A Metal-Organic Framework Constructed of 1,4-Di(pyridin-4-yl)-buta-1,3-diyne and Nickel(II) Nitrate

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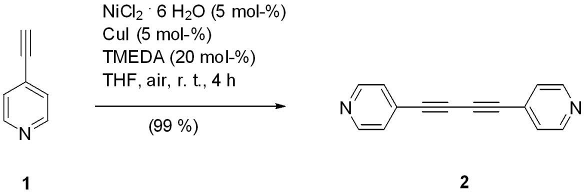
A metal-organic framework (MOF) was prepared from 1,4-di(pyridin-4-yl)buta-1,3-diyne and nickel(II) nitrate hexahydrate in methanol and dichloromethane at room temperature. The crystals are orthorhombic, space group $C222_1$, $Z = 4$. The rhombic cavities of the MOF are occupied by disordered molecules of dichloromethane.

Key words: MOF, Pyridine, Rhombic Cavities, Coordination Polymer

Introduction

Coordination polymers (CP) are solid materials consisting of a network of metal ions which are coordinated to multidentate organic molecules. This definition includes a large variety of materials. Among this broader family metal-organic frameworks (MOF) form a subclass of ever growing importance [1]. Three important characteristics have caused an increasing interest in this class of materials, *viz.* their crystallinity, their porosity, and the existence of strong metal – ligand interactions. The use of organic building blocks as spacer elements that serve to separate the metal nodes provides a unique opportunity to form new materials with tunable pore sizes and properties. Thus, the microporous structures have surface areas up to 5900 $m^2 g^{-1}$ and pore volumes up to 2 $cm^3 g^{-1}$ [2]. Metal-organic frameworks belong to the second or third generation of coordination polymers as they possess either a robust porous system with permanent porosity after removal of the guest molecules, or a flexible pore system which changes reversibly. They contain sorting domains [3], wherein the pore apertures act as sieves based on size- and shape-selectivity and/or a coverage domain [4–6], and wherein the guest molecules bind non-covalently to the internal pore surfaces. A new type of distribution domain – the active domain with specific features and functions – has been designed recently [7]. These properties have led to applications in heterogeneous catalysis [8], gas separation and storage [9–12], chiral recognition [13], and many others. We describe here a novel metal-organic framework constructed of 1,4-di(pyridin-4-yl)buta-1,3-diyne and nickel(II) nitrate.



Scheme 1. Synthesis of 1,4-di(pyridin-4-yl)buta-1,3-diyne (**2**).

Results and Discussion

We chose 1,4-di(pyridin-4-yl)buta-1,3-diyne (**2**) as the organic building block. This ligand was formed from 4-ethynyl-pyridine (**1**) which was oxidatively coupled by nickel(II) chloride and copper(I) iodide in the presence of tetramethylethylenediamine (TMEDA) in anhydrous THF to give **2** in quantitative yield (Scheme 1).

A metal-organic framework **3** was prepared from **2** and a solution of nickel(II) nitrate hexahydrate in methanol as slightly orange crystals. Single crystals were obtained within 3 d by carefully layering a solution of 1,4-di(pyridin-4-yl)buta-1,3-diyne **2** in dichloromethane onto a solution of $Ni(NO_3)_2$ hexahydrate in methanol at r. t. The results of a single-crystal X-ray structure analysis are given in Table 1 and shown in Figs. 1 and 2. Selected bond lengths and bond angels are presented in Table 2. The obtained species crystallized in the non-centrosymmetric orthorhombic space group $C222_1$ with $Z = 4$.

Four 1,4-di(pyridin-4-yl)buta-1,3-diyne ligands and two nitrate anions form a pseudooctahedral coordination environment of the Ni(II) ion as shown in Fig. 1, similar to a metal organic framework of **2**

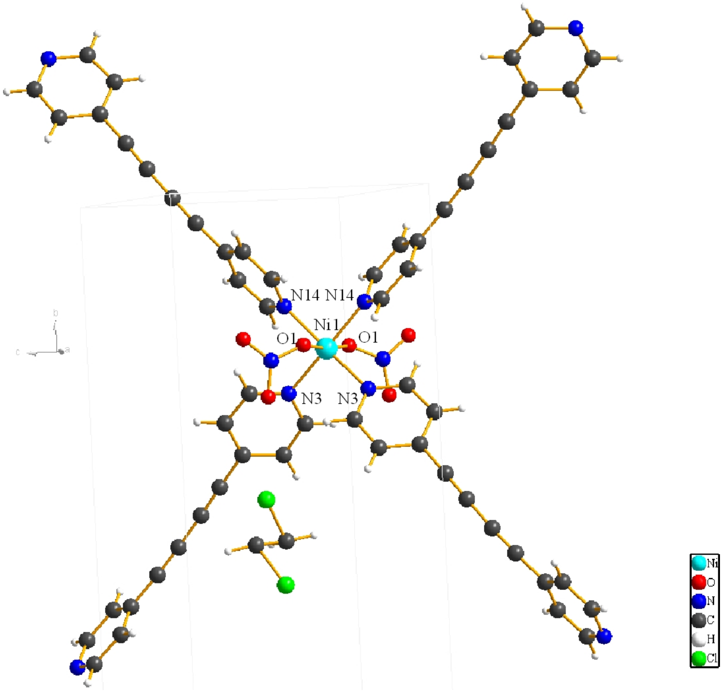


Fig. 1. Coordination environment of the Ni atom in the MOF **3**.

