

A Metal-Organic Framework Constructed of 1,2-Di(pyridin-4-yl)ethyne, Terephthalic Acid, and Zinc(II) Nitrate

Marcel Albrecht^a, Martin Nieger^b, and Andreas Schmidt^a

^a Clausthal University of Technology, Institute of Organic Chemistry, Leibnizstraße 6, 38678 Clausthal-Zellerfeld, Germany

^b University of Helsinki, Laboratory of Inorganic Chemistry, Department of Chemistry, 00014 University of Helsinki, Finland

Reprint requests to Prof. Dr. Andreas Schmidt. Fax: +49-5323-722858. E-mail: schmidt@ioc.tu-clausthal.de

Z. Naturforsch. **2012**, 67b, 103 – 106; received January 12, 2012

A metal-organic framework (MOF) was prepared from 1,2-di(pyridin-4-yl)ethyne, terephthalic acid and zinc(II) nitrate in dimethylformamide, water and ethanol at 80 °C. The cavities of the MOF are occupied by disordered molecules of dimethylformamide. The crystals are monoclinic, space group $P2_1/c$ with $Z = 4$.

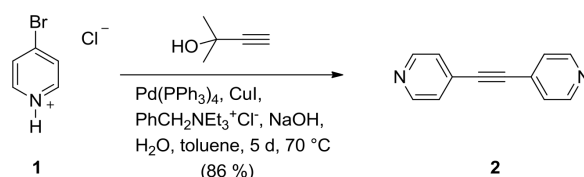
Key words: MOF, Coordination Polymer

Introduction

Metal-organic frameworks (MOF) [1–3] combine properties of both organic and inorganic porous materials as they are stable, ordered, and possess high surface areas ($> 3000 \text{ m}^2 \text{ g}^{-1}$). The combination of metal ions with polytopic organic linkers allows for a fascinating diversity of structures which have been the subject of extensive exploration during the last decade. Potential applications of microporous (pores less than 20 Å), mesoporous (pores between 20–500 Å), and macroporous metal-organic frameworks (openings > 500 Å) in hydrogen [4, 5] and methane [6] gas storage, selective gas absorption [7, 8], sensing [9] and drug storage [10] have been reviewed recently [11–13]. A great deal of attention has also been directed toward catalytic properties of metal-organic frameworks [14, 15], among those catalytic Mukaiyama aldol reactions [16], transesterifications [17], and the chiral secondary alcohol synthesis by addition of diethyl zinc to aromatic aldehydes in the presence of a chiral MOF [18]. In continuation of our studies in preparative organic and heterocyclic chemistry [19–23], catalysis [24–27], materials chemistry [28], and metal-organic frameworks [29], we report here the preparation and structure of a MOF constructed of 1,2-di(pyridin-4-yl)ethyne, terephthalic acid and zinc(II) nitrate.

Results and Discussion

The ligand 1,2-di(pyridin-4-yl)ethyne (**2**) was prepared according to a modified literature procedure [30]



Scheme 1. Synthesis of di(pyridin-4-yl)ethyne (**2**).

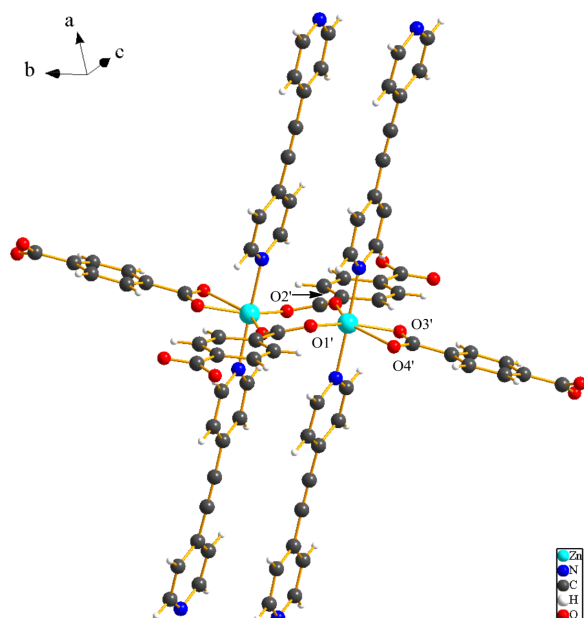
by a palladium-catalyzed one-pot reaction of 4-bromopyridine hydrochloride with 2-methyl-but-3-yn-2-ol in 86 % yield in a two-phase system consisting of toluene and aqueous sodium hydroxide (Scheme 1).

