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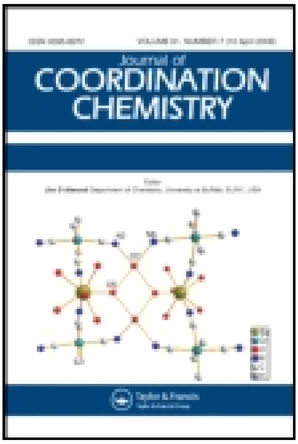

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From discrete dinuclear to 1-D and 2-D structures: nickel dipicolinate complexes with flexible bis(imidazole) ligands

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From discrete dinuclear to 1-D and 2-D structures: nickel dipicolinate complexes with flexible bis(imidazole) ligands

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Three new complexes, $[Ni_2(dpc)_2(L_1)_2(H_2O)_2]\cdot 4H_2O$ (**1**), $[Ni(dpc)(L_2)_{1.5}]_n$ (**2**), and $\{[Ni(dpc)(L_3)_{1.5}]\cdot 2H_2O\}_n$ (**3**), where H_2dpc = dipicolinic acid, L_1 = 1,4-bis(2-methylimidazol-1-yl)butane, L_2 = 4,4′-bis(2-methylimidazol-1-ylmethyl)biphenyl, and L_3 = 1,4-bis(benzimidazol-1-yl)-2-butylene, have been synthesized by hydrothermal methods and characterized by elemental analyses, infrared spectra, thermogravimetric analysis, and X-ray crystallography. The common structural characteristic of the three complexes is that the Ni^{2+} is coordinated by tridentate dipicolinate through nitrogen of pyridine and oxygen of carboxylate, serving as a terminal ligand. In **1**, two L_1 link two $[Ni(dpc)(H_2O)]$ units to a discrete binuclear metallomacrocycle with a 22-membered ring, which is assembled through multiple O–H $\cdots$ O hydrogen bonds to form a 3-D supramolecular framework. Complex **2** exhibits a 1-D ladder-like chain structure constructed by *cis*/*trans*-conformation L_2 linking metal centers; **3** displays a 2-D (6,3) topology, being constructed from the linking of [Ni(pdc)] by L_3. These results indicate the merits of flexible bis(imidazole) ligands as building blocks with dipicolinate for the construction of complexes with diverse structural motifs.

Keywords: Bis(imidazole) ligand; Crystal structure; Nickel-dipicolinate complex

1. Introduction

Research has focused on crystal engineering of metal–organic coordination architectures due to their diversity of structural topologies and potential applications in functional materials [1–4]. Construction of such molecular architecture depends on coordination number and geometry of metal ions, nature of organic ligands and solvents, ratio of metal-to-ligand, counterions, etc. [5]; selection of organic bridging ligand is extremely important. However, understanding of how these considerations affect metal coordination and influence crystal packing remains a great challenge.

Dipicolinic acid (H_2dpc) plays important roles in a variety of processes, enzyme inhibition [6], plant preservation [7], and food sanitation [8]. This aromatic dicarboxylic acid and its anions are widely used in the assembly of coordination frameworks because

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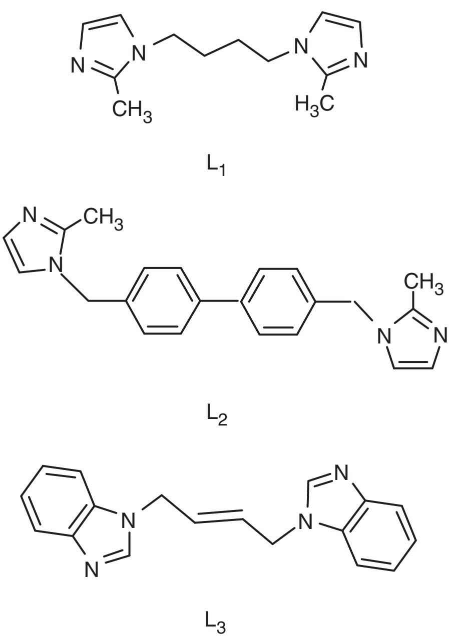

Scheme 1. The selected $L_1 + L_3$ ligands.

