# Characterization and Crystal Structure of a Novel Two-dimensional Coordination Polymer: $[Ni(bpdc)(bix)_{1.5} \cdot H_2O]_n$

Lin Heng Wei[a], Zi-Liang Wang[b], and Ming-Xue Li[b]

[a] Institute of Natural Resources and Environmental Science, College of Environment and Planning, Henan University, Kaifeng 475001, P. R. China
[b] College of Chemistry and Chemical Engineering, Henan University, Kaifeng 475001, P. R. China

Reprint requests to Lin Heng Wei. E-mail: linhengw@henu.edu.cn
or Zi Liang Wang. E-mail: zlwang@henu.edu.cn

*Z. Naturforsch.* **2011**, *66b,* 681 – 684; received January 10, 2011

The two-dimensional coordination polymer $[Ni(bpdc)(bix)_{1.5} \cdot H_2O]_n$ ($H_2$bpdc = 2,4′-biphenyldicarboxylic acid; bix = 1,4-bis(imidazol-1-ylmethyl)benzene) was hydrothermally synthesized and structurally characterized. In the tile compound, the octahedral coordination environment around the $Ni^{2+}$ ion is established by two oxygen atoms from two $bpdc^{2-}$ anions, one water molecule and three nitrogen atoms from three bix ligands. One bix ligand in the asymmetric unit lies on an inversion center at 1, 0.5, 0.5, and the other bix molecule resides on a general position. Each of the two bix molecules is coordinated to four $Ni^{2+}$ ions, forming a 52-membered ring which is further assembled into a one-dimensional tape structure running parallel to the [100] direction. By a combination of the O2 and O4 oxygen atoms of one $bpdc^{2-}$ anion coordinating two $Ni^{2+}$ ions, adjacent tapes are joined together, forming a layer structure parallel to the (010) plane. A 22-membered ring is formed by means of two bpdc anions binding to two $Ni^{2+}$ ions.

*Key words:* Crystal Structure, Coordination Polymer, Carboxylate, Topology

## Introduction

Rational design and synthesis of metal-organic frameworks have attracted considerable attention owing to their intriguing architectures and potential applications in catalysis and in gas storage fields [1, 2]. During the past decades, many metal-organic frameworks have been reported, in which polycarboxylates are used as bridging ligands owing to their multiple coordination sites and versatile coordination modes [3 – 6].

2,4′-Biphenyldicarboxylic acid is a flexible ligand for coordinating transition metals, because it has two carboxyl groups that can supply four potential O-donor atoms. Moreover, the two carboxyl groups are in asymmetric positions, and the two phenyl rings can be rotated around the C–C single bond. To the best of our knowledge, coordination polymers with 2,4′-biphenyldicarboxylate groups have been rarely reported [7]. Herein we present the coordination polymer $[Ni(bpdc)(bix)_{1.5} \cdot H_2O]_n$ (**1**).

## Experimental Section

### General

All chemicals were of reagent grade as received from commercial sources and used without further purification. C, H, N elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. The infrared spectrum was recorded on KBr pellets with a Nicolet 170SXFT-IR spectrometer in the range of 400 – 4000 $cm^{-1}$. The UV spectrum was obtained on a Shimzu UV-250 spectrometer in the range 190 $\sim$ 400 nm. TG measurements were performed on a Perkin-Elmer7 thermal analyzer in flowing nitrogen gas with a heating rate of 10 °C $min^{-1}$.

### *Synthesis of* $[Ni(bpdc)(bix)_{1.5} \cdot H_2O]_n$ (**1**)

A mixture of $NiSO_4 \cdot 7H_2O$ (0.5 mmol, 0.14 g), $H_2$bpdc (0.5 mmol, 0.12 g), bix (0.5 mmol, 0.12 g), NaOH (1 mmol, 0.04 g), and $H_2O$ (15 mL) was placed in a Parr Teflon-lined stainless-steel vessel (23 mL), which was sealed and heated at 130 °C for 3 d. After the mixture had slowly cooled to r. t., green block-shaped crystals were obtained. – Elemental analysis: calcd. C 62.34, H 4.63, N 12.46; found C 62.46, H 4.69, N 12.19. – IR (film): $\nu$ = 3127(m), 3025(w), 1601(m), 1579(m), 1555(m), 1518(m), 1440(m), 1423(w), 1390(s), 1279(s), 1234(s), 1101(m), 936(s), 818(m), 790(s), 674(m) $cm^{-1}$.

