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Crystal structure, sorption properties, and electronic structure of flexible MOF, (Ni-4,4'azopyridine)[Ni(CN)₄]



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ABSTRACT

The flexible metal organic framework (MOF) compound, Ni(L)[Ni(CN)₄], (L = 4,4'azopyridine (C₁₀N₄H₈), nicknamed AzoPyr) is a 3D porous material that adopts the Hofmann-type structure. This paper reports our synthesis of Ni-AzoPyr and its structural, bonding, and sorption characterization. The red monoclinic crystals (with space group *P2/n*) were found to be multiple twins with three main components related by twin laws. The lattice parameters are a = 7.102 (3) Å, b = 14.154 (4) Å, c = 25.655 (10) Å, $\beta = 92.575$ (12)°, and V = 2577 (2) Å³. Ni-AzoPyr adopts a pillared structure with layers defined by the 2-D Ni [Ni(CN)₄]_n nets and AzoPyr ligands as pillars linking between 6-fold coordinated Ni3 sites. An additional AzoPyr ligand was found to cross link between the 6-fold Ni1 sites to the open ends of the four-fold Ni2 sites. This arrangement results in a 5-fold pseudo square-pyramid for Ni2 and a significantly long Ni2–N distance of 2.436 (11) Å. Density functional theory (DFT) calculations show that almost all states in the conducted at the 5-fold coordinated Ni site. Water molecules were found to be entrapped in the cavities of the structure. In addition to the gating adsorption feature of Ni-AzoPyr, using computational approach, we found that in the absence of water molecules, the pores were found to have a local diameter of 5.8 Å with a maximum number of 15.5 CO₂ molecules per unit cell. The inclusion of disordered water solvent molecules gives rise to the formula of Ni(AzoPyr)[Ni(CN)₄]-0.8H₂O, or C₁₉H₁₂N₁₀Ni₂-0.8(H₂O).

1. Introduction

Porous sorbent materials offer a wide range of structures, compositions, and cost-effective ways that are suitable for adsorption and capture of CO₂ at around atmospheric pressure and at different temperatures, resulting in rapid advances in carbon capture and storage technology. An increasing number of potential solid sorbents have been reported throughout literature [1–21]. Recently, a Sc₂CO₂ monolayer has been demonstrated to be a prospective solid gas sorbent [22]. Flexible porous coordination polymers (or flexible metal organic frameworks (MOFs)) have been developed at a fast pace which show reversible structural transitions between low porosity and high porosity

phases during the adsorption and desorption of guests [4].

The Ni-containing flexible Hofmann-type host structures are described by the general formula $[Ni(L)Ni(CN)_4]n$ (L = pillar ligand), and are collectively called pillared cyanonickelates, or PICNICs [4]. The PICNIC family of compounds was developed for systematic studies of the effect of pore structure and functionality on CO₂ capture and separations. These cyano-bridged complexes have been shown to form polymeric structures with 3-D microporous frameworks [4,5,21]. The sorbents are based on 2-D planar tetracyano-nickelate coordination complex (Fig. 1). The nitrogen-end of the cyanide ligand from NiA coordinates to a 6-fold coordinated transition metal, Ni (NiB). NiB acts as a linear linker between the tetracyano-nickelate groups, creating a 2-D

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Fig. 1. Schematic of the 2D Ni(CN) $_4$ planar structure. NiA represents a 4-fold coordination site and NiB represents a 6-old coordination site.

square grid network (*xy*-plane). NiB in general has a 6-fold octahedral coordination and the organic pillar ligands frequently coordinate along the z-axis. The size of the pores in these materials are partly determined by the lengths of the pillared ligands. Certain PICNICs exhibit hysteretic adsorption-desorption behaviors which is often associated with the 'gate-opening' effect. They also show dynamic host-guest behavior due to structural transitions that occur between the guest-free and guest-loaded states.

Information of the crystal structures of PICNICs is crucial for interpreting sorption data, for modeling calculations, for in-depth understanding of sorption mechanism, and for developing new porous materials. However, structural analyses of these materials can often be complicated by the tendency of these materials to form multiple twinned crystals with disordered ligands and guests. The use of synchrotron Xray diffraction often allow structural analysis to be conducted on micron-sized crystals which might minimize complications associated with crystal twinning. Previously we have studied the crystallography of a number of flexible $[Ni(L)Ni(CN)_4]_n$ compounds and their sorption properties [21], for example, with L = 1,2-bis(4-pyridyl) ethylene (Bpene) (Fig. 2a) [23], and Dpbz (Fig. 2b) [24,25].

Recently, we have been interested in a PICNIC type $[Ni(L)Ni(CN)_4]_n$ compound with L = 4,4'azopyridine (nickname AzoPyr) (Fig. 2c). For simplicity, we refer to the sorbent, Ni(AzoPyr)[Ni(CN)_4], as Ni-AzoPyr.



