹ selectivities for Fe₂Cl₂(bbta) are shown in Figure 3.5 which show a moderate selectivity of 5.8 for acetylene over ethane for an equimolar mixture of gas at 298 K. This selectivity is divergent from what is seen in a comparable framework Fe₂(dobdc) which exhibits a reverse selectivity for ethylene over acetylene under the same conditions.⁷ Fe₂Cl₂(bbta) similarly shows a moderate selectivity of 3.7 for ethylene in a room temperature equimolar mixture of ethylene and ethane and 1.6 at 218 K which is significantly lower than that of Fe₂(dobdc) with a selectivity of 13.7 at 318 K.²²

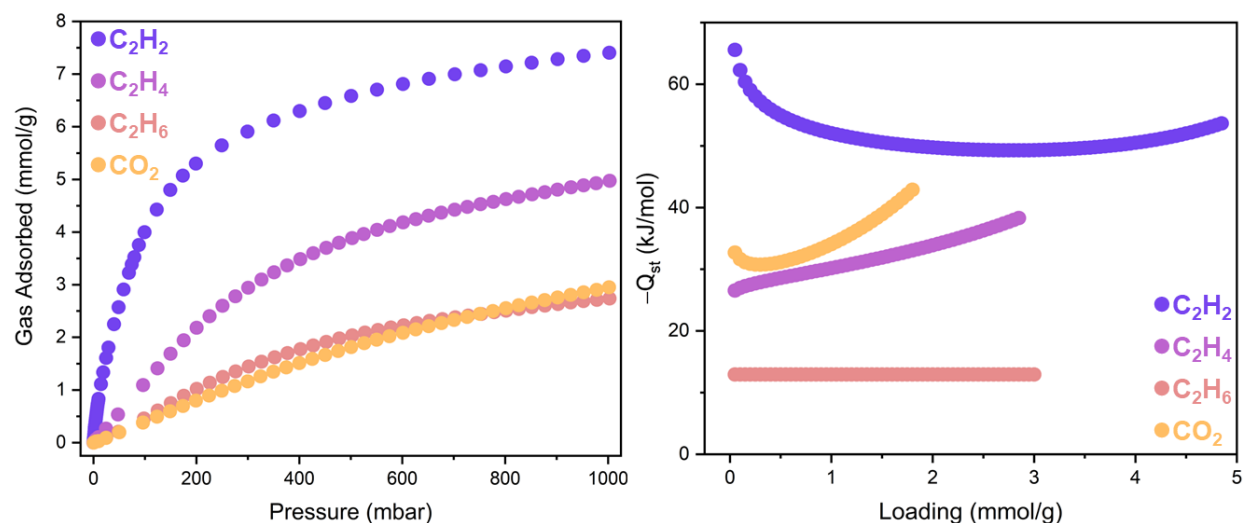
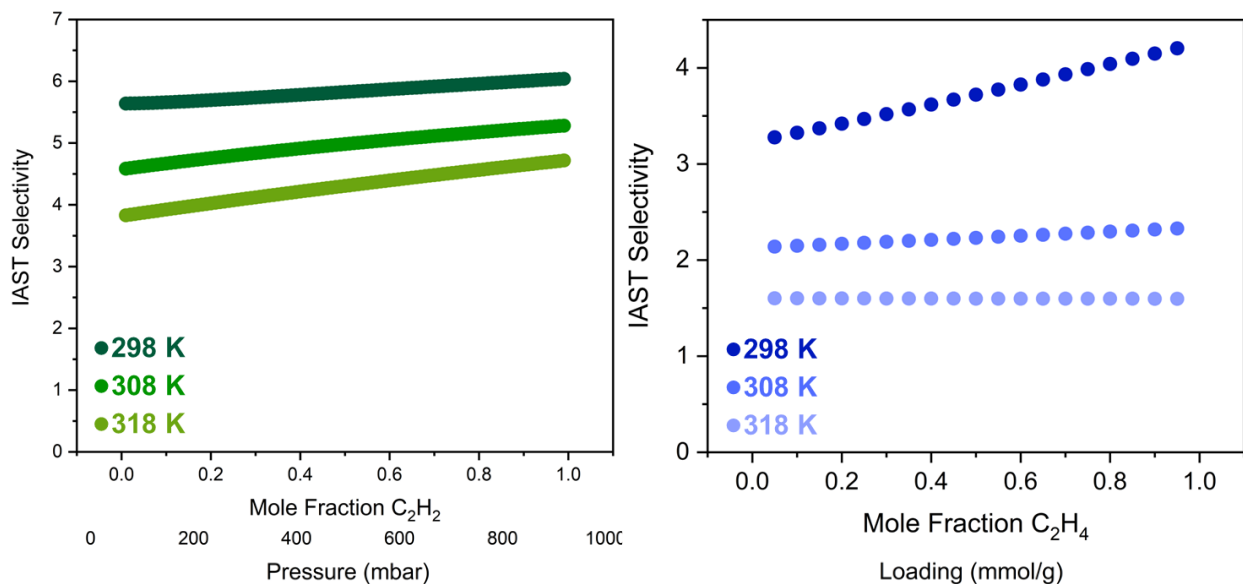


Figure 3.4. Left: Acetylene (purple), ethylene (dark pink), ethane (light pink), and carbon dioxide (yellow) isotherms collected for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ at 298 K. Right: isosteric heats of adsorption or $-Q_{\text{st}}$ values, calculated for acetylene (purple), ethylene (dark pink), ethane (light pink), and carbon dioxide (yellow).

Figure 3.5. Left: IAST selectivities for acetylene over ethylene calculated from data collected for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ at 298 K, 308 K and 318 K. Right: IAST selectivities for ethylene over ethane calculated from data collected at 298 K, 308 K and 318 K.

$\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ was subjected to the same set of gas adsorption experiments, the results of which are shown in Figure 3.6 along with calculated isosteric heats of adsorption for acetylene, ethylene, ethane and CO_2 . Notably the isosteric heat of adsorption for acetylene is higher than that of the all-Fe(II) framework with a value of -62.5 kJ/mol at 1 mmol/g loading which suggests a stronger chemisorptive interaction in this framework. The Q_{st} values show the expected trend of decreasing value with decreasing propensity for π -backbonding with the metal site which corresponds to values of -50 kJ/mol, -35 kJ/mol and -31 kJ/mol for ethylene, ethane and CO_2 respectively. The resultant IAST selectivities are reported in Figure 3.7 which show lower values for both acetylene over ethylene and ethylene over ethane than $\text{Fe}_2\text{Cl}_2(\text{bbta})$ which is a result of



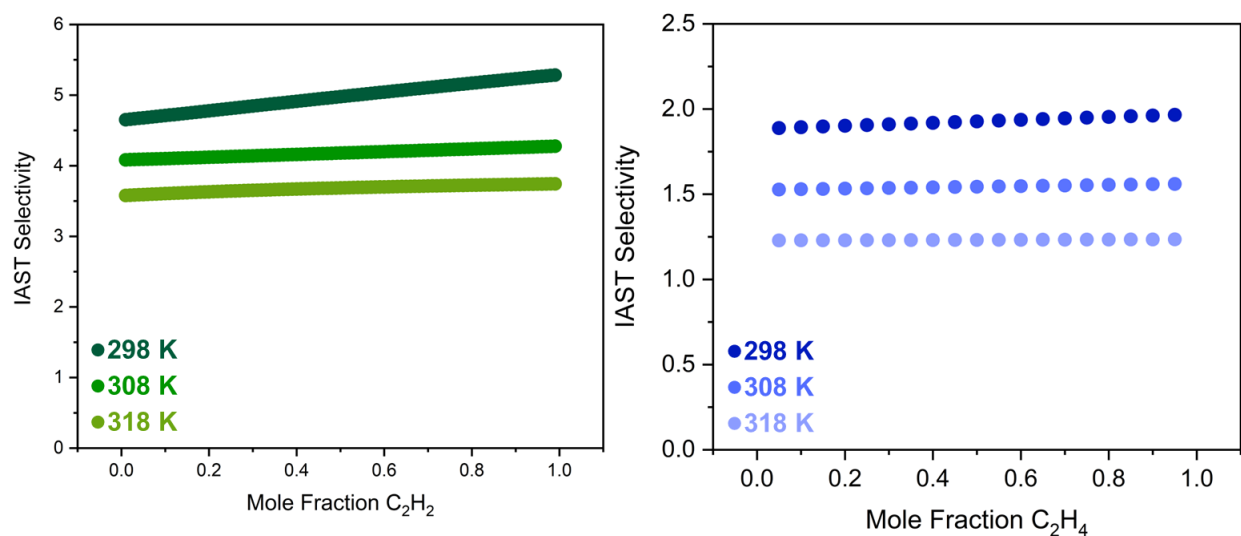
the higher isosteric heat of adsorption for ethylene in this framework.

Figure 3.6. Left: Acetylene (purple), ethylene (dark pink), ethane (light pink), and carbon dioxide (yellow) isotherms collected for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ at 298 K. Right: isosteric heats of adsorption or Q_{st} values, calculated for acetylene (purple), ethylene (dark pink), ethane (light pink), and carbon dioxide (yellow).

Figure 3.7. Left: IAST selectivities for acetylene over ethylene calculated from data collected for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ at 298 K, 308 K and 318 K. Right: IAST selectivities for ethylene over ethane calculated from data collected at 298 K, 308 K and 318 K.

3.3.4. Structural Characterization via Powder X-ray Diffraction

To investigate the origins of the changes in gas adsorption behavior between the $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{bbta})$ variants, powder X-ray diffraction was employed. Variable pressure *in situ* gas dosing measurements were performed using acetylene, which are shown for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ in Figure 3.8. A clear unit cell contraction can be seen as the pressure is incrementally increased from 0.01 bar to 1 bar. This unit cell contraction correlates to a 1.5% change in overall unit cell volume which is far less than that the 11.7% decrease seen upon spin crossover as a result of CO binding.¹²



Therefore, the contraction can be attributed to strong binding of the acetylene molecule, which is supported by the acetylene isothermal data and the calculated Q_{st} value, but confirms that spin crossover and cooperative binding is absent in this system. Detailed unit cell parameters derived from Rietveld refinements can be seen in Table 3.S6.

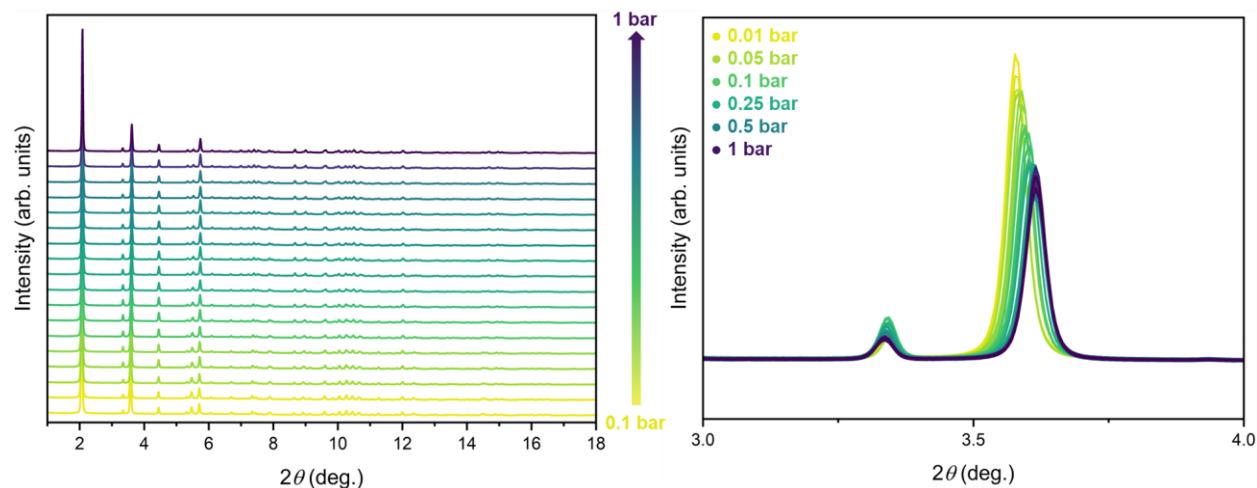


Figure 3.8. Variable pressure *in situ* acetylene dosed PXRD patterns of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ collected at 298 K over a pressure range of 0.01 bar to 1 bar. The unit cell undergoes a contraction as the pressure of acetylene in the system increases. $\lambda = 0.45192 \text{ \AA}$.

Structural models for acetylene dosed $\text{Fe}_2\text{Cl}_2(\text{bbta})$ at variable pressures were obtained through Rietveld refinement to elucidate the binding motifs present and identify a secondary binding site responsible for the increased capacity of this material. Structural solutions for experiments performed at 0.05 and 0.5 bar are shown in Figure 3.9. At a pressure of 0.05 bar, one acetylene molecule per metal site with an occupancy of 0.96(2) can be identified. This corresponds well to the acetylene uptake observed for this framework at 50 mbar, which is close to the maximum capacity of the open metal sites of 4.0 mmol/g as indicated by the CO isotherms that can serve as a proxy for the number of available open metal sites. At a pressure of 0.5 bar, an additional binding site becomes apparent along the *c*-axis of the framework in a diagonal stacking pattern as depicted in Figure 3.9. These secondary acetylene molecules have a refined occupancy of 0.37(2), a reasonable value based on the isotherm data which has an uptake of ~6.5 mmol/g at 0.5 bar.

At both a pressure of 0.05 and 0.5 bar, the acetylene molecule has an elongated C–C bond length relative to that of free acetylene at 1.2026 Å, which is indicative of a π -backbonding interaction with the open metal site.²³ The refined C–C and Fe–C bond lengths differ slightly at both pressures, but they can be considered equivalent within the error of the experiment. The bond length of the pore-dwelling acetylene is also slightly elongated which can be attributed to interactions with the neighboring acetylene molecules due to their short intermolecular distances.²⁴ However, the short C $\cdots$ C contacts are also likely an artifact of the disorder caused by symmetry of the space group which generates the second pore dwelling acetylene molecule through a two-fold rotational axis. The acetylene bond distances observed for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ are similar to of $\text{Fe}_2(\text{dobdc})$ which has a C–C bond length of 2.282 Å and two separate Fe–C bond lengths of 2.52(1) Å and 2.48(1) Å due to the slight reduction in space group symmetry to *R*-3.⁷ These similar bond lengths correlate well with the comparable Q_{st} values for these two frameworks, which are –52 and –47 kJ/mol for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ and $\text{Fe}_2(\text{dobdc})$, respectively. There does not appear to be any significant interaction with the framework lattice that brings about the diagonal stacking orientation of the acetylene molecules relative to one another, but this conformation is analogous to one of the two lowest energy geometries adopted by acetylene in the solid state crystal structure which has C $\cdots$ C contacts of 3.63 Å.^{25,26} Therefore, it is likely that this arrangement arises from the distance between

the two open metal binding sites along the *c*-axis being advantageous for the packing of two acetylene molecules between the metal-bound molecules.

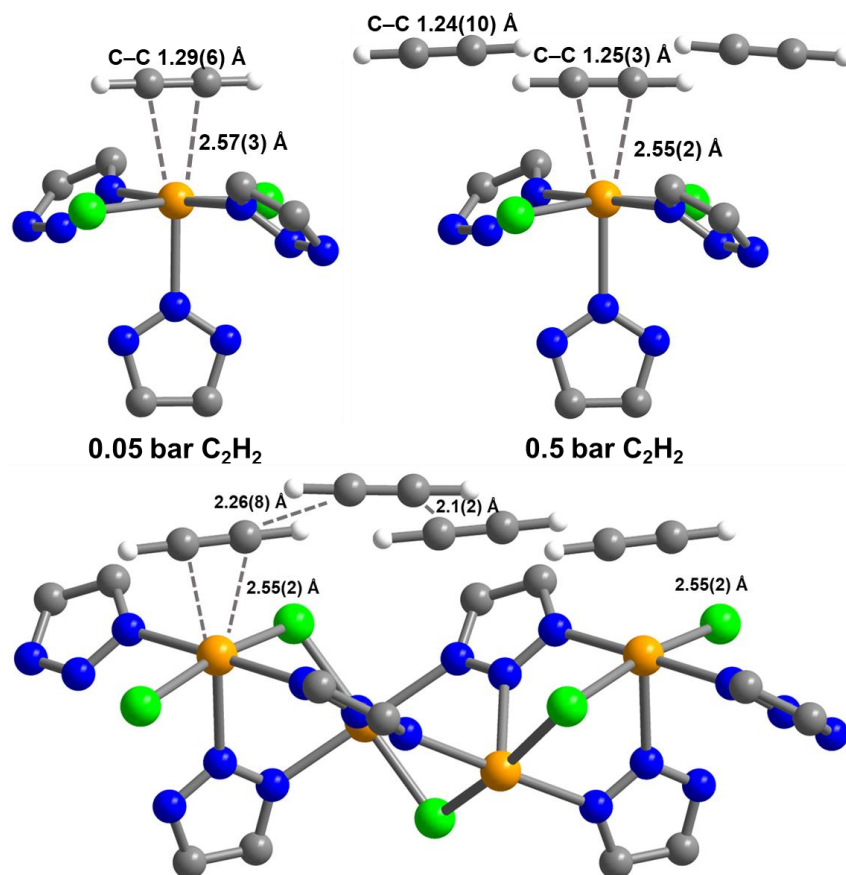


Figure 3.9. Acetylene binding motifs at the first coordination sphere of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ at pressures of 0.05 bar (top left) and 0.5 bar (top right). At low pressures, acetylene is bound to the open metal site alone. Since the metal site lies on a special position, the full metal-bound acetylene molecule is generated by symmetry. At higher pressures acetylene occupies a secondary binding site along the *c*-axis of the framework (bottom center), shown here at 0.5 bar. The pore-dwelling acetylene molecules have a partial occupancy and the second molecule is generated by symmetry elements inherent to the $R\bar{3}m$ space group. All gas molecules have high thermal displacement parameters indicating that significant disorder is likely present, but could not be modeled due to the limitations of powder diffraction. The short inter-acetylene distances can likewise be attributed to disorder.

Structural solutions were also obtained for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ dosed with ethylene and ethane. In these experiments the framework was sealed in a capillary under an intermediate pressure of gas and the temperature was varied to simulate an isothermal experiment. Powder diffraction patterns for these experiments can be seen in Figure 3.S7-2.S8 and unit cell parameters can be found in Table 3.S7. The resultant structural models are shown in Figure 3.10 which show binding motifs for ethylene and ethane that are analogous to those seen in $\text{Fe}_2(\text{dobdc})$. The C–C bond length of ethylene is slightly elongated relative to free ethylene at 1.3390 Å suggesting there could be some degree of π -backbonding with the bound gas, however this elongation is within error of the experiment.²³ The Fe–C bond of 2.55(5) Å is much longer than that observed in $\text{Fe}_2(\text{dobdc})$ of 2.42(2) Å, which is in line with the much lower isosteric heat of adsorption in $\text{Fe}_2\text{Cl}_2(\text{bbta})$ of –30 kJ/mol versus that of $\text{Fe}_2(\text{dobdc})$ at –45 kJ/mol. The weakness of the Fe– C_2H_4 interaction is confirmed by the absence of a significant unit cell contraction upon binding, as the lattice only contracts 0.4% when ethylene is bound. An even weaker interaction is seen for ethane, which is canted away from the metal site making the hydrogen atoms the closest metal-gas contacts at a distance of 2.351 Å. This interaction geometry is similar to that of $\text{Fe}_2(\text{dobdc})$ with ethane which has closest Fe–C and Fe–H contacts of 3.09 Å and 2.59 Å respectively. The ethane molecule is slightly more canted in $\text{Fe}_2\text{Cl}_2(\text{bbta})$ which could be due to ligand-adsorbate hydrogen bonding interactions with the chloride, where there is a distance of 2.1 Å. It should be noted that hydrogen atoms cannot be located by powder X-ray diffraction and were added after the refinement; therefore no errors are reported on these values and C–H distances used are standard values.

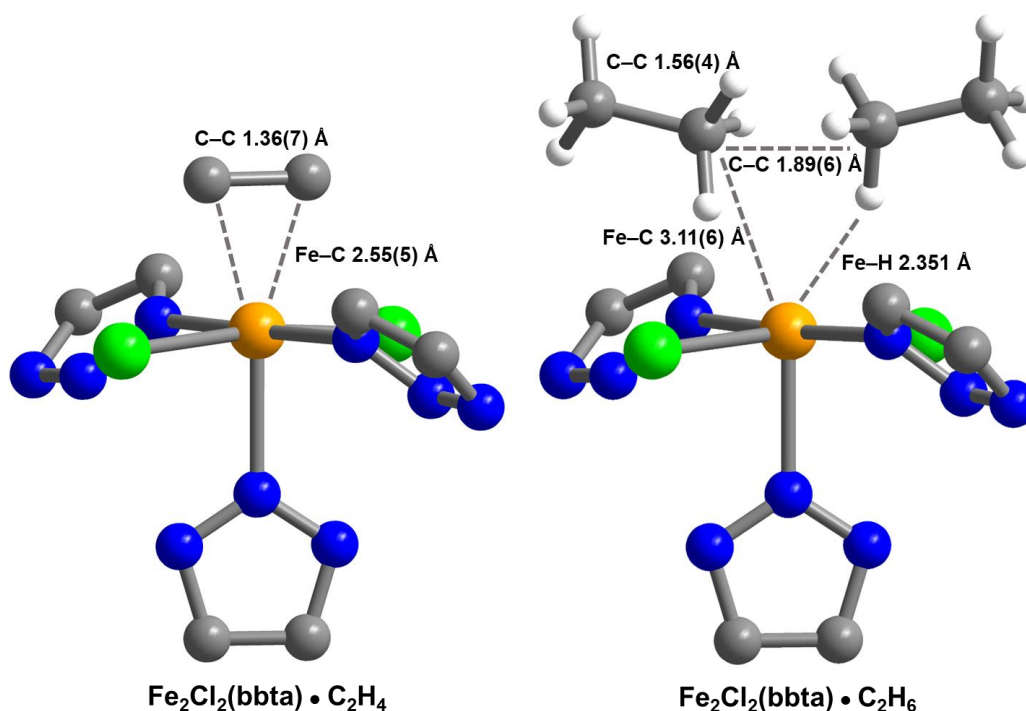


Figure 3.10. Structural solutions of binding motifs of ethylene (left) and ethane (right) in $\text{Fe}_2\text{Cl}_2(\text{bbta})$ at a pressure of 0.5 bar and temperature of 223 K. The carbon atom of ethylene has a partial occupancy of 0.589(4) and the second atom is generated by a two-fold rotational axis. In the ethane bound structure, the two carbon atoms were located independently and their occupancies were made equivalent and calculated to be 0.69(2). The second molecule of ethane is generated by the same two-fold rotational axis and the position of the molecule is therefore disordered over these two positions.

An analogous set of diffraction experiments was performed for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ where acetylene was dosed at variable pressures under a constant temperature seen in Figure 3.11. Unlike in the all-Fe(II) material, there is no measurable lattice contraction that occurs (Table 3.S8) indicating that there is not a significant change in the crystal lattice upon gas binding, despite the high Q_{st} value of -62.5 kJ/mol. Isobaric, variable temperature experiments were undertaken by dosing $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ with CO, ethylene and ethane, the patterns for which can be seen in Figures 2.S10-2.S12 and unit cell parameters for which are listed in Table 3.S9. Carbon monoxide produces a unit cell contraction of 0.5%, but none of the other gases produce a statistically significant change in unit cell volume. Due to the presence of the terminal chloride atom in this framework, which causes significant disorder at the open metal site, structural solution of the gas-bound frameworks is an ongoing challenging. Preliminary structural solutions for CO, acetylene, ethylene and ethane bound to $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ can be seen in Figure 3.S13.

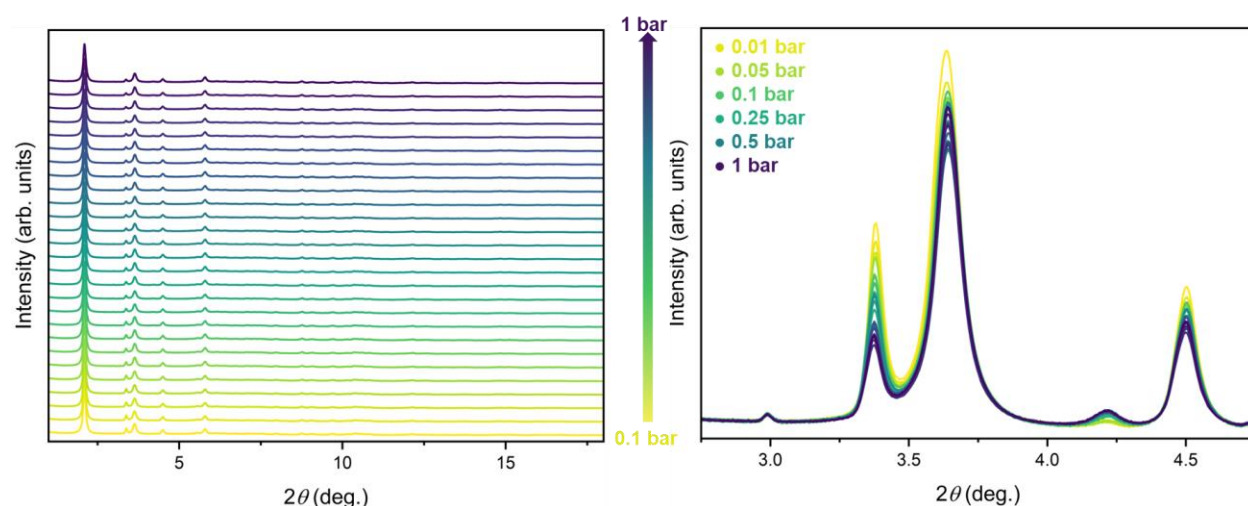


Figure 3.11. Variable pressure *in situ* acetylene dosed PXRD patterns of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ collected at 298 K over a pressure range of 0.01 bar to 1 bar. The unit cell undergoes a contraction as the pressure of acetylene in the system increases. $\lambda = 0.45192$ Å.

