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Synthesis, structural and sorption characterization of a Hofmann compound, Ni(3-methy-4,4'-bipyridine)[Ni(CN)₄]



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ABSTRACT

Acetone extraction of crystalline Ni(CN)4-based metal organic framework Ni(3-Methy-4,4'-bipyridine)[Ni (CN)₄] which has dimethyl sulfoxide "DMSO" as guest molecules (nicknamed Ni-BpyMe(D) followed by evacuation yielded the guest-free crystalline framework, (Ni-BpyMe(A)). Ni-BpyMe(A) was determined to be orthorhombic, *Pmma*, *a* = 12.6025(4) Å, *b* = 7.3324(3) Å, *c* = 11.3095(4) Å, *V* = 1045.07 (2) Å³ and *Z* = 2. The structure of Ni-BpyMe(A) consists of a 3-D net built from extended 2-D [Ni(CN)₄] groups. These layers are connected to each other via the BpyMe ligands at the six-fold coordinated Ni1 site while Ni2 has a four-fold coordination environment. While forming infinite square nets, the [Ni(CN)4] chains progress in a zig-zag fashion along the *ab*-direction; they can be projected along *a* or *b* directions. Another feature of this structure is that instead of locating the $-CH_3$ group in one position of the pyridine ring as expected, it appears to be in two mirror-related positions on the same pyridine ring. The structure represents an average of two configurations which gives rise to the pseudosymmetry. The methyl group is distributed equally among each side of the pyridine ring; therefore, the occupancy of the methyl group is 50%. The compound exhibits a Type-I sorption characteristic. The absence of a hysteresis loop indicates that it is not likely a flexible MOF. A comparison of the structure of Ni-BpyMe(A) with the previously reported structure of Ni-BpyMe(D) with DMSO as guest molecules revealed a different structure (Monoclinic P2/ n) as a result of significant increase in the bipyridyl dihedral angle from 34.87° to 90.00° after removal of the guest molecules in the pores. The change in ring orientation of the BpyMe ligands stabilize the pore structure against collapse. The structural change is relevant to gate opening behaviors observed in other MOFs although no gating behavior was indicated in the gas adsorption behavior.

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1. Introduction

Carbon dioxide is known to be the main anthropogenic contributor to global climate change, and carbon mitigation approaches are critical for maintaining a sustainable future [1–3]. Therefore, it is important to have state-of-the-art technologies for capture and storage of CO_2 and other harmful gases. Since gas retention in porous solids is technically and economically feasible, development of solid sorbent materials could provide a cost-effective way to capture CO_2 . According to Zhou and Kitagawa [4], the research field of porous metal-organic frameworks (MOF) has been growing in the past two decades due to five factors: (1) Progress in cluster chemistry, (2) maturation of organic synthesis (ligand design and post-synthetic modification of linkers), (3) advancements in

* Corresponding author. E-mail address: winnie.wong-ng@nist.gov (W. Wong-Ng). evaluation of sorption and structural properties, (4) increase in interdisciplinary MOF investigations, and (5) expanding areas for applications [5,6].

Among various porous materials, multidimensional cyanidebridged complexes prepared by the self-assembly approach are playing an increasingly important role in areas such as ion exchange, materials for gas storage, separation, catalysis and sensing and detection [7-17]. These polymeric metal complexes are special macromolecules formed by metal-ligand-metal bridge connections in one, two, or three-dimensional frameworks. The choice of designed bridging ligands based on functionality, shape, flexibility length, symmetry, and with appropriate coordination sites that can link to the metal-ion connectors is crucial to the construction of desirable Hofmann-type framework [18].

Designs of nanoporous cyanide-bridged coordination polymers are known to involve various flexible pillars with bidentate heteroaromatic *N*-atom donor ligands [19]. As part of the design



and synthesis of a new structural type of flexible MOF materials with Hofmann-type networks [18], Culp et al. [7] reported the successful synthesis of forty-two Ni-tetracyanometallates-based compounds which were nicked-name PICNICS. In general, the framework of PICNICS is built up in a unique manner. In the NiLNi(CN)₄ Hofmann-type structure, the host consists of 2D polymeric layers from Ni_AL₂ cations and Ni_B(CN)₄ anions. The Ni_A atom is coordinated to four C atoms of the CN groups forming a square-planar geometry. The Ni_B ion is octahedrally surrounded by six N atoms, four from the CN units and the other two from two ligand molecules. Fig. 1 gives the schematic of the 2D Ni(CN)₄ layer but omitting the CN units.