Structures of Fe-analogs ([Fe (AzoPyr)[M(CN)₄], M = Ni, Pd and Pt) were reported by Agusti et al. [26]. They found ([Fe (AzoPyr)[Pt (CN)₄] (or FePt-AzoPyr) to be disordered, which is tetragonal with space group P4/mmm, a = 7.1670 (5) Å, c = 13.0330 (13) Å. Because of the similar chemical formula of FePt-AzoPyr and Ni-AzoPyr, one might expect similar structure between them. On the other hand, due to the fact that the ligands AzoPyr and 1,2-bis(4-pyridyl) ethylene (Bpene) [23] only differ in the C=C and N=N moiety between the two pyridine rings in the chemical formula, it is also reasonable to expect possible similar structures between Ni-AzoPyr and Ni-Bpene.

The main goal of the present work is to determine the structure/ bonding characteristics of the Ni-AzoPyr compound and to understand the structure and sorption relationships by conducting a comparison of the structures among several other PICNICS and related compounds. In this paper, we summarize our structure determination effort of Ni-AzoPyr using synchrotron X-ray diffraction, the understanding of its bonding characteristics using DFT calculations, the determination of the accessible pore volume and pore surface area using pore size distribution calculations, and the estimation of the maximum amount of CO_2 captured by studying the adsorption/desorption isotherms. The result of comparison of the structures of Ni-Bpene, Ni-Dpbz and Ni-AzoPyr will also be discussed.

2. Experimental methods

2.1. Material synthesis and crystal growth

A technique [23] that we have found to be versatile for crystallization of the PICNIC family of compounds is a modification of a procedure originally used by Černák et al. to prepare crystalline 1-D [Ni(CN)₄] containing chain compounds [27]. The approach involves the use of NH₃ as a blocking ligand since a sufficient concentration of NH3 will prevent the formation of Ni-CN-Ni and Ni-L-Ni bridges which are required for polymerization. If the reaction mixture is contained in an open flask, NH₃ will outgas from the solution. Once the concentration of NH₃ drops below a threshold level, assembly of the Ni(L)[Ni(CN)₄] material will commence. Using a H₂O/DMSO mixture as the solvent and a reaction temperature of \approx 90 °C provided the necessary combination of NH₃ out gassing rate and oligomer solubility to produce the polymeric structures. A good crop of crystals can typically be obtained in 24 h-72 h. The technique has been found to be adaptable to various organic bridging ligands (L) in our laboratory. Crystalline Ni-AzoPyr was prepared from polymeric Ni [Ni(CN)₄]_n (H₂O)₃ and 4,4'-azopyridine in a mixture of water, concentrated aqueous ammonia, and dimethyl sulfoxide (DMSO) at 90 °C in an open flask using the method previously reported for the preparation of Ni-Bpene wherein 4,4'-azopyridine was substituted for the 1,2-bis(4-pyridyl)ethylene ligand in the original synthesis [23]. Water was purified by an in-house reverse osmosis system. All other reagents were purchased from Sigma Aldrich and used as received.

2.2. Synchrotron X-ray diffraction, structure solution and refinements

As most crystals are multiple twins, the crystals that we used for data collection in general have very small dimensions (for example the crystal used for structure determination has a dimension of 0.010 \times 0.007 \times 0.003 mm³ and has a thin-plate morphology). The crystal was mounted on the tip of a glass fiber with Paratone oil and was cooled down to 100 K with an Oxford Cryojet.¹ X-ray diffraction experiments (λ = 0.49594 Å) were performed with a Bruker D8 diffractometer in the vertical mount with a APEX II CCD detector using double crystals

¹ The purpose of identifying the equipment and software in this article is to specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology.

technique with Si(111) monochromator at 30 keV at Sector15 (Chem-MatCARS), Advanced Photon Sources (APS).

The data set was processed using Bruker software (CELL_NOW for identification of twin domains; SAINT for data integration; TWINABS for scaling and multi-scan absorption correction and analysis [28]; (XPREP for space group determination) prior to generating a preliminary structural model (SHELXT, intrinsic phasing method) [29]. Refinement of the structural model was finalized with SHELXL2017 [30]. SHELXL DISP instructions were obtained using the Brennan values within the XDISP program. Two "most disagreeable reflections" with $F_0^2 \ll F_c^2$, (0 1 0) and (0 0 2), were omitted for being partially blocked by the beam-stop.

Carbon-bound hydrogen atomic sites were refined in "riding" (AFIX) positions. For partially occupied H_2O molecules, hydrogen atoms were restrained to chemically reasonable bond distances (DFIX) while maintaining an appropriate H–O–H bond angle (DANG). The Ni sites were refined in an anisotropic manner while isotropic refinements of the C and N sites were performed.

