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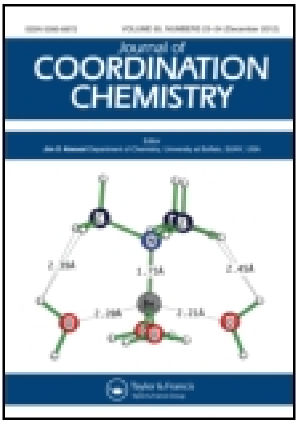

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Two solvent directed zinc(II) coordination polymers with 1-D single-zigzag chain and 1-D double-zigzag chains

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Accepted author version posted online: 17 Oct 2012.Published online: 31 Oct 2012.

To cite this article: Xiao-Jian Kong , Xiao-Zeng Li & Li-Na Zhu (2012) Two solvent directed zinc(II) coordination polymers with 1-D single-zigzag chain and 1-D double-zigzag chains, Journal of Coordination Chemistry, 65:24, 4315-4326, DOI: 10.1080/00958972.2012.740666

To link to this article: http://dx.doi.org/10.1080/00958972.2012.740666

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Journal of Coordination Chemistry
Vol. 65, No. 24, 20 December 2012, 4315–4326

Two solvent directed zinc(II) coordination polymers with 1-D single-zigzag chain and 1-D double-zigzag chains

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(*Received 14 March 2012; in final form 7 September 2012*)

Two coordination polymers, $\{[Zn(NiL)(DMA)(H_2O)_2]\ (DMA)(H_2O)\}_n$ (**1**) (DMA = *N*,*N*-dimethylacetamide) and $\{[Zn_2(NiL)_2(DMF)(H_2O)_4] \cdot 3DMF\}_n$ (**2**) (DMF = *N*,*N*-dimethylformamide), have been prepared by reactions of $Zn(NO_3)_2 \cdot 6H_2O$ and NiL in CH_2Cl_2-DMA–H_2O and CH_2Cl_2-DMF–H_2O, respectively. H_2L denotes dimethyl 5,6,7,8,15,16-hexahydro-6,7-dioxodibenzo-9,10-benzo-[1,4,8,11]tetraazacyclotetradecine-13,18-dicarboxylate. Single-crystal X-ray diffraction analyses reveal that coordination geometries around Ni(II) are identical with slightly distorted square planar and all Ni–N bonds are very short. Complex **1** shows 1-D zigzag chain structure, while **2** has 1-D double-zigzag chains. The chains, which are packed parallel in **1** and **2**, are interconnected by lattice solvent through O–H···O and C–H···O hydrogen bonds to form 3-D supramolecular networks. We discuss solvent effects on assembly of the two coordination polymers. The results reveal that coordinated solvent has influence on the assembly procedure.

Keywords: Synthesis; Crystal structure; Macrocyclic complex; Solvent effects; Coordination polymers

1. Introduction

Coordination polymers have useful properties, potential applications, and interesting architectures [1–12]. The topology of coordination polymers can be obtained by assembling metal centers and functionality of the ligands. Much effort has been devoted to transition metal coordination polymers based on multiple N- and O-donors. The formation of coordination polymers is dependent on the coordination geometries of the metal ions, flexibility of the ligands, metal/ligand ratios, and the presence of counterions and solvents [13–15]. Counterion and solvent effects on assembly of metal ions and ligands give a variety of self-assembled coordination polymers [16]. Hydrogen-bonding and coordinative bonds are involved in generation of supramolecular multimetallic assemblies [17, 18]. Zn(II) macrocyclic complexes have received attention owing to their relationship to biological activities [19–21], drugs for the treatment of Alzheimer disease [22], DNA-binding [23], and applications in optical devices [24]. In this article, we chose $Zn(NO_3)_2 \cdot 6H_2O$ to react with NiL in different solvent systems

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.740666

and isolated two metal–organic coordination polymers $\{[Zn(NiL)(DMA)(H_2O)_2]\cdot(DMA)(H_2O)\}_n$ (**1**) and $\{[Zn_2(NiL)_2(DMF)(H_2O)_4]\cdot 3DMF\}_n$ (**2**). L denotes dimethyl 5,6,7,8,15,16-hexahydro-6,7dioxodibenzo-9,10-benzo-[1,4,8,11]tetraazacyclotetradecine-13,18-dicarboxylate. We report crystal structures of **1** and **2** and discuss the effect of solvent on assembly.

2. Experimental details

2.1. *Materials and measurements*

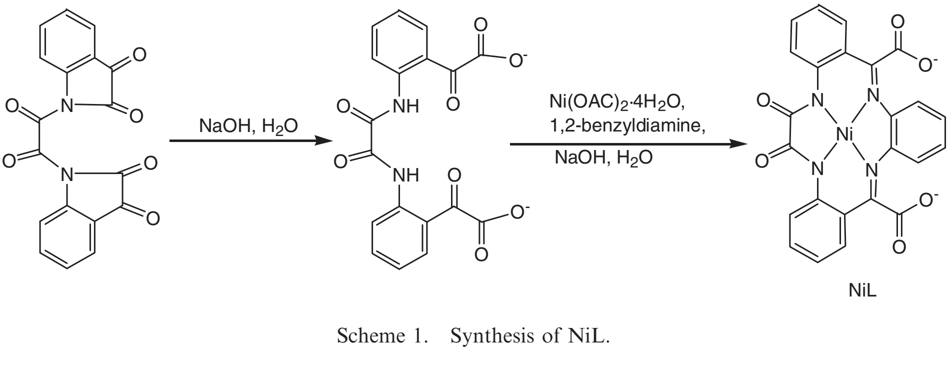
All materials and solvents were purchased commercially and used without purification. 1,1′-Oxalylbisisatin was prepared by the literature method [25]. IR spectra were recorded as KBr discs on a BIO-RAD 3000 infrared spectrophotometer from 4000 to 400 cm^{-1}. Elemental analyses (C, H, and N) were carried out on a Perkin-Elmer 240 analyzer.

