SYNTHESIS AND CHARACTERIZATION OF FLEXIBLE PILLARED-LAYER STRUCTURED POROUS COORDINATION POLYMERS AND DETERMINATION OF GAS ADSORPTION-DESORPTION PROPERTIES

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ABSTRACT

Porous coordination pillared-layer structured polymers are a particular category of 3D uniform crystal materials constituted by well-defined two-dimensional layers (specially formed by a combination of metal ion or metal cluster and anionic organic ligands) interconnected by organic molecules used as pillars. A thorough research study has been dedicated to a subset of porous coordination polymers with $Cu_2(pzdc)(L)$ frameworks, which are prepared using copper (Cu^{2+}) and pyrazine-2,3-dixarboxylate (pzdc) as layers and a series of N-donor bi-pyridyl ligands (L) as pillars. An important characteristic associated to this type of material is its designability, namely, a variety of isostructural crystals could be synthesized with a diversity of pore sizes and surface chemical content upon substitution of the pillar ligand. Therefore, this work focuses on the development of two new pillared-layer porous materials using (1) 1,3-bis(4-pyridyl)propane (bpp) and (2) 1,3-bis(imidazol-1-yl)benzene (bix) as organic pillars (L) in an attempt to improve properties related to structural flexibility and thermal stability; and to provide a porous surface that interacts significantly with CO₂, either for its storage/delivery or for its separation from light gas mixtures. These two porous coordination polymers were successfully synthesized, and their crystal structures refined using a combination of high resolution X-ray diffraction (XRD) patterns and Rietveld refinement techniques. Both materials crystallized in a monoclinic $P2_1/c$ space group in which the copper atom coordinates to three pzdc units and a half of the pillar unit with a distorted square-pyramidal geometry. Thermal studies based on thermal gravimetric analysis (TGA) and in situ XRD/differential scanning calorimetry (DSC) showed that the material containing bix has a significantly improved thermal stability, by an average margin of 55 K when compared with other isostructural materials. This is due to the presence of imidazole groups in the pillar in comparison to traditional di-pyridyl-based ligand. Furthermore, determination of N2 and CO2 adsorption isotherms at cryogenic conditions for both materials presented a phenomenon associated to framework expansion in concomitant with the uptake of CO₂. This was also confirmed at 298 K and gas pressures up to 50 atm. Meticulous experiments at ambient temperature and CO₂ pressure up to 7 atm varying the equilibration time interval evidenced that the aforementioned structural expansion had a larger time scale than the adsorption kinetic. On the other hand, although the pillared-layer built with bpp showed a stronger interaction with CO₂, the presence of di-imidazole fractions in bix resulted in an interesting pore surface with higher affinity toward CO₂.

RESUMEN

Los polímeros de coordinación porosa estructurados de capa pilar son una categoría particular de materiales cristalinos uniformes tridimensionales constituidos por capas bidimensionales bien definidas (especialmente formadas por una combinación de ión metálico o grupo metálico y ligandos orgánicos aniónicos) interconectadas por moléculas orgánicas utilizadas como pilares. Se ha dedicado un estudio exhaustivo de investigación a un subconjunto de polímeros de coordinación porosa con estructuras $Cu_2(pzdc)(L)$, que se preparan utilizando cobre (Cu^{2+}) y pirazina-2,3dixarboxilato (pzdc) como capas y una serie ligandos (L) de bipiridil donadores N como pilares. Una característica importante asociada a este tipo de material es su diseñabilidad, es decir, una variedad de cristales isoestructurales se podrían sintetizar con una diversidad de tamaños de poro y contenido químico superficial con la sustitución del pilar. Por lo tanto, este trabajo se centra en el desarrollo de dos nuevos materiales porosos de capa pilar usando (1) 1,3-bis(4-piridil)propano (bpp) y (2) 1,3-bis(imidazol-1-yl)benceno (bix) como pilares orgánicos (L) en un intento de mejorar las propiedades relacionadas con la flexibilidad de la estructura y la estabilidad térmica del material; y además, para proporcionar una superficie porosa que interactúe significativamente con el CO₂, ya sea para aplicaciones relacionadas con su almacenamiento y entrega continua o para su separación de mezclas de gases ligeros. Estos dos polímeros de coordinación porosa se sintetizaron con éxito, y sus estructuras cristalinas se refinaron usando una combinación de patrones de difracción de rayos-X de alta resolución y técnicas de refinamiento mediante el método de Rietveld. Ambos materiales cristalizaron con un grupo espacial monoclínico P2₁/c y en ellos el átomo de cobre se coordinó a tres unidades de pzdc y a la mitad de un pilar con una geometría piramidal cuadrada distorsionada. Los estudios térmicos basados en análisis gravimétrico térmico y difracción de rayos-X in situ / calorimetría diferencial de barrido mostraron que el material que contiene bix tiene una estabilidad térmica significativamente mejorada, por un margen promedio de 55 K en comparación con otros materiales isosestructurales. Esto se debe a la presencia de grupos de imidazol en el pilar en comparación con el ligando los tradicionales basados en dipiridilo. Además, la determinación de isotermas de adsorción de N₂ y CO₂ en condiciones criogénicas para ambos materiales presentó un fenómeno asociado a la expansión de la estructura en concomitancia con la adsorción de CO₂. Esto también se confirmó a 298 K y presiones de gas de hasta 50 atm. Experimentos meticulosos a temperatura ambiente y presiones de CO₂ de hasta 7 atm variando el intervalo de tiempo de equilibrio evidenciaron que la expansión estructural antes

mencionada tenía una escala de tiempo mayor que la asociada a la cinética de adsorción. Por otro lado, aunque el material construido con bpp mostró una interacción fuerte con CO₂, la presencia de fracciones de di-imidazol en bix dió como resultado una superficie de poro interesante con mayor afinidad hacia el CO₂.

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Peer Reviewed Publications

- Rodinson R. Arrieta-Pérez, Samuel D. Marks, Karina Riascos-Rodríguez, Paul G. Evans, Arturo J. Hernández-Maldonado. Development of Semi-empirical CO₂ Adsorption Isotherm Model onto Porous Coordination Cu₂(pzdc)₂(L) [pzdc: pyrazine-2,3-dixarboxylate, L: pillar ligand] Polymers. *In Preparation*, 2018.
- Rodinson R. Arrieta-Pérez, José N. Primera-Pedrozo, Jason Exley, and Arturo J. Hernández-Maldonado. Synthesis and Characterization of a Cu₂(pzdc)₂(bix) [pzdc = 2,3pyrazinedicarboxylate; bix = 1,3-bis(imidazol-1-yl)benzene] Porous Coordination Pillared-Layer Network. Cryst. Growth Des. 2018, 18, 1676-1685.
- Paul J. Meza-Morales, Diego A. Gómez-Gualdrón, <u>Rodinson A. Arrieta-Perez</u>, Arturo J. Hernandez-Maldonado, Randall Q. Snurr, and María C. Curet-Arana. CO₂ Adsorption-Induced Structural Changes in Coordination Polymer Ligands Elucidated via Molecular Simulations and Experiments. *Dalton Trans.* 2016, 45, 17168-17178.
- Arturo J. Hernández-Maldonado, <u>Rodinson R. Arrieta-Pérez</u>, José N. Primera-Pedrozo, and Jason Exley. Structure of a Porous Cu₂(pzdc)₂(bpp) (pzdc: Pyrazine-2,3-dicarboxylate, bpp: 1,3-Bis(4-pyridyl)propane) Coordination Polymer and Flexibility upon Concomitant Hysteretic CO₂ Adsorption. *Crys. Growth Des.* 2015, 15, 4123-4131.

Oral Presentations

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- **Rodinson R. Arrieta-Pérez**, Marietta E. Marcano-González, John Hogan, and Arturo J. Hernández-Maldonado. Synthesis and Characterization of a Cu₂(pzdc)₂(bix) [pzdc = 2,3-pyrazinedicarboxylate; bix = 1,3-bis(imidazol-1-yl)benzene] Pillared-Layer Structure. *UPRM Chemical Engineering Graduate Research Symposium*. PR December **2015**.
- <u>Rodinson R. Arrieta-Pérez</u>, José N. Primera-Pedrozo and Arturo J. Hernández-Maldonado. Synthesis and Characterization of Pillared-Layer Structure Nanoporous Coordinations Polymers for Carbon Dioxide Storage and Continuous Delivery. UPRM Chemical Engineering Graduate Research Symposium. PR - May 2014.

Poster Presentations

- <u>Rodinson R. Arrieta-Pérez</u>, Marietta E. Marcano-González, John Hogan, and Arturo J. Hernández-Maldonado. Synthesis and Characterization of a Cu₂(pzdc)₂(bix) [pzdc = 2,3-pyrazinedicarboxylate; bix = 1,3-bis(imidazol-1-yl)benzene] Pillared-Layer Material for CO₂ Storage. 2017 External Advisory Board Meeting. PR February 2017.
- Rodinson R. Arrieta-Pérez, Marietta E. Marcano-González, John Hogan, and Arturo J. Hernández-Maldonado. Synthesis and Characterization of a Cu₂(pzdc)₂(bix) [pzdc = 2,3-pyrazinedicarboxylate; bix = 1,3-bis(imidazol-1-yl)benzene] Pillared-Layer Material for CO₂ Storage. 2016 External Advisory Board Meeting. PR January 2016.
- Rodinson R. Arrieta-Pérez, Marietta E. Marcano-González, and Arturo J. Hernández-Maldonado. Synthesis and Characterization of a Pillared-Layer Structured CPL-N2-UPRM Material: A Nanoporous Coordination Polymer for CO₂ Storage and Sustained Delivery. *Fostering Collaborations Between UPR and UCF Meeting*. PR - June 2014.

CHAPTER 1

Introduction



1.1. Background and Justification

Metal-organic frameworks (MOFs) or porous coordination polymers (PCPs) are attractive as platforms for applications in areas that include light harvesting, sensors, drug delivery, membranes, water treatment, heterogeneous catalysis, and gas separation and storage.¹⁻¹³ The ubiquitous status is certainly due to the tremendous amount of knowledge that has been gathered during the last two decades on the assembly of these materials. What started with the simple notion of building structures by association of metal centers or clusters with bridging organic linkers to form a one-, two- or three-dimensional coordination structure has now turned into offerings of chemical function versatility paired with tailored framework dimensions and, in many cases, an unprecedented large and permanent porosity. For instance, reports of PCPs with structures made of a metal-organic polymeric layers interconnected by organic pillars have shown that these materials offer potential for scalability to industrial scale due to in part to tunable pore dimensions and functionalities, including those that arise from application of external stimuli.¹⁴⁻¹⁶ Some PCP

structures offer a "manifold" type design, an advantage over classical zeolitic systems, but their chemical and thermal stability are generally lower in comparison owing to relatively weak coordination bonds that connect the metal and ligand molecules.¹ Still, such coordination environment also lends unique performance during processes such as adsorption, storage and delivery, and guest recognition, yet another reflection of unique properties, including size and shape of the pores, and the chemical environment of the pore surface.^{2, 17-19}

These materials include pillared-layer coordination polymers, formed by combination of a thermodynamically stable layer [i.e., Cu(pzdc)] (pzdc: pyrazine-2,3-dicarboxylate) and a choice of a wide range of pyridyl-type pillar ligands and are known as CPL-*n* series materials.^{16, 20-22} Such assembly is simple yet successful in the tailoring of both the size and chemical environment of the framework pores and channels. CPL-n materials were originally developed by Kitagawa and coworkers,²⁴⁻³² and have been recently studied by Hernández-Maldonado et al. to elucidate properties that are relevant to the use of these materials as gas adsorption platforms.^{19, 23, 33-35} Among the ligands that have been employed to tailor the CPL-*n* are pyridine (pyz) for CPL-1, 4,4'-bipyridine (bpy) for CPL-2, 2,7-diazapyrene (dap) for CPL-3, 4,4'-azopyridine (apy) for CPL-4, 1,2-di-(4pyridyl)-ethylene (bpe) for CPL-5, N-(4-pyridyl)-isonicotinamide (pia) for CPL-6 and 1,2-di-(4pyridyl)-glycol (dpyg) for CPL-7. Some of the aforementioned studies have attempted to explain the structural behavior of some of these CPL-*n* variants to external stimuli, motivated by findings from Kitagawa and co-workers about structural changes induced by incorporation of guest molecules such as water and benzene onto Cu₂(pzdc)₂(bpy).³⁶ This material in particular exhibited remarkable contraction or expansion breathing framework behavior called "shape-responsive fitting" transformation at ambient conditions. Hernandez-Maldonado and co-workers have also documented the effect of activation temperature as external stimuli on the structures of some CPL-

n materials. For example, *in situ* high-temperature X-ray powder diffraction (XRD) and ¹³C crosspolarization magic angle spinning nuclear magnetic resonance (CP NMR) spectroscopy were used to elucidate the effect of the activation temperature on the long and local-range changes in the 1D channels of $Cu_2(pzdc)_2(bpy)$.^{33, 34} The results signaled to an apparent local framework distortion as responsible for a drastic reduction in the materials effective surface area within a temperature range of 373 - 423 K. On the other hand, $Cu_2(pzdc)_2(bpy)$ also evidenced a long-range structural changes upon CO₂ uptake at moderate pressure and ambient temperature.³⁵ According to a set of *in situ* XRD adsorption tests, the structural changes are apparently linked to a combination of local changes induced by adsorbate-adsorbent interactions and external forces being exerted onto the crystals.

The ligands employed to synthesize the CPL-*n* series are usually based on a family of 2-connecting N-donor di-pyridyl-based neutral organic molecules and rigid in the sense that rotation is observed only at the pyridine ring or rings of the (*L*) ligand. In addition, differences between these ligands lie in the characteristic functional group that resides between the pyridine rings, also known as a spacer group and that gives unique chemical properties to the moiety and, as a consequence, to the framework. Thus, the structural changes investigated so far in many of the CPL-*n* materials are related to weak coordination bindings that probably take place within the frameworks in the presence of a Jahn-Teller distortion around the Cu²⁺ complex. In order to expand the investigations to include other possible scenarios, we present in this doctoral dissertations the synthesis and meticulous characterization of a CPL-like coordination polymer containing the flexible ligand 1,3-bis(4-pyridyl)propane or bpp and 3-bis(imidazol-1-yl)benzene or bix³⁷⁻³⁹. The former ligand contains -CH₂CH₂CH₂- as a spacer and can exist in *anti-anti, gauche-anti, gauche-gauche* and *gauche-gauche'* conformations upon coordination to give rise to a variety of interpenetrating or

non-interpenetrating coordination network topology.⁴⁰⁻⁴³ The latter is introduced in an attempt to increase both flexibility and thermal stability, due to the presence of imidazole fractions, particularly in light of potential adsorption based applications for these materials.

1.2. Goals and Specific Aims

The main goal of this doctoral dissertation is to develop pillared-layer nanoporous coordination polymers using di-pyridyl and di-imidazol based ligands capable of introducing flexibility and thermal stability in an attempt to develop platforms for superior CO_2 adsorption, storage and sustained delivery at moderate pressure. The followings are the specific objectives:

1.2.1. Objective 1: Synthesis of pillared-layer polymers using 2D copper + pyrazine-2,3-dicarboxylates and the *N*-donor ligands shown below.