of their diverse coordination modes and bridging abilities [9–12]. Flexible bis(imidazole) ligands are a good choice of N-donors with the flexible nature of spacers allowing the ligands to bend and rotate when coordinating to metal centers so as to conform to the coordination geometries of metal ions [13]. We and other groups [14–18] have focused on the synthesis and structural exploration of coordination polymers with mixed dicarboxylates and flexible N-ligands, with a view to understanding how the nature of metal ions and structures of ligands affect the architectures assembled *via* coordination bonds. In this article, we continue to investigate the influence of nature of bis(imidazole) ligands (including chain length, rigidity of spacer, and diimidazolyl functionality) on the formation of transition metal dipicolinate coordination compounds. Three bis(imidazole) derivatives with different flexible spacers, 1,4-bis(2-methylimidazol-1-yl)butane (L_1), 4,4′-bis(2-methylimidazol-1-ylmethyl)biphenyl (L_2), 1,4-bis(benzimidazol-1-yl)-2-butylene (L_3) have been synthesized (scheme 1) and employed in reaction with dipicolinate and nickel nitrate hexahydrate under hydrothermal conditions, yielding three nickel–dipicolinate complexes with different topologies $[Ni_2(dpc)_2(L_1)_2(H_2O)_2] \cdot 4H_2O$ (**1**), $[Ni(dpc)(L_2)_{1.5}]_n$ (**2**), and $\{[Ni(dpc)(L_3)_{1.5}] \cdot 2H_2O\}_n$ (**3**), ranging from discrete dinuclear to 1-D and 2-D frameworks.

2. Experimental

2.1. *Materials and physical measurements*

All commercially available chemicals were of analytical reagent grade and used without purification. L_1, L_2, and L_3 were prepared according to the literature method [19].

Elemental analyses were made on a Perkin-Elmer 240 C automatic analyzer. IR spectra were recorded on a FT-IR AVATAR 360 (Nicolet) spectrophotometer from 4000 to 400 cm^{-1} by using KBr pellets. Thermogravimetric (TG) measurements were carried out on a NETZSCH TG 209 thermal analyzer from room temperature to 800°C, under N_2 with a heating rate of 10°C min^{-1}.

2.2. *Synthesis of the complexes*

2.2.1. Synthesis of $[Ni_2(dpc)_2(L_1)_2(H_2O)_2]\cdot 4H_2O$ (1). A mixture of nickel nitrate hexahydrate (1.0 mmol, 290.8 mg), L_1 (1.0 mmol, 218.3 mg), dipicolinic acid (1.0 mmol, 167.0 mg), NaOH (2.0 mmol, 80.0 mg), and H_2O (10 mL) was placed in a Teflon-lined stainless vessel, heated to 140°C for 4 days under autogenous pressure, and then cooled to room temperature at a rate of 5°C h^{-1}. Green crystals of **1** were obtained in 61.5% yield based on Ni. Anal. Calcd for $C_{38}H_{54}N_{10}Ni_2O_{14}$ (%): C, 46.05; H, 5.50; N, 14.14. Found (%): C, 46.57; H, 5.28; N, 13.99. IR (KBr pellet, cm^{-1}): 3310(s), 3094(w), 2921(w), 1641(s), 1580(m), 1514(m), 1439(w), 1410(w), 1375(m), 1349(m), 1266(w), 1220(m), 1110(m), 1022(w), 853(w), 725(m), 660(m).

2.2.2. Synthesis of $[Ni(dpc)(L_2)_{1.5}]_n$ (2). Preparation of **2** was similar to **1** except that L_2 was used instead of L_1. Green crystals of **2** were obtained in 59.6% yield based on Ni. Anal. Calcd for $C_{40}H_{36}N_7NiO_4$ (%): C, 65.15; H, 4.92; N, 13.30. Found (%): C, 63.29; H, 5.37; N, 12.41. IR (KBr pellet, cm^{-1}): 3420(s), 3063(w), 1630(s), 1500(m), 1470(w), 1430(m), 1370(s), 1280(w), 1080(m), 995(m), 862(w), 810(w), 768(w), 675(w), 536(m).

2.2.3. Synthesis of $\{[Ni(dpc)(L_3)_{1.5}]\cdot 2H_2O\}_n$ (3). Preparation of **3** was similar to **1** except that L_3 was used instead of L_1. Green crystals of **3** were obtained in 49.3% yield based on Ni. Anal. Calcd for $C_{34}H_{31}NiN_7O_6$ (%): C, 59.03; H, 4.52; N, 14.18. Found (%): C, 58.45; H, 4.33; N, 14.65. IR (KBr pellet, cm^{-1}): 3440(s), 3058(m), 2370(w), 1630(s), 1510(m), 1430(w). 1380(m), 1260(w), 1200(m), 1080(m), 991(w), 943(w), 762(w), 536(m).

2.3. *X-ray crystallography*

Suitable single crystals of **1**–**3** were mounted on the top of a glass fiber with epoxy cement for X-ray measurement. The crystallographic data collections were carried out on a Bruker Smart 1000 CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) and ω–2θ scan mode at 293 K. All absorption corrections were applied using SADABS [20a]. The structures were solved by direct methods and refined anisotropically by full-matrix least-squares using Bruker's SHELXTL program package [20b]. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogens of water were located on a difference Fourier map, while other hydrogens were included in calculated positions and refined with anisotropic thermal parameters riding on the corresponding parent atoms. Details of data collection and structure refinement for **1**, **2**, and **3** are summarized in table 1. Because the crystal size of

Table 1. Crystallographic data for **1**, **2**, and **3**.