2.2. *Syntheses of the complexes*

NiL was prepared following the steps shown in scheme 1. The reactions are similar to those in the syntheses of analogous macrocyclic oxamide complexes [25]. Soldium amido bisgloylate is a substrate for the synthesis of NiL. This step is necessary because of cleavage of N–C bonds (belonging to two five-membered rings) and the formation of N–H bonds. Excess $Zn(NO_3)_2\cdot 6H_2O$ and solvent (including DMA/CH_2Cl_2 and DMF/CH_2Cl_2) were needed for formation of crystalline **1** and **2**, respectively, similar to cases reported by our group [26]. There was a different procedure for NiL [26], using NaOH to replace triethylamine. We obtained pure NiL through the new method but the yield decreased. Metalloligand NiL is characterized in this article.

2.2.1. Synthesis of NiL

2.2.1.1. *Synthesis of soldium amido bisgloylate.* A mixture of 1,1′-oxalylbisisatin (3.4832 g, 10.0 mmol) and solution of 0.8000 g (20.0 mmol) NaOH in 100 mL water was



Scheme 1. Synthesis of NiL.

stirred at 40°C for 1 h to give a yellow solution and then cooled to room temperature and filtered. The filtrate was concentrated to remove most water to give a yellow paste by rotary evaporation. The solid was dried under vacuum at room temperature to afford a yellow powder. Yield: 89.5% (3.8322 g). Anal. Found (Calcd for $C_{18}H_{10}N_2O_8Na_2$ (%)): C 50.29 (50.48), H 2.42 (2.35), N 6.43 (6.54). Main IR bands (KBr, cm^{-1}): 1728(m), 1616(s), 1514(s), 1460(m), 1395(m), 1331(s), 1270(m), 1202(m), 1095(m), 1014(m), 946(m), 770(m), 725(m). ^1H NMR (400 MHz, DMSO-d_6) δ 13.16 (s, br, 2H), 8.73 (d, $J = 8.4$ Hz, 2H), 7.91 (d, $J = 7.6$ Hz, 2H), 7.70 (t, $J = 7.6$ Hz, 2H), 7.31 (t, $J = 8.4$ Hz, 2H). ^{13}C NMR (400 MHz, DMSO-d_6) δ 201.20, 168.06, 158.26, 138.90, 134.11, 133.98, 123.79, 120.28, 119.54. EI-MS Calcd. for $C_{18}H_{10}N_2O_8^{2-}$ $[M+H]^-$ 383.0, Found 383.0.

2.2.1.2. *Synthesis of NiL.* Soldium amido bisgloylate (2.1405 g, 5.0 mmol) in 50 mL water was stirred to give a yellow solution. To the solution was added $Ni(OAc)_2 \cdot 4H_2O$ (1.4428 g, 5.0 mmol) and 0.4000 g (10.0 mmol) NaOH (drop by drop). To the above solution was then added dropwise a solution of 1,2-benzenediamine (0.5408 g, 5.0 mmol) in 10 mL water for 2 h under stirring at 75°C, and the solution was kept stirring for an additional 6 h at 75°C. The resulting mixture was then cooled to room temperature and filtered. The filtrate was evaporated by heating on a water bath of 55°C to afford a dark red paste. The paste and 10 mL of ethanol was stirred for 30 min and then filtered. The solid was dried under vacuum to afford a dark red powder. Yield: 55.9% (1.5578 g). Anal. Found (Calcd for $C_{24}H_{12}N_4NiO_6Na_2$ (%)): C 51.40 (51.75), H 2.28 (2.17), N 10.25 (10.06). Main IR bands (KBr, cm^{-1}): 1632(s), 1586(s), 1537(s), 1472(m), 1454(m), 1374(s), 1251(m), 1171(m), 1113(m), 994(m), 784(m), 749(m). ^1H NMR (400 MHz, DMSO-d_6) δ 8.50 (t, $J = 8.4$ Hz, 4H), 7.77 (d, $J = 8.4$ Hz, 2H), 7.36 (t, $J = 7.2$ Hz, 2H), 7.15 (d, $J = 7.6$ Hz, 2H), 6.96 (t, $J = 7.2$ Hz, 2H). EI-MS Calcd for $C_{24}H_{12}N_4NiO_6^{2-}$ $[M+H]^-$ 512.0, Found 512.1.

2.2.2. Synthesis of $\{[Zn(NiL)(DMA)(H_2O)_2] \cdot (DMA)(H_2O)\}_n$ (1). A mixture of the above dark red powder (0.0305 g, 0.055 mmol), $Zn(NO_3)_2 \cdot 6H_2O$ (0.0242 g, 0.081 mmol), DMA (20 mL), CH_2Cl_2 (20 mL), and water (5 mL) was stirred to form a red solution. The filtrate of the solution was then stored at room temperature for a few days and red crystals suitable for single-crystal X-ray analysis were formed. Yield: 0.0102 g. Anal. Found (Calcd for $C_{32}H_{36}N_6NiO_{11}Zn$ (%)): C 47.56 (47.76), H 4.35 (4.51), N 10.56 (10.44). IR (KBr cm^{-1}): 3411(m), 1621(s), 1593(s), 1547(s), 1471(m), 1455(m), 1371(s), 1255(m), 1173(m), 1120(m), 995(m), 783(m), 751(m).

2.2.3. Synthesis of $\{[Zn_2(NiL)_2(DMF)(H_2O)_4] \cdot 3DMF\}_n$ (2). Red crystals suitable for single-crystal X-ray analysis were afforded by the same method used to prepare **1** except utilizing DMF (20 mL) to replace DMA (20 mL). Yield: 0.0115 g. Anal. Found (Calcd for $C_{60}H_{59}N_{12}Ni_2O_{20}Zn_2$ (%)): C 47.56 (47.52), H 4.02 (3.92), N 11.22 (11.08). Main IR bands: 3419(m), 1615(s), 1589(s), 1539(s), 1476(m), 1448(m), 1372(s), 1253(m), 1172(m), 1109(m), 989(m), 779(m), 739(m).