Information on the crystal structure of the MOF materials is essential for understanding their physical properties, for performing first-principle calculations and for an in-depth understanding of the mechanisms underlying CO₂ adsorption/desorption processes. Previously in our laboratory we have studied the structure of Ni(3-Methy-4,4'-bipyridine)[Ni(CN)₄] with dimethyl-sulfonyl oxide (DMSO) as a solvent of crystallization (Ni-BpyMe (D)) [20] (Monclinic P2/n). Fig. 2 gives the schematic drawing of the BpyMe ligand. However, to study CO₂ sorption properties of singe crystals, it is necessary to remove DMSO guests from the pores of the single crystals without disrupting the crystalline state. Hot acetone or methanol (MeOH) extraction of the crystals followed by evacuation was found to be effective at removing DMSO guests while preserving the crystalline state of the guest-free material. We performed various characterization of evacuated solvent free Ni(3-Methy-4,4'-bipyridine)[Ni(CN)₄] (or Ni-BpyMe(A)), including computational pore size studies, as well as adsorption/desorption studies of Ni-BpyMe(A). It was interesting to find that the guest-free structure is significantly different. In this paper, we also compare the structures of Ni-BpyMe(A) with Ni-BpyMe(D).

2. Experimental

2.1. Materials synthesis of evacuated Ni-BpyMe(A)

A technique [7,15, 21] that we have found to be versatile for crystallization of $Ni(L)[Ni(CN)_4]$ compounds is a modification of a procedure originally used by Černák *et al.* to prepare crystalline 1-D [Ni(CN)_4] containing chain compounds [22]. In brief, the approach involves the use of NH₃ as a blocking ligand since a suf-



Fig. 1. Schematic of the 2D Ni(CN)₄ planar structure. The C≡N units are omitted.



Fig. 2. Schematic drawing of the BpyMe ligand.

ficiently large 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, the 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. For example, 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 to 72 h. The technique has been found to be adaptable to various organic bridging ligands (L) in our laboratory. The general synthetic strategy has been reported previously [7,15].

To prepare guest-free Ni(3-Methy-4,4'-bipyridine)[Ni(CN)₄], crystals of Ni(3-Methy-4,4'-bipyridine)[Ni(CN)₄](DMSO) prepared as previously described [20] were suspended in acetone or MeOH, and refluxed under N₂ for approximately 4 h at which point TGA tests indicated complete removal of the DMSO guests. The acetone or MeOH was subsequently removed from the pores by evacuation of the isolated crystals at 90 °C for 4 h. The evacuated crystals, Ni-BpyMe(A), were stored under N₂ for three days prior to X-ray diffraction analysis.

We have performed preliminary single crystal X-ray diffraction experiments and found out that the activated samples resulting from MeOH and acetone solvent exchanged samples have the same space group (orthorhombic *Pmma*) and similar lattice parameters. The single crystal quality of the MeOH evacuated crystals were not as good as the acetone ones, therefore we performed detailed crystal structure only using the acetone-evacuated crystals. We have studied the sorption experiments using the MeOH evacuated samples [20]. Since the resulting evacuated samples from both MeOH and acetone have similar structure, we will report the sorption results for the MeOH evacuated sample Here also to demonstrate the feature of the sorption curves as compare with the sorption behavior of a flexible MOF, Ni-Bpene [15].

2.2. Synchrotron X-ray experiments

As most crystals are twins, the crystals that we used for potential data collection in general have very small dimensions (for example the final crystal chosen for this study has a dimension of $0.05 \times 0.03 \times 0.02 \text{ mm}^3$). The crystal was mounted with paratone oil on the tip of a glass fiber and cooled down to 100 K with an Oxford Cryojet. Single crystal X-ray diffraction experiments were performed with a Bruker D8 diffractometer in the vertical mount with an APEX II CCD detector using the double crystal technique (with a Si(111) monochromator at 30 keV and the λ used was 0.41328 Å). The experiments were performed at sector15 (ChemMatCARS), Advanced Photon Sources (APS), Argonne National Laboratory, IL). Data were processed with APEX2 suite software [23] for cell parameter refinements and data reduction. The structure was solved using the direct method and refined on F^2 (SHELXTL) [24]. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms on carbons were placed in idealized positions.

