Electronic Supplementary Material (ESI) for Dalton Transactions

Electronic Supplementary Information

A polydalton@rsc.orghedron–based metal–organic framework with *reo-e* net

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Material and Methods.

All the starting materials were purchased commercially as reagent grade and used without further purification. The IR spectra in KBr pellets were recorded in the range 400-4000 cm^{-1} with an Alpha Centaurt FT/IR spectrophotometer. Thermogravimetric analyses were carried out by using a Perkin-Elmer TGA7 instrument, with a heating rate of 10 °C /min, under a nitrogen atmosphere. Powder X-ray diffraction measurements were performed on a Rigaku D/MAX-3 instrument with Cu KR radiation in the angular range 2θ = 3-90 ° at 293 K. X-ray photoelectron spectroscopy (XPS) was performed on a thermo ESCALAB 250 electron spectroscopy with a standard and monochromatic source. Gas adsorption measurements were performed with a Hiden Isochema Intelligent Gravimetric Analyser (IGA-100B). High purity gases (N_2, 99.999%; H_2, 99.9995%) were used for the gas adsorption measurements performed at 77 K.

Single-crystal X-ray crystallography

The reflection intensity data of **1** were collected on a SMART CCD diffractometer equipped with graphite monochromatic Mo KR radiation (λ = 0.71073 Å) at 293 K. The linear absorption coefficients, scattering factors for the atoms, and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography. The structure was solved by the direct method and refined by the full-matrix least squares method on F^2 using the SHELXTL crystallographic software package. All H atoms were placed geometrically for **1**. Anisotropic thermal parameter was used to refine all nonhydrogen atoms. Solvents within the channels were not crystallographically well defined and these data were treated with the SQUEEZE routine within PLATON.

Bond valence sum of Ni1

Ni2+	r_0	r_{ij}	B	$S_{ij}=\exp[(r_0-r_{ij})/B]$
Ni1-O3	1.670	2.082	0.370	0.328
Ni1-O4	1.670	2.078	0.370	0.332
Ni1-O6	1.670	2.077	0.370	0.333
Ni1-O7	1.670	2.082	0.370	0.328
Ni1-O1	1.670	1.998	0.370	0.412
Ni1-N1	1.647	2.122	0.370	0.277

$V_{Ni1}=\sum S_{ij}=2.010$

Ni3+	r_0	r_{ij}	B	$S_{ij}=\exp[(r_0-r_{ij})/B]$
Ni1-O3	1.750	2.082	0.370	0.408
Ni1-O4	1.750	2.078	0.370	0.412
Ni1-O6	1.750	2.077	0.370	0.413
Ni1-O7	1.750	2.082	0.370	0.408
Ni1-O1	1.750	1.998	0.370	0.512
Ni1-N1	1.731	2.122	0.370	0.348

$V_{Ni1}=\sum S_{ij}=2.501$

Bond valence sum of Ni2

Ni2+	r_0	r_{ij}	B	$S_{ij}=\exp[(r_0-r_{ij})/B]$
Ni2-O2	1.670	2.037	0.370	0.371
Ni2-O2	1.670	2.037	0.370	0.371
Ni2-O5	1.670	2.034	0.370	0.374
Ni2-O5	1.670	2.034	0.370	0.374
Ni2-O1	1.670	1.981	0.370	0.431
Ni2- O10	1.670	2.177	0.370	0.254

$V_{Ni2}=\sum S_{ij}=2.175$

Ni3+	r_0	r_{ij}	B	$S_{ij}=\exp[(r_0-r_{ij})/B]$
Ni2-O2	1.750	2.037	0.370	0.460
Ni2-O2	1.750	2.037	0.370	0.460
Ni2-O5	1.750	2.034	0.370	0.464
Ni2-O5	1.750	2.034	0.370	0.464
Ni2-O1	1.750	1.981	0.370	0.536
Ni2- O10	1.750	2.177	0.370	0.316

$V_{Ni2}=\sum S_{ij}=2.700$

XPS spectrum

As shown in Fig S1, the peak 1 at 855.4 eV and peak 2 at 856.2 eV are characteristic of Ni^{2+} $2p_{3/2}$ and Ni^{3+} $2p_{3/2}$ peaks, respectively. The results indicate that the mean percentages of Ni^{2+} and Ni^{3+} are 72% and 28%. So there are five Ni^{2+} and two Ni^{3+} per molecule unit. One of the three Ni atoms in trinuclear cluster is trivalent. It has also been observed that the Ni3 is Ni^{2+}.