2.3. *X-ray structure determinations*

Single crystals were selected for X-ray measurements and mounted on a glass fiber [27]. Crystallographic data for **1** were collected at 113(2) K and for **2** at 298(2) K on a Bruker Smart-1000-CCD area detector with Mo-Kα radiation ($\lambda = 0.71073$ Å). The absorption correction was based on multiple and symmetry-equivalent reflections in the data set using SADABS. The structures were solved by direct methods and refined with full-matrix least-squares on F^2 using SHELXL97 [28] and SHELXTL [29]. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on calculated positions and refined as riding with common fixed isotropic thermal parameters. Crystal data and pertinent information are summarized in table 1. Selected bond lengths and angles are given in table 2 for **1** and in table 3 for **2**.

3. Results and discussion

3.1. *Descriptions of the structures*

X-ray diffraction reveals that **1** crystallizes in the $P2(1)/n$ space group and is an infinite 1-D single-zigzag chain (figure 1b). The asymmetric unit is composed of Zn(NiL)(DMA)$(H_2O)_2$ (figure 1a), one lattice water molecule and one lattice DMA. X-ray diffraction also reveals that **2** crystallizes in the $P2(1)/c$ space group and has infinite 1-D double-zigzag chains (figure 2b) containing $Zn_2(NiL)_2$(DMF)$(H_2O)_4$ (figure 2a) and three lattice DMF. In the binuclear entity of **1** and tetranuclear entity of **2**, Zn(II) and Ni(II) are both linked by oxamido groups from the macrocyclic ligand. Ni(II) of NiL has a slightly distorted square-planar environment defined by four nitrogen atoms. The largest deviations of Ni and N from the corresponding NiN_4 planes are 0.0016–0.0473 Å in **1** and 0.0033–0.0750 Å in **2**. All Ni–N bonds are quite short (1.845–1.872 Å in **1** and 1.848–1.891 Å in **2**), suggesting that coordination of the deprotonated oxamido and imino nitrogen atoms are strong. In **1**, Zn coordinates with two oxygen atoms from oxamido of one NiL fragment, one oxygen atom from carboxyl of another NiL fragment, two oxygen atoms from water, and one oxygen atom from DMA, forming a slightly distorted octahedral coordination geometry. In each dinuclear entity, the Ni···Zn distance is 5.267 Å. In **2**, there are two kinds of Zn ions. One coordinates with two oxygen atoms from oxamido of one NiL fragment, one oxygen atom from carboxyl of another NiL fragment, two oxygen atoms from water, and one oxygen atom from DMF, forming a slightly distorted octahedral coordination geometry. The other zinc coordinates with two oxygen atoms from oxamido of one NiL fragment, two oxygen atoms from carboxyl groups of another two NiL fragments, and two oxygen atoms from water, also forming a similar distorted octahedral geometry. In each tetranuclear entity, the Ni···Zn distances are 5.278 Å and 5.331 Å. In **1** the N(1)–C(1) and N(2)–C(2) bond lengths in oxamido groups are 1.324 Å and 1.350 Å, respectively, longer than N = C double bonds (N(3)–C(9) (1.302 Å) and N(4)–C(17) (1.309 Å)), but shorter than N–C single bonds (N(3)–C(11) (1.424 Å) and N(4)–C(16) (1.431 Å)). The sum of the three bond angles around each amidate nitrogen atom is close to 360° (372.7–373.3°). Thus the amidate nitrogen atoms are sp^2-hybridized and the π-electrons on these atoms are delocalized into carbonyl and stabilized. C(1)–C(2)

Table 1. Crystal data and structure refinements of **1** and **2**.

Molecular formula	$C_{32}H_{36}N_6NiO_{11}Zn$	$C_{60}H_{59}N_{12}Ni_2O_{20}Zn_2$
Molecular weight	804.75	1516.35
Temperature (K)	113(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	*P*2(1)/*n*	*P*2(1)/*c*
Unit cell dimensions (Å, °)		
a	11.242(3)	22.163(16)
b	14.248(4)	14.194(10)
c	21.185(5)	22.615(16)
α	90	90
β	97.709(4)	117.618(7)
γ	90	90
Volume (Å^3), *Z*	3362.5(14), 4	6304(8), 4
Calculated density (Mg m^{-3})	1.590	1.598
Absorption coefficient (mm^{-1})	1.344	1.426
Crystal size (mm^3)	$0.16 \times 0.14 \times 0.10$	$0.20 \times 0.20 \times 0.20$
F(000)	1664	3116
θ range for data collection (°)	1.73–27.88	3.04–27.50
Index ranges	$-14 \le h \le 10$; $-16 \le k \le 18$; $-27 \le l \le 27$	$-28 \le h \le 28$; $-18 \le k \le 18$; $-29 \le l \le 29$
Reflections collected/unique	34,574/7990 [*R*(int) = 0.0601]	63,768/14,424 [*R*(int) = 0.1804]
Completeness to $\theta = 99.6$ (%)	27.88	27.50
Absorption correction	Semi-empirical	Semi-empirical
Max. and min. transmission	0.8773 and 0.8137	0.7635 and 0.7635
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	7990/81/482	14,424/102/877
Goodness-of-fit on F^2	1.081	1.021
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0521$, $wR_2 = 0.1110$	$R_1 = 0.0923$, $wR_2 = 0.1829$
R indices (all data)	$R_1 = 0.0671$, $wR_2 = 0.1185$	$R_1 = 0.1802$, $wR_2 = 0.2269$
Largest difference peak and hole (e Å^{-3})	1.428 and −0.688	1.145 and −0.893