2.3. Electronic structure calculations

We employed the Vienna *ab initio* simulation package (VASP) [31] to calculate the ground state energy of the Ni-AzyPyr structure. The projector-augmented wave (PAW) pseudo-potentials were applied with the generalized gradient approximation (GGA) exchange correlation with an energy convergence of 1×10^{-7} eV. A gamma-centered $8\times 4\times 2$ k-point mesh was used to sample first Brillouin zone [32]. Ni is highly correlated, so Coulomb potentials of $U_{\rm Ni}=8.0$ eV and an on-site exchange potential of $J_{\rm Ni}=1.0$ eV were applied to Ni with Liechtenstein et al. method [33]. Local Density of States (LDoS) was calculated to understand the bonding behavior and hybridization throughout the framework. Partial charge density maps were also calculated for valence band maximum (VBM), from -1 eV to the Fermi energy, and conduction band minimum (CBM), from the Fermi energy to 1 eV, to map electron densities.

2.4. Computational surface characterization

Computational methods were used to estimate the pore size distribution (PSD), to characterize the pore volume and surface area, and to obtain a visualization of the maximum space available for the uptake of CO₂ in the pore. We chose the technique the method of Gelb and Gubbins to compute the PSD [34]. In this method the local pore size at any given location in the material is equal to the diameter of the largest sphere that contains that point without overlapping the material framework. The value of the PSD at a particular pore diameter is the fraction of the free volume with local pore size equal to that diameter. We first reconstructed the Ni-AzoPyr framework from the crystal structure data, identified the coordinates of each atom in the framework, and then drew a van der Waals exclusion sphere around each atom. (van der Waals radii used were 1.63 Å for Ni, 1.09 Å for H, 1.70 Å for C, and 1.55 Å for N) [35,36]). The PSD was then numerically calculated via the voxel technique described by Palmer et al. [37], using cubic voxels with side length 0.1 Å or smaller. We computed the PSD for the structure with the solvent H₂O molecules removed. The pore volume and surface area were characterized by the accessible volume and accessible surface area metrics, which were computed as described by Düren and coworkers [38]. The framework atoms were assigned the radii listed above, and N₂ with assigned diameter of 3.681 Å was used as the probe gas. Use of N2 with this diameter as the computational probe is expected to yield an accessible surface area that correlates well with the BET surface area measured by N₂ adsorption [39]. Lastly, we estimated the CO₂ capacity using a simple, but rapid, technique that we have described in earlier related work [25].

2.5. Adorption/desorption experiments

Gravimetric gas adsorption measurements for the Ni-AzoPyr sample were conducted on a Hiden IGA microbalance. The crystalline sample was first extracted by refluxing in toluene overnight to remove the "extra" guest 4,4'-azopyridine ligand. The isolate solid was then extracted for several hours in boiling acetone until TGA samples showed complete replacement of the toluene guests with acetone. The acetone exchanged sample (\approx 25 mg) was activated by heating under vacuum at 100 °C until the sample weight stabilized. Isotherms were then measured under flowing gas regulated by a mass flow controller and back pressure regulator. Equilibrium was determined at each pressure step using an internal fitting algorithm in the instrument control software. Buoyance corrections were then applied to the final equilibrium weights using the sample crystal density and the known densities of all components in the sample and counterweight chambers with gas densities calculated using REFPROP software [40].

3. Results and discussion

The detailed data collection parameters and refinement results are listed in supplementary Table S1 [30,41]. Atomic coordinates and displacement parameters are given in Table S2. In brief, crystal data for the structure of Ni-AzoPyr C₁₉H₁₂N₁₀Ni₂. 0.8(H₂O) are: M = 512.22, Monoclinic, a = 7.102 (3) Å, b = 14.154 (4) Å, c = 25.655 (10) Å, $\beta = 92.575$ (12)°, V = 2576.5 (16) Å³, T = 100 K, space group P2/n, Z = 4, Synchrotron radiation $\lambda = 0.49594$ Å, $\mu = 0.56$ mm⁻¹.

The solvent DMSO was not found during the structure solution and refinement processes. Although the solvent H₂O water molecule being identified could be highly disordered DMSO molecule, there is not crystallographic evidence to provide a conclusive identification. The 5 highest residuals ($2.15 \text{ e}\text{Å}^{-3}$ to $3.75 \text{ e}\text{Å}^{-3}$) are either near (less than 1 Å) a Ni atomic site or nearly in plane with four Ni atomic site coordinated with CN linkers (residuals are 1.45 Å - 1.67 Å from the carbon atom in CN linker). Most likely these residuals are a result of the multicomponent twinning.