Name and Structure	Relevant Characteristics	Thermal Stability
1,3-bis(imidazol-1-yl)benzene: bib	Widely used in non-pyrazine based 2D coordination polymers because of variable coordination positions conformations, and structural diversity. ⁴⁴	2D compounds synthesized using 1,3-bib have shown thermal stabilities at temperatures higher than 630 K. ⁴⁴
1,3-bis(4-pyridyl)propane: bpp	It is a rigid ligand. Its stiffness allows synthesizing pillar-layer structured polymeric structures. The bpp ligand has a flexible trimethyl group and can supply a variety of structural conformations. ⁴⁵	Compounds synthesized using bpp ligands have shown thermal stabilities at temperatures higher than 500 K. ⁴⁵

1.2.2. Objective 2: Obtain the refined molecular structure of the PCPs that will result from the use of the aforementioned *N*-donor pillar ligands. This was accomplished via analysis of high

resolution X-ray diffraction (XRD) data to determine space group and unit cell parameters followed by generation of the fine structure via a Rietveld refinement. The results helped to set a benchmark for structural and textural properties prior to the gas adsorption-desorption tests and, and therefore, allowed the elucidation of local level changes that occur concomitant upon the gas uptake.

1.2.3. Objective 3: Determination of chemical, textural and adsorption properties of the PCPs and development of correlations between these and local and long-range structural changes. Specifically:

- Chemical composition determination via thermal gravimetric analysis (TGA)
- Evaluation of PCP framework thermal stability via *in situ* high temperature XRD combined with TGA and differential scanning calorimetric (DSC) analysis.
- Determination of textural properties including surface area, pore volume and pore size distribution (PSD) of as-synthesized materials by nitrogen and carbon dioxide adsorption at 77 and 194.5 K, respectively. Textural properties were estimated using classical BET modeling as well as more advances methods to correct for adsorption processes involving micropore filling as well as deviations from Henry's law. PSD was determined using a corrected Horvath-Kawazoe method.

1.2.4. Objective 4: Adsorption-desorption performance tests

 Measurement and evaluation of CO₂, CH₄ and N₂ pure component adsorption-desorption isotherms at different temperatures and different PCP pre-activation temperatures. The tests were also focused on the effect of employing different equilibration time intervals since it is well known that some PCPs display slow structural transformations upon the concomitant adsorption of certain gases. The isotherm data allowed the determination of isosteric heats of adsorption profiles; these were employed to elucidate the level of interactions between the adsorbate and the PCP, and characterization of the level of surface heterogeneity.

• Develop a thermodynamically sound adsorption isotherms model that incorporates dependency on structural dynamic of the structure porous materials.

1.3. Overview of the Dissertation

Chapter 1 of this doctoral dissertation presents a brief background and justification of the present research and also, the general and specific goals. Chapter 2 shows details of the synthesis and characterization of a CPL-like coordination polymer containing the flexible ligand 1,3-bis(4-pyridyl)propane (*bpp*), namely Cu₂(pzdc)₂(bpp). The Cu₂(pzdc)₂(bpp) long-range manifold-like structure was verified via Rietveld refinement and the material was thoroughly characterized via *in situ* XRD, thermal gravimetric analysis (TGA), and porosimetry, as well as via CO₂ adsorption. Furthermore, the chapter 2 shows results that evidence the effect of adsorption equilibrium time intervals onto the uptake capacity of the material and probably as a direct reflection of concomitant structural changes. Finally, in attempt to elucidate the adsorption capacity and selectivity toward CO₂, adsorption equilibrium isotherms CH₄ and N₂ were also gathered.

Chapter 3 presents details of the synthesis and characterization of a $Cu_2(pzdc)_2(L)$ based on the diimidazole-based ligand L = 1,3-bis(imidazol-1-yl)benzene or bix in an attempt to increase both flexibility and thermal stability of the structure, particularly in light of potential CO₂-based applications for these materials. The material was characterized via thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), *in situ* high-temperature XRD, and N₂ and CO₂ adsorption at cryogenic temperatures. The Chapter 3 also present results of CO₂ adsorption isotherms at ambient temperature, moderate/high gas pressures, and at different equilibration time intervals (t_e), which allowed probing the structural dynamics of the framework material upon interactions with the adsorbate. The adsorption selectivity capabilities of Cu₂(pzdc)₂(bix) were estimated via isosteric heats of adsorption and adsorption of single component CH₄ and N₂ also at ambient temperature.

In Chapter 4, the development of a semi-empirical isotherm adsorption mathematical model to is detailed predict CO₂ uptake amounts in Cu_x(pzdc)_y(*L*) like MOFs. *In situ* CO₂ adsorption and synchrotron X-ray powder diffraction data were employed to observe unit cell expansion and elucidate a model to predict how the effective pore volume changes as a function of gas pressure. This model was then incorporated into a Dubinin isotherm model and tested for prediction of CO2 uptake onto Cu₂(pzdc)₂(bpy), Cu₂(pzdc)₂(bpe) and Cu₂(pzdc)₂(bix).

The final remarks including contributions of the dissertation and recommendations for future work are presented in Chapter 5.

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CHAPTER 2

Structure of a Porous Cu₂(pzdc)₂(bpp) (pzdc: pyrazine-2,3dicarboxylate; bpp: 1,3-bis(4-pyridyl)propane) Coordination Polymer and Flexibility Upon Concomitant Hysteretic CO₂ Adsorption.



2.1. Introduction

A porous coordination polymer was prepared using pyrazine-2,3-dicarboxylate (pzdc) and a dipyridyl ligand that contains -CH₂CH₂CH₂- as a spacer, namely 1,3-bis(4-pyridyl)propane (bpp). This spacer group can exist in *anti-anti*, *gauche-anti*, *gauche-gauche* and *gauche-gauche'* conformations upon coordination to give rise to a variety of interpenetrating or non-interpenetrating coordination network topology.¹⁻³ It is known that the ligands employed to synthesize the CPL-*n* series are usually rigid in the sense that rotation is observed only at the pyridine ring or rings of the *N*-donor ligand.^{4, 5-18} Thus, the structural changes investigated so far in many of the CPL-*n* materials are related to weak coordination bindings that probably take place

within the frameworks in the presence of a Jahn-Teller distortion around the Cu²⁺ complex. Therefore, the main objective of this chapter is the synthesis and characterization of a CPL-like coordination polymer containing the aforementioned flexible spacer ligand, namely Cu₂(pzdc)₂(bpp). This long-range manifold-like structure^{19-21, 5} was verified via Rietveld refinement and the material was thoroughly characterized via *in situ* XRD, thermal gravimetric analysis (TGA), scanning electron microscopy (SEM), and porosimetry, as well as via CO₂ adsorption in an attempt to elucidate structural flexibility in the absence of a gate opening pressure phenomenon. Additionally, in an attempt to determine the adsorption capacity and selectivity toward CO₂, adsorption equilibrium isotherms CH₄ and N₂ were also gathered.

The periodic framework (monoclinic, $P2_1/c$, a = 13.300(3), b = 13.112(7), c = 10.808(5) Å, $\beta = 101.28(4)$) composition was Cu₂(pzdc)₂(bpp))•4H₂O, with an overall structural arrangement similar to those present in other 2D copper + pzdc based coordination polymers, but showcasing a heavily distorted, parallelogram shaped gallery along c. The structure also appeared stable up to 510 K based on TGA and *in situ* high temperature XRD and the complete elimination of water took place at 373 K. Upon activation, the material effective surface area and pore volume were much smaller than those of other Cu₂(pzdc)₂ structures, probably because of the constricted void space. Still, a corrected Horvath-Kawazoe method points to a 4.2 Å average pore size. Uptake of CO₂ at 194.5 K revealed a hysteretic adsorption-desorption phenomenon, probably due to a concomitant pore width expansion process that is analogous to the one reported for Cu₂(pzdc)₂(bpy) (bpy: 4,4'-bipyridine). The phenomenon is amplified at 298 K, and remains at pressures up to 50 atm of CO₂. Furthermore, it appears that the dynamics of structural changes are slower than those of the adsorption process; equilibrium seems to take place at equilibration time interval of at least 120 s. In contrast with isostructural Cu₂(pzdc)₂(dpyg) (dpyg: 1,2-di-(4-pyridyl)-

glycol),⁶⁻¹⁰ Cu₂(pzdc)₂(bpp) appears to have stronger interaction with CO₂ as evidenced by the isosteric heats of adsorption profiles and probably due to the flexibility introduced by the bpp ligand.

2.2. Experimental Section

2.2.1. Materials

Reagents employed for the synthesis of $Cu_2(pzdc)_2(bpp)$ were 2,3-pyrazinedicarboxylic acid (H₂*pzdc*, 97% purity), copper(II) perchlorate hexahydrate (Cu(ClO₄)·6H₂O, 98% purity) and 1,3bis(4-pyridyl)propane (*bpp*, 98% purity). All three were obtained from Sigma-Aldrich and used as received. Ethanol and methanol were used during synthesis and for sample washing upon recovery, respectively. Ultra-high purity grade CO₂, N₂ and CH₄ gases (Praxair, Inc.) were employed during the measurements of adsorption data. High purity grade He gas (Praxair, Inc.) was used as a carrier gas during thermogravimetric analysis and *in situ* high temperature XRD tests. These gases were pre-treated with zeolite and hydrocarbon traps beds upstream to remove any traces of impurities and humidity.

2.2.2. Synthesis of Cu₂(pzdc)₂(bpp)

 $Cu_2(pzdc)_2(bpp)$ was synthesized at ambient pressure and temperature adapting procedures previously reported for other CPL-n materials^{6, 16-18}. One mmol of H₂*pzdc* (0.1681 g) and 0.5 mmol of *bpp* (0.09913 g) were dissolved in a solution containing 1:1 NaOH 0.04M and ethanol. The resulting homogeneous mixture was dropwise added to a solution containing 1 mmol of $Cu(ClO_4)$ ·6H₂O (0.37 g). The final solution was stirred for 24 h and the precipitate vacuum filtered and washed with equal amounts of methanol and distilled/deionized water. The solid obtained was dried overnight at 363 K to remove excess solvents.

2.2.3. Thermal Gravimetric Analysis (TGA)

Thermogravimetric analysis was carried out using a TA-Q500 unit. A sample of $Cu_2(pzdc)_2(bpp)$ (~10 mg) was placed onto a platinum holder suspended from the instrument weight balance and heated from ambient to 1,173 K at 10 K min⁻¹ under a constant helium flow rate of 60 mL min⁻¹. This analysis was conducted to investigate the thermal behavior of the sample, to determine its thermal decomposition temperature and identify the degassing temperature for the adsorption analyses.

2.2.4. Powder X-ray Diffraction (XRD) Patterns and Refinement

XRD patterns were gathered using a Rigaku ULTIMA III X-ray diffraction unit. The diffractometer is equipped with cross beam optics and a CuK_a target operating at 40 kV and 44 mA. A high-resolution diffraction pattern was collected for as-synthesized Cu₂(pzdc)₂(bpp) at a scanning speed of 0.04° min⁻¹ and a step size of 0.005° in the 2 - 60° 2 θ range. The unit cell parameters were determined by indexing the collected X-ray data using CRYSFIRE program and the DICVOL91 indexing routine.²² Afterwards, a set of refined unit cell parameters were obtained using a structure-less Le Bail fitting method.²³ A isostructural model based on Cu₂(pzdc)₂(dpyg) was employed as a starting point for the structural determination of Cu₂(pzdc)₂(bpp).¹⁰ The model was then refined via the Rietveld method using the using GSAS routine and the EXPGUI graphical interface^{24, 25} with a pseudo-Voigt peak profile and a background function of 18-term shifted Chebyshev polynomials. Soft constraints with high weight factor for bond and angles were applied through the refinement process, while the unit cell parameters were refined only in the last stages. Hydrogen atoms were added to the refined structure and their parameters were not refined. The refined crystal structure was visualized with VESTA.²⁶

2.2.5. In Situ High-Temperature Powder X-ray Diffraction (XRD) Patterns

In situ high-temperature XRD measurements were obtained using a Rigaku ReactorX attachment fitted with a continuous beryllium window. This allows for complete enclosure and heating of the sample under an inert atmosphere and still permits the passages of X-ray. Upon calibration of the ULTIMA III goniometer in a Bragg-Brentano focusing mode, the ReactorX module was attached to the system. Diffraction analyses were performed using a helium flow of 60 mL min⁻¹ for a constant 2θ diffraction angle range, voltage, current, and step size. Powders were loaded onto a thin black quartz sample plate and heated from 303 K to 903 K by means of infrared heating and using a temperature ramp of 1 K min⁻¹. The diffraction scanning speed was raised to 3.5° min⁻¹ to avoid large temperature differences between the starting and ending points of each diffraction pattern. Temperature differences were no greater of 15 K.

2.2.6. Textural Properties

Low-pressure equilibrium adsorption data were acquired using a Micromeritics ASAP 2020 volumetric adsorption unit fitted with turbo molecular drag pumps. Activation of the sample was carried out prior to each adsorption test using the ASAP 2020 thermal vacuum-degassing module. A sample was loaded (~100 mg) into a quartz-made tube fitted with isolation valve. The sample was evacuated at a rate of 50 mmHg s⁻¹ to reach a degassing pressure of ca. 20 µmHg, and heated at a rate of 10 K min⁻¹ *in situ* to 373 K (activation temperature) and soaked at that temperature for 10 h. Upon completion of the degassing stage, the sample was allowed to cool to ambient temperature under vacuum. The sample was then backfilled with helium to allow its transfer to the analysis port under isolation. Prior to the adsorption test, the sample was evacuated using high vacuum provided by the turbo molecular drag pump to remove the inert gas.

Textural properties were estimated by means of nitrogen and carbon dioxide equilibrium adsorption data gathered at 77 and 194.5 K, respectively. Surface area was estimated using a BET isotherm model while the average pore size was calculated from a pore size distribution (PSD) generated using the Horvath-Kawazoe method with the Cheng-Yang correction (HK-CY) and assuming a slit-shaped pore.²⁷⁻²⁹ The sample pore volume was estimated by assuming that the adsorbed phase behaved similar to that of a liquid (*i.e.*, molecules tightly packed) and applying the Modified Dubinin-Astakhov (MDA) isotherm model.^{30, 31} The model is given by the following expression:

$$q = q_0 \left[\beta_1 \exp\left[-\left(C \ln\left(P_o / P\right)\right)^n \right] + \beta_2 KP \right]$$
$$\beta_1 = 1 - \exp\left(-\alpha \frac{P}{P_o}\right)$$
$$\beta_2 = \exp\left(-\alpha \frac{P}{P_o}\right)$$
$$C = \frac{RT}{\beta E}$$
$$K = \frac{q_1}{P_o}$$

where q is the equilibrium adsorption loading amount, q_0 is the adsorption loading amount at saturation (complete pore filling), R is the universal gas constant, β is the affinity coefficient of the adsorbate, E is the characteristic energy of adsorption, P/P_o is the relative pressure, n is the heterogeneity coefficient, α is a fitting parameter and K is Henry's law constant.

