



Two Zn(II) and Co(II) compounds with dicarboxylates and curved 4,4'-azopyridine ligands: Syntheses, crystal structures and gas sorption properties

Jue Wang, Ying Zhang, Xiao-Qing Liu, Jie Xiao, Hu Zhou, Ai-Hua Yuan *

School of Biology and Chemical Engineering, Jiangsu University of Science and Technology, Zhenjiang 212003, China

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ABSTRACT

Two new compounds Zn(PDA)(AZPY)·4H₂O (**1**) and [Co(NDC)(AZPY)]₂·2H₂O·DMF (**2**) (H₂PDA = pyridine-2,6-dicarboxylic acid, AZPY = 4,4'-azopyridine, H₂NDC = 2,6-naphthalenedicarboxylic acid) were prepared through solvothermal reactions and characterized. Single crystal X-ray diffraction analysis indicates that compound **1** exhibits a one-dimensional chain structure, while compound **2** features a three-dimensional framework. Notably the bridged AZPY ligands involved in both compounds exhibit rare bent configurations. The thermal stability and gas sorption properties of compound **2** have also been studied. A normal amount (2.8 mmol g⁻¹) of hydrogen uptake at 1 atm and -196 °C for compound **2** were observed, which can be attributed to the presence of micropores.

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1. Introduction

In recent years, metal organic frameworks (MOFs) have attracted extensive attention due to their unusual topological architectures [1] and potential applications in gas storage, drug delivery, and separations [2–4]. Although large numbers of MOFs have been produced [5,6], the design and structural control on self-assemble MOFs still remain a long process. The success syntheses of MOFs are mainly based on the concept of network design [7] and the structures of organic ligands have played a key role in the formation of the coordinated crystal engineering [8]. Several groups have used copolymerization synthesis approach for the construction of novel MOFs in the latest studies, among which the dipyrindyl-type ligands (N-donors) and polycarboxylic acids (O-donors) with more tunable factors were widely employed [9–12].

The aromatic *N*-heterocyclic, electron-rich 4,4'-azopyridine ligand (AZPY), because of its ability to form hydrogen bonds with anions or with solvent molecules, as well as π -back-donating to generate electron transfer and delocalization, has been used as an excellent linker for constructing architectures of MOFs, which possibly exhibit some potential gas sorption and photoelectric properties [13–24]. Furthermore, it has been chosen to build MOFs together with diverse polycarboxylates, which are either aliphatic (glutarate [13], ethylmalonic acid [14]) or aromatic (H₂BDC = 1,4-benzenedicarboxylate [15,16], *o*-phthalate [17], 1,2,4,5-benzenetetracarboxylic acid [18], H₄bpta = 1,1'-biphenyl-2,2',6,6'-tetracarboxylic acid [19], methanetetra benzoic acid [20], 2,3,6,7-anthracenetetracarboxylic

acid [21]), or *N*-heterocyclic acid (pyrazine-2,3-dicarboxylate [22], dipicolinate [23,24]). Our tentative idea is to design porous frameworks with long spacer AZPY and rigid aromatic polycarboxylic acids, which could be considered for potentially gas sorption properties. Recently, we have prepared and structurally characterized a new compound [Co(BDC)(AZPY)]₂·2DMF·0.5 H₂O [25]. In the structure, both AZPY and carboxylate terephthalic acid are coordinated with the metal to form a 2D layer.

As a subsequent work, two kinds of carboxylic acid, being pyridine-2, 6-dicarboxylic acid (H₂PDA) and aromatic 2, 6-naphthalenedicarboxylate (H₂NDC), were employed as bidentate O-donor ligands, due to their robust structure and commercial availability. H₂NDC, belonging to the aromatic carboxylate homologs, has participated in making up series of excellent MOFs with high surface area. An intriguing example is DUT-6 with the high total pore volume of 2.02 cm³ g⁻¹ [26]. So the rigid H₂PDA as well as H₂NDC and the semi-rigid AZPY were applied as mixed ligands to coordinate with metal Zn(II) and Co(II) and two coordinated polymers possessing interesting frameworks have emerged. Herein we present the syntheses, structures and characterizations for two compounds Zn(PDA)(AZPY)·4H₂O (**1**) and [Co(NDC)(AZPY)]₂·2H₂O·DMF (**2**). The thermal stability and gas sorptions for compound **2** were also studied.