2.3. Adsorption/desorption experiments

Gravimetric gas adsorption measurements for the evacuated Ni-BpyMe sample were conducted on a Hiden IGA microbalance. Sorption experiments are performed on the guest evacuated samples. As mentioned earlier, we have conducted sorption experiments on MeOH exchanged samples, followed by evacuation of MeOH. In brief, the MeOH-containing sample (≈ 25 mg) was activated by heating under vacuum at 90 °C for approximately 1 h 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 known densities of all components in the sample and counter-weight chambers from gas densities calculated using REFPROP [25] software.

2.4. Computational pore size characterization

Ni-BpyMe(A) and Ni-BpyMe(D) have been characterized using computational techniques to estimate the gas-accessible pore volume and porosity, the surface area, and the pore-size distribution (PSD), and to obtain a visualization of the maximum space available for the uptake of CO₂ in the pore. We have used the geometric techniques of Gelb and Gubbins, and of Palmer et al. [26–29] which were discussed in our previous works [17,30–34]. In this study, the pore size of Ni-BpyMe(D) was estimated by theoretically removing DMSO for comparison purpose. For consistency with our previous disclosures, we used the same atomic radii (van der Waals radii were 1.63 Å for Ni, 1.09 Å for H, 1.70 Å for C, and 1.55 Å for N) [35,36]. For clarity, the geometric estimation of surface area presented here should approximate the results of experimental BET measurements [37]. Uncertainties in all quantities were estimated via jackknife analysis over at least ten replicate computational experiments.

To estimate the CO_2 capacity, we computed a highly simplified estimate based on the free volume fraction from the pore-size distribution calculation- Our objective is to achieve a rough estimate of CO_2 capacity based solely on the crystalline adsorbent structure and a minimal set of assumptions, in contrast to a more costly molecular simulation that would also require assignment of a tuned force field and atomic partial charges. The maximum CO_2 capacity may be roughly estimated by representing CO_2 as a sphere of diameter 4.2 Å (larger than C at 3.4 Å diameter and smaller than the major axis of 5.36 Å of CO_2), and then assuming the sphere can access all free volume with local pore size greater than 4.2 Å.

3. Results and discussion

3.1. Crystal structure of Ni(3-methyl-4,4'-bipyridine)[Ni(CN)₄] (Ni-BpyMe(A))

Table S1 gives the crystal data for Ni-BpyMe(A). Fig. 3 gives the crystallographic independent unit with a complete labeling. Tables 1 to 2 list the atomic coordinates of nonhydrogen atoms, and selected bond distances for Ni-BpyMe(A), respectively. The anisotropic displacement parameters, atomic coordinates for the hydrogen atoms and a wider range of bond distances and angles are given in Tables S2 to S4.



Fig. 3. Basic motif of disordered Ni(BpyMe)[Ni(CN)₄] with labels (C-dark grey, *N*-blue, Ni-green, and H-light grey; probability ellipsoids drawn at 50%). The presence of two CH₃ groups was due to disorder. One of the CH₃ group should be replaced by a hydrogen (labeled as H(2) (Table 4)) due to the disordered situation.

The Ni-BpyMe crystal is orthorhombic with space group Pmma (No.51), a = 12.6025(4) Å, b = 7.3324(3) Å, c = 11.3095(4) Å, V = 1045.07 (2) Å³ and Z = 2. (The uncertainties of the lattice parameters are expressed as standard deviations). The structure of Ni-BpyMe(A) consists of a 3-D net built from extended 2-D [Ni (CN)₄] groups. These layers are connected to each other via the BpyMe ligands at the six-fold coordinated Ni1 site. Ni2 has a four-fold coordination environment. One unexpected feature of this structure is that instead of locating the -CH₃ group in one position of the pyridine ring, it appears in two positions. The structure represents an average of two configurations which give rise to the pseudosymmetry. The disordered –CH₃ groups were found to be on either side of the o-position of the pyridine ring, therefore, the occupancy of each methyl group is 50%. In Fig. 3, the presence of two CH₃ groups indicates disorder. One of the CH₃ group is replaced by a hydrogen with an occupancy of 50% (labeled as H (2) (Table S3)). The packing diagrams of Ni-BpyMe(A) are shown in Figs. 4-6.