3.1. Crystal structure of Ni(AzoPyr)[Ni(CN)₄]·0.8H₂O

Most crystals in the sample batches consist of multiple twins. Fig. 3 (a) and (b) and 3(c) are the representative precession images of the reciprocal lattices of the Okl, hOl and hkO domains of one of the crystals that we used to solve the structure (more detailed precession images are shown in supplementary Figs. S1, S2 and S3). Our crystal structure model was found to be a 3-component non-merohedral twin. Nonmerohedral twinning occurs when the lattices of the contact twins superimpose in three dimensions, such as by relative rotation of one twin from the other. In our crystal, the second domain is rotated from first domain by 180° about reciprocal axis (-0.006 0.003 1.000) and real axis (0.069 0.011 1.000). The twin law to convert hkl from first to second domain is (-1.001 0.000-0.012, 0.002-1.000 0.006, 0.137 0.023 1.001). The third domain is rotated from first domain by 180° about reciprocal axis (0.001-0.001 1.000) and real axis (0.161 0.000 1.000). The twin law to convert hkl from first to third domain is (-1.000 -0.002 0.003, 0.006-1.000 -0.001, 0.323 0.000 1.000). The refined BASF fractional volume contributions of the twin components is: 1st domain \approx 45%, 2nd domain \approx 27.5%, and 3rd domain \approx 27.5%. As one of our main goals was to understand the relationships of structure and adsorption and electronic properties, our chemically sound structure is sufficed for this purpose.

Ni-AzoPyr was found to adopt the 3-D Hofmann-type structure [42]. The molecular structure of the asymmetric unit with partial labeling is shown in Fig. 4 (The complete labeling is given in Fig. S4). All \equiv CN groups are bridging, creating a 2-D square grid network. The framework of Ni(AzoPyr) is based on the 2-D infinite layer-like tetracyanonickelate Ni [Ni(CN)₄]²⁻ planar complex, or referred to as the square net. The



(a) Okℓ domain

(b) h0ℓ domain

(c) hk0 domain





Fig. 4. A basic motif of the Ni(AzoPyr)[Ni(CN)₄] molecules (including water molecule as solvent), with a partial labeling scheme provided (green-Ni, blue-N, grey-C, red-oxygen). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

chains that make up the 2-D Ni [Ni(CN)₄] square nets are arranged in a zig-zag manner in the order of Ni1, Ni2, Ni3 and repeat (Fig. 5, viewed along *a*-axis). These three Ni sites are crystallographically independent. The Ni1 and Ni3 sites are octahedrally surrounded by six N sites, four



Fig. 5. 3-D grid network (form by tetracyanonickelate molecules) showing the bridging AzoPyr group (Green-Ni, blue-N, grey-C), and the water moleclues. View along a-axis. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

from the CN units and the other two from two AzoPyr ligands. These AzoPyr ligands further bridge together the 2-D Ni [Ni(CN)₄] sheets to form the 3-D pillared-layered structure as shown in Figs. 5 and 6 (viewed along *b*-axis). Ni2 is (4 + 1) fold coordinated, where (4 + 1) fold refers to 4 Ni-C regular bonds and one unusually long Ni-N bond. More specifically, Ni2 is coordinated to four C atoms of the CN groups, but also to the N4 site of an additional AzoPyr ligand, resulting in a long Ni2-N4 distance of 2.436 (11) Å.

Instead of forming an expected parallelepiped shape cavity where the "boundary ligands" of the parallelepipeds are parallel to each other, the AzoPyr ligands originated from Ni1 bonding via N1 on one end was found weakly bonded to the 4-fold Ni2 on the neighboring square net via N4. These ligands while parallel to each other, are perpendicular to the boundary ligands connecting the 6-fold Ni3 via N5 to the Ni3 of the neighboring 2-D net. Using polyhedral representation (Fig. 7, view along



Fig. 6. Framework structure of Ni(AzoPyr)[Ni(CN)₄] viewed along the *b*-axis showing the 2D nets connected by the bpene ligands to form a 3D network (Green-Ni, blue-N, grey-C). The solvent is not included. One sees the alternate empty parallelepiped-shape cavity. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 7. Polyhedral view of the octahedral and square-pyramidal coordination environments of Ni1 (blue), Ni2 (yellow), and Ni3 (pink), respectively, in Ni (AzoPyr)[Ni(CN)₄], view along *a* axis. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

a-axis), one notes small rectangular shape cavities form by the parallel 'extra ligands' alternating with the sets of AzoPyr boundary ligands. One end of the extra ligand is part of the 6-fold ligand from Ni1 (Ni1–N1) and at the other end (Fig. 8, blue octahedra) forms the apex of the square pyramid enclosing the five-fold Ni2 (Ni2–N4) (Fig. 8 yellow pyramid). The Ni2–N4 bond distance is unusually long as mentioned earlier (2.438 (11) Å). In summary, there are two sets of parallel ligands in the Ni-AzoPyr structure that are perpendicular to each other, as can be seen in Figs. 7 and 8. In addition, in each ligand it is seen that the two pyridine rings are almost coplanar.