2. Experimental

2.1. Materials and physical measurements

Pyridine-2,6-dicarboxylic acid (H₂PDA), 2,6-naphthalenedicarboxylate (H₂NDC), *N,N*-dimethylamide (DMA), *N,N*-dimethylformamide

* Corresponding author.

E-mail address: aihuayuan@163.com (A.-H. Yuan).

(DMF), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ were purchased from J&K CHEMICA in a reagent grade and used without any purification. 4,4'-azopyridine (AZPY) was prepared according to the literature procedure [27,28]. Infrared spectra as KBr pellets were recorded using Avatar Nicolet FT-1703x FT-IR spectrophotometer from 4000 to 400 cm^{-1} . Thermogravimetric analyses (TGA) were taken on a Pyris Diamond analyzer heated from room temperature to $550\text{ }^\circ\text{C}$ in nitrogen atmosphere at a heating rate of $10\text{ }^\circ\text{C min}^{-1}$. Powder X-ray diffraction (PXRD) measurements were performed on a Shimadzu XRD-6000 diffractometer with $\text{CuK}\alpha$ radiation ($\lambda = 1.5418\text{ \AA}$). The nitrogen and hydrogen adsorption isotherms were measured using an automatic volumetric adsorption equipment (ASAP 2020, Micromeritics). Preceding to gas sorption experiments, the guest solvent molecules were removed by thermal activation at temperature of $180\text{ }^\circ\text{C}$ under vacuum over 24 h. The adsorption isotherms of N_2 and H_2 were measured at $-196\text{ }^\circ\text{C}$.

2.2. Syntheses

2.2.1. Preparation of $\text{Zn}(\text{PDA})(\text{AZPY}) \cdot 4\text{H}_2\text{O}$ (**1**)

A mixture of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.0297 g, 0.1 mmol), H_2PDA (0.01667 g, 0.1 mmol), AZPY (0.0184 g, 0.1 mmol) combined with 6 mL DMF was stirred for 20 min at room temperature. Then the solution was heated in a 30 mL Teflon-lined stainless-steel vessel at $160\text{ }^\circ\text{C}$ for 3 days, and then cooled to room temperature at the rate of $10\text{ }^\circ\text{C h}^{-1}$. The colorless block-shaped crystalline product was collected by filtration, washed with DMA, and then air-dried.

2.2.2. Preparation of $[\text{Co}(\text{NDC})(\text{AZPY})]_2 \cdot 2\text{H}_2\text{O} \cdot \text{DMF}$ (**2**)

A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.0238 g, 0.1 mmol), 2,6-NDC (0.0216 g, 0.1 mmol), AZPY (0.0184 g, 0.1 mmol) combined with 10 mL DMF was stirred for 20 min at room temperature. Then the solution was heated in a 30 mL Teflon-lined stainless-steel vessel at $140\text{ }^\circ\text{C}$ for 2 days, and then cooled to room temperature at the rate of $3\text{ }^\circ\text{C h}^{-1}$. The purple block-shaped crystalline product was collected by filtration, washed with DMF and then air-dried.

2.3. Crystallographic data collection and structure determination

Single-crystal X-ray diffraction of compounds **1** and **2** were performed on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated $\text{MoK}\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$). The structure were solved by patterson method using SHELXS-97 program and refined on F^2 within SHELXL-97 [29,30]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated at idealized positions. The H atoms bound to water

Table 1
Crystallographic data and refinement details for compounds **1** and **2**.