The metal-organic framework **3** was then prepared starting from 1,2-di(pyridin-4-yl)ethyne (**2**), terephthalic acid and a solution of zinc(II) nitrate hexahydrate in a solvent mixture of dimethylformamide, water, and ethanol in a closed vessel at 80 °C over a period of 3 d in 90 % yield. The results of a single-crystal X-ray structure determination are given in Table 1 and are shown in Figs. 1, 2, and 3. Selected bond lengths and bond angles are presented in Table 2. The obtained species crystallized in the monoclinic space group $P2_1/c$ with $Z = 4$.

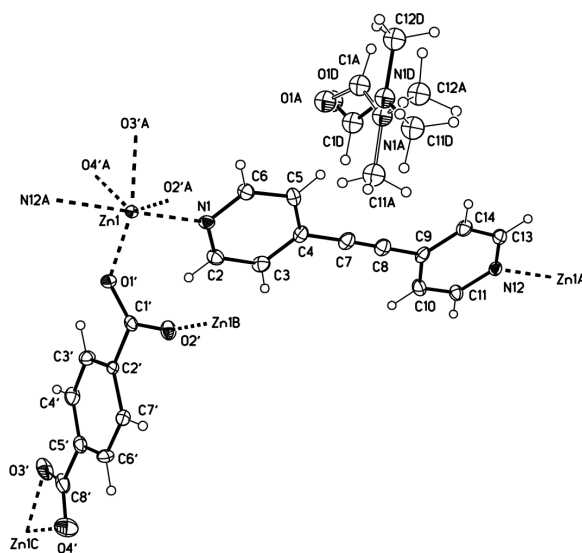
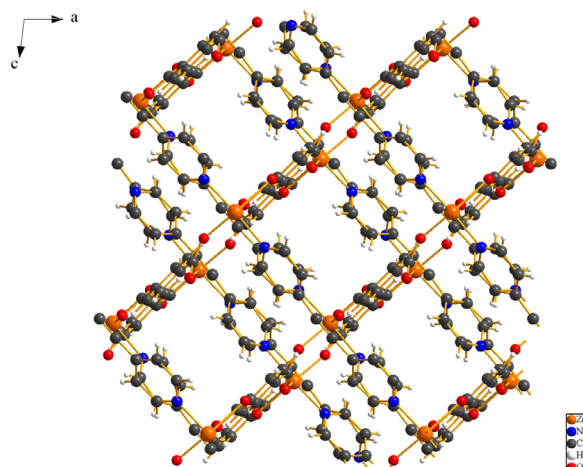
As shown in Fig. 1 three terephthalic acid molecules and two 1,2-di(pyridin-4-yl)ethyne molecules form a pseudooctahedral coordination environment of the Zn(II) ion. The dicarboxylic acid linkers occupy the equatorial positions of the octahedron. One carboxylate group of each terephthalic acid molecule serves as bidentate-chelating ligand to the zinc atom, whereas the other carboxylate group bridges two zinc atoms.

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

Formula	C ₂₀ H ₁₂ N ₂ ZnO ₄ · C ₃ H ₇ NO
<i>M_r</i>	482.78
Crystal size, mm ³	0.24 × 0.12 × 0.06
<i>T</i> , K	123(2)
Crystal system	monoclinic
Space group	<i>P</i> 2 ₁ / <i>c</i> (no. 14)
<i>a</i> , Å	10.400(1)
<i>b</i> , Å	19.294(2)
<i>c</i> , Å	10.706(1)
β, deg	96.94(19)
<i>V</i> , Å ³	2132.5(4)
<i>Z</i>	4
<i>D</i> _{calcd} , g cm ^{−3}	1.50
μ (MoKα), cm ^{−1}	1.2
<i>F</i> (000), e	992
<i>hkl</i> range	±13, ±25, ±13
2θ _{max} , deg	55
Refl. measured / unique / <i>R</i> _{int}	28598 / 4884 / 0.059
Param. refined / restraints / data	284 / 61 / 4884
<i>R</i> (<i>F</i>) (<i>I</i> ≥ 2σ(<i>I</i>)) / <i>wR</i> (<i>F</i> ²) (all refl.)	0.042 / 0.089
GoF (<i>F</i> ²)	1.05
Δρ _{fin} (max / min), e Å ^{−3}	0.56 / −0.37

Fig. 1. Coordination environment of the Zn atom in **3**.

