Yan-Hong Li and Min-Le Han*

Crystal structure of poly[diaqua-(μ_2 -4,4'-bipyridine- $\kappa^2N:N'$)-(μ_2 -3,4,5,6-tetrafluorophthalato- $\kappa^2O:O'$)nickel(II)], $C_{18}H_{12}F_4NiN_2O_6$

Table 1: Data collection and handling.

Crystal:	Block, clear light green
Size:	0.17 × 0.16 × 0.13 mm
Wavelength:	Cu K α radiation (1.54184 Å)
μ :	2.32 mm ⁻¹
Diffractometer, scan mode:	XtaLAB Pro, ω -scans
$\theta_{\max}$, completeness:	66.6°, >99%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	5233, 1609, 0.031
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1435
$N(\text{param})_{\text{refined}}$:	151
Programs:	CrysAlis ^{PRO} [1], SHELX [2, 3]

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Ni1	0.7500	0.2500	0.69933(2)	0.02072(17)
F1	0.42940(17)	0.47055(12)	0.58105(5)	0.0389(3)
F2	0.3341(2)	0.36136(13)	0.47825(5)	0.0454(4)
O1	0.24633(17)	0.41046(16)	0.72524(7)	0.0401(4)
O2	0.52662(18)	0.36524(13)	0.70260(5)	0.0269(3)
O3	0.89240(19)	0.41454(14)	0.69982(6)	0.0269(3)
N1	0.7500	0.2500	0.60577(10)	0.0234(5)
N2	0.7500	0.2500	0.29381(10)	0.0269(5)
C1	0.6919(3)	0.15118(19)	0.57490(8)	0.0284(4)
H1	0.6523	0.0811	0.5953	0.034*
C2	0.6880(3)	0.14852(19)	0.51426(8)	0.0302(5)
H2	0.6437	0.0785	0.4948	0.036*
C3	0.7500	0.2500	0.48220(12)	0.0263(6)
C4	0.7500	0.2500	0.41710(12)	0.0275(6)
C5	0.6025(3)	0.2116(2)	0.38528(9)	0.0408(6)
H5	0.5004	0.1840	0.4047	0.049*
C6	0.6065(3)	0.2142(2)	0.32459(9)	0.0393(5)
H6	0.5044	0.1898	0.3042	0.047*
C7	0.3630(3)	0.36474(17)	0.69261(8)	0.0222(4)
C8	0.2997(2)	0.30524(17)	0.63545(8)	0.0212(4)
C9	0.3416(3)	0.36100(18)	0.58245(8)	0.0253(4)
C10	0.2940(3)	0.3059(2)	0.52967(8)	0.0293(4)
H3A	0.844(3)	0.469(2)	0.7228(10)	0.043(7)*
H3B	1.003(2)	0.411(2)	0.7073(10)	0.045(8)*

<https://doi.org/10.1515/ncrs-2019-0808>

Received October 31, 2019; accepted January 8, 2020; available online February 7, 2020

Abstract

$C_{18}H_{12}F_4NiN_2O_6$, orthorhombic, *Pccn* (no. 56), $a = 7.4650(2)$ Å, $b = 10.6954(2)$ Å, $c = 22.7513(5)$ Å, $V = 1816.49(7)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0304$, $wR_{\text{ref}}(F^2) = 0.0898$, $T = 293$ K.

CCDC no.: 1976169

A part of the title crystal structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

A mixture of 3,4,5,6-tetrafluorophthalic acid (H_2F_4ph , 9.5 mg, 0.04 mmol), 4,4'-bipyridine (4,4'-bipy, 6.2 mg, 0.04 mmol), and $Ni(OAc)_2 \cdot 4H_2O$ (0.04 mmol, 9.9 mg), was added to water (6 mL) and KOH (0.1 M, 0.4 mL) in a 25 mL Teflon-lined autoclave. The mixture was heated at 393 K for 3 days and then slowly cooled down to room temperature. Light green block crystals of the title compound were obtained.

*Corresponding author: Min-Le Han, College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang, Henan 471934, P.R. China, e-mail: minle_han@163.com. <https://orcid.org/0000-0003-3934-3345>

Yan-Hong Li: College of Chemistry and Chemical Engineering, Henan Key Laboratory of Function-Oriented Porous Materials, Luoyang Normal University, Luoyang, Henan 471934, P.R. China

Experimental details

The carbon bound hydrogen atoms were placed in calculated positions using a riding model on attached atoms.

Discussion

In the last two decades, a large number of mixed ligands-metal-organic frameworks (MOFs) have been reported in the

literature [4–8]. Mixed ligands-MOFs can be constructed from metal ions and carboxylic acid and nitrogen-containing ligands. In most situations, *N*-containing ligands are electrically neutral, while carboxylate ligands are negatively charged. Among organic aromatic multicarboxylates like the phthalates can yield predetermined networks and have been widely utilized to construct MOFs [9–12]. On the other hand, 4,4'-bipy serves as bridging ligand to coordinate to two metal ions [13, 14].