Compounds	1	2
Chemical formula	$\text{C}_{17}\text{H}_{19}\text{ZnN}_5\text{O}_8$	$\text{C}_{47}\text{H}_{39}\text{Co}_2\text{N}_9\text{O}_{11}$
Formula weight	486.74	1023.73
Crystal system	Orthorhombic	Monoclinic
Space group	<i>Cmc</i> 21	<i>C2/c</i>
<i>a</i> / \AA	10.509(5)	31.781(2)
<i>b</i> / \AA	24.643(12)	16.4904(12)
<i>c</i> / \AA	12.359(6)	23.2119(18)
α / $^\circ$	90.00	90.00
β / $^\circ$	90.00	117.2850(10)
γ / $^\circ$	90.00	90.00
<i>V</i> / \AA^3	3201(3)	10811.2(14)
<i>Z</i>	4	8
Calculated density / g cm^{-3}	1.010	1.258
μ / mm^{-1}	0.803	0.675
<i>F</i> (000)	1000	4208
<i>S</i>	1.056	1.092
$R_1, \omega R_2$ [$I > 2\sigma(I)$]	0.0426, 0.1166	0.0541, 0.1455
$R_1, \omega R_2$ (all data)	0.0607, 0.1203	0.0686, 0.1503

Table 2
Selected bond lengths (\AA) and angles ($^\circ$) for compounds **1** and **2**.

Compound 1			
N1–Zn1	1.950(4)	O1–Zn1	2.138(6)
N2–Zn1	2.071(3)	O3–Zn1	2.181(5)
Zn1–N2 ⁱⁱⁱ	2.071(3)		
N1–Zn1–N2	128.62(9)	N1–Zn1–O3	78.6(3)
N2–Zn1–N2 ⁱⁱⁱ	102.05(17)	N2–Zn1–O3	101.53(16)
N1–Zn1–O1	78.6(3)	O1–Zn1–O3	157.17(14)
N2–Zn1–O1	92.70(18)		
Compound 2			
Co1–N1	2.034(2)	Co2–N5	2.058(2)
Co1–O1	2.044(2)	Co2–O5	2.131(2)
Co1–N8 ^{iv}	2.075(3)	Co2–O6	2.181(2)
Co1–O3 ^v	2.113(2)	Co2–O7	2.234(2)
Co1–O4 ^v	2.184(2)	Co2–O8	2.156(2)
Co2–N4	2.064(2)		
N1–Co1–O1	84.41(10)	N5–Co2–O8	98.96(9)
N1–Co1–N8 ^{iv}	105.33(11)	N4–Co2–O8	93.46(9)
O1–Co1–N8 ^{iv}	96.80(11)	O5–Co2–O8	146.00(9)
N1–Co1–O3 ^v	145.30(9)	N5–Co2–O6	104.89(9)
O1–Co1–O3 ^v	116.81(9)	N4–Co2–O6	150.60(9)
N8 ^{iv} –Co1–O3 ^v	99.25(9)	O5–Co2–O6	58.57(8)
N1–Co1–O4 ^v	92.08(9)	O8–Co2–O6	100.73(10)
O1–Co1–O4 ^v	160.34(9)	N5–Co2–O7	148.81(9)
N8 ^{iv} –Co1–O4 ^v	102.78(10)	N4–Co2–O7	104.90(9)
O3 ^v –Co1–O4 ^v	58.40(8)	O5–Co2–O7	86.68(8)
N5–Co2–N4	98.07(9)	O8–Co2–O7	59.32(9)
N5–Co2–O5	111.86(8)	O6–Co2–O7	62.54(10)
N4–Co2–O5	95.99(8)		

Symmetry codes:

Compound **1**: (iii) $-x + 2, y, z$.

