Journal of Molecular Structure 1128 (2017) 103-110

Contents lists available at ScienceDirect

Journal of Molecular Structure

journal homepage: http://www.elsevier.com/locate/molstruc

Six complexes based on bis(imidazole/benzimidazole-1-yl)pyridazine ligands: Syntheses, structures and properties



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ARTICLE INFO

Article history: Received 25 June 2016 Received in revised form 16 August 2016 Accepted 17 August 2016 Available online 19 August 2016

Keywords: Bis(imidazole/benzimidazole-1-yl) pyridazine Complex Crystal structure Luminescence property

ABSTRACT

Herein we reported six new Ni(II)/Cu(II)/Zn(II) complexes, namely, $[Ni(L^1)_4(OH)_2]$ (1), $[Cu(L^1)_4(OH)_2]$ (2), $[Cu(L^1)_2(SiF_6)]_n$ (3), $\{[Cu(L^2)(HCOO)_2] \cdot H_2O \cdot CH_3OH\}_n$ (4), $[Ni(L^2)_2(NO_3)_2]_n$ (5) and $\{[Zn(L^2)Cl_2] \cdot DMF\}_n$ (6) ($L^1 = 3,6$ -bis(imidazole-1-yl)pyridazine, $L^2 = 3,6$ -bis(benzimidazole-1-yl)pyridazine), which were characterized by single-crystal X-ray diffraction, elemental analysis, IR, PXRD. These complexes have been successfully constructed under interface diffusion process, heating reflux or hydrothermal conditions. The structures of 1 and 2 are mononuclear complexes. Complex 3 exhibits a 6-connected 3D topology network with the Schläfli symbol of ($4^{12} \cdot 6^3$). In complex 4, two Cu(II) were connected through two HCOO⁻ anions to form dinuclear structure unit, which is arranged into a 1D ladder-like structure by μ_2 - L^2 ligands. Complexes 5 and 6 are 1D zigzag chains connected by L^2 ligands, but the Ni(II) ion is four-coordinated in 6. Moreover, the solid-state luminescence property and UV–vis diffuse reflection spectrum of complex 6 have been investigated and discussed.

1. Introduction

Recently, the design and synthesis of coordination polymers have attracted increasing attention, due to not only intriguing topological structures, but also their applications as new materials such as gas storage/separation, catalysis, fluorescent materials, nonlinear optics and magnetism, anticancer drug [1]. Many spectacular metal-organic framework (MOF) have been reported, such as zero-dimensional (0D) complexes, one-dimensional (1D) chains, two-dimensional (2D) grids, three-dimensional (3D) microporous networks and interpenetrated modes [2]. Therefore, much work has focused on the rational design of such complexes by controlling the favored geometry of ligands and metals. Nevertheless, it is still a great challenge to rationally design and construct the desired polynuclear metal complexes in coordination chemistry. The assembly of coordination polymers can dramatically been changed by very small tuning factors, such as metal-ligand ratio, metal ions, pH, solvents system, temperature and number of coordination sites provided by organic ligands [3–9]. In previous studies, researchers

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spent most time on the design and synthesis of the multifunctional organic bridging ligands to get desired complexes.

From a synthetic point of view, organic ligands provide the opportunity to tailor the inorganic aggregation and to achieve interesting inorganic motifs by means of connection or separation of the building units [10]. Until now, some versatile ligands containing N-donor atoms have been extensively employed in the construction of polymers. Because of the special metalcoordinating ability of imidazoles, research on imidazolecontaining ligands has experienced a drastic development, and a large number of networks have been reported [11]. The semirigid ligands with multinitrogen heterocycles, such as 1,4-bis(1imidazolyl)benzene [12], 1,4-bis(benzoimidazol-1-yl)benzene [13], 1,4-bis(benzoimidazol-1-yl)butane [14], 1,2,4,5-tetrakis(imidazol-1-ylmethyl)benzene [15] and 1,4-bis(imidazol-1-ylmethyl)-naphthalene [16], are also widely utilized to construct coordination polymers. The ligand 3,6-bis(imidazole-1-yl)pyridazine [17] was reported the synthesis and structure of several perchlorometallate complexes as the functional organic ammonium cations.