Complexes	**1**	**2**	**3**
Empirical formula	$C_{38}H_{54}N_{10}Ni_2O_{14}$	$C_{40}H_{36}N_7NiO_4$	$C_{34}H_{31}N_7NiO_6$
Formula weight	992.33	737.47	692.37
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	*C2/c*	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å,°)			
a	19.455(2)	13.111(3)	9.3163(3)
b	17.684(1)	13.657(3)	19.6622(7)
c	15.554(1)	14.245(3)	18.7964(7)
α	90	66.57(3)	90
β	123.562(1)	83.14(3)	111.337(3)
γ	90	61.95(3)	90
Volume (Å^3), *Z*	4459.1(6), 4	2058.3(8), 2	3207.1(2), 4
Calculated density (g cm^{-3})	1.478	1.190	1.434
Absorption coefficient (mm^{-1})	0.920	0.527	0.663
F(000)	2080	770	1440
Crystal size (mm^3)	0.19 × 0.18 × 0.16	0.18 × 0.17 × 0.14	0.20 × 0.20 × 0.19
θ range for data collection (°)	2.30–25.02	3.00–25.02	3.03–25.02
Reflections collected	14,884	17,287	13,354
Independent reflections	3933 [*R*(int) = 0.0388]	7227 [*R*(int) = 0.1349]	5642 [*R*(int) = 0.0333]
Completeness to $\theta = 25.02$ (%)	99.8	99.4	99.8
Goodness-of-fit on F^2	1.043	0.930	0.867
Final *R* indices $[I > 2\sigma(I)]^{a,b}$	$R_1 = 0.0442$, $wR_2 = 0.1118$	$R_1 = 0.0959$, $wR_2 = 0.1819$	$R_1 = 0.0390$, $wR_2 = 0.0850$
R indices (all data)^{a,b}	$R_1 = 0.0601$, $wR_2 = 0.1226$	$R_1 = 0.2003$, $wR_2 = 0.2225$	$R_1 = 0.0786$, $wR_2 = 0.0907$
Largest difference peak and hole (e Å^{-3})	0.689 and −0.471	0.378 and −0.286	0.446 and −0.379

$^aR_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $^bR_1 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$.

2 is small and not of good quality, the *R*(int) of **2** is high. In the structure of **2**, the two lattice water molecules are disordered, thus this structure was refined by the SQUEEZE routine of PLATON [21].

3. Results and discussion

3.1. *Description of crystal structures*

Selected bond lengths and angles for **1**–**3** are given in table 2, and the main hydrogen bond data for **1** and **3** are listed in table 3.

3.1.1. Crystal structures of $[Ni_2(dpc)_2(L_1)_2(H_2O)_2]\cdot 4H_2O$ (1). Crystal structure analysis of **1** reveals a binuclear structure. As shown in figure 1, each Ni(II) is six-coordinate by two oxygens from two monodentate carboxylates (Ni1–O1 = 2.135(2), Ni1–O3 = 2.132(2) Å) and one nitrogen from pyridyl (Ni – N1 = 1.978(3) Å) of a dipicolinate, two nitrogens from two L_1 (Ni1–N2 = 2.042(3), Ni1–N4 = 2.124(3) Å), and one oxygen from a coordinated water (Ni1–O3w = 2.173(2) Å) O1, O3, N1, and N2 occupy the equatorial plane, while N4 and O3w complete the apical positions. The three Ni–O and

Table 2. Selected bond lengths and angles for **1**–**3**.

