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Solvothermal Synthesis and Crystal Structure of a 1D Coordination Polymer: $[Ni(1,4\text{-}BDC)(N\text{-}MIM)_2]_n$ (1,4-BDC = 1,4-Benzenedicarboxylic Acid, N-MIM = *N*-Methylimidazole)[1]

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Abstract—A new metal-organic coordination polymer, namely $[Ni(1,4\text{-}BDC)(N\text{-}MIM)_2]_n$ (**I**) (1,4-BDC = 1,4-benzenedicarboxylic acid and N-MIM = *N*-methylimidazole), has been synthesized under solvothermal conditions by using N-MIM as solvent and characterized by elemental analysis, IR, and X-ray single-crystal diffraction. The X-ray diffraction analysis reveals that **I** crystallizes in the monoclinic system, space group *C*2/*c*. The 1,4-BDC ligand adopts a *bis*(bidentate) chelating mode to connect two adjacent Ni(II) centers to form a one-dimensional (1D) zigzag chain. The adjacent chains are further linked through hydrogen bonds and π–π stacking interactions, forming a three-dimensional (3D) supramolecular framework. The unit cell parameters for I: $a = 17.250(10)$, $b = 7.214(4)$, $c = 16.506(7)$ Å, $\beta = 125.53(4)°$, $V = 1671.6(15)$ Å^3, $Z = 4$.

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INTRODUCTION

The design and synthesis of metal-organic frameworks (MOFs) has attracted much attention in recent decades, not only because of their intriguing variety of architectures and topologies but also owing to their potential applications as functional materials, such as porous materials, catalysis, chirality, magnetic materials, etc. [1–6]. One of the successful approaches to construct MOFs is to employ suitable multidentate organic ligands and metal ions as building blocks. Among them, carboxylate ligands have been demonstrated as top-ranking candidates for the construction of novel coordination frameworks due to the controllable length of ligand and the various coordination modes of the carboxyl group [7]. In this paper, we report the synthesis and structural characterization of a new coordination polymer $[Ni(1,4\text{-}BDC)(N\text{-}MIM)_2]_n$ (**I**) (1,4-BDC = 1,4-benzenedicarboxylic acid and N-MIM = *N*-methylimidazole), which exhibits a new 1D zigzag chain structure. Adjacent chains are further linked via strong intermolecular hydrogen bonds and π–π stacking interactions to form a 3D supramolecular structure.

EXPERIMENTAL

Materials and methods. All reagents employed were commercially available and used as received without further purification. The C, H, and N microanalyses were carried out with a PerkinElmer 240 elemental analyzer. The FTIR spectra were recorded from KBr pellets in the 4000–400 cm^{-1} range on a Nicolet 5DX spectrometer.

Solvothermal synthesis. Compound **I** was obtained by the solvothermal reaction of $Ni(NO_3)_2 \cdot 6H_2O$ (0.4361 g, 1.5 mmol), 1,4-BDC (0.1661 g, 1.0 mmol), and N-MIM (10 mmol) in a 23-mL Teflon flask at 110°C for five days followed by cooling to a needed temperature at a rate of 5 K/h. The resulting green block crystals of **I** were isolated after being washed with methanol and dried in air (the yield is ~40%).

For $C_{16}H_{16}N_4NiO_4$			
anal. calcd., %:	C, 49.65;	H, 4.17;	N, 14.48.
Found, %:	C, 49.67;	H, 4.15;	N, 14.45.

IR spectrum (KBr; ν, cm^{-1}): 1557 v.s, 1536 m, 1504 s, 1440 w, 1397 v.s, 1282 m, 1240 m, 840 s, 747 s, 657 s, 530 s.

X-ray crystal determination. Single-crystal X-ray diffraction measurements were carried out on a Bruker P4 diffractometer at 293(2) K temperature. The data collections were performed with MoK_α radiation ($\lambda = 0.71073$ Å) and a graphite monochromator using the ω scan mode. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL [8–10]. All non-hydrogen atoms were treated anisotropically. Positions of hydrogen atoms were generated geometrically. Crystallographic

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Table 1. Crystallographic parameters and summary of data collection for **I**

