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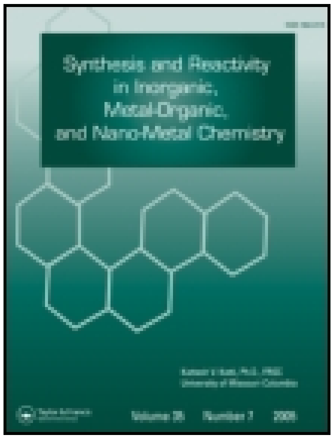

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Hydrothermal Synthesis of Two Ni(II) Metal-Organic Coordination Polymers Constructed From Dicarboxylate and Nitrogen-Contained Ligands

Feng Guo [a], Jian-Jun Li [b], Xian-Jiang Li [c], Bao-Yong Zhu [a] & Xiu-Ling Zhang [a]
[a] Department of Chemistry, De Zhou University, Shandong, P. R. China
[b] Weifang Entry-Exit Inspection and Quarantine Bureau, Shandong, P. R. China
[c] Shangdong ShengLi Co. Ltd, Shandong, P. R. China

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Hydrothermal Synthesis of Two Ni(II) Metal-Organic Coordination Polymers Constructed From Dicarboxylate and Nitrogen-Contained Ligands

Feng Guo,[1] Jian-Jun Li,[2] Xian-Jiang Li,[3] Bao-Yong Zhu,[1] and Xiu-Ling Zhang[1]
[1]*Department of Chemistry, De Zhou University, Shandong, P. R. China*
[2]*Weifang Entry-Exit Inspection and Quarantine Bureau, Shandong, P. R. China*
[3]*Shangdong ShengLi Co. Ltd, Shandong, P. R. China*

Two new coordination polymers $[Ni(2,4'\text{-oba})(1,10\text{-phen})]_n$ (1) and $\{[Ni(2,4'\text{-Hoba})_2\ (4,4'\text{-}\ bipy)(H_2O)_2]\cdot 2H_2O\}_n$ (2) have been synthesized [2,4′-H_2oba=2-(4-carboxyphenoxy)benzoic acid, 1,10-phen=1,10-phenanthroline and 4,4′-bipy=4,4′-bipyridine]. The framework structures of these polymeric complexes have been determined by single-crystal X-ray diffraction studies. Complex 1 exhibits double-helical chains formed by π-π stacking interactions from the phenyl rings of the 1,10-phen ligands. Complex 2 forms a two-dimensional supramolecular architecture directed by hydrogen bonding. In compounds 1 and 2, the oba^{2-} ligands exhibit two coordination modes to link metal ions: bidentate chelating and monodenate modes.

Keywords crystal structure, hydrothermal syntheses, nickel(II) complex

INTRODUCTION

The interest in the construction of metal-organic frameworks (MOFs) is rapidly increasing in crystal engineering owing to their ability to provide diverse assemblies with fascinating topological structures and material properties that make them potential applications relating to magnetism, porous materials, and luminescence.[1–8] Selection of the appropriate multidentate ligand to link metal ions is a key strategy for the building MOFs. Therefore, a considerable number of transition metal compounds using carboxylates have been reported during the last decade due to the diversity of bonding modes of carboxylate groups.[9–13]

Semirigid V-shaped multicarboxylate ligands with two benzene rings of central molecular framework bridged by a nonmetallic atom (C, O, S, or N) are excellent ligands and can freely twist around the nonmetallic atom to meet the requirements of the coordination geometries of metal atoms in the assembly process.[14–16]

In view of previous points, we chose 2-(4-carboxy phenoxy)benzoic acid along with nitrogen-contained auxiliary ligands to construct two new metal coordination polymers $[Ni(2,4'\text{-oba})(1,10\text{-phen})]_n$ (**1**) and $\{[Ni(2,4'\text{-Hoba})_2\ (4,4'\text{-}bipy)(H_2O)_2]\cdot 2H_2O\}_n$ (**2**).