In this article, we selected 3,6-bis(imidazole-1-yl)pyridazine (L^1) and 3,6-bis(benzimidazole-1-yl)pyridazine (L^2) (Scheme 1) as organic linkers, six Ni(II)/Cu(II)/Zn(II) complexes [Ni(L¹)₄(OH)₂] (1), [Cu(L¹)₄(OH)₂] (2), [Cu(L¹)₂(SiF₆)]_n (3), {[Cu(L²)(HCOO)₂].



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Scheme 1. The ligands L¹ and L² used in this work.

 $H_2O \cdot CH_3OH_n$ (**4**), $[Ni(L^2)_2(NO_3)_2]_n$ (**5**) and $\{[Zn(L^2)Cl_2] \cdot DMF\}_n$ (**6**) were synthesized. All complexes were structurally characterized by elemental analysis, IR spectra, single crystal X-ray diffraction and powder X-ray diffraction(PXRD). Furthermore, the photoluminescence property and UV–vis diffuse reflection spectrum of complex **6** have been investigated and discussed.

2. Experimental section

2.1. Materials and general methods

The chemicals in organic synthesis and all solvents were commercially available and used without further purification. FT-IR spectra were measured with a Brucker Equinox 55 spectrometer on KBr Pellets in the range of 4000–400 cm⁻¹. C, H and N elemental analyses were carried out by Thermo Flash EA 1112-NCHS-O analyzer. ¹H NMR data were collected using an INOVA-400 NMR spectrometer in DMSO medium at 25 °C with TMS as the internal reference. The X-ray powder diffraction (PXRD) was recorded on a Rigaku D/Max-2500 diffractometer at 40 kV, 100 mA for a Cu-target tube and a graphite monochromator. Luminescence spectra were measured by a Hitachi F-4500 Fluorescence Spectrophotometer, equipped with a Xe arc lamp excitation source and bandwidths of 2.5 nm at room temperature. Fluorescence lifetime data were acquired on Fluorolog-3 Spectrophotometer equipped with nanoled as the light source. UV–Vis absorption spectra were obtained using a Hitachi UV-3010 UV-Vis Spectrophotometer.

2.2. Preparation of ligands

2.2.1. Preparation of ligand L^1

3.6-bis(imidazole-1-yl)pyridazine (L¹) A mixture of imidazole (3.4 g, 49.9 mmol) and sodium (1.2 g, 26.1 mmol) were dissolved in THF (80 mL). After heating reflux for 40 min, a solution of 3,6dichloropyridazine (3.7 g, 24.8 mmol) in THF (10 mL) was added to the mixture within 40 min. The mixture was refluxed for 4 h under N₂, then stirring for 30 min. After the reaction mixture was cooled to ambient temperature. Poured reactor into ice water mixture, an earthy yellow solid of L¹ was obtained after filtering and distilling off the filtrate, recrystallized from absolute ethanol to give pure ligand L¹ as white crystals, yield 80%, m.p. 281–282 °C. ¹H NMR (DMSO-*d*₆): δ: 8.69 (s, 2H, imidazole-2), 8.48 (s, 2H, pyridazine), 8.11 (s, 2H, imidazole-5), 7.23 (s, 2H, imidazole-4); Anal. Calcd for C₁₀H₈N₆: C, 56.60; H, 3.79; N, 39.60; Found: C, 56.75; H, 3.75; N, 39.54. IR (cm⁻¹, KBr pellets): 3176(w), 3145(m), 3109(m), 3047(m), 3018(m), 2946(m), 2782(w), 2621(w), 2526(w), 2408(w), 2214(w), 1991(w), 1903(w), 1795(w), 1727(w), 1692(w), 1645(w), 1577(s), 1519(s), 1490(s), 1459(s), 1371(m), 1321(s), 1277(m), 1237(m), 1163(m), 1106(m), 1059(m), 1031(s), 962(m), 903(m), 861(s), 823(s), 766(s), 749(s), 645(s), 613(m), 507(w), 487(m), 421(m).