The bond distances of Ni-N and Ni-C within the 2-D sheet are all within the expected range (Table 1 and Table S3). The mean Ni-C (1.849 Å) and CN (1.18 Å) bond lengths agree with the values reported for other tetracyanonickelate salts [43-46]. The Ni-N distances (range from 2.047 (15) Å to 2.107 (11) Å) in the 6-fold coordination environment are substantially longer than the Ni–C distances (1.83 (2) Å to 1.88 (2) Å), which also conform to the literature values [47–51]. The 6-fold coordinated Ni sites are of high spin configuration because N is acting as a weak-field ligand. When the Ni atom only has 4-coordination (such as that in Ni(CN)₂) [52], the low spin square-planar coordination of the Ni²⁺ ions results in a contraction. Angles around the Ni site of the zig-zag chains that are 180° were determined to be: N1-Ni1-N1, N7-Ni1-N7, N8-Ni1-N8, N5-Ni3-N5, N9-Ni3-N9, and N10-Ni3-N10. Those that are deviated from 180° are: C16-Ni2-C19 (178.2 (8)°) and C17-Ni2-C18 (171.0 (8)°). In the other part of the net, deviations of bond angles from 180° are observed in the followings: N8-C17-Ni2 (170.1 (15)°), N7-C16-Ni2 (175 (2)°), C16-N7-Ni1 (160.2 (13)°, C17-N8-Ni1 (164.0 (13)°), N9-C18-Ni2 (179 (2)°), C18-N9-Ni3 (169.5 (14)°), N10-C19-Ni2 (176 (2)°), and C19-N10-Ni3 (171.2 ((12)°) (Table S4).



Fig. 8. Polyhedral view of the octahedral and square-pyramidal coordination environments of Ni1 (blue) and Ni2 (yellow), respectively, in Ni(AzoPyr)[Ni (CN)₄], view along *b* axis. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

3.2. A comparison of the structure of Ni-AzoPyr with previousy studied Fe (AzoPyr)[Pt(CN)4], Ni-Bpene, and Ni-Dpbz

Despite same ligand in Ni-AzoPyr and FePt-AzoPyr [26], and a slightly different ligand (an azo group vs. ethylene group) in Ni-Bpene, the crystal structures of these materials are substantially different (Fig. 5, S5 and S6). One of the structural features for Ni-AzoPyr is that there is no connection between Ni1 to Ni1 via the AzoPyr ligands. In other words, the blue to blue octahedra are not connected directly (Fig. 8). This feature distinguishes the structure difference between Ni-AzoPyr and that of other PICNICs (such as Ni-Bpene (Fig. S6) [23], Ni-dpbz (Fig. S7) [24,25]), and FePt-AzoPyr (Fig. S5) [26].

FePt-AzoPyr is tetragonal and the structure consists of disordered pyridine rings and disordered N—N groups. The structure was reported as having a parallelepiped type of channels. Back in 2003, Real et al. [53] found interesting communication between Fe(II) building blocks,

Table 1

Selected bond distances (Å) for Ni-AzoPyr.

Bond	Bond Length	Bond	Bond length
Ni1–N8 ⁱ	2.052 (15)	C6–C7	1.36 (2)
Ni1-N8 ⁱⁱ	2.052 (15)	C7–C8	1.387 (19)
Ni1-N7 ⁱⁱⁱ	2.061 (15)	C8–N4	1.359 (18)
Ni1-N7 ^{iv}	2.061 (15)	C9–N4	1.327 (18)
Ni1–N1	2.107 (11)	C9–C10	1.39 (2)
Ni1-N1 ^v	2.107 (11)	N5-C15	1.33 (2)
Ni2-C16	1.83 (2)	N5-C11	1.39 (2)
Ni2-C19	1.841 (18)	C11-C12	1.43 (2)
Ni2-C17	1.843 (19)	C12-C13	1.45 (3)
Ni2-C18	1.88 (2)	C12-C13	1.45 (3)
Ni2–N4	2.438 (11)	C13–N6	1.37 (2)
Ni3–N9 ^{vi}	2.047 (15)	C13-C14	1.42 (3)
Ni3–N9 ^{vii}	2.047 (15)	C14-C15	1.43 (2)
Ni3–N10 ^{viii}	2.064 (15)	N6–N6ix	1.31 (3)
Ni3-N10	2.064 (15)	C16–N7	1.19 (2)
Ni3–N5 ^{viii}	2.100 (12)	N7–Ni1iv	2.061 (15)
Ni3–N5	2.100 (12)	C17–N8	1.17 (2)
N1C1	1.317 (19)	N8–Ni1ii	2.052 (15)
N1-C5	1.362 (18)	C18–N9	1.16 (2)
C1–C2	1.409 (19)	N9–Ni3x	2.047 (15)
C2–C3	1.34 (2)	C19-N10	1.18 (2)
C3–C4	1.41 (2)		
C3–N2	1.451 (19)		
C4–C5	1.42 (2)		
N2-N3	1.261 (18)		
N3-C6	1.471 (19)		
C6–C10	1.34 (2)		