EXPERIMENTAL

Materials and Physical Measurements

All reagents and solvents employed were commercially available and were used as received without further purification. Elemental analysis was carried out on a Carlo Erba 1106 full-automatic trace organic elemental analyzer (Germany). FT-IR spectra were recorded with a Bruker Equinox 55 FT-IR spectrometer (Germany) as a dry KBr pellet in the 400∼4000 cm^{-1} range.

Synthesis of $[Ni(2,4'\text{-oba})(1,10\text{-phen})]_n$ (1)

A mixture of $NiCl_2\cdot 6H_2O$ (0.238 g, 1 mmol), H_2oba (0.258 g, 1 mmol), NaOH (0.08 g, 2 mmol), 1,10′-phen(0.180 g, 1 mmol), and distillated water (15 mL) was heated to 160°C for 96 h in a 25 mL stainless steel reactor with a Teflon liner. Green block crystals of **1** were obtained with 42% yield on Ni basis. Elemental Anal. Calcd. (%) for $C_{26}H_{16}NiN_2O_5$: C, 63.07; H, 3.26; N,5.66. Found: C, 62.58; H, 3.24; N, 5.59. IR: 1543(s),1408(s), 1016(w),928(m),851(m),763(m).

Synthesis of $[Ni(2,4'\text{-Hoba})_2\ (4,4'\text{-bipy})(H_2O)_2]\cdot 2H_2O\}_n$(2)

A mixture of $NiCl_2\cdot 6H_2O$ (0.238 g, 1 mmol), H_2oba (0.258 g, 1 mmol), and 4,4′-bipy (0.156 g,1 mmol) and distillated water (15 mL) was heated to 160°C for 96 h in a 25 mL stainless steel reactor with a Teflon liner. Green block crystals of **2** were obtained with 65% yield on Ni basis. Elemental Anal. Calcd. (%) for $C_{38}H_{34}NiN_2O_{14}$: C, 56.95; H, 4.28; N, 3.50. Found:

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Address correspondence to Feng Guo, Department of Chemistry, De Zhou University, Shandong 253023, P. R. China. E-mail: guofeng1510@yeah.net

C, 57.42; H, 4.26; N, 3.45. IR: 3360(br), 1639(s),1394(s), 1113(m),887(s),653(w).

Crystallographic Measurement

Diffraction intensity data of the single crystal of the two compounds were collected on a Bruker SMART APEX CCD diffractometer equipped with a graphite monochromated Mo-$K\alpha$ radiation ($\lambda = 0.71073$ Å) by using a ω-scan mode. Empirical absorption correction was applied using the SADABS programs.[17] All the structures were solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHEXL 97-[18] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for coordination polymers are summarized in Table 1. Selected bond and angle parameters are listed in Table 2.

TABLE 1
Crystallographic data and structure refinement summary for complexes **1** and **2**

Empirical formula	$C_{26}H_{16}N_2NiO_5$	$C_{38}H_{34}N_2NiO_{14}$
Formula weight	495.12	801.38
Crystal system space group	Monoclinic $P2_1/n$	Monoclinic $P2/n$
Unit cell dimensions	$a = 7.740(2)$ Å	$a = 12.415\ (2)$ Å
	$b = 15.388(3)$Å	$b = 111.269\ (1)$ Å
	$c = 18.991(4)$ Å	$c = 13.632\ (2)$ Å
	$\alpha = 90.00°$	$\alpha = 90.00°$
	$\beta = 98.107(2)$ °	$\beta = 107.452\ (1)$ °
	$\gamma = 90.00°$	$\gamma = 90.00°$
Volume(Å^3)	2239.3(8)	1819.4 (4)
Z	4	2
Calculated density(mg/m^3)	1.469	1.463
Reflections collected	5215	3203
Independent reflections ($I > 2\sigma(I)$)	2993	2782
F(000)	1016	832
θ range for data collection	2.54–27.72	2.39–24.99
Limiting indices	$–10 \leq h \leq 9–$	$–14 \leq h \leq 12$
	$20 \leq k \leq 20$	$–10 \leq k \leq 13$
	$–24 \leq l \leq 24$	$–16 \leq l \leq 12$
Goodness-of-fit on F^2	1.000	1.050
R_1[a],wR_2 [b] [$I > 2\sigma$(I)]	$R_1 = 0.0546$	$R_1 = 0.0304$
	$wR_2 = 0.0956$	$wR_2 = 0.0755$
R_1,wR_2 (all data)	$R_1 = 0.1175$	$R_1 = 0.0370$
	$wR_2 = 0.1144$	$wR_2 = 0.0779$
Largest diff. peak and hole (e/Å^3)	0.479 and –0.376	0.284 and –0.221