### *Crystal structure determination*

The data collection was made on a Bruker SMART APEX CCD area detector diffractometer using graphite-monochromatized Mo$K_\alpha$ radiation ($\lambda$ = 0.71073 Å) at 298(2) K.

0932–0776 / 11 / 0700–0681 $ 06.00 © 2011 Verlag der Zeitschrift für Naturforschung, Tübingen · http://znaturforsch.com

Table 1. Crystallographic data for [Ni(bpdc)(bix)$_{1.5}$· $H_2O$]$_n$ (**1**).

| | |
|---|---|
| Formula | $C_{35}H_{31}N_6NiO_5$ |
| $M_r$ | 674.37 |
| Crystal size, mm$^3$ | 0.10 × 0.06 × 0.04 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| $a$, Å | 13.559(2) |
| $b$, Å | 23.860(3) |
| $c$, Å | 10.027(2) |
| $\beta$, deg | 91.55(2) |
| $V$, Å$^3$ | 3242.7(9) |
| $Z$ | 4 |
| $D_{calcd}$, g cm$^{-3}$ | 1.38 |
| $\mu$(Mo$K_\alpha$), cm$^{-1}$ | 6.5 |
| $F$(000), e | 1404 |
| Refl. measured / unique / $R_{int}$ | 23055 / 6385 / 0.079 |
| Param. refined | 432 |
| $R1$ / $wR2$ [$I \geq 2\sigma(I)$]$^a$ | 0.0529 / 0.0932 |
| $R1$ / $wR2$ (all data)$^a$ | 0.0872 / 0.1024 |
| GoF ($F^2$)$^b$ | 0.986 |
| $\Delta\rho_{fin}$ (max / min), e Å$^{-3}$ | 0.45 / −0.36 |

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.0334P)^2]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0) + 2F_c{}^2)/3$; [b] GoF $= [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$.

Table 2. Selected bond lengths (Å) in the Ni coordination sphere of **1**$^a$.

| | | | |
|---|---|---|---|
| Ni(1)–N(5) | 2.053(2) | Ni(1)–N(1) | 2.079(2) |
| Ni(1)–O(4) | 2.0852(17) | Ni(1)–O(2)A | 2.0888(16) |
| Ni(1)–O(5) | 2.1030(18) | Ni(1)–N(4)B | 2.105(2) |

[a] Symmetry transformations used to generate equivalent atoms: (A) $-x+2$, $-y+1$, $-z+2$; (B) $x-1$, $y$, $z$.

The intensities were corrected for Lorentz and polarization effects, and empirically for absorption. The structure was solved by Direct Methods and refined by full-matrix least-squares techniques on $F^2$ using the program SHELXTL-97 [8]. All non-hydrogen atoms were refined anisotropically. H atoms bound to water were located from a difference map. All remaining H atoms were positioned geometrically. Crystallographic data are listed in Table 1. Selected bond lengths and angles are given in Table 2.

CCDC 806661 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.

## Results and Discussion

### *Crystal and molecular structure of [Ni(bpdc)(bix)$_{1.5}$ · $H_2O$]$_n$ (**1**)*

As shown in Fig. 1, the asymmetric unit of **1** contains one Ni$^{2+}$ ion, one bpdc$^{2-}$ anion, one and a half of the bix ligand and one Ni-coordinated water molecule. The Ni$^{2+}$ ion is coordinated by two oxygen atoms from different bpdc$^{2-}$ anions, one water molecule and three nitrogen atoms from three bix ligands, constructing a distorted coordination octahedron. In addition to being Ni-coordinated, the O5 water molecule is hydrogen-bonded to two carboxylate O atoms [O1 ($-x+2$, $-y+1$, $-z+2$) and O3]. The Ni–O distances range from 2.085(2) to 2.103(2) Å, and the Ni–N bond lengths fall in the range 2.053(2) – 2.105(2) Å, comparable to those in some analogous compounds [7]. The two crystallographically independent bix ligands adopt an *anti*-conformation each. For one bix ligand, the dihedral angles of the two imidazole rings with respect to the average plane of the central phenyl ring are almost equal at 79.0 and 79.3°. For the other, centrosymmetric bix molecule, the corresponding angles are both 76.6°. Each of the two bix molecules is linked to four Ni$^{2+}$ ions, forming a 52-membered ring with Ni···Ni distances of 13.559(1) and 13.745(1) Å. These 52-membered rings are further assembled into a one-dimensional tape structure running parallel to the [100] direction by sharing the symmetrical bix bridge (Fig. 2). By the interactions of the carboxylate atoms O2 and O4 coordinating to two Ni$^{2+}$ ions residing on two different tape structures,