A current hypothesis for the increase in the binding strength of acetylene with the inclusion of chromium into the $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{bbta})$ lattice is that the 4.7% contraction of the unit cell afforded by the metal dilution generates a more optimal metal-metal distance. This allows the acetylene molecules to interact along the pore of the framework in a more favorable manner, akin to that seen in the lowest energy conformations of the acetylene dimers formed in gas phase calculations which bear resemblance to the stacking arrangement seen for $\text{Fe}_2\text{Cl}_2(\text{bbta})$.²⁴ A similar effect was calculated for the framework UTSA-74 which experiences an increased heat of adsorption for acetylene due to favorable acetylene-acetylene interactions brought about by decreased distance between open metal sites relative to Zn-MOF-74.²⁷ Since the structural solution for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ at 0.5 bar of acetylene shows that the acetylene molecules prefer to pack along the *c*-axis, small changes in the distance between open metal sites could play a role in the strength of gas binding. Additionally, interactions between the acetylene molecules and the terminal chlorides could provide further stabilization of these stacking arrangements due to the polarizability of the chloride anion.

3.3.5. Infrared Spectra

To investigate the electronic interaction between acetylene and the $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{bbta})$, *in situ* acetylene dosing infrared spectroscopy was employed. The resultant spectra for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ and $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ are shown in Figure 3.12. Both frameworks exhibit two red-shifted stretches in the region of the C–C stretch of acetylene which occurs at 1974 cm^{-1} in free acetylene, the values for which are listed in Table 3.²³ The decrease in the stretching frequency indicates that there is some degree of π -backbonding from the Fe(II) open metal site to the acetylene antibonding orbitals. The two different stretches can be assigned to the two crystallographically distinct sites determined by powder diffraction. The lower energy stretch which occurs at $\sim 1946\text{ cm}^{-1}$ in $\text{Fe}_2\text{Cl}_2(\text{bbta})$ and $\sim 1941\text{ cm}^{-1}$ in $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ is assigned to the metal-bound species whereas the higher energy stretch located at $\sim 1959\text{ cm}^{-1}$ in $\text{Fe}_2\text{Cl}_2(\text{bbta})$ and $\sim 1956\text{ cm}^{-1}$ in $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ corresponds to the pore dwelling acetylene molecule. Both stretches in the $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ are at lower energies than those of the all-Fe(II) framework, which is indicative of a slightly stronger framework-gas interaction, corroborating the higher isosteric heat of adsorption in that material. Interestingly, there is also a slight evolution of the higher energy stretch with increasing pressure. This could be due to changes in inter-acetylene interactions as excess acetylene diffuses through the material and compresses the pore-dwelling species in the secondary binding site towards neighboring molecules.

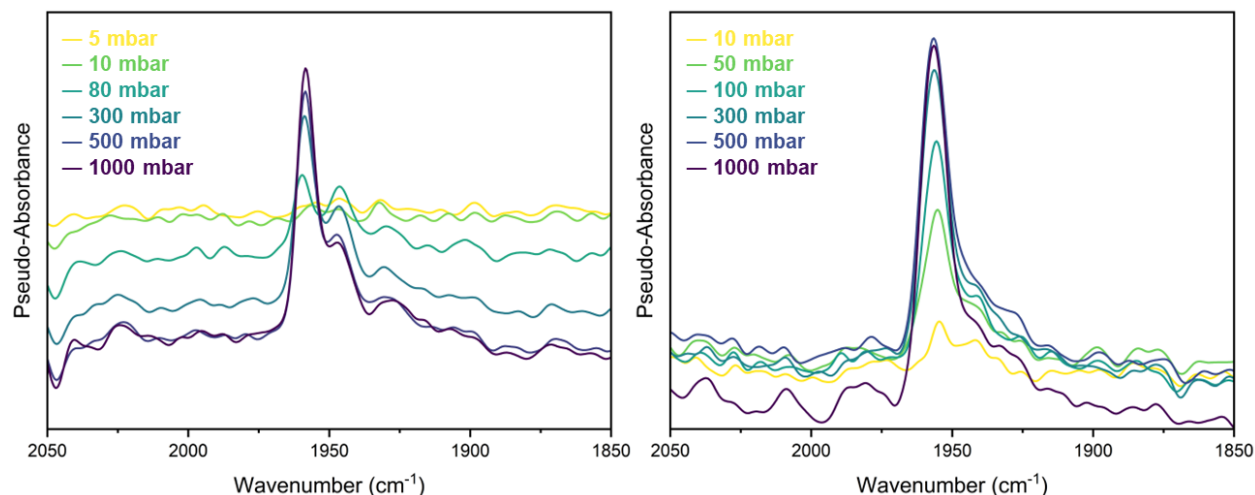


Figure 3.12. Left: Difference plot of the infrared spectrum of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ dosed with 5-1000 mbar of acetylene. This plot highlights the C–C stretch of acetylene which shows two different frequencies that correspond to the two binding sites determined by X-ray diffraction. Right: Difference plot of the infrared spectrum of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ dosed with 10-1000 mbar acetylene.

Table 3.2. Acetylene C–C stretching frequencies for dosed $\text{Fe}_{2-x}\text{Cr}_x\text{Cl}_{2+x}(\text{bbta})$ frameworks. Free $\text{C}_2\text{H}_2 = 1974\text{ cm}^{-1}$.

$\text{Fe}_2\text{Cl}_2(\text{bbta})$		$\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$	
Pressure (mbar)	C–C Stretch (cm^{-1})	Pressure (mbar)	C–C Stretch (cm^{-1})
5	1946.4	10	1954.6/1941.6
10	1955.6/1946.4	50	1955.1/1941.1
80	1959.4/1945.9	100	1955.6/1940.6
300	1958.5/1946.4	300	1956.0/1941.1
500	1958.5/1947.4	500	1956.5/1939.6
1000	1958.5/1946.4	1000	1956.5/1941.1

3.4. Conclusions

Metal dilution was used as a technique to modify the structure of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ -type frameworks. The inclusion of Cr(III) led to an expected contraction in the crystal lattice, which was confirmed by structural solution of powder X-ray diffraction data. Gas adsorption experiments reveal that metal dilution leads to a decrease in the onset of step pressure in CO isotherms, which is consistent with what was seen for the isoreticular $\text{Fe}_2\text{Cl}_2(\text{btdd})$ frameworks. A series of hydrocarbon gas adsorption measurements were undertaken to see if spin-crossover would occur upon binding of weaker π -acidic gases. Cooperative binding behavior was not observed, but large isosteric heats of adsorption were calculated for acetylene, and larger than expected uptake suggested that there are multiple binding sites in the crystal lattice for this gas. Additional gas adsorption experiments show the Q_{st} value for acetylene adsorption increases upon dilution with Cr(III). IAST calculations reveal that both $\text{Fe}_2\text{Cl}_2(\text{bbta})$ and $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ are selective for acetylene over ethylene and ethylene over ethane.

Powder X-ray diffraction allowed for the location of a secondary binding site for acetylene along the *c*-axis of the framework where an additional two molecules are stabilized by inter-acetylene interactions. Structural solutions also showed that the acetylene molecules bound to the open metal sites have elongated C–C bonds which is suggestive of π -back donation. This is corroborated by *in situ* gas dosing IR experiments which show the presence of two distinct redshifted acetylene C–C stretches which can be assigned to each of the crystallographically distinct acetylene species. It is hypothesized that the increased heat of adsorption in the Cr(III) diluted framework is due to optimization of the secondary binding site by decreasing the distance between open metal sites.

3.5. Supplementary Information

3.5.1. Gas Adsorption

Dual-Site Langmuir-Freundlich Fits of Pure Component Isotherms

The adsorption isotherms were fit with a dual-site Langmuir model (1), where n is the amount of gas adsorbed by the material in mmol/g, $q_{sat,i}$ is the saturation capacity in mmol/g, P is the pressure in bar, b_i is the Langmuir parameter in bar^{-1} and v_i is the Freundlich parameter. The fitted parameters for each adsorption isotherm can be found in Tables 2.S1-2.S5.

$$n = \frac{q_{sat,1}b_1P^{v_1}}{1+b_1P^{v_1}} + \frac{q_{sat,2}b_2P^{v_2}}{1+b_2P^{v_2}} \quad (1)$$

$$b_i = e^{\frac{-S_i}{R}} e^{\frac{E_i \times 1000}{RT}} \quad (2)$$

An expansion of the Langmuir parameter is shown in (2), where S_i is the site-specific integral entropy of adsorption in J/mol·K, E_i is the site-specific differential enthalpy of adsorption in kJ/mol, R is the gas constant in J/mol·K, and T is the temperature in K. Isotherms collected for Fe_2Cl_2 -(bbta) were fit independently for each temperature (see Figure 3.S2), while isotherms for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}$ -(bbta) were fit simultaneously. Adsorption parameters for fits for Fe_2Cl_2 -(bbta) can be found in Table 3.S1-2.S4 and those for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}$ -(bbta) can be found in Table 3.S5.

Isosteric Heats of Adsorption

The isosteric heats of adsorption ($-Q_{st}$) were calculated by solving (1) for explicit values of n at a minimum of 3 temperatures, in this work 298, 308 and 318 K. The isosteric heats of adsorption as a function of the amount of gas adsorbed were determined using the integrated form of the Clausius-Clapeyron equation (3) by calculating the slope of $\ln(p)$ vs $1/T$ for each loading.

$$(\ln p)_n = \left(\frac{Q_{st}}{R} \right) \left(\frac{1}{T} \right) + C \quad (3)$$

Ideal Adsorbed Solution Theory (IAST) Selectivity Calculations

Ideal Adsorbed Solution Theory (IAST) was used along with the solutions to the Langmuir-Freundlich fits to simulate dual component isotherms and estimate the selectivity of the material as a function of the mole fraction of gas in the stream. The selectivities for acetylene over ethylene, ethane and CO_2 as well as ethylene over ethane were calculated with relation (4) where n is the amount of each gas adsorbed and x is the mole fraction of each gas.

$$S = \frac{n_{gas1}/n_{gas2}}{x_{gas1}/x_{gas2}} \quad (4)$$

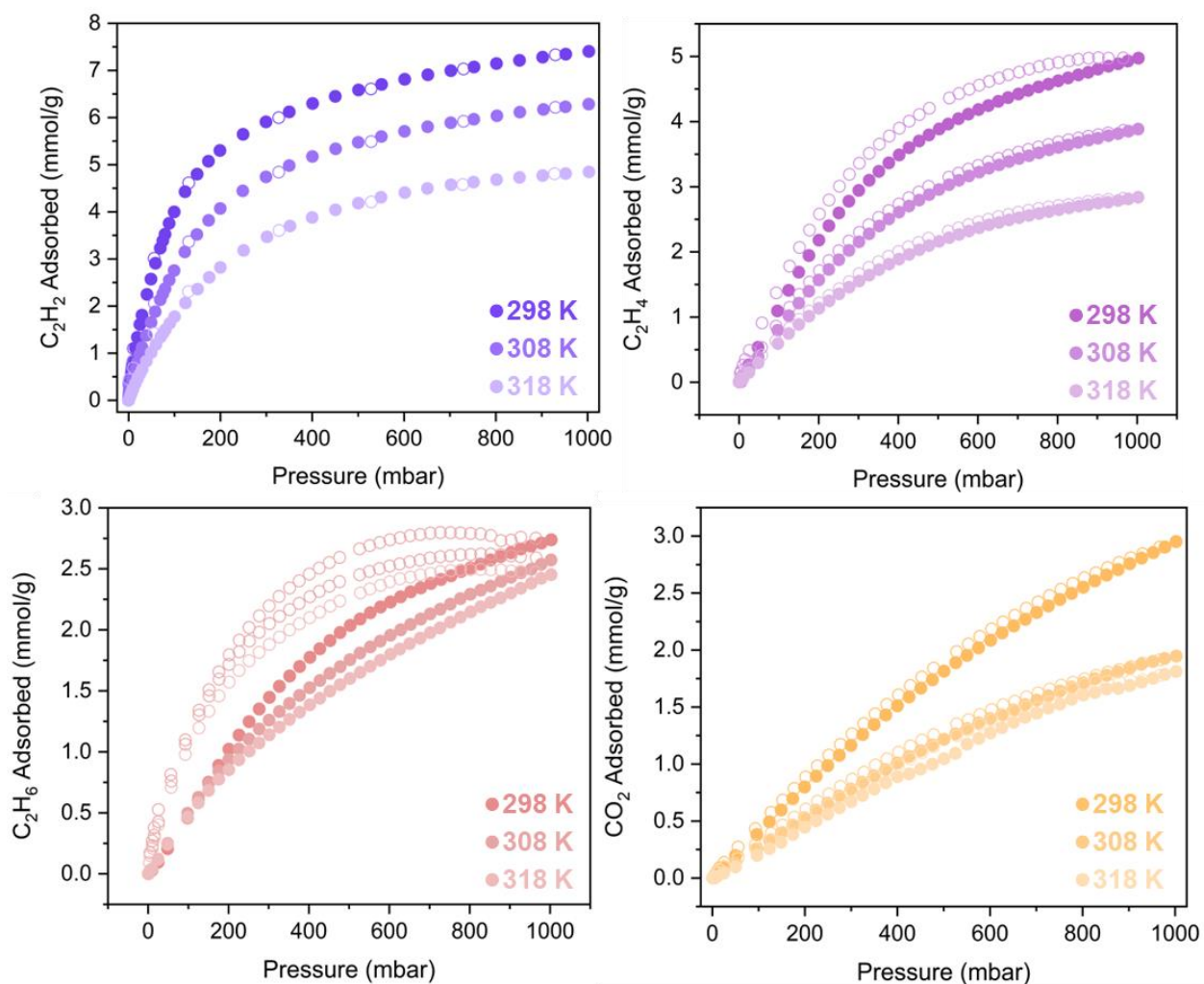


Figure 3.S1. Top Left: Acetylene isotherms for $\text{Fe}_2\text{Cl}_2(\text{bbta})$ collected at 298 K, 308 K and 318 K. Top Right: Ethylene isotherms collected at 298 K, 308 K and 318 K. Bottom Left: Ethane isotherms collected at 298 K, 308 K and 318 K. Bottom Right: Carbon dioxide isotherms collected at 298 K, 308 K and 318 K.

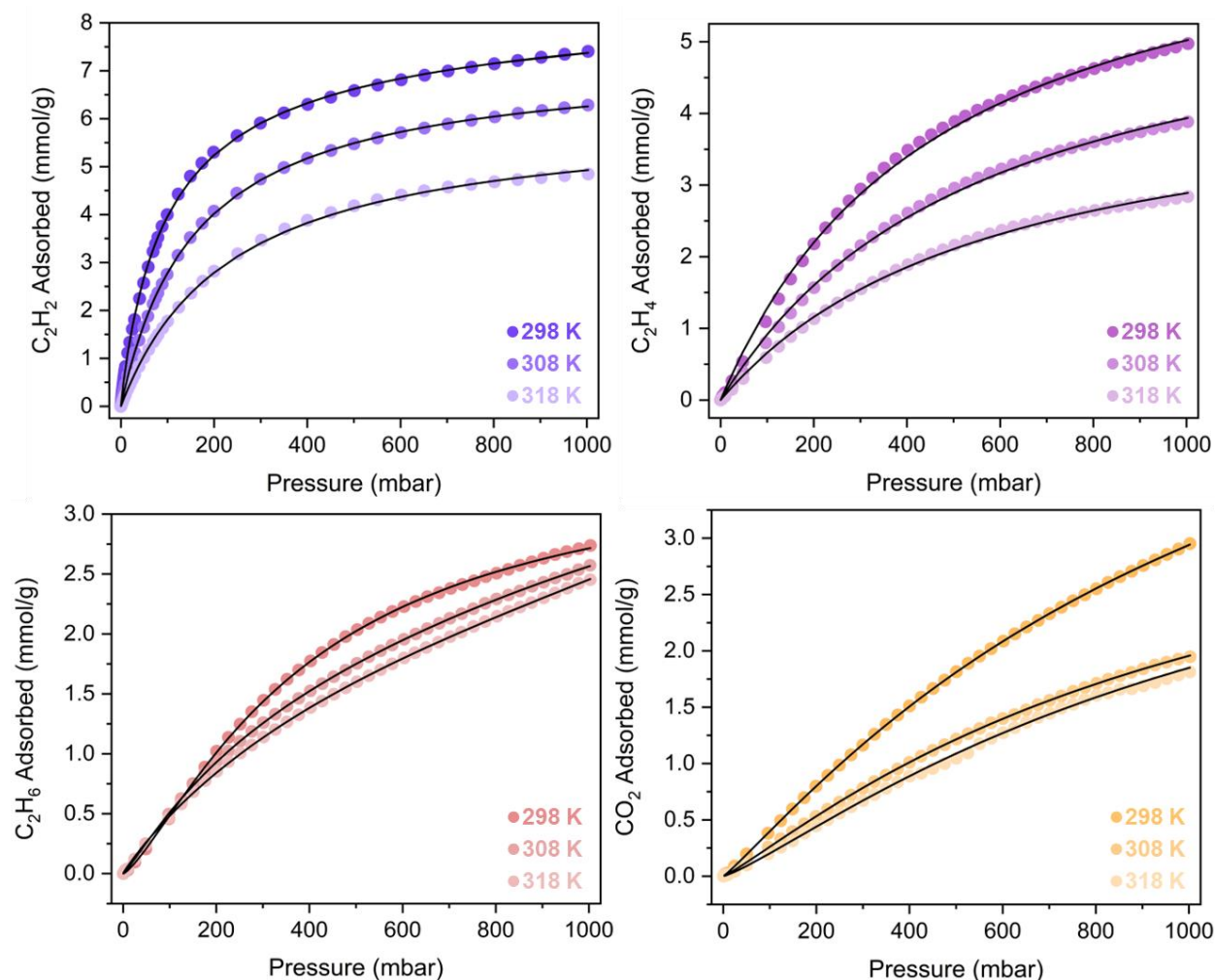


Figure 3.S2. Dual-site Langmuir-Freundlich fits of variable temperature acetylene (top left), ethylene (top right), ethane (bottom left), and carbon dioxide (bottom right) isotherms of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ collected at 298 K, 308 K and 318 K.

Table 3.S1. Acetylene adsorption parameters for Fe₂Cl₂(bbta) for the individual temperature dual site Langmuir-Freundlich equation. Note that the values are representative of the best mathematical fit, not necessarily true thermodynamic parameters.

	298 K	308 K	318 K
$q_{\text{sat},1}$ (mmol/g)	4.27	2.34	2.11
E_1 (–kJ/mol)	21.7	22.1	21.4
S_1 (–R)	11.1	6.98	6.66
v_1	0.771	1	1
b_1	0.980	5.12	4.22
$q_{\text{sat},2}$ (mmol/g)	7.78	4.94	3.99
E_2 (–kJ/mol)	38.5	29.7	23.5
S_2 (–R)	13.4	9.69	7.43
v_2	0.945	1	1
b_2	8.81	6.77	4.22

Table 3.S2. Ethylene adsorption parameters for Fe₂Cl₂(bbta) for the individual temperature dual site Langmuir-Freundlich equation. Note that the values are representative of the best mathematical fit, not necessarily true thermodynamic parameters.

	298 K	308 K	318 K
$q_{\text{sat},1}$ (mmol/g)	3.10	2.09	1.33
E_1 (–kJ/mol)	16.9	16.3	16.3
S_1 (–R)	6.03	5.77	5.63
v_1	1.02	1.01	1.01
b_1	2.21	1.78	1.72
$q_{\text{sat},2}$ (mmol/g)	4.20	4.05	3.24
E_2 (–kJ/mol)	27.2	27.2	25.4
S_2 (–R)	10.2	10.1	9.06
v_2	1.01	1.01	1.01
b_2	2.19	1.79	1.72

Table 3.S3. Ethane adsorption parameters for Fe₂Cl₂(bbta) for the individual temperature dual site Langmuir-Freundlich equation. Note that the values are representative of the best mathematical fit, not necessarily true thermodynamic parameters.

	298 K	308 K	318 K
$q_{\text{sat},1}$ (mmol/g)	3.49	1.74	3.66
E_1 (–kJ/mol)	8.44	3.78	4.10
S_1 (–R)	2.17	0.000376	4.71
v_1	1.33	1.14	3.27
b_1	3.44	4.38	0.0426
$q_{\text{sat},2}$ (mmol/g)	0.0231	3.85	4.61
E_2 (–kJ/mol)	2.83	0.00239	11.1
S_2 (–R)	1.73	0.857	4.21
v_2	0.858	1.22	0.933
b_2	0.555	0.425	1.00

Table 3.S4. CO₂ adsorption parameters for Fe₂Cl₂(bbta) for individual temperature dual site Langmuir-Freundlich equation. Note that the values are representative of the best mathematical fit, not necessarily true thermodynamic parameters.

	298 K	308 K	318 K
$q_{\text{sat},1}$ (mmol/g)	6.36	3.93	3.91
E_1 (–kJ/mol)	5.60	5.81	5.73
S_1 (–R)	2.42	2.29	2.29
v_1	1.11	1.14	1.22
b_1	0.852	0.979	0.886
$q_{\text{sat},2}$ (mmol/g)	0.0260	0.0260	0.0260
E_2 (–kJ/mol)	3.06	3.06	3.07
S_2 (–R)	1.52	1.52	1.52
v_2	0.816	0.821	0.819
b_2	0.753	0.724	0.698

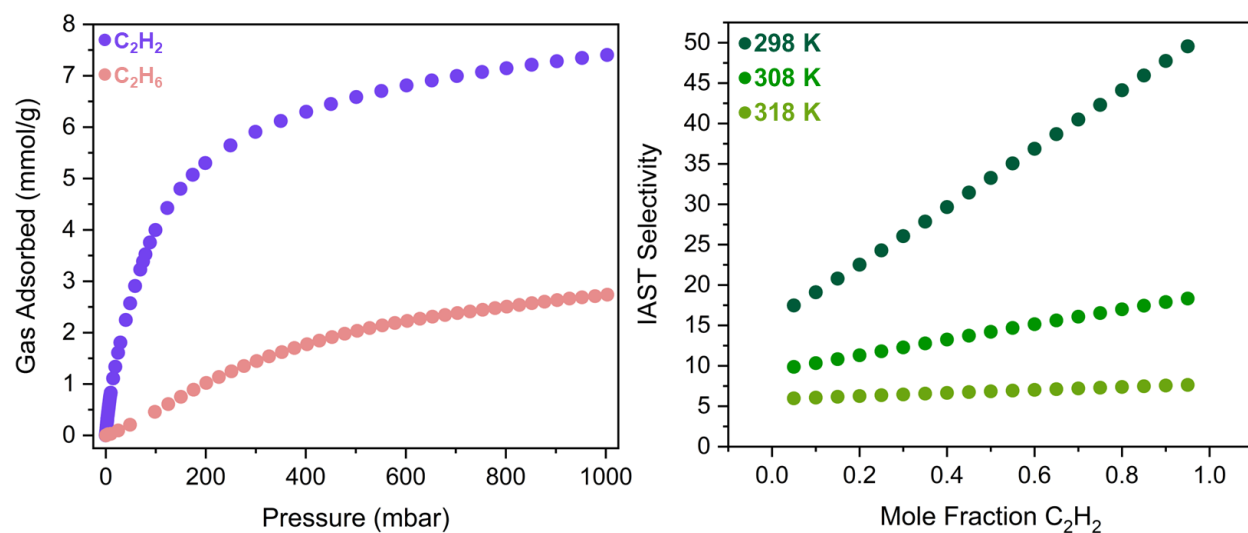


Figure 3.S3. Left: Acetylene and ethane isotherms for $Fe_2Cl_2(bbta)$ collected at 298 K. Right: IAST selectivities for acetylene over ethane calculated from data collected at 298 K, 308 K and 318 K.

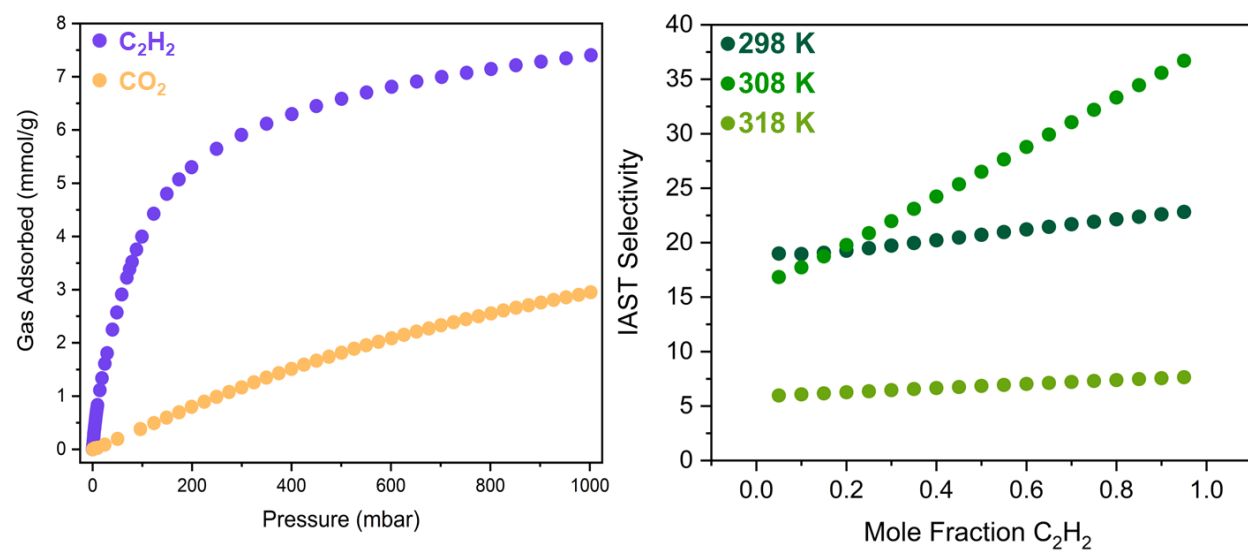


Figure 3.S4. Left: Acetylene and carbon dioxide isotherms for $Fe_2Cl_2(bbta)$ collected at 298 K. Right: IAST selectivities for acetylene over carbon dioxide calculated from data collected at 298 K, 308 K and 318 K.