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Zn(1)–O(8)	2.024(2)	O(9)–Zn(1)–O(7)	174.3(2)
Zn(1)–O(9)	2.063(2)	O(4)^a–Zn(1)–O(7)	89.6(2)
Zn(1)–O(4)^a	2.076(2)	O(8)–Zn(1)–O(2)	86.2(2)
Zn(1)–O(7)	2.106(2)	O(9)–Zn(1)–O(2)	98.6(2)
Zn(1)–O(2)	2.142(2)	O(4)^a–Zn(1)–O(2)	172.8(2)
Zn(1)–O(1)	2.186(2)	O(7)–Zn(1)–O(2)	83.3(2)
Ni(1)–N(2)	1.845(2)	O(8)–Zn(1)–O(1)	158.9(2)
Ni(1)–N(4)	1.866(2)	O(9)–Zn(1)–O(1)	82.8(2)
Ni(1)–N(3)	1.869(2)	O(4)^a–Zn(1)–O(1)	103.3(2)
Ni(1)–N(1)	1.871(2)	O(7)–Zn(1)–O(1)	92.4(2)
O(1)–C(1)	1.245(3)	O(2)–Zn(1)–O(1)	76.9(2)
O(2)–C(2)	1.235(3)	N(2)–Ni(1)–N(4)	178.2(2)
O(3)–C(10)	1.236(3)	N(2)–Ni(1)–N(3)	93.1(2)
O(4)–C(10)	1.263(3)	N(4)–Ni(1)–N(3)	85.8(2)
O(4)–Zn(1)^b	2.076 (2)	N(2)–Ni(1)–N(1)	86.3(2)
O(5)–C(18)	1.246(3)	N(4)–Ni(1)–N(1)	94.9(3)
O(6)–C(18)	1.248(4)	N(3)–Ni(1)–N(1)	177.1(2)
O(8)–Zn(1)–O(9)	87.34(9)	C(1)–O(1)–Zn(1)	112.6(3)
O(8)–Zn(1)–O(4)^a	95.11(9)	C(2)–O(2)–Zn(1)	113.5(3)
O(9)–Zn(1)–O(4)^a	88.54(8)	C(10)–O(4)–Zn(1)^b	130.6(3)
O(8)–Zn(1)–O(7)	98.21(9)	C(26)–O(9)–Zn(1)	136.8(2)

Symmetry transformations used to generate equivalent atoms: ^{a} $x, y-1, z$; ^{b} $x, y+1, z$.

Table 3. Selected bond lengths (Å) and angles (°) for **2**.

Ni(1)–N(1)	1.853(5)	Zn(2)–O(2)^{b}	2.116(5)	O(9)–Zn(2)–O(11)	90.1(2)
Ni(1)–N(4)	1.856(6)	Zn(1)–O(20)^{b}	2.091(5)	O(12)–Zn(2)–O(11)	98.4(3)
Ni(1)–N(3)	1.876(6)	N(8)–Ni(4)–N(6)	93.42(3)	O(8)–Zn(2)–O(11)	87.7(3)
Ni(1)–N(2)	1.890(5)	N(5)–Ni(4)–N(6)	86.5(2)	O(2)^{b}–Zn(2)–O(11)	166.7(3)
Ni(2)–N(8)	1.848(5)	N(8)–Ni(4)–N(7)	86.4(3)	O(9)–Zn(2)–O(10)	89.8(2)
Ni(2)–N(5)	1.872(6)	N(5)–Ni(4)–N(7)	93.4(3)	O(12)–Zn(2)–O(10)	172.6(2)
Ni(2)–N(6)	1.879(6)	N(6)–Ni(4)–N(7)	176.5(2)	N(8)–Ni(4)–N(5)	174.9(2)
Ni(2)–N(7)	1.882(6)	N(1)–Ni(6)–N(4)	179.2(3)	O(8)–Zn(2)–O(10)	88.5(2)
C(15)–O(17)	1.253(8)	N(1)–Ni(6)–N(3)	93.0(2)	O(2) ^{b}–Zn(2)–O(10)	90.3(3)
C(16)–O(16)	1.241(8)	N(4)–Ni(6)–N(3)	86.5(2)	O(11)–Zn(2)–O(10)	76.6(3)
C(15)–C(16)	1.538(10)	N(1)–Ni(6)–N(2)	85.8(2)	O(15)–Zn(1)–O(20)^{b}	95.3(2)
C(25)–O(11)	1.239(8)	N(4)–Ni(6)–N(2)	94.7(2)	O(15)–Zn(1)–O(18)	99.1(2)
C(26)–O(10)	1.246(8)	N(3)–Ni(6)–N(2)	176.7(2)	O(20)^{b}–Zn(1)–O(18)	88.3(2)
C(25)–C(26)	1.538(9)	C(26)–O(10)–Zn(2)	113.3(4)	O(15)–Zn(1)–O(17)	90.9(2)
O(2)–Zn(2)^{a}	2.116(5)	C(25)–O(11)–Zn(2)	114.7(4)	O(20^{b}–Zn(1)–O(17)	172.8(2)
O(8)–Zn(2)	2.098(5)	C(24)–O(12)–Zn(2)	131.6(5)	O(18)–Zn(1)–O(17)	87.2(2)
O(9)–Zn(2)	2.051(5)	C(55)–O(14)–Zn(1)	120.8(6)	O(15)–Zn(1)–O(14)	87.2(2)
O(10)–Zn(2)	2.189(5)	C(16)–O(16)–Zn(1)	110.1(5)	O(20) ^{b}–Zn(1)–O(14)	85.4(2)
O(11)–Zn(2)	2.153(5)	C(15)–O(17)–Zn(1)	116.5(5)	O(18)–Zn(1)–O(14)	171.5(2)
O(12)–Zn(2)	2.062(5)	C(8)–O(20)–Zn(1)^{a}	131.7(5)	O(17)–Zn(1)–O(14)	98.5(2)
O(14)–Zn(1)	2.115(6)	O(9)–Zn(2)–O(12)	95.7(2)	O(15)–Zn(1)–O(16)	161.2(2)
O(15)–Zn(1)	2.006(6)	O(9)–Zn(2)–O(8)	177.5(2)	O(20) ^{b}–Zn(1)–O(16)	98.4(2)
O(16)–Zn(1)	2.263(5)	O(12)–Zn(2)–O(8)	85.8(2)	O(18)–Zn(1)–O(16)	94.1(2)
O(17)–Zn(1)	2.107(5)	O(9)–Zn(2)–O(2)^{b}	92.0(2)	O(17)–Zn(1)–O(16)	76.4(3)
O(18)–Zn(1)	2.095(6)	O(12)–Zn(2)–O(2)^{b}	94.4(3)	O(14)–Zn(1)–O(16)	81.2(2)
O(20)–Zn(1)^{a}	2.091(5)	O(8)–Zn(2)–O(2) ^{b}	90.0(3)	O(15)–Zn(1)–O(18)	99.1(2)