Symmetry codes: (i) x+1/2, -y, z-1/2; (ii) -x+1/2, y, -z+1/2; (iii) x-1/2, -y, z-1/2; (iv) -x+3/2, y, -z+1/2; (v) -x+1, -y, -z; (vi) -x+1, -y+1, -z+1; (vii) x-1, y, z; (viii) -x, -y+1, -z+1; (ix) -x+1/2, y, -z+3/2; (x) x+1, y, z.

and intermolecular interactions play an important role in the π -interactions in mononuclear complexes. In FePt-AzoPyr, the two transition metals have different coordination preference: Fe prefers 6-fold and Pt-4 fold coordination. When both metals are Ni, as in Ni-AzoPyr, the (4 + 1) bond or 5-fold coordination characteristics on the Ni2 site of was observed. Although uncommon, the (4 + 1) fold bonding site has also been found previously in the Ni-Dpbz compound [24,25].

Similar to Ni-Bpene (Fig. S6 [23]) and Ni-dpbz (Fig. S7 [24,25]) where there are guest ligands in the cavities of the structure, we also found guest ligands that are coordinated to the 4-fold Ni sites in the Ni-AzoPyr structure. Also, while DMSO solvent molecules of crystallization were found in Ni-Bpene and Ni-Dpbz, they were not located in the cavities of Ni-AzoPyr, other than a small amount of disordered water molecules (Fig. 5).

3.3. Electronic structure of Ni(Azopyr)Ni(CN)₄

Using DFT calculations, the optimized Ni-AzoPyr lattice parameters are a = 7.28 b = 13.85 c = 26.19 with $\alpha = 90 \beta = 94.34 \gamma = 90$ within 3% of the experimental measurements. The Ni–N bond length for the 6-fold coordinated Ni is 2.07 Å while the longer Ni–N bond length for the 5-fold coordinated Ni is 2.45 Å, both agreeing well with experimental measurements.

The electronic structure of the Ni-AzoPyr framework is detailed in the LDoS, as seen in Figs. 9 and 12. The contributions of the Ni and N atomic species around the 6-fold coordinated Ni are plotted in red while the contributions of the Ni, N, and C atomic species around the 5-fold coordinated Ni are plotted in blue. Bond hybridization occurs around the 6-fold coordinated Ni with the N atom from the -1 eV to Fermi energy 0 eV at the VBM. The 6-fold coordinated Ni also contributes significantly at the CBM. The 5-fold coordinated Ni with the N and C atoms plotted in blue exhibits a significant difference. At the VBM, the majority of bond hybridization occurs between the Ni and N atoms but not with C rings. almost of the states in the CBM are contributed by the 6-fold coordinated Ni, implying that little to no electrons are conducted



Fig. 9. The Local Density of States (LDoS) of Ni-AzoPyr. The electronic contributions for the 6-fold coordinated Ni and surrounding N atoms are accounted for in red, and the 5-fold coordinated Ni and surrounding N and C atoms in blue. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

at the 5-fold coordinated Ni.

The partial charge density map gives the potential locations of electrons at the valence and conduction band edges, as seen in Fig. 10. The yellow isosurfaces indicate the locations of available states where electrons could congregate. The partial charge density map of the VBM shows available states around both the 6 and 5-fold coordinated Ni (Fig. 10a). Specifically, the 6-fold coordinated Ni demonstrates bond hybridization with the surrounding N atoms, while the 5-fold coordinated N i experiences limited interactions with the associated N atoms. The CBM partial charge density map indicates available states around the 6-fold coordination and absence of states at the 5-fold coordination (Fig. 10b). The local density of states (LDoS) and partial charge densities both demonstrate that conduction occurs at the 6-fold coordinated Ni.

3.4. Pore size distribution, pore volume, and surface area

Fig. 11 displays a schematic representation of Ni-AzoPyr in the absence of water molecules. The voids are located near fractional coordinates 0, 1/4, 3/4 and 0, 3/4, 1/4 (\approx 2 Å away from the solvent H₂O molecules). van der Waals radii have been drawn about each constituent atom to indicate the approximate space taken up by the framework atoms. There is an unobstructed pore of approximate width 5.9 Å. Without the solvent molecules, the free volume (volume that are not occupied by the framework atoms) is with approximate 46% of the total volume.