Figs. 4, 5, and 6 provide different views of the packing of the Ni-BpyMe(A) structure. In Fig. 4, while viewing along *b*, the 2D plane appears in wave form. Along these chains, the angles around C-N-Ni1 and N-C-Ni2 are much deviated from 180°. For example, the angle of C(9)-N(8)-Ni(1) is 161.43(12)° while the N(8)-C (9)-Ni(2) is 174.79(14)° (refer to Fig. 3 for atomic labeling). It is also seen that the two wavy chains of $Ni(CN)_4$ are connected to each other via the 'N' atoms of the pyridine rings. In Fig. 5, the view of the structure is along the *ab* direction, again featuring the wavy form of the Ni(CN)₄ net. It is obvious that the two pyridine rings in the BpyMe ligand are perpendicular to each other, avoiding steric hindrance between the two rings due to the bulky methyl group. In Fig. 6, viewed along the *c*-axis, the projected square-planar 2D net is neatly displayed, and one can see alternate porous channels running along the c-axis. These rows of channels can be considered as parallel to the *a*-axis, alternating with filled channels by the BpyMe ligands.

The bond distances of Ni1-N in the six-fold coordination environment (an average of 2.083 Å) are longer than that of the fourfold coordinated Ni2-C (an average of 1.8601 Å), as expected. The C \equiv N distance was found to be 1.148(2) Å. Bond distances within the bipyridine rings are as expected (Table 2). The average Ni-N distances are substantially longer than the average Ni-C distances, which also conform to the literature values [15]. The 6-fold coordinated Ni are of high spin configuration because nitrogen is acting as a weak-field ligand. When the Ni atom only has 4-coordinations

Table 1

Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (A^2) (x10³) for Ni-BpyMe(A). U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2}U^{11} + ... + 2h k a^* b^* U^{12}]$. 'occ' stands for occupancy.

	х	у	Z	U(eq)	Wyckoff Multiplicity
Ni(1)	7500	5000	1073(1)	15(1)	2f
Ni(2)	5000	0	0	20(1)	2a
N(1)	7500	5000	2931(2)	23(1)	2f
N(2)	7500	5000	9183(3)	25(1)	2f
C(1)	8408(2)	5000	8577(2)	33(1)	4j
C(2)	8450(2)	5000	7351(2)	38(1)	4j
C(3)	7500	5000	6717(3)	32(1) 2f	
C(4)	7500	5000	5410(3)	35(1)	2f
C(5)	7500	6584(5)	4770(3)	69(1)	4k
C(6)	7500	6542(4)	3537(2)	57(1)	4k
C(7)	9520(7)	5000	6767(7)	68(3)	4f (occ. 0.5)
N(8)	6363(1)	2974(2)	1019(1)	25(1)	8ℓ
C(9)	5832(1)	1811(2)	683(1)	23(1)	8ℓ

Table 2

Selected bond lengths [Å] for Ni-BpyMe(A).

Length [Å]
2.0651(12)
2.0651(12)
2.0651(12)
2.0651(12)
2.102(2)
2.138(3)
1.8601(13)
1.8601(13)
1.8601(13)
1.8601(13)
1.322(3)
1.322(3)
1.334(3)
1.334(3)
1.387(3)
1.395(3)
1.501(8)
1.479(5)
1.368(4)
1.338(4)
1.394(4)
1.148(2)

Symmetry transformations used to generate equivalent atoms:

#1 -x + 3/2,-y + 1,z #2 x,-y + 1,z #3 -x + 3/2,y,z.

#4 x,y,z-1 #5 -x + 1,-y,-z #6 x,-y,z #7 -x + 1,y,-z.

#8 x,y,z + 1.

(such as that in $Ni(CN)_2$), the low-spin square-planar coordination of Ni^{2+} ions results in a contraction.