Symmetry transformations used to generate equivalent atoms: ^{a} $x, -y+1/2, z-1/2$; ^{b} $x, y+1/2, z+1/2$.

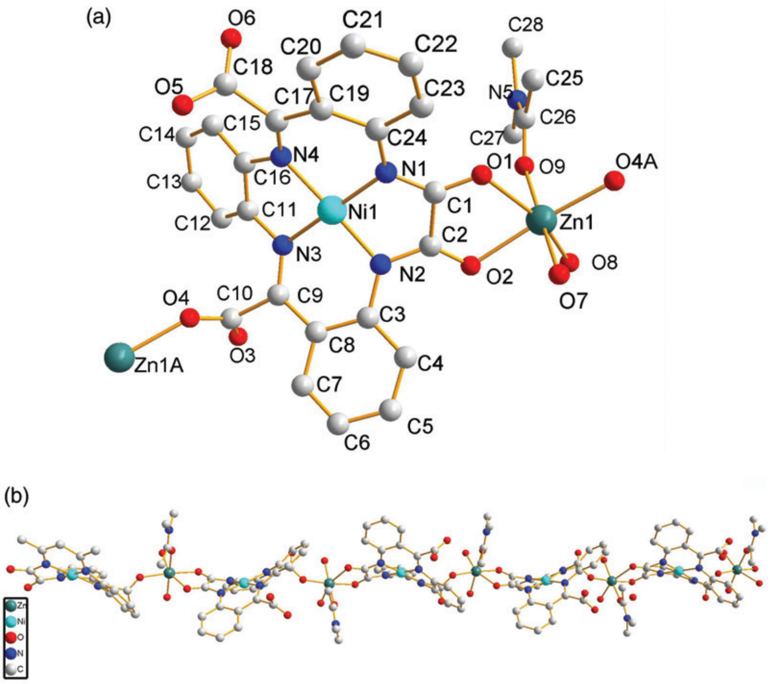


Figure 1. (a) Coordination environments of Ni and Zn in **1** and (b) 1-D zigzag chain structure of **1**. Hydrogen atoms have been omitted for clarity.

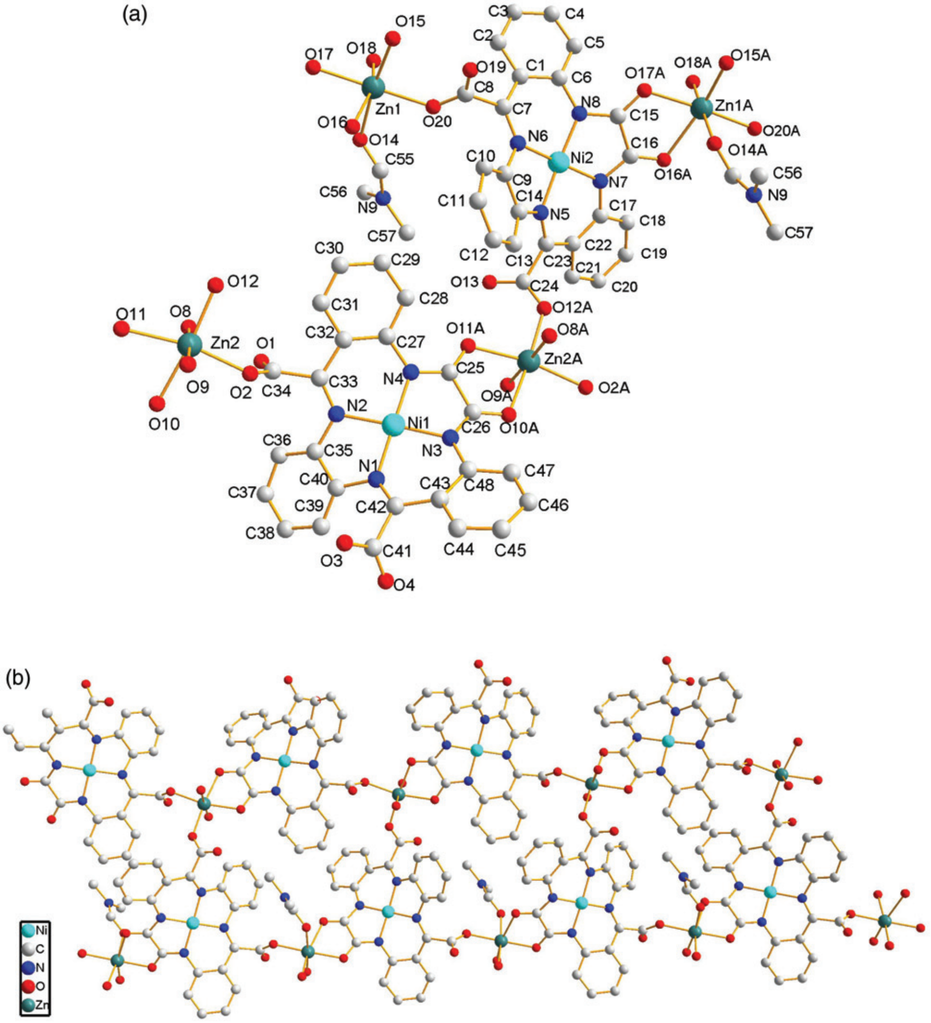


Figure 2. (a) Coordination environments of Ni and Zn in **2** and (b) 1-D double-zigzag chain structure of **2**.