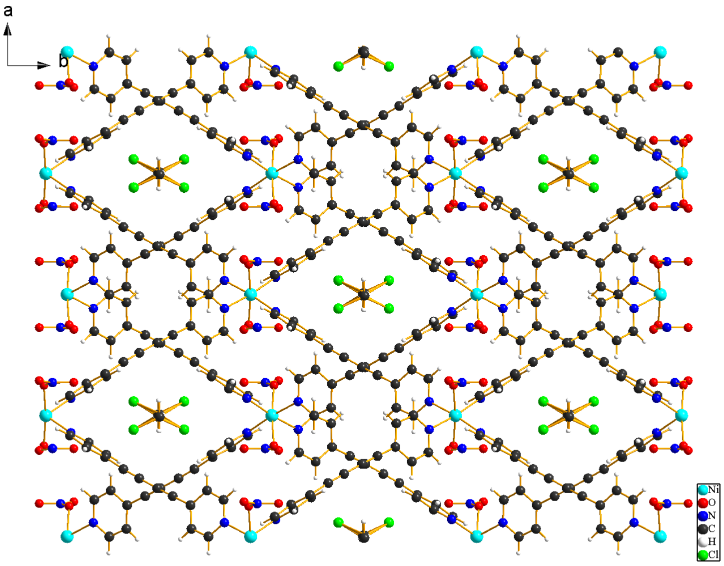


Fig. 2. Crystal structure of the MOF **3**. Direct view down the channel direction which runs parallel to the crystallographic *c* axis.

and copper(II) nitrate described earlier [14]. Two crystallographically equivalent nitrate oxygen atoms occupy the axial positions, whereas the organic linkers are located in a square-planar arrangement about the nickel center. The nickel atom is located on a twofold axis of symmetry which is parallel to the crystallographic *b* axis, *i. e.* the MOF **3** possesses crystallographic C_2 (2) symmetry. The absolute structure of the chiral space group was determined by refinement of Flack's x parameter [15–17]. The distances between the ligand and the central atom were determined to be 2.096(1) (Ni1–N3) and 2.090(1) Å (Ni1–N14). The Ni–O distances of the two nitrate anions to the nickel atom were found to be 2.104(1) Å. The pyridine rings are twisted by 84.3° around the triple bonds. The resulting network consists of 2 two-dimensional interca-

Table 1. Crystal structure data for the MOF **3**.

Formula	$C_{28}H_{16}N_6NiO_6 \cdot 0.5\ CH_2Cl_2$
M_r	633.64
Crystal size, mm^3	$0.32 \times 0.16 \times 0.08$
T, K	123(2)
Crystal system	orthorhombic
Space group	$C222_1$ (no. 20)
a, Å	13.905(2)
b, Å	23.540(3)
c, Å	8.954(1)
V, Å^3	2930.9(7)
Z	4
D_{calcd}, g cm^{-3}	1.4
μ (MoK_α), cm^{-1}	0.8
$F(000)$, e	1292
hkl range	$\pm 18, \pm 30, \pm 11$
$2\theta_{\max}$, deg	55
Refl. measd. / unique / R_{int}	25119 / 3353 / 0.053
Param. refined	199
$R(F)[I \geq 2\sigma(I)]/wR(F^2)$ (all reflections)	0.038 / 0.092
x (Flack)	$-0.008(16)$
GoF (F^2)[a]	0.99
$\Delta\rho_{\text{fin}}$ (max / min), e Å^{-3}	0.64 / -0.34

lating square-grid-type layers with an inner square cavity of 8.35 (C9$\cdots$C9) × 13.70 (Ni$\cdots$Ni) Å^2, which interpenetrate at an angle of 74.3° (Fig. 2). The rhombic cavities are occupied by one disordered molecule of dichloromethane.

Thermogravimetric analyses (TGA) and differential scanning calorimetric measurements (DSC) of **3** were performed. A weight loss of 6.6 % from the initial temperature (30 ℃) to approximately 240 ℃ can be attributed to the desorption of the guest molecule dichloromethane from the pores of the MOF (calculated weight loss: 6.6 %). This desorption is very slightly endothermic as evidenced by the DSC measurement. A stepwise weight-loss pattern between 250 – 800 ℃ is observed. This can be attributed to the subsequent decomposition of the organic struts which begins with a strongly exothermic reaction between 245 and 260 ℃.