Parameter	Value
Formula weight	387.02
Crystal system	Monoclinic
Space group	$C2/c$
Unit cell dimensions:	
a, Å	17.250(10)
b, Å	7.214(4)
c, Å	16.506(7)
β, deg	125.53(4)
V, Å^3	1671.6(15)
Z	4
ρ_{calcd}, mg cm^{-3}	1.538
Absorption coefficient, mm^{-1}	1.190
F(000)	800
Crystal size, nm	0.37 × 0.31 × 0.27
θ Range, deg	2.72–26.10
Limiting indeces, h, k, l	$-21 \le h \le 21$,
	$-8 \le k \le 8$
	$-20 \le l \le 20$
Scan mode	ω
Reflections collected	8234
Independent reflections (R_{int})	1657(0.0483)
Data/restraints/parameters	1657/0/114
Goodness-of-fit on F^2	1.039
Final R indices ($I > 2\sigma(I)$)*	$R_1 = 0.0381$, $wR_2 = 0.0904$
R indices (all data)	$R_1 = 0.0565$, $wR_2 = 0.0982$
Largest diff. peak and hole, e/Å^3	0.426 and −0.240

* $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

data and experimental details for structural analyses are summarized in Table 1, and the selected bond lengths and angles are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (no. 794369; deposit@ccdc.cam.ac.uk).

RESULTS AND DISCUSSIONS

The asymmetric unit consists of one nickel(II) center on the 2-fold axis, one molecule of 1,4-BDC, and two molecules of N-MIM (Fig. 1). The nickel(II) ion is surrounded by two nitrogen atoms from two individual N-MIM molecules and four oxygen atoms

Table 2. Selected lengths (Å) and angles (deg) for **I***

Bond	d, Å	Bond	d, Å
Ni(1)–O(1)	2.186(2)	Ni(1)–N(1)	2.018(2)
Ni(1)–O(2)	2.063(2)		
Angle	**ω, deg**	**Angle**	**ω, deg**
N(1)$^{\#1}$Ni(1)N(1)	97.59(13)	O(2)$^{\#1}$Ni(1)O(1)	100.26(8)
N(1)Ni(1)O(2)$^{\#1}$	93.99(9)	O(2)Ni(1)O(1)	61.51(8)
N(1) Ni(1)O(2)	101.35(9)	N(1)$^{\#1}$Ni(1)O(1)$^{\#1}$	94.06(10)
O(2)$^{\#1}$Ni(1)O(2)	156.68(12)	O(2)Ni(1)O(1)$^{\#1}$	100.26(8)
N(1)$^{\#1}$Ni(1)O(1)	154.60(8)	O(1)Ni(1)O(1)$^{\#1}$	84.64(12)
N(1)Ni(1)O(1)	94.06(10)		

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, y, -z + 1/2$.

from two individual chelating *bis*-bidentate 1,4-BDC ligands with the bond lengths ranging from 2.018(2) to 2.186(2) Å and bond angles ranging from 61.51(8)° to 101.35 (90)° and from 154.60(8)° to 156.68(12)° to give a distorted octahedral geometry around of the mental center (Table 2). The 1,4-BDC ligand acting in a *bis*-bidentate chelating mode to connect two individual Ni(II) center to form a 1D zigzag chain with a Ni···Ni distance of 10.562(4) Å (Fig. 2). The Ni–O bond distances are in the range of 2.063(2)–2.186(2) Å for Ni–$O_{carboxylic}$, which are comparable to those reported for other nickel–oxygen donor compounds [11, 12]. Weak π–π stacking is observed between the imidazole rings of the lateral N-MIM ligand with a perpendicular separation of 3.6127(14) Å and a centroid-to-centroid distance of 4.340(3) Å.

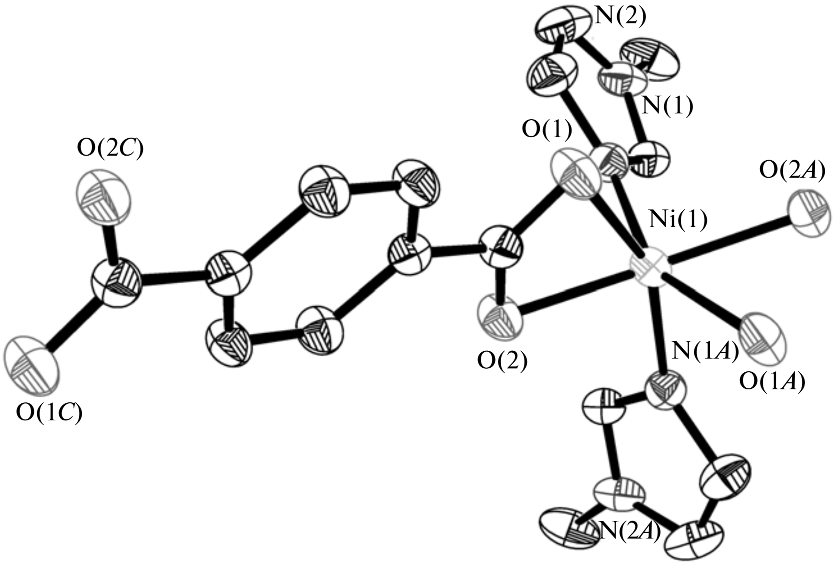

Fig. 1. Coordination environment of the Ni(II) center in **I**.