having a single bond length in the oxamido is 1.530 Å. In **2**, the N(3)–C(26), N(4)–C(25), N(7)–C(16), and N(8)–C(15) bond lengths in the oxamido groups are 1.346, 1.343, 1.330, and 1.357 Å, respectively, longer than N = C double bonds (N(2)–C(33) (1.290 Å), N(1)–C(42) (1.316 Å), N(6)–C(7) (1.313 Å), and N(5)–C(23) (1.316 Å)), but shorter than N–C single bonds (N(2)–C(35) (1.433 Å), N(1)–C(40) (1.445 Å), N(6)–C(9) (1.434 Å), and N(5)–C(14) (1.433 Å)). The sum of the three bond angles around each amidate nitrogen atom is close to 360° (372.4–373.6°), sp^2-hybridized, similar to **1**. The C(15)–C(16) and C(25)–C(26) bonds have single bond lengths in the oxamido group of 1.540 and 1.538 Å, respectively. The above analyses of **1** and **2** suggest that each oxamido is divided into two π-systems, each of which includes an amidate nitrogen and a carbonyl. Normal lengths of the C–C single bonds (C(8)–C(9), C(9)–C(10), C(17)–C(18), and C(17)–C(19) in **1** and C(1)–C(7),

Table 4. Contact distances (Å) between neighboring binuclear cations of **1**.

Ni1–C27^{g}	3.492(4)	C20–C6^{i}	3.551(5)
Ni1–C32^{f}	3.680(4)	C21–C3^{g}	3.456(4)
C3–C21^{h}	3.456(4)	C24–C32^{c}	3.465(5)
C6–C31^{d}	3.371(5)	C27–C9^{h}	3.466(4)
C6–C20^{e}	3.551(5)	C27–N4^{h}	3.419(4)
C7–O6^{e}	3.385(4)	C27–Ni1^{h}	3.492(4)
C9–C27^{g}	3.466(4)	C31–C6^{a}	3.371(5)
C9–C22^{h}	3.488(4)	C32–Ni1^{h}	3.680(4)
C32–C24^{b}	3.465(5)		

Symmetry codes: ^{a} $-1/2-x$, $-1/2+y$, $3/2-z$; ^{b} x, $-1+y$, z; ^{c} x, $1+y$, z; ^{d} $-1/2-x$, $1/2+y$, $3/2-z$; ^{e} $-1+x$, y, z; ^{f} $1/2-x$, $1/2+y$, $3/2-z$; ^{g} $1/2-x$, $1/2+y$, $3/2-z$; ^{h} $1/2-x$, $-1/2+y$, $3/2-z$; ^{i} $1+x$, y, z.

C(7)–C(8), C(22)–C(23), C(23)–C(24), C(32)–C(33), C(33)–C(34), C(41)–C(42), and C(42)–C(43) in **2**) are 1.456–1.543 Å. The normal length of N–C single bonds (N(3)–C(11) and N(4)–C(16) in **1** and N(1)–C(40), N(2)–C(35), N(5)–C(44), and N(6)–C(9) in **2**) are 1.424–1.445 Å. So, normal lengths of the C–C and C–N single bonds around the C=N double bond indicate that the Schiff-base groups are not involved in conjugated systems.

Each NiL of every binuclear **1** and two NiL fragments of every tetranuclear **2** overlaps with NiL fragments of neighbors with close distances; many distances between the benzene ring of each NiL and the nickel and separate π-systems around other NiL metalloligands are shorter than 3.80 Å (tables 4 and 5), revealing $\pi\cdots\pi$ interactions [30, 31]. The benzene ring, nickel, and the separate unclosed π-systems around nickel in NiL are complementary and this kind of $\pi\cdots\pi$ interaction plays an important role in self-complementary for NiL [31].

Intermolecular hydrogen bonds of O–H···O and C–H···O types were observed in **1** and **2**. Parameters of hydrogen bonds are given in tables 6 and 7. Hydrogen bonds involve coordinated solvent (DMA and H_2O of **1** and DMF and H_2O of **2**) in forming 3-D supramolecular networks. Infinite arrays of molecular units are parallel in crystals of the two compounds with different packing modes (figures 3 and 4) of the infinite arrays of molecular units in **1** and **2**.

3.2. *Solvent effects*

DMF, DMA, and water with different coordination abilities and steric effects play roles as both ligand and guest in the final structures. DMF, DMA, and water show affinities to Zn ions, resulting in coordination. DMF, DMA, and water as guests in the crystalline frameworks with different volumes and polarities induce distinct coordination patterns and packing lattices. Coordination polymers **1** and **2** and polymer **4** $\{[Zn_2(NiL)_2(H_2O)_6]\cdot 8H_2O\}_n$ [26] were attained by changing the volume ratio of the mixed solvent. The reaction of NiL with zinc(II) in water/DMF or water/DMA at 3 : 1 volume ratio gave **4** [26]. When the water/CH_2Cl_2 volume ratio was 5 : 4, **4** was also attained [26]. However, when the water/DMA/CH_2Cl_2 and water/DMF/CH_2Cl_2 volume ratios were both at 1 : 4 : 4 volume ratio, **1** and **2** were formed, respectively. Coordination abilities of DMA, DMF, and water are different and they can be used as gradual neutralization agents in the reactions. DMA, DMF, and

Table 5. Contact distances (Å) between neighboring tetranuclear cations of **2**.