2.2.7. Equilibrium Gas Adsorption Measurements

Pure single component gas equilibrium adsorption and desorption isotherms were obtained at pressures up to 7 atm using a Micromeritics ASAP 2050 extended pressure volumetric adsorption instrument. The adsorption equilibration time intervals (t_e) were varied to check for the apparent equilibrium state and corroborated by a near-zero slope condition present in at least eleven
consequent pressure transient points (e.g., for $t_e = 100$ s, a total of 1100 s worth of data per section per pressure step). The intervals tested were 15, 60 and 120 seconds. The adsorbent sample activation was carried out similarly to the procedure employed in ASAP 2020 unit. As will be discussed later, the desorption isotherms gathered at each t_e where fitted with the MDA model. In addition, high-pressure CO₂ adsorption isotherms were measured using the Particulate Systems HPVA-II 100 at Micromeritics Instrument Corporation (Georgia, US), a static volumetric system, connected to a high vacuum source. Between 250-450 mg of each material was used for these tests. Samples were heated to 373 K under vacuum for a minimum of four hours preceding analyses. Prior to each analysis on the HPVA-II 100 system a blank run was carried out with the same analysis gas, temperature, and pressure steps as the sample experiment. Blank run data were extracted from the sample analysis data to correct for small errors resulting from the increasing density of CO₂ at elevated pressures. A wait time of at least 10 minutes was implemented after equilibrium at each adsorption/desorption pressure step before continuing the experiment. This equilibration time was the maximum allowable due to instrument usage logistics. Sample temperature was maintained at 298 K using a recirculating water bath.

2.2.8. Isosteric Heat of Adsorption

Carbon dioxide isosteric heat of adsorption ΔH_{ads} was estimated using equilibrium adsorption data at different temperatures (273 - 323 K) and evaluated at constant surface loading. The calculations were made using the classic Clausius-Clapeyron equation.

2.3. Results and Discussion

2.3.1. Crystal Structure Determination and Thermal Stability

Cu₂(pzdc)₂(bpp) was prepared using a flexible and neutral ligand *bpp* that can acquire different structural conformations.^{1, 2, 26} Figure 2.1. shows the XRD pattern of the as-synthesized material,

evidencing a highly crystalline phase. The first three peaks $(6.47^{\circ}, 10.41^{\circ} \text{ and } 13.01^{\circ})$ are characteristic of pillared-layer structures of the CPL-*n* type.^{6, 16, 17, 32} A single-phase Rietveld refinement of the XRD data was employed to further confirm the material manifold-like structure (see Figure 2.1.).



Figure 2.1. Observed and calculated powder X-ray diffraction patterns for Cu₂(pzdc)₂(bpp). The observed data are shown with markers points with the position of the Bragg reflections and difference between calculated and observed intensities shown below.

Cu₂(pzdc)₂(bpp) crystallizes in a monoclinic P2₁/c (no. 14) space group, with a structure consisting of a 3D porous coordination polymer composed by one copper cation coordinated to a half nitrogen *bpp* donor molecule, one *pzdc* dianion, and two guest water molecules located within the asymmetric unit (see Figure 2.2.A). The Cu₂(pzdc)₂(bpp) framework also contains 2D [Cu(*pzdc*)]_n sheets in the *bc* plane connected by *bpp* bis-monodentated pillar ligands. The latter are spaced ca. 9.101 Å along [010] to form a pillared-layer structure with 1D channels along (Figure 2.2.A). Cu(1) has a distorted squared-pyramidal geometry constituted by linkage of the metal to three *pzdc* units and one *bpp* pillar ligand (Figure 2.2.A). Cu(1) is also coordinated to nitrogen N(1) and oxygen (O(1)) from a *pzdc* ligand, two oxygen atoms (O(3) and O(3')) from the carboxylate groups in the *pzdc* units and nitrogen (N(3)) from the *bpp* pillar ligand. The Cu•••O and Cu•••N bond lengths are ca. 2.15 and 2.0 Å, respectively. The unit cell and refinement parameters are presented in Table 2.1. For a full list of atomic parameters, interatomic distances and angles please refer to the Appendix A.

Figure 2.2.B shows the anticipated extension of pzdc layers parallel to the bc plane as well as the bpp pillars aligned in single-file fashion along c. Plane (100) (Figure 1) corresponds to the distance between the pzdc layers, characteristic of the polymeric character of the material and directly related to one of the pore gallery dimensions. Meanwhile, (110) intersects both the layers pillars, passing through the pores channels of the material. In other words, the changes in the pore gallery dimension could be reflected by changes in distances associated to these two planes.



Figure 2.2. (A) Copper coordination environment in $Cu_2(pzdc)_2(bpp)$ and (B) structural views along [001] and [010], respectively. Hydrogen atoms and water molecules were omitted for clarity. A half occupancy in the C(13) atom is denoted by a partially color filled sphere.

Information about the chemical composition and thermal stability of $Cu_2(pzdc)_2(bpp)$ was verified by means of TGA and *in situ* high-temperature XRD (Figure 2.3.). From the data it seems apparent that the material has an effective thermal stability of ca. 510 K. Furthermore, the elimination or decomposition sequence shown by the TGA weight loss profile matched very well with those observed in other CPL's^{6, 16, 33} The first weight loss (300 - 350 K) corresponds to the release of water molecules that were physisorbed within the structure galleries; this amounts to ca. 10 wt.%. Assuming that the structural decomposition proceeds in a similar fashion to that of $Cu_2(pzdc)_2(bpy)$, then the second weight loss step observed in Figure 2.3.A (ca. 510 K) corresponds to the decomposition of the pyrazine groups and probably some of the *bpp* ligands (a total of ca. 47.32 wt.%). It should be noted that decomposition of the $Cu_2(pzdc)_2(bpy)$ structure was verified by means TGA/time-evolved FTIR tests.¹⁶ The third TGA weight loss shown in Figure 3A (ca. 22.98 wt.%) corresponds to the organic portion of the $Cu_2(pzdc)_2(bpp)$ corresponds to copper (ca. 19.70 wt.%). Completion of a mass balance analysis confirmed a structural chemical stoichiometry similar to that of other CPL-*n* materials. A mass composition calculation based on the crystal structure yields the following distribution (in wt. %): H₂O 9.87, *pzdc* 45.53, *bpp* 27.18, and Cu 17.4; this matches well with the TGA mass balances.

Data collection		Phase	
X-ray source	CuKα	Formula	$C_{25}H_{18}Cu_2N_6O_{12}$
Wavelength (Å)	1.5418	Molecular Weight (g mol ⁻¹)	721.55
Step (°)	0.005	ρ (g cm ⁻³)	1.296
2θ range (°)	2 - 50	<i>T</i> (K)	298
Unit cell		Refinement	
Crystal system	Monoclinic	R_p	0.111
Space group	$P2_{1}/c$	wR_p	0.150
<i>a</i> (Å)	13.300 (3)	Rexp	0.012
b (Å)	13.112(7)	$R(F^2)$	0.262
<i>c</i> (Å)	10.808(5)		
β (°)	101.28(4)		
Volume (Å ³)	1848.5(9)		
Ζ	2		

Table 2.1. Data collection, crystallographic data and refinement parameters for Cu₂(pzdc)₂(bpp).

In situ high-temperature XRD data (Figure 2.3.B) presented long-range changes upon the application of an external thermal stimulus and observed mainly in (100). Upon the release of physisorbed water (300-350 K range), the peak related to this plane shifts to larger diffraction angles (*i.e.*, decrease in *d*-spacing), corresponding to a reduction in the pore gallery dimensions of ca. 0.6 Å. This is a common occurrence in many porous materials, even zeolites, and known as structural breathing upon desorption of guest molecules. However, it is important to highlight that such behavior in $Cu_2(pzdc)_2(bpp)$ also leads to an irreversible trend since the diffraction peak in discussion did not return to its original position, even at temperatures above 350 K. This contrasts considerably with the thermal related structural changes observed in other CPL-*n* like materials, where the peak corresponding to (100) displays reversible expansion/contraction paths upon the release of physisorbed water.^{6, 16} The difference in behavior is plausibly associated to the presence of a -CH₂CH₂CH₂- spacer as part of the ligand employed for Cu₂(pzdc)₂(bpp), leading to a shorter *N-N* distance upon an increase in temperature.^{34, 35}



Figure 2.3. (A) Thermal gravimetric analysis profile and (B) *in situ* high temperature diffraction patterns gathered for as-synthesized $Cu_2(pzdc)_2(bpp)$. Both tests were performed using a dry helium atmosphere and heating rates of 10 and 1 K min⁻¹, respectively.

In the case of the diffraction peak corresponding to (110) (Figure 2.3.B), the changes observed during the *in situ* tests were not prominent, suggesting that most of the structural changes experienced by the structure during the elimination of water could be visualized as small distortion of the gallery cross-section. At temperatures above 510 K the Cu₂(pzdc)₂(bpp) structure collapses (XRD data not shown here), in agreement with what was inferred by the TGA data. In general, the TGA and XRD data suggest that a temperature of 373 K suffices to effectively activate the material for adsorption measurements.

2.3.2. Textural Properties

Figure 2.4.A shows nitrogen equilibrium adsorption and desorption isotherms gathered at 77 K after thermal activation of the material in vacuum 373 K. From these data, the BET surface area and pore volume are around 40 m² g⁻¹ and 0.010 cm³ g⁻¹, respectively, values much smaller than those observed on other PCPs such as Cu₂(pzdc)₂(bpy), but in line with what has been reported for the isostructural PCP $Cu_2(pzdc)_2(dpyg)$ or even Cu(pyrdc)(bpp) ([pyrdc = pyridine-2,3dicarboxylate).^{10, 36} Cu₂(pzdc)₂(dpyg) showcases a surface area of ca. 37 m² g⁻¹ only upon a gate opening pressure like phenomenon takes place during the adsorption of methanol.¹⁰ An average pore size of 4.2 Å in Cu₂(pzdc)₂(bpp) was estimated using a PSD profile (Figure 4B) that was generated using the HK-CY method.²⁷⁻²⁹ Interestingly, the average pore size differs considerably from the gallery dimensions as measured from the crystal model structure (4.45 x 6.78 Å), probably due to a structural contraction upon the removal of water. In perspective, Cu₂(pzdc)₂(bpy) has a pore gallery dimension of 5.6 x 7.2 Å and, upon activation at 373 K, a surface area and pore volume of 633 m² g⁻¹ and 0.165 cm³ g⁻¹.^{16, 32} The results obtained for Cu₂(pzdc)₂(bpp) therefore suggests that access of N₂ molecules (kinetic diameter, $\sigma_{N2} = 3.65$ Å) to the apohost structure is severely limited, likely due to a distorted pore channel as suggested by the *in situ* high temperature XRD data (Figure 3). To further validate this, we tested for the adsorption of a slightly smaller probe adsorbate, namely CO₂ ($\sigma_{N2} = 3.2$ Å).

Figure 2.4.A also shows CO₂ equilibrium adsorption-desorption data gathered at 194.5 K. Interestingly, the adsorption data follow a Type I isotherm (according to International Union of Pure and Applied Chemistry classification), as opposed to that exhibited by N₂ that resemble a Type II isotherm. The former is typical of a microporous and, at first glance, suggests that CO₂ is able to access the voids in better fashion due to its smaller kinetic diameter. However, a BET analysis based on the CO₂ uptake yields a surface area value of ca. 48 m² g⁻¹, which is just slightly larger than the one reported above for N₂ as a probe molecule. If a BET analysis is performed on the CO₂ desorption leg of the data shown in Figure 4A, the surface area increases to ca. 60 m² g⁻¹. Meanwhile, a fit with the MDA model yields a pore volume of ca. 0.020 cm³ g⁻¹, suggesting a structural expansion. This should not be considered far fetching since there is direct evidence of structural expansion in Cu₂(pzdc)₂(bpy) and Cu₂(pzdc)₂(dpyg) upon adsorption-desorption of CO₂ at ambient conditions.^{10, 18}

Interestingly, the CO₂ adsorption-desorption data shown in Figure 2.4.A lack the gate opening pressure step seen in Cu(pyrdc)(bpp) upon adsorption of CO₂ also at the same conditions,³⁶ which points to a unique synergistic behavior between pzdc and bpp during the gas uptake. Kitagawa and co-workers have ascribed structural changes in Cu₂(pzdc)₂(bpy) in the absence of a gate opening upon adsorption of vapors to a cleavage of Cu-O bonds in the Cu geometry followed by rotation of the carboxyl groups,³² which may also explain the hysteretic CO₂ adsorption shown in Figure 2.4.A.



Figure 2.4. (A) N_2 and CO_2 adsorption isotherms gathered for $Cu_2(pzdc)_2(bpp)$ at 77 and 194.5 K, respectively. (B) Pore size distribution profile of $Cu_2(pzdc)_2(bpp)$ estimated from the N_2 adsorption data.

2.3.3. Hysteretic Carbon Dioxide Adsorption at High Pressure and Ambient Temperature

Several CPL-*n* type materials exhibit hysteretic gas or vapor adsorption-desorption paths at ambient conditions.^{6, 10} In the case of $Cu_2(pzdc)_2(bpy)$ (i.e., CPL-2), the hysteretic CO₂ adsorption is linked to a structural expansion that onsets right after the pore volume is filled to capacity by the adsorbate while in the relaxed state.¹⁸ The observation was made possible via a meticulous *in situ* diffraction study.

Among CPL-*n* materials, so far Cu₂(pzdc)₂(dpyg) (i.e., CPL-7) has displayed the most prominent

CO₂ hysteretic adsorption-desorption at ambient temperature and moderate pressures (up to ca. 9

atm) and, remarkably, the adsorption leg corresponded to a Type III isotherm (i.e., concave downwards).⁶ Since CPL-*n* materials exhibit a manifold-like structure based on polymeric Cupyrazine-2,3-dicarboxylate layers linked to one another through *N*-donor ligands, it is plausible to assume that all will exhibit analogous structural changes that arise upon hysteretic adsorption paths, at least when adsorbing CO_2 .

In the case of $Cu_2(pzdc)_2(bpp)$, CO_2 does adsorb and desorb in a hysteretic fashion at ambient temperature, even when employing a gas pressure near the 50 atm mark (see Figure 2.5.). Adsorbate capillary condensation is in the vicinity at such conditions, perhaps evident by the shape of the adsorption isotherm. The appearance of a nearly pressure independent hysteresis gap upon desorption suggests that the structure of $Cu_2(pzdc)_2(bpp)$ has expanded considerably. It is important to mention at this point of the discussion that our group has previously found that achieving structural expansion or contraction equilibrium in $Cu_2(pzdc)_2(bpy)$ (i.e., CPL-2) upon adsorption of CO_2 involves time intervals that are much shorter than the characteristic adsorbate diffusion time, meaning that the equilibrium adsorption amounts will increase upon an increase in equilibrium time interval (i.e., t_e).¹⁸ Due to instrument usage logistics, the results shown in Figure 5 were gathered upon waiting a maximum of 10 min between each uptake datum. However, CO_2 adsorption data at moderate pressures for $Cu_2(pzdc)_2(bpp)$ were gathered at different t_e values and the results are shown in Figure 2.6.



