

Flexible Metal Organic Framework {[Ni(L)][Ni(CN)₄]}_n, (L=Dpbz and Azopyr), with an Unusual Ni-N Bond

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To mitigate global warming as a major result of fossil fuel burning, CO₂ capture and storage (CCS) technology is critical. Effective sorbent materials are needed for carbon capture because coal-fired electrical power plants, the largest emitters of the greenhouse gas, will continue to produce much of our nation's electricity for at least several decades. Within the family of pillared layer metal organic frameworks (MOFs), the Ni-based Hofmann compounds [Ni'(L)Ni(CN)₄]_n (L=pillar ligand), have been shown to be especially diverse. To understand the CO₂ sorption mechanism of these MOFs, and enable the design of more efficient sorbent materials, detailed knowledge of the crystal structure is necessary. Two selected flexible MOFs, [Ni'(L)Ni(CN)₄]_n ((L=1,4-Bis(4-pyridyl)benzene, or Dpbz) and L= 4,4'-azopyridine, or AzoPyr) that show a reversible structural transition between low porosity and high porosity phases during the sorption of CO₂ have been synthesized and analyzed using synchrotron single crystal diffraction, powder X-ray diffraction, and adsorption/desorption isotherm measurements. Both structures consist of an unusual 5-fold pseudo square-pyramid environment for Ni and a significantly long Ni-N distance. DFT calculations have been conducted to understand the charge distribution in these unusual Hoffmann compounds.