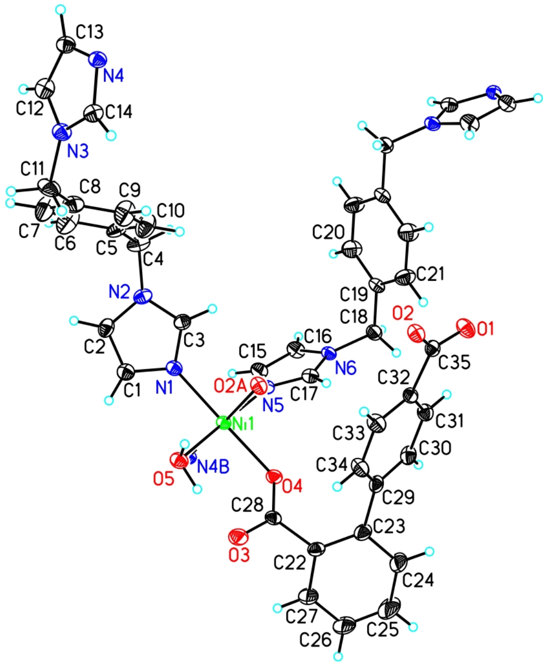

Fig. 1. The asymmetric unit of **1** showing the atom-numbering scheme adopted. Displacement ellipsoids are drawn at the 30 % probability level. Symmetry codes: (A) $-x+2$, $-y+1$, $-z+2$; (B) $x-1$, $y$, $z$.

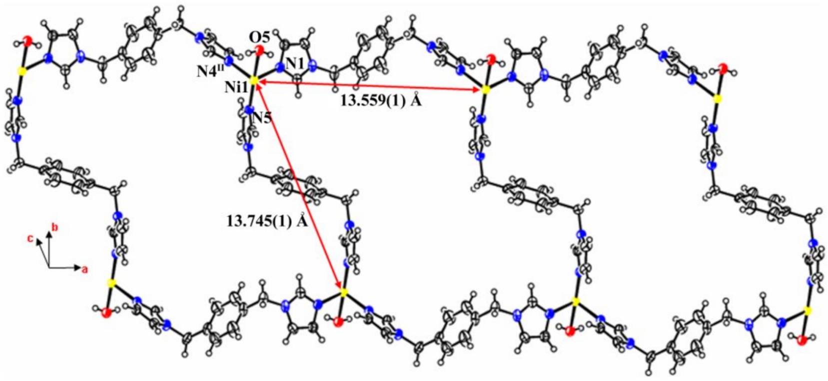

Fig. 2. Part of the structure of **1**, showing the formation of the one-dimensional tape structure by the interactions of the bix molecules with the $Ni^{2+}$ ions. The $bpdc^{2-}$ anions have been omitted for clarity. Symmetry code: (II) $x-1, y, z$.

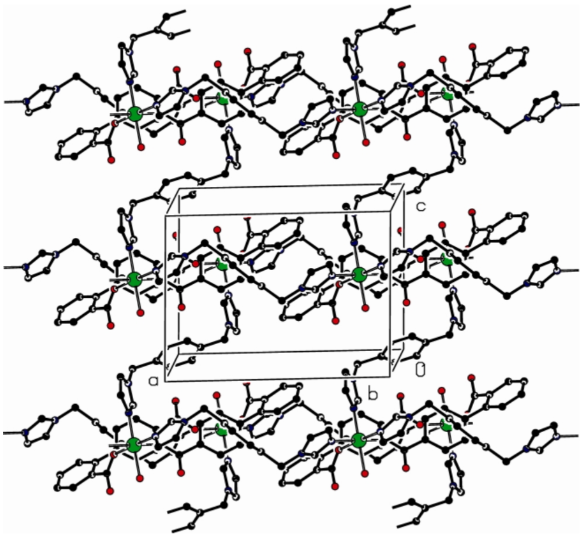

Fig. 3. Part of the structure of **1**, showing the formation of the two-dimensional network formed by coordination of bix and $bpdc^{2-}$ ligands to the $Ni^{2+}$ ions.