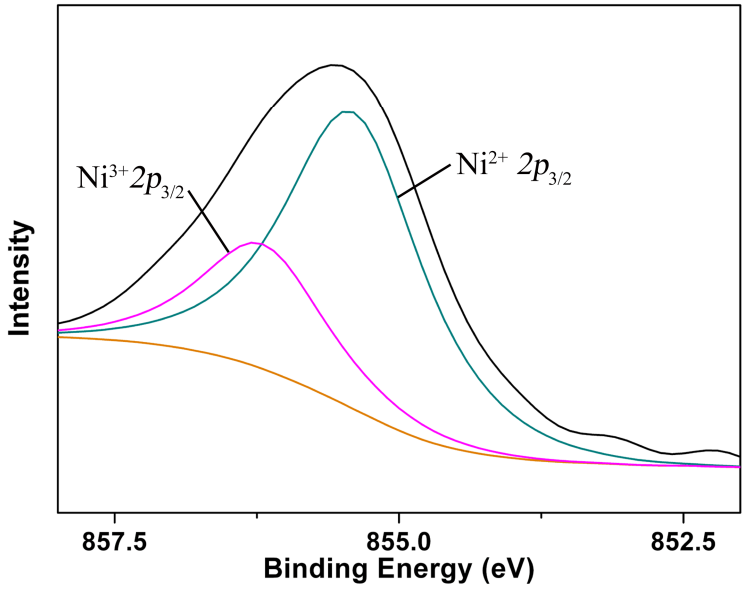

Fig. S1 XPS spectra of compound **1**.

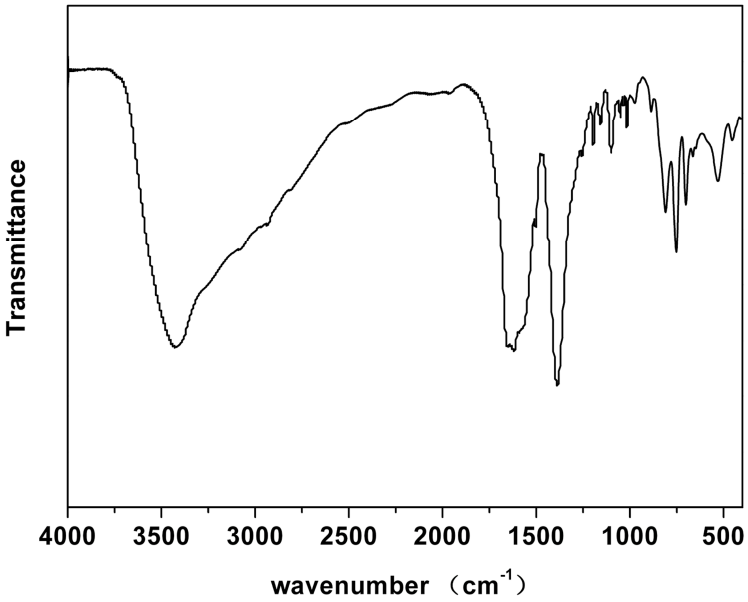

Fig. S2 IR spectrum of the as-synthesized sample of **1**.

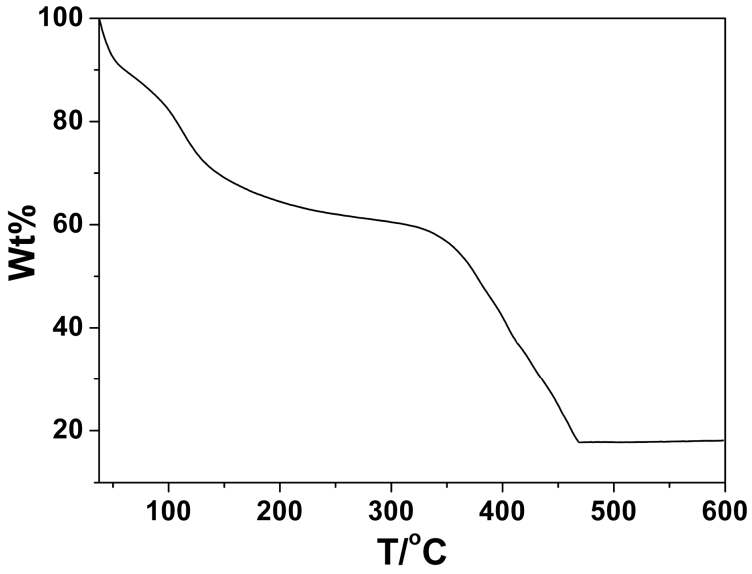

Fig. S3 TGA curve of **1**.