Figure 2.5. High pressure CO₂ adsorption (filled symbols) and desorption (empty symbols) isotherms gathered for Cu₂(pzdc)₂(bpp) at 298 K. Maximum time elapsed each pressure increment was 10 min.

An increase in t_e does result in a significant increase in adsorption amounts. CO₂ uptake at $t_e = 120$ s and 7 atm is significant larger than the one exhibited by the material at 45-50 atm (Figure 2.5). The total amount of time necessary to determine the first apparent equilibrium datum at $t_e = 120$ s was nearly 90 min. In an attempt to indirectly quantify the expansion of the Cu₂(pzdc)₂(bpp) structure at different t_e and, therefore, present evidence of the slow dynamics that may govern such changes, the isotherm data were fitted against the MDA isotherm model. This is an appropriate approach since the model was originally developed for prediction of adsorption onto micropores (i.e., pore volume filling instead of monolayer formation). The MDA model also covers Henry's law region as well as high-pressure adsorption. Furthermore, the model characteristic energy of adsorption (*E*) is known to be inversely proportional to the pore width, particularly in slit shaped pores.³⁷



Figure 2.6. CO₂ adsorption (filled symbols) and desorption (empty symbols) isotherms gathered for Cu₂(pzdc)₂(bpp) at 298 K and different equilibration time intervals.

Table 2.2. collects the MDA isotherm parameters obtained from fitting the desorption legs of the data shown in Figure 6. Upon inspection of the MDA isotherm parameter *C* it is evident that the characteristic energy of adsorption *E* decreases as t_e increases or, therefore, that the pore width increases as t_e increases. The pore volume values shown in Table 2.2. were estimated using the adsorption amount at saturation q_0 (complete pore filling) and using the classical assumption that the adsorbed phase resembles that of a liquid. It should be noted that the heterogeneity parameter *n* also increases as t_e increases, meaning that the adsorption effective surface is less heterogeneous. A hypothesis to explain this could be based on the interaction between the CO₂ permanent quadrupole moment and the electric field generated by the copper centers nodes present in the Cu₂(pzdc)₂(bpp) structure. Since the apohost Cu₂(pzdc)₂(bpp) exhibits a distorted pore gallery, projection and interaction with the metal electric field could be sterically hindered. Concomitant pore expansion upon adsorption could eliminate this problem, allowing for better adsorbate-

adsorbent interactions. This might explain why the Henry's law constant values increased at longer t_e (Table 2.2.), which were calculated based on the desorption legs. These specific interactions have been identified via DFT studies involving CO₂ adsorption and Cu₂(pzdc)₂(bpy).⁵

Table 2.2. MDA model parameters and pore volume data obtained from CO₂ desorption at 298 K.

Equilibration Time Interval (s)	Modified Dubinin-Astakhov (MDA) Parameters						
	qo (mmol g ⁻¹)	С (-)	<i>K</i> (mmol g ⁻¹ atm ⁻¹)	α (-)	n (-)	Std. Deviation *	<i>V</i> _{mp} (cm ³ g ⁻¹)
15	1.898	0.188	101.410	6498.976	1.723	± 0.001	0.054
60	2.840	0.193	125.235	4051.304	1.756	± 0.007	0.109
120	4.340	0.252	111.074	5374.623	1.183	± 0.008	0.166

^a Standard deviation calculated based on residuals between the observed and calculated equilibrium loading amounts for the complete pressure range.

2.3.4. Isosteric Heat of Adsorption and Single Component Adsorption Selectivity

A comparison between CO₂ adsorption isotherms gathered for isostructural Cu₂(pzdc)₂(bpp) and Cu₂(pzdc)₂(dpyg) at low pressure (Figure 2.7.A) suggests that adsorbate-adsorbent interactions are prominent in the former, even when relatively low adsorption capacities were observed for both cases. Profiles for isosteric CO₂ heat of adsorption (Figure 2.7.B) clearly show that the adsorbate-adsorbent interactions are stronger in Cu₂(pzdc)₂(bpp), but still within the range of physical adsorption (<40 kJ mol⁻¹). Exposed hydroxyl pendant-like groups of the *dpyg* pillars should facilitate electron donor-acceptor and even dipolar interactions with CO₂, but at the same time should offer resistance to the transport of the adsorbate. Therefore, the results shown in Figure 2.7. suggest that the pore channels of Cu₂(pzdc)₂(dpyg) are too small to accommodate CO₂ molecules at low pressure, at least in a fashion favorable to the occurrence of the aforementioned interactions. In contrast, it appears that the flexibility bought by the -CH₂CH₂CH₂- group of the *bpp* pillar to the CPL structure in general allows the pore gallery to be more accessible upon activation for adsorption of guest molecules.



Figure 2.7. (A) CO₂ adsorption isotherms at 298 K and (B) CO₂ isosteric heat of adsorption (ΔH) profiles for Cu₂(pzdc)₂(bpp) and Cu₂(pzdc)₂(dpyg). The data presented for Cu₂(pzdc)₂(dpyg) was reproduced with permission of The Royal Society of Chemistry.⁶

Despite the low adsorption capacity exhibited by $Cu_2(pzdc)_2(bpp)$ in comparison to other CPL materials, it appears that its pore galleries dimensions could serve for size exclusion separations. Figure 2.8. data show that $Cu_2(pzdc)_2(bpp)$ has less affinity toward CH_4 or N_2 perhaps due exclusion of these from access to the pore gallery. These adsorbates are much larger than CO_2 . Still CH_4 , being a symmetrical adsorbate, adsorbs better than the linear N_2 .



Figure 2.8. Pure component CO₂, CH₄ and N₂ adsorption isotherms gathered for Cu₂(pzdc)₂(bpp) at 298 K and $t_e = 120$ s.

2.4. Conclusions

An as prepared $Cu_2(pzdc)_2(bpp)$ porous coordination polymer exhibited pore galleries that are significantly constricted probably due to the greater flexibility introduced by the many possible conformations of the 1,3-bis(4-pyridyl)propane pillar. The material composition and structure is stable up to ca. 510 K and a porous structure can be attained upon removal of water at 373 K. Adsorption of N₂ at 77K was severely limited due to the relatively large kinetic diameter of the adsorbate; this was confirmed upon CO₂ adsorption at 194.5 and 298 K. Adsorption-desorption of CO₂ presented a hysteretic process that was related to an concomitant structural expansion previously reported for other $Cu_2(pzdc)_2(L)$ (L = bipyridyl ligands). The hysteretic adsorption process also involves what appears to be dual dynamics: structural expansion dynamics are much slower than those of the CO₂ adsorption. In terms of adsorbate-adsorbent interactions, CO₂ heat of adsorption energies are significant in $Cu_2(pzdc)_2(bpp)$ in comparison to isostructural $Cu_2(pzdc)_2(dpyg)$, probably due to the flexibility of the pillar in the former, allowing for better access to the electric field generated by the copper nodes.

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CHAPTER 3

Synthesis and Characterization of a Cu₂(pzdc)₂(bix) (pzdc: pyrazine-2,3-dicarboxylate; bix: 1,3-bis(imidazole-1-yl)benzene) Porous Pillared-Layer Coordination Polymer Network.



3.1. Introduction

Porous PCPs that contain copper nodes (Cu₂(pzdc)₂(*L*); i.e., *L* = pillar ligand), sometimes known as CPL-*n*, were discovered by Kitagawa and co-workers. These manifold-like frameworks consist of 3-D structures that exhibit a 1-D pore channel system.^{1, 2-13} CPL-*n* materials have also been extensively studied by Hernandez-Maldonado and co-workers to establish relationships between chemical, structural, textural, and adsorption properties.¹⁴⁻¹⁹ An interesting aspect of Cu₂(pzdc)₂(*L*) materials is the capability for tailoring the accessible surface for the uptake of light gases such as CO₂.

The pillar ligands usually employed for the syntheses of $Cu_2(pzdc)_2(L)$ are commonly based on a family of 2-connecting N-donor di-pyridyl-based neutral organic molecules. Differences between these ligands lie in the characteristic functional group that resides between the pyridine rings, also known as a spacer group and that gives unique chemical properties to the moiety and, as a consequence, to the framework. In general, these N-donor pyridyl-type ligands are also considered rigid, imposing this limits on both flexibility and stability in $Cu_2(pzdc)_2(L)$ frameworks. In this

chapter we present the synthesis and characterization of a $Cu_2(pzdc)_2(L)$ based on the di-imidazolebased ligand L = 1,3-bis(imidazol-1-yl)benzene or bix²⁰⁻²² with the objective of increasing both flexibility and thermal stability, particularly in light of potential CO₂ adsorption based applications for these materials. The Cu₂(pzdc)₂(bix) crystal structure was elucidated using a combination of high resolution X-ray diffraction (XRD) and Rietveld refinement techniques. The material was also characterized via thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), *in situ* high-temperature XRD, and N₂ and CO₂ adsorption at cryogenic temperatures. In addition, we present results of CO₂ adsorption isotherms at ambient temperature, moderate/high gas pressures, and at different equilibration time intervals (t_e), which allows probing the structural dynamics of the framework material upon interactions with the adsorbate. The adsorption selectivity capabilities of Cu₂(pzdc)₂(bix) were estimated via isosteric heats of adsorption and adsorption of single component CH₄ and N₂ also at ambient temperature.

3.2. Experimental Section

3.2.1. Materials

Reagents used for the synthesis of 1,3-bis(imidazole-1-yl)benzene (*bix*) and Cu₂(pzdc)₂(bix) were potassium carbonate (K₂CO₃, 99% purity), 1,3-diaza-2,4-cyclopentadiene (imidazole, 99% purity), α,α '-dichloro-p-xylene (C₆H₄(CH₂Cl)₂, 98% purity), 2,3-pyrazinedicarboxylic acid (H₂*pzdc*, 97% purity) and copper(II) perchlorate hexahydrate (Cu(ClO₄)·6H₂O, 98% purity). Methanol (99.8% purity) was used during the syntheses or for washing samples upon recovery; denatured ethanol (95% purity) was used during synthesis of Cu₂(pzdc)₂(bix). All reagents were obtained from Sigma-Aldrich and used as received. Ultra-high purity grade CO₂, N₂ and CH₄ gases (Praxair, Inc.) were used during the acquisition of adsorption data. High purity grade He gas (Praxair, Inc.) was used as a carrier gas during thermogravimetric analysis and *in situ* high-temperature XRD tests. All gases were pre-treated with zeolitic and hydrocarbon traps beds to remove any traces of impurities and humidity.

3.2.2. Synthesis of 1,3-bis(imidazole-1-yl)benzene

1,3-bis(imidazole-1-yl)benzene (*bix*) was synthesized as prescribed in a recipe presented elsewhere.²³ A solution containing 46.4 mmol of imidazole (3.16 g) and 4.46 mmol of α , α' -dichloro-p-xylene (0.78 g) in 50 mL of methanol was heated under reflux at 338 K. After 18 h, methanol was removed via evaporation; leaving a yellow remainder which was later dissolved in a solution containing 6.13 g of K₂CO₃ in 100 mL of water. The resulting mixture was held overnight at ambient pressure and temperature. Upon filtration, the resulting product was a white dehydrated crystalline solid (i.e., bix).

3.2.3. Synthesis of Cu₂(pzdc)₂(bix)

 $Cu_2(pzdc)_2(bix)$ was synthesized at ambient pressure and temperature adapting procedures previously reported for the preparation of CPL-n type materials.¹⁴ One mmol of H₂*pzdc* (0.1681 g) and 0.5 mmol of *bix* (0.1006 g) were dissolved in 100 mL of a solution containing 1:1 NaOH 0.04M and ethanol. The resulting solution mixture was dropwise added to 100 mL of a aqueous solution containing 1 mmol of Cu(ClO₄)·6H₂O (0.37 g). The final solution was stirred for 24 h and the precipitate was then vacuum filtered and washed with equal amounts of methanol and distilled/deionized water. The resulting blue solid crystals were dried overnight at 363 K to remove excess solvents.

3.2.4. Thermal Gravimetric Analysis (TGA)

All TGA tests were carried out using a TA-Q500 unit. A sample of $Cu_2(pzdc)_2(bix)$ (~10 mg) was placed onto a platinum holder suspended from the instrument weight balance and heated from ambient temperature to 1,173 K at 5 K min⁻¹ under a constant flow helium (60 mL min⁻¹). TGA was realized to verify its thermal decomposition temperature profile, and to identify the optimal degassing temperature for activation of the material prior to adsorption tests.

3.2.5. Differential Scanning Calorimetry (DSC)

DSC tests were performed in the Galbraith Laboratories, Inc. facilities in Knoxville, TN, USA. A Mettler-Toledo DSC instrument was employed for those tests; a heating rate of 5 K min-1 was employed during the tests. Further details about the standard DSC procedures can be found elsewhere.

3.2.6. Powder X-ray Diffraction (XRD) Patterns and Refinement

XRD patterns were gathered using a Rigaku ULTIMA III X-ray diffraction unit. The diffractometer is equipped with cross beam optics and a CuK_a target operating at 40 kV and 44 mA. XRD was employed for the following purposes: (1) verify the structure of the as-synthesized pillar ligand *bix* and (2) collect a high-resolution diffraction data for as-synthesized Cu₂(pzdc)₂(bix) for structure refinement. All XRD tests were performed with a scanning speed of 0.04° min⁻¹ and a step size of 0.005° in the 2 - 60° 2θ range. The unit cell parameters of Cu₂(pzdc)₂(bix) were determined using the CRYSFIRE program and the DICVOL91 indexing routine.²⁴ Afterwards, a set of refined unit cell parameters were obtained using a structure-less Le Bail fitting method.²⁵ A combination of two isostructural models based on Cu₂(pzdc)₂(dpyg) (or CPL-7) and Cu₂(pzdc)₂(bpp) were employed as a starting point for the elucidation of the fine

structure of Cu₂(pzdc)₂(bix).^{6, 26} The resulting model was then refined via the Rietveld technique using GSAS and the EXPGUI graphical interface, with a pseudo-Voigt peak profile and a background function of 22-term shifted Chebyshev polynomials.^{27, 28} The unit cell parameters were refined during the last stages of the overall refinement procedure; hydrogen atoms were directly added to the refined, final structure.

3.2.7. In Situ High-Temperature Powder X-ray Diffraction (XRD) Patterns

In situ high-temperature XRD measurements were obtained using a Rigaku ReactorX attachment fitted with a continuous beryllium window. This allows for complete enclosure and heating of the sample under an inert atmosphere and still permits the passages of X-ray. Upon calibration of the goniometer in a Bragg-Brentano focusing mode, the ReactorX module was attached to the system. Diffraction analyses were performed using a helium flow of 60 mL min⁻¹ for a fixed 2θ diffraction angle range, voltage, current, and step size. Powders of as-synthesized Cu₂(pzdc)₂(bix) were loaded onto a thin black quartz sample plate and heated from 303 K to 903 K by means of infrared heating and using a temperature ramp of 1 K min⁻¹. The diffraction scanning speed was raised to 3.5° min⁻¹ to avoid large temperature differences between the starting and ending points of each diffraction pattern. Temperature differences were no greater of 15 K. In situ ramp and hold XRD measurements were performed to further verify the structural stability of Cu₂(pzdc)₂(bix) at a degassing or activation temperature prescribed by the TGA tests. The as-synthesized sample was heated to that activation temperature at 5 K min⁻¹ and held/soaked at that condition for 10 h. X-ray diffraction patterns were collected every hour at a scanning speed of 2° min⁻¹ in the 2 - 60° 20 range.