[a]$R = \Sigma(||F_0|-|F_C||)/\Sigma|F_0|$. [b]$wR = [\Sigma w(|F_0|^2-|F_C|^2)^2/\Sigma w(F_0{}^2)]^{1/2}$.

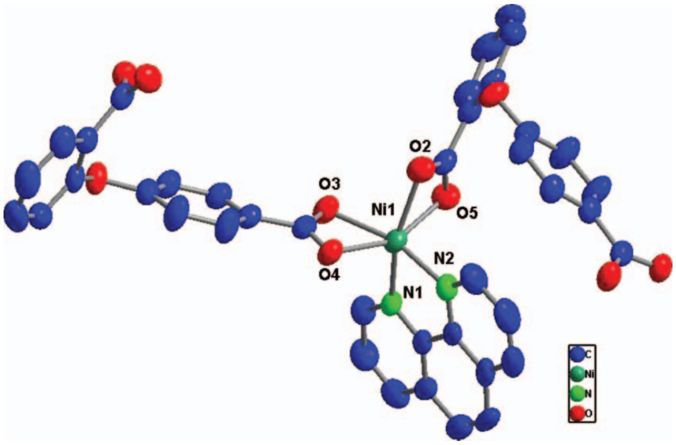

FIG. 1. The coordination environments of nickel(II) atoms in complex **1** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity (color figure available online).

RESULTS AND DISCUSSION

Structure Description of 1

X-ray diffraction analysis shows that the asymmetric unit of complex 1 contains one crystallographic independent Ni(II) atom, one oba^{2-} ligand, and one 1,10-phen ligand. A view of the Ni^{II} atom coordination environment is presented in Figure 1. Each Ni(II) atom is located in a distorted octahedral geometry and is coordinated to four oxygen atoms of two oba^{2-} ligands and two nitrogen atoms of 1,10-phen. The Ni-O bond distances vary from 2.076 Å to 2.142 Å, Ni-N bond lengths are 2.042 Å and 2.056 Å. Each oba^{2-} ligand adopts a bis(chelating bidentate)mode (Scheme 1a), linking two Ni^{II} ions.

The adjacent Ni(II) ions are bridged by V-shaped oba^{2-} ligands to form a helical chain *b*-axis (Figure 2). The helix is generated around the crystallographic 2_1 axis with a pitch of 15.464 Å. The two benzene rings of the oba^{2-} ligand are bent (the dihedral angle of the two benzene rings is ~77.27°). The dihedral angles of carboxylate groups and the corresponding linking rings are 12.62° and 34.27°. Obviously, this twist is an important factor is forming the helical structure.

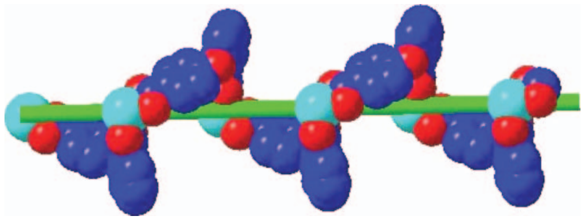

FIG. 2. The helical chain of complex **1** along *b*-axis (color figure available online).