3.2. A comparison of structure of Ni-BpyMe(A) with Ni-BpyMe(D)

The detailed structure of Ni-BpyMe(D) which has DMSO as solvent of crystallization has been described previously [20]. It is interesting that the structures of Ni-BpyMe(D) and Ni-BpyMe(A) are significantly different. The structure of Ni-BpyMe(D) is monoclinic with space group P2/n, a = 13.3483(14) Å, b = 7.1002(7) Å, c = 13.5625(14) Å, and $\beta = 114.834(2)^\circ$, V = 1166.5(2) Å³ and Z = 2. Figs. 7 and 8 give the simulated powder X-ray diffraction patterns for Ni-BpyMe(A) and Ni-BpyMe(D) using the software MER-CURY [38]. It is obvious that the two patterns are substantially different. The basic motif of the Ni-BpyMe(D) molecules and a complete labeling of the crystallographic independent unit is given in Fig. 9. In this case, the structure adopts a more expanded structure in order to accommodate the guest DMSO molecules. The increased volume is obtained via a reduction in the puckering of the Ni[$Ni(CN)_4$]_n sheets. As a result, the volume of the unit cell of Ni-BpyMe(D) of 1166.5(2) Å³ is substantially larger than that of Ni-BpyMe(A) (1045.07(7) Å³).



Fig. 4. Structure of Ni-BpyMe(A) view along the *b*-axis (C-dark grey, *N*-blue, Ni-green).

Fig. 10 shows the packing of Ni-BpyMe(D) along the *b*-axis. The structure and disordered solvent of crystallization, DMSO, was found in the channels of the structure. In each cluster of DMSO, there are two disordered positions of S (S1a and S2b) and O atoms (O1a and O2b), but the two carbon positions are not disordered (C9 and C10) (Fig. 9). The two resolved DMSO molecules are labeled as S1aO1aC9C10 and S2bO2bC9C10 (hydrogen atoms not included).



Fig. 5. Structure of Ni-BpyMe(A) showing that the pyridine rings are perpendicular to each other (C-dark grey, *N*-blue, Ni-green).



Fig. 6. Structure of Ni-BpyMe(A) view along the c-axis, featuring the 2D net and the ligands along the c-axis (C-dark grey, *N*-blue, Ni-green).



Fig. 7. Simulated powder X-ray diffraction pattern for Ni-BpyMe(A) using λ of 1.54056 Å and the software Mercury [38].



Fig. 8. Simulated powder X-ray diffraction pattern for Ni-BpyMe(D) using λ of 1.54056 Å and the software Mercury [38].



Fig. 9. Basic motif of the Ni(BpyMe)(D) molecules (C-dark grey, *N*-blue, Ni-green, and H-light grey; probability ellipsoids drawn at 50%). (C-dark grey, *N*-blue, Ni-green, S-yellow, O-red, and H-white).

Similar to the structure of Ni-BpyMe(A), instead of locating the –CH₃ group in one position of the pyridine ring as expected, it also appears in two positions. The structure Ni-BpyMe(D) represents an average of two configurations which gives rise to the pseudosymmetry. The methyl group is distributed equally among the two pyridine rings (instead of being present on either side of one pyridine ring as found in Ni-BpyMe(A) (Fig. 9)), therefore, the occupancy of



Fig 10. Structure of Ni-BpyMe(D) with disordered DMSO solvent inside the rectangular cage (view along the *b*-axis; C-dark grey, *N*-blue, Ni-green, S-yellow, O-red, and H-white).

the methyl group in each pyridine ring site is also 50%. It is again the over-all randomization that creates the resulting local symmetry. It is likely that the disordered structure gives rise to a lower energy of crystallization.

The bond distances in Ni-BpyMe(A) and Ni-BpyMe(D) are comparable to each other. For example, the bond distances of Ni1-N in the six-fold coordination environment (an average of 2.083 Å) are the same in both compounds, and they are longer than that of the four-fold coordinated Ni2-C distance (an average of 1.8601 Å in Ni-BpyMe(A) as compared to 1.862 Å in Ni-BpyMe(D)), as expected. The average C≡N distance was found to be 1.148 Å in Ni-BpyMe (A) and 1.152 Å in Ni-BpyMe(D). Bond distances within the bipyridine rings are also as expected. The main difference in the geometry of the BpyMe ligands in the two structures is the dihedral angles between the two pyridine rings. In the Ni-BpyMe(D) structure, the dihedral angle is relatively small (34.87°) as compared to the 90.00° angle in Ni-BpyMe(A). In the evacuated structure, the perpendicular arrangement of the two pyridyl rings on the BpyMe ligand allows a close contact between the methyl group of one BpyMe ligand and a neighboring ligand. As discussed below, these molecular contacts help to reduce the crystal free volume while also preventing a more drastic or total collapse of the pillar, thus preserving access to the pore space for small gaseous molecules such as CO₂, N₂, and CH₄.