The pore size distribution in Fig. 12 was computed using the structure shown in Fig. 5. Much of the free volume has local pore size less than 2 Å which is practically inaccessible to sorbates of any size. The main pore channel with diameter 5.9 Å is visible and most prominent in the PSD. These larger pores are voids in the material where a relatively large sphere can reside.

The accessible surface areas for Ni-AzoPyr were computed using N_2 and He as the probe gases. The structure without guest molecules, was found to have an accessible surface area of 633.8216 m²/g with N_2 probe. With the same N_2 probe, the accessible pore volume (e.g., the pore volume available to N_2 centers [34]) for the structure in Fig. 11 was computed as 0.03405 cm³/g, and 0.08938 cm³/g using the He probe. While the N_2 porosity was estimated to be 0.04369, the He porosity was 0.1147.

A comparison of the accessible volume and surface area of Ni-Dpbz



Fig. 10. Partial charge densities of Ni-AzoPyr are plotted down the *a* axis for the VMB (a) and CBM (b) where the yellow isosurfaces represent electron density. The green, blue, grey, red, and white atoms represent the Ni, N, C, O, and H atoms respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 11. Molecular structure of Ni(AzoPyr)[Ni(CN)₄] (without solvent), with van der Waals exclusion volume of all atoms shown by colored spheres. Atomic positions were obtained via the crystallographic information from this work. Color codes for atoms: cyan, C; blue, N; white, H; green, Ni. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

with a well-known rigid MOF (ZIF-8) [19] and two other PICNIC compounds Ni-Bpene [23] and Ni-Dpbz [24,25] whose structures were determined previously in our laboratories calculated using the same method is shown in Table 2. In the case of Ni-Bpene, the disordered DMSO were removed. While all three PICNIC compounds have similar Hofmann structure type and have entrapped ligands in the pores, the extra Bpene ligands in Ni-Bpene are not bonded to the framework. However, in Ni-Dpbz and Ni-AzoPyr, the extra ligands are weakly bonded to the 4-fold Ni, resulting in a five-fold pentagonal pyramid geometry. The difference is that in Ni-dpbz, the resulting ligand and boundary ligands are all nominally parallel to each other, whereas in Ni-AzoPyr, while the 'extra ligands are parallel to each other, they are



Fig. 12. Pore Size Distribution (PSD) of Ni-AzoPyr as a function of local pore diameter, as calculated by the method of Gelb and Gubbins [34]. The solid black line is the PSD for the material with only the bound AzoPyr ligands (i.e., the free ligands in the pore channels have been removed) and the solid red line is the PSD for the material with all AzoPyr ligands present. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Accessible pore volume and pore area for Ni-AzoPyr, Ni-dpbz, Ni-bpene and ZIF-8 using N₂ probe.

	Ni-dpbz	Ni-Bpene	Ni-AzoPyr	ZIF-8
N_2 Accessible pore volume (cm ³ /g)	0.00699	0.00990	0.03405	0.172
N_2 Accessible pore area (m ² /g)	507.77	411.65	633.82	1459

perpendicular to the boundary ligands. In Table 2, one also notes that among the three PICNICS, Ni-AzoPyr has the largest accessible pore volume and accessible pore area, followed by Ni-Dpbz and Ni-Bpene. Therefore, despite similar chemical formula of Ni-AzoPyr and Ni-bpene, they have significantly different pore size distribution. However, all these values are much smaller than those in many reported open structures, with ZIF- 8 as an example [19].

3.5. CO₂ sorption isotherms

As was previously done with the Ni-Bpene and Ni-Dpbz materials, the guest ligand in the Ni-AzoPyr material was removed by extraction with boiling toluene in order to increase the available pore space within structure. The Ni-AzoPyr compound, after undergoing an activation procedure to remove the remaining guest solvent, showed flexible behavior during the adsorption and desorption process of CO_2 similar to the absorption behavior of Ni-Bpene and Ni-Dpbz. The threshold pressure (P_{th}) (or gating pressure) associated with the pore opening transition illustrates the characteristics of flexible MOFs for all three samples with the gating pressure dependent on the pillar ligand incorporated into the structure.

In Fig. 13, CO₂ sorption isotherms of Ni-AzoPyr crystals after removal of the guest ligand are depicted at three different temperatures, namely, 0 °C, 25 °C, and 40 °C. It is seen that as the temperature at which the sorption experiments took place, the higher the temperature, the higher the hysteresis pressure or the gate opening pressure (namely, from 0 °C, 25 °C, to 40 °C, the gate opening pressure increases from approximately 1.5 bar, to 2 bar, to 3 bars, respectively. This is likely because as temperature increases, the maximum amount of CO₂ adsorption decreases as a result of greater thermal energy of molecules at increasing temperature. At 8 bar, the maximum amount of CO₂ adsorbed approaches 240 mg/g at 0 °C. As the temperature is warmed to 25 °C, the maximum amount of CO₂ adsorbed is about 220 mg/g. At 40



Fig. 13. Adsorption/desorption curves of Ni-AzoPyz at different temperature (0 °C, 25 °C and 40 °C). The adsorption and desorption behavior for CO_2 show hysteresis loops in all three cases which is the characteristic of a flexible MOF.



