

Selective Gas Adsorption in Highly Porous Chromium(II)-Based Metal-Organic Polyhedra

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Supporting Information

Porous solids, including zeolites,¹ activated carbons,² and metal–organic frameworks,^{3–6} have been extensively studied for their gas adsorption properties. Particularly in the case of the latter, their high surface areas,⁷⁻⁹ tunable syntheses,^{10,11} and large variety of pore geometries and functionalities have garnered them attention for many applications. These have included hydrogen, ^{12,13} methane, ^{14–17} and acetylene storage, ¹⁸ hydrocarbon separations, ^{19,20} carbon dioxide storage and separation, ^{21–23} and more recently, water capture and delivery. ^{24,25} Metal–organic polyhedra, a related class of potentially porous materials, have been investigated for over a decade yet still exhibit a relative dearth of adsorption studies.

Metal-organic polyhedra are discrete metal-organic molecular assemblies, and although they have been reported with a large variety of ligand functional groups, most typically contain carboxylate-based ligands. The most common example of this are the isophthalic acid containing cuboctahedra structures (Figure 1). These contain 24 dicarboxylate bridging ligands and 12 bimetallic paddlewheels. This pore structure is pervasive in metal-organic framework chemistry. It is the basic pore building unit in the NU-111, NOTT-119, and PCN-69 family of framework materials.²⁶⁻²⁸ It is also present as the largest of three pores in the well-known $M_3(btc)_2$ (M = Cr, Fe, Co, Ni,



Figure 1. Structure of Cr ^tBu-bdc. Green, red, and gray spheres represent Cr, O, and C atoms, respectively. Solvent molecules are omitted for clarity.

Cu, Zn, Mo, Ru; $btc^{3-} = 1,3,5$ -benzenetricarboxylate; HKUST-1) structure type.²⁹⁻³¹ However, the chemistry of discrete metal-organic polyhedra is relatively underdeveloped with homobimetallic structures of M X-bdc only reported for Cu, Mo, Rh, Ru, and very recently \overline{Cr} .^{32–36} We have considerable interest in expanding the number of accessible structures as these materials conceptually serve as soluble metal-organic framework pore analogs and have considerable potential utility in gas storage and small-molecule activation.

Chromium(II)-based metal-organic polyhedra are an intriguing target given the redox-active nature of this unit and the well-developed fundamental chemistry of this quadruply bonded species. Additionally, Zhou and co-workers have recently prepared three novel chromium paddlewheel-based polyhedra.³⁶ Analogous to the synthesis of previously reported M_X-bdc (M = Cu^{2+} , Mo²⁺; X = OH, ^tBu; bdc²⁻ = benzene-1,3-dicarboxylate) polyhedra,^{37,38} the solvothermal reaction of $Cr_2(OAc)_4$ with $H_2^{t}Bu$ -bdc (or H_2OH -bdc) in a 4:1 (5.7:1) N,N'-dimethylformamide/methanol mixture at 343 K for 24 h affords phase pure Cr X-bdc·nDMF as large brick-red octahedral crystals. Utilizing alternative chromium(II) sources for synthesis routinely afforded amorphous, red powder. This is consistent with previous observations that many paddlewheelbased materials require preformation of the metal building unit prior to material synthesis.³⁹ For both materials, addition of 2 equivalents of pyridine significantly increases the crystal size of the resulting product. While visual inspection of crystals suggested single-crystal quality, diffraction data was poor. Soaking the as-synthesized crystals in fresh DMF significantly increased the diffraction quality. However, structural characterization via single-crystal X-ray diffraction was unsuccessful as the data indicated the presence of interpenetrated twin crystals. We alternatively turned to powder X-ray diffraction for structural characterization.

To confirm the phase purity and crystal structures of the materials, initial structures were created based on the isostructural phases, Mo_OH-bdc and Cu_tBu-bdc. 37,38 Initial refinements gave poor fits (Figure S7) as a result of the lack of solvent molecules in the starting structures. However, attempts

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to remove disordered solvent from our materials led to a significant loss in crystallinity (Figure S18). This observation is consistent with the long-range crystal structure, consisting of body center cubic packing of the pore shown in Figure 1. Each pore is not bound to neighboring pores, rather van der Waals forces from metal-bound solvent molecules are the only interactions between polyhedra. Hence solvent removal decreases long-range crystallinity. Ultimately, Pawley refinement of powder patterns collected on DMF-solvated materials afforded unit cells of $P4_2/mnm$ with a = 29.422(5) Å and c = 41.181(14) for Cr_OH-bdc and $P4_2/mnm$ with a = 29.726(6) Å and c = 41.769(11) Å for Cr_^tBu-bdc. See Supporting Information for additional powder diffraction details.