Eight-membered rings of two zinc atoms plus two carboxylate groups are formed. Thus, each terephthalic acid molecule in **3** serves as a ligand of three zinc atoms in such a way that one carboxylate group is a bidentate and the other one a bis-monodentate ligand. The distances between the oxygen atoms of the bidentate terephthalic acid ligand and the zinc atom were determined to be 2.028(1) Å (Zn–O3') and 2.483(1) Å

Fig. 2. 1,2-Di(pyridin-4-yl)ethyne, terephthalic acid and the zinc atom dissected from the crystal structure of **3** (displacement parameters are drawn at the 50% probability level; crystallographic numbering).Fig. 3. Crystal structure of **3**. Direct view down the channels which run parallel to the crystallographic *b* axis (solvent molecules omitted).

(Zn–O4'), whereas the distances to the bridging carboxylate group were determined to be 1.988(1) Å (Zn–O1') and 2.019(1) Å (Zn–O2'). The Zn–N distances of the two 1,2-di(pyridin-4-yl)ethyne molecules to the zinc atom were determined to be 2.199(1) Å (Zn–N1) and 2.174(1) Å (Zn–N12'). Additional bond lengths, bond angles, and dihedral angles are summarized in Table 2. The linkage to additional zinc atoms through the axial 1,2-di(pyridin-4-yl)ethynes forms layers at a

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

Zn1–O1'	1.988(2)	Zn1–O2' ^{#1}	2.019(2)
Zn1–O3' ^{#2}	2.028(2)	Zn1–N12 ^{#3}	2.174(2)
Zn1–N1	2.199(2)	Zn1–O4' ^{#2}	2.483(3)
N1–C2	1.336(3)	C2–C3	1.386(4)
C3–C4	1.396(4)	C4–C7	1.435(3)
C7–C8	1.195(4)	O1'–C1'	1.261(3)
O2'–C1'	1.251(3)	C8'–O3'	1.265(4)
C8'–O4'	1.236(4)		
O1'–Zn1–O2' ^{#1}	120.15(8)	O1'–Zn1–O3' ^{#2}	147.42(9)
O2' ^{#1} –Zn1–O3' ^{#2}	92.41(9)	O1'–Zn1–N12 ^{#3}	89.54(8)
O2' ^{#1} –Zn1–N12 ^{#3}	86.20(7)	O1'–Zn1–N1	92.36(8)
O3' ^{#2} –Zn1–N1	88.54(8)	N12 ^{#3} –Zn1–N1	176.11(8)
O2' ^{#1} –Zn1–O4' ^{#2}	149.35(8)		
O1'–Zn1–N1–C2	16.9(2)	O2' ^{#1} –Zn1–N1–C2	137.1(2)
N12 ^{#3} –Zn1–N1–C2	136.1(11)	O4' ^{#2} –Zn1–N1–C2	–73.6(2)
C8' ^{#2} –Zn1–N1–C2	–101.7(2)	O2' ^{#1} –Zn1–N1–C6	–40.84(19)
O4' ^{#2} –Zn1–N1–C6	108.54(19)	C5–C4–C7–C8	–145(4)
O2' ^{#1} –Zn1–O1'–C1'	–34.7(2)	O3' ^{#2} –Zn1–O1'–C1'	147.51(19)

Symmetry transformation used to generate equivalent atoms: ^{#1} $-x, -y+1, -z+1$; ^{#2} $-x+0.5, y+0.5, z+0.5$; ^{#3} $x-1, y, z-1$.

distance of 13.995(2) Å. Two pyridine rings connected *via* one zinc atom are slightly twisted to each other by an angle 5.6°. The resulting network is shown in Fig. 3. The inner cavities are occupied by one molecule of DMF per zinc atom, which is omitted in the drawing for clarity. The porosity (solvent area) of the MOF is 22.3 % and the packing index 56.2. The volume of one cave (4 per unit cell) is 120 Å³ [31, 32].

A thermogravimetric analysis (TGA) of **3** was performed. A weight loss of approximately 10 % in the temperature range between approximately 150 and 270 °C can be attributed to the partial desorption of the DMF from the pores of **3** (calculated weight loss: 16 %). Stepwise weight-loss patterns from 330 °C to 420 °C (25 %) and 420 °C to 540 °C (21 %) can be attributed to the subsequent decomposition of the organic components.