TABLE 2
Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Compound **1**			
Ni(1)—N(1)	2.042 (3)	Ni(1)—O (4)	2.083 (2)
Ni(1)—N(2)	2.056 (3)	Ni(1)—O(3)	2.124 (2)
Ni(1)—O(5)	2.076 (2)	Ni(1)—O(2)	2.142 (2)
N(1)—Ni(1)—N(2)	80.72 (11)	N(2)—Ni(1)—O(3)	161.54 (10)
N(1)—Ni(1)—O(5)	99.21 (9)	O(5)—Ni(1)—O(3)	98.26 (10)
N(2)—Ni(1)—O(5)	99.92 (10)	O(4)—Ni(1)—O(3)	62.79 (9)
N(1)—Ni(1)—O(4)	99.54 (9)	N(1)—Ni(1)—O(2)	161.09 (9)
N(2)—Ni(1)—O(4)	100.79 (10)	N(2)—Ni(1)—O(2)	97.15 (10)
O(5)—Ni(1)—O(4)	153.97 (9)	O(5)—Ni(1)—O(2)	62.46 (8)
N(1)—Ni(1)—O(3)	93.26 (10)	O(4)—Ni(1)—O(2)	99.32 (9)
Compound **2**			
Ni(1)—O(1W)$^{\#1}$	2.0659 (13)	Ni(1)—O(4)$^{\#1}$	2.0811 (12)
Ni(1)—O(1WA)	2.0659 (13)	Ni(1)—O(4A)	2.0811 (12)
Ni(1)—N(1)	2.107 (2)	Ni(1)—N(2)	2.085 (2)
O(1W)$^{\#1}$—Ni(1)—O(1WA)	174.90 (7)	O(1WA)—Ni(1)—O(4A)	92.82 (5)
O(1W)$^{\#1}$—Ni(1)—O(4A)	87.18 (5)	O(1W)$^{\#1}$—Ni(1)—O(4)$^{\#1}$	92.82 (5)
O(1WA)—Ni(1)—O(4)$^{\#1}$	87.18 (5)	O1W^{i}—Ni(1)—N(2)	87.45 (3)
O(1WA)—Ni(1)—N(1)	92.55 (3)	O(1WA)—Ni(1)—N(2)	87.45 (3)
O(4A)—Ni(1)—N(1)	89.98 (3)	O(4A)—Ni(1)—N(2)	90.02 (3)
O(4)$^{\#1}$—Ni(1)—N(1)	89.98 (3)	O(4)$^{\#1}$—Ni(1)—N(2)	90.02 (3)
N2—Ni(1)—N(1)	180.000 (1)	O(1W)$^{\#1}$—Ni(1)—N(1)	92.55 (3)

Symmetry code for compounds: (2)#1:$-x+3/2$, y, $-z+3/2$

The 1,10-phen ligands are alternately attached to both sides of the helical chain, providing potential supramolecular recognition sites for π-π stacking interactions. Two adjacent helical chains with different handedness are assembled by intermolecular π-π stacking. The interchain distance between parallel 1,10-phen ligands is ~3.447 Å and the corresponding centroid-to-centroid distance is ~3.826 Å, indicating face to face π-π stacking interactions that further stabilize the crystal structure (Figure 3).

Structure Description of 2

X-ray diffraction analysis reveals that complex **2** is a 2D supramolecular assembly based on a 1D alternate polymeric