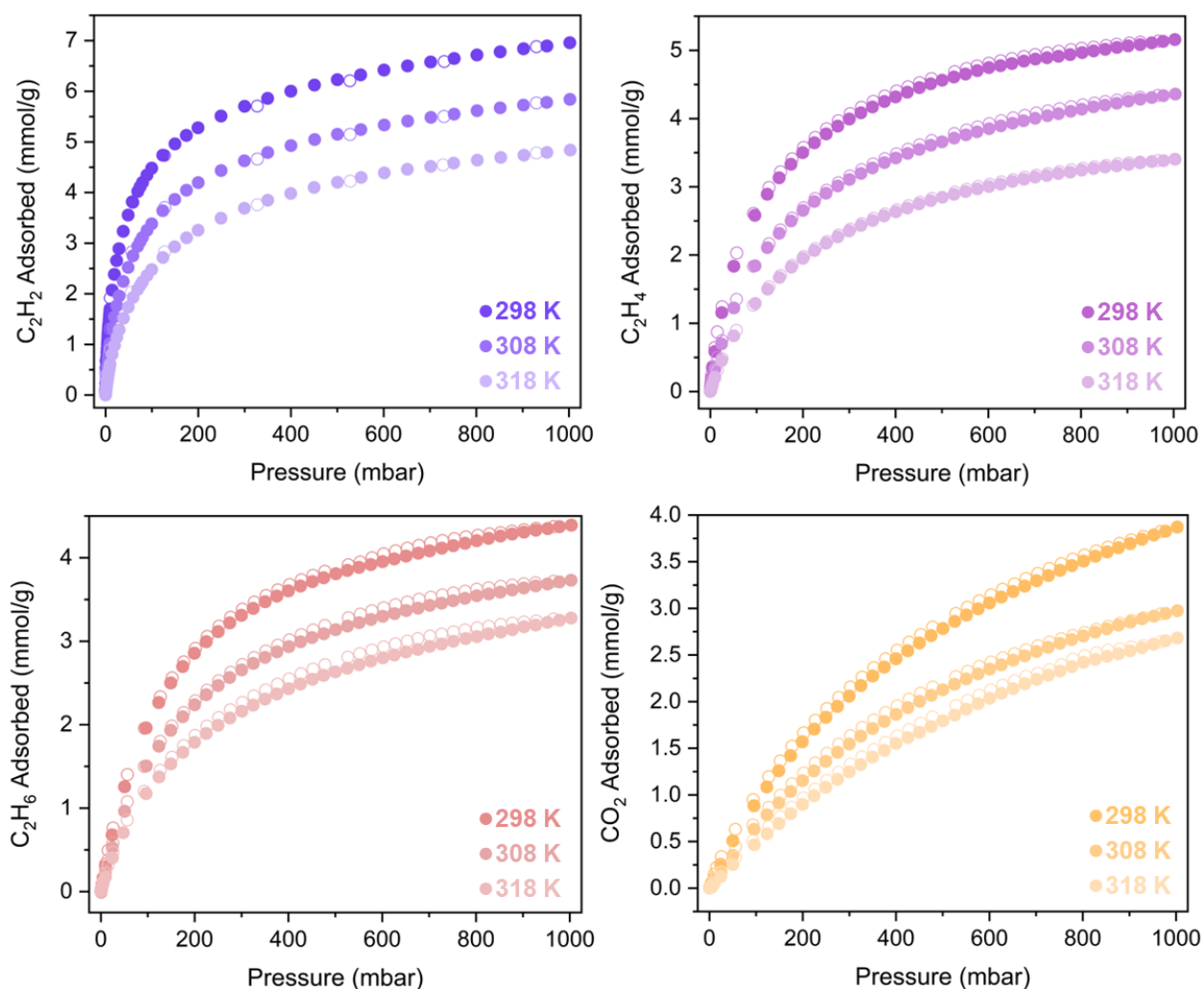


Figure 3.S5. Top Left: Acetylene isotherms for Fe_{1.5}Cr_{0.5}Cl_{2.5}(bbta) collected at 298 K, 308 K and 318 K. Top Right: Ethylene isotherms collected at 298 K, 308 K and 318 K. Bottom Left: Ethane isotherms collected at 298 K, 308 K and 318 K. Bottom Right: Carbon dioxide isotherms collected at 298 K, 308 K and 318 K.

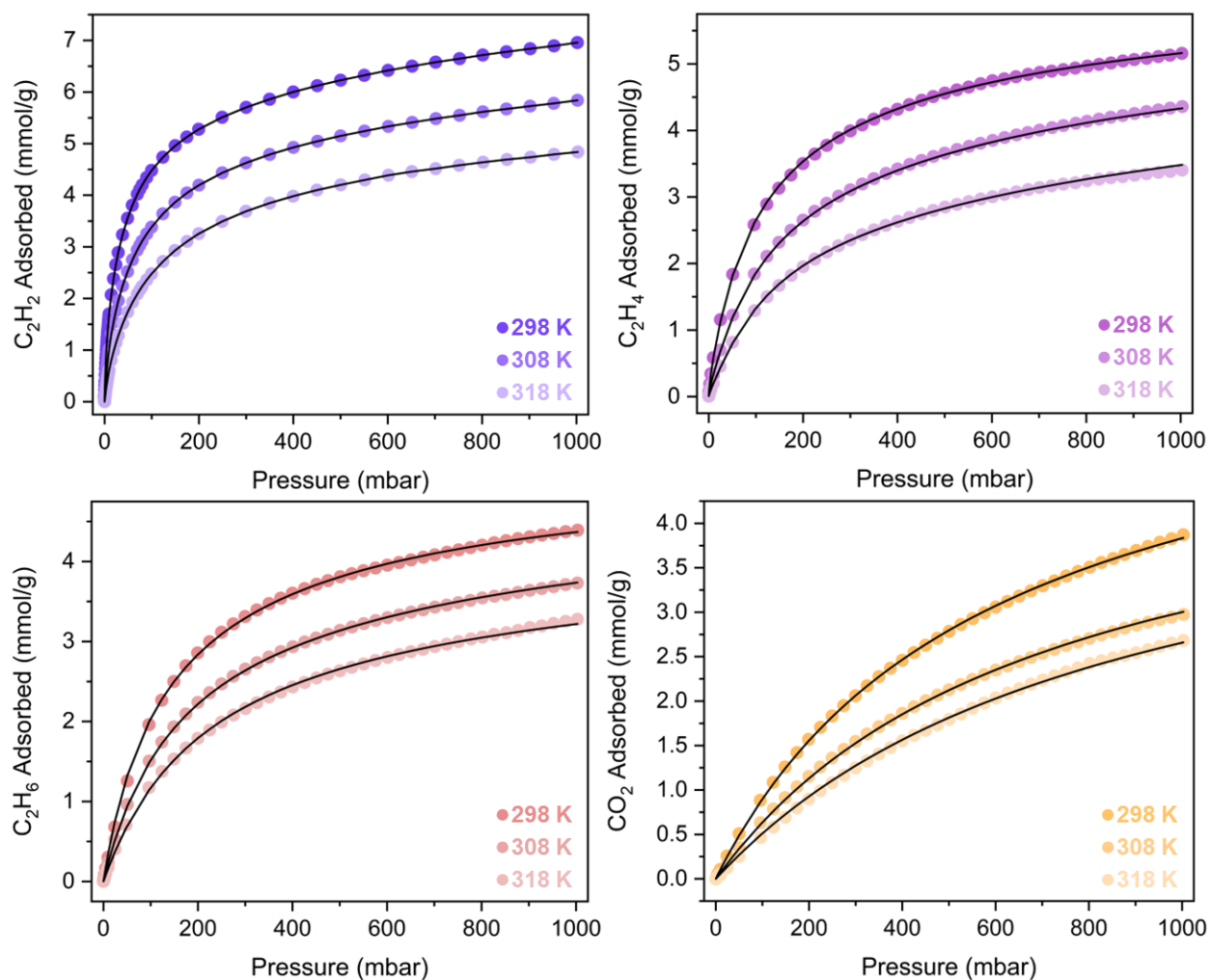


Figure 3.S6. Dual-site Langmuir-Freundlich fits of variable temperature acetylene (top left), ethylene (top right), ethane (bottom left), and carbon dioxide (bottom right) isotherms of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ collected at 298 K, 308 K and 318 K.

Table 3.S5. Adsorption parameters for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ the simultaneous-fit dual site Langmuir-Freundlich equation. Note that the values are representative of the best mathematical fit, not necessarily true thermodynamic parameters.

	Acetylene	Ethylene	Ethane	Carbon Dioxide
$q_{\text{sat},1}$ (mmol/g)	4.06	1.44	3.57	4.93
E_1 (–kJ/mol)	47.4	17.0	28.0	19.0
S_1 (–R)	15.9	3.36	9.02	7.04
v_1	0.866	1.37	1.01	1
$b_{1,298}$	25.2	33.5	9.61	1.89
$b_{1,308}$	13.6	26.8	6.67	1.47
$b_{1,318}$	7.59	21.7	4.73	1.17
$q_{\text{sat},2}$ (mmol/g)	5.71	5.22	1.73	1.43
E_2 (–kJ/mol)	53.7	53.0	91.3	207
S_2 (–R)	21.5	20.4	36.2	83.6
v_2	0.569	0.689	0.962	0.909
$b_{2,298}$	1.12	2.59	1.90	0.753
$b_{2,308}$	0.556	1.29	0.575	0.0503
$b_{2,318}$	0.288	0.674	0.188	0.00399

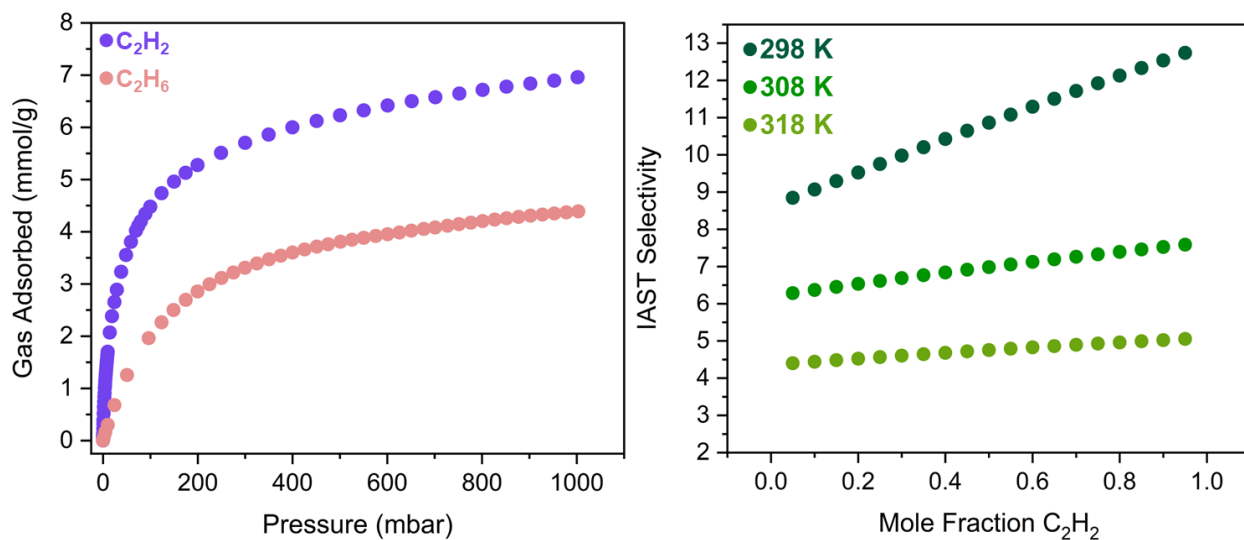


Figure 3.S7. Left: Acetylene and ethane isotherms for $Fe_{1.5}Cr_{0.5}Cl_{2.5}(bbta)$ collected at 298 K. Right: IAST selectivities for acetylene over ethane calculated from data collected at 298 K, 308 K and 318 K.

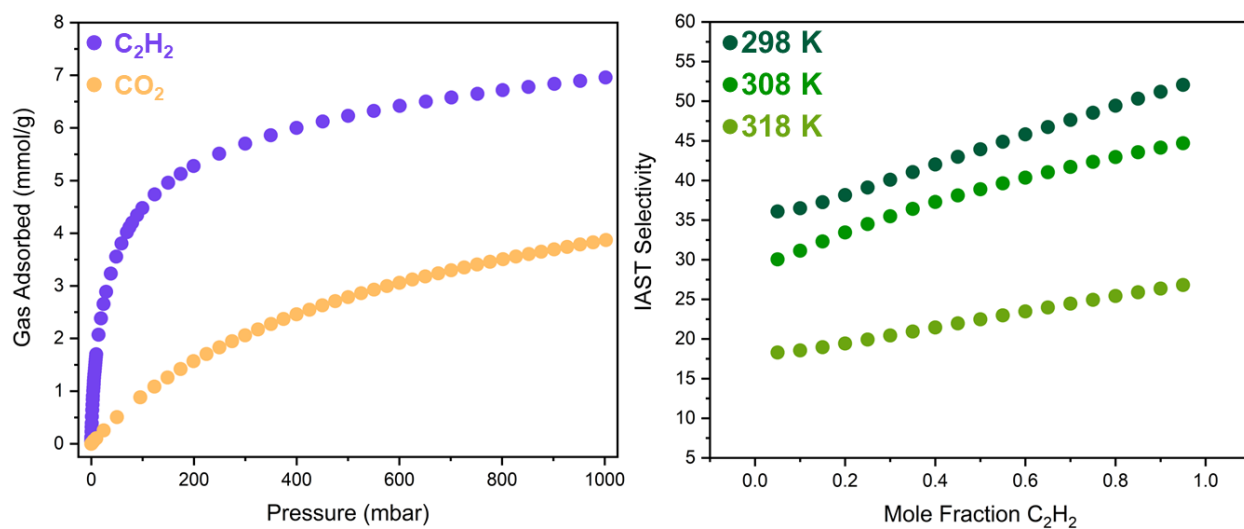


Figure 3.S8. Left: Acetylene and carbon dioxide isotherms for $Fe_{1.5}Cr_{0.5}Cl_{2.5}(bbta)$ collected at 298 K. Right: IAST selectivities for acetylene over carbon dioxide calculated from data collected at 298 K, 308 K and 318 K.

3.5.2. Powder X-ray Diffraction

Table 3.S6. Unit cell parameters for Fe₂Cl₂(bbta) dosed with varying pressures of acetylene at 298 K. Note, unit cell parameters for Fe₂Cl₂(bbta) at 0 bar were taken from the literature.¹²

Pressure (bar)	Space Group	<i>a</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
0	<i>R</i> – <i>3m</i>	25.157(1)	8.2321(4)	4511.7(5)
0.05	<i>R</i> – <i>3m</i>	24.936(2)	8.2909(5)	4464.5(7)
0.1	<i>R</i> – <i>3m</i>	24.868(2)	8.2987(5)	4444.4(7)
0.25	<i>R</i> – <i>3m</i>	24.809(2)	8.3101(4)	4429.6(7)
0.5	<i>R</i> – <i>3m</i>	24.796(2)	8.3150(5)	4427.5(7)
1.0	<i>R</i> – <i>3m</i>	24.790(2)	8.3192(4)	4427.7(7)

Table 3.S7. Unit cell parameters for Fe₂Cl₂(bbta) dosed with 500 mbar of ethylene and ethane at 223 K and 333 K. This variable temperature experiment mimics an isothermal variable pressure experiment in a sealed capillary. Note, unit cell parameters for experiments at 223 K were determined by Rietveld refinement whereas parameters for experiments at 333 K were determined by structureless Pawley refinement.

Gas	Temperature (K)	Space Group	<i>a</i> (Å)	<i>c</i> (Å)	Volume (Å ³)
Ethylene	223	<i>R</i> – <i>3m</i>	24.893(6)	8.341(1)	4476(2)
Ethylene	333	<i>R</i> – <i>3m</i>	24.975(3)	8.3184(7)	4494(1)
Ethane	223	<i>R</i> – <i>3m</i>	24.934(3)	8.3221(7)	4482(1)
Ethane	333	<i>R</i> – <i>3m</i>	24.972(2)	8.3230(4)	4481(1)

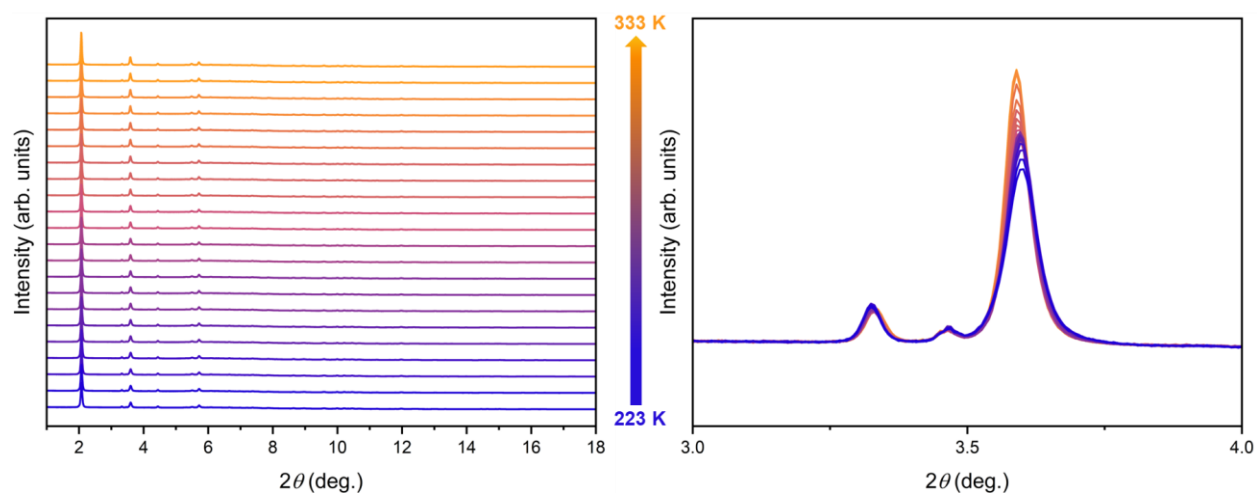


Figure 3.S9. Variable temperature PXRD patterns of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ dosed with 500 mbar ethylene collected over a temperature range of 223 K to 333 K. $\lambda = 0.45192 \text{ \AA}$.

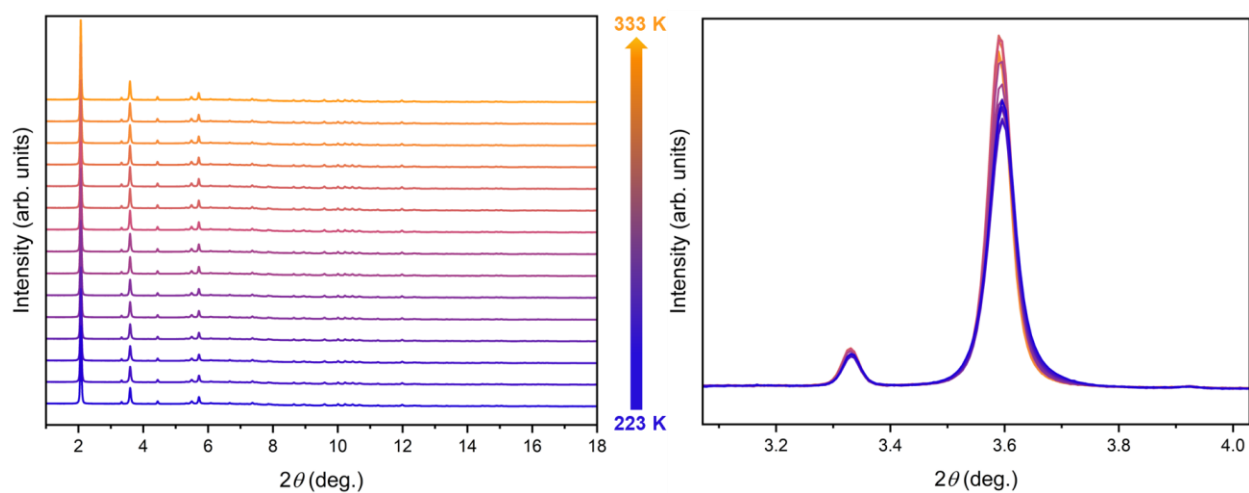


Figure 3.S10. Variable temperature PXRD patterns of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ dosed with 500 mbar ethane collected over a temperature range of 223 K to 333 K. $\lambda = 0.45192 \text{ \AA}$.

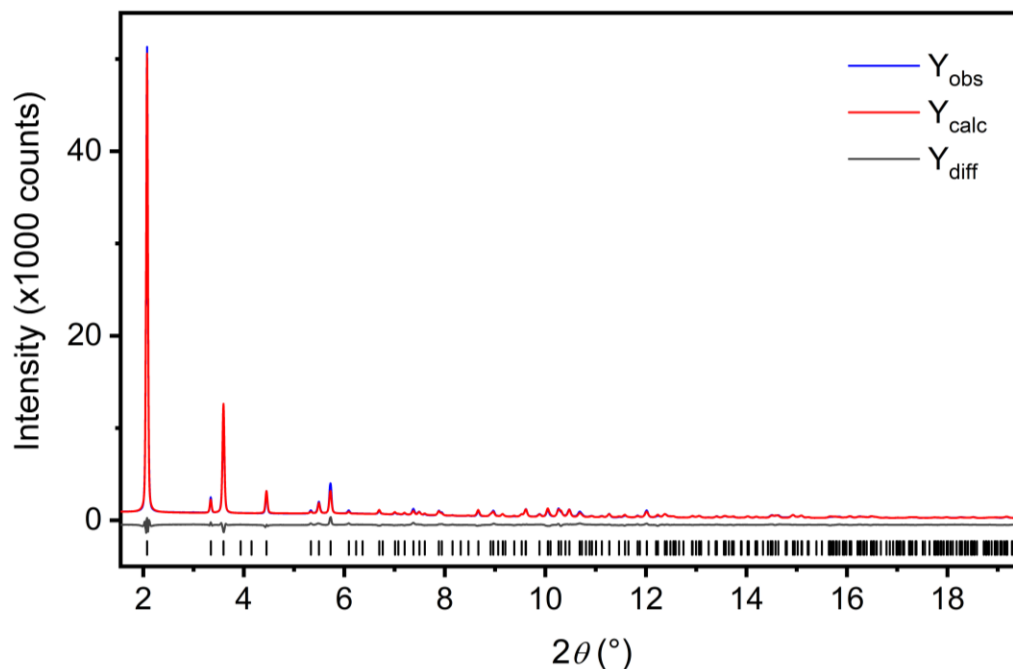


Figure 3.S11. Rietveld refinement of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ dosed with 0.05 bar of acetylene at 298 K. The unit cell parameters are listed in Table 3.S6. Figures of Merit (as determined by TOPAS): $R_{\text{wp}} = 5.39\%$, $R_{\text{exp}} = 3.63\%$, $R_p = 3.83\%$, $\text{GoF} = 1.48$ ($\lambda = 0.45192 \text{ \AA}$).

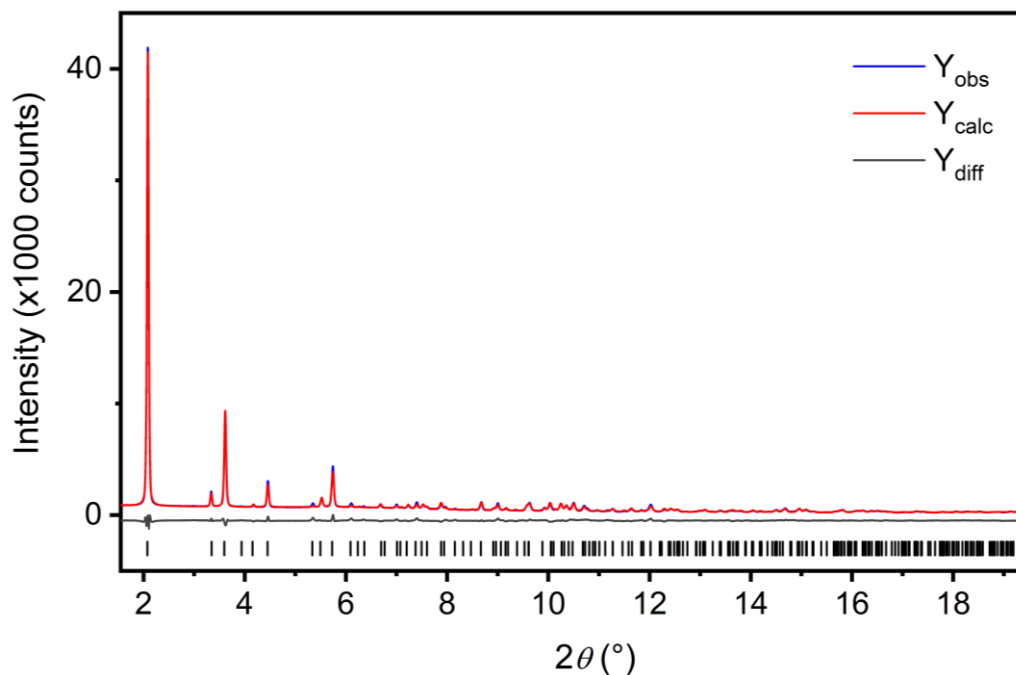


Figure 3.S12. Rietveld refinement of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ dosed with 0.5 bar of acetylene at 298 K. The unit cell parameters are listed in Table 3.S6. Figures of Merit (as determined by TOPAS): $R_{\text{wp}} = 5.24\%$, $R_{\text{exp}} = 3.85\%$, $R_p = 3.64\%$, $\text{GoF} = 1.36$ ($\lambda = 0.45192 \text{ \AA}$).