Fig. 14. CO_2 adsorption (solid symbols) and desorption (open symbols) isotherms at 10 °C for a crystalline sample of Ni-dpbz prepared as described in Ref. [24].



Fig. 15. CO_2 adsorption/desorption isotherms at 30 °C for Ni-Bpene crystals [23].

°C, the maximum has been reduced to about 190 mg/g.

For comparisons, Fig. 14 gives the CO_2 adsorption behavior at 0 °C for Ni-Bpene [4,54] and Fig. 15 gives the sorption behavior of Ni-Dpbz [24] at 0 °C. The gate opening pressure increases from approximately 1.5 bar in the Ni-AzoPyr material to about 5 bar with bpene as the pillar ligand and close to 8 bar with dpbz as the pillar ligand. The isotherms in Figs. 13–15 all show desorption hysteresis loops associated with the energy barrier of the structure transition. The width and shape of the desorption hysteresis region changes as the pillar ligand is varied. The isotherm behavior for each material is summarized in Fig. 16. The shift in gate-opening pressure across the series is indicative of an inherent energy difference between the closed-pore and open-pore structures for the three materials. All three compounds have 3D monoclinic structures with 2D layers connected via ligands in c-direction, however, the length and chemical nature of the ligand affects the stability of the structural phases. This influence is initially observed by the orientation of the extra "guest ligand" in the single crystal analysis. Each structure incorporates this ligand in a different way. When the extra ligand is removed to yield a material with increased free volume, each material will respond to additional void space in a different way. Hypothetically, this free volume will be reduced through a titling orientation of the pillar ligand.



Fig. 16. Summary of the isotherm behavior of Ni-Bpene, Ni-Dpbz, and Ni-AzoPvr.

The nature of this final tilted pillar arrangement will be a function of the initial guest loaded structural motif, the volume of the free space after the guest ligand is removed, and the ability of the pillar to organize into a close packed state. The more dense and more stable this collapsed phase is, the higher the pressure that will be required to reopen it. It is an interesting observation how a basic pillared layer structural motif can yield a complex interaction of structural variables which affect the structurally dynamic gas adsorption behavior and in doing so provide a rather simple and direct means of tuning this structural response via ligand substitution.

4. Summary

As a summary, Ni-AzoPyr is an intriguing flexible MOF compound that crystallizes with an extra ligand in the unit cell. One end of the extra ligand is bonded to the 6-fold Ni1 and the other end forms a weak bond to the four-fold coordinated Ni2 in a neighboring 2-D Ni(CN)₄ net, resulting in a five-fold square-pyramidal coordination around Ni2. Therefore, Ni2 has a (4 + 1) bond environment, that is a four typical Ni–C bonds and one long Ni–N interatomic distance of 2.438 (11) Å. As synthesized, much of the free volume in the structure has local pore size less than 2 Å which is practically inaccessible to sorbates of any size. The main pore channel with diameter 5.9 Å is visible and most prominent in the PSD. From DFT calculations, the 6-fold Ni1 and Ni3 sites have stronger covalent bond and ionic bond characters, and are more active electron conduction sites than the 5-fold Ni2 site. The Ni-AzoPyr compound after undergoing an activation procedure wherein the extra guest ligand is removed shows a transition to a more porous material with flexible behavior during the adsorption and desorption process of CO₂. The higher the temperature at which the sorption experiments took place the higher the hysteresis pressure (or the gate opening pressure). We plan to continue to understand the mechanism of the sorption process, the hysteresis loop, and the structure/sorption property relationship by developing time-resolved in situ X-ray technique to study the structure of these flexible coordination frameworks as a function of partial pressure of CO₂.

Author statement

W. Wong-Ng - conceptualization, supervision, formal analysis and write original draft. G. T. McCandless - data analysis and writing. J. T. Culp - conceptualization, data curation, formal analysis and writing, M. Lawson-computational modeling and writing, Y. Chen - data curation, formal analysis and writing. D. W. Siderius - data curation, formal analysis and writing. Lan Li- computational modeling and writing. Y. P. Chen - data analysis.

Data availability statement

The data that supports the findings of this study are available within the article (and its supplementary material).

X-ray crystallographic data (Electronic materials as Table S1 to Table S4; Fig. S1 to S7). CCDC 2080844 contains the supplementary crystallographic data for Ni-AzoPyr. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam. ac.uk. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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