3.2.8. Equilibrium Gas Adsorption Measurements

Low-pressure equilibrium adsorption data were obtained using a Micromeritics ASAP 2020 volumetric adsorption unit fitted with turbo molecular drag pumps. Activation of the sample was carried out prior to each adsorption test using the ASAP 2020 thermal vacuum-degassing stage or module. A sample of as-synthesized $Cu_2(pzdc)_2(bix)$ was loaded (~100 mg) into a quartz-made tube fitted with an isolation valve. The sample was then evacuated at a rate of 50 mmHg s⁻¹ to reach a degassing pressure of ca. 10 µmHg, heated at a rate of 10 K min⁻¹ *in situ* to 373 K (activation temperature), and held at that condition for 10 hours. Upon completion of the degassing stage, the sample was allowed to reach ambient temperature under vacuum and then backfilled with helium (inert gas) to allow its transfer to the analysis port under isolation. Prior to each adsorption test, the samples were evacuated using vacuum provided by a turbo molecular drag pump to effectively remove all the inert gas.

Moderate high pressure CO₂ single component gas equilibrium adsorption and desorption isotherms were obtained using a Micromeritics ASAP 2050 extended pressure volumetric adsorption instrument (up to 7 atm). In an attempt to assess the dynamics behind the concomitant CO₂ adsorption/ Cu₂(pzdc)₂(bix) framework relaxation/expansion process, each set of isotherms was gathered using equilibration time intervals (t_e) of 15, 60 and 120 seconds. All the adsorbent samples were activated using the procedure that was employed for ASAP 2020 adsorption tests. As will be discussed later, the desorption isotherms legs at each t_e were fitted with the MDA model (Eqn. 1).

High-pressure (up to 50 atm) CO₂ single component adsorption isotherms were measured using the Particulate Systems HPVA-II 100 at Micromeritics Instrument Corporation (Georgia, US), a

static volumetric system, connected to a high vacuum source. Between 250-450 mg of each material was used for these tests. Samples were heated to 373 K under vacuum for a minimum of four hours preceding analyses. Prior to each analysis on the HPVA-II 100 system a blank run was carried out with the same analysis gas, temperature, and pressure steps as the sample experiment. Blank run data were extracted from the sample analysis data to correct for small errors resulting from the increasing density of CO_2 at elevated pressures. A wait time of at least 10 minutes was implemented after equilibrium at each adsorption/desorption pressure step before continuing the experiment. This equilibration time was the maximum allowable due to instrument usage logistics. Sample temperature was maintained at 298 K using a recirculating water bath.

3.2.9. Estimation of Textural Properties

 $Cu_2(pzdc)_2(bix)$ textural properties were estimated by means of nitrogen and carbon dioxide equilibrium adsorption data gathered at 77 and 194.5 K, respectively. Surface area was estimated using the BET isotherm model. Pore volume was estimated with the Modified Dubinin-Astakhov (MDA) isotherm model^{29, 30} and assuming a liquid-like adsorbed phase at pore saturation (*i.e.*, molecules tightly packed). The MDA model is given by the following expression:

$$q = q_0 \left[\beta_1 \exp\left[-\left(C \ln\left(P_o / P\right)\right)^n \right] + \beta_2 K P \right]$$

$$\beta_1 = 1 - \exp\left(-\alpha \frac{P}{P_o}\right)$$

$$\beta_2 = \exp\left(-\alpha \frac{P}{P_o}\right)$$

$$C = \frac{RT}{\beta E}$$

$$K = \frac{q_1}{P_o}$$

(1)

where q is the equilibrium adsorption loading amount, q_0 is the adsorption loading amount at saturation (complete pore filling), R is the universal gas constant, T is temperature (K), β is the affinity coefficient of the adsorbate, E is the characteristic energy of adsorption, P/P_o is the relative pressure, n is the heterogeneity coefficient, α is a fitting parameter and K is Henry's law constant.

3.2.10. Isosteric Heat of Adsorption

Carbon dioxide isosteric heat of adsorption ΔH_{ads} was estimated using single component equilibrium adsorption data at different temperatures (273 - 323 K) and evaluated at constant surface loading. The calculations were made using the classic Clausius-Clapeyron equation:

$$-DH_{ads} = R \frac{d \ln P}{d(1/T)} \bigg|_{\substack{\text{at constant} \\ \text{loading}}}$$
(2)

3.3. Results and Discussion

3.3.1. Crystal Structure Determination and Thermal Behavior

Figure 3.1. shows that the as-synthesized $Cu_2(pzdc)_2(bix)$ possesses a highly crystalline structure that exhibits characteristic peaks found also in CPL-like solid frameworks, namely those that appear at 7.7, 11.3 and 13.32° in 20. These correspond to crystalline planes (100), (110) and (011) and are directly related to the formation of 2D Cu(pzdc) layers. In other words, these reflections are closely associated to geometry of the material pore gallery. In general, the Cu₂(pzdc)₂(bix) structure consists of a 3D framework with 1D channels along *c* direction, as shown in Figure 3.2., with pillar ligand molecules interconnecting pzdc layers along *a*. The distance between them is c.a. 10.050 Å when measured along *b*. From a chemical ambient perspective, the coordination complex around the copper metal nodes is exactly like the one found in CPL-*n* porous coordination polymers. It consists of a distorted square-pyramidal configuration due to the presence of a Jahn-Teller distortion around Cu^{2+} . The five complexing agents linked to the coordination center are delineated by three pzdc units and a half a bix pillar. The $Cu_2(pzdc)_2(bix)$ crystalline structure was refined by a combination of high-resolution diffraction and Rietveld refinement techniques, as shown in Figure 3.1. and Table 3.1. A full list of atomic parameters, interatomic distances, and angles are presented in the Appendix B.



Figure 3.1. Observed and calculated powder X-ray diffraction patterns for $Cu_2(pzdc)_2(bix)$. The observed data are shown with markers points with the position of the Bragg reflections and difference between calculated and observed intensities shown below.

Attempts to explain the structural response of CPL-*n* variants to external stimuli such as pressure or temperature have been made in the past.^{13, 16, 18, 31} Motivated by those findings, we subjected $Cu_2(pzdc)_2(bix)$ to TGA, DSC, and *in situ* high-temperature XRD tests (Figure 3.1.).

Data collection		Phase			
X-ray source	CuKα	Formula	$C_{3}H_{9}CuN_{4}O_{6}$		
Wavelength (Å)	1.5418	Molecular Weight (g mol ⁻¹)	380.78		
Step (°)	0.005	ρ (g cm ⁻³)	1.514		
2θ range (°)	2 - 50	<i>T</i> (K)	298		
Unit cell		Refinement			
Crystal system	Monoclinic	R_p	0.0881		
Space group	$P2_{1}/c$	wR_p	0.1150		
<i>a</i> (Å)	11.836	R _{exp}	0.0076		
<i>b</i> (Å)	13.005	$R(F^2)$	0.44208		
<i>c</i> (Å)	11.389				
β (°)	107.64				
Volume (Å ³)	1670.7				
Ζ	4				

 Section Control and Control and

 $Cu_2(pzdc)_2(bix)$ has a thermal stability of up to about 510 K and the profile decomposition shape is very similar to those observed in other CPL-like framework material. The first weight loss observed corresponds to the release of water that is loosely bound or contained within the pore gallery structures (8.46 wt. %). This amount corresponds to two guest water molecules located within the asymmetric unit cell. The second weight loss corresponds to organic pyrazine groups and a small fraction of *bix* (total of 49.24 wt.%) while the third weight loss corresponds to the complete elimination of the rest of the pillar ligand *bix* (22.14 wt. %). The remnant corresponds to copper (about 20 wt. %). These results commensurate with those based on the chemical composition observed in the crystal-refined structure: 8.20, 47.30, 28.13 and 16.13 wt.%, respectively.



Figure 3.2. Structural views along [001] and [010], respectively. Hydrogen atoms and water molecules are omitted for clarity.

Figure 3.3. also shows DSC and stacks of *in situ* high-temperature X-ray diffraction patterns. Nonuniform shifting and broadening of diffraction peaks were observed upon an increase in temperature. For instance, peak reflections corresponding to (100) and (110) (associated with the pore galleries of the PCP) experienced changes associated with diffraction angle and peak broadening. The specific diffraction pattern changes can be related to expansion in the pore gallery and structural breathing due to release of the physisorbed water. DSC measurements meanwhile showed two endothermic peaks centered at 368 and 428 K, suggesting that removal of water is taking place stepwise. The former peak is related to bulk water (W1) release, as readily observed in the TGA profile, while the latter is attributed to water molecules strongly adsorbed or coordinated to the PCP structure (W2). From Figure 3.4., the W1 water molecules are plausibly located near the benzene ring of the bix ligand while W2 water molecules are coordinated to imidazole rings. It is known that the dipole moment for benzene and for imidazole rings are is 0 and 3.61 D, respectively, suggesting that there is a stronger interaction between W2 molecules and the PCP framework. This correlates well with (110) peak shifting to lower diffraction angles being more pronounced at higher temperatures (> 400 K). These results also correlate well with data gathered from TGA profile, which indicated that the material continues to lose weight upon treatment at temperatures greater of 373 K (Figure 3.3.).



Figure 3.3. Thermal gravimetric analysis and differential scanning calorimetry profiles, and *in situ* high temperature diffraction patterns gathered for Cu₂(pzdc)₂(bix). Both tests were performed using a dry helium atmosphere and heating rates of 10 and 1 K min⁻¹, respectively.

It can be seen from the *in* situ XRD data that peak broadening for both (100) and (110) planes increases as temperature increases. This suggests that, in principle, a structural defect within the framework might be taking place, which in turn could induce inhomogeneous strain within the crystal. This could also lead to a pore that is both contracted and expanded. It should be noted that a non-identifiable phase transition was observed in the DSC profile at temperatures below 450 K, indicating maybe that a microporous-to-mesoporous material transition is primarily associated to structural defects.



Figure 3.4. Approximate location of water molecules along the pore galleries of $Cu_2(pzdc)_2(bix)$. The DSC profile also shows a pronounced exothermic peak centered at 467 K and another one centered at 465 K. Pyrazine ligands and bix pillars both decompose at temperatures near to the temperature of $Cu_2(pzdc)_2(bix)$ destruction, which is ca. 556 K. Therefore, the endothermic peak at 465 K and the exothermic peak at 467 K are both associated to decomposition and phase transition of the framework, respectively. The phase transition is linked to a crystal symmetry change evidenced by the shifts to higher and lower diffraction angles for (100) and (110) planes, respectively (Figure 3.3.). It should be noted that in the process of decomposition, $Cu_2(pzdc)_2(bix)$ could plausibly reach a non-reversible new phase before undergoing a complete decomposition. This contrasts somewhat with studies that were made for $Cu_2(pzdc)_2(bpy)$ (bpy: 4,4'-bipyridine) or CPL-2,³² which found that the thermally induced structural changes were mainly related to a shift of (100) to higher diffraction angles. Furthermore, the decomposition temperature limit of $Cu_2(pzdc)_2(bix)$ (556 K) is higher than that of $Cu_2(pzdc)_2(bpy)$ (523 K), $Cu_2(pzdc)_2(apy)$ (510 K),

Cu₂(pzdc)₂(bpe) (490 K), Cu₂(pzdc)₂(pia) (520 K) or Cu₂(pzdc)₂(dpyg) (453 K), probably due to the imidazole groups. Bix ligands have been used in non-pyrazine based 2D coordination polymers because of variable coordination positions conformations, which also results in improved thermal stability.²³

3.3.2. Estimation of Textural Properties from Gas Adsorption at Cryogenic Temperatures

Figure 3.5. shows the N₂ and CO₂ equilibrium adsorption isotherms gathered for Cu₂(pzdc)₂(bix) at 77 and 194.5 K, respectively, after activating the sample at 373 K under vacuum for several hours. The adsorption/desorption profiles follow a Type I isotherm as suggested by International of Pure and Applied Chemistry (IUPAC) classifications and this is characteristic of microporous solids. Using the N₂ adsorption data, we estimated a BET surface area of ca. 100 m² g⁻¹ and a pore volume of 0.09 cm³ g⁻¹. While the adsorption saturation loading for N₂ can be readily obtained from in Figure 2.5. (i.e., 1.215 mmol g⁻¹), for CO₂ the isotherm profile indicates that saturation was not achieved within the prescribed relative pressure range. Still, a theoretical value can be calculated under the assumption that both adsorbates would yield similar surface areas (i.e., kinetic diameters are similar) and based on the following relationships:

$$S_{N_2} a q_{N_2,sat} S_{N_2}^2 \qquad S_{CO_2} a q_{CO_2,sat} S_{CO_2}^2$$
(3)

$$\frac{q_{CO_2,sat}}{q_{N_2,sat}} \approx \left(\frac{S_{N_2}}{S_{CO_2}}\right)^2 \tag{4}$$

where S_i is the surface estimated for adsorbate *i*, $q_{i,sat}$ the adsorption loading amount at saturation, and σ_i is the adsorbate kinetic diameter ($\sigma_{N2} = 3.65$ Å and $\sigma_{CO2} = 3.2$ Å). Assuming also that the adsorbent framework remains rigid during the adsorption, equation 4 yields a CO₂ adsorption loading at saturation of ca. 1.5 mmol g⁻¹. This value contrasts considerably with what the adsorption isotherm data suggest, even without extrapolation. A possible explanation to this is that the crystal structure is perhaps undergoing a concomitant structural expansion during CO_2 adsorption; this has been reported before for $Cu_2(pzdc)_2(bpy)$ materials also at cryogenic temperatures.³¹ The CO_2 isotherm as shown in Figure 3.5.B also suggests a dynamical adsorption behavior that is represented by a inflections points at low relative pressure and changes in slope that are absent in the case of N₂.



Figure 3.5. (A) N_2 and CO_2 adsorption (filled markers) and desorption (empty marker) isotherms gathered for $Cu_2(pzdc)_2(bix)$ at 77 and 194.5 K, respectively; (B) Log-log scale plot for data shown in (A).

3.3.3. CO₂ Adsorption at Ambient Temperature and Equilibration Time Intervals (t_e)

High pressure CO₂ adsorption and desorption data gathered for as-synthesized Cu₂(pzdc)₂(bix) at 298 K (Figure 3.6.) present a hysteretic pathway probably associated to a pore expansion and contraction. These data were captured upon an equilibration time of 10 min for each point due to instrument usage logistics. However, our group has already shown that equilibration time intervals (t_e) play an important role in the determination of actual structural relaxation upon changes induced by CO₂ adsorption.^{18, 19} The rate of structural expansion is smaller than the rate of adsorption and

therefore the equilibrium adsorption amounts will increase simultaneous an increase t_e . In an attempt to verify such behavior Cu₂(pzdc)₂(bix), we gathered CO₂ adsorption isotherm data at ambient temperature and pressures up to 7 atm using different t_e values. The apparent equilibrium state for each adsorption or desorption datum was corroborated by a near-zero slope condition present in at least 11 consequent pressure transient points (e.g., for $t_e = 100$ sec, a total of 1100 sec worth of data per section per pressure step).