Given their lack of extended three-dimensional structure, the activation of metal-organic polyhedra to achieve porous material is particularly challenging. For example, whereas Mo₃(btc)₂ and Cu₃(btc)₂ have Langmuir surface areas of 2010 and 2175 m^2/g respectively,^{31,40} their metal-organic polyhedra analogues based on substituted isophthalic acid ligands have been shown to display surface areas ranging from zero to 504 m²/g depending on activation conditions.³⁸ To the best of our knowledge, the highest reported surface area for a carboxylate based metal-organic polyhedron is $1100 \text{ m}^2/\text{g}^{41}$ In an attempt to desolvate Cr_OH-bdc and Cr_^tBu-bdc, we first sought to replace DMF with more volatile solvents prior to evacuation. However, these attempts either led to dissolution or decomposition of the materials. Ultimately, the solids were desolvated by heating the DMF exchanged materials under vacuum for 24 h. For Cr_OH-bdc, heating at 323 K afforded a solid with a Langmuir surface area of 187 m²/g. Interestingly, Cr_^tBu-bdc was found to be significantly more thermally stable with an optimal activation temperature of 448 K (Figure S17). Under these conditions, the polyhedra showed a Langmuir (BET) surface area of 1796 (1135) m²/g. These values are moderately higher than those recently reported for Cr_^tBu-bdc $(1406/1044 \text{ m}^2/\text{g})^{36}$ and represent the highest surface area achieved for metal-organic polyhedra. In fact, the Langmuir surface area is approaching the values of 2420 and 2722 m^2/g reported for M_bdc_dabco (M^{2+} = Co, Zn; dabco = 1,4diazabicyclo[2.2.2]octane), two metal-organic frameworks featuring dabco-pillared metal-organic polyhedra as their building units.^{42,43} Although the surface area of Cr ^tBu-bdc decreased upon heating above 448 K, the material retained significant surface area $(1588 \text{ m}^2/\text{g})$ upon heating to 548 K. Powder X-ray diffraction indicated significant loss of crystallinity of Cr ^tBu-bdc upon desolvation (Figure S10). Pore-size distribution calculated from an N2 isotherm collected at 77 K confirms a material with predominantly 13.7 Å pores (Figure 2). This pore size corresponds to the intrapolyhedron cavity with M–M distance of \sim 17 Å, taking the van der Waals radii of the metal cations into consideration. However, in addition to the pores within individual polyhedra, the solid displayed a significant fraction of pores with approximately 29 Å diameter, similar to those within the aforementioned dabco-pillared materials (Figure S12).

Given the impressive porosity of $Cr_t^{t}Bu$ -bdc, coupled with the potential presence of open metal sites in the material, the solid was tested for the selective uptake of gases. As is the case for most metal—organic framework-type materials, $Cr_t^{t}Bu$ -bdc adsorbs significantly more CO_2 than N_2 at 298 K, with uptakes of 11.2 wt % (2.88 mmol/g) and 0.4 wt % (0.15 mmol/g) at one bar (Figures S19, S20). The water-sensitive nature of the material precludes its use for the separation of CO_2 from flue



Figure 2. Nitrogen adsorption in Cr_^tBu-bdc at 77 K. Closed and open symbols represent adsorption and desorption, respectively. Inset: pore size distribution indicating the intrapolyhedron pore is dominant.

gas mixtures.²¹ However, temperature dependence of CO₂ and N₂ adsorption isotherms can be used to calculate isosteric heats of adsorption to give insights into gas binding mechanisms. Here, the low-coverage CO₂ adsorption enthalpy of -37.9 kJ/ mol is consistent with the enthalpy displayed by analogous paddlewheel-based three-dimensional framework materials with open metal sites.^{44,45} Given its diminished polarizability and quadrupole moment, N₂ was found to have an adsorption enthalpy of just -15 kJ/mol.

To assess the ability of the chromium(II) cations in Cr_^tBubdc to selectively transfer electron density to unsaturated small molecule substrates, we measured the uptake of carbon monoxide. The related rhodium(II)-based material was found to strongly bind carbon monoxide at a capacity of one molecule per paddlewheel unit. Infrared spectroscopy confirmed strong π -back bonding from the $d\pi^*$ orbital of the Rh–Rh bond to CO.³⁵ Here, CO adsorption reaches just 0.36 mmol/g at 298 K and one bar (Figure S21). This value is significantly lower than the value expected if one CO molecule is adsorbed per open metal site (3.67 mmol/g). This observation is consistent with the presence of a strong Cr-Cr quadruple bond in the material resulting in significantly reduced back bonding to carbon monoxide. The isosteric heat of CO adsorption calculated from isotherms collected at 298, 308, and 318 K reveals a binding enthalpy of approximately -18 kJ/mol, consistent with the value displayed by Cu₃(btc)₂.⁴⁶ Carbon monoxide adsorption was too low under ambient conditions to observe a C-O stretch via infrared spectroscopy.

