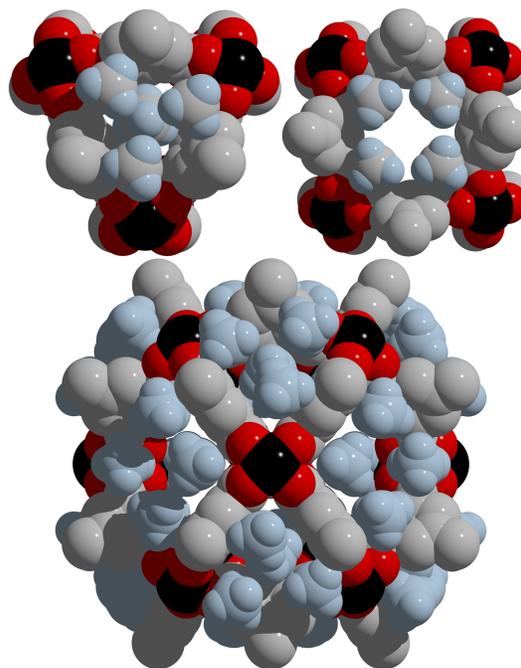


Methane is becoming an increasingly important fuel for a variety of factors. The constantly increasing levels of accessible natural gas reserves, coupled with the mature natural gas infrastructure in the United States, makes it an attractive fuel. Although more than 64 million American homes utilize natural gas for heating, its poor volumetric energy density of just 0.04 MJ/L, compared to 32.4 MJ/L for gasoline, has prevented the widespread use of natural gas in the transportation sector. Adsorbed gas systems offer promise in this regard, contingent on the advent of porous storage materials with sufficient capacity. Porosity in network solids, including zeolites, activated carbons, and metal-organic frameworks, has been widely interrogated for decades. In molecular systems, however, it is a relatively novel phenomenon. This is somewhat surprising given the fact that porous molecules can display surface areas that rival those of metal-organic frameworks. This work has focused on the design, synthesis, and characterization of highly porous coordination cages for small molecule storage. We have recently shown that these materials, which conceptually serve as soluble metal-organic framework analogs, display impressive porosity under specific synthesis and activation conditions. Although these cages are typically amorphous upon activation, a strategy in which pillaring ligands are utilized endow the materials with high crystallinity and thus compatibility with diffraction methods for the identification and optimization of gas binding sites.

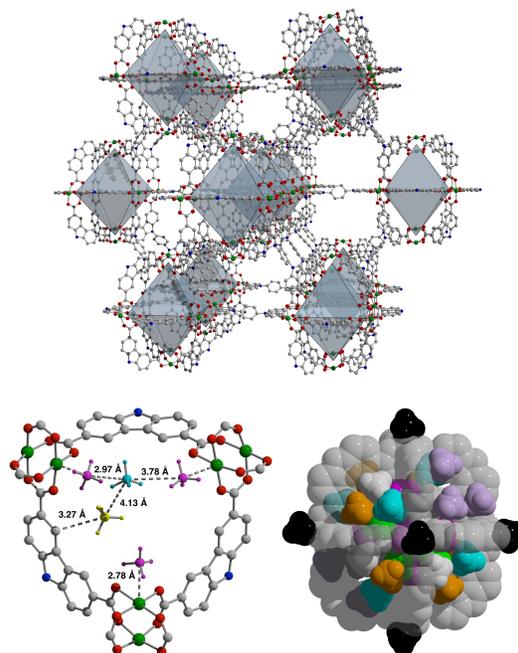
Work on this project has focused on a series of isostructural cuboctahedral, paddlewheel-based coordination cages,  $M_{24}(\text{}^t\text{Bu-bdc})_{24}$  ( $M = \text{Cr, Mo, Ru}$ ;  $\text{}^t\text{Bu-bdc}^{2-} = 5\text{-tert-butylisophthalate}$ ), for high-pressure methane storage. As the decrease in crystallinity upon activation of these porous molecular materials precluded the use of diffraction studies, we turned to a related class of pillared coordination cage-based metal-organic frameworks,  $M_{24}(\text{Me-bdc})_{24}(\text{dabco})_6$  ( $M = \text{Fe, Co}$ ;  $\text{Me-bdc}^{2-} = 5\text{-methylisophthalate}$ ;  $\text{dabco} = 1,4\text{-diazabicyclo}[2.2.2]\text{octane}$ ) for neutron diffraction studies. The five porous materials display BET surface areas from 1,057 – 1,937  $\text{m}^2/\text{g}$  and total methane uptake capacities of up to 143  $\text{cm}^3/\text{cm}^3$ . Both the porous cages and cage-based frameworks have methane adsorption enthalpies of –15 to –22 kJ/mol. Neutron diffraction studies indicate that the triangular windows of the cage are optimal methane adsorption sites with  $\text{CD}_4\text{-arene}$  interactions between 3.7 and 4.1 Å. At both low and high loadings two additional methane adsorption sites on the exterior surface of the cage are apparent for a total of 56 adsorption sites per cage (Figure 1). These results show that  $M_{24}L_{24}$  cages are competent gas storage materials and further adsorption sites may be optimized by judicious ligand functionalization to control extra-cage pore space. Further, by optimizing synthesis, solvent exchange, and activation conditions, surface areas of porous coordination cages can approach those displayed by three-dimensional metal-organic frameworks. This is particularly the case for this family of *tert*-butyl-functionalized cuboctahedral coordination cages. The  $\text{Cr}^{2+}$ ,  $\text{Mo}^{2+}$ , and  $\text{Ru}^{2+/3+}$  analogs of these molecules display high BET surface areas, with  $\text{Mo}_{24}(\text{}^t\text{Bu-bdc})_{24}$  having a porous cage record surface area of 1320  $\text{m}^2/\text{g}$ . Although the methane storage properties of these materials are not remarkable when compared to flexible, or ultra-high surface area metal-organic frameworks, the fact that they are molecular renders them significantly more tunable than their MOF counterparts. Moving forward, this insight will aid in the development of future porous metal-organic materials. In particular, by precisely tuning both the pore size and