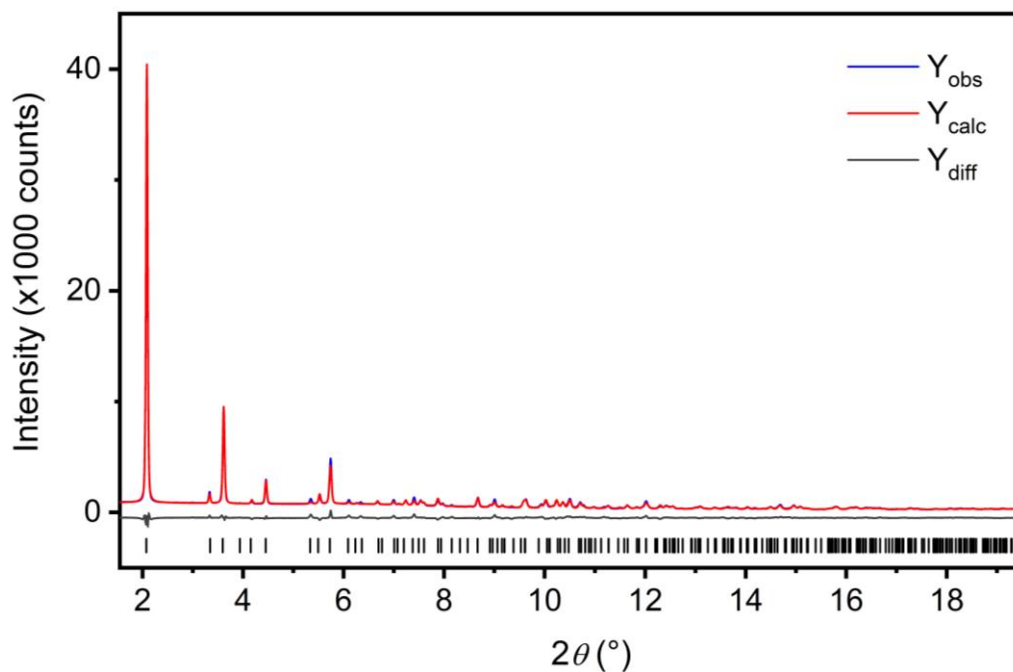


Figure 3.S13. Rietveld refinement of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ dosed with 0.5 bar of ethylene at 298 K. The unit cell parameters are listed in Table 3.S7. Figures of Merit (as determined by TOPAS): $R_{\text{wp}} = 3.67\%$, $R_{\text{exp}} = 4.50\%$, $R_p = 2.68\%$, $\text{GoF} = 0.82$ ($\lambda = 0.45192 \text{ \AA}$).

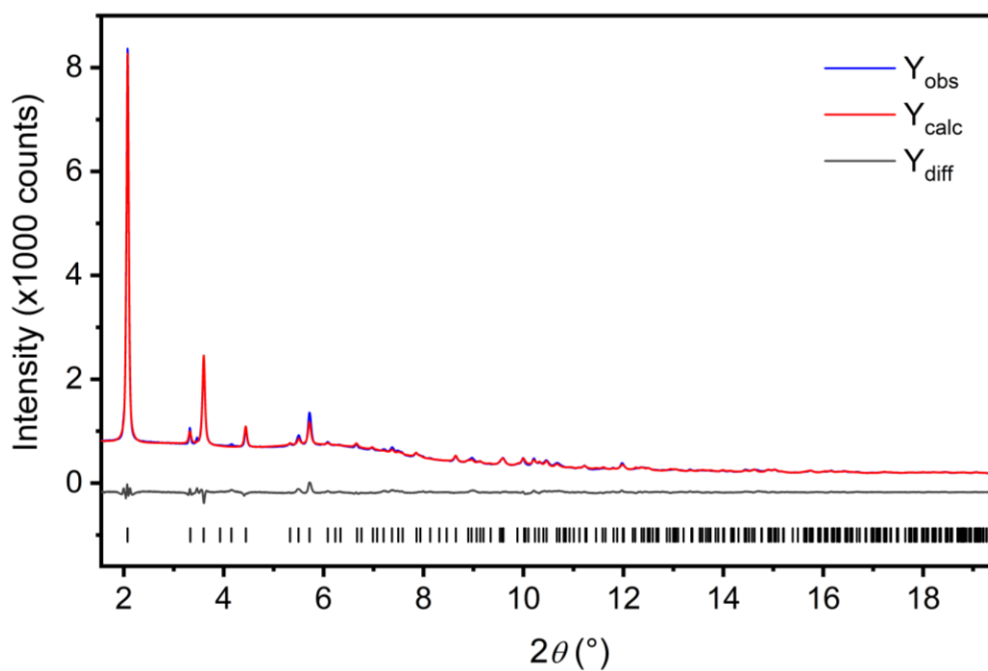


Figure 3.S14. Rietveld refinement of $\text{Fe}_2\text{Cl}_2(\text{bbta})$ dosed with 0.5 bar of ethane at 298 K. The unit cell parameters are listed in Table 3.S7. Figures of Merit (as determined by TOPAS): $R_{\text{wp}} = 3.37\%$, $R_{\text{exp}} = 3.91\%$, $R_p = 2.35\%$, $\text{GoF} = 0.86$ ($\lambda = 0.45192 \text{ \AA}$).

Table 3.S8. Unit cell parameters for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ dosed with varying pressures of acetylene at 298 K. Note that the unit cell parameters for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ at 0 bar were determined by Rietveld refinement and the parameters for pressures between 0.01 and 1 bar were determined by structureless Pawley refinement.

Pressure (bar)	Space Group	a (Å)	c (Å)	Volume (Å ³)
0	$R\bar{3}m$	24.602(5)	8.197(2)	4297(2)
0.01	$R\bar{3}m$	24.634(8)	8.120(2)	4309(3)
0.05	$R\bar{3}m$	24.607(8)	8.209(2)	4304(3)
0.1	$R\bar{3}m$	24.599(8)	8.212(2)	4303(3)
0.25	$R\bar{3}m$	24.595(7)	8.215(2)	4304(3)
0.5	$R\bar{3}m$	24.598(7)	8.217(2)	4306(3)
1.0	$R\bar{3}m$	24.596(7)	8.222(2)	4307(2)

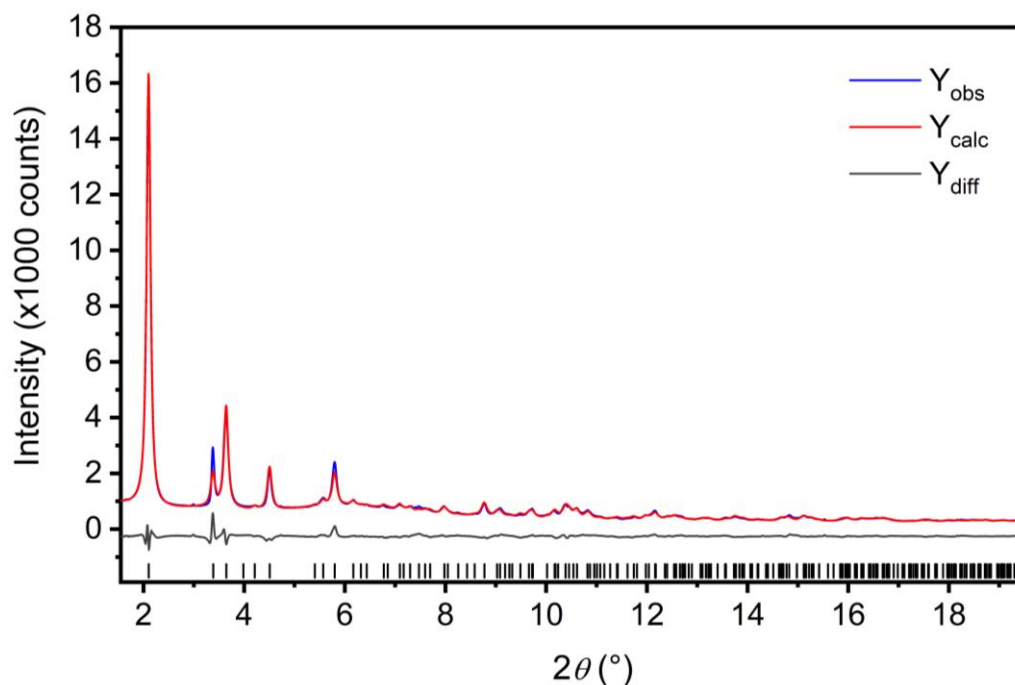


Figure 3.S15. Rietveld refinement of evacuated $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ at 298 K. The unit cell parameters are listed in Table 3.S8. Figures of Merit (as determined by TOPAS): $R_{\text{wp}} = 4.82\%$, $R_{\text{exp}} = 3.61\%$, $R_p = 3.26\%$, $\text{GoF} = 1.34$ ($\lambda = 0.45192$ Å)

Table 3.S9. Unit cell parameters for $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ dosed with 500 mbar of carbon monoxide, ethylene and ethane at 223 K and 333 K. This variable temperature experiment mimics an isothermal variable pressure experiment in a sealed capillary. Note, unit cell parameters for the CO experiment were determined by Rietveld refinement whereas parameters for experiments for ethylene and ethane were determined by structureless Pawley refinement.

Gas	Temperature (K)	Space Group	a (Å)	c (Å)	Volume (Å ³)
CO	223	$R\bar{3}m$	24.583(5)	8.168(1)	4275(2)
Ethylene	223	$R\bar{3}m$	24.566(7)	8.211(2)	4291(3)
Ethylene	333	$R\bar{3}m$	24.595(8)	8.201(2)	4296(3)
Ethane	223	$R\bar{3}m$	24.596(9)	8.188(2)	4290(3)
Ethane	333	$R\bar{3}m$	24.613(8)	8.186(2)	4295(3)

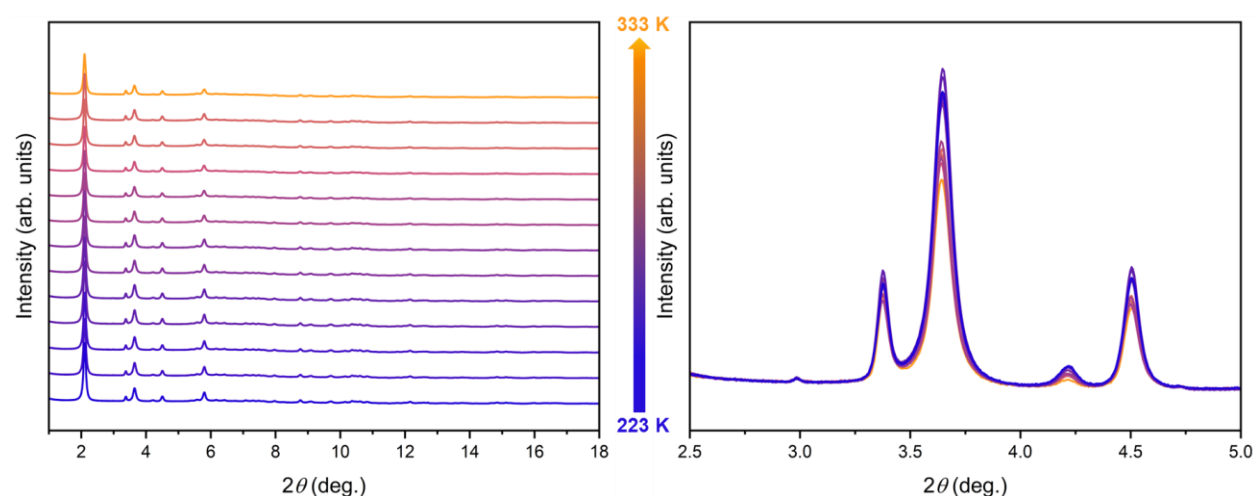


Figure 3.S16. Variable temperature PXRD patterns of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ dosed with 500 mbar ethylene collected over a temperature range of 223 K to 333 K. $\lambda = 0.45192$ Å.

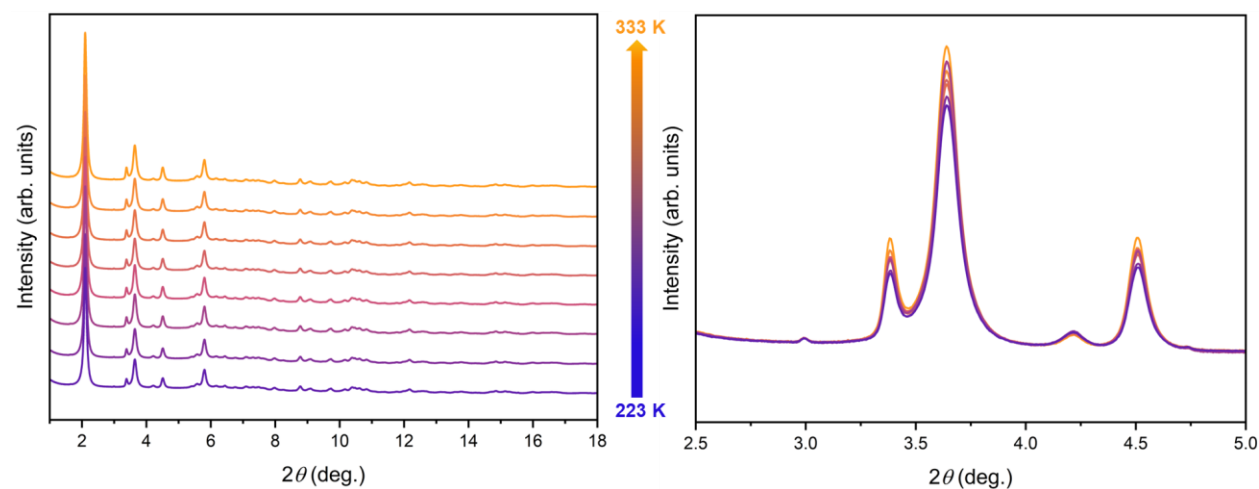


Figure 3.S17. Variable temperature PXRD patterns of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ dosed with 500 mbar ethane collected over a temperature range of 223 K to 333 K. $\lambda = 0.45192$ Å.

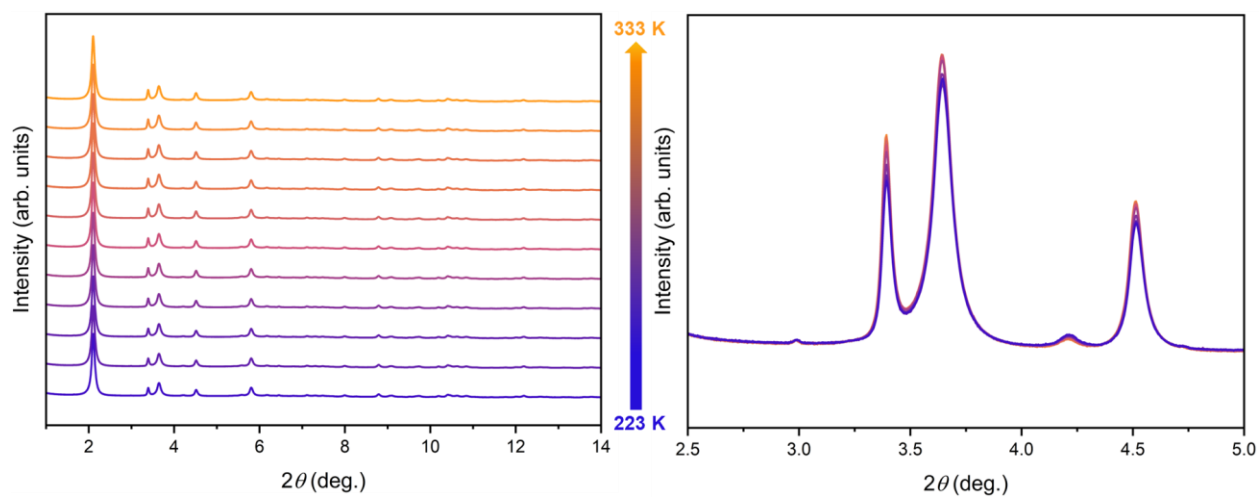


Figure 3.S18. Variable temperature PXRD patterns of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ dosed with 500 mbar carbon monoxide collected over a temperature range of 223 K to 333 K. $\lambda = 0.45192 \text{ \AA}$.

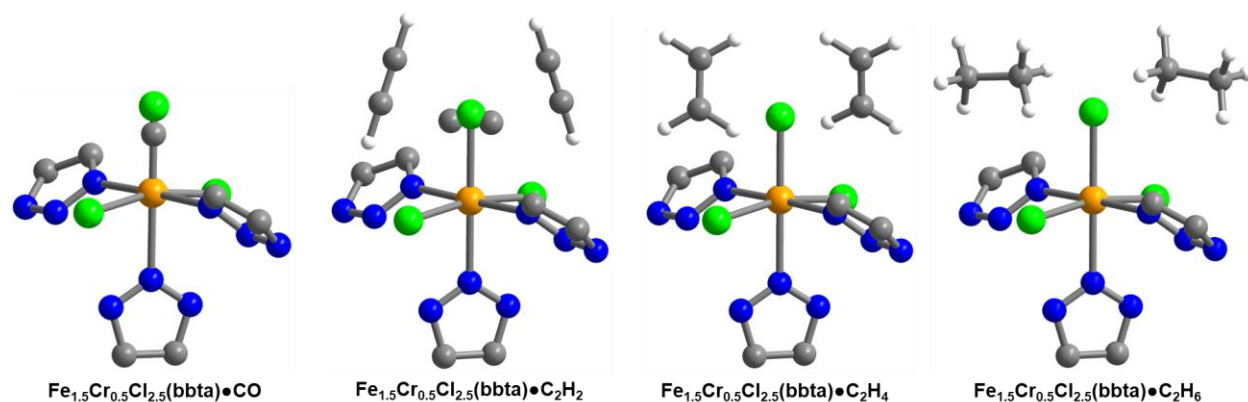


Figure 3.S19. Preliminary structural solutions of $\text{Fe}_{1.5}\text{Cr}_{0.5}\text{Cl}_{2.5}(\text{bbta})$ dosed with carbon monoxide (leftmost), acetylene (center left), ethylene (center right) and ethane (rightmost).

3.5.3 Diffuse Reflectance Infrared Fourier Transform Spectroscopy

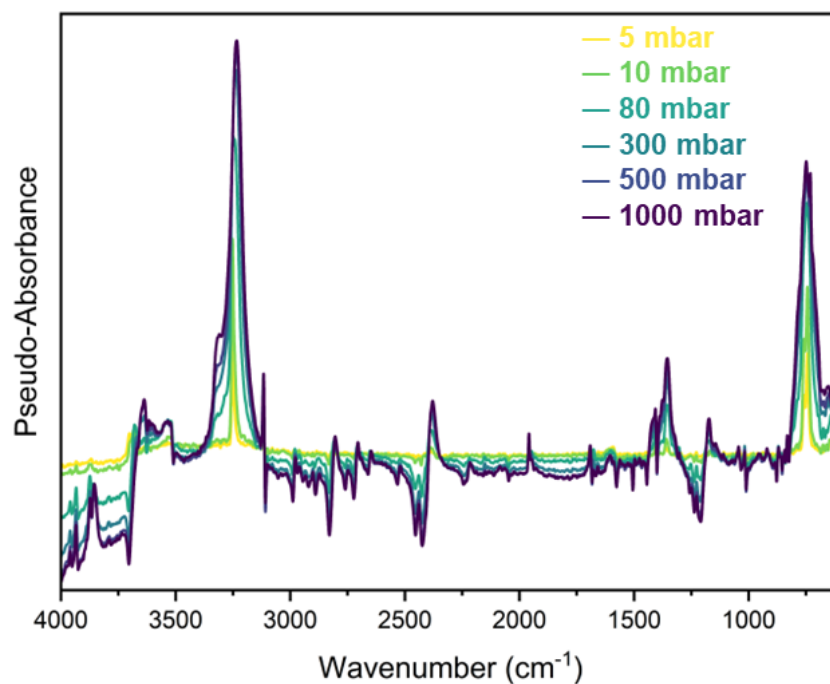


Figure 3.S20. Difference plot of the infrared spectrum of Fe₂Cl₂(bbta) dosed at variable pressures between 5 mbar and 1000 mbar. Spectrum was obtained by subtracting that of the bare framework from that of the dosed framework to highlight changes upon gas dosing.

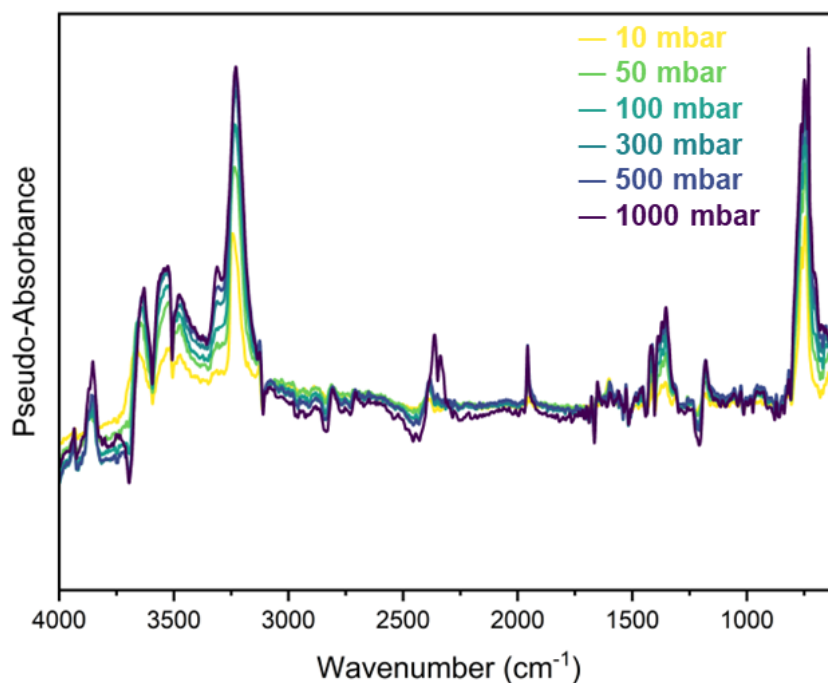


Figure 3.S21. Difference plot of the infrared spectrum of Fe_{1.5}Cr_{0.5}Cl_{2.5}(bbta) dosed at variable pressures between 10 mbar and 1000 mbar.

3.6. References

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3.7. Acknowledgements

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Chapter 4: Investigating Structure-Function Relationships in Metal–Organic Frameworks through Powder X-Ray Diffraction

4.1. Introduction

Metal–organic frameworks are unique materials because they provide a rigid scaffold to access ligand coordination environments and geometries that are often inaccessible or challenging to isolate in molecular inorganic complexes. For example, the unsaturated open metal sites that provide many MOFs with interesting functionalities would typically be occupied with solvent or require the synthesis of a complex sterically-hindering ligand to be accessed in a small molecule.^{1,2} One of the most comprehensive and satisfying characterization tools available to inorganic chemists is single crystal X-ray diffraction (SCXRD); however, the generally low solubility of MOF linkers and their reliance on solvothermal synthesis conditions makes single crystal growth exceedingly difficult.^{3,4} In order to study the chemical interactions at these sites of interest in frameworks where single crystals cannot be obtained, it is necessary to employ a host of bulk materials characterization techniques such as electron diffraction, powder neutron diffraction and, most accessible to the common chemist, powder X-ray diffraction (PXRD).^{5–7}

Of course, with ease of data collection comes increased difficulty of data analysis. PXRD is an excellent tool for routine phase identification or monitoring framework degradation during any step of synthesis.⁸ However, if a structure solution from powder diffraction data is desired, both the material and the data quality must be high, oftentimes requiring the use of a synchrotron source to obtain patterns suitable for solution. Many crystal properties can affect the data quality, including the crystallite size, which can impact peak shape, or defect sites, which can impact peak intensity due to unit cell contents being non-uniform.⁹ Even when all of these material and experimental factors align to produce a satisfactory powder pattern, structure solution remains a non-trivial endeavor. This is mainly caused by all the information contained in a three-dimensional lattice being compressed into a one-dimensional data set, and extraction of that information requires patience, skill and chemical intuition.

