Supplementary Information ESI

Nickel(II)-Azido Ferromagnetic Chains in 3D Porous Metal-Organic Framework with Breathing Guest Molecules

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Materials, Methods, Syntheses and Characterizations

All the reagents for synthesis were obtained commercially and used as received.

Complex $\{[\mathrm{Ni}(\mathrm{N}_3)_{0.5}(\mathbf{L})_{1.5}\mathrm{H}_2\mathrm{O}]\cdot\mathrm{EtOH}\}_n$ **1** was prepared by hydrothermal reaction. A mixture of NaN_3, $Ni(NO_3)_2\cdot 6H_2O$, isonicotinic acid (**L**H) and urea at a ratio of 1.5:2:2:0.3 in 15 mL 50% aqueous ethanol was sealed in a Teflon-lined stainless steel vessel, heated at 140 °C for 2 days under autogenous pressure, and then cooled to room temperature. Green block crystals of **1** were harvested in a yield of 48%.

CAUTION: *Azide complexes are potentially explosive. Only a small amount of the materials should be prepared, and it should be handled with care.*

We tried to obtain **1** without the presence of the apparently innocent urea or using other solvents systems, but all attempts were unsuccessful. For the nature of urea, we speculate that it may mainly affect the pH of the reaction mixture, along with the mixed-solvent medium, and playing the key role in the formation of **1**.

The phase purity of **1** is confirmed by the X-ray powder diffraction. XRPD was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Simulation of the XRPD spectra was carried out by the single-crystal data and diffraction-crystal module of the *Mercury* program available free of charge *via* internet at *http://www.iucr.org.* XRPD patterns are shown in Fig. 1S.

Single-crystal X-ray diffraction measurement for **1** and **2** were carried out on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam. The determinations of unit cell parameters and data collections were performed with Mo-Kα radiation (λ = 0.71073 Å) at 294(2) K and unit cell dimensions were obtained with least-squares refinements. The program SAINT (Bruker, *SAINT Software Reference Manual*, Madison, Wisconsin, 1998) was used for integration of the diffraction profiles and semi-empirical absorption corrections were applied using SADABS program (Bruker, *SADABS: Program for Expirical Absorption Correction of Area Detector Data*, Madison, Wisconsin, 1998). The positions of metal atoms were located from direct-method E map, other non-hydrogen atoms were located in difference Fourier syntheses and and least-squares refinement cycles, and finally refined anisotropically. The hydrogen atoms of the ligands were placed theoretically onto the specific atoms and refined isotropically as riding atoms. The hydrogen atoms of hydroxyl were added by difference Fourier maps and the location of water hydrogen atoms were calculated by programme WinGx. Crystallographic data (excluding structure factors) for **1** has also been deposited on the Cambridge Crystallographic Data Centre as supplementary publication (no. CCDC-668703). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (.44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Single-crystal X-ray diffraction of **1** and **2** reveal that they crystallize in the monoclinic space group C2/c and have a 3D framework structure. Ni(1) is coordinated by two oxygen atoms from two isonicotinate ligands of type (1) (isonic(1)) with μ_2 bridge mode, two oxygen atoms from two water molecules, and one nitrogen atoms from another type of isonic(2) with μ_3 bridge mode. The equatorial plane of Ni(2) consists of two nitrogen atoms from two azide ions in the end-on (EO) mode coordination and two nitrogen atoms from two equivalent isonic(1), while two oxygen atoms from two isonicotinate ligands of type (2), isonic(2), occupy the axial sites. Ni(1) lies on a twofold axis and that Ni(2) lies on an inversion centre. At the same time, the asymmetric unit has one isonicotinate in a general position and another lying about the same twofold axis as Ni(1). Selected bond distances (Å) and angles (deg) for complexes **1** and **2** are shown in Table 1S.

The asymmetric unit, the linkage and coordination mode in **1** are shown in Fig. 2S.

Thermal analyses of **1** were performed in the temperature range of 25 ~ 800 °C on a Rigaku standard TG-DTA analyzer in N_2 with an increasing temperature rate of 10 °C/min^{-1}. An empty Al_2O_3 crucible was used as reference (Fig. 3S).

Magnetic data were collected at the Unitat de Mesures Magnètiques at the Universitat de Barcelona using crushed crystals of the sample on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5T magnet. The data were corrected for TIP and the diamagnetic corrections were calculated using Pascal's constants; an experimental correction for the sample holder was applied.