2.2.2. Preparation of ligand L^2

3,6-bis(benzimidazole-1-yl)pyridazine (L^2) The synthetic method of L^2 is the same as the L^1 , except for using benzimidazole instead of imidazole, then crude product were recrystallized by the

mixed solution of methanol and DMF (1:1). Yield 76%, m.p. 283–284 °C. ¹H NMR (DMSO- d_6): δ : 9.130 (s, 2H, imidazole-2), 8.653 (s, 2H, pyridazine), 7.388–8.384 (m, 8H, benzene); Anal. Calcd for C₁₈H₁₂N₆: C, 69.21; H, 3.87; N, 26.91; Found: C, 69.34; H, 3.56; N, 27.41. IR (cm⁻¹, KBr pellets): 3082(m), 3058(m), 2924(w), 2854(w), 2773(w), 2371(w), 1921(w), 1783(w), 1739(w), 1669(w), 1609(m), 1590(m), 1558(s), 1497(s), 1459(s), 1359(m), 1338(m), 1308(m), 1279(m), 1238(m), 1190(s), 1163(m), 1138(m), 1035(m), 992(m), 979(m), 962(m), 939(m), 884(m), 830(m), 769(s), 753(s), 732(s), 644(m), 623(m), 575(m), 538(m), 486(m), 427(m).

2.3. Synthesis of complexes 1~6

2.3.1. Preparation of $[Ni(L^1)_4(OH)_2]$ (1)

A mixture of Ni(ClO₄)₂·6H₂O (0.035 g, 0.1 mmol), **L**¹ (0.021 g, 0.1 mmol), and distilled water (5 mL) was placed in a 25 mL Teflonlined stainless steel vessel and heated at 140 °C for 2 days. After the mixture had been cooled to room temperature at a rate of 5 °C h⁻¹, green crystals of **1** were obtained with a yield of 43% (based on **L**¹). Anal. Calcd (%) for C₄₀H₃₄N₂₄O₂Ni (%): C, 51.02; H, 3.64; N, 35.70. Found: C, 50.30; H, 3.28; N, 35.52. IR (KBr pellets, cm⁻¹): 3572(m), 3389(m), 3150(m), 3115(m), 2591(w), 2558(w), 2511(w), 2417(w), 2338(w), 2212(w), 2015(w), 1913(w), 1872(w), 1809(w), 1580(s), 1523(s), 1480(s), 1370(m), 1319(s), 1242(s), 1097(s), 1065(s), 1032(s), 967(m), 934(m), 915(m), 837(m), 737(m), 653(m), 620(m), 493(m), 419(m).

2.3.2. Preparation of $[Cu(L^1)_4(OH)_2]$ (2)

A solution of L^1 (0.021 g, 0.1 mmol) in MeOH (3 mL) was carefully layered on top of MeOH/H₂O (10 mL, middle), and a solution of Cu(BF₄)₂·6H₂O (0.035 g, 0.1 mmol) in H₂O (3 mL, bottom) at room temperature. The blue block-shaped crystals were formed after 5 days with the evaporation of the filtrate. The crystalline product was obtained after filtering and washed with distilled water (ca. 38% yield based on L¹). Anal. Calcd (%) for C₄₀H₃₄N₂₄O₂Cu (%): C, 54.42; H, 3.88; N, 38.07. Found: C, 54.54; H, 3.82; N, 38.42. IR (KBr pellets, cm⁻¹): 3601(m), 3384(m), 3155(m), 3118(m), 2870(w), 2788(w), 2738(w), 2592(w), 2530(w), 2418(w), 2339(w), 2212(w), 2083(w), 2009(w), 1914(w), 1872(w), 1809(w), 1716(m), 1581(s), 1522(s), 1481(s), 1370(m), 1321(s), 1243(s), 1067(s), 1033(s), 968(s), 942(m), 912(m), 838(m), 739(m), 652(m), 613(m), 493(m).