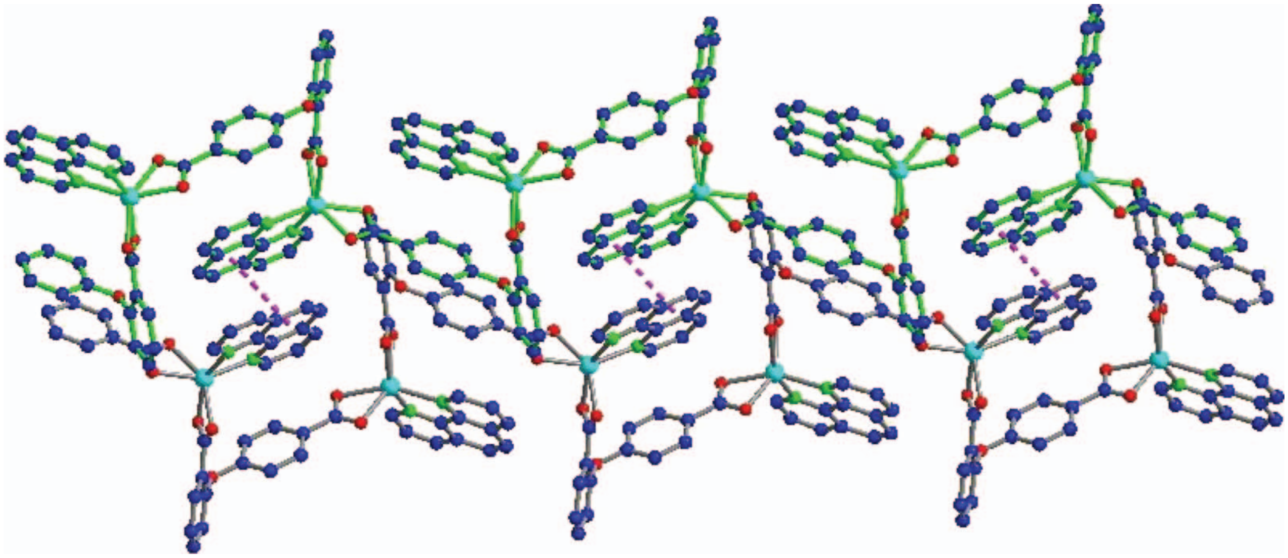

FIG. 3. The 2D supramolecular structure through π-π interceptions (color figure available online).

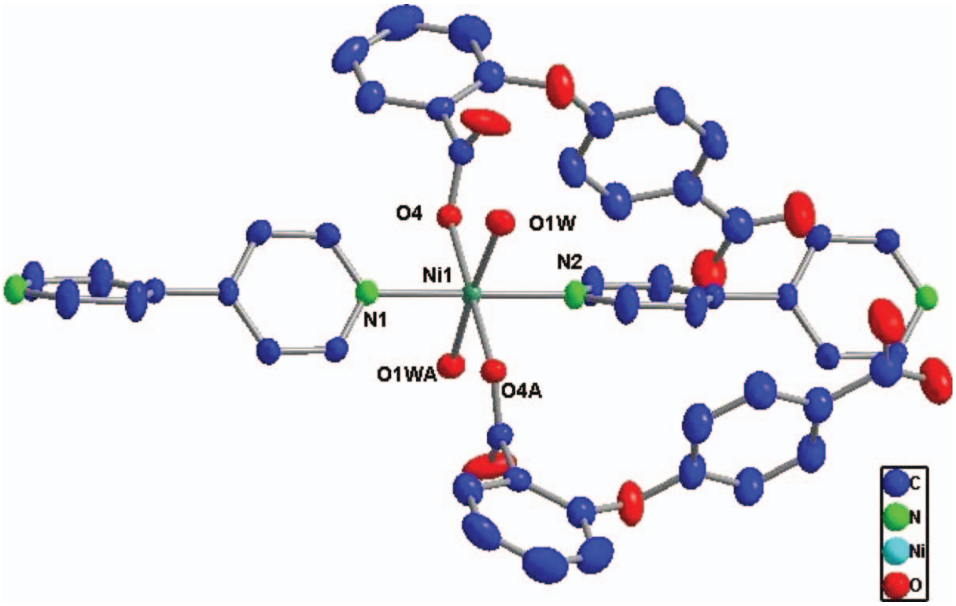

FIG. 4. The coordination environments of nickel(II) atoms in complex **2** with 50% thermal ellipsoids. All hydrogen atoms are omitted for clarity (color figure available online).

chain substructure of Ni(Hoba)$_2$ bridged by 4,4′-bipy. As illustrated in Figure 4, the six-coordinated center shows a octahedral geometry [NiO$_4$N$_2$], with two oxygen atoms from two different oba^{2-} ligands and two nitrogen atoms of separate 4,4′-bipy ligands in the equatorial plane, as well as two oxygen atoms from two water molecules in the axial position. The extended structure of **1** through 4,4′-bipy displays neutral 1D linear [Zn(4,4′-bipy)]chains. H$_2$oba is monodeprotonated