Experimental Section

^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance III (600 MHz) spectrometer. Multiplicities are described by using the abbreviation "d" for doublet; chemical shifts δ are given in ppm. FT-IR spectra were obtained on a Bruker Vektor 22 in the range of 400 to 4000 cm^{-1} (2.5 % pellets in KBr). TGA measurements were performed on a TGA 2950, and DSC examinations on a DSC 2920 TA instrument. The DSC scan rate was 5 K min^{-1}. Nitrogen purge gas was used at a flow rate of 24 mL min^{-1}.

Table 2. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **3** with estimated standard deviations in parentheses[a].

Ni1–N14	2.090(2)	Ni1–N3	2.096(2)
Ni1–O1	2.1037(18)	N1–O3	1.222(4)
N1–O2	1.235(3)	C1–C2	1.380(4)
C1–C6	1.399(4)	C2–N3	1.344(4)
N3–C4	1.334(3)		
N14$^{\#1}$–Ni1–N14$^{\#2}$	88.1(1)	N14$^{\#1}$–Ni1–N3	89.7(1)
N14$^{\#2}$–Ni1–N3	174.4(1)	N14$^{\#1}$–Ni1–N3$^{\#3}$	174.4(1)
N14$^{\#2}$–Ni1–N3$^{\#3}$	89.7(1)	N3–Ni1–N3$^{\#3}$	93.1(1)
N14$^{\#1}$–Ni1–O1	87.4(1)	N14$^{\#2}$–Ni1–O1	88.3(1)
N3–Ni1–O1	96.7(1)	N3$^{\#3}$–Ni1–O1	87.5(1)
N3$^{\#3}$–Ni1–O1$^{\#3}$	96.7(1)	N1–O1–Ni1	126.2(2)

[a] Symmetry operations: $^{\#1}$ $0.5-x, 0.5+y, 1.5-z$; $^{\#2}$ $0.5+x, 0.5+y, -1+z$; $^{\#3}$ $1-x, y, 0.5-z$.

*1,4-Di(pyridin-4-yl)buta-1,3-diyne (**2**)*

A suspension of copper(I) iodide (10 mg, 0.05 mmol), nickel(II) chloride hexahydrate (12 mg, 0.05 mmol) and tetramethylethylenediamine (0.03 mL, 0.2 mmol) in 5 mL of anhydrous THF was stirred under an inert atmosphere (N_2) for 2 min. Then, 4-ethynylpyridine **1** (206 mg, 2 mmol) was added, and the mixture was stirred at r. t. over a period of 4 h while air was bubbled through the mixture. After evaporation of the solvent the resulting residue was chromatographed on silica gel (petroleum ether : ethyl acetate = 1 : 1) to give a colorless solid: 204 mg (99 %), m. p. 201 ℃ (ref. [18]: 198 – 201 ℃). – ^{1}H NMR (600 MHz, $CDCl_3$): δ = 8.64 (dd, J = 4.6 Hz, J = 1.6 Hz, 4H), 7.50 (dd, J = 4.6 Hz, J = 1.6 Hz, 4H) ppm. – IR (KBr, cm^{-1}): ν = 3326, 1654, 1584, 1506, 1442, 1397, 1259, 814, 777, 542, 460. All spectroscopic data are in agreement with those reported in the literature [18].

*$[Ni(NO_3)_2(C_{14}H_8N_2)_2 \cdot 0.5\ CH_2Cl_2]_n$ (**3**)*

A solution of 1,4-di(pyridin-4-yl)buta-1,3-diyne **2** (20 mg, 0.1 mmol) in 5 mL of dichloromethane was carefully layered onto a solution of $Ni(NO_3)_2$ hexahydrate (29 mg, 0.1 mmol) in 3 mL of methanol. After 3 days at r. t. slightly orange crystals precipitated from the solution which were filtered off and washed with methanol. The yield was 47 % based on nickel nitrate. – IR (KBr, cm^{-1}): ν = 3053, 2225, 1606, 1535, 1493, 1448, 1281, 1019, 971, 550, 490 cm^{-1}. – Analysis: calcd. C 54.02, H 2.70, N 13.26; found C 53.16, H 2.68, N 13.36.

*X-Ray structure determination of **3***

Intensity data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at $T = -150$ ℃. The structure was solved by Patterson Methods and refined by full-matrix least-squares on F^2 [19]. A semi-empirical absorption correction was applied. All non-hydrogen atoms in **3** were refined anisotropically, and hydrogen atoms were located from

ΔF maps and refined at idealized positions using a riding model. The solvent CH_2Cl_2 is disordered about two positions.

CCDC 796244 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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