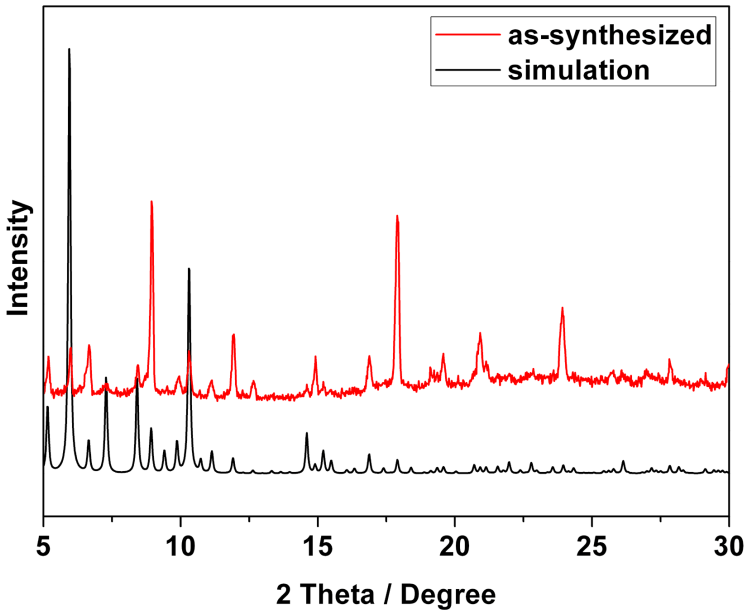

Fig. S4 Power X-ray diffraction (PXRD) of **1**.

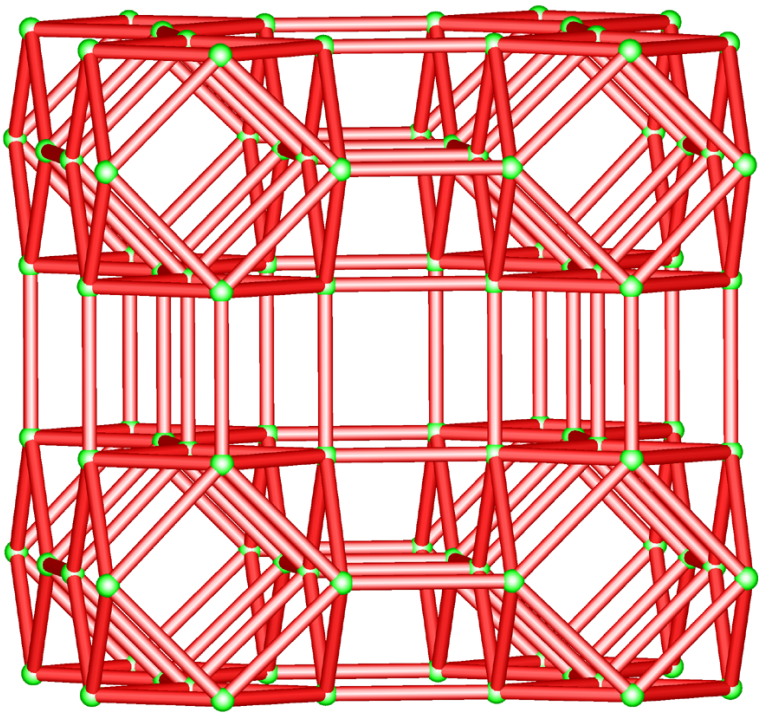

Fig. S5 The topology of the **1**.