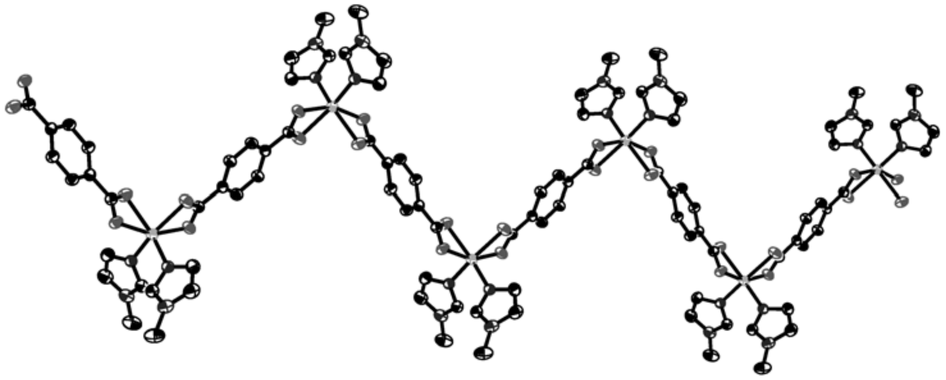

Fig. 2. Fragment of the zigzag $[Ni(1,4\text{-}BDC)(N\text{-}MIM)_2]_n$ chain.

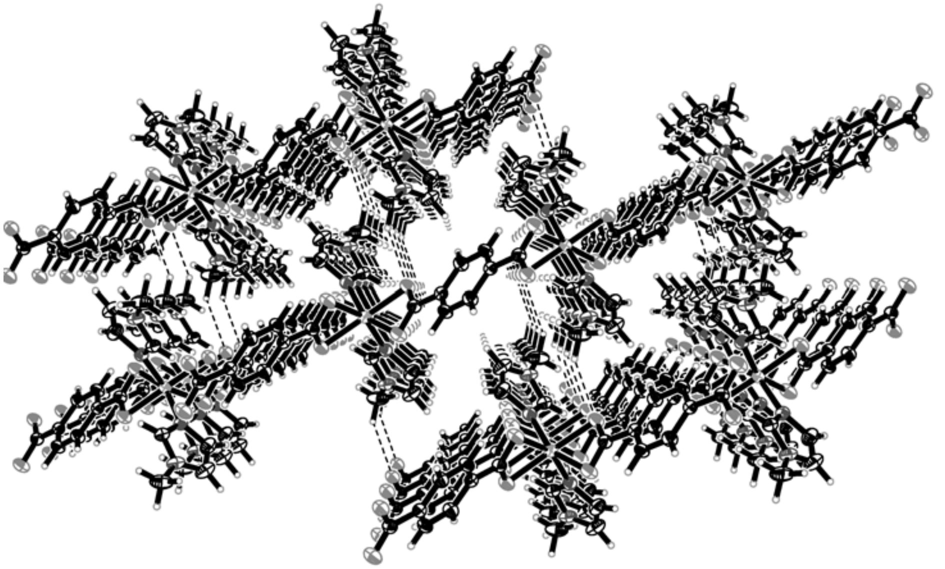

Fig. 3. The 3D supramolecular structure of **I** showing the hydrogen bonds and π–π stacking interactions viewed along the *y* axis.

These values are typical of π–π stacking interactions [13]. Adjacent zigzag chains are further linked via the hydrogen bonding to form a 3D supramolecular framework (Fig. 3). The hydrogen bonding and π–π stacking interactions enhance the stability of the complex [14, 15]. Parameters of bond C(9)–H(9B)···O(2)$^\#$ ($^\#$ $x + 1/2$, $-y + 1/2$, $z - 1/2$) are: D–H 0.96, H···A 2.46, D···A 3.276(5) Å, angle D–H···A 143°.

The IR spectrum of complex **I** shows characteristic bands of the dicarboxylate groups in the usual region at 1557 and 1536 cm^{-1} for the antisymmetric stretching and at 1440 w, 1397 vs for symmetric stretching. The separations (Δ) between $\nu_{as}(CO_2)$ and $\nu_s(CO_2)$ are at 117 and 139 cm^{-1}, respectively. The values of $\Delta(\nu_{as} - \nu_s) < 200$ cm^{-1} indicate that the coordination of carboxyl group is chelating bidentate [16, 17]. The absence of the absorption band around 1700 cm^{-1} confirms that the carboxylate groups are completely deprotonated [18, 19] that is in accord with the results of the X-ray analysis.

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