Experimental Section

The ¹H and ¹³C NMR spectra were recorded on a Bruker Avance DPX 200 (200 MHz) spectrometer. Multiplicities are described by using the abbreviation “d” for doublet. FT-IR spectra were obtained on a Bruker Vektor 22 instrument in the range of 400 to 4000 cm^{–1} (2.5 % pellets in KBr). The TGA was performed with a TGA 2950 instrument. Nitrogen purge gas was used at a flow rate of 24 mL min^{–1}.

1,2-Di(pyridin-4-yl)ethyne (**2**)

A solution of 37.5 mL 5.5 M sodium hydroxide in water, tetrakis(triphenylphosphine)palladium(0) (0.5 g, 0.43 mmol), copper(I) iodide (0.5 g, 2.6 mmol), and benzyltriethylammonium chloride (0.5 g, 2.2 mmol) was treated with a suspension of 2-methyl-3-butyn-2-ol (3.05 mL, 31.3 mmol) and 4-bromopyridine hydrochloride (12.1 g, 62.5 mmol) in 25 mL of toluene. The mixture was stirred at 70 °C over a period of 5 d, and then treated with 100 mL of a saturated ammonium chloride solution in water. After stirring for 1 h at r. t., the mixture was extracted four times with 100 mL of toluene. The organic layer was separated, dried over magnesium sulfate, and evaporated to dryness. Column chromatography (silica gel; CH₂Cl₂ · MeOH = 40 : 1) gave 4.85 mg (86 %) of a colorless solid, m. p. 162 °C (ref. [30]: 163–164 °C). – ¹H NMR (CDCl₃): δ = 8.65 (d, *J* = 4.5 Hz, 4H, α-H), 7.40 (d, *J* = 4.5 Hz, 4H, β-H) ppm. – ¹³C NMR (CDCl₃): δ = 149.9, 130.1, 125.5, 90.5 ppm. – IR (KBr): ν = 3034, 1944, 1597, 1540, 1499, 1412, 1216, 1088, 993, 827, 553, 528 cm^{–1}. All spectroscopic data are identical to those reported in ref. [33].

[C₂₀H₁₂N₂ZnO₄·C₃H₇NO]_n (**3**)

1,2-Di(pyridin-4-yl)ethyne (**2**) (14.0 mg, 0.078 mmol), terephthalic acid (9.0 mg, 0.054 mmol) and zinc(II) nitrate hexahydrate (15.0 mg, 0.051 mmol) were dissolved in a solvent mixture of 8 mL of dimethylformamide, 1 mL of water, and 1 mL of ethanol, and heated in a closed vessel to 80 °C over a period of 3 d. The resulting colorless crystals were filtered off. The MOF **3** was obtained in 90 % yield (22.0 mg) with respect to the zinc salt.

X-Ray structure determination

Data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromatized MoK_α radiation (λ = 0.71073 Å) at *T* = –150 °C, and the structure was solved by Direct Methods and refined by full-matrix least-squares on *F*² [34]. A semi-empirical absorption correction was applied. All non-hydrogen atoms in **3** were refined anisotropically, and hydrogen atoms were located from Δ*F* maps and refined at idealized positions using a riding model. The solvent molecule DMF was found to be disordered. In the refinement it was modelled using geometrical restraints for the 1,2- and 1,3-distances (SADI) as well as constraints (EADP) and restraints (SIMU) for the displacement parameters.

