Highly-Selective and Reversible O2 Binding in Cr3(1,3,5-benzenetricarboxylate)2

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The separation of O2 from air is carried out in industry using cryogenic distillation on a scale of 100 Mtons/year,1 as well as using zeolites in portable devices for medical applications.2 Thus, there is a clear benefit to developing materials that might enable this process to be carried out with a lower energy cost. Recently, the need for such materials has become even more apparent, owing to the potential for using oxyfuel combustion as a means of eliminating CO2 emissions from fossil fuel-fired power plants.3 Here, instead of separating CO2 from N2, as in postcombustion capture, O2 is separated from the N2 in air prior to combustion. Advantages of this scenario include the greater partial pressure of O2 in air (0.21 bar) compared to CO2 in a typical flue gas (0.10−0.15 bar) and the fact that, although pure O2 is needed, it is not necessary to remove 100% of it from the air stream.

In addition, there is the chemical advantage of being able to distinguish O2 from N2 via its greater propensity for accepting negative charge transferred from a redox-active transition metal center. Indeed, this mechanism provided the foundation for a great deal of chemistry involving molecular complexes, particularly of cobalt(II), used for the reversible capture and transport of O2.4 By isolating such transition metal centers within the pores of a zeolite,5 it is further possible to inhibit the formation of O2-brided structures that can diminish the performance of molecular complexes. For example, Cr2+ ions exchanged into zeolite A led to a reversible O2 loading of 2.7 wt % at 298 K.5a We envision that metal−organic frameworks, which can present both high surface areas and open metal coordination sites,6 may form the basis for a new generation of O2 capture materials with good air permeability, a high loading capacity, and a tunable O2 adsorption enthalpy. Herein, we report the synthesis of the first Cr-based metal−organic framework, Cr3(BTC)2 (BTC=1,3,5-benzenetri-carboxylate), which displays both a high O2 loading capacity and strong selectivity for binding O2 over N2 at 298 K.

Analogous to the synthesis of Mo3(BTC)2,7 the reaction of Cr(NO3)3 with trimesic acid in DMF yielded Cr3(BTC)2·nDMF as a purple microcrystalline solid. X-ray powder diffraction data revealed the compound to be isostructural with Cu3(BTC)2·3H2O.8 It thus features the porous three-dimensional framework structure depicted in Figure 1A, wherein Cr3O2C3n(DMF)2 paddle-wheel complexes are linked via triangular BTC3− bridging ligands. The DMF solvent was exchanged with methanol, and the material was desolvated by heating at 160 °C under vacuum for 48 h to afford Cr3(BTC)2 as a yellow-green solid. Once activated, the compound reacts rapidly in air to generate a deep forest green solid.

Rietveld analysis of powder neutron diffraction data collected for Cr3(BTC)2 showed retention of the framework structure, albeit with a shortening of the intermetal separation within the paddle-wheel units. The observed distance of 2.06(2) Å is in line with the formation of a Cr−Cr quadruple bond upon loss of the axial solvent molecules.9 Consistent with this open framework structure, the N2 gas adsorption isotherm measured at 77 K revealed a type I adsorption isotherm with BET and Langmuir surface areas of 1810 and 2040 m2/g, respectively (Figure S1). The latter value is comparable to the Langmuir surface areas of 2175 and 2010 m2/g determined for Cu3(BTC)2·10 and Mo3(BTC)2,7 respectively.

Figure 1. Portions of the structure of Cr3(BTC)2, where green, red, and gray spheres represent Cr, O, and C atoms, respectively, while large red spheres represent either bound DMF molecules in the solvated structure or bound O2 molecules upon desolvation and exposure to O2. Atomic positions shown correspond to the results obtained from Rietveld refinement of powder neutron diffraction data for activated (B) and O2-loaded (A and C) samples. Note that the Cr−Cr distance lengthens from 2.06(2) Å in B to 2.8(1) Å in C upon coordination of O2.

The separation of O2 from 298 K (Figure 2). Indeed, while the N2 adsorption isotherm climbs gradually to a capacity of 0.58 wt % at 1 bar, the O2 isotherm rises sharply, reaching 11 wt % at just 2 mbar. The latter loading corresponds to ~0.8 molecules of O2 per Cr center, near the value of 1 (or 14.4 wt %) expected if every metal in the framework were available to bind an O2 molecule. Based on interpolated uptakes of 0.73 mmol/g O2 at 0.21 bar and 0.033 mmol/g N2 at 0.78 bar (reflecting the corresponding partial pressures in air), Cr3(BTC)2 exhibits an exceptional O2/N2 selectivity factor of 22. To our knowledge, the highest selectivity factor observed previously is ~4 for cobalt(II) complexes appended to a silica support.11 Moreover, both the selectivity and gravimetric capacity are much greater than previously reported for O2 uptake in any metal−organic framework.12

The temperature and evacuation time required to release O2 to regenerate the capture material were tested. Heating at 50 °C under dynamic vacuum for 48 h was optimal and afforded a material that readsobered O2 with a somewhat reduced capacity of 9.1 wt % at 0.21 bar. As shown in the inset of Figure 2, repeated cycling performed on a separate sample under such conditions indicated a gradual reduction...
in the $O_2$ loading capacity. This behavior is likely a consequence of incomplete release of bound $O_2$ under the regeneration conditions and/or partial decomposition of the material as a result of the highly exothermic reaction with $O_2$. Consistently, we observed a 5% loss in surface area of the material after the two cycles (Figure S1), only minor changes to the powder X-ray diffraction patterns upon oxygenation (Figure S3), and an increase in sample weight after the first $O_2$ desorption cycle.

The nature of the interaction between Cr$_3$(BTC)$_2$ and $O_2$ was probed using a variety of spectroscopic techniques. As shown at the right in Figure 3, upon exposure to $O_2$ an infrared absorption band at 1129 cm$^{-1}$ appears and increases in intensity with dosage (Figures 3, S6). We assign this band to a $\nu_{\text{vO}}$ vibrational mode and note that its frequency lies between those previously assigned for a Cr$^{III}$/O$_2$ superoxide species (1027–1104 cm$^{-1}$)$^{13}$ and a putative end-on superoxide moiety bound to a Cr$^{III}$ porphyrin complex (1142 cm$^{-1}$).$^{14}$ Two additional, weaker absorption features are also observed, and we attribute these to an overtone of the 1129 cm$^{-1}$ mode and to a $\nu_{\text{vO}}$ mode arising from a superoxide or peroxide adduct (see Supporting Information). In the UV–vis–nIR spectra, new absorption features at 13 430, 15 840, and 20 600 cm$^{-1}$ are evident in the spectrum (Figure S3), and an increase in sample weight after the first $O_2$ desorption cycle.

We note that although the resolution of the data was insufficient to determine the orientation of $O_2$, the observed metal–center distance is more likely consistent with a side-on coordination mode.

The foregoing results demonstrate the reversible, selective binding of $O_2$ at a high loading capacity within Cr$_3$(BTC)$_2$, a metal–organic framework featuring open Cr$^{III}$ coordination sites. Future work will attempt to improve framework stability and reduce the energy required for deoxygenation by varying the metal or attenuating the donor strength of the bridging ligand through addition of electron-donating/withdrawing substituents.

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Supporting Information Available: Full experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

References


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