A common procedure for approaching a powder solution is to begin by indexing the peak positions to determine possible space groups and unit cell parameters. Once a suitable set of lattice parameters and a potential space group is obtained, a structureless Pawley or Le Bail refinement of the peak shape and positions, but not intensities, can be performed to refine the unit cell parameters.¹⁰ Finally, if an appropriate model is available, be that from an existing crystal structure or a DFT model, a Rietveld refinement can be performed to obtain a structural solution. A Rietveld refinement relies on a least squares minimization approach to achieve a solution with the lowest possible difference between the experimental and calculated patterns. Equation 1 shows the minimization used where W is the statistical weight, c is the scale factor, y_i^{obs} is the experimental pattern, and y_i^{calc} is the calculated fit.¹¹ A minimization for any pattern can be achieved with a variety of possible structures, whether or not the resultant solution is chemically reasonable is up to the crystallographer to decide.

$$M = \sum_i W_i \{y_i^{obs} - \frac{1}{c} y_i^{calc}\}^2 \quad (1)$$

Despite the challenges discussed above, many remarkable structural solutions have been obtained *via* Rietveld refinement in the MOF literature. This is thanks to the variety of sample

environments accessible with microcrystalline powders including *in situ* variable pressure, temperature and even ball milling environments.^{12–14} Here, I discuss several investigations into structure function relationships in metal–organic frameworks which were undertaken where only microcrystalline samples were accessible. Variable temperature and variable pressure sample environments were used to study gas binding at open metal sites, as well as structural transformations at variable pressures and temperatures. Rietveld refinements were performed, which shed light on these phenomena.

4.2. Examination of Butene Binding in Thermodynamic Separations

The frameworks $M_2(\text{dobdc})$ ($M = \text{Mn, Fe, Co, Ni}$; $\text{dobdc}^{4-} = 2,5\text{-dioxidobenzene-1,4-dicarboxylate}$) and $M_2(m\text{-dobdc})$ ($m\text{-dobdc}^{4-} = 4,6\text{-dioxidobenzene-1,3-dicarboxylate}$) have been shown to have selectivity for a variety of gases under a myriad of conditions including hydrocarbons, hydrogen, noble gases and oxygen.^{15–18} This versatility arises from the tunability of the metal site identity as well as the slight variations in ligand electronic contributions from the functional groups of the meta- and para- isomers.¹⁶ Additionally, this framework has a high density of open metal sites that arises from its hexagonal structure where the open metal sites dwell in the helical chains that proceed down the *c*-axis, shown in Figure 4.1. Both of these qualities were exploited to find an optimal framework to perform a thermodynamic separation on a mixture of butene isomers.¹⁹ It was found that in general the increase in electron density at the metal site afforded by the *m*-dobdc⁴⁻ ligand led to increased selectivity for 1-butene over the *cis* and *trans* isomers in all variants.

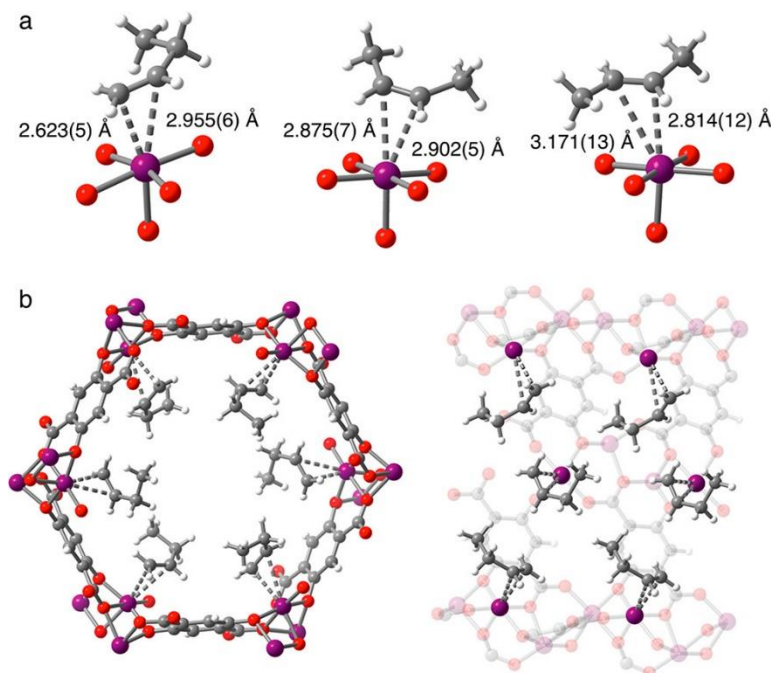


Figure 4.1. a) Views of the primary coordination spheres in $\text{Co}_2(\text{dobdc})(1\text{-butene})_{1.59}$, $\text{Co}_2(\text{dobdc})(\text{cis-2-butene})_{1.58}$, and $\text{Co}_2(\text{dobdc})(\text{trans-2-butene})_{1.48}$ as determined by single-crystal X-ray diffraction. b) Views of the structure of $\text{Co}_2(\text{dobdc})(1\text{-butene})_{1.59}$ as viewed in the crystallographic *ab* plane (left) and along the one-dimensional pores (right), showing the proximity of adsorbed 1-butene molecules. Purple, red, gray, and white spheres represent Co, O, C, and H atoms, respectively.

Structural impacts on this separation process were investigated in the $M_2(\text{dobdc})$ frameworks using single crystal X-ray diffraction (SCXRD) due to the relative ease single crystal synthesis of the $\text{Co}_2(\text{dobdc})$ framework. Gas dosing experiments revealed relatively weak, mainly electrostatic interactions with the open metal site evidenced by the elongated Co–C distances. Additionally, the hydrogen atoms were found to be canted down towards the open metal site, suggesting that the p-orbitals of the olefin were not directly interacting with the metal d-orbitals. The hydrogen atoms were also found to be located within H-bonding distance of the hydroxyl and carboxylate oxygens, which implies that $\text{O}\cdots\text{H}$ bonding may provide additional stabilization to the adsorbate.

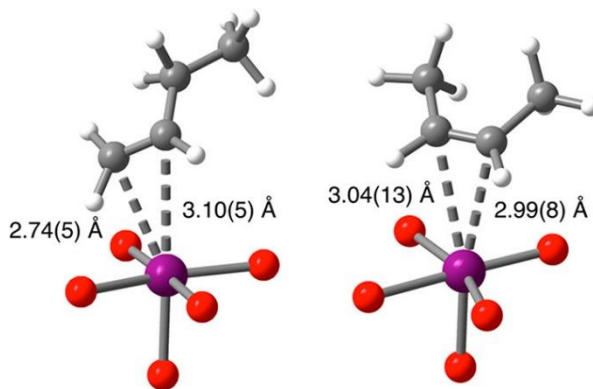


Figure 4.2. Views of the primary coordination spheres in $\text{Co}_2(m\text{-dobdc})(1\text{-butene})_{1.64}$ and $\text{Co}_2(m\text{-dobdc})(\text{cis-2-butene})_{2.88}$. Purple, red, gray, and white spheres represent Co, O, C, and H atoms, respectively.

As was previously mentioned, an advantage of powder X-ray diffraction is that it can be used as a resource to gain structural information when single crystals are not synthetically accessible, as is the case with the $M_2(m\text{-dobdc})$ frameworks. To gain insight into why the selectivity for 1-butene is higher in the meta- version of these frameworks, powder diffraction was used to obtain structural solutions with Rietveld refinement. Due to the relative challenge of powder refinement, only structural solutions for 1-butene and cis-butene were obtained, as trans-butene could not be located within the framework pore. The Co–C distances obtained for $\text{Co}_2(m\text{-dobdc})$ -cis and 1-butene interactions are slightly longer than those of the para- isomer, which can be attributed to the diffraction patterns being collected at a higher temperature than the single crystal experiments. Due to the additional mirror plane present in the $R3m$ space group which the meta- isomer crystallizes into, there is also significant disorder along the plane bisecting the ligand. This leads to short inter-butene distances in both structures. However, this geometry also likely contributes to the selectivity found in this framework by allowing for stabilization of the butene molecules by the ligand π -system as well as intermolecular interactions with butenes at neighboring metal sites. The conformational flexibility present in 1-butene which is absent in the cis- and trans- isomers likely leads to advantageous packing arrangements in the pore which contribute to the selectivity found for this isomer.

4.3. Structural Studies of Ammonia Capture via Ligand Insertion

Cooperative gas adsorption mechanisms have been of great interest due to the superior working capacity when applied to industrial separations.^{13,20,21} This allows for additional energy savings during a temperature or pressure swing regeneration process which has the added benefit of

reducing carbon dioxide emissions. Recently, a novel material which exhibits exceptionally high ammonia uptake was found to adsorb this important commodity chemical *via* a cooperative ligand insertion mechanism.²² Figure 4.3 shows how this material, *cis*-Cu(cyhdc) (cyhdc²⁻ = *trans*-1,4-cyclohexanedicarboxylate), which forms initially as discrete one-dimensional chains, converts to a distinct one-dimensional structure upon binding two ammonia molecules per copper atom and then undergoes another transition to a three-dimensional framework upon adsorption of another two ammonia molecules. These structural transformations upon binding yield a step-shaped adsorption profile. Initial attempts at structural solutions of the methanol bound and ammonia bound frameworks were performed by using Density Functional Theory (DFT) models as a starting point for Rietveld refinement, but attempts were unsuccessful due to contamination of the sample with water which causes the emergence of a different crystallographic phase. The structure of the copper variant in both its pristine and ammonia bound states were determined by single crystal X-ray diffraction.

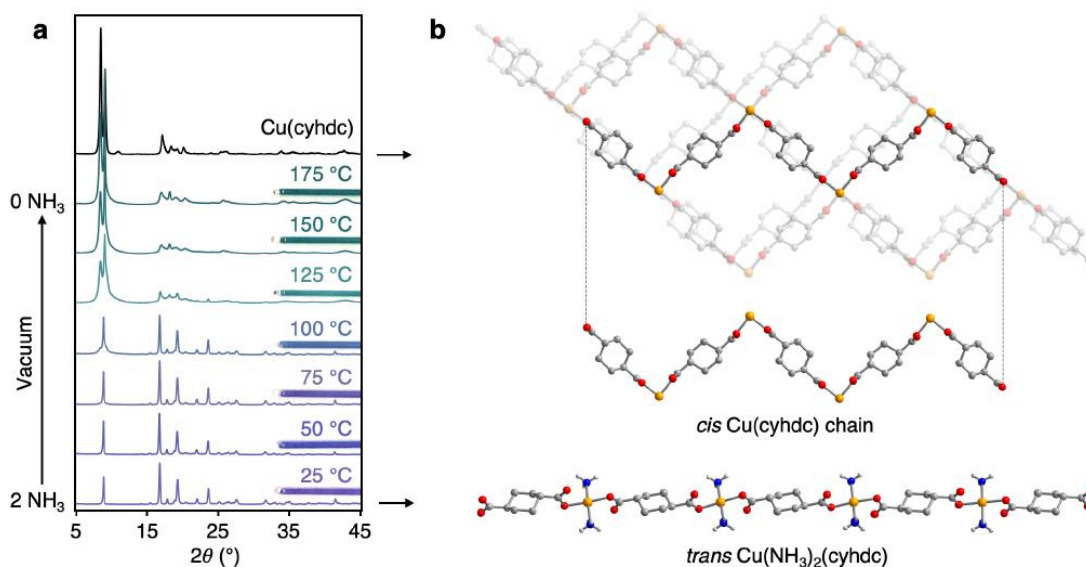


Figure 4.3. a) Powder X-ray diffraction data collected while heating ammonia-bound $\text{Cu}(\text{NH}_3)_2(\text{cyhdc})$ (purple trace) under dynamic vacuum to regenerate $\text{Cu}(\text{cyhdc})$ (green trace). b) Illustration of the relationship between the structures of $\text{Cu}(\text{NH}_3)_2(\text{cyhdc})$ (bottom) and $\text{Cu}(\text{cyhdc})$ (top) as discussed in the text. Orange, red, blue, grey, and white spheres represent Cu, O, N, C, and H atoms, respectively; H atoms are omitted for clarity. Adsorption of two additional ammonia molecules yields a three-dimensional framework isostructural to that shown in Figure 4.4.

Additional variants were synthesized to determine if this mechanism could be tuned by inclusion of a different metal atom. Single crystals of these variants were not synthetically accessible and were structurally characterized using powder X-ray diffraction. The crystal structure of $\text{Fe}(\text{cyhdc})$ was determined using Rietveld refinement and it was confirmed to be isostructural to the copper variant (Figure 4.4). It was determined through ammonia adsorption isotherms that changing the identity of the metal from copper to iron caused a shift in the step pressure onset to higher pressures. This was attributed to an increase in the metal ligand bond strength impeding the insertion of the ammonia into the metal-ligand bonds. A $\text{Cr}(\text{cyhdc})$ variant was also synthesized, the crystallinity of which was insufficient to perform a Rietveld refinement, but structureless Pawley refinement shows that this material has crystallizes in the same space

group and has similar unit cell parameters to the iron and copper materials (Figure 4.S5) suggesting that it is isostructural. Synchrotron powder diffraction experiments were performed on several other variants, Cu(tfbdc) (cyhdc²⁻ = 2,3,5,6-tetrafluoro-1,4-cyclohexanedicarboxylate), Cu(bpdc) (bpdc²⁻ = 4,4'-biphenyldicarboxylate) and Cu(bipy) (bpdc²⁻ = 4,4'-bipyridinedicarboxylate). Predicted powder patterns based on DFT models were used to suggest a structure for these materials. Pawley refinement of Cu(bipy) shows that it crystallizes in the same space group as the cyclohexane-dicarboxylate materials with an expanded unit cell volume, however the refinement reveals that there is likely a second phase present due to the poor fit (Figure 4.S6).

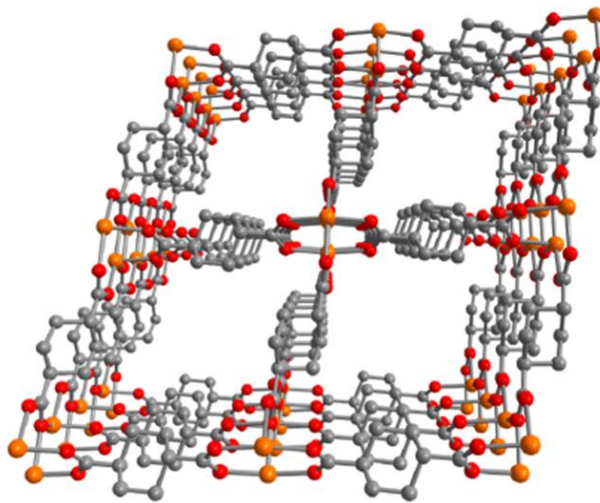


Figure 4.4. Structural model of Fe(cyhdc) derived from Rietveld refinement. Orange, red, and gray spheres represent Fe, O, and C atoms, respectively; H atoms have been omitted for clarity.

4.4. Controlling Methane Storage through π -Stacking Interactions in Flexible MOFs

As has been discussed, cooperative gas adsorption mechanisms are of great interest due to their advantageous thermodynamic properties for utilization in industrial separation processes that arise from their step-shaped isothermal profile.²¹ Several mechanisms that yield this isothermal profile have been discussed thus far including spin crossover and ligand insertion. A third type of mechanism that leads to step-shaped isotherms is pressure-induced pore opening in flexible metal-organic frameworks. It was discovered that in the frameworks Co(BDP) and Fe(BDP) (BDP²⁻ = 1,4-benzenedipyrzolate) which after activation exist in a closed-pore “collapsed phase”, that by exposing the material to a high pressure of methane gas at ambient temperature, at a certain pressure the material will expand to an open-pore phase allowing for the uptake of a large amount of gas.²⁰ It was later shown that this mechanism could be tuned by varying the substituents on the benzene ring to control the π - π -stacking interactions between the benzene rings that stabilize the closed pore phase, allowing for an increase or decrease in step pressure according to the benzene interaction strength.²³ A new strategy for tuning the π - π interactions of the dipyrzolate ligands has recently been explored which involved the synthesis of a new framework Zn(BDP), which has superior air and water stability to the cobalt and iron analogues, as well as analogous zinc MOFs synthesized using a series of heterocyclic dipyrzolate ligands including 1,4-pyridinedipyrzolate

(PyDP), 1,4-pyrimidinedipyrzolate (PymDP), 1,4-pyrazinedipyrzolate (PyzDP) and 1,4-pyridazinedipyrzolate (PydDP).²⁴

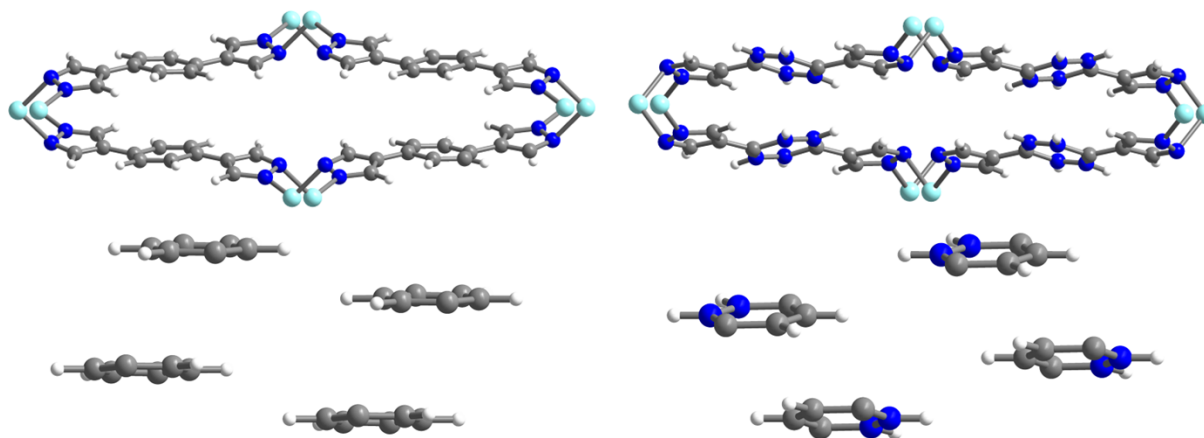


Figure 4.5. Left: *c*-axis view of collapsed Zn(BDP) and a view of the benzene ring stacking motif. Right: *c*-axis view of Zn(PydDP) and a view of the pyridazine stacking motif. Due to the space group symmetry of the framework, the heteroatoms are disordered over two positions. The lowest energy conformation where the electronegative atoms are canted away from one another is depicted in the bottom right-hand corner, but a second conformation is also possible since the rings are able to freely around the heterocycle-pyrzolate single bond.

It was found through high-pressure methane isotherms that the heterocyclic frameworks experience an increase in step pressure in the order Zn(BDP), Zn(PyDP), Zn(PymDP), Zn(PyzDP) and Zn(PydDP). This was hypothesized to be the result of stronger π - π interactions due to electrostatics from the inclusion of electronegative nitrogen atoms into the heterocycles. To investigate this structurally, a series of variable pressure PXRD experiments were performed. Structural solutions were obtained through Rietveld refinements of the evacuated closed-pore phase which crystallize in the $C2/c$ space group. Several structural metrics can be used to evaluate how closely stacked the adjacent heterocycles are, which are listed in Table 4.1. The *c*-axis unit cell parameter measures roughly the distance across the pore as shown in Figure 4.5, which decreases in the same order as the step pressure increases. Additionally, the center of mass distance, *R*, which is a typical metric used to measure the distance between parallel displaced aromatic rings in theoretical calculations of π - π stacking interactions, between the rings in each framework was determined, which also decreases in the expected order.²⁵ Lastly, as was used by Mason et. al, the angle between the planes defined by the Zn, N1 and N2 atoms and the pyrazolate rings which decreases with pore opening, was determined and likewise decreases in the expected order. This structural study of the closed pore phase confirms that heterocyclic distances are an indicator of π - π stacking interaction strength and in turn the expected gas adsorption properties.

Table 4.1. Selected crystal metrics for Zn-pyrazolate frameworks. Row 1: *c*-axis unit cell parameters determined by Rietveld refinement, Row 2: center of mass distances between aromatic rings in each framework (see Figure 4.S18), Row 3: the angle between the Zn-N1-N2 plane and the plane of the pyrazolate ring (see Figure 4.S17)

Selected Metrics	Zn(BDP)	Zn(PyDP)	Zn(PymDP)	Zn(PyzDP)	Zn(PydDP)
<i>c</i> (Å)	6.861(1)	6.814(2)	6.747(2)	6.670(1)	6.657(3)

R (Å)	3.84	3.60	3.44	3.39	3.12
$\angle \Pi_{\text{Zn-N}} \Pi_{\text{py}}$ (°)	50.02	55.10	56.23	56.81	67.88

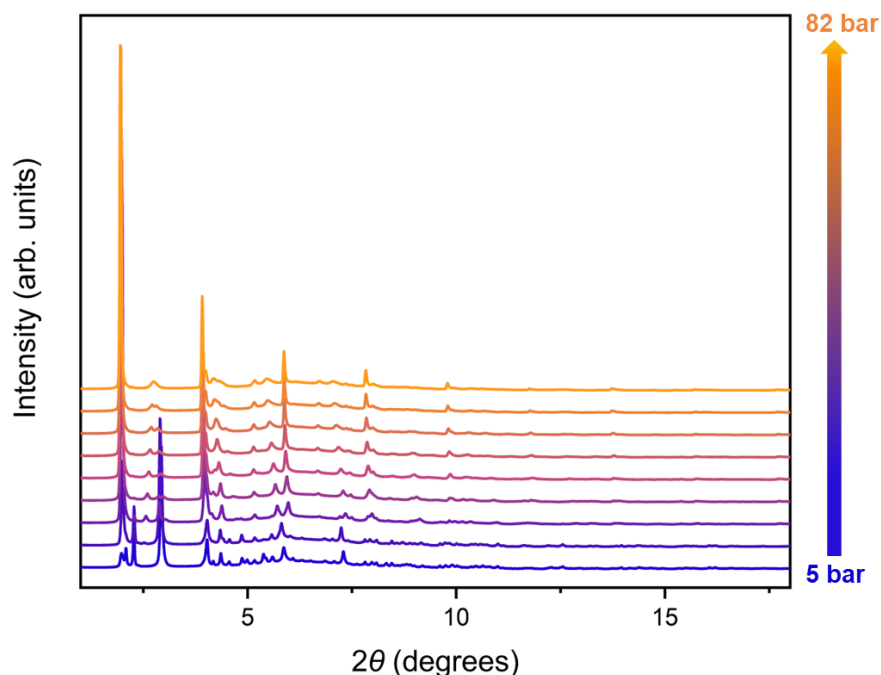


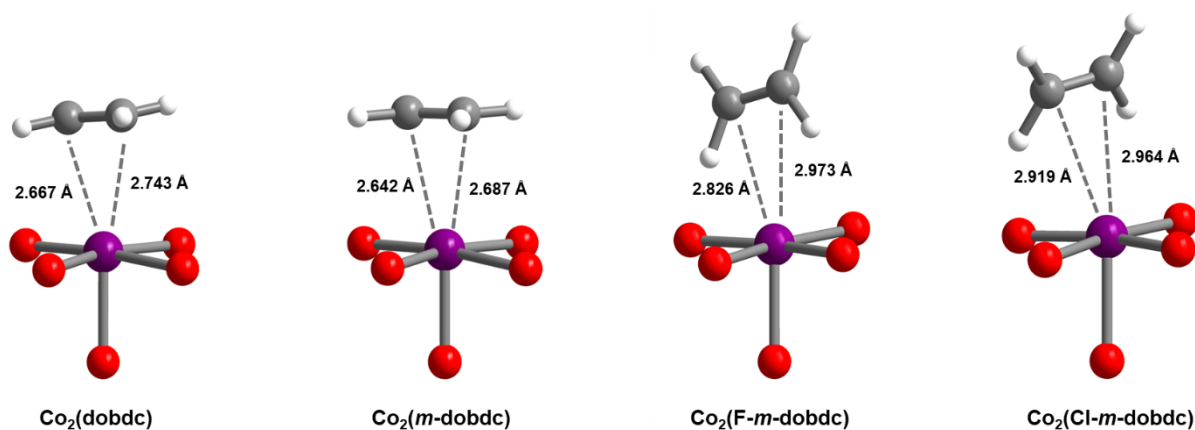
Figure 4.6. Variable pressure diffraction data of Zn(BDP) measured in steps of 10 bar between 5 bar and 82 bar at 298 K. ($\lambda = 0.45191$ Å)

Additionally, *in situ* high pressure methane dosing experiments were performed to directly observe the phase change that occurs in these materials upon exposure to high pressures of gas. These experiments were undertaken with the frameworks Zn(BDP), Zn(PymDP) and Zn(PydDP), and the results for Zn(BDP) are shown in Figure 4.6. Upon pressurizing to a sufficient extent, the material undergoes a phase change from the closed-pore $C2/c$ phase to the open pore, higher symmetry $P42/mmc$ phase. As is discussed in more detail in the supplemental information, the open pore phase of this framework exhibits paracrystallinity which affects the resultant peak shapes in the pattern significantly. This can be seen in the orange trace of Figure 4.6, where there are several very intense reflections with narrow peak widths which corresponds to those which result from diffraction along the $0k0$ planes. The remaining peaks are broad and low intensity which makes a full structural solution challenging, since all peaks are fit to the same set of shape parameters, but evidence of the phase change and space group of the assignment is unambiguous.