In the title complex, there are one half of a Ni(II) ion, one coordinated water molecule, one half of the F₄ph ligand, and one half of the 4,4'-bipy ligand in the asymmetric unit. Ni1 is six-coordinated with a distorted octahedral geometry by two O atoms from two F₄ph and two coordinated water molecules, located at the basal equatorial plane, and a pair of N atoms of two 4,4'-bipy ligands from the axial positions (see the figure). The Ni–N bond lengths are 2.129(2) and 2.150(2) Å and the Ni–O ones are in the range of 2.0560(14) to 2.0750(13) Å. All geometric parameters are comparable to related ones [15]. Ni(II) ions are linked by 4,4'-bipy ligands and F₄ph ligands to form a 2-D layer. In the title complex, there are hydrogen bonds between water and carboxylate O atoms. So an extended three-dimensional network of hydrogen bonds contributes to the stability of the structure.

Acknowledgements: This work was supported financially by the Natural Science Foundation of Henan province (no. 182300410238).

References

1. Agilent Technologies: CrysAlis^{PRO} Software system, version 1.171.35.15. Agilent Technologies UK Ltd, Oxford, UK (2011).
2. Sheldrick, G. M.: SHELXL – Integrated space-group and crystal structure determination. *Acta Crystallogr.* **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. *Acta Crystallogr.* **C71** (2015) 3–8.
4. Han, M.-L.: Crystal structure of diaqua-bis(3-carboxy-5-bromoisophthalato-κO)-bis(1-(3-(1*H*-benzo[d]imidazol-1-yl)propyl)-1*H*-benzo[d]imidazol-3-ium-κN)nickel(II) bis(3-carboxy-5-bromoisophthalate), C₆₆H₅₄Br₄N₈NiO₁₈. *Z. Kristallogr. NCS* **234** (2019) 655–657.
5. Wu, Y.-P.; Tian, J.-W.; Liu, S.; Li, B.; Zhao, J.; Ma, L.-F.; Li, D.-S.; Lan, Y.-Q.; Bu, X.: Bi-microporous metal-organic frameworks with cubane [M₄(OH)₄] (M = Ni, Co) clusters and pore-space partition for electrocatalytic methanol oxidation reaction. *Angew. Chem. Int. Ed.* **131** (2019) 12313–12317.
6. Chang, X.-H.; Ma, L.-F.; Hui, G.; Wang, L.-Y.: Four low-dimensional cobalt(II) coordination polymers based on a new isophthalic acid derivative: Syntheses, crystal structures, and properties. *Cryst. Growth Des.* **12** (2012) 3638–3646.
7. Li, D.-S.; Zhao, J.; Wu, Y.-P.; Liu, B.; Bai, L.; Zou, K.; Du, M.: Co₅/Co₈-Cluster-based coordination polymers showing high-connected self-penetrating networks: syntheses, crystal structures and magnetic properties. *Inorg. Chem.* **52** (2013) 8091–8098.
8. Wu, Y.-P.; Zhou, W.; Zhao, J.; Dong, W.-W.; Lan, Y.-Q.; Li, D.-S.; Sun, C.; Bu, X.: Surfactant-assisted phase-selective synthesis of new cobalt MOFs and their efficient electrocatalytic hydrogen evolution reaction. *Angew. Chem. Int. Ed.* **56** (2017) 13001–13005.
9. Han, M.-L.; Ling, X.-L.; Chang, X.-H.; Liu, G.-Z.; Du, D.-G.: Syntheses, structures and characteristics of two new Cu(II) coordination polymers based on 4-*tert*-butyl-phthalate and different bis(1,2,4-triazol-1-yl) co-ligands. *Chinese J. Struct. Chem.* **34** (2015) 543–550.
10. Farnum, G. A.; Pochodylo, A. L.; LaDuca, R. L.: Tether length control of topology in cadmium 4-methylphthalate two-dimensional coordination polymers: an acentric buckled grid and a rare self-catenated layer. *Cryst. Growth Des.* **11** (2011) 678–683.
11. Han, M.-L.; Zhao, Y.; Li, D.-S.; Wu, Y.-P.; Ma, L.-F.: Bis(pyridyl)-based ligands driven Ni^{II} entangled metal-organic frameworks: From a new 1-D + 2-D → 3-D polythreading motifs to a rare 3-fold interpenetrating **ths** network. *Inorg. Chem. Commun.* **52** (2015) 1–4.
12. Liu, G.-Z.; Li, S.-H.; Li, X.-L.; Xin, L.-Y.; Wang, L.-Y.: Three series of MOFs featuring various metal(II)-carboxylate chains cross-linked by dipyrindyl-typed coligands: synthesis, structure, and solvent-dependent luminescence. *CrystEngComm* **15** (2013) 4571–4580.
13. Zhou, P.; Yao, J. F.; Sheng, C. F.; Li, H.: A continuing tale of chirality: metal coordination extended axial chirality of 4,4'-bipy to 1D infinite chain under cooperation of a nucleotide ligand. *CrystEngComm* **15** (2013) 8430–8436.
14. Karmakar, A.; da Silva, M. F. C. G.; Pombeiro, A. J. L.: Zinc metal-organic frameworks: efficient catalysts for the diastereoselective Hery reaction and transesterification. *Dalton Trans.* **43** (2014) 7795–7810.
15. Zhang, M.-N.; Zheng, X.-L.; Qu, X.-L.; Li, X.; Gao, Y.; Xuebao, W. H.: Synthesis, crystal structures and fluorescence sensing for Fe³⁺ of transition metal complexes with 3,4,5,6-tetrafluorophthalic acid and *N*-Donor Ligands. *Chinese J. Inorg. Chem.* **33** (2017) 1172–1180.