Table S1

Complex 1			
Ni(1)-O(1)$^{\#1}$	2.024(3)	Ni(1)-O(1W)	2.083(3)
Ni(1)-N(5)$^{\#2}$	2.045(5)	Ni(2)-O(3)$^{\#3}$	2.084(3)
Ni(2)-N(4)$^{\#3}$	2.145(3)	Ni(2)-N(1)$^{\#3}$	2.157(2)
O(1)-Ni(1)-N(5)$^{\#2}$	93.04(10)	O(1)-Ni(1)-O(1W)$^{\#1}$	91.05(12)
O(3)-Ni(2)-N(4)$^{\#3}$	91.99(11)	O(3)-Ni(2)-N(1)	86.22(13)
N(4)-Ni(2)-N(1)	88.15(9)		
Complex 2			
Ni(1)-O(1)$^{\#1}$	2.000(2)	Ni(1)-O(1W)	2.035(2)
Ni(1)-N(5)$^{\#2}$	2.020(3)	Ni(2)-O(3)$^{\#3}$	2.0537(18)
Ni(2)-N(4)	2.126(2)	Ni(2)-N(1)$^{\#3}$	2.1158(15)
O(1)-Ni(1)-N(5)$^{\#2}$	93.01(7)	O(1)-Ni(1)-O(1W)$^{\#1}$	91.25(11)
O(3)-Ni(2)-N(4)$^{\#3}$	92.16(9)	O(3)-Ni(2)-N(1)	86.46(9)
N(1)-Ni(2)-N(4)	88.17(7)		

* Symmetry mode: For **1**, #1, -x,y,-z+1/2; #2, x-1/2,y-1/2,z; #3, -x+1,-y+1,-z+1. For **2**, #1, -x,y,-z+1/2; #2, x-1/2,y-1/2,z; #3, -x+1,-y+1,-z+1.

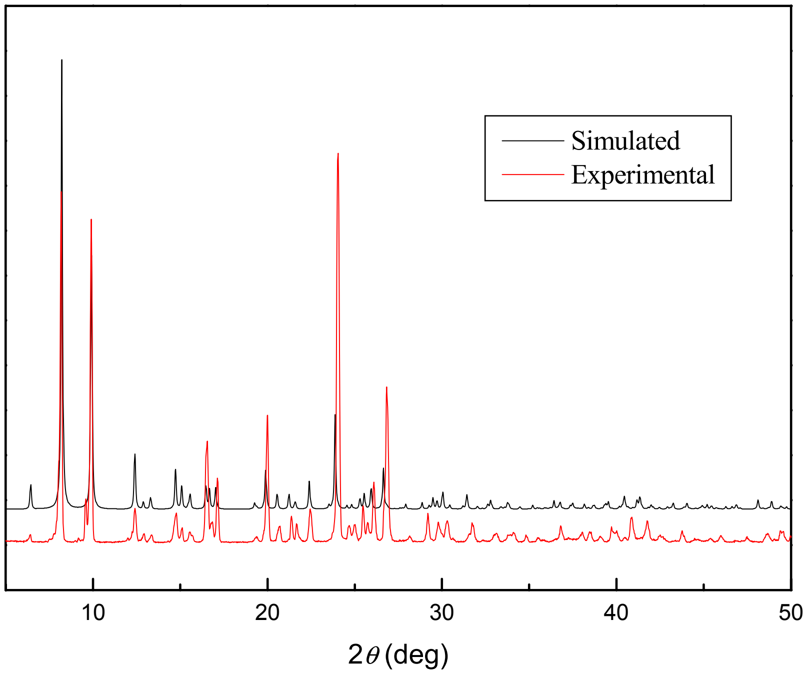

Fig. S1 XRPD patterns for **1**, and the simulated one based on the single crystal structure.