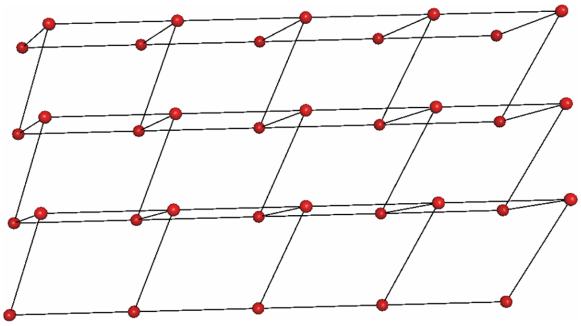

Fig. 4. Schematic view of the ($4^4$, $6^2$) net (node: Ni) in the crystal structure of **1**.

these adjacent tapes are further joined together forming a two-dimensional network running parallel to the (010) plane (Fig. 3). A 22-membered ring is formed by means of two $bpdc^{2-}$ anions binding to two $Ni^{2+}$ ions with a Ni···Ni distance of 8.821(5) Å. Both carboxylate groups of the $bpdc^{2-}$ unit coordinate to one $Ni^{2+}$ ion in a monodentate mode with a dihedral angle of 132.7° between the two phenyl rings. In order to simplify the description of the network, we have carried out a topological analysis. When both $bpdc^{2-}$ anions and bix ligands are regarded as 2-connectors, and the $Ni^{2+}$ ions as 4-connected nodes, then the title compound can be identified as a ($4^4$.$6^2$) net [9] (Fig. 4).

The Co complex related to the title compound, [Co(2,4′-bpdc)(bix)], has recently been reported by Liu [7]. Although their components are similar except for the metal atom, the spatial arrangements are very different. For instance, the bpdc anion in [Co(2,4′-bpdc)(bix)] has two coordination modes: the 2-carboxylate group coordinates to one $Co^{2+}$ cation as a monodentate ligand, and the 4′-carboxylate group in a chelating mode. A two-dimensional wave-like network with (4,4) topology is thus formed by these coordination motifs. In another related compound, $[Co(2,4'\text{-bpdc})(bix)_{0.25}] \cdot 0.25H_2O$ [7], the two carboxylate groups in the $bpdc^{2-}$ anion also adopt two different coordination modes: the 2-carboxylate group coordinates to two $Co^{2+}$ cations in a bidentate bridging mode, and the 4′-carboxylate group coordinates to one Co(II) cation in a monodentate fashion. A sheet structure with a ($6^3$)($6^3$.$10^3$) topology is thus formed in $[Co(2,4'\text{-bpdc})(bix)_{0.25}] \cdot 0.25H_2O$. In comparison, although both compounds have the same organic bridging ligands, including 2,4′-bpdc and bix molecules, they have distinctly different topologies mainly caused by the different metal coordination modes of $Ni^{2+}$ *versus* $Co^{2+}$.

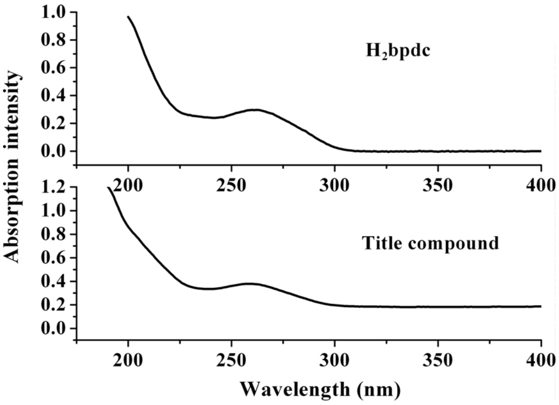

Fig. 5. UV spectrum of the **1** and of $H_2$bpdc.