Compound **2**: (v) $x, -y, z + 1/2$; (vi) $x + 1/2, y + 1/2, z$.

molecules were located from difference Fourier maps and refined as riding mode. The crystallographic data and refinement details of compounds **1** and **2** are given in Table 1. Selected bond lengths and bond angles are summarized in Table 2.

3. Results and discussion

3.1. IR analysis of compounds **1** and **2**

IR spectra of compounds **1** and **2** are shown in Fig. 1. The existence of AZPY ligands was reflected by the bands of aromatic $\nu(\text{C}-\text{H})$ vibrations and characteristic band at 1541 cm^{-1} . The bands of stretching vibrations $\nu(\text{O}-\text{H})$ were found at 3427 cm^{-1} for compound **1**, 3446 cm^{-1} for compound **2**, indicating that the water molecules exist in the structures. The bands of antisymmetric carboxylate stretch, $\nu_{\text{as}}(\text{COO}^-)$, were found at 1620 cm^{-1} for compound **1**, 1616 cm^{-1} for compound **2**. And the bands of symmetric

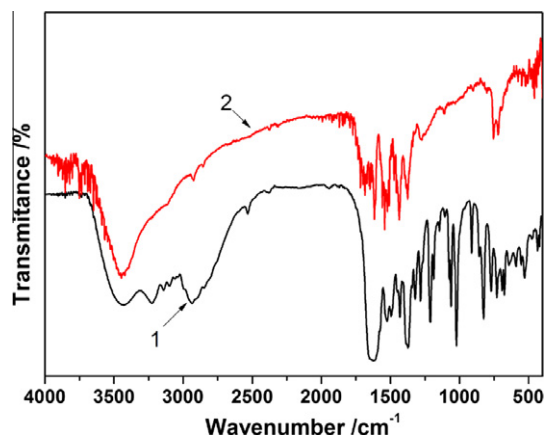


Fig. 1. Infrared spectra of compounds **1** and **2**.

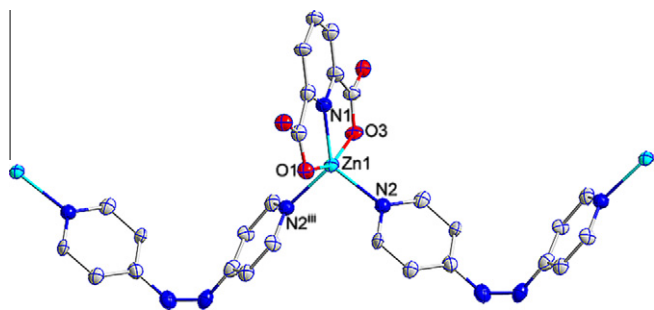


Fig. 2. ORTEP diagram of compound **1** with displacement ellipsoids drawn at 30% probability level. Crystallized water molecules and all hydrogen atoms have been omitted for clarity. Symmetry codes: (iii) $-x + 2, y, z$.

$\nu_s(\text{COO}^-)$ stretches were found at 1373 cm^{-1} for **1**, 1436 cm^{-1} and 1375 cm^{-1} for **2**. In compound **1** the $\Delta\nu(\text{COO}^-) = \nu_{as}(\text{COO}^-) - \nu_s(\text{COO}^-)$, is 247 cm^{-1} (more than 200 cm^{-1}), indicating that the carboxylate group belongs to the monodentate coordination mode. And the fact that the $\Delta\nu(\text{COO}^-)$ of compound **2** is 180 cm^{-1} (less than 200 cm^{-1}) and 241 cm^{-1} , reveals there are both bidentate and monodentate coordination circumstances for the COO^- groups of NDC.