**Figure 1.** Methane binding sites in  $M_{24}(\text{Me-bdc})_{24}(\text{dabco})_6$  as determined by powder neutron diffraction. At loadings up to 1.5  $\text{CD}_4/\text{M}^{2+}$ , four binding sites are apparent: the center of the triangular window, corners of the triangular window, corners of the square window, and open metal coordination sites on the interior surface of the cage. Black, red, gray, and blue spheres represent metal cation, oxygen, carbon, and deuterium, respectively.

shape of the cage, in addition to the pore space between cages, adsorbents with true molecular level control are attainable.

Along these lines, we have targeted the synthesis of smaller cage structures in order to avoid the intra-cage pore space that has been shown to be detrimental to total volumetric capacity. For this, a previously reported carboxylate-based family of cages ( $M_{12}cdc$ ) ( $M = Cu, Mo$ ;  $cdc =$  carboxylate) were an intriguing target, although they were previously reported to be nonporous. However, our newly synthesized chromium(II)-based cage,  $Cr_{12}(cdc)_{12}$ , displayed a then coordination cage record B.E.T. (Brunauer–Emmett–Teller) surface area of  $1235 \text{ m}^2/\text{g}$ . By using precise synthesis and activation procedures, the previously reported copper(II) and molybdenum(II) cages similarly displayed high surface areas. The materials exhibit high methane adsorption capacities at 65 bar with the chromium(II) cage displaying total  $CH_4$  capacities of  $194 \text{ cm}^3/\text{g}$  and  $148 \text{ cm}^3/\text{cm}^3$ . Similar to the aforementioned  $M_{24}(\text{Bu-bdc})_{24}$  cages, these  $M_{12}(cdc)_{12}$  materials displayed appreciable losses in crystallinity upon activation that precluded the use of diffraction studies to interrogate gas binding sites. Instead, we turned to an analogous MOF, PCN-81 (Figure 2) as it is based on similar octahedral pores. These studies indicated the octahedral cage displays favorable methane binding at a capacity of up to 49 molecules per cage. Work going forward will focus on strategies to tune inter-cage pore space to more favorably tune adsorption and deliverable capacities of these molecular adsorbents.



**Figure 2.** (Upper) Structure of activated PCN-81. (Lower)  $CD_4$  adsorption in PCN-81 as determined by powder neutron diffraction. (Left) At low loading three sites in the  $Cu_{12}(cdc)_{12}$  portion of the structure are populated. (Right) Up to 4.0  $CD_4/Cu$ , methane exclusively resides in the octahedral cage.

This funding has been invaluable on both the career of the PI and the career of the student that it supported. The preliminary work that it supported has already resulted in a manuscript published in the *Journal of the American Chemical Society*. It is further expected that additional publications will be forthcoming. Additionally, a portion of the work supported by the ACS PRF was used as the basis for a proposal submitted to the Department of Energy, Energy Efficiency and Renewable Energy (DOE EERE), that was recently funded. The first graduate student on this project has done significant work and was rewarded for such with a NASA Delaware Space Grant (DESG) Graduate Fellowship. As a result, another student will be funded for this project and will continue to develop porous molecular materials for gas storage applications.