2.3.3. Preparation of $[Cu(L^1)_2(SiF_6)]_n$ (3)

The synthesis procedure of **3** was similar to complex **2**, except for using $\text{CuSiF}_{6} \cdot \text{6H}_2\text{O}$ (0.031 g, 0.1 mmol) instead of $\text{Cu}(\text{BF}_4)_2 \cdot \text{6H}_2\text{O}$. The solution was allowed to stand for approximately two weeks, resulting in the formation of blue block-shaped crystals of **3** that were obtained. Yield: 32% based on **L**¹. Anal. Calcd (%) for $\text{C}_{20}\text{H}_{16}\text{N}_{12}\text{F}_6\text{SiCu}$ (%): C, 38.13; H, 2.56; N, 26.68. Found: C, 38.47; H, 2.28; N, 27.52. IR (KBr pellets, cm⁻¹): 3520(m), 3136(m), 2596(w), 240(w), 2350(w), 2216(w), 2026(w), 1915(w), 1639(m), 1580(s), 1497(s), 1454(s), 1376(m), 1310(s), 1278(s), 1248(m), 1147(m), 1121(m), 1102(m), 1076(s), 1037(m), 970(m), 859(m), 712(s), 650(s), 498(m), 473(m), 429(m).

2.3.4. Preparation of $\{[Cu(\mathbf{L}^2)(HCOO)_2] \cdot H_2O \cdot CH_3OH\}_n$ (**4**)

A mixture of Cu(NO₃)₂·3H₂O (0.024 g, 0.1 mmol), **L**² (0.031 g, 0.1 mmol) was dissolved in 15 mL mixed solvent (H₂O: DMF: CH₃OH = 1:1:1). The solution was refluxed for 3 h and allowed to evaporate for seven days and finally suitable blue block crystals were formed. The crystalline product was obtained after filtering and washed with distilled water (ca. 53% yield based on **L**²). Anal. Calcd (%) for C₂₁H₂₀N₆O₆Cu (%): C, 48.88; H, 3.91; N, 16.29. Found: C, 47.37; H, 3.35; N, 15.30. IR (KBr pellets, cm⁻¹): 3485(m), 3155(w),

3112(w), 2924(w), 2858(w), 2825(w), 2713(w), 2608(w), 1913(w), 1738(w), 1622(s), 1593(s), 1515(s), 1461(s), 1439(s), 1370(m), 1341(m), 1303(s), 1250(m), 1221(m), 1153(m), 1040(m), 1006(w), 941(w), 915(w), 868(w), 848(w), 769(m), 747(m), 650(w), 618(w).

2.3.5. Preparation of $[Ni(L^2)_2(NO_3)_2]_n$ (5)

A mixture of L^2 (0.031 g, 0.1 mmol) and Ni(NO₃)₂·6H₂O (0.029 g, 0.1 mmol) was added to a 5 mL methanol, which was placed in a 25 mL Teflon-lined stainless steel vessel and heated at 140 °C for 2 days, and then the mixture was cooled to room-temperature at a rate of 5 °C h⁻¹. The green block crystals of **5** were obtained (ca. 32% yield based on L^2). Anal. Calcd (%) for C₃₆H₂₄N₁₄O₆Ni (%): C, 53.56; H, 3.00; N, 24.29. Found: C, 52.35; H, 3.32; N, 24.23. IR (KBr pellets, cm⁻¹): 3109(w), 3081(w), 3060(w), 2500(w), 2341(w), 1676(w), 1611(w), 1586(m), 1561(m), 1503(s), 1467(s), 1443(s), 1365(w), 1320(s), 1282(s), 1241(s), 1194(m), 1167(m), 1038(m), 1014(m), 907(w), 860(w), 832(w), 811(w), 767(m), 747(m), 625(w), 608(w).

2.3.6. Preparation of $\{[Zn(L^2)Cl_2] \cdot DMF\}_n$ (6)

Complex 6 was synthesized in a similar way as described for 4,

 Table 1

 Crystal data and structure refinement summary for complexes 1–6.