Ni1–C56^{c}	3.748(12)	Ni2–C59^{e}	3.685(14)
N2–C56^{c}	3.400(12)	C13–C58^{e}	3.577(13)
C17–C30^{b}	3.526(14)	C18–C30^{b}	3.493(13)
C19–C30^{b}	3.558(12)	C19–C33^{f}	3.450(10)
C20–C27^{f}	3.357(10)	C22–C30^{b}	3.584(12)
C30–C18^{a}	3.493(13)	C30–C22^{a}	3.584(12)
C30–C17^{a}	3.526(14)	C30–C19^{a}	3.558(12)
C33–C56^{c}	3.568(13)	C33–C19^{f}	3.450(10)
C44–C3^{d}	3.595(13)	C51–O3^{b}	3.322(14)
C54–C15^{f}	3.443(15)	C54–C16^{f}	3.440(17)
C56–N2^{c}	3.400(12)	C56–Ni1^{c}	3.748(12)
C56–C33^{c}	3.568(13)	C59–Ni2^{c}	3.685(14)

Symmetry codes: ^{a} x, $1/2-y$, $-1/2+z$; ^{b} x, $1/2-y$, $1/2+z$; ^{c} x, $1+y$, z; ^{d} $-1+x$, $1/2-y$, $-1/2+z$; ^{e} $-1+x$, y, z; ^{f} $1/2-x$, $1/2+y$, $3/2-z$.

Table 6. Hydrogen-bonding parameters of **1**.

Donor–H···Acceptor	D–H (Å)	D···A (Å)	H···A (Å)	D–H···A (°)
O7–H7A···O3^{b}	0.890	1.820	2.691(3)	166.0
O7–H7B···O10^{c}	0.840	1.890	2.723(3)	175.0
O8–H8A···O6^{d}	0.860	1.770	2.608(3)	164.0
O8–H8B···O5^{a}	0.810	2.070	2.856(3)	163.0
O11–H11A···O5^{b}	0.990	1.910	2.891(3)	173.0
O11–H11B···O2^{f}	0.950	2.230	3.088(3)	151.0
O11–H11B···O8^{f}	0.950	2.550	3.278(3)	134.0
C4–H4···O2	0.950	2.370	2.928(4)	118.0
C12–H12···O3	0.950	2.480	3.268(4)	140.0
C13–H13···O3^{i}	0.950	2.540	3.378(4)	148.0
C15–H15···O6	0.950	2.310	3.130(4)	144.0
C22–H22···O3^{g}	0.950	2.410	3.344(4)	168.0
C23–H23···O1	0.950	2.200	2.848(3)	124.0
C25–H25C···O1	0.980	2.550	3.127(4)	118.0
C27–H27A···O9	0.980	2.200	2.621(4)	105.0
C27–H27B···O4^{h}	0.980	2.540	3.477(4)	159.0
C28–H28A···O11	0.980	2.490	3.372(5)	149.0
C28–H28C···O8^{e}	0.980	2.520	3.454(5)	159.0

Symmetry codes: ^{a} $3/2-x$, $-1/2+y$, $3/2-z$; ^{b} $1/2+x$, $3/2-y$, $1/2+z$; ^{c} x, $1+y$, z; ^{d} $-1/2+x$, $3/2-y$, $1/2+z$; ^{e} $1-x$, $1-y$, $2-z$; ^{f} $1+x$, y, z; ^{g} $1/2-x$, $1/2+y$, $3/2-z$; ^{h} $1/2-x$, $-1/2+y$, $3/2-z$; ^{i} $-x$, $1-y$, $1-z$.

water coordinate with zinc and solvent effects play roles in formation of the ultimate chain structures. These solvents are widely used in syntheses of coordination polymers. Different polymers can be achieved by changing the volume ratio of the mixed solvents.

3.3. *IR spectroscopic properties*

The IR spectrum of NiL shows an absorption at 1632 cm^{-1} attributed to stretch of oxamido C=O. Bands at 1621 cm^{-1} for **1** and 1615 cm^{-1} for **2** can be assigned to

Table 7. Hydrogen-bonding parameters of **2**.

Donor–H···Acceptor	D–H (Å)	D···A (Å)	H···A (Å)	D–H···A (°)
O8–H8A···O7	0.850	1.830	2.666(8)	165.0
O8–H8B···O1^{b}	0.850	1.850	2.651(9)	157.0
O9–H9A···O6	0.870	1.850	2.715(14)	170.0
O9–H9B···O13^{a}	0.840	1.980	2.803(9)	169.0
C2–H2A···O4^{c}	0.930	2.600	3.271(12)	130.0
C5–H5A···O17	0.930	2.340	2.914(12)	119.0
C10–H10A···O19	0.930	2.410	3.237(12)	148.0
C12–H12A···O7	0.930	2.530	3.420(13)	160.0
C13–H13A···O8	0.930	2.510	3.290(12)	142.0
C13–H13A···O12	0.930	2.340	3.163(10)	147.0
C18–H18A···O16	0.930	2.270	2.873(10)	122.0
C19–H19A···O1^{a}	0.930	2.590	3.521(11)	177.0
C28–H28A···O11	0.930	2.240	2.843(11)	122.0
C36–H36A···O1	0.930	2.350	3.154(12)	144.0
C39–H39A···O4	0.930	2.410	3.200(12)	142.0
C47–H47A ···O10	0.930	2.270	2.889(10)	124.0
C50–H50A···O6	0.960	2.320	2.755(17)	107.0
C51–H51C···O3^{b}	0.960	2.490	3.321(14)	144.0
C52–H52A···O5	0.960	2.370	2.78(2)	105.0
C56–H56A···O14	0.960	2.310	2.744(13)	107.0
C60–H60A···O7	0.960	2.300	2.730(14)	106.0

Symmetry codes: ^{a} $1-x, -y, 1-z$; ^{b} $x, 1/2-y, 1/2+z$; ^{c} $1+x, 1/2-y, 1/2+z$.