1			
Ni(1)–O(1)	2.135(2)	Ni(1)–O(3)	2.132(2)
Ni(1)–N(1)	1.978(3)	Ni(1)–N(2)	2.042(3)
Ni(1)–N(4)	2.124(3)	Ni(1)–O(3 W)	2.173(2)
N(1)–Ni(1)–N(2)	177.44(11)	N(1)–Ni(1)–N(4)	93.42(10)
N(2)–Ni(1)–N(4)	89.01(11)	N(1)–Ni(1)–O(3)	77.98(10)
N(2)–Ni(1)–O(3)	101.22(10)	N(4)–Ni(1)–O(3)	89.80(10)
N(1)–Ni(1)–O(1)	77.71(10)	N(2)–Ni(1)–O(1)	103.00(11)
N(4)–Ni(1)–O(1)	93.13(10)	O(3)–Ni(1)–O(1)	155.64(10)
N(1)–Ni(1)–O(3 W)	87.48(10)	N(2)–Ni(1)–O(3 W)	90.09(10)
N(4)–Ni(1)–O(3 W)	179.09(10)	O(3)–Ni(1)–O(3 W)	90.27(9)
O(1)–Ni(1)–O(3 W)	87.18(9)	–	–
2			
Ni(1)–N(1)	1.983(5)	Ni(1)–O(1)	2.140(4)
Ni(1)–O(3)	2.165(4)	Ni(1)–N(4)	2.057(5)
Ni(1)–N(2)	2.123(6)	Ni(2)–N(6)	2.130(6)
N(1)–Ni(1)–N(4)	176.7(2)	N(1)–Ni(1)–N(2)	91.6(2)
N(4)–Ni(1)–N(2)	89.8(2)	N(1)–Ni(1)–N(6)	93.0(2)
N(4)–Ni(1)–N(6)	85.6(2)	N(2)–Ni(1)–N(6)	175.4(2)
N(1)–Ni(1)–O(1)	77.5(2)	N(4)–Ni(1)–O(1)	99.5(2)
N(2)–Ni(1)–O(1)	89.7(2)	N(6)–Ni(1)–O(1)	91.4(2)
N(1)–Ni(1)–O(3)	76.5(2)	N(4)–Ni(1)–O(3)	106.5(2)
N(2)–Ni(1)–O(3)	90.6(2)	N(6)–Ni(1)–O(3)	90.4(2)
O(1)–Ni(1)–O(3)	154.0(2)	–	–
3			
Ni(1)–N(1)	2.039(3)	Ni(1)–O(1)	2.164(2)
Ni(1)–O(3)	2.163(2)	Ni(1)–N(2)	2.162(2)
Ni(1)–N(4)	2.093(2)	Ni(1)–N(6)	2.195(2)
N(1)–Ni(1)–N(4)	171.88(9)	N(1)–Ni(1)–O(3)	75.83(9)
N(4)–Ni(1)–O(3)	103.29(8)	N(1)–Ni(1)–O(1)	75.53(8)
N(4)–Ni(1)–O(1)	105.48(8)	O(3)–Ni(1)–O(1)	151.21(8)
N(1)–Ni(1)–N(2)	100.27(9)	N(4)–Ni(1)–N(2)	87.72(9)
O(3)–Ni(1)–N(2)	87.34(8)	O(1)–Ni(1)–N(2)	94.93(8)
N(1)–Ni(1)–N(6)	87.70(9)	N(4)–Ni(1)–N(6)	84.31(9)
O(3)–Ni(1)–N(6)	94.25(8)	O(1)–Ni(1)–N(6)	87.45(9)
N(2)–Ni(1)–N(6)	172.02(9)	–	–

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1** and **3**.

Complex	D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠DHA
1	O(1W)–H(1A)···O(3)	0.94	1.91	2.812(4)	162
	O(1W)–H(1B)···O(4)^{i}	0.90	1.99	2.823(4)	153
	O(2W)–H(2A)···O(1)^{ii}	0.82	2.57	3.143(7)	127
	O(2W)–H(2A)···O(2)^{ii}	0.82	2.57	3.195(8)	176
	O(3W)–H(3A)···O(2W)	0.87	1.94	2.738(7)	150
3	O(1W)–H(1A)···O(3)	0.86	2.14	2.927(4)	153
	O(1W)–H(1B)···O(2)^{i}	0.85	2.32	2.905(5)	126
	O(2W)–H(2B)···O(4)^{ii}	0.85	2.05	2.898(4)	178
	O(2W)–H(2C)···O(2)^{i}	0.85	2.59	3.274(5)	138

Symmetry code for **1**: $^{i}-x, -y, 1-z$; $^{ii}-1/2+x, 1/2-y, -1/2+z$; for **3**: $^{i}x, 1/2-y, -1/2+z$; $^{ii}1+x, y, z$.