3.2. Structural descriptions of compounds **1** and **2**

Single-crystal X-ray diffraction analysis reveals that the asymmetric unit of compound **1** consists one Zn(II) center, one deprotonated PDA^{2-} , one AZPY and four guest water molecules (Fig. 2). The zinc atom is coordinated by two oxygen atoms (O1, O3) and one nitrogen atom (N1) from the same PDA^{2-} ligand, and two nitrogen atoms (N2, N2ⁱⁱⁱ); symmetric code: (iii) $-x + 2, y, z$), from two different pyridine rings of AZPY to furnish a distorted trigonal bipyramid geometry. The average distances of Zn1–O and Zn1–N are 2.1595 and 2.0105 Å, respectively. The AZPY, acting as a bridging ligand, connects the adjacent Zn atoms (Zn...Zn distance is 10.509 Å) to form a 1D zigzag chain (Fig. 3). The PDA^{2-} ligand fails to construct the skeleton and turns out to be an auxiliary ligand. It is worth noting that the AZPY ligand in compound **1** exhibits rare bending configuration, which has been observed in the 2D compound [25]. In addition, the AZPY *gauche* arrangement in our case is also different from the *trans* configuration in other MOFs [23,24].

Compared with compound **1**, compound **2** crystallizes in the monoclinic space group $C2/c$. In the structure (Fig. 4), the NDC^{2-} ligands adopts two coordinated modes: monodentate and bidentate. There are two crystallographically independent cobalt(II) centers (Co1 and Co2). The Co1 atom is five-coordinated by two nitrogen atoms from two AZPY and three oxygen atoms from two NDC^{2-} ligands, forming a distorted CoN_2O_3 pyramid geometry, in which O1, O3^v and O4^v occupy the equator plane, and N1 and N8^{iv} are in axis direction. The bond lengths of Co1–O range from 2.044(2) to 2.184(2) Å, and Co1–N from 2.034(2) to 2.075(3) Å. The Co2 atom is six-coordinated by two nitrogen atoms from two AZPY ligands and four oxygen atoms from two NDC^{2-} ligands to afford a distorted CoN_2O_4 octahedral geometry. The average bond lengths of

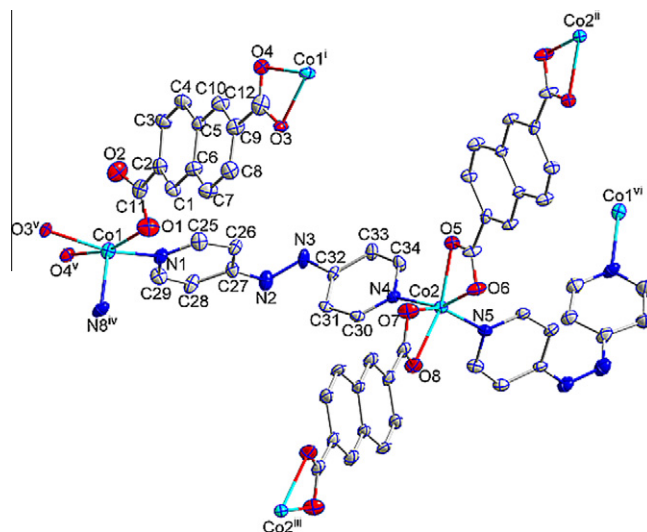


Fig. 4. ORTEP diagram of compound **2** with displacement ellipsoids drawn at 30% probability level. Crystallized water and DMF molecules and all hydrogen atoms have been omitted for clarity. Symmetry codes: (i) $x, -y, z - 1/2$; (ii) $-x + 1/2, -y + 1/2, -z$; (iii) $-x, -y + 1, -z$; (iv) $x - 1/2, y - 1/2, z$; (v) $x, -y, z + 1/2$; (vi) $x + 1/2, y + 1/2, z$.