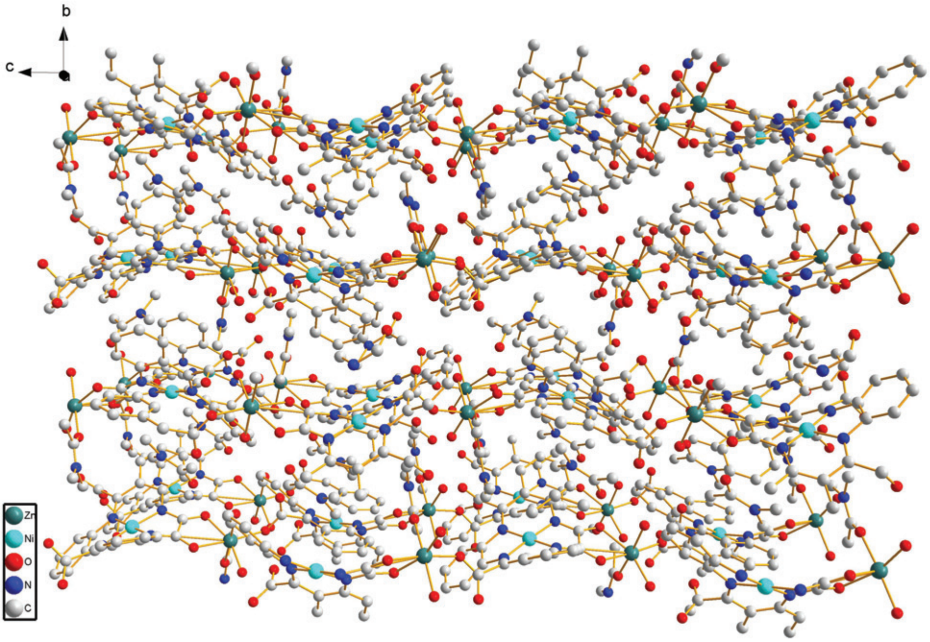


Figure 3. Packing diagram of the infinite molecular structure in **1**. Solvent and hydrogen atoms are omitted for clarity.

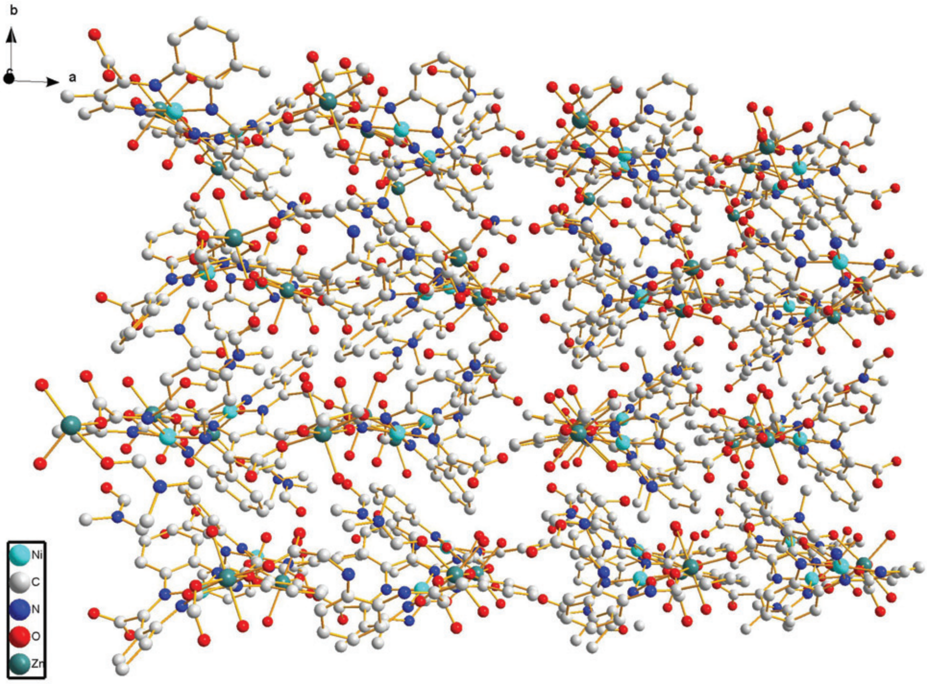


Figure 4. Packing diagram of the infinite molecular structure in **2**. Solvent and hydrogen atoms are omitted for clarity.

absorptions of oxamido C=O coordinated to Zn^{2+}. Bands at $1593\,cm^{-1}$ for **1** and $1589\,cm^{-1}$ for **2** are attributed to $\nu(C{=}N)$.

4. Conclusion

$\{[Zn(NiL)(DMA)(H_2O)_2]\cdot(DMA)(H_2O)\}_n$ (**1**) and $\{[Zn_2(NiL)_2(DMF)(H_2O)_4]\cdot 3DMF\}_n$ (**2**) synthesized from mixed solvents with different structure motifs have been structurally characterized. Complex **1** is a 1-D single-zigzag chain while **2** contains 1-D double-zigzag chains. Both **1** and **2** were obtained by solvent induced assembly of Zn(II) and NiL. We highlight the delicate coordinated-solvent induced assembly in crystal engineering in this work, which is useful to construct metal–organic frameworks with desirable structures.

Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC Nos 871022 for **1** and 871023 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgments

We acknowledge support by the National Natural Science Foundation of China (No. 20801040).

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