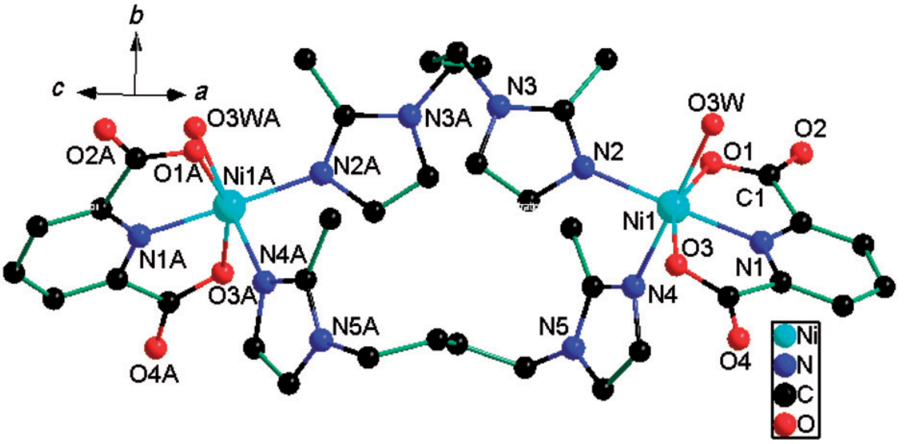

Figure 1. A view of the coordination environment of Ni(II) in **1**; all hydrogens were omitted for clarity. Symmetry transformations used to generate equivalent atoms: A: $-x+1$, y, $-z+3/2$.

three Ni–N distances all are within normal ranges [22]. Each dipicolinate bonds tridentate to a Ni, then two L_1 ligands link two [Ni(pdc)(H_2O)] units to form a 22-membered metallomacrocycle, having a Ni···Ni distance of 10.502(1) Å. The N–Ni–N coordination angles between two L_1 ligands of 89.0(1)° are much smaller than those observed in related structures (117.4(2)° and 115.4°) [18c, 23]. In contrast, for a similar complex $\{[Cu(pdc)(bib)_{1.5}]\cdot 4H_2O\}_n$ (bib = 1,4-bis(imidazol-1-yl)butane) [24], the bib ligands adjust their conformation for the Cu(II)-connected metal nodes to a ladder chain.

Furthermore, there are strong multiple intermolecular hydrogen bonds (O–H···O) in **1** involving lattice water (O1w and O2w), coordinated water (O3w), and carboxylate oxygen of dipicolinate (O1, O2, O3, and O4). These hydrogen-bonding interactions lead to a 3-D architecture. The O···O distances fall in the normal range of 2.73–3.20 Å (table 3).

3.1.2. Crystal structures of $[Ni(dpc)(L_2)_{1.5}]_n$ (2).

Replacement of L_1 in **1** with L_2 results in a 1-D ladder-like double chain structure of **2**. The crystallographic asymmetric unit of **2** consists of one Ni(II), one dipicolinate dianion, and one and a half L_2. Each Ni(II) is coordinated by one dipicolinate dianion and three L_2's, affording a distorted $[NiO_3N_3]$ octahedral geometry (figure 2). The equatorial positions are occupied by one nitrogen and two oxygens from a dipicolinate (Ni1–N1 = 1.983(5) Å, Ni1–O1 = 2.140(4) Å, and Ni1–O3 = 2.165(4) Å) and one nitrogen from a L_2 ligand (Ni1–N4 = 2.057(5) Å), while apical positions are completed by two nitrogens from another two L_2 ligands (Ni1–N2 = 2.123(6) Å and Ni1–N6 = 2.130(6) Å). The spatial constraint prevents the two imidazole rings which ligate to one metal in apical positions from being parallel. As in **1**, the dipicolinate in **2** is a tridentate terminal ligand to Ni(II), producing similar coordination bond lengths with **1**.

In **2**, two kinds of L_2 can be found, one in a *cis*-coordination mode links [Ni(pdc)] to 1-D polymeric chains, separating the neighboring Ni···Ni distance of 15.321(7) Å, while the other adopts *trans*-conformation to connect two neighboring 1-D chains, generating

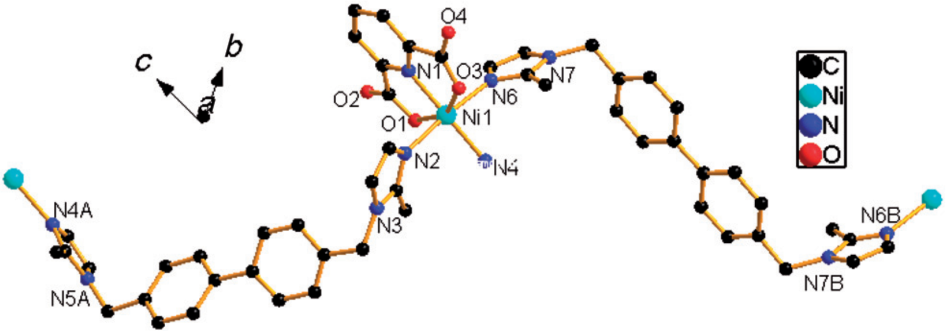

Figure 2. A view of the coordination environment of Ni(II) in **2**; all hydrogens were omitted for clarity. Symmetry transformations used to generate equivalent atoms: A = x, $y-1$, $z+1$; B = $-x+1$, $-y+1$, $-z$.