Figure 3.6. High pressure CO₂ adsorption (filled marker) and desorption (empty markers) isotherms gathered for Cu₂(pzdc)₂(bix) at 298 K.

Figure 3.7. shows that, once again, the hysteretic loop persists even at large t_e values. The loadings observed at 7 atm increased considerably between a t_e of 15 and 60 sec, but appeared to level of afterwards. Furthermore, hysteresis gap increased with t_e , which suggests dynamics between framework relaxation time, adsorbate-adsorbent interactions and external force exerted onto the Cu₂(pzdc)₂(bix) crystals.



Figure 3.7. CO₂ adsorption (filled markers) and desorption (empty markers) isotherms gathered for $Cu_2(pzdc)_2(bix)$ at 298 K and different equilibration time intervals, t_e .

In an attempt to quantify this expansion, we estimated textural properties by fitting the MDA model to the desorption profiles shown in Figure 3.6. The results are presented in Table 3.2. The results show that an increase in t_e results in an increase in micropore volume and this suggests the Cu₂(pzdc)₂(bix) framework is expanding. The *C* parameter also increases with t_e , not surprisingly since the former is directly proportional to the pore width of the framework (i.e., surface energy potential decreases as *C* increases.²⁶

Equilibration - Time Interval (s)	Modified Dubinin-Astakhov (MDA) Parameters						
	<i>q</i> ₀ (mmol g ⁻¹)	С (-)	<i>K</i> (mmol g ⁻¹ atm ⁻¹)	α (-)	n (-)	Std. Deviation ^a	V _{mp} (cm ³ g ⁻¹)
15	3.686	0.214	8.220	6498.976	1.723	± 0.0030	0.141
60	4.558	0.217	7.913	4051.304	1.756	± 0.0095	0.174
120	5.008	0.220	8.229	5374.623	1.183	± 0.0098	0.192

Table 3.2. Modified Dubinin-Astakhov model parameters and pore volume data obtained from CO₂ desorption at 298 K.

^a Standard deviation calculated based on residuals between the observed and calculated equilibrium loading amounts for the complete pressure range.
3.3.4. Isosteric Heat of Adsorption of Carbon Dioxide and Selectivity

The imidazole-based ligand *bix*, unlike the di-pyridyl-based ligand traditionally used in CPL-*n* materials, will produce specific adsorbate-adsorbent interactions that are significant. Imidazole rings have a dipole moment, or polarity, larger than that of pyridyl rings (3.6 vs. 2.2 D, respectively). Such difference will result in better, stronger interactions with adsorbates possessing large dipole or quadrupole moments; the location of the imidazole rings within the $Cu_2(pzdc)_2(bix)$ pore galleries make them readily accessible to small molecules such as CO_2 , which has a quadrupole moment that is an three times as large as that of N₂ and an order of magnitude larger than that of O₂. Possible evidence of the interaction of CO_2 with the imidazole rings comes in the form of the MDA *n* parameter (heterogeneity factor) values presented in Table 3.2.

Figure 3.8. makes comparison of low pressure CO₂ equilibrium adsorption data and isosteric heat profiles in Cu₂(pzdc)₂(bix), Cu₂(pzdc)₂(bpp) and Cu₂(pzdc)₂(dpyg).²⁶ In general, all the apparent interaction energies fall within the physical adsorption range ($\Delta H_{iso} <40$ kJ mol⁻¹). However, it is evident from the data that the interactions between CO₂ and Cu₂(pzdc)₂(bix) are significant in comparison. Furthermore, at 0.85 atm CO₂, the uptake in Cu₂(pzdc)₂(bix) is three times that the one seen in Cu₂(pzdc)₂(bpp) and an order of magnitude larger than the seen in Cu₂(pzdc)₂(dpyg). Given that these adsorbent materials are isostructural to one another, it is evident that the imidazole based ligands play a significant role in the adsorption of CO₂. The ligand along with the copper node is a significant contributor to the overall surface potential or field.

To compare the CO_2 adsorption capacity over N_2 and CH_4 , we also gathered single component adsorption isotherms for those gases. The results are collected in Figure 3.9.; selectivity toward CO_2 is quite evident, most certainly because of specific interactions between its strong permanent quadrupole moment, and the imidazole based ligands and metal node (i.e., Cu). It should be noted that the CH₄ adsorbed amounts are larger compared to those obtained for N₂ and this plausibly attributed to the induced octopole moment that CH₄ exhibits when in contact with the electric field generated by the adsorbent surface generated by metals³³⁻³⁶ and its slightly large polarizability.^{37,} ³⁸



Figure 3.8. (A) CO₂ adsorption isotherms at 298 K and (B) CO₂ isosteric heat of adsorption (ΔH_{iso}) profiles for Cu₂(pzdc)₂(bix), Cu₂(pzdc)₂(bpp) and Cu₂(pzdc)₂(dpyg). The data presented for Cu₂(pzdc)₂(bpp) was reproduced with permission of the American Chemical Society. Copyright 2015.²⁶ The data presented for Cu₂(pzdc)₂(dpyg) was reproduced with permission of The Royal Society of Chemistry. Copyright 2012.¹⁶

CO₂/CH₄ selectivity profiles were generated using the adsorption data shown in Figure 3.9. and the Ideal Adsorbed Solution Theory (IAST). This theory provides a framework to elucidate the suitability of an adsorbent to achieve a particular separation under equilibrium conditions and involves the assumption that the mixing of the adsorbed phases is ideal. The selectivity is calculated using the following expression:

$$S_{LAST} = \frac{\left(x_{CO_2} / x_{CH_4}\right)}{\left(y_{CO_2} / y_{CH_4}\right)}$$
(7)

where x_i and y_i are the molar fraction of CO₂ or CH₄ in the adsorbed and gas phase, respectively. Details on the equations that govern IAST as well as the calculations methods is available elsewhere.³⁰



Figure 3.9. Single component CO₂, N₂ and CH₄ adsorption isotherms for Cu₂(pzdc)₂(bix) at 298 K. Figure 3.10. shows IAST profiles for Cu₂(pzdc)₂(bix) and different gas phase CO₂/CH₄ compositions (i.e., 10/90, 20/80, and 50/50), representing bulk level separation case scenarios. IAST phase diagrams are shown in the Supplementary Information file (Figure C1). For the case of 10/90 gas mixtures, Cu₂(pzdc)₂(bix) showcases a maximum IAST selectivity of 8.4, which is a 10 and 75% increase in comparison with selectivity values reported for Cu₂(pzdc)₂(bpy) and Cu₂(pzdc)₂(bpe), respectively, at similar gas composition and pressure.¹⁹



Figure 3.10. Adsorption selectivity (CO₂/CH₄) on Cu₂(pzdc)₂(bix) at 298 K based on the Ideal Adsorbed Solution Theory (IAST). Ratios shown are in molar basis.

3.4. Conclusions

A porous coordination pillared-layer network based on bis(imidazole) N-donor pillar ligand was synthesized and characterized. A Rietveld refinement confirmed a material structurally similar to those found in the $Cu_2(pzdc)_2(L)$ family. Results based on thermogravimetric analysis and *in situ* high temperature XRD reported that the material composition and structure is stable up to ca. 556 K, an increase in stability of an average of 55K compared to previous $Cu_2(pzdc)_2(L)$ materials. *In situ* tests also evidenced a non-typical behavior of the structure using temperature as external stimuli in which the structure experimented a pore gallery expansion and distortion upon the release of physisorbed and coordinated water. Adsorption of N₂ at 77 K and CO₂ at 194.5 K confirmed the porous nature of the material while suggesting a concomitant pore expansion upon the uptake of the latter. The expansion was further demonstrated with results of CO₂ adsorption at 298 K and at different equilibration time intervals, *t_e*. The presence of a hysteretic adsorption

desorption pathway moderate pressure and still present a higher pressure (50 atm) was related to a structural expansion previously reported for $Cu_2(pzdc)_2(L)$ materials. Both isosteric heats of adsorption as well as IAST based selectivity calculations suggest that the bix imidazole rings are responsible for additional CO₂ interactions within the $Cu_2(pzdc)_2(bix)$ framework, in contrast with di-pyridyl-based $Cu_2(pzdc)_2(L)$ materials.

3.5. References

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CHAPTER 4

A Semi-Empirical Isotherm Model for CO₂ Adsorption onto Flexible Porous Coordination Cu₂(pzdc)₂(L) (pzdc: pyrazine-2,3dicarboxylate, L: Pillar Ligand) Polymers.

4.1. Introduction

Since their discovery in the 1990s, a wide number of reports for synthesis and characterization of MOFs or PCPs have been made available in literature.^{1, 2} In perspective, the Cambridge Crystallographic Data Centre (CCDC) databases list structural information for more than 75,000 materials under the ordered MOFs subset. Due to the covalent character of the structure coordination environment, most PCP's or MOF's are classified as highly flexible materials and, therefore, are also attractive as platforms for processes in the areas of catalysis, separations, energy, and biomedical applications.³⁻¹⁷

Copper-based PCPs, also known as CPL-n, have been extensively studied to understand their structural changes upon external stimuli, including those induced by thermal energy input and concomitant adsorption.^{2, 4, 18-28} The CPL-n series was coined by Kitagawa's group and have been extensively studied by Hernandez-Maldonado's group and others. This subset of materials is constituted by 2D [Cu(pzdc)]_n (pzdc: pyrazine-2,3-dicarboxylate) layers interconnected by *L* pillar ligands (i.e., *N*-donor bidentate ligands) to form 3D pillared-layer structures with accessible 1D channels. Several Cu_x(pzdc)_y(*L*) variants experience remarkable channel contraction or expansion upon the adsorption of vapors or gases, a phenomenon known as "shape-responsive fitting" transformation.^{2, 19, 23, 24, 27, 29-32}

 $Cu_x(pzdc)_y(L)$ structural changes that take place concomitant with CO₂ adsorption at room temperature, for instance, do not correlate with gate-opening like adsorbent behavior and are

completely absent during the uptake of other gases such as N₂ and CH₄ also at room temperature.^{24,} ²⁶ Therefore, modeling CO₂ uptakes in materials for selectivity and working capacity predictions in gas separation processes with $Cu_x(pzdc)_y(L)$ materials requires consideration of the effect of the structural changes. Previous attempts made by our group to model the adsorption of CO₂ onto $Cu_x(pzdc)_y(L)$ variants have been limited to the use of the classical micropore filling theory of Dubinin and co-workers. The models encompassed by this theory all assume that a whole adsorbate phase volume instead of a monolayer (i.e., Langmuir) interacts with the adsorbent surface (i.e., galleries of $Cu_x(pzdc)_y(L)$). Although fits of CO₂ equilibrium adsorption data with such Dubinin models yield acceptable statistics, they make little physical sense since the Dubinin work theory, as well as other well-known equilibrium adsorption models, implies an adsorbent remains with a rigid structure. In other words, that the CO₂ adsorption saturation capacity is independent of gas pressure. This is certainly not the case in $Cu_x(pzdc)_y(L)$ materials.

In this chapter, we present the development of a semi-empirical isotherm adsorption mathematical model to predict CO₂ uptake amounts in $Cu_x(pzdc)_y(L)$ like MOFs. *In situ* CO₂ adsorption and synchrotron X-ray powder diffraction data were employed to observe unit cell expansion and elucidate a model to predict how the effective pore volume changes as a function of gas pressure. This model was then incorporated into a Dubinin isotherm model and tested for prediction of CO2 uptake onto $Cu_2(pzdc)_2(bpy)$, $Cu_2(pzdc)_2(bpe)$ (bpe: 1,2-di(4-pyridyl)-ethylene) and $Cu_2(pzdc)_2(bix)$ (bix: 1,3-bis(imidazol-1-yl)benzene).

4.2. Experimental Section

4.2.1. Materials

Reagents employed for the synthesis of $Cu_2(pzdc)_2(L)$ were potassium carbonate (K₂CO₃, 99% purity), 1,3-diaza-2,4-cyclopentadiene (imidazole, 99% purity), α,α' -dichloro-p-xylene (C₆H₄(CH₂Cl)₂, 98% purity), 4,4'-bipyridine (for Cu₂(pzdc)₂(bpy)), 1,2-di(4-pyridyl)-ethylene (for Cu₂(pzdc)₂(bpe)), 2,3-pyrazinedicarboxylic acid (H₂*pzdc*, 97% purity) and copper perchlorate hexahydrate (Cu(ClO₄)·6H₂O, 98% purity). All were obtained from Sigma-Aldrich and used as received. Methanol (99.8% purity) was used during synthesis of bix and for Cu₂(pzdc)₂(L) washing upon recovery; and denatured ethanol (95% purity was used during synthesis of Cu₂(pzdc)₂(L). Ultra-high purity grade CO₂ gas (Praxair, Inc.) was employed during the measurements of adsorption data. This gas was pre-treated with zeolite and hydrocarbon traps beds upstream to remove any traces of impurities and humidity.

4.2.2. Synthesis of 1,3-bis(imidazole-1-yl)benzene

1,3-bis(imidazole-1-yl)benzene (bix) was synthesized following procedures available elsewhere.³³ A solution containing 46.4 mmol of imidazole (3.16 g) and 4.46 mmol of α , α '-dichloro-p-xylene (0.78 g) in 50 mL of methanol was heated under reflux at 338 K. After 18 h, methanol was removed by evaporation giving a yellow remainder, which was dissolved in a solution containing 6.13 g of K₂CO₃ in 100 mL of water. The resulting heterogeneous mixture was held at ambient pressure and temperature overnight. A white dehydrated crystalline solid (i.e., bix) was recovered via filtration.

4.2.3. Synthesis of Cu₂(pzdc)₂(*L*)

 $Cu_2(pzdc)_2(L)$ was synthesized at ambient pressure and temperature based on procedures reported elsewhere.^{2, 21, 24, 25} One mmol of H₂*pzdc* (0.1681 g) and 0.5 mmol of the corresponding ligand *L* (i.e., bpy, bpe or bix) were dissolved in 100 mL of a solution containing 1:1 NaOH 0.04 M and ethanol. The resulting solution was dropwise added to 100 mL of an aqueous solution containing 1 mmol of $Cu(ClO_4)$ ·6H₂O (0.37 g). The final solution was stirred for 24 h and the precipitate was then vacuum filtered and washed with equal amounts of methanol and distilled/deionized water. The blue solid obtained was dried overnight at 363 K to remove excess solvents.