CCDC 861982 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

- [1] O. M. Yaghi, H. L. Li, *J. Am. Chem. Soc.* **1995**, *117*, 10401–10402.
- [2] H. Li, M. Eddaoudi, M. O’Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276–279.
- [3] J. L. C. Rowsell, O. M. Yaghi, *Micropor. Mesopor. Mater.* **2004**, *73*, 3–4.
- [4] N. L. Rosi, J. Eckert, M. Eddaoudi, D. T. Vodak, J. Kim, M. O’Keeffe, O. M. Yaghi, *Science* **2003**, *300*, 1127–1129.
- [5] L. J. Murray, M. Dinca, J. R. Long, *Chem. Soc. Rev.* **2009**, *38*, 1294–1314.
- [6] M. Kondo, T. Yoshitomi, K. Seki, H. Matsuzaka, S. Kitagawa, *Angew. Chem.* **1997**, *109*, 1844–1846; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1725–1727.
- [7] J.-R. Li, R. J. Kuppler, H. C. Zhou, *Chem. Soc. Rev.* **2009**, *38*, 1477–1504.
- [8] J.-R. Li, Y. Ma, M. C. McCarthy, J. Sculley, J. Yu, H.-K. Jeong, P. B. Balbuena, H.-C. Zhou, *Coord. Chem. Rev.* **2011**, *255*, 1791–1823.
- [9] B. V. Harbuzaru, A. Corma, F. Rey, P. Atienzar, J. L. Jordá, H. García, D. Ananias, L. D. Carlos, J. Rocha, *Angew. Chem.* **2008**, *120*, 1096–1099; *Angew. Chem. Int. Ed.* **2008**, *47*, 1080–1083.
- [10] P. Horcajada, C. Serre, M. Vallet-Regí, M. Sebban, F. Taulelle, G. Férey, *Angew. Chem.* **2006**, *118*, 6120–6124; *Angew. Chem. Int. Ed.* **2006**, *45*, 5974–5978.
- [11] R. J. Kuppler, D. J. Timmons, Q.-R. Fang, J.-R. Li, T. A. Makal, M. D. Young, D. Yuan, D. Zhao, W. Zhuang, H.-C. Zhou, *Coord. Chem. Rev.* **2009**, *253*, 3042–3066.
- [12] S. T. Meek, J. A. Greathouse, M. D. Allendorf, *Adv. Mater.* **2011**, *23*, 249–267.
- [13] B. Chen, S. Xiang, G. Qian, *Acc. Chem. Res.* **2010**, *43*, 1115–1124.
- [14] M. Ranocchiari, J. A. van Bokhoven, *Phys. Chem. Chem. Phys.* **2011**, *13*, 6388–6396.
- [15] A. Corma, H. García, F. X. Llabrés i Xamena, *Chem. Rev.* **2010**, *110*, 4606–4655.
- [16] S. Horike, M. Dinca, K. Tamaki, J. R. Long, *J. Am. Chem. Soc.* **2008**, *130*, 5854–5855.
- [17] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986.
- [18] C. D. Wu, W. B. Lin, *Angew. Chem.* **2007**, *119*, 1093–1096; *Angew. Chem. Int. Ed.* **2007**, *46*, 1075–1078.
- [19] A. Schmidt, N. Münster, A. Dreger, *Angew. Chem.* **2010**, *122*, 2851–2854; *Angew. Chem. Int. Ed.* **2010**, *49*, 2790–2793.
- [20] A. Dreger, R. Cisneros Camuña, N. Münster, T. A. Rokob, I. Pápai, A. Schmidt, *Eur. J. Org. Chem.* **2010**, 4296–4305.
- [21] A. Schmidt, A. Beutler, M. Albrecht, B. Snovydyovych, F. J. Ramírez, *Org. Biomol. Chem.* **2008**, *6*, 287–295.
- [22] A. Schmidt, A. Beutler, T. Habeck, T. Mordhorst, B. Snovydyovych, *Synthesis* **2006**, 1882–1894.
- [23] A. Schmidt, M. Nieger, *Heterocycles* **1999**, *51*, 2119–2126.
- [24] A. Rahimi, J. C. Namyslo, M. Drafz, J. Halm, E. Hübner, M. Nieger, N. Rautzenberg, A. Schmidt, *J. Org. Chem.* **2011**, *76*, 7316–7325.
- [25] A. Schmidt, A. Rahimi, *Chem. Commun.* **2010**, *46*, 2995–2997.
- [26] A. Rahimi, A. Schmidt, *Synthesis* **2010**, 2621–2625.
- [27] A. Rahimi, A. Schmidt, *Synlett* **2010**, 1327–1330.
- [28] M. Albrecht, M. Yulikov, T. Kohn, G. Jeschke, J. Adams, A. Schmidt, *J. Mater. Chem.* **2010**, *20*, 3025–3034.
- [29] M. Albrecht, M. Nieger, A. Schmidt, *Z. Naturforsch.* **2011**, *66b*, 209–212.
- [30] A. Carpita, A. Lessi, R. Rossi, *Synthesis* **1984**, 571–572.
- [31] Porosity defined as total potential solvent area volume per unit cell volume: A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.
- [32] For the packing index, see: A. I. Kitajgorodskij, *Molecular Crystals and Molecules*, New York, Academic Press, **1973**.
- [33] N. R. Champness, A. N. Khlobystov, A. G. Majuga, M. Schröder, N. V. Zyk, *Tetrahedron Lett.* **1999**, *40*, 5413–5416.
- [34] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467–473; *ibid.* **2008**, *A64*, 112–122.