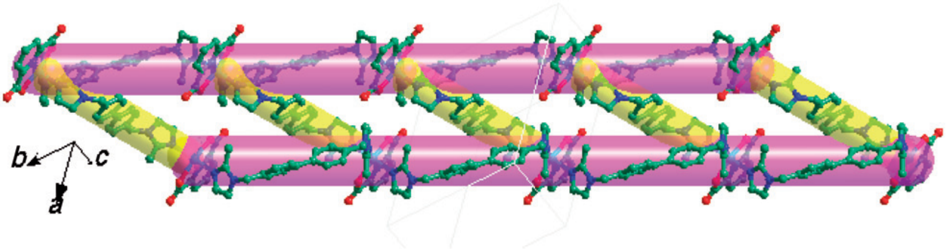

Figure 3. A ladder-like chain structure in **2**.

a ladder-like chain (figure 3), which is very different from the binuclear metallomacrocycle structure of reported L_2 complexes [25]. The dihedral angles between imidazole rings in same L_2 are 52.1(3)° for the former and 0° for the latter, respectively. In the crystal structure of $\{[Pb(dimb)_{1.5}(NO_3)_2](DMF)\}_n$ (dimb = 4,4′-bis(imidazol-1-methyl)biphenyl) [26], Pb(II) nodes also linked by three dimb ligands generate a ladder chain, but in which the bridging dimb ligands all exhibit *trans*-conformation.

3.1.3. Crystal structures of $\{[Ni(dpc)(L_3)_{1.5}]\cdot 2H_2O\}_n$ (3). When we used L_3 instead of the neutral ligands in **1** or **2**, a different topology of **3** was obtained, containing one Ni(II), one dipicolinate dianion, one and a half L_3, and two water molecules. As illustrated in figure 4, the Ni(II) is octahedral, coordinated by nitrogen and two oxygens from a dipicolinate (Ni1–N1 = 2.039(2) Å, Ni1–O1 = 2.164(2) Å, and Ni1–O3 = 2.163(2) Å) and three nitrogens from three L_3 ligands (Ni1–N2 = 2.162(2) Å, Ni1–N4 = 2.093(2) Å, and Ni1–N6 = 2.195(2) Å). The Ni–O and Ni–N bond lengths are slightly larger than the corresponding values observed in **1** and **2**, which may be attributed to the effect of the spatial constraint of benzimidazole rings. Dipicolinate chelates to Ni(II) through two oxygens from two monodentate carboxylates and one nitrogen from pyridyl ring, forming [Ni(pdc)]. There are two kinds of L_3 ligands around each Ni(II), all adopting *trans*-conformation, but with different dihedral angles between benzimidazole rings within same neutral ligand, 0° and 14.94(7)°, respectively.

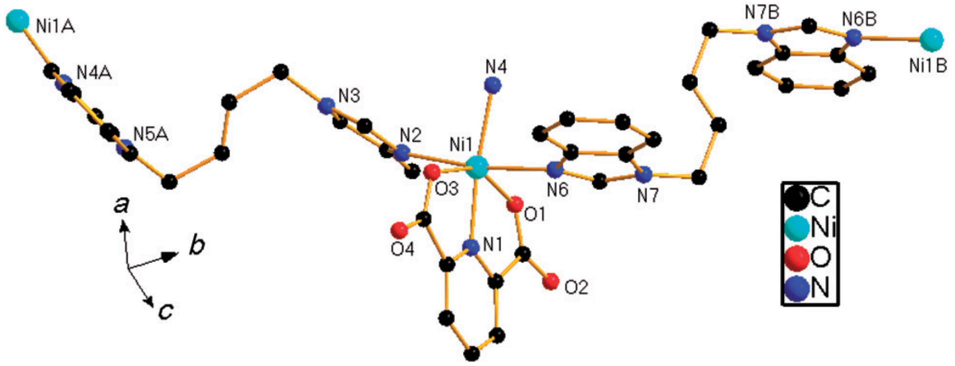

Figure 4. A view of the coordination environment of Ni(II) in **3**; all hydrogens were omitted for clarity. Symmetry transformations used to generate equivalent atoms: $A = -x+1,\ y-1/2,\ -z+1/2$; $B = -x+1,\ -y+1,\ -z+1$.