4.2.4. In situ CO₂ adsorption and Synchrotron X-ray Powder Diffraction

The lattice distortions induced by gas sorption in Cu₂(pzdc)₂(bpy) and Cu₂(pzdc)₂(bpe) were measured with synchrotron x-ray powder diffraction. Experiments were conducted at station 17-BM of the Advanced Photon Source of Argonne National Laboratory using an x-ray wavelength of 0.72768 Å. Diffraction data were collected with an amorphous Si flat panel detector (Perkin Elmer, Inc.) positioned at a distance of 500 mm from the sample. Powder specimens were loaded into cylindrical quartz capillaries with a 1 mm diameter. Glass wool was packed into both ends of the capillary to reduce sample displacement during gas flow and a thin wire K-type thermocouple was inserted into the capillary near the sample to monitor the temperature. The x-ray probe was positioned immediately adjacent to the thermocouple to ensure accurate temperature resolution. The capillaries were mounted to a non-ambient x-ray scattering sample holder equipped with two resistive heaters mounted 5 mm from opposite sides of the capillary. The capillary was attached to the sample holder with gas fittings.

Before each adsorption experiment, the samples were purged of small-molecule impurities in order to activate the pores for adsorption. The activation procedure consisted of heating the adsorbent powders in helium gas while collecting diffraction data to monitor the structural changes resulting from activation. After one hour under flowing ultrahigh purity (UHP) helium at atmospheric pressure and 30 minutes at 373 K, the atmosphere was switched from helium to UHP CO₂ at 0 atm (gauge). Two key experimental signatures of the activation were a transient shift by 0.09° to higher 20 angle and a factor of three increase in intensity of the (020) peak.

X-ray scans were conducted with in situ sorption and desorption of CO_2 in $Cu_2(pzdc)_2(bpy)$ and $Cu_2(pzdc)_2(bpe)$ as the pressure was increased from 0 to 50 atm and subsequently decreased from 50 to 0 atm. Diffraction data were acquired after allowing the gas pressure to equilibrate for at least 3 minutes following each pressure step. A syringe pump was used to deliver pressurized gas to the sample cell at a ramp rate of 1 bar/s during the experiments. In order to obtain sufficient counting statistics while avoiding detector saturation, scans were repeated ten times with a 3 s acquisition time per exposure. The diffraction patterns were constructed by summing the intensities of the ten exposures. The angular range in 2 θ for each scan was 2-20°.

4.2.5. Equilibrium CO₂ Adsorption Measurements

High-pressure CO_2 adsorption isotherms were measured using the Particulate Systems HPVA-II 100 at Micromeritics Instrument Corporation (Georgia, US), a static volumetric system, connected to a high vacuum source. Between 250-450 mg of each material was used for these tests. Samples were heated to 373 K under vacuum for a minimum of four hours preceding analyses. Prior to each analysis on the HPVA-II 100 system, a blank run was carried out with the same analysis gas, temperature, and pressure steps as the sample experiment. Blank run data were extracted from the sample analysis data to correct for small errors resulting from the increasing density of CO_2 at elevated pressures. Sample temperature was maintained at 298 K using a recirculating water bath.

4.3. Results and Discussion

4.3.1. In situ CO₂ Adsorption and Synchrotron XRD

The porous coordination polymers $Cu_2(pzdc)_2(bpy)$ and $Cu_2(pzdc)_2(bpe)$ are pillar-layered structures classified as microporous material according to IUPAC classification (pore diameter < 20 Å or 2 nm). Differences between the N-donor ligands in these two materials lie in the functional (spacer) group located between the pyridine rings and it imparts unique physical and chemical properties.²¹⁻²³ The metal node present in these materials (i.e., Cu^{2+}) is surrounded via coordination bond by three units of pyrazine groups and a half of pillar ligand. In addition, the dimensions of pore channel are 8.2 x 6.0 Å, 10.3 x 6.0 Å for $Cu_2(pzdc)_2(bpy)$ and $Cu_2(pzdc)_2(bpe)$, respectively. Figure 4.1. shows synchrotron XRD data as well views of super-cell crystal structures for both $Cu_2(pzdc)_2(bpy)$ and $Cu_2(pzdc)_2(bpe)$.

One of the feature of these pillar-layered materials is their structural flexibility, particularly upon an external stimulus. To date, computational and experimental studies have been used to explore the behavior of the structures upon thermal treatment, and adsorption of CO_2 .^{4, 21, 23, 24, 27, 32} In the case of the latter, studies have strongly suggested the structural changes are induced by adsorbateadsorbent interactions and that the framework expansion/contraction takes place gradually rather than suddenly as in the gate opening phenomenon observed in many MOFs. However, these studies were performed for CO_2 pressures up to about 10 atm, leaving the possibility of the structure undergoing a gate opening at much higher pressures as unknown.



Figure 4.1. Observed powder X-ray diffraction patterns (left side) and structural arrange along [100] (right side) for Cu₂(pzdc)₂(bpy) and Cu₂(pzdc)₂(bpe).

Figure 4.2. shows stacks of synchrotron XRD patterns gathered for $Cu_2(pzdc)_2(bpy)$ and $Cu_2(pzdc)_2(bpe)$ during the concomitant adsorption of CO₂ at pressures up to 50 atm and a temperature of 298 K. It is evident from the (020) and (011) reflections trajectory that both adsorbent materials undergo gradual expansion and contraction upon CO₂ uptake at pressures up to 50 atm. Furthermore, the original crystal framework is recovered upon complete CO₂ desorption, which is of great importance for usage of these materials in multi-cycle gas storage or even separation applications.

Figure 4.3. shows total accessible volume profiles for $Cu_2(pzdc)_2(bpy)$ and $Cu_2(pzdc)_2(bpe)$ estimated from unit cell volume data generated from the data shown in Figure 4.2. and employing a Connolly surface method. It should be noted that both $Cu_2(pzdc)_2(L)$ variants have structures that are described by a monoclinic P2₁/c space group.^{2, 21, 25}



Figure 4.2. *In situ* CO₂ adsorption and desorption synchrotron X-ray powder diffraction (XRD) patterns for Cu₂(pzdc)₂(bpy) (A) and Cu₂(pzdc)₂(B) (bottom) gathered at 298 K.

As shown in Figure 4.3., both $Cu_2(pzdc)_2(bpy)$ and $Cu_2(pzdc)_2(bpe)$ experience a considerable increase in accessible volume increase upon adsorption of CO₂. A 7% increase in volume was observed in the case of $Cu_2(pzdc)_2(bpe)$, compared to about 3% in the other material. However, it is evident that the total volume increase in $Cu_2(pzdc)_2(bpy)$ is attained at a much lower gas pressures, perhaps due to faster re-coordination of the framework upon adsorption of CO_2 .



Figure 4.3. Apparent void volume for $Cu_2(pzdc)_2(bpy)$ (A) and $Cu_2(pzdc)_2(bpe)$ (B) as function of carbon dioxide pressure at 298 K. Data estimated from indexing of individual XRD patterns shown in Figure 4.2. The solid lines correspond to data fits for a first order model. Fit parameters are presented in Table 4.1.

The expansion in both materials seems to follow a first order dynamic mechanism, in other words:

$$V_{a} = V_{a_{1}} + V_{a_{2}} \left(1 - e^{-\frac{P}{P}} \right)$$
(1)

where V_a is the total accessible volume, P is the gas pressure, V_{a1} is the adsorbent accessible volume at a given initial P, and \overline{P} is the gas pressure to reach 63.2% of the adsorbent accessible

volume increase (V_{a2}) upon saturation with CO₂. A fit of the data shown in Figure 4.3. with the model shown in equation 1 results in the parameters presented in Table 4.1.

Adsorbent	Val	Val	Va	P	
	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(cm ³ g ⁻¹)	(atm)	
Cu2(pzdc)2(bpy)	0.184	0.007	0.191	5.297	
Cu2(pzdc)2(bpe)	0.242	0.017	0.259	1.688	

 Table 4.1. Mathematical model parameters for prediction of total accessible volume in the adsorbents.

^a Standard deviation calculated based on residuals between the observed and calculated equilibrium loading amounts for assigned pressure range.

4.3.2. Isotherm Model for CO₂ Uptake in Cu₂(pzdc)₂(L)

The results discussed in the preceding section strongly suggest that the CO₂ saturation loadings in $Cu_2(pzdc)_2(L)$ materials will be a function of the ultimate framework expansion and this should be considered explicitly in the isotherm model. Since CPL-n like materials are classified as microporous, their gas adsorption equilibrium isotherms can be fitted by models developed under the known Dubinin Theory, (i.e., micropore volume filling). This theory is based on the Polanyi adsorption potential theory, which assumes that the chemical potential is a function of the adsorbed amount. The molar work of adsorption, *A*, difference between the adsorbed phase and a saturated liquid adsorbate at the same temperature in terms of free energy is given by:³⁴

$$A = -RT\ln\left(\frac{P}{P_o}\right) \tag{2}$$

where the parameter P_o is the pressure vapor of the adsorbate. Another important aspect considered in the Dubinin Theory is that the adsorbent structure is assumed rigid and implies a constant saturation loading amount during adsorption. In other words, the pore volume of the structure and therefore the dimensionality of them are constant while the gas adsorption is taking place. Equation 3 shows the resulting prediction model, known as the Dubinin-Astakhov isotherm model:

$$q = q_s \exp\left(-\left[C\ln\frac{P_o}{P}\right]^n\right)$$
(3)

$$C = \frac{RT}{bE} \tag{4}$$

where q is the equilibrium adsorption loading amount, q_s is the adsorption loading amount at saturation (complete pore filling), R is the universal gas constant, β is the affinity coefficient of the adsorbate, E is the characteristic energy of adsorption, P/P_o is the relative pressure, and n is the heterogeneity coefficient. To account for the increase in saturation capacity due to volume increase and based on the results shown in Figure 4.3. and the profile suggested by equation 1, we have redefined the saturation loading amount presented in equation 3 as follows:

$$q_{s} = q_{s_{1}} + q_{s_{2}} \left(1 - e^{-\frac{P}{P}} \right)$$
 (6)

where q_{s} , q_{s1} , q_{s2} , and \overline{P} are constant parameters. Both the original and modified Dubinin-Astakhov models were used to fit high pressure CO₂ adsorption data gathered for Cu₂(pzdc)₂(bpy) and Cu₂(pzdc)₂(bpe). In addition, we have applied the model to data gathered for Cu₂(pzdc)₂(bix), a Cu₂(pzdc)₂(*L*) variant with a imidazole based pillar ligand that improves the material overall thermal stability and is known to also introduce additional surface-adsorbate interactions.³⁵ Figure 4.4. shows both the XRD pattern for this material as well as a relative view of the framework super cell.



Figure 4.4. Observed powder X-ray diffraction patterns and structural arrange along [001] for Cu₂(pzdc)₂(bix).

Figure 4..5 shows high pressure CO₂ adsorption data for all three $Cu_2(pzdc)_2(L)$ materials as well as the resulting fit with the modified Dubinin-Astakhov model. The fit parameters are shown in Table 2 and the residuals are stacked in Figure 6. The latter also includes data for fits with the original Dubinin-Astakhov model. It should be noted that the adsorption of other gases such as N₂ is negligible in all three of these materials.^{4, 21, 23-26, 32, 35}

	Dubinin-Astakhov			Modified Dubinin-Astakhov							
Adsorbent	q S (mmol g ⁻¹)	С (-)	n (-)	Std. Dev. ^a	q S1 (mmol g ⁻¹)	q S2 (mmol g ⁻¹)	q S (mmol g ⁻¹)	P (atm)	С (-)	n (-)	Std. Dev. ^a
Cu ₂ (pzdc) ₂ (bpy)	3.123	0.250	1.987	0.054	0.000	3.346	3.346	1.017	0.181	1.069	0.02
Cu ₂ (pzdc) ₂ (bpe)	4.989	0.299	2.098	0.040	0.545	4.650	5.195	1.688	0.247	1.396	0.02
Cu ₂ (pzdc) ₂ (bix)	4.301	0.312	1.067	0.037	2.141	2.693	4.834	1.608	0.306	0.718	0.01

 Table 4.2. Mathematical model parameters obtained from CO2 adsorption equilibrium data for different adsorbents at 298 K.

^a Standard deviation calculated based on residuals between the observed and calculated equilibrium loading amounts for assigned pressure range.

Figure 4.6. shows that the correction made to the saturation loading in equation 3 does allow for better fit statistics while introducing some quantitative physical reasoning to the observed crystal volume expansion. The parameter C suggests that the adsorption interactions are stronger in

 $Cu_2(pzdc)_2(bpy)$ compared to the other variant. When considering the saturation loading correction, the new isotherm model suggests that these interactions are stronger than those predicted by the original Dubinin-Astakhov model. Predicted *E* values are 20% larger in comparison, and this is possibly ascribed to the framework re-coordination during the CO₂ uptake, leading perhaps to an improved surface electric field upon a greater exposure of the Cu nodes.



Figure 4.5. CO_2 adsorption isotherms gathered at 298 K for $Cu_2(pzdc)_2(bpy)$, $Cu_2(pzdc)_2(bpe)$ and $Cu_2(pzdc)_2(bix)$. The solid lines correspond to data fits with the modified Dubinin-Astakhov isotherm model. Fit parameters are presented in Table 4.2.



Figure 4.6. Residual plots for the isotherm model fits on CO_2 adsorption data gathered at 298 K for $Cu_2(pzdc)_2(bpy)$, $Cu_2(pzdc)_2(bpe)$ and $Cu_2(pzdc)_2(bix)$. Profiles shown in (A, C, E) correspond to fits with the Dubinin-Astakhov isotherm model, while those in (B, D, F) correspond to fits with the modified Dubinin-Astakhov isotherm model.

4.4. Conclusions

A new semi-empirical adsorption isotherm mathematical model was proposed and developed. This model took in consideration the fact of that the predicted available void volume and therefore the saturation adsorption loading both change as a function of gas pressure. Results based on *in situ* CO_2 adsorption and synchrotron X-ray powder diffraction evidenced a clear expansion of the unit cell volume and therefore an augmentation of the free space volume or adsorption saturation loading. The new isotherm model adequately fitted high pressure CO_2 adsorption data up to 50 atm of pressure for a $Cu_2(pzdc)_2(bpy)$, $Cu_2(pzdc)_2(bpe)$ and $Cu_2(pzdc)_2(bix)$ adsorbents.

4.5. References

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CHAPTER 5

Final Remarks: General Contibutions and Recommendations

The main objective of this work was the isostructural synthesis of two new Porous Coordination Pillared-Layer $Cu_2(pzdc)_2(L)$ (L: Pillar Ligand) Polymers in an attempt to improve their physical and chemical properties, such as flexibility, thermal stability and affinity to Carbon Dioxide, due to great potential CO₂-based physical adsorption applications of these materials. Two pillar ligands with different chemical nature were proposed in order to tackle this challenge. The first one was the *bpp* (1,3-bis(4-pyridyl)propane) pillar, due to the variety in structural conformations, in an attempt to provide flexibility to the resulting pillared-layer structure. The second was the bix (1,3bis(4-imidazole-1-yl)), due to the presence of imidazole fractions, in an attempt to provide not only flexibility but also thermal stability and high interactions toward CO₂. Significant contributions were obtained with the development of this doctoral dissertations: (1) in terms of flexibility both assembled materials evidence hysteretic adsorption process in their CO₂ adsorption isotherm involving what appears to be dual dynamics: structural expansions dynamics much slower compared to those of the CO_2 kinetic adsorption; (2) in accordance to thermal stability the results suggest that the presence of di-imidazole fractions in pillar ligand in comparison with the traditional di-pyridyl contributes to an improvement of the thermal stability of the framework materials. In perspective $Cu_2(pzdc)_2(L)$ built with bix pillar ligand reported an increase in stability of an average of 55 K compared to previous isostructural pillared-layer materials. (3) finally, in terms of affinity toward CO_2 , and in perspective, toward light molecule with presence of strong polarity (for instance: dipole moment, quadrupole moment, etc.), and although the pillared-layer built with *bpp* pillar ligand showed a stronger interaction with CO₂, once again the presence of diimidazole fractions in bix resulted in an interesting pore surface with higher affinity toward CO₂.