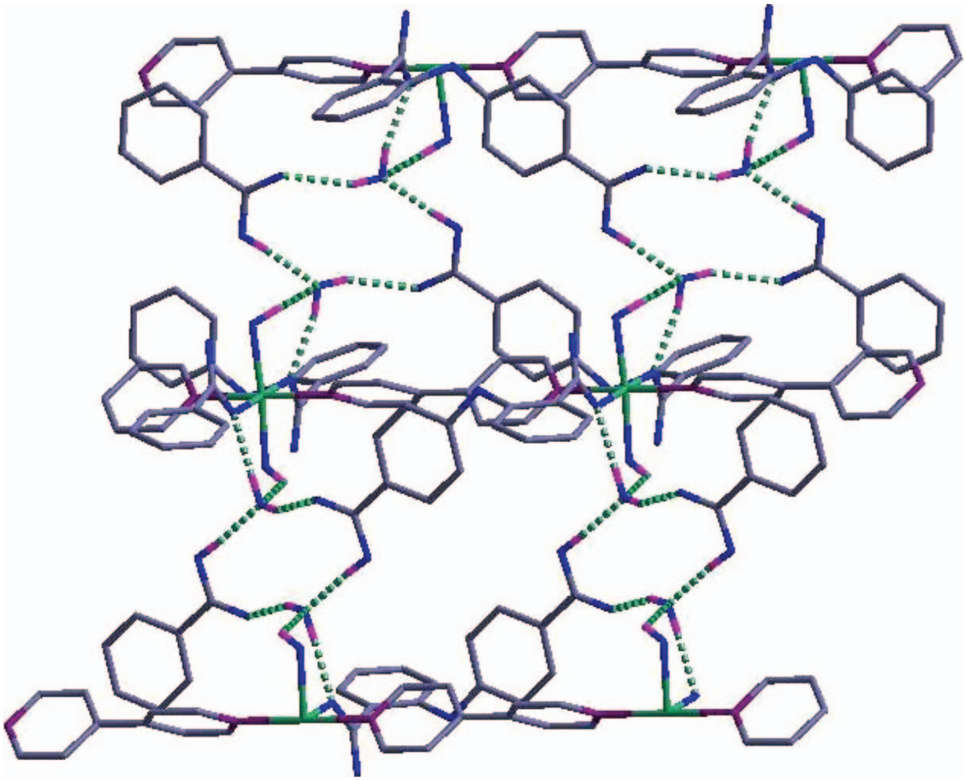

FIG. 5. 2D supramolecular network formed through hydrogen bonding (color figure available online).

TABLE 3

Hydrogen bond lengths(Å) and bond angles (°) for compound 2

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(2W)—H(22W)···O(1)$^{\#1}$	0.84	2.06	2.867 (2)	160
O(2W)—H(21W)···O(4)$^{\#2}$	0.85	1.92	2.733 (2)	160
O(1W)—H(12W)···O(2W)$^{\#3}$	0.84	2.34	2.888 (2)	123
O(1W)—H(11W)···O(5)	0.85	1.84	2.621 (2)	152
O(2)—H(2)···O(2W)$^{\#4}$	0.82	1.83	2.648 (2)	175

Symmetry codes: #1:$-x+1$, $-y+2$, $-z+1$; #2: $-x+1$, $-y+1$, $-z+1$; #3:$x+1/2$, $-y+1$, $z+1/2$; #4:x, $y+1$, $z+1$.

to give Hoba^{-1} to meet the requirement of charge balance requirement.

In compound **2**, O2W of the guest water is involved in a "saturated" hydrogen-bond pattern between the 1D chains (Table 3), acting as a double donor and a double acceptor to three carboxylate oxygen atoms and one oxygen atom from a coordinated water molecule (Figure 5).

CONCLUSION

Two new Ni(II) metal coordination polymers assembled from 2,4′-H_2oba and auxiliary ligands have been successfully prepared under hydrothermal conditions. The differences of neutral ligands and pH value affect the frameworks of the compounds.

SUPPLEMENTARY MATERIALS

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC reference number 780021 and 780022. These data can be obtained fee of charge at: http://www.ccdc.cam.ac.uk (or Cambridge Crystallographic Data Center, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44–1223–336–033; e-mail: deposit @ccdc.cam.ac.uk).

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