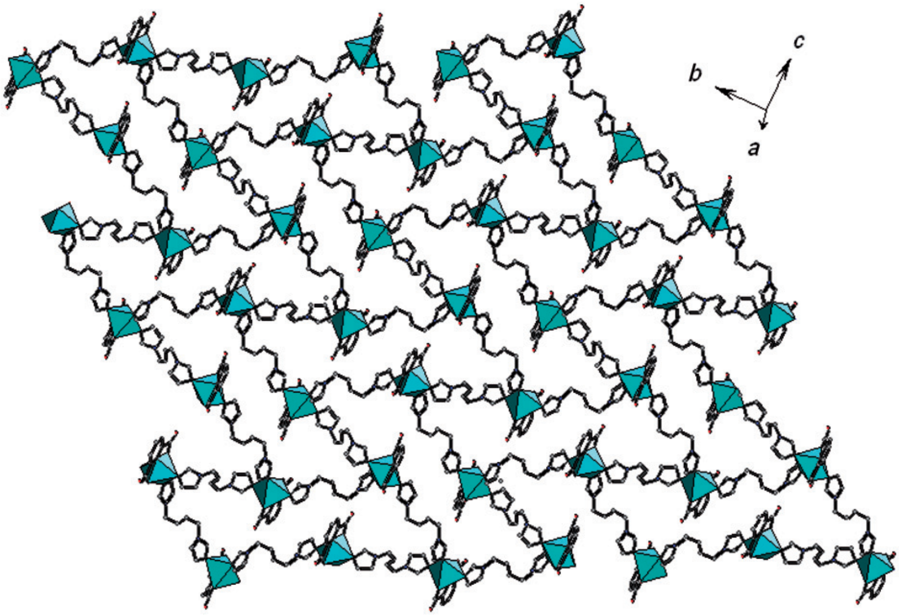

Figure 5. A view of 2-D (6,3) topology in **3**.

Therefore, the L_3 in **3** bridge adjacent [Ni(pdc)] units forming a 2-D (6,3) network (figure 5), separating two adjacent Ni $\cdots$ Ni distances of 11.8177(7) and 12.1798(7) Å. A reported L_3 complex, $[Co(L_3)_{1.5}(SO_4)]_n$ [27], also exhibits a 2-D (6,3) net connected by L_3, in spite of completely different reaction condition than **3**. Two related picolinate-containing Ni(II) complexes $[Ni(bbma)(pic)(H_2O)](ClO_4) \cdot CH_3OH$ and $[Ni(ntb)(pic)]Cl \cdot CH_3OH \cdot 3H_2O$ with poly-benzimidazole tridentate and tripodal tetradentate ligand are both mononuclear [28]. The two lattice waters in **3** form intermolecular hydrogen bonds ($O(1W)–H(1B) \cdots O(2)^{i}$, $O(2W)–H(2B) \cdots O(4)^{ii}$, and $O(2W)–H(2C) \cdots O(2)^{i}$, symmetric code: $i = x,\ 1/2-y,\ -1/2+z$; $ii = 1+x,\ y,\ z$) with

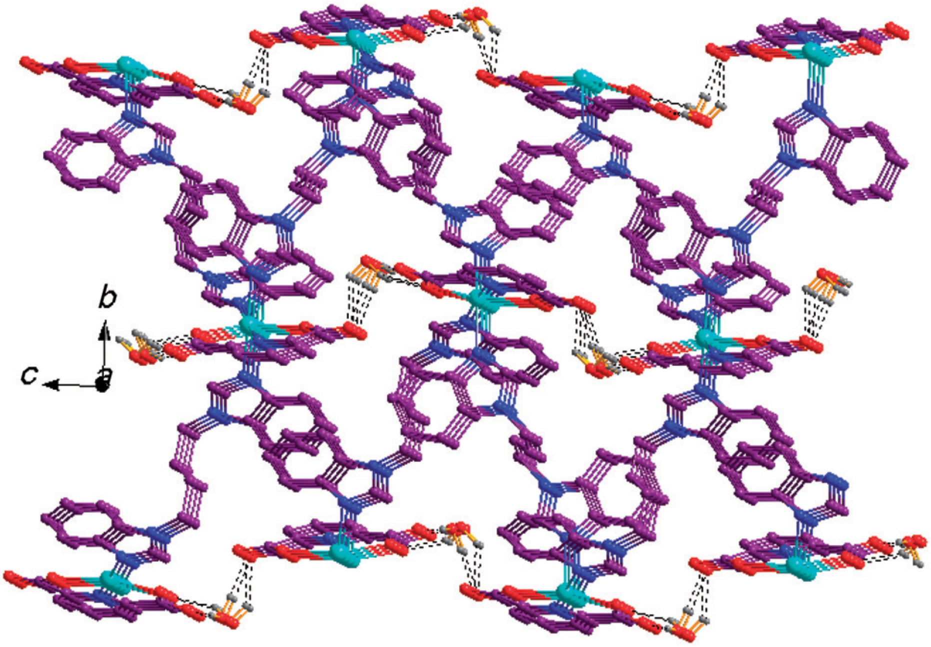

Figure 6. The 3-D packing view of **3** constructed by hydrogen-bonding interactions along the *a*-axis.

carboxylate group oxygen (O2 and O4) of the chelating dipicolinate, which extend the 2-D network into a 3-D framework (figure 6). The O(1w) ··· O(2)^{i}, O(2w) ··· O(4)^{ii}, and O(1w) ··· O(2)^{i} distances of 2.905(5), 2.898(4), and 3.274(5) Å are falling in the normal O(aqua) ··· O hydrogen bond range.