3.3. Pore size analysis of Ni-BpyMe(A) and Ni-BpyMe(D)

Results of the computational pore size analysis of Ni-BpyMe(A) and Ni-BpyMe(D) are summarized in Table 3. Uncertainty in the last digit of each metric is given in parentheses and corresponds to 95% confidence intervals of the geometric estimates computed via jackknife resampling. Fig. 11 shows an overlay of the PSDs for Ni-BpyMe(A) and Ni-BpyMe(D). Figs. 12–15 display schematic representations of Ni-BpyMe(A) and Ni-BpyMe(D) in the absence of DMSO solvent. Van der Waals radii have been drawn about each constituent atom to indicate the approximate space taken up by

Table 3

Summary of computational structural characterization estimates for Ni-BpyMe(A) and Ni-BpyMe(D). Material porosity is dimensionless. Uncertainty in the last digit of each metric is given in parentheses and corresponds to 95% confidence intervals of the geometric estimates computed via jackknife resampling.

Metric	Ni-BpyMe(A)	Ni-BpyMe(D)
N ₂ Porosity	0.00837(2)	0.01731(1)
He Porosity	0.00673(2)	0.13635(3)
N ₂ volume (cm ³ /g)	0.06720(1)	0.08364(2)
He volume (cm ³ /g)	384.6(4)	0.01552(1)
Surface area (m ² /g)	492(2)	0.12228(2)
CO_2 ratio (mg CO_2 /g adsorbent)	271.7(17.1)	781.8(5)



Fig. 11. Pore Size Distribution (PSD) of Ni-BpyMe(D), blue; Ni-BpyMe(A), orange as a function of local pore diameter, as calculated by the method of Gelb and Gubbins [26] and described in the text; PSD(D) is the volume fraction of the free-volume with local pore size D. Error bars on the PSD of are estimates of the 95% confidence bounds computed via jackknife resampling analysis of at least 10 random realizations of the voxel grid.

the framework atoms. The accessible surface areas for the structures shown in these figures were computed using N_2 as the probe gas. As suggested by structural schematics, both materials have a few primary pores that may admit molecular adsorbates, centered near diameters of 4.5 Å.

Ni-BpyMe(A) shows a split peak in the main pore (Fig. 11), with local maxima at 4.1 Å and near 4.5 Å to 4.7 Å. The split peaks indicate some variability in the local pore structure. A closer examination of the Ni-BpyMe(A) structure (Fig. 12) shows that the pore is fully connected, but with localized regions of different local pore diameter. Fig. 13 gives the graphic of the pores (4.1 Å, 4.3 Å, 4.5 Å, and 4.7 Å). Note that the pores are continuous; the difference in pore diameter in the PSD in this case does not indicate separate pores, but just regions of the same continuous pore space that have different local diameter. As with the pore volume and surface area, this is a result of the sinusoidal sheet form of the Ni backbone. For Ni-BpyMe(D) (Fig. 14), the PSD has a single obvious peak, indicating relative monodispersity in the local pore diameter and a consistent, homogenous pore structure (the cavities on each side of the methyl are symmetric, therefore the PSD has a single peak). Fig. 15 gives the graphic of the Ni-BpyMe(D) pores with same diameters labeled as in Fig. 13 and color-coded identically. Note that the pore structure is also continuous. The major difference

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Fig. 12. Schematic representations of acetone evacuated Ni-BpyMe(A). Van der Waals radii have been drawn about each constituent atom to indicate the approximate space taken up by the framework atoms (Color scheme for framework atoms: Ni-gold, *N*-dark blue, C-light blue, H-white).



Fig. 13. Schematic representations of acetone evacuated Ni-BpyMe(A) showing the pore with local diameters 4.1 Å (green), 4.3 Å (grey), 4.5 Å (orange), and 4.7 Å (red). Note that the pores are continuous. (Color scheme for framework atoms: Ni-gold, *N*-dark blue, C-light blue, H-white).

in the pore structure between the (A) and (D) forms is the significantly smaller volume-fraction of pore space with local diameter 4.3 Å for the (A) form, which is visualized in Fig. 13 by the proportionate reduction in pore space color-coded orange.