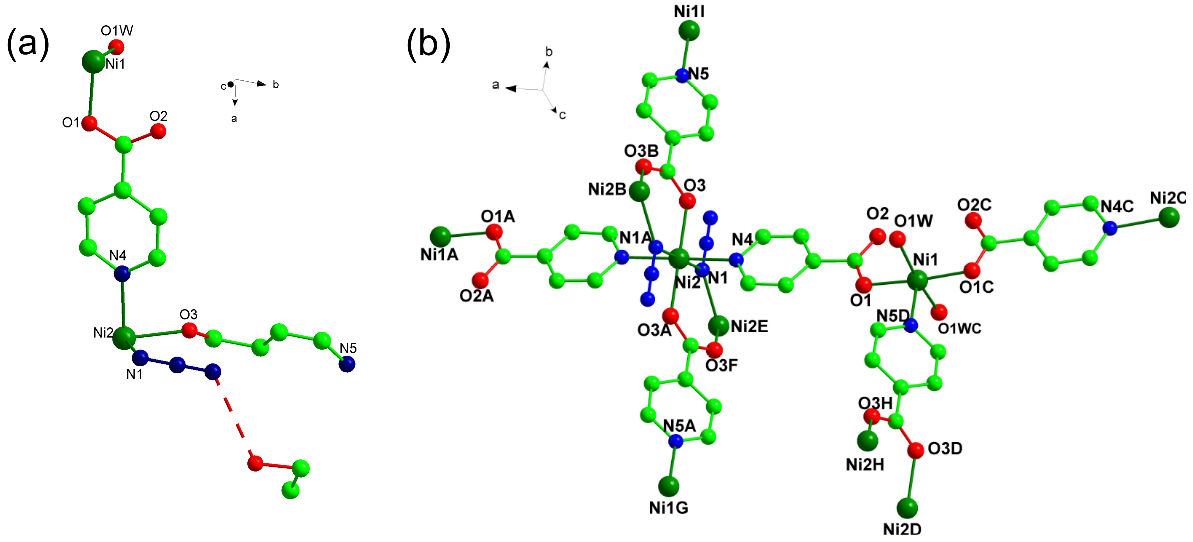

Fig. S2 (a) The asymmetric unit of **1**. The red dashed represents weak O-H...N hydrogen bond. Atom color codes: dark green, Ni; red, O; blue, N and light green, C. (b) The linkage and coordination mode in **1**. Symmetry mode: A, -x+1, -y+1, -z+1; B, -x+1, y, -z+1/2; C, -x, y, -z+1/2; D, x-1/2, y-1/2, z; E, -x+1, y, -z+3/2; F, x, -y+1, z+1/2; G, -x+1/2, -y+1/2, -z+1; H, -x+1/2, y-1/2, -z+1/2; I, x+1/2, y+1/2, z.

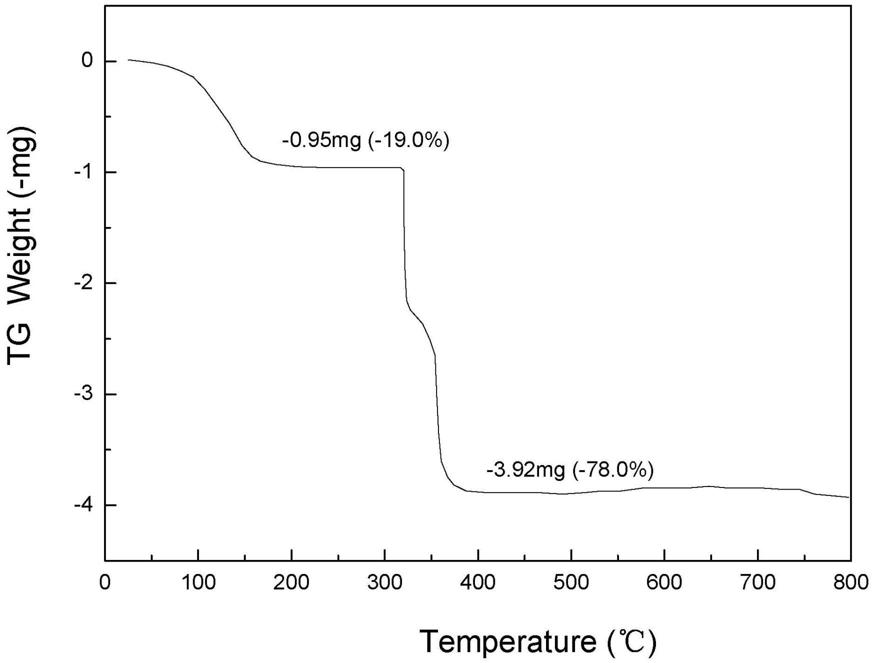

Fig. S3 The TGA curve of **1.**