4.5. Tuning Hydrocarbon Separations and Hydrogen Storage in $M_2(X-m\text{-dobdc})$

As was discussed in Chapter 3, hydrocarbon separations are an area of active interest in the study of metal–organic frameworks due to the prevalence of frameworks with positively charged open metal sites that have the ability to form π -bonding interactions with olefins and alkynes.¹⁵ Previously reported frameworks such as $\text{Fe}_2(m\text{-dobdc})$ have performed remarkably well in hydrocarbon separations such as that of ethylene from ethane, however the selectivity of these frameworks is still insufficient for producing gas of a purity sufficient for usage in polymer

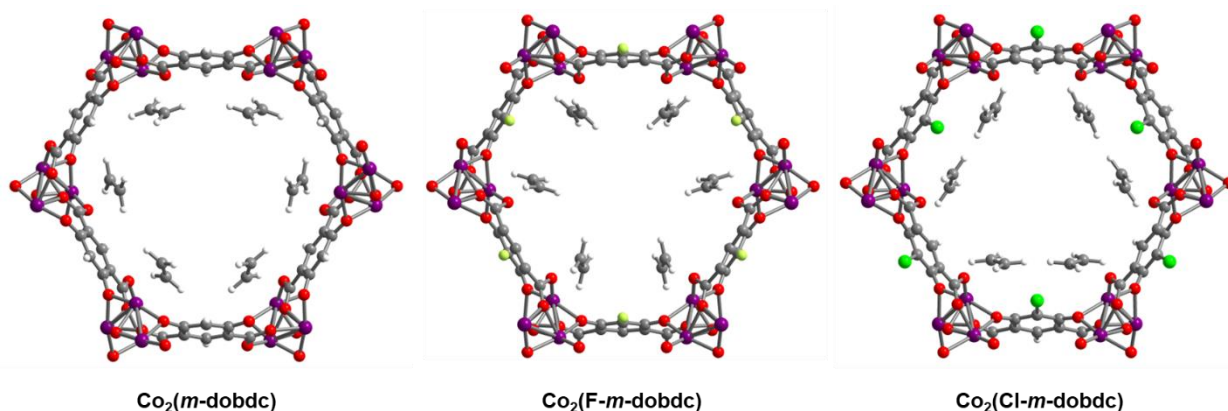
synthesis.^{26,27} Towards that end, based on the success of using the *m*-dobdc⁴⁻ ligand for use in separations involving π -acidic adsorbates due to its increased electron donation to bound metals, two new halogenated linkers, F-*m*-dobdc⁴⁻ and Cl-*m*-dobdc⁴⁻, were synthesized and used to form the new frameworks Ni₂(F-*m*-dobdc), Co₂(F-*m*-dobdc) and Co₂(Cl-*m*-dobdc).²⁸ A series of ethylene and ethane isotherms were performed which reveals that all of these frameworks have a



selectivity for ethylene over ethane, with Co₂(Cl-*m*-dobdc) having the highest followed by Co₂(F-*m*-dobdc) then Ni₂(F-*m*-dobdc). As compared to the parent framework Co₂(*m*-dobdc), the chlorinated variant has a higher selectivity while the fluorinated variant has a similar selectivity. To elucidate the mechanism behind this selectivity, powder X-ray diffraction was employed to obtain a structural solution of the new frameworks and their ethylene binding motifs.

Figure 4.7. Primary coordination spheres of Co₂(dobdc), Co₂(*m*-dobdc), Co₂(F-*m*-dobdc), and Co₂(Cl-*m*-dobdc) bound to ethylene.

Figure 4.7 shows the primary coordination spheres of four M₂(dobdc)-type frameworks with ethylene bound to the cobalt open metal sites.²⁶ What is readily apparent is the increased distance of the ethylene molecule from the metal sites of the halogenated frameworks relative to the parent frameworks. Additionally, there is clear π -complexation with the open metal sites in Co₂(dobdc) and Co₂(*m*-dobdc) as evidenced by the shorter C–C distances as well as the orientation of the hydrogen atoms relative to the metal. The ethylene bound to the halogenated frameworks is canted away from the open metal site and becomes increasingly drawn from the center of the metal towards the ligand going from the fluorine to the chlorine variant. This seems to be in direct



opposition with the selectivity values which are highest for the chlorine variant which seemingly has the weakest structural interaction with the metal site.

Figure 4.8. Views down the *c*-axis of $\text{Co}_2(m\text{-dobdc})$, $\text{Co}_2(\text{F-}m\text{-dobdc})$, and $\text{Co}_2(\text{Cl-}m\text{-dobdc})$ bound to ethylene.

However, when taking into account the orientation of the ethylene within the larger MOF pore, secondary ligand interactions become much more apparent. It can be seen in Figure 4.8 that the ethylene molecules are clearly oriented towards the chlorine atom in $\text{Co}_2(\text{Cl-}m\text{-dobdc})$, the hydrogen atoms of the ethylene have $\text{Cl}\cdots\text{H}$ distances of 3.487 Å and 3.715 Å which fall within the accepted range for halogen bonding.²⁹ Additionally the benzene ring of the chlorinated ligand is clearly canted into the pore of the framework at larger angle than that of the parent framework or the fluorinated framework, which likely facilitates this interaction. The fluorinated variant exhibits a much less obvious interaction between the halogen and the adsorbed ethylene which accounts for the selectivity for ethylene and enthalpy of adsorption being overall similar to the parent framework. From the structural solutions it is quite apparent that the chlorinated framework exhibits a preferential interaction for ethylene not because of electronic changes at the metal center but because of secondary interactions with the halogen atom.

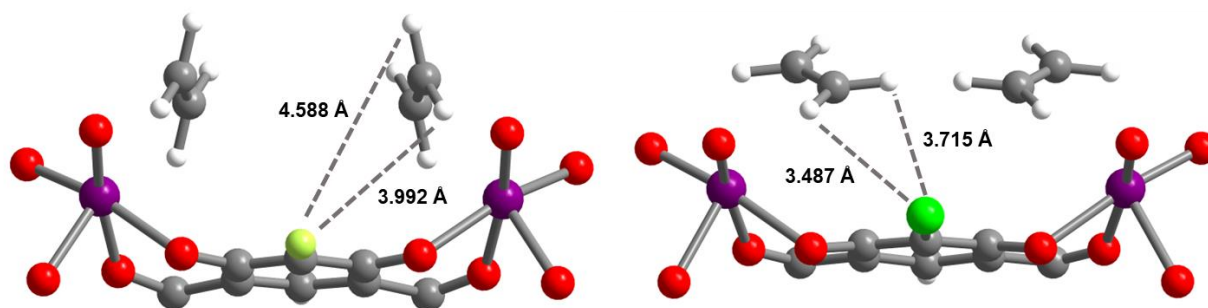


Figure 4.9. Hydrogen-halogen distances in $\text{Co}_2(\text{F-}m\text{-dobdc})$, and $\text{Co}_2(\text{Cl-}m\text{-dobdc})$ bound to ethylene.

4.6. Conclusions

Powder X-ray diffraction is a versatile and complex tool which can be used to obtain insights into a variety of structural phenomena. In the study of metal–organic frameworks for gas storage and separations, it is clear that PXRD plays an essential role in aiding in the characterization of gas-framework interactions. This is especially important for materials such as $\text{Co}_2(m\text{-dobdc})$, which have many potential applications, but cannot be isolated in a single crystalline form. Additionally, the range of sample environments available for *in situ* experiments such as the high pressure adsorption measurements performed for $\text{Zn}(\text{BDP})$, provide the ability to answer a wide range of questions about the mechanisms of structural changes. Although not without its setbacks, for example the inability to perform a structural solution for trans-butene bound to $\text{Co}_2(m\text{-dobdc})$, PXRD can oftentimes lead to satisfying answers to structural questions and shed light on interactions, like in the case of the halogenated frameworks, that are unclear based on other techniques.

4.7. Supplementary Information

4.7.1. Powder X-ray Diffraction Analysis of Co₂(*m*-dobdc)

High-resolution synchrotron X-ray powder diffraction data for all Co₂(*m*-dobdc) samples were collected at beamline 17-BM at the Advanced Photon Source at Argonne National Laboratory with a Perkin-Elmer a-Si flat panel detector. Diffraction patterns for Co₂(*m*-dobdc) dosed with 1-butene and *trans*-butene were collected at a wavelength of 0.45415 Å, while the temperature was held constant at 250 K with an Oxford Cryosystems Cryostream 800. Diffraction patterns for *cis*-butene dosed Co₂(*m*-dobdc) were collected at 125 K with a wavelength of 0.45411 Å. The crystal structure analyses (indexing, Pawley and Rietveld refinement) were performed with the program TOPAS-Academic v4.

To obtain patterns of Co₂(*m*-dobdc) dosed with 1-butene and *trans*-butene, the activated framework was loaded into 1.0 mm borosilicate capillaries inside an argon glovebox. The capillaries were then placed in a gas-dosing cell which was attached to a Micromeritics 3Flex gas adsorption analyzer and dosed with 250 mbar of 1-butene and 200 mbar of *trans*-butene, respectively, and flame sealed. For measurements of *cis*-butene dosed onto Co₂(*m*-dobdc), the activated framework was loaded into a 1.0 mm borosilicate capillary inside a nitrogen glovebox, attached to a gas-dosing cell connected to a custom gas-dosing manifold, turbomolecular pump, and fixed to a goniometer. The framework was first evacuated, then was dosed *in situ* with 4 mbar of *cis*-butene at 298 K, and cooled slowly to 125 K at a rate of 3 K/min.

Upon inspection of the diffraction patterns, it was found that Co₂(*m*-dobdc) exhibits noticeable changes in peak intensity upon adsorption of 1-butene and *trans*-butene, and more pronounced changes upon adsorption of *cis*-butene. These changes in intensity are particularly apparent upon cooling and is indicative of gas molecules occupying the pores of the framework. Precise unit cell parameters of all dosed samples were first obtained by Pawley refinement.

Using the refined structure of activated Co₂(*m*-dobdc) as a starting reference, a Fourier difference map was calculated after Rietveld refinement. Excess electron density was observed most clearly above the Co open metal site with all three butenes. When atoms were placed in the region with the highest concentration of electron density and their atomic coordinates and occupancies were refined the goodness-of-fit parameters showed a marked improvement. In the initial stages of the refinement, C–C bond distances were refined with soft constraints. In the final stages of the refinement, the adsorbed gas occupancies and thermal and unit cell parameters were fully refined and convoluted with the sample and instrument parameters and Chebyshev background polynomials. The calculated diffraction pattern for the final structural models of Co₂(*m*-dobdc) dosed with 1-butene and *cis*-butene agree well with the experimental data (Rietveld plots in Figures 4.S1-4.S2 and crystallographic details in Table 4.S1).

In the refinement of Co₂(*m*-dobdc) dosed with 1-butene, the olefinic carbons C6 and C7 were easily located over the Co open metal site and refined to a reasonable C–C double bond distance of 1.26(9) Å. The alkyl groups were challenging to model due to the disorder imposed by the mirror plane characteristic to the R3*m* space group which bisects the framework ligand. This mirror plane places the terminal carbon C8 of the alkyl chain close to the neighboring butene, however

the large atomic displacement parameter of 0.13(3) suggests that there is significant disorder at this position caused by the flexibility of the alkyl chain and steric hinderance of the neighboring butene, in addition to the crystallographic mirror plane.

In the refinement of Co₂(*m*-dobdc) dosed with *cis*-butene, the olefinic carbons C6 and C7 of the butene were located above the Co centers without difficulty. However, only one other carbon atom belonging to the butene, C9, could be found using the Fourier difference map. The final carbon of the butene, C10 could not be located using this method and was instead attached to the partial molecule using Mercury CSD v4.1.0, based on the expected structural parameters of *cis*-butene determined from single-crystal x-ray diffraction experiments of Co₂(dobdc). As a result, this carbon's atomic positions were not freely refined.

The Fourier difference map indicated there was unmodelled electron density in the middle of the MOF pore. This led to the addition of C8 to the structure, which greatly improved the statistics of the refinement (reduction of ~2% in the R_{wp} to 7.69%) and is assigned as an additional molecule of *cis*-butene at the center of the pore which is highly disordered, as evidenced by the high value of the thermal displacement parameter and inability to resolve all carbons of the butene molecule. The close C and H distances between neighboring butenes should not be regarded as accurate, due to significant disorder imposed by the ligand-bisecting mirror plane.

Finally, attempts to conduct a Rietveld refinement to obtain the *trans*-butene-dosed Co₂(*m*-dobdc) structural model were unsuccessful. The Fourier difference map clearly shows excess electron density centered over the open metal site, however, attempts to fit it with defined atom positions resulted in unreasonable occupancies and bond distances. A plot of the Pawley refinement has been provided in Figure 4.S3.

Table 4.S1. Experimental conditions, unit cell parameters, figures-of-merit, butene occupancy values, and metal–olefinic carbon distances, as determined by Rietveld refinement of powder X-ray diffraction patterns of Co₂(*m*-dobdc) dosed with 250 mbar 1-butene and 4 mbar *cis*-butene respectively.

	Co ₂ (<i>m</i> -dobdc)•(1-butene)	Co ₂ (<i>m</i> -dobdc)•(<i>cis</i> -butene) _{1.5}
λ (Å)	0.45415	0.45411
Temp. (K)	250 K	125 K
Space Group	<i>R</i> 3m	<i>R</i> 3m
a (Å)	25.982(18)	26.089(3)
c (Å)	6.8437(5)	6.8483(8)
V (Å ³)	4001.0(5)	4036.7(12)
R _{wp}	6.36%	7.69%
R _{exp}	1.57%	2.70%
R _{Bragg}	3.18%	3.11%
R _p	4.42%	5.0%
GoF	4.05	2.58
Butene occupancy	0.82(15)	0.91(5)
Co–C6 dist. (Å)	2.74(5)	2.99(8)
Co–C7 dist. (Å)	3.10(5)	3.04(13)
C6–C7 dist. (Å)	1.26(9)	1.25(2)

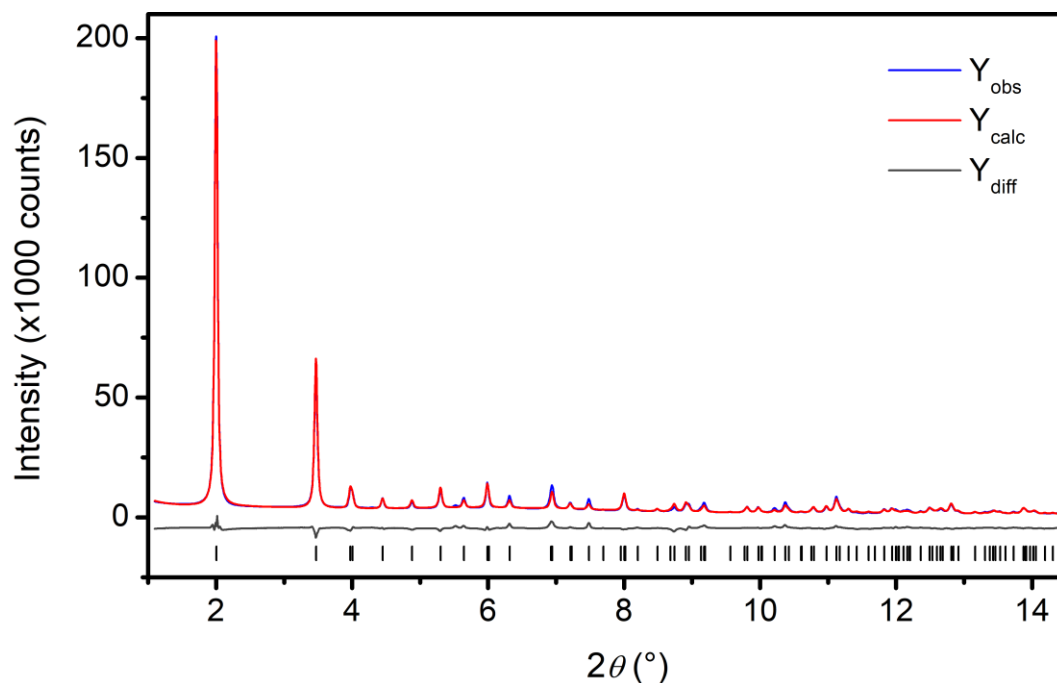


Figure 4.S1. Rietveld refinement of $\text{Co}_2(m\text{-dobdc})$ dosed with 250 mbar of 1-butene at 250 K from 1.0° to 14.80° . Blue and red lines represent the observed and calculated diffraction patterns, respectively. The gray line represents the difference between observed and calculated patterns, and the black tick marks indicate calculated Bragg peak positions. Figures-of-merit (as defined by TOPAS): $R_{\text{wp}} = 6.36\%$, $R_p = 4.42\%$, $R_{\text{exp}} = 1.57\%$, $R_{\text{Bragg}} = 3.18\%$, $\text{GoF} = 4.05$. The wavelength was $0.45415 \text{ \AA}$.

Table 4.S2. Structural model obtained by Rietveld refinement of the synchrotron powder X-ray diffraction pattern of $\text{Co}_2(m\text{-dobdc})$ dosed with 250 mbar of 1-butene at 250 K. The wavelength was $0.45415 \text{ \AA}$. Values in parenthesis indicate one standard deviation from the parameter value.

atom	x	y	z	multiplicity	occupancy	$U_{\text{iso}} (\text{\AA}^2)$
Co	0.2956(2)	0.0096(4)	-0.119(5)	18	1	0.0105(1)
C1	0.3201(16)	0.114(2)	0.175(7)	18	1	0.0244(4) ^a
C2	0.337(3)	0.169(4)	0.078(9)	9	1	0.0244(4) ^a
C3	0.3047(18)	0.107(2)	0.374(8)	18	1	0.0244(4) ^a
C4	0.3000(17)	0.058(2)	0.483(6)	18	1	0.0244(4) ^a
C5	0.2954(18)	0.1477(20)	0.497(9)	9	1	0.0244(4) ^a
O1	0.3356(10)	0.0763(13)	0.088(5)	18	1	0.0244(4) ^a
O2	0.3153(9)	0.0231(14)	0.438(6)	18	1	0.0244(4) ^a
O3	0.2767(10)	0.0474(14)	0.6710(10)	18	1	0.0244(4) ^a
C6	0.1748(19)	-0.0370(2)	-0.106(11)	18	0.82(15)	0.13(2)
C7	0.1744(17)	-0.0257(18)	0.073(7)	18	0.82(15)	0.01(17)
C8	0.1537(13)	0.059(3)	0.192(9)	18	0.82(15)	0.13(3)

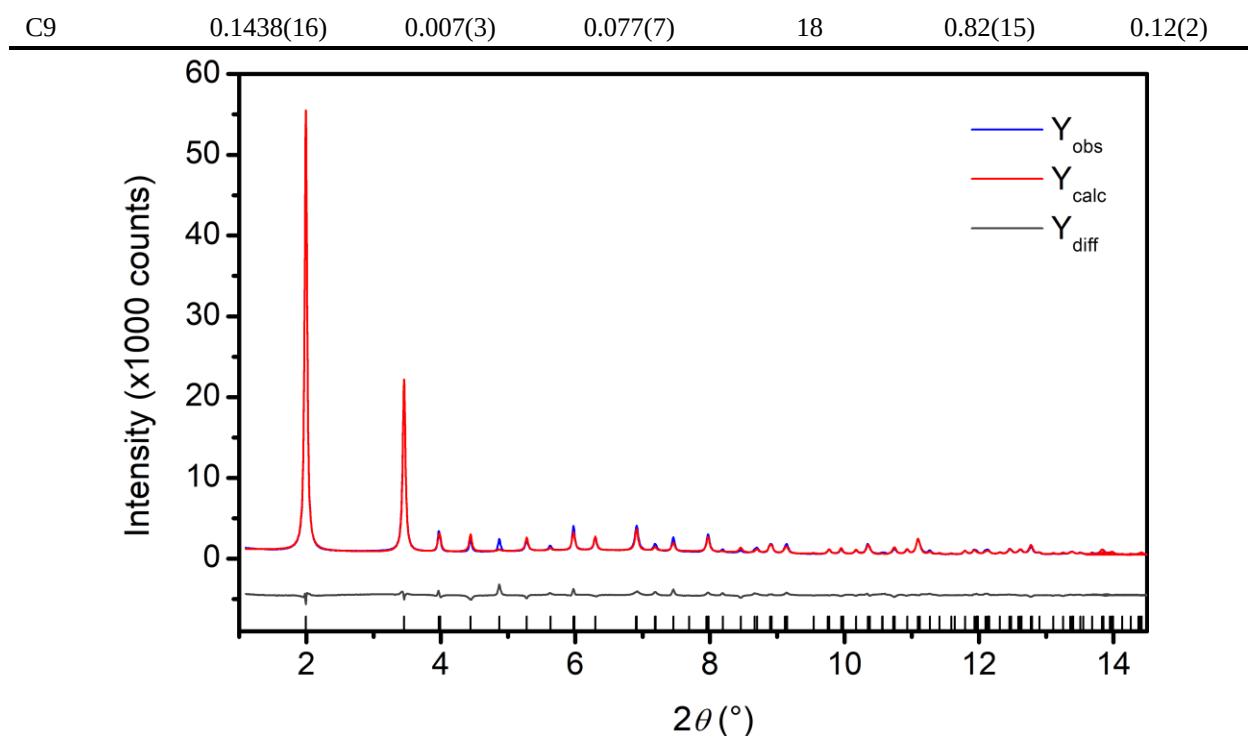


Figure 4.S2. Rietveld refinement of $\text{Co}_2(m\text{-dobdc})$ dosed with 4 mbar of *cis*-butene at 125 K from 1.0° to 14.80° . Blue and red lines represent the observed and calculated diffraction patterns, respectively. The gray line represents the difference between observed and calculated patterns, and the black tick marks indicate calculated Bragg peak positions. Figures-of-merit (as defined by TOPAS): $R_{\text{wp}} = 7.69\%$, $R_p = 5.0\%$, $R_{\text{exp}} = 2.70\%$, $R_{\text{Bragg}} = 3.11\%$, $\text{GoF} = 2.58$. The wavelength was $0.45411 \text{ \AA}$.

Table 4.S3. Structural model obtained by Rietveld refinement of the synchrotron powder X-ray diffraction pattern of $\text{Co}_2(m\text{-dobdc})$ dosed with 4 mbar of *cis*-butene at 125 K. The wavelength was $0.45411 \text{ \AA}$. Values in parenthesis indicate one standard deviation from the parameter value.

atom	x	y	z	multiplicity	occupancy	$U_{\text{iso}} (\text{\AA}^2)$
Co	0.2956(2)	0.0096(4)	-0.119(5)	18	1	0.01(6)
C1	0.3201(16)	0.114(2)	0.175(7)	18	1	0.03(14) ^a
C2	0.337(3)	0.169(4)	0.078(9)	9	1	0.03(14) ^a
C3	0.3047(18)	0.107(2)	0.374(8)	18	1	0.03(14) ^a
C4	0.3000(17)	0.058(2)	0.483(6)	18	1	0.03(14) ^a
C5	0.2954(18)	0.1477(20)	0.497(9)	9	1	0.03(14) ^a
O1	0.3356(10)	0.0763(13)	0.088(5)	18	1	0.03(14) ^a
O2	0.3153(9)	0.0231(14)	0.438(6)	18	1	0.03(14) ^a
O3	0.2767(10)	0.0474(14)	0.6710(10)	18	1	0.03(14) ^a
C6	0.175(4)	0.185(4)	-0.031(17)	18	0.91(5)	0.01(5)
C7	0.198(5)	0.193(5)	0.134(20)	18	0.91(5)	0.01(5)
C8	0.074(8)	0.064(7)	0.57(3)	18	0.53(7)	0.1(10)
C9	0.157(5)	0.122(5)	-0.11(3)	18	0.91(5)	0.13(9)
C10	0.205(6)	0.143(4)	0.23(2)	18	0.91(5)	0.13(6)

^aThe thermal parameters for all of atoms of the ligand were constrained to be equivalent.

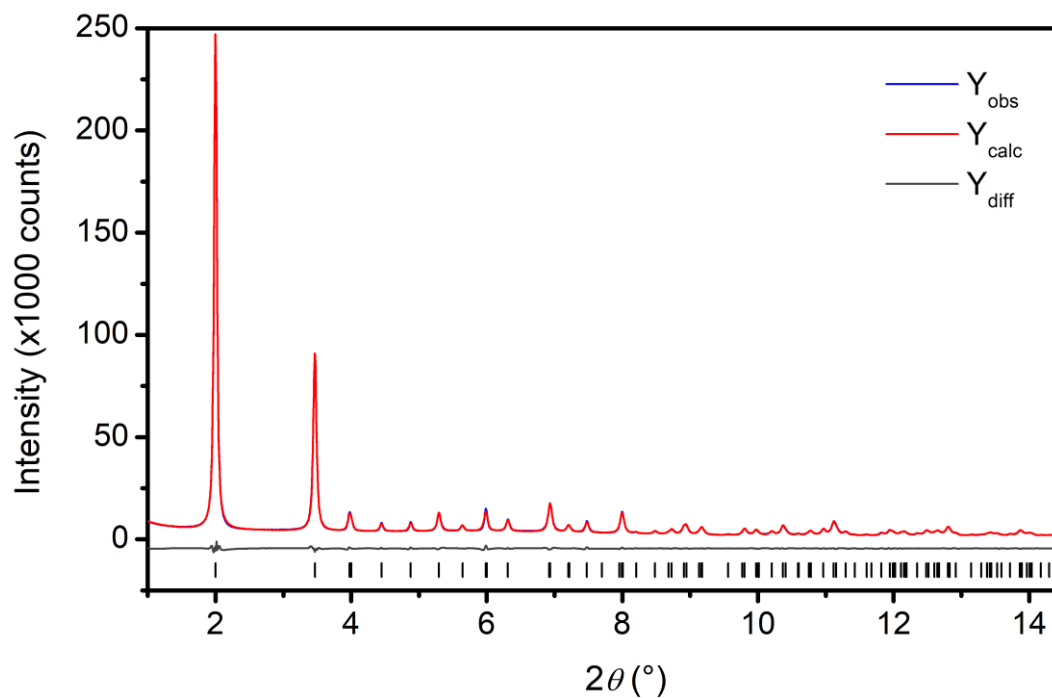


Figure 4.S3. Pawley refinement of Co₂(*m*-dobdc) dosed with 200 mbar of *trans*-butene at 250 K from 1.0° to 14.80°. Blue and red lines represent the observed and calculated diffraction patterns, respectively. The gray line represents the difference between observed and calculated patterns, and the black tick marks indicate calculated Bragg peak positions. Space group *R3m*, $a = 25.995(1) \text{ \AA}$, $c = 6.8395(3) \text{ \AA}$, $V = 4002.4(4) \text{ \AA}^3$. Figures-of-merit (as defined by TOPAS): $R_{wp} = 2.11\%$, $R_p = 1.44\%$, $R_{exp} = 1.46\%$. The wavelength was $0.45415 \text{ \AA}$.