Co–O and Co–N are 2.178 and 2.061 Å, respectively. Similar to compound **1**, two AZPY ligands in compound **2** are also bent and connect adjacent Co(II) centers. The two pyridine cycles in AZPY appear bending and the C27–N2–N3–C32 torsion angle between the two planes is 90.14° . Thus, the distance between Co1 and Co2 (Co1...Co2 distance is 10.771 Å) bridged by AZPY are less longer than those bridged by the rigid linker 2,6- H_2NDC (Co1...Co1 and Co2...Co2 distances are 12.893 Å and 13.030 Å, respectively) [31]. So each Co center connects to four adjacent Co atoms via two NDC^{2-} ligands and two AZPY spacers to form a 3D framework. The solvent accessible void in the structure accounts for approximately 32% of the crystal volume calculated with PLATON software [32], and the voids were occupied by guest DMF and water molecules. To further explore the network, the topology method based on the connectivity was considered. Co1 and Co2 are viewed as four-connected nodes, and the bridged ligands (AZPY and NDC^{2-}) are both simplified to be linear connectors; then the combination of nodes and connectors gives a 3D porous framework (Fig. 5).

It should be noted that, AZPY ligands in both compounds showed rare bending configurations, and there are no other examples instead of some *cis* isomers appeared in the articles. The photosensitive azobispyridine gold(I) complexes in solution isomerize to the *cis* azo isomer under UV irradiation [33]; and the two compounds $[(\text{Cp}^*_2\text{Ti})_4(\mu_2\text{-N,N}';\eta^2\text{-N,N}'\text{-C}_{10}\text{H}_8\text{N}_4)_2]$ and $[(\text{tBuCp}_2\text{Ti})_4(\mu_2\text{-N,N}';\eta^2\text{-N,N}'\text{-C}_{10}\text{H}_8\text{N}_4)_2]$ the azo ligands experience a conformational rearrangement from *trans* to *cis* within self-assembly process [34]. We suppose that the bending of semi-rigid AZPY in compound **1** and **2** can be ascribed to the high reaction temperature. During the solvothermal process, a free rotation along C–N σ -bond is possible by heating, resulting in the *trans* to *gauche*

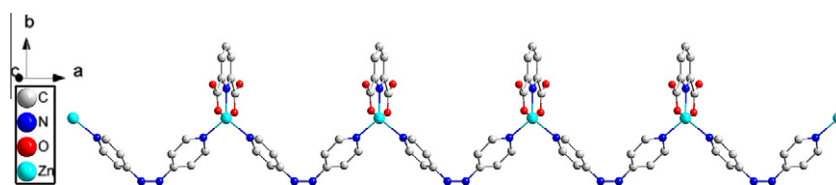


Fig. 3. The 1D zigzag chain of compound **1**. Crystallized water molecules and all hydrogen atoms have been omitted for clarity.

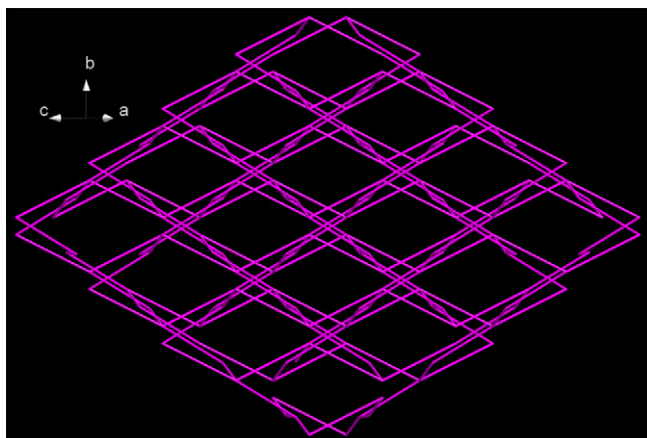


Fig. 5. The 3D open network of compound 2.