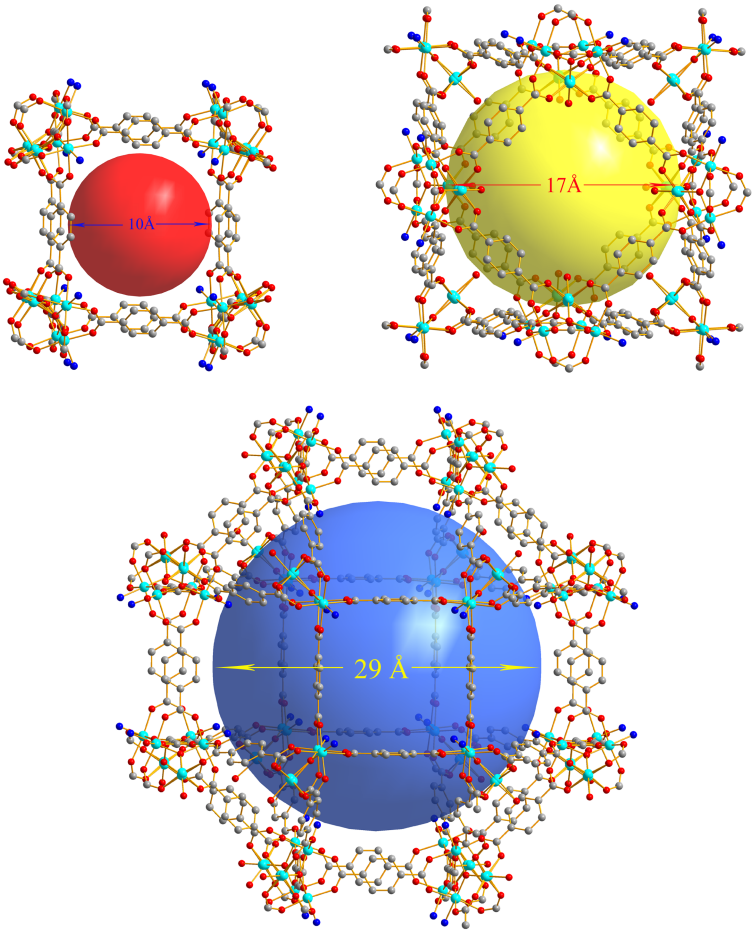

Fig. S6 The diameter of hexahedron, cuboctahedron and rhombicuboctahedron are 10 Å, 17 Å and 29 Å, respectively.

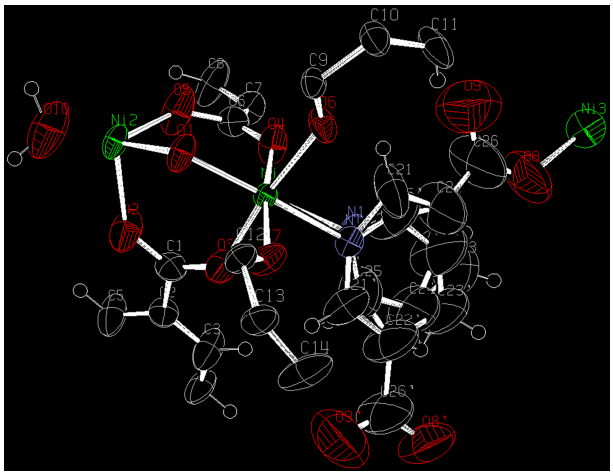

Fig. S7 ORTEP view of the asymmetry unit of **1** with displacement ellipsoids drawn at 50% probability level.

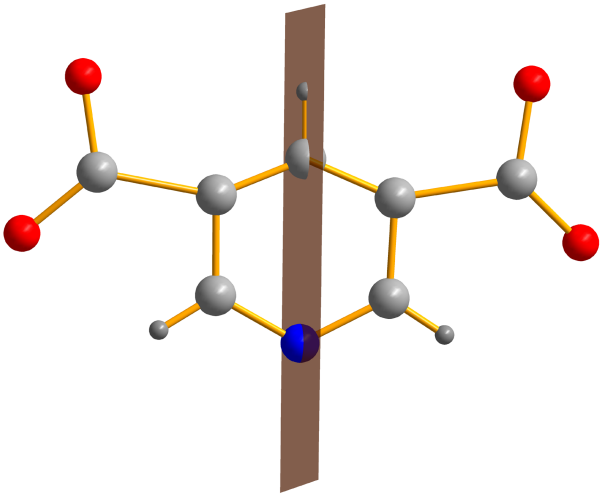

Fig. S8 One type of na disordered at two positions in **1**.

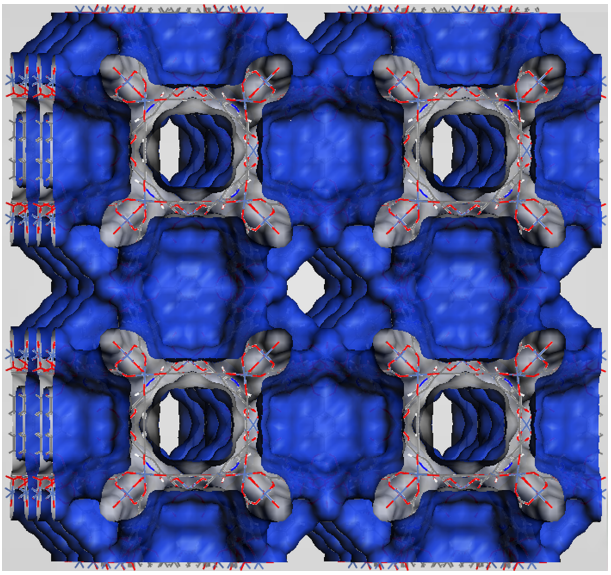

Fig. S9 Connolly surface of **1** (Connolly radius 1.40 Å).