4.7.2. Powder X-ray Diffraction Analysis of MOFs with Dicarboxylate Ligands

High-resolution synchrotron X-ray powder diffraction data for all samples were collected at beamline17-BM at the Advanced Photon Source at Argonne National Laboratory with a Perkin-Elmer a-Si flat panel detector. Diffraction patterns were collected at a wavelength of 0.44850 Å, while the temperature was held constant at 298 K with an Oxford Cryosystems Cryostream 800. The crystal structure analyses (indexing and Pawley refinements) were performed with the program TOPAS-Academic v4.1.16

The structural solution of Fe(cyhdc) was obtained by first indexing the powder patterns and performing a subsequent Pawley refinement to determine the goodness of fit for that combination of unit cell parameters. After obtaining accurate lattice parameters, rigid body structural model of the ligand was based on the asymmetric unit of related frameworks³ as a reference to perform simulated annealing refinements. The model was constructed using z-matrix notation and then allowed refine along three rotational and translational axes. Once the simulated annealing calculation reached a minimum the atom positions were extracted and used for a Rietveld refinement. All hydrogen atoms were added to the final refined structure using the program Mercury and therefore no error values are reported for these atoms in the structure information files.

Table 4.S3. Unit cell parameters for three dicarboxylate-based frameworks.

	Fe(cyhdc)	Cr(cyhdc)	Cu(bipy)
Space Group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	5.2395(2)	5.252(7)	14.904(5)
<i>b</i> (Å)	9.9305(4)	9.937(8)	5.60(2)
<i>c</i> (Å)	10.8125(4)	10.86(1)	13.418(5)
<i>α</i> (°)	107.741(5)	106.23(5)	90.7(1)
<i>β</i> (°)	81.419(6)	82.25(9)	90.2(5)
<i>γ</i> (°)	92.401(4)	93.3(1)	89.4(5)
Volume (Å³)	529.83(4)	539(4)	1119(4)

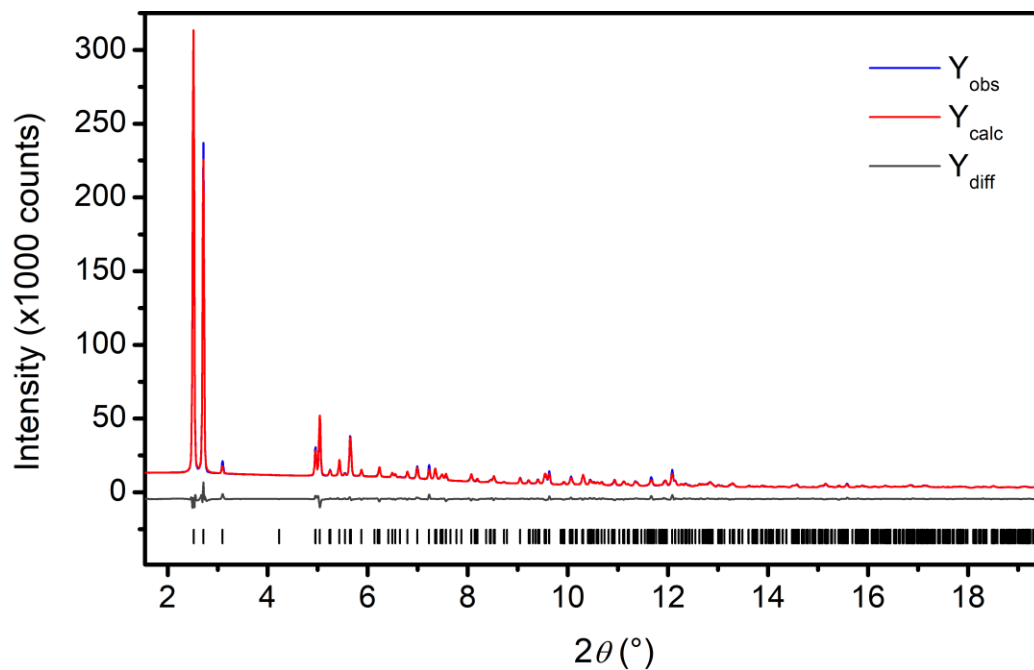


Figure 4.S4. Rietveld refinement of Fe(cyhdc) at 295 K. Figures of Merit (as defined by TOPAS): $R_{wp} = 3.63\%$, $R_{exp} = 1.04\%$, $R_p = 2.41\%$, $R_{bragg} = 2.27\%$, GoF = 4.21 ($\lambda = 0.44850 \text{ \AA}$).

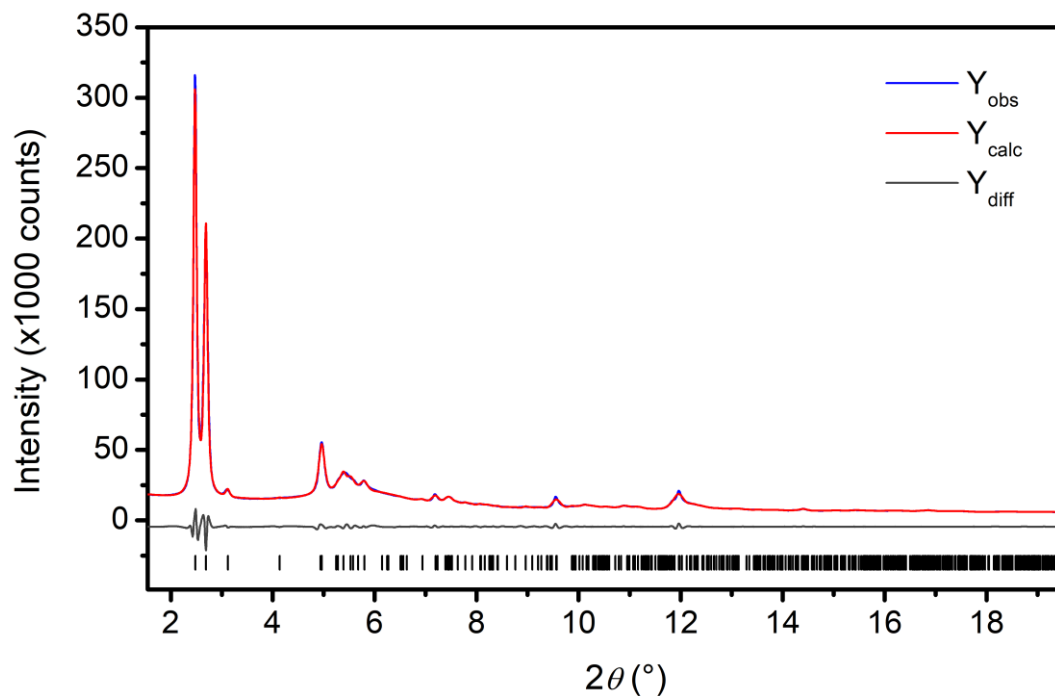


Figure 4.S5. Pawley refinement of Cr(cyhdc) at 295 K. Figures of Merit (as defined by TOPAS): $R_{wp} = 2.91\%$ ($\lambda = 0.44850 \text{ \AA}$).

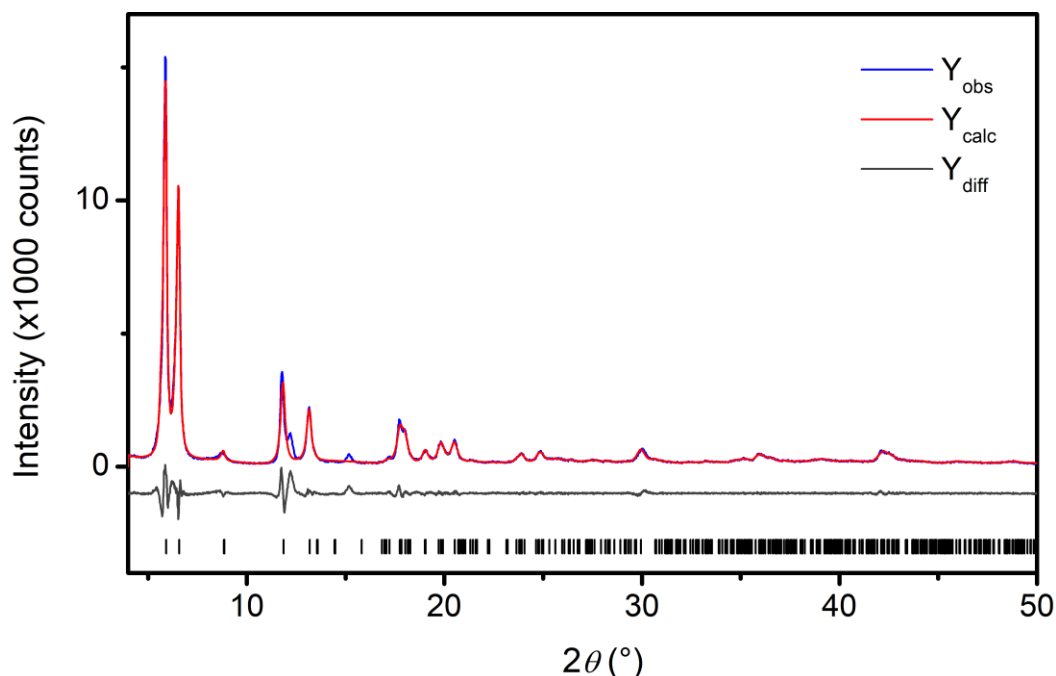


Figure 4.S6. Pawley refinement of Cu(bipy) at 295 K. Figures of Merit (as defined by TOPAS): $R_{wp} = 12.84\%$ ($\lambda = 0.44850$ Å).

4.7.3. Powder X-ray Diffraction Analysis of Zn(BDP) and Analogous Frameworks

High-resolution synchrotron X-ray powder diffraction data for all samples were collected at beamline 17-BM at the Advanced Photon Source at Argonne National Laboratory with a Perkin-Elmer a-Si flat panel detector. Diffraction patterns of Zn(PyridineDP), Zn(PyridazineDP) and Zn(PyrazineDP) were collected at a wavelength of 0.44850 Å, while Zn(BDP), Zn(PyrimidineDP) and Zn(Tetrazine) were collected at 0.45191 Å. Samples were prepared in borosilicate glass capillaries which were then placed under vacuum and flame sealed. The temperature was held constant at 100K or 298 K during these measurements with an Oxford Cryosystems Cryostream 800. The crystal structure analyses including indexing, Pawley and Rietveld refinements were performed with the program TOPAS-Academic v4.1.16.^{30,31} In-situ high pressure measurements were conducted using a specialized gas cell in which the samples were packed into quartz capillaries and pressurized using a syringe pump provided by beamline 17-BM.

The space group of the collapsed phases were determined by first indexing the powder patterns and performing a subsequent Pawley refinement to determine the goodness of fit for that combination of unit cell parameters. After obtaining accurate lattice parameters, rigid body structural model of the ligand was based on the asymmetric unit of related frameworks³ as a reference to perform simulated annealing refinements. The model was constructed using z-matrix notation and then allowed refine along three rotational and translational axes. The angles and torsions between the pyrazolate rings and the heterocyclic six-membered rings were also allowed to freely refine. A Fourier difference map was used to locate the position of the zinc atom which was then fixed in space, after which the ligand was allowed to refine along the parameters previously described. Once the simulated annealing calculation reached a minimum the atom positions were extracted and used for a Rietveld refinement. All hydrogen atoms were added to

the final refined structure using the program Mercury and therefore no error values are reported for these atoms in the structure information files.

It should be noted that these frameworks are known to be paracrystalline which prohibits the Lorentzian and Gaussian line widths and crystal strain parameters to be accurately calculated.²⁰ Additionally, the expanded phase of the framework can be seen in varying amounts in all of these patterns and as such, the data sampled in the refinement was selected to exclude the highest intensity peak of this expanded phase occurring at around 2 degrees 2θ . These factors contribute to higher than typical goodness of fit parameters and sections of the pattern that have a poorer than average fit.

This phenomenon is especially apparent in the high pressure measurements of Zn(BDP), Zn(PymDP), and Zn(PyzDP). In these frameworks at pressures in excess of 50 bar, the expanded phase becomes visible and is characterized by a set of sharp asymmetric peaks that correspond to reflections along the crystallographic $0k0$ planes. This is consistent with what was seen for isostructural frameworks Fe(BDP) and Co(BDP). For the Zn(PymDP), and Zn(PyzDP) frameworks, the collapsed phase can still be observed even at the highest pressures that could be achieved with the high pressure sample cell. Due to the presence of mixed phases and the challenges afforded by the atypical peak shapes, a refinement of atom positions for the expanded phases of Zn(BDP), Zn(PymDP), and Zn(PyzDP) was not undertaken, instead the atom positions were extracted from an existing structural model of the expanded phase of this framework type, and the unit cell parameters were refined via the Rietveld method.

Table 4.S4. Unit cell parameters for Zn(BDP) and four heterocyclic derivatives.

	Zn(BDP)	Zn(PyDP)	Zn(PymDP)	Zn(PyzDP)	Zn(PydDP)	Zn(TDP)
Space Group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>	<i>P21/c</i>
<i>a</i> (Å)	9.032(1)	8.372(2)	7.431(2)	7.519(2)	7.579(3)	7.217(2)
<i>b</i> (Å)	23.140(3)	22.768(5)	22.230(6)	22.130(4)	22.139(7)	22.550(9)
<i>c</i> (Å)	6.861(1)	6.814(2)	6.747(2)	6.670(1)	6.657(3)	6.815(1)
α (°)	90	90	90	90	90	90
β (°)	124.091(5)	123.14(1)	59.46(1)	120.58 (1)	61.93(2)	67.69(2)
γ (°)	90	90	90	90	90	90
Volume (Å³)	1187.6(3)	1087.4(5)	959.9(5)	955.5(4)	985.6(7)	1026.1(5)
Density (g/cm³)	1.51(4)	1.66(1)	1.87(9)	1.89(2)	1.84(1)	---

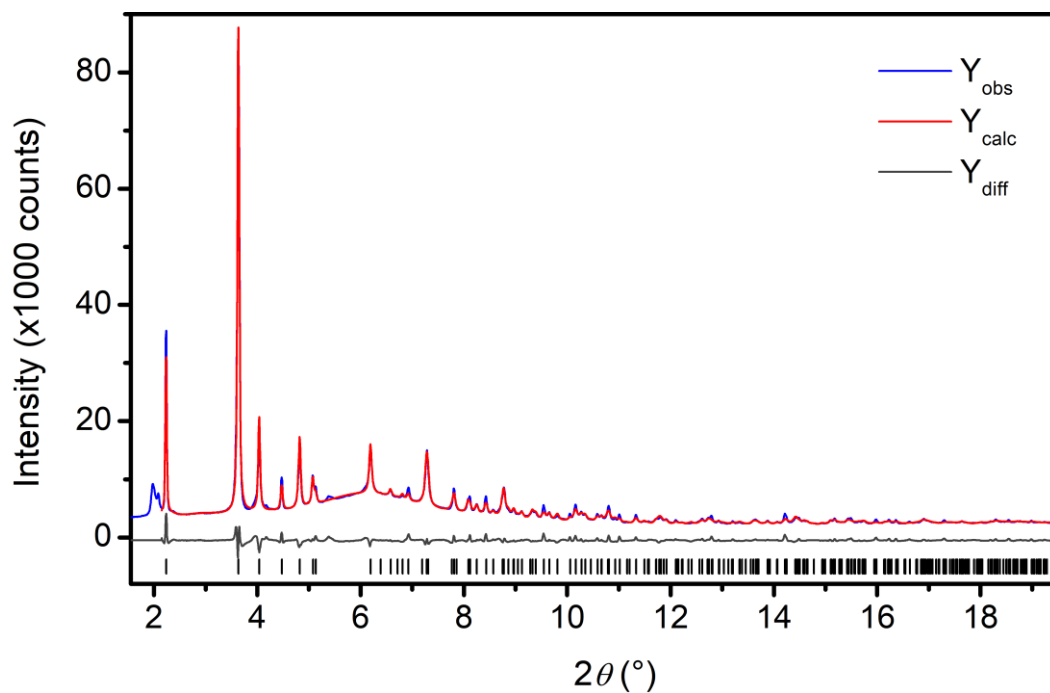


Figure 4.S7. Rietveld refinement of evacuated Zn(BDP) at 298 K. Figures of Merit (as defined by TOPAS): $R_{\text{wp}} = 4.62\%$, $R_{\text{exp}} = 1.47\%$, $R_p = 3.20\%$, $R_{\text{bragg}} = 2.05\%$, GoF = 3.14 ($\lambda = 0.45191 \text{ \AA}$).

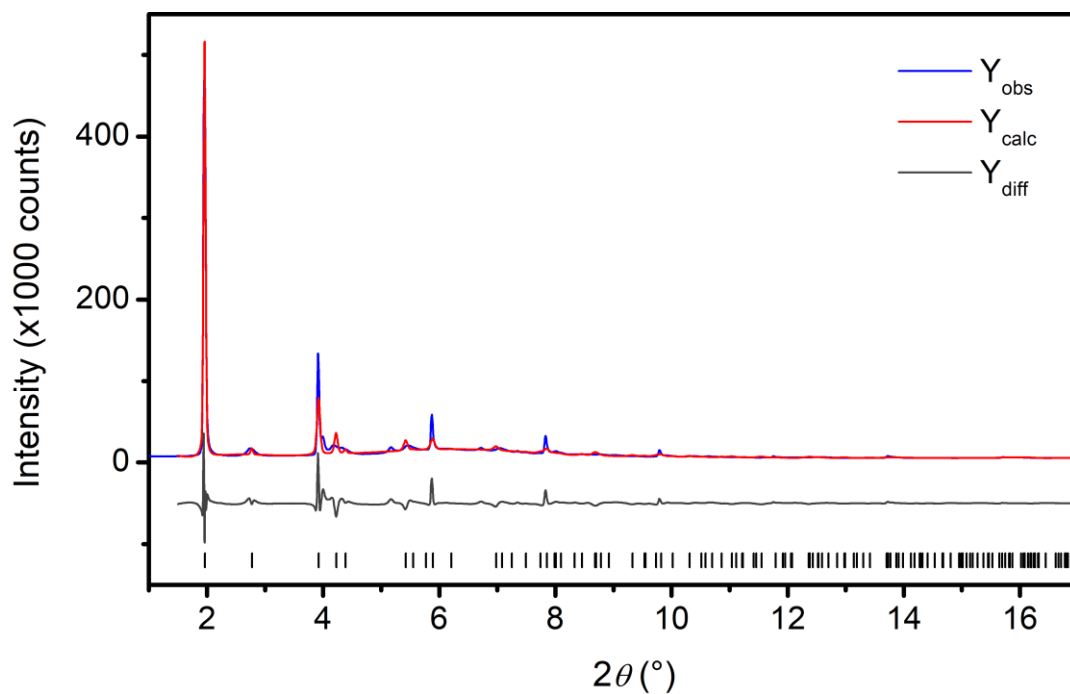


Figure 4.S8. Rietveld refinement of Zn(BDP) under 82 bar methane at 298 K. Figures of Merit (as defined by TOPAS): $R_{\text{wp}} = 15.8\%$, $R_{\text{exp}} = 0.92\%$, $R_p = 10.5\%$, GoF = 17.1 ($\lambda = 0.45191 \text{ \AA}$).

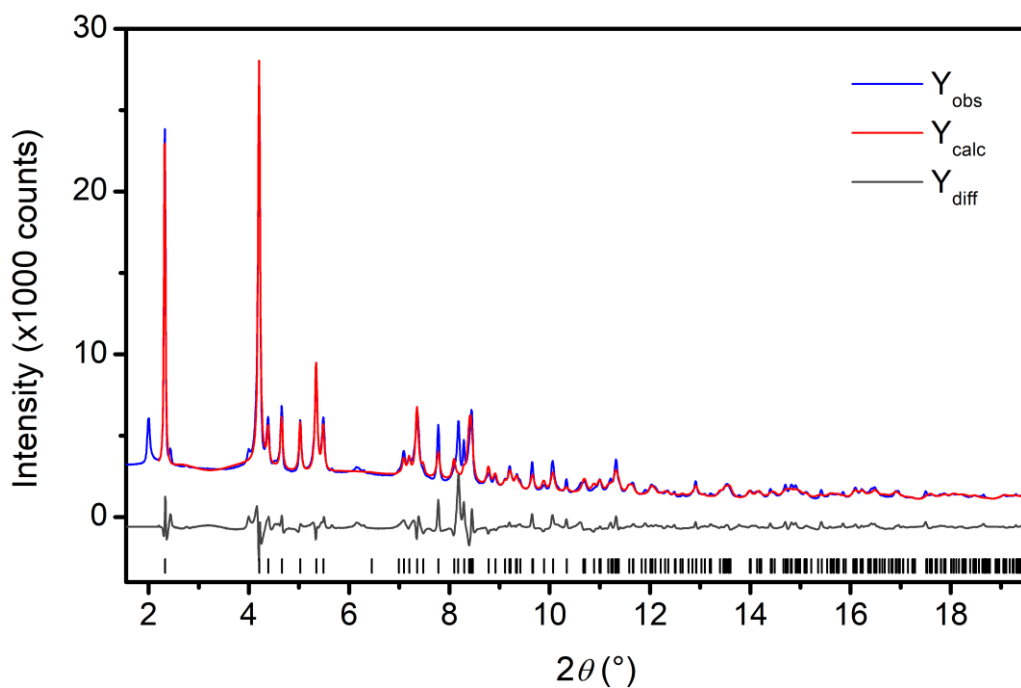


Figure 4.S9. Rietveld refinement of evacuated Zn(PymDP) at 100 K. Figures of Merit (as defined by TOPAS): $R_{wp} = 8.34\%$, $R_{exp} = 2.03\%$, $R_p = 5.88\%$, $R_{bragg} = 2.53\%$, $GoF = 4.21$ ($\lambda = 0.45191 \text{ \AA}$).

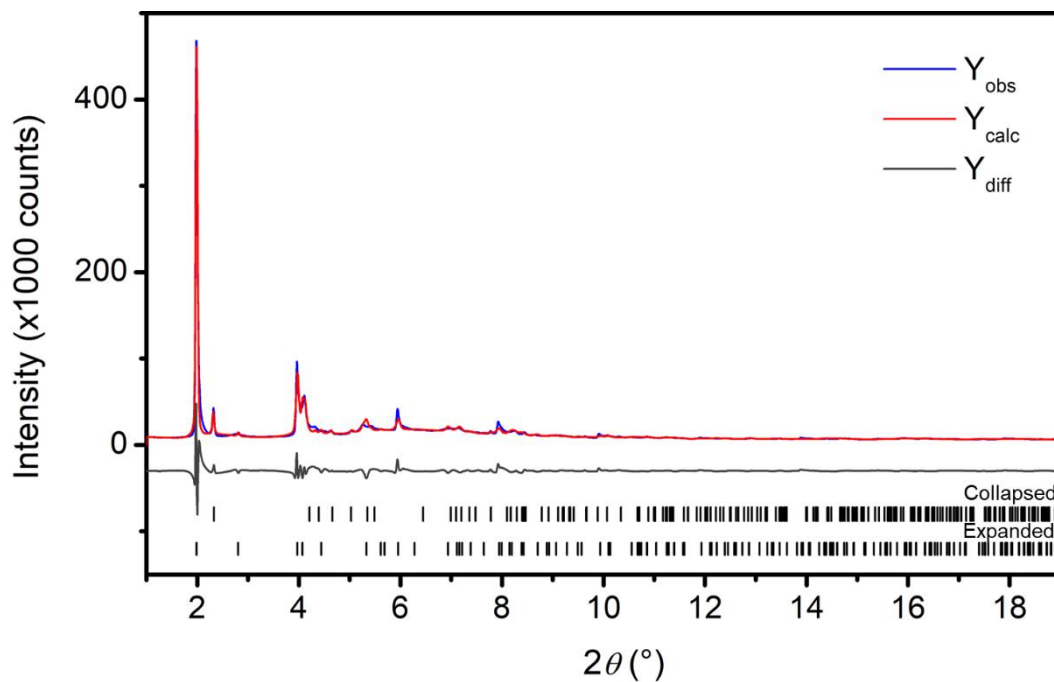


Figure 4.S10. Multi-phase Rietveld refinement of Zn(PymDP) under 79 bar methane. Collapsed phase ($C2/c$) and expanded phase ($P42/mmc$) are labelled accordingly. Figures of Merit (as defined by TOPAS): $R_{wp} = 11.5\%$, $R_{exp} = 0.83\%$, $R_p = 7.38\%$, $GoF = 13.1$ ($\lambda = 0.45191 \text{ \AA}$).