The limited ability of Cr_^tBu-bdc to engage in π -back bonding with unsaturated substrates is further illustrated by ethylene/ethane uptake in the material. This is a particularly challenging separation most effectively performed by metal– organic frameworks featuring high densities of strongly backdonating metal cation sites.¹⁹ Solids completely lacking these sites typically have inverse adsorption selectivities as a result of the slightly higher polarizability of ethane compared to ethylene.⁴⁶ At 298 K, Cr_^tBu-bdc adsorbs only slightly more ethylene than ethane over the entire pressure range measured with one bar uptakes of 3.51 and 3.06 mmol/g (Figures S22, S23) and corresponding adsorption enthalpies of -32.0 and -29.0 kJ/mol, respectively.

The quadruple bonds present in Cr_X-bdc limit the ability of the chromium(II) cations to backbond with unsaturated substrates. However, their redox-active nature makes the materials particularly interesting for the selective adsorption

of O_2 over N_2 based on selective electron transfer.^{47,48} Indeed, at 298 K Cr_'Bu-bdc adsorbs significantly more O_2 than N_2 . Specifically, at one bar the solid adsorbs 5.3 wt % (1.76 mmol/ g) O_2 and just 0.4 wt % (0.15 mmol/g) N_2 . The former value is approaching the value predicted if each paddlewheel binds a single oxygen molecule (1.83 mmol/g). The O_2 isotherm is incredibly steep, reaching a value of 1.64 mmol/g at 0.10 mbar (Figure 3). Infrared spectra of Cr_'Bu-bdc in the presence of



Figure 3. Adsorption of oxygen (red squares) and nitrogen (blue squares) in Cr_tBu-bdc at 298 K. Closed and open symbols represent adsorption and desorption, respectively.

 O_2 show an O–O stretch at 1051 cm⁻¹ that shifts to 993 upon ¹⁸O₂ isotope labeling (Figures S26, S27. This stretching frequency is in line with typical values seen for side-on superoxide complexes.^{49,50} Although previously reported Cr²⁺-based porous frameworks that formed chromium-superoxide adducts upon oxygen binding displayed modest cycling ability,⁴⁷ subsequent O₂ uptake in Cr_^tBu-bdc was greatly diminished. This is likely partially a result of further loss of long-range order/pore collapse as evidenced by the decreased Langmuir surface area of 582 m²/g. Powder X-ray diffraction patterns collected in the presence of oxygen reveal a significant reduction in crystallinity upon O₂ binding (Figure S29), further indicative of loss of long-range order and significant pore blocking upon oxidation.

To find conditions under which O_2 adsorption is reversible, we turned to low-temperature isotherms (Figure 4). At 195 K, the material remains highly selective. Notably, an O_2 saturation



Figure 4. Adsorption of oxygen (red squares) and nitrogen (blue squares) in $Cr_{t}^{t}Bu$ -bdc at 195 K. The low-pressure O_{2} saturation capacity of 3.07 mmol/g corresponds to 0.84 O_{2}/Cr .

capacity of 3.07 mmol/g is achieved by 10 μ bar. This corresponds to the adsorption of 0.84 O₂ molecules per open metal site. This suggests the inability of the material to achieve O₂ adsorption of one molecule per metal site may be a result of inaccessibility of the metal cations on the exterior surface of the polyhedra upon collapse of the structure, as was postulated for the aforementioned Rh_bdc material in the presence of CO,³⁵ rather than an inherent lack of reactivity of the metal cations. Under these conditions, however, a significant loss in surface area was observed after O₂ adsorption at 195 K decreasing from 1818 to 760 m²/g. As a result of this, we were unable to achieve any appreciable O₂ cycling in the material under the reactivation conditions we employed as we consistently observed diminished surface areas upon O₂ adsorption.

The foregoing results detail the synthesis and characterization of two chromium(II)-based metal—organic polyhedra, Cr_OH-bdc and Cr_'Bu-bdc. The latter exhibits a record high surface area for a metal—organic polyhedra-based porous solid. Furthermore, this material displays excellent O_2/N_2 selectivity based on selective electron transfer. Future work will attempt to improve upon the cycling ability of the material through ligandbased functionalization, which is expected to significantly alter the stability of the materials via, for example, ligand-based $\pi - \pi$ interactions. Additionally, efforts are underway to assess the reactivity of the chromium(III)-superoxide adduct.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.7b03361.

Detailed experimental procedures, powder X-ray diffraction data, gas adsorption isotherms, thermal data, and spectroscopic data (PDF)

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Notes

The authors declare no competing financial interest.

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