3.1.4. Effect of flexible bridging ligands on the frameworks. In this study, **1**–**3** are obtained under similar conditions, displaying discrete binuclear, 1-D ladder-like chain, and 2-D (6,3) network structures. As described above, the dipicolinate is a tridentate terminal ligand, showing similar coordination modes in the three compounds. The three flexible ligands L_1, L_2, and L_3 all have the ability to adjust configuration to meet the coordination requirements of the metal centers. As a comparison, the complexities of the title compounds strongly rely on the nature of flexible bridging ligands, which may be tuned by changing the flexibility and length of the spacer groups between the two imidazole rings, as well as diimidazolyl functionality. For example, in $[Ni_2(dpc)_2(L_1)_2(H_2O)_2] \cdot 4H_2O$ (**1**), a pair of L_1 ligands with highly flexible butanediyl spacer bridge two $[Ni(dpc)(H_2O)]$ units to form a binuclear metallomacrocycle. Nevertheless, when L_2 with a long semi-flexible spacer between two imidazole rings was employed in place of L_1, a 1-D ladder-like chain $[Ni(dpc)(L_2)_{1.5}]_n$ (**2**), arising from L_2 which exhibits both *cis*- and *trans*-conformations and the Ni(II) ions are obtained. Likewise, the L_3 with linking of dibenzimidazole by a butenediyl spacer was used to react with nickel nitrate hexahydrate and dipicolinate, adopting a preparation similar to **1** and **2**, then a quite different topology, $\{[Ni(dpc)(L_3)_{1.5}] \cdot 2H_2O\}_n$ (**3**), was produced. Unlike **2**, the [Ni(dpc)] is connected by three L_3 ligands, forming a (6,3) grid network.

Apparently, the spacer of bis(imidazole) ligands between two imidazole rings have significant influence on the structures of resulting coordination architectures.

3.2. *Thermal properties of the complexes*

The TG analyses for the three compounds have been investigated under N_2. Complex **1** is stable up to 124.6°C, then 9.78% weight loss is between 124.6°C and 156.3°C, corresponding to the removal of coordinated and uncoordinated water (Calcd 10.90%). Next, mass loss is from 248.7°C to 446.2°C, assigned to the decomposition of L_1 and dipicolinate, leading to the formation of NiO as the residue observed 9.22% (Calcd 7.53%). Complex **2** has three weight-loss processes between 67 and 495.5°C. The first mass loss of 3.88% at 67.2°C to 113.1°C corresponds to the release of free water molecule. The second loss of 62.94% takes place from 294.6°C to 423.7°C, being assigned to the loss of L_2 (Calcd 65.66%). The third weight loss from 438.6°C to 495.8°C can be attributed to the decomposition of dipicolinate (Obsd 22.36%, Calcd 19.05%). The remaining mass of 8.82% is consistent with a remnant mass of NiO (Calcd 9.55%). Complex **3** releases lattice water from 60.7°C to 116.2°C, with a mass loss of 5.45% (Calcd 5.20%). Decomposition of L_3 occurs gradually from 288.7°C to 465.2°C, having a mass loss of 65.19% (Calcd 62.37%). Mass loss of 19.38% is observed from 480°C to 568.3°C, assigned to the decomposition of dipicolinate (Calcd 21.49%). The remaining weight corresponds to the formation of NiO (Obsd 10.03%, Calcd 10.77%).

4. Conclusion

Three new complexes with different structures have been obtained by hydrothermal reactions of nickel nitrate hexahydrate, bis(imidazole) ligands, and dipicolinic acid under similar conditions. Complex **1** exhibits a binuclear metallomacrocycle with a 22-membered ring; **2** displays a ladder-like chain structure, while for **3**, the [Ni(pdc)] unit is connected by L_3 ligands to a 2-D (6,3) grid network. The structural analyses demonstrate that the flexible bis(imidazole) ligand can bend and rotate freely to coordinate to metal, and the nature of the spacer of bis(imidazole) ligands between two imidazole rings can exert significant influence on the topologies of final nickel-dipicolinate complexes with bis(imidazole).

Supplementary material

X-ray crystallographic files in CIF format for **1**–**3** have been deposited at the Cambridge Crystallographic Data Centre with CCDC No: 785996, 785998, and 785997. This data can be freely obtained from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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