On the other hand, and profiting from our extensive knowledge about the flexibility of this subset of materials upon concomitant CO_2 adsorption, an interesting contributions was realized developing a new semi-empirical adsorption isotherm mathematical model taking in consideration the fact of that the $Cu_2(pzdc)_2(L)$ materials evidenced a clear expansion with CO_2 adsorption.

For future works, it is recommendable to use other straight (without alkyl groups) pillar ligand that contains imidazole fractions. The presence of alkyl groups provide a scenario of structural distortion and diversity. The synthesis of these new materials will require to use refinement tools to verify the obtained phase. We also recommends to verify the behavior of these type of materials in presence of other light gases and molecules with strong polarity. Finally, measurement of transient fractional uptake data for the estimation of diffusion time constants.

APPENDIX A

Full list of atomic parameters, interatomic distances and angles of the porous coordination $Cu_2(pzdc)_2(bpp)$ pillared-layer structure polymer.

atom	x	у	Z	occupancy	Uiso
Cu(1)	-0.3918 (7)	-0.419 (6)	-0.0499 (7)	1	0.2716 (16)
O(1)	-0.362 (3)	-0.2779 (7)	0.011 (3)	1	0.0366 (4)
O(2)	-0.4348 (5)	-0.1293 (14)	-0.0668 (5)	1	0.5330 (10)
O(3)	-0.638 (3)	-0.071 (3)	-0.3927 (17)	1	0.0481 (4)
O(4)	-0.6174 (19)	-0.063 (3)	-0.153 (2)	1	0.3552 (8)
O(5)	-0.0986 (5)	-0.3514 (4)	-0.0919 (8)	1	0.0145 (5)
O(6)	-0.8655 (4)	-0.5577 (5)	-0.9059 (7)	1	0.008 (3)
N(1)	-0.4676 (6)	-0.372 (3)	-0.2187 (6)	1	0.1220 (8)
N(2)	-0.6304 (10)	-0.2743 (17)	-0.3671 (10)	1	0.0105 (4)
N(3)	-0.2707 (15)	-0.4712 (7)	0.075 (2)	1	0.3887 (11)
C(1)	-0.4844 (8)	-0.2716 (4)	-0.2027 (12)	1	0.5435 (18)
C(2)	-0.5697 (11)	-0.2245 (5)	-0.2734 (15)	1	0.3733 (11)
C(3)	-0.6211 (17)	-0.375 (3)	-0.369 (3)	1	0.138 (3)
C(4)	-0.537 (2)	-0.4261 (11)	-0.3 (4)	1	0.1193 (7)
C(5)	-0.423 (2)	-0.2315 (7)	-0.0744 (17)	1	0.0199 (8)
C(6)	-0.5973 (6)	-0.113 (2)	-0.2675 (8)	1	0.4174 (15)
C(7)	-0.269 (3)	-0.5642 (11)	0.130 (3)	1	0.1771 (7)
C(8)	-0.1832 (17)	-0.5925 (5)	0.219 (3)	1	0.3209 (10)
C(9)	-0.1091 (17)	-0.5233 (10)	0.269 (3)	1	0.4925 (13)
C(10)	-0.1177 (18)	-0.4267 (17)	0.2188 (4)	1	0.2549 (14)
C(11)	-0.201 (3)	-0.3985 (16)	0.1272 (5)	1	0.3382 (13)
C(12)	-0.051 (6)	-0.534 (3)	0.400 (3)	1	0.3559 (9)
C(13)	0.014 (2)	-0.4523 (16)	0.4716 (6)	0.5	0.2932 (4)

Table A1. Refined atomic parameters for $Cu_2(pzdc)_2(bpp)$ in space group $P2_1/c$ (Z = 2)

bond	distance (Å)	atoms	angle (°)
C(1)—C(2)	1.3834 (5)	C(2)—C(1)—C(5)	124.86 (3)
C(1)—C(5)	1.5552 (7)	C(2) - C(1) - N(1)	120.112 (17)
C(2)—C(6)	1.5084 (8)	C(5) - C(1) - N(1)	111.863 (14)
C(3)—C(4)	1.3858 (5)	C(1)—C(2)—C(6)	125.982 (13)
C(7)—C(8)	1.3904 (6)	C(1) - C(2) - N(2)	120.63 (3)
C(8)—C(9)	1.3702 (4)	C(6)—C(2)—N(2)	112.94 (2)
C(9)—C(10)	1.3727 (7)	C(4)—C(3)—N(2)	122.803 (15)
C(9)—C(12)	1.4878 (8)	C(3) - C(4) - N(1)	118.44 (4)
C(10)—C(11)	1.3838 (6)	C(1)—C(5)—O(1)	129.82 (3)
C(12)—C(13)	1.4919 (5)	C(1)—C(5)—O(2)	110.072 (14)
C(13)—C(12)	1.3873 (7)	O(1)—C(5)—O(2)	119.809 (18)
N(1) - C(1)	1.3569 (7)	C(2)—C(6)—O(3)	112.181 (17)
N(1) - C(4)	1.3453 (5)	C(2)—C(6)—O(4)	111.524 (4)
N(2)—C(2)	1.3349 (5)	O(3)—C(6)—O(4)	106.03 (3)
N(2)—C(3)	1.3243 (7)	C(8)—C(7)—N(3)	118.978 (10)
N(3)—C(7)	1.3547 (6)	C(7)—C(8)—C(9)	121.69 (3)
N(3)—C(11)	1.3712 (5)	C(8)—C(9)—C(10)	117.24 (3)
Cu(1) - N(1)	1.9993 (10)	C(8)—C(9)—C(12)	120.80 (3)
Cu(1) - N(3)	2.0081 (8)	C(10)-C(9)-C(12)	116.959 (11)
Cu(1) - O(1)	1.9777 (10)	C(9) - C(10) - C(11)	121.402 (8)
$Cu(1) - O(3)^{a}$	2.1472 (10)	C(10) - C(11) - N(3)	119.42 (3)
O(1)—C(5)	1.2610 (5)	C(9) - C(12) - C(13)	124.24 (3)
O(2)—C(5)	1.3536 (7)	$C(9) - C(12) - C(13)^{b}$	169.883 (6)
O(3)—C(6)	1.4655 (7)	N(1)— $Cu(1)$ — $N(3)$	155.813 (15)
O(4)—C(6)	1.1997 (4)	N(1) - Cu(1) - O(1)	92.91 (3)
		$N(1)$ — $Cu(1)$ — $O(3)^{a}$	96.27 (2)
		N(3) - Cu(1) - O(1)	90.81 (3)
		$N(3) - Cu(1) - O(3)^{a}$	72.99 (2)
		$O(1) - Cu(1) - O(3)^{a}$	158.208 (12)
		C(1) - N(1) - C(4)	118.894 (19)
		C(1) - N(1) - Cu(1)	104.329 (17)
		C(4) - N(1) - Cu(1)	126.63 (3)
		C(2) - N(2) - C(3)	116.96 (2)
		C(7) - N(3) - C(11)	119.51 (3)
Symmetry code:	(a) -x-1, y-1/2, -z-1/2	C(11) - N(3) - Cu(1)	115.36 (3)
	(b) $-x, -y-1, -z+1$	C(5) - O(1) - Cu(1)	98.56 (3)
	(c) $-x-1$, $y+1/2$, $-z-1/2$	$C(6) - O(3) - Cu(1)^{c}$	124.181 (12)

Table A2. Interatomic distances and angles from the refinement of Cu₂(pzdc)₂(bpp).

APPENDIX B

Full list of atomic parameters, interatomic distances and angles of the porous coordination $Cu_2(pzdc)_2(bix)$ pillared-layer structure polymer.

atom	x	у	Z	occupancy	$oldsymbol{U}_{iso}$
Cu(1)	-0.4307 (35)	-0.40856 (29)	-0.10192 (30)	1	0.03027 (9)
O(1)	-0.39113 (19)	-0.29545 (10)	-0.0492 (20)	1	0.29849 (30)
O(2)	-0.42583 (22)	-0.12689 (29)	-0.08381 (29)	1	0.41549 (6)
O(3)	-0.56718 (22)	-0.04226 (12)	-0.40357 (20)	1	0.11665 (15)
O(4)	-0.6645 (13)	-0.07888 (14)	-0.277 (17)	1	0.00388 (10)
O(5)	-0.23265 (13)	-0.03448 (22)	-0.02757 (25)	1	0.131 (9)
O(6)	-0.11139 (22)	0.11504 (19)	0.69768 (15)	1	0.36 (12)
N(1)	-0.51901 (20)	-0.35633 (14)	-0.22597 (15)	1	0.0425 (28)
N(2)	-0.65325 (22)	-0.26158 (15)	-0.46395 (20)	1	0.04862 (34)
N(3)	-0.1975 (18)	-0.40825 (18)	0.20429 (13)	1	0.06728 (8)
N(4)	-0.33609 (26)	-0.45947 (25)	0.04362 (26)	1	0.33682 (4)
C(1)	-0.22528 (5)	-0.40766 (7)	0.07871 (5)	1	0.1548 (15)
C(2)	-0.52423 (5)	-0.26628 (35)	-0.24095 (5)	1	0.03552 (14)
C(3)	-0.59013 (4)	-0.21598 (4)	-0.35265 (4)	1	0.03703 (6)
C(4)	-0.64813 (5)	-0.35918 (4)	-0.46375 (29)	1	0.05454 (4)
C(5)	-0.58253 (4)	-0.41118 (5)	-0.35415 (6)	1	0.04876 (15)
C(6)	-0.45073 (4)	-0.22048 (6)	-0.16233 (5)	1	0.04315 (6)
C(7)	-0.58615 (4)	-0.10519 (4)	-0.34092 (4)	1	0.0435 (7)
C(8)	-0.0128 (4)	-0.60464 (23)	0.4989 (5)	1	0.66522 (24)
C(9)	-0.27646 (6)	-0.44599 (13)	0.24815 (9)	1	0.38048 (8)
C(10)	-0.36916 (6)	-0.47785 (7)	0.14962 (8)	1	0.18508 (6)
C(11)	-0.10855 (12)	-0.54635 (17)	0.39303 (16)	1	0.2786 (10)
C(12)	-0.07379 (32)	-0.43953 (6)	0.39577 (27)	1	0.71682 (6)
C(13)	-0.1301 (20)	-0.36391 (15)	0.28823 (15)	1	0.8000 (5)

Table B1. Refined atomic parameters for $Cu_2(pzdc)_2(bix)$ in space group $P2_1/c$ (Z = 4)

bond	distance (Å)	atoms	angle (°)
Cu(1)—O(1)	1.6220 (21)	O(1)—Cu(1)—O(3)	152.66 (5)
Cu(1) - O(3)	1.7403 (27)	O(1) - Cu(1) - N(1)	89.32 (10)
Cu(1) - N(1)	1.5984 (23)	O(1) - Cu(1) - N(4)	86.10 (9)
Cu(1) - N(4)	1.8737 (29)	O(3) - Cu(1) - N(1)	117.49 (5)
C(2)—C(3)	1.4330 (21)	O(1) - Cu(1) - N(4)	66.94 (4)
C(2)—C(6)	1.2005 (16)	N(1) - Cu(1) - N(4)	175.217 (8)
C(3)—C(7)	1.4464 (22)	C(2) - N(1) - C(5)	108.76 (8)
C(4)—C(5)	1.4251 (21)	C(3) - N(2) - C(4)	114.28 (5)
C(6)—C(2)	1.2005 (14)	C(1) - N(3) - C(9)	115.90 (9)
C(8)—C(11)	1.5763 (20)	C(1) - N(3) - C(13)	136.62 (7)
C(8)—C(12)	1.4402 (20)	C(9)—N(3)—C(13)	105.19 (11)
C(9)—C(10)	1.3743 (19)	C(1) - N(4) - C(10)	109.98 (9)
C(9)—C(13)	1.9670 (15)	N(1) - C(2) - C(3)	124.81 (4)
C(11)—C(12)	1.4465 (21)	N(1)—C(2)—C(6)	112.92 (7)
C(12)—C(13)	1.5546 (21)	C(3)—C(2)—C(6)	120.81 (11)
N(1) - C(2)	1.1824 (25)	N(2)—C(3)—C(2)	127.64 (11)
N(1) - C(5)	1.5938 (25)	N(2)—C(3)—C(7)	120.09 (4)
N(1)—C(6)	1.9861 (25)	C(2)—C(3)—C(7)	112.27 (7)
N(2)—C(3)	1.3938 (21)	N(2)—C(4)—C(5)	119.25 (6)
N(2)—C(4)	1.2707 (20)	N(1) - C(4) - C(5)	124.79 (11)
N(3) - C(1)	1.3670 (27)	O(1)—C(6)—O(2)	93.20 (13)
N(3)—C(10)	1.1919 (10)	O(1)—C(6)—C(2)	109.97 (12)
N(3)—C(13)	1.3712 (16)	O(3)—C(7)—O(4)	115.95 (9)
N(4) - C(1)	1.4202 (11)	O(3)—C(7)—C(3)	131.12 (8)
N(4)—C(10)	1.3688 (22)	O(4)—C(7)—C(3)	106.650 (20)
O(1)—C(6)	1.5992 (21)	C(8) - C(11) - C(12)	127.63 (10)
O(2)—C(6)	1.4860 (18)	N(3)—C(9)—C(10)	107.03 (11)
O(3)—C(7)	1.1517 (13)	N(4)—C(10)—C(9)	106.48 (11)
O(4)—C(7)	1.3843 (14)	C(8) - C(11) - C(12)	108.15 (7)
		C(8) - C(12) - C(11)	121.8 (5)
		C(8)—C(12)—C(13)	115.52 (11)
Symmetry code:	(a) -x-1, y-1/2, -z-1/2	C(11) - C(12) - C(13)	122.64 (8)
	(b) -x, -y-1, -z+1	N(3)—C(3)—C(12)	110.42 (12)
	(c) $-x-1$, $y+1/2$, $-z-1/2$		

Table B2. Interatomic distances and angles from the refinement of Cu₂(pzdc)₂(bix).

APPENDIX C

Adsorption isotherm profiles obtained from the applications of the Ideal Adsorbed Solution Theory (IAST) for selectivity calculations.



Figure C1. Ideal Adsorbed Solution Theory (IAST) phase diagrams for Cu₂(pzdc)₂(bix) at 25°C.