The pore space with local diameter larger than 3.5 Å accounts for 62% and 70% of the non-occluded pore volume for the Ni-BpyMe(A) and Ni-BpyMe(D), respectively. The pore volume inaccessible to N₂ (e.g., that with local diameter smaller than 3.681 Å) accounts for 38% and 30% for the Ni-BpyMe(A) and Ni-BpyMe(D), respectively. We estimated the maximum CO₂ capacity to be about 4.8(3) and 8.75(3) CO₂ molecules per unit cell for Ni-BpyMe(A) and Ni-BpyMe(D), respectively. Currently work is underway to use density functional theory (DFT) calculations to study the CO₂ sorption process as a function of CO₂ partial pressure.



Fig. 14. Schematic representations of Ni-BpyMe(D) in the absence of DMSO solvent. Van der Waals radii have been drawn about each constituent atom to indicate the approximate space taken up by the framework atoms. (Color scheme for framework atoms: Ni-gold, *N*-dark blue, C-light blue, H-white).



Fig. 15. Schematic representations of Ni-BpyMe(D) in the absence of DMSO solvent, showing the pore with local diameters 4.1 Å (green), 4.3 Å (grey), 4.5 Å (orange), and 4.7 Å (red). Note that the pores are continuous. (Color scheme for framework atoms: Ni-gold, *N*-dark blue, C-light blue, H-white).

3.4. Guest molecules sorption Isotherms

The gas adsorption properties of a large number of PICNIC derivatives were recently reported [7], in which powder materials were prepared by a heterogeneous ligand intercalation reaction. Figs. 16 and 17 give the CO_2 , CH_4 and N_2 adsorption curves for evacuated crystalline Ni-BpyMe (as mentioned before we used the MeOH exchanged samples followed by solvent removal) at 20 °C and 40 °C [20]. As is typically observed with porous materials, the trend of these curves indicate that the crystal has the highest adsorption capacity for CO₂ as compare to that of CH₄, and N₂ probably due to the fact that CO₂ molecules possess quadrupole moments, therefore enabling interactions with the BpyMe molecules. As the temperature increases from 20 °C to 40 °C, the adsorption amount decreases relatively. This is due to the fact that as temperature increases the thermal energy of the molecules also increases. This behavior is consistent with a physisorption mechanism. Ni-BpyMe(A) shows a typical Type I adsorption isotherm for each gas with no indication of a structure transition or significant interaction of CO₂ with Ni-BpyMe(A) over the measured range of temperature and pressure. The experimental CO₂ capacity at 20 °C of approximately 5 mmol/g agrees well with the computational estimate given above of 4.8 mmol/g for Ni-BpyMe(A). Based on this analysis, the structure appears to remain with the perpendicular arrangement of the BpyMe ligands during CO₂ adsorption



Fig. 16. Adsorption data for CO₂ (diamonds), CH₄ (circles) and N₂ (triangles) at 20 °C on a crystalline sample of Ni-BpyMe(A) [20]. The sample used was the MeOH exchanged sample followed by evacuation.



Fig. 17. Adsorption data for CO₂ (diamonds), CH₄ (circles) and N₂ (triangles) at 40 °C on a crystalline sample of Ni-BpyMe(A) [20]. The sample used was the MeOH exchanged sample followed by evacuation.

and not transition into the larger pore volume structure observed for the Ni-BpyMe(D) with DMSO in the pores. This Type I isotherm behavior is in contrast with the sorption curves of the MOF Ni(1,2bis(4-pyridyl)ethylene)[Ni(CN)₄] (or Ni-Bpene) compound that we studied previously [15]. Ni-Bpene is a flexible MOF that shows a hysteresis adsorption/desorption loop at 30 °C (adsorption (solid)-desorption (open) (Fig. 18)). Description of the structural and flexible adsorption behavior of Ni-Bpene has been given by Allen et al. [14].