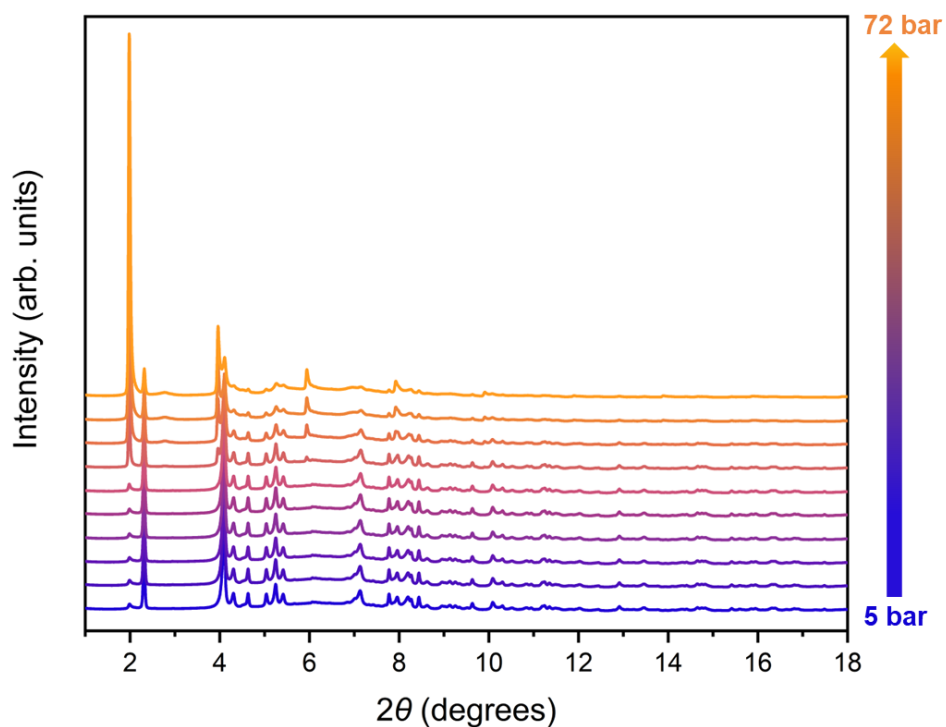


Figure 4.S11. Variable pressure diffraction data of Zn(PyMDP) measured in steps of 10 bar between 5 bar and 72 bar at 298 K. ($\lambda = 0.45191 \text{ \AA}$)

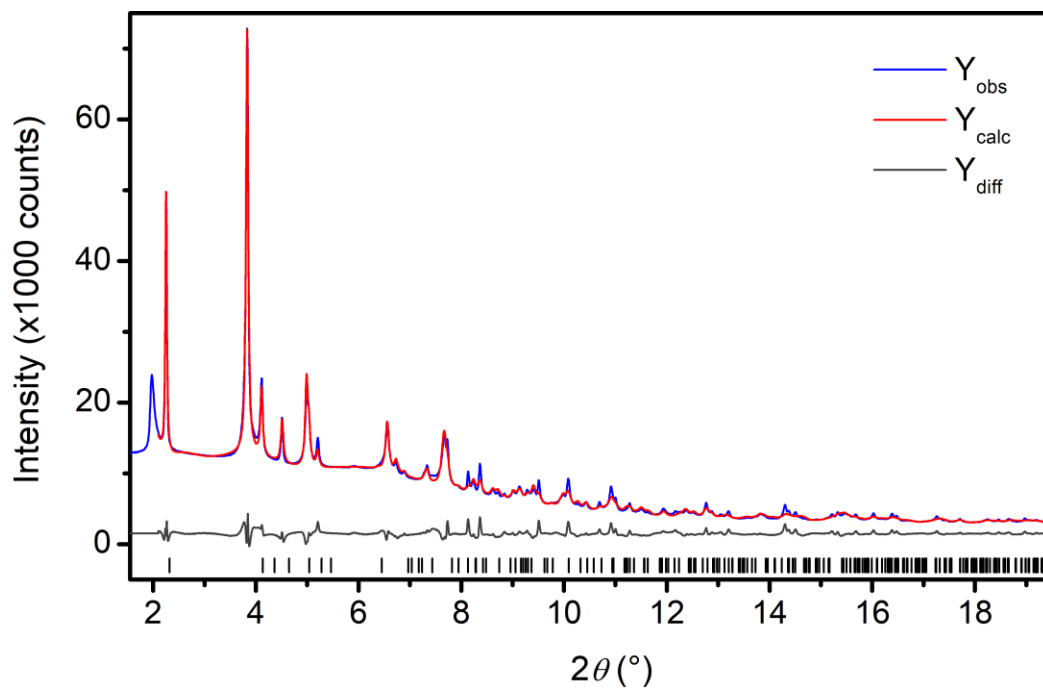


Figure 4.S12. Rietveld refinement of evacuated Zn(PyZDP) at 298 K. Figures of Merit (as defined by TOPAS): $R_{wp} = 6.81\%$, $R_{exp} = 2.31\%$, $R_p = 4.54\%$, $R_{bragg} = 2.38\%$, $GoF = 3.14$ ($\lambda = 0.45191 \text{ \AA}$).

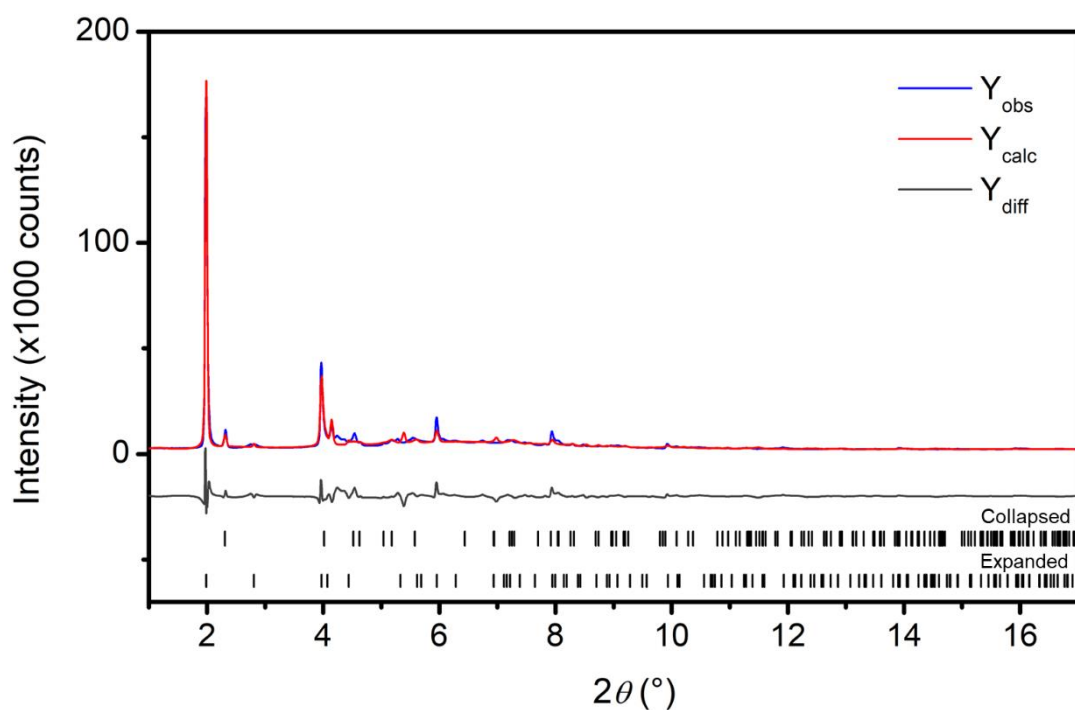


Figure 4.S13. Multi-phase Rietveld refinement of Zn(PyzDP) under 90 bar methane at 298 K. Collapsed phase (*C2/c*) and expanded phase (*P42/mmc*) are labelled accordingly. Figures of Merit (as defined by TOPAS): $R_{\text{wp}} = 13.6\%$, $R_{\text{exp}} = 1.54\%$, $R_p = 9.25\%$, GoF = 8.86 ($\lambda = 0.45191 \text{ \AA}$).

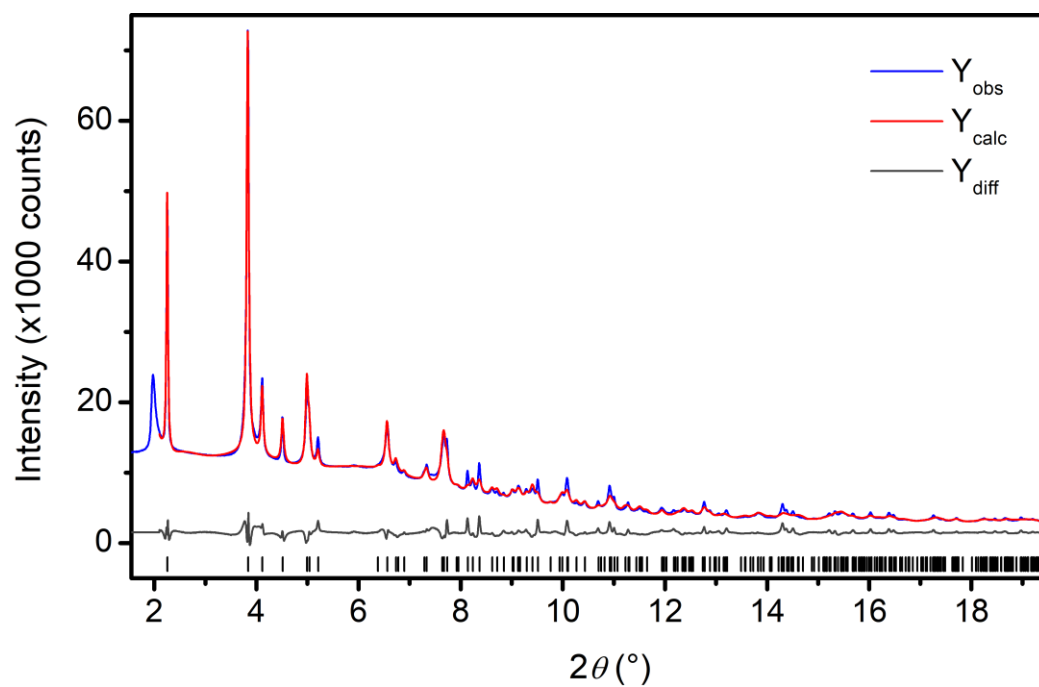


Figure 4.S14. Rietveld refinement of evacuated Zn(PyDP) at 298 K. Figures of Merit (as defined by TOPAS): $R_{wp} = 3.98\%$, $R_{exp} = 1.14\%$, $R_p = 2.66\%$, $R_{bragg} = 1.60\%$, GoF = 3.50 ($\lambda = 0.44850 \text{ \AA}$).

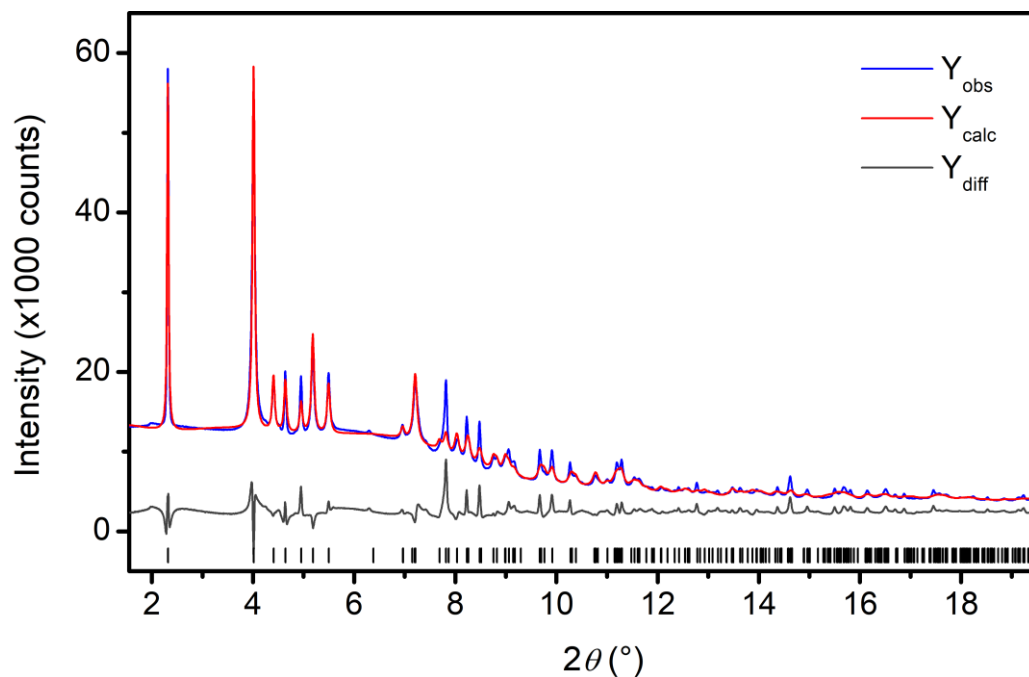


Figure 4.S15. Rietveld refinement of evacuated Zn(PydDP) at 298 K. Figures of Merit (as defined by TOPAS): $R_{wp} = 5.26\%$, $R_{exp} = 1.06\%$, $R_p = 3.55\%$, $R_{bragg} = 2.25\%$, GoF = 4.98 ($\lambda = 0.44850 \text{ \AA}$).

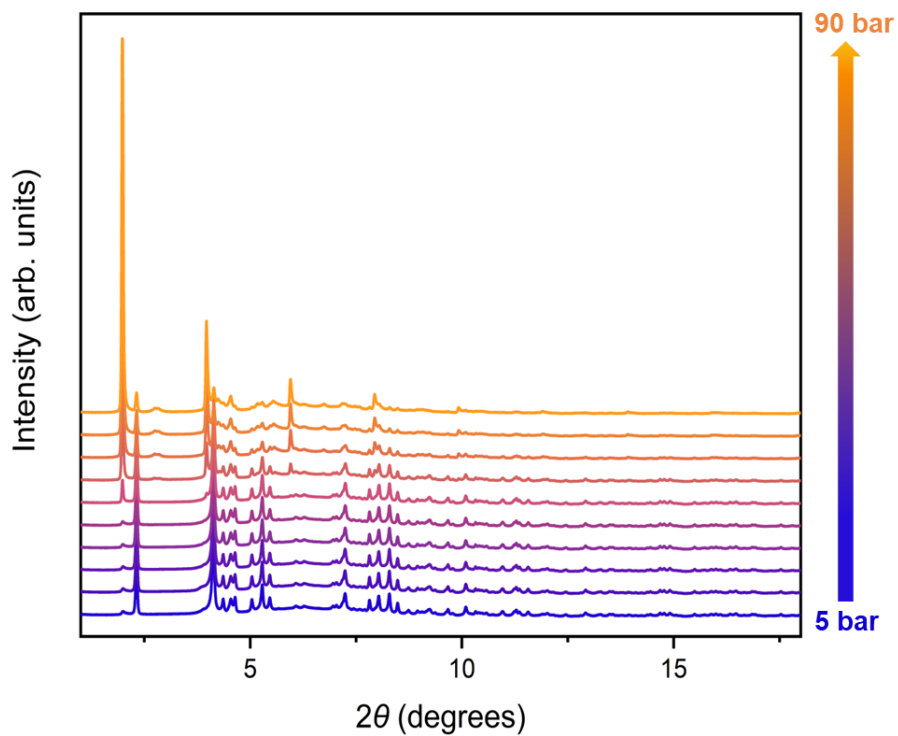


Figure 4.S16. Variable pressure diffraction data of Zn(PydDP) measured in steps of 10 bar between 5 bar and 90 bar at 298 K. ($\lambda = 0.45191 \text{ \AA}$).

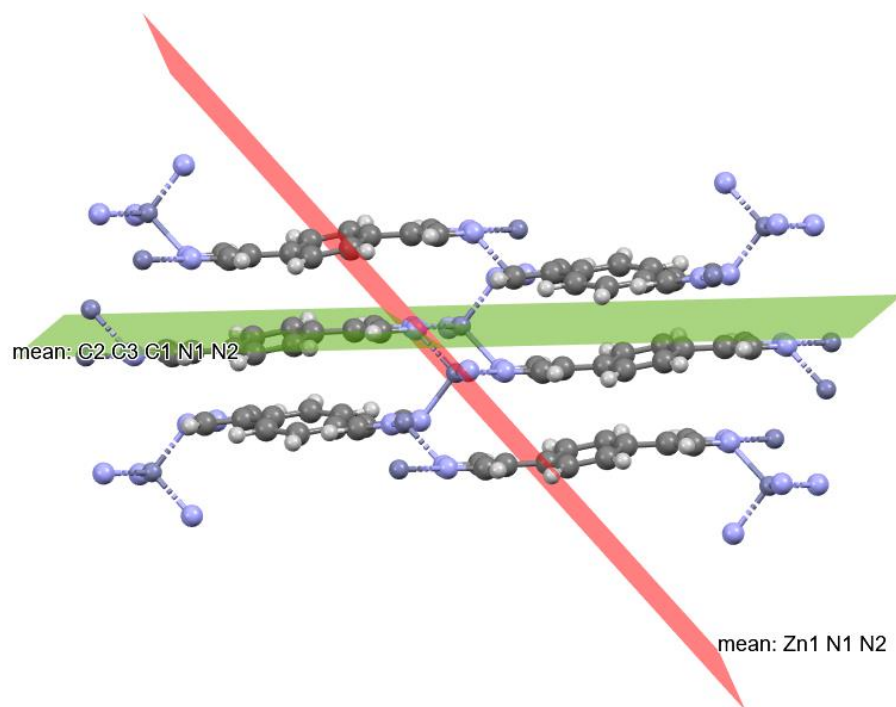


Figure 4.S17. Depiction of the planes that pass through Zn, N1 and N2 (red plane) and N1, N2, C1, C2 and C3 (green plane) or the atoms that compose the pyrazolate ring.

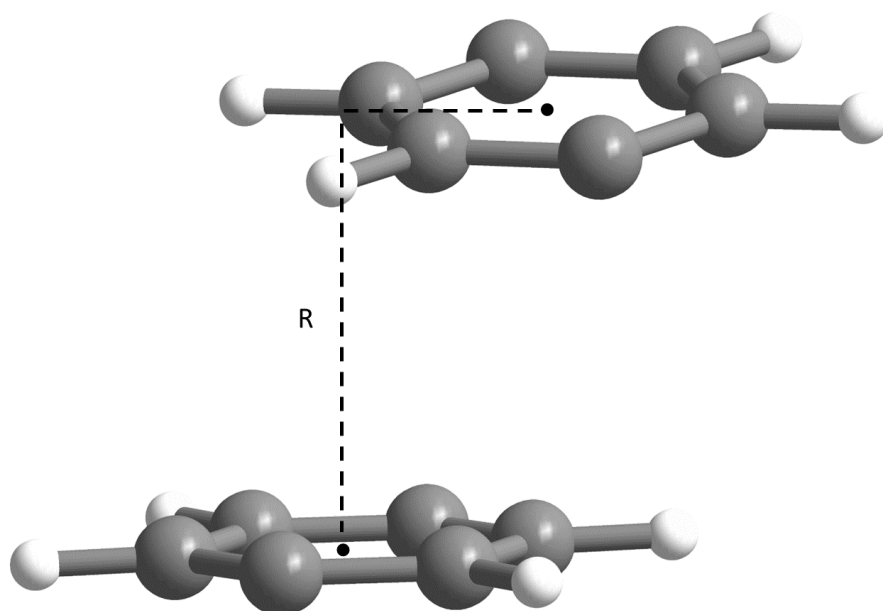


Figure 4.S18. Depiction of the center of mass distance, R , as calculated for Zn-dipyrzolate frameworks. The center of mass of the atoms in the aromatic ring was calculated and the vertical displacement of the ring was calculated based on the Pythagorean theorem.

4.7.4. Powder X-ray Diffraction Analysis of $M_2(X-m-dobdc)$ Frameworks

High-resolution synchrotron X-ray powder diffraction data for all samples were collected at beamline 17-BM at the Advanced Photon Source at Argonne National Laboratory with a Perkin-Elmer a-Si flat panel detector. Diffraction patterns of Zn(PyridineDP), Zn(PyridazineDP) and Zn(PyrazineDP) were collected at a wavelength of 0.44850 Å, while Zn(BDP), Zn(PyrimidineDP) and Zn(Tetrazine) were collected at 0.45192 Å. Samples were prepared in borosilicate glass capillaries which were dosed with ethylene, ethane, propylene or propane at a pressure of 500 mbar with a Micromeritics 3-flex gas adsorption analyzer and flame sealed. The temperature was held constant at 100K or 298 K during these measurements with an Oxford Cryosystems Cryostream 800. The crystal structure analyses including indexing, Pawley and Rietveld refinements were performed with the program TOPAS-Academic v4.1.16.^{30,31}

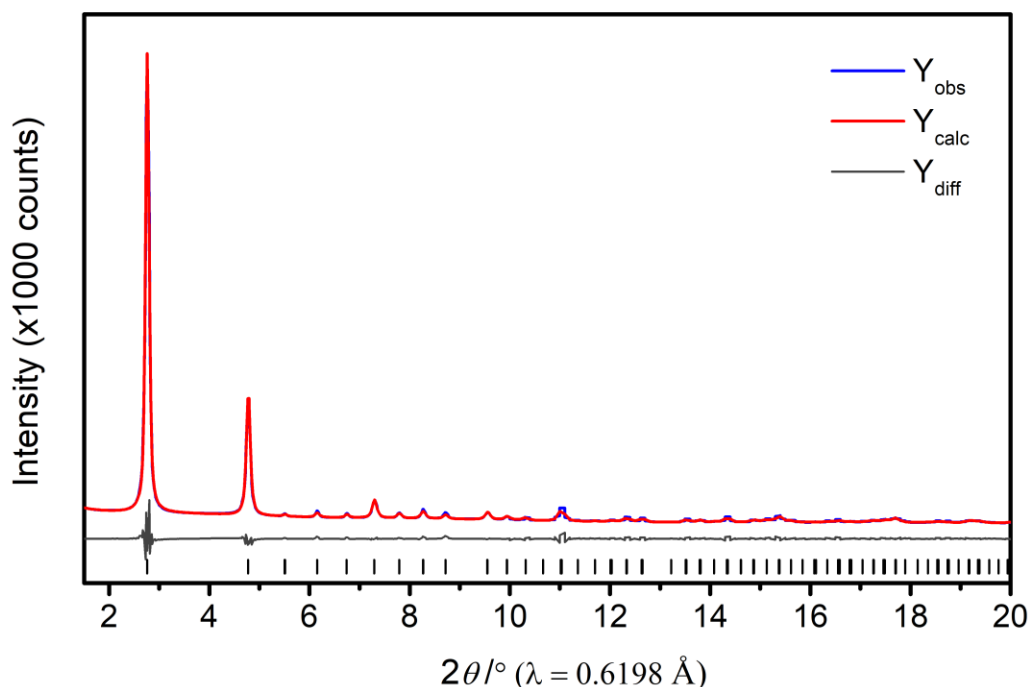


Figure 4.S19. Rietveld refinement of evacuated Co(F-*m*-dobdc) at 298 K. Space Group: $R3m$, $a = 25.778(6)$ Å, $c = 6.746(2)$ Å. Figures of Merit (as defined by TOPAS): $R_{wp} = 5.61\%$, $R_p = 3.79\%$ ($\lambda = 0.6198$ Å).

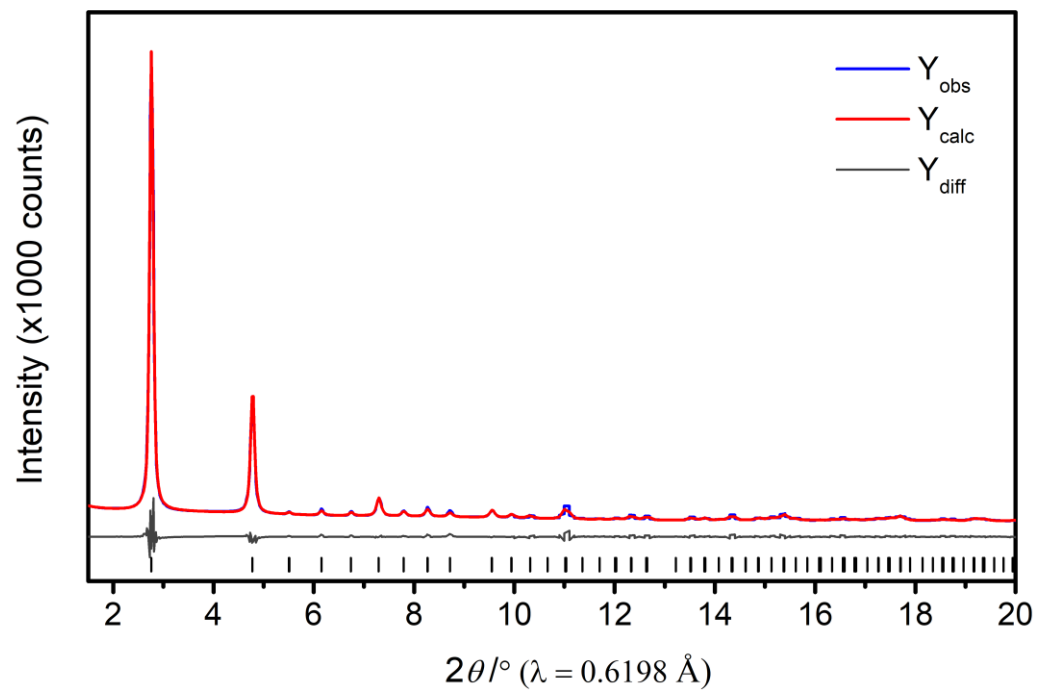


Figure 4.S20. Rietveld refinement of evacuated Ni(F-*m*-dobdc) at 298 K. Space Group: *R3m*, $a = 25.779(6)$ Å, $c = 6.747(2)$ Å. Figures of Merit (as defined by TOPAS): $R_{wp} = 5.68\%$, $R_p = 3.85\%$ ($\lambda = 0.6198$ Å).

4.8. References

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