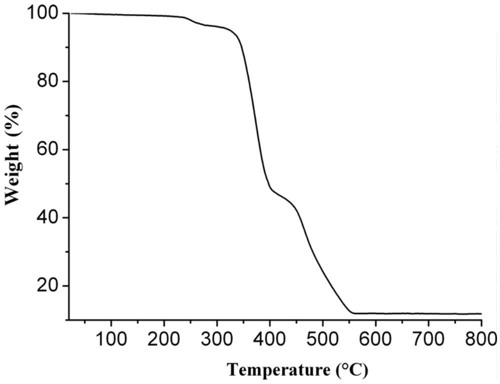

Fig. 6. TGA curve of **1**.

### *IR spectrum of* ***1***

The IR spectra of **1** shows the characteristic bands of carboxylate groups in the region 1579–1602 $cm^{-1}$ for the $\nu_{as}(COO^-)$ and 1390–1423 $cm^{-1}$ for the $\nu_s(COO^-)$ vibrations. The values $\Delta\nu = 189$ and 179 $cm^{-1}$ indicate that two carboxylate groups are coordinated in a mono-dentate fashion [10], which is consistent with the results of the X-ray analysis. Peaks at 1555 and 1440 $cm^{-1}$ are assigned to the vibrations of C=N and C=C in the imidazole rings of the bix ligands [11].

### *UV spectrum of* ***1***

The UV spectra of **1** and of the $H_2$bpdc and bix ligands were investigated in the solution state in the range of 190 ~ 400 nm. For the bix ligand, there is no absorption band. The title compound and $H_2$bpdc display one absorption peak at 260 nm (Fig. 5), attributed to an $n \rightarrow \pi^*$ transition of $H_2$bpdc [12]. However, the absorption intensity in the title compound is slightly increased, which indicates that the coordination of $bpdc^{2-}$ to $Ni^{2+}$ does not affect the absorption maximum but weakly changes the absorption intensity.

### *Thermal properties of* ***1***

The results of a thermogravimetric analysis (TGA) of **1** measured under a $N_2$ atmosphere are shown in Fig. 6. The weight loss of 3.2 % from r. t. to 267 °C (calcd. 2.67 %) corresponds to the loss of one coordinated water molecule per formula unit. A further rapid weight loss of 50.6 % (calcd. 50.60 %) can be observed from 276 to 409 °C, which is attributed to the decomposition of the bix ligands. The third step with a loss of 34.3 % (calcd. 35.58 %) can be detected from 422 to 573 °C corresponding to the decomposition of the $bpdc^{2-}$ anions.

*Acknowledgement*

This work was supported by the Natural Science Foundation of Henan Province (grant Nos. 092300410119 and 102300410093).

[1] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469.

[2] J. L. Belof, A. C. Stern, M. Eddaoudi, B. Space, *J. Am. Chem. Soc.* **2007**, *129*, 15202.

[3] X. Y. Duan, Y. Z. Li, Y. Su, S. Q. Zang, C. J. Zhu, Q. J. Meng, *CrystEngComm* **2007**, *9*, 758.

[4] Y. Y. Liu, J. Yang, J. C. Ma, J. F. Ma, *Acta Crystallogr.* **2008**, *C64*, m33.

[5] Y. J. Jiang, J. Huang, B. Kasumaj, G. Jeschke, M. Hunger, T. Mallat, A. Baiker, *J. Am. Chem. Soc.* **2009**, *131*, 2058.

[6] S. Wang, D. Q. Wang, J. M. Dou, D. C. Li, *Acta Crystallogr.* **2010**, *C66,* m141.

[7] Y. Liu, Y. Qi, Y. H. Su, F. H. Zhao, Y. X. Che, J. M. Zhen, *CrystEngComm* **2010**, *12*, 3283.

[8] 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; *ibid.* **2008**, *A64*, 112.

[9] V. A. Blatov, A. P. Shevchenko, V. N. Serezhkin, *J. Appl. Crystallogr.* **2000**, *33*, 1193.

[10] G. P. Yang, Y. Y. Wang, L. F. Ma, J. Q. Liu, Y. P. Wu, W. P. Wu, Q. Z. Shi, *Eur. J. Inorg. Chem.* **2007**, 3892

[11] S. R. Zhu, H. Zhang, Y. M. Zhao, M. Shao, Z. X. Wang, M. X. Li, *J. Mol. Struct.* **2008**, *892*, 420.

[12] G. G. Mohamed, N. E. A. El-Gamel, *Spectrochim. Acta, Part A* **2004**, *60*, 3141.