It is possible that the presence of the bulky –CH₃ groups and the geometry of the pyridine rings play a role in influencing the adsorption of guest molecules, and subsequently the appearance of adsorption curves. The free volume of the pore is partly governed by the dihedral angles between the two pyridine rings. In Ni-BpyMe(A), the two pyridine rings (with the bulky methyl group) are perpendicular to each other to avoid steric hindrance in the surrounding environment. As a result, there is not much



Fig. 18. Adorption (solid)–desorption (open) behavior for CO_2 at 30 °C on the flexible PICNIC Ni-Bpene [15].

space and freedom for the pillars to tilt as a function of p_{CO2} (and eventually progress to a near-collapsed state). In the Bpene case, the pyridine rings of the ligands are approximately parallel to each other at the high porosity state, therefore it is possible to tilt. Furthermore, the pore volume in the Ni-BpyMe(A) (0.0067 cm3/g) is about 30% smaller than that of Ni-Bpene (0.0090 cm3/g), therefore we observe gate opening and structural transition at high partial pressure (at about 12 bar) and a wide hysteresis region in Ni-Bpene.

4. Conclusions

The structure of Ni(3-methyl-4,4'-bipyridine)[Ni(CN)₄] (Ni-BpyMe) was determined to have different symmetry when dimethyl sulfonate, DMSO (Ni-BpyMe(D) was adsorbed in the pores and when guests were absent in the pores (Ni-BpyMe(A). The structure of Ni-BpyMe in general consists of a 3-D net built from extended 2-D [Ni(CN)₄] groups. These layers are connected via the BpyMe ligands at the six-fold Ni1 sites, while Ni2 has a four-fold coordination environment. The interesting feature of this structure is that instead of locating the $-CH_3$ group in one position of the pyridine ring, it appears in two positions in both cases due to disorder.

The Type-I adsorption curve indicates Ni-BpyMe(A) to be a relatively rigid MOF during adsorption of weakly interacting guests such as CO₂, CH₄, and N₂ as no hysteresis loop was observed. A review of the structures and guest adsorption behaviors of Ni-BpyMe(A) and Ni-Bpene shows that while both materials adopt a similar pillared layer motif, the Bpene compound shows structurally dynamic behavior that transitions between a low porosity and high porosity state during the adsorption and desorption of guests, such as CO₂. The Ni-BpyMe material, in contrast, shows an initial structural transition between the as-synthesized crystal with DMSO guests in the pores and the guest-free structure, but then appears to retain a relatively rigid structure with insignificant variation in pore structure between the guest-loaded and guestfree states during CO₂ adsorption/desorption. One possible explanation is that the bulky pyridine rings with the methyl group which are perpendicular to each other resulted in insufficient space or freedom for the pillars to tilt as a function of p_{CO2} , whereas in the Ni-Bpene case, the pyridine rings of the ligand are approximately parallel to each other in the high porosity state. In addition, the adsorption enthalpy of CO_2 does not appear to be enough to

provide the energy need to change the dihedral angle of the BpyMe ligand and further expand the crystal free volume as observed for the DMSO loaded crystal. Furthermore, the pore volume of Ni-Bpene is greater than that in Ni-BpyMe(A) by about 30%. As a result, it is possible to have a large tilt angle, or a near-collapsed state in Ni-Bpene.

To understand the differences in the sorption characteristics of various cyanide-bridged MOFs, it is important to study the *in-situ* sorption mechanism as well as performing first-principle density functional theory (DFT) calculations of the stable arrangement of CO_2 as a function of p_{CO2} . DFT calculations have been reported in literature for understanding electronic structure and location of CO_2 in the pores/channels of the MOF materials [17,39,40]. We are in the process of using DFT to study the electronic structure as well as the energetics of the system. We are also in the process of studying the *in situ operando* small-angle neutron and X-ray scattering, neutron diffraction and X-ray diffraction under relevant gas pressure and flow conditions (including adsorption under supercritical pressure conditions) to determine possible enhancements of CO_2 gas adsorption.

CRediT authorship contribution statement

W. Wong-Ng: Conceptualization, Supervision, Formal analysis, Writing - original draft. **J. Culp:** Conceptualization, Data curation, Formal analysis, Writing - review & editing. **D.W. Siderius:** Data curation, Formal analysis, Writing - review & editing. **Y. Chen:** Data curation, Formal analysis. **S.Y.G. Wang:** Data curation, Formal analysis. **A.J. Allen:** Formal analysis. **E. Cockayne:** Formal analysis.

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

X-ray crystallographic data (Electronic materials as Table S1 to Table S4). CCDC 2046166 contains the supplementary crystallographic data for Ni-BPyMe(A). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 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. Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2021.115132.

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