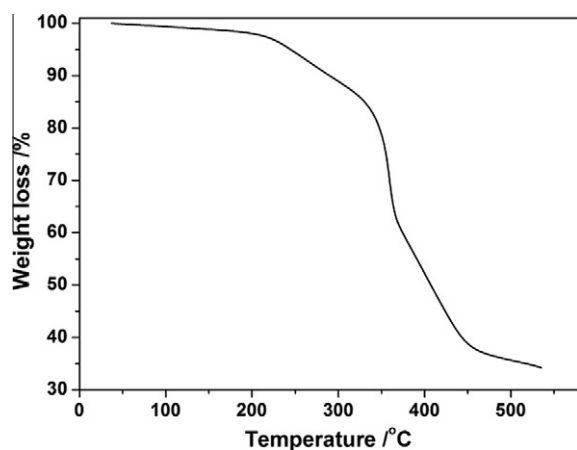


Fig. 6. Thermogravimetric curve of compound 2.

rearrangement when less special obstruction between the two pyridine planes occurs.

3.3. Thermal stability and gas sorption properties of compound 2

The TG curve of compound 2 was shown in Fig. 6. The initial weight loss (3.19%) in the range of 37–225 °C corresponds to the loss of two guest water molecules (calcd. 3.51%). The second weight loss was in the range 225–290 °C and the mass loss of 6.80% observed which attributes to one DMF molecule (calcd. 7.13%). And after 290 °C the framework collapsed.

To investigate the characteristics of the porous framework, N₂ and H₂ adsorption experiments were carried on at –196 °C. The nitrogen adsorption isotherm (Fig. 7) of compound 2 can be classified as type I, typical of microporous materials. Fitting the Brunauer-Emmett-Teller (BET) equation gives the surface area of 38 m² g^{–1}, which is close to that of {[Zn₂(OH)(AZPY)(BDC)_{1.5}](H₂O)_n} (32 m² g^{–1}) [15]. A small additional amount at higher pressures is adsorbed, most probably multilayers on the external surface. The lower porosity can be attributed to the very small micropore size (average pore diameter of 3.11 Å) in the structure. The hydrogen loading at 1 atm and –196 °C was 2.8 mmol g^{–1}, which is remarkably high when compared to the nitrogen micropore capacity. The kinetic diameters for N₂ and H₂ molecules are 3.64 and 2.8 Å, respectively. The greater molar uptake of H₂ over that of N₂ under the same conditions can be attributed to the closer packing of the smaller H₂ molecule in the ultramicropores. The hydrogen uptake for

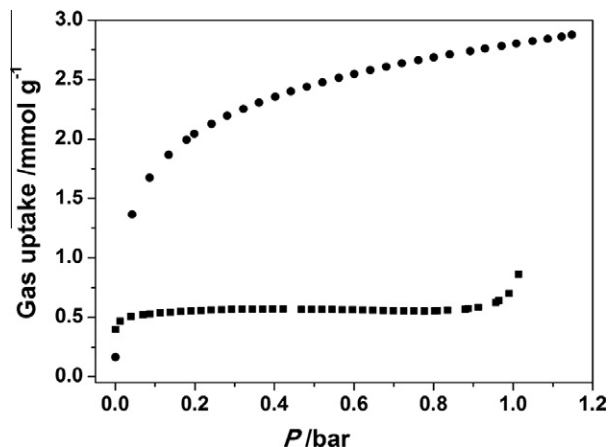


Fig. 7. N₂ (■) and H₂ (●) sorption isotherms at –196 °C for compound 2.

compound 2 is higher than that of Co₃(NDC)₃DMF₄ (2.0 mmol g^{–1}) and Mn₃(NDC)₃DMF₄ (1.8 mmol g^{–1}) with the surface areas are 110 m² g^{–1} and 18 m² g^{–1}, respectively [30].

4. Conclusion

We have synthesized two new compounds (1 and 2) constructed by aromatic dicarboxylic acids (H₂PDA, H₂NDC) and AZPY linkers, in which the AZPY units are unusually bent. The ultramicropores involved in the structure of compound 2 are responsible for the higher uptake of H₂ over N₂ under the same conditions. Our continuous attempts are underway to prepare new compounds with potential functionalities, employing other mixed ligands.

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