	1	2	3
Formula	C40H34N24O2Ni	C40H34N24O2Cu	C20H16N12F6SiCu
Formular wt	941.59	946.45	632.97
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	Aba2	Pc	P21/c
T/K	293(2)	293(2)	293(2)
a/Å	13.716(5)	15.429(8)	12.697(8)
b/Å	13.757(5)	13.874(7)	25.099(15)
c/Å	28.738(11)	13.882(7)	12.664(8)
α/deg	90	90.00	90
β/deg	90	113.352(8)	117.423(8)
γ/deg	90	90.00	90
$V/Å^3$	5423(3)	2728(2)	3582(4)
z	4	2	4
$D/g \text{ cm}^{-3}$	1.151	1.151	1.174
μ/mm^{-1}	0.412	0.454	0.712
F(000)	1935	972	1272
Crystal size (mm ³)	$0.20 \times 0.20 \times 0.20$	$0.22 \times 0.20 \times 0.18$	$0.15 \times 0.10 \times 0.10$
Theta range (deg)	1.42-24.99	1.44-29.22	1.62-25.00
GOOF(F ²)	1 016	0 905	0.987
Messured reflns	16422	21760	14144
Obsd refins	4017	10005	5709
Rint	0.0583	0 0797	0.0651
R^a/wR^b	0.0951/0.2312	0.0718/0.2123	0.0654/0.1768
,			
	4	F	C
	4	5	6
Formula	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn
Formula Formular wt	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70
Formula Formular wt Crystal system	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic
Formula Formular wt Crystal system Space group	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic P21/n
Formula Formular wt Crystal system Space group T/K	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic P-1 293(2)	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2)	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2)
Formula Formular wt Crystal system Space group T/K a/Å	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1 293(2) 8.5791(3)	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11)	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5)
Formula Formular wt Crystal system Space group T/K a/Å b/Å	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1 293(2) 8.5791(3) 11.5009(5)	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12)	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5) 18.729(9)
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic P-1 293(2) 8.5791(3) 11.5009(5) 11.7865(5)	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18)	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic P21/n 296(2) 10.434(5) 18.729(9) 12.619(6)
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å α/deg	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1 293(2) 8.5791(3) 11.5009(5) 11.7865(5) 70.7230(10)	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18) 79.403(3)	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5) 18.729(9) 12.619(6) 90
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å a/deg β/deg	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1 293(2) 8.5791(3) 11.5009(5) 11.7865(5) 70.7230(10) 78.2360(10)	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18) 79.403(3) 80.933(3)	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5) 18.729(9) 12.619(6) 90 110.996(14)
Formula Formular wt Crystal system Space group T/K <i>a</i> /Å <i>b</i> /Å <i>c</i> /Å <i>a</i> /deg β/deg γ/deg	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1 293(2) 8.5791(3) 11.5009(5) 11.7865(5) 70.7230(10) 78.2360(10) 68.6200(10)	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18) 79.403(3) 80.933(3) 66.993(2)	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5) 18.729(9) 12.619(6) 90 110.996(14) 90
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å a/deg β/deg γ/deg V/Å ³	$\begin{array}{c} 4 \\ \hline \\ C_{21}H_{20}N_6O_6Cu \\ 515.96 \\ Triclinic \\ P-1 \\ 293(2) \\ 8.5791(3) \\ 11.5009(5) \\ 11.7865(5) \\ 70.7230(10) \\ 78.2360(10) \\ 68.6200(10) \\ 1017.57(7) \end{array}$	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18) 79.403(3) 80.933(3) 66.993(2) 1650.0(3)	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5) 18.729(9) 12.619(6) 90 110.996(14) 90 2302.3(19)
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å α/deg β/deg γ/deg γ/deg $V/Å^3$ Z	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1 293(2) 8.5791(3) 11.5009(5) 11.7865(5) 70.7230(10) 78.2360(10) 68.6200(10) 1017.57(7) 2	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18) 79.403(3) 80.933(3) 66.993(2) 1650.0(3) 2	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5) 18.729(9) 12.619(6) 90 110.996(14) 90 2302.3(19) 4
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å α/deg β/deg γ/deg $V/Å^3$ Z D/g cm ⁻³	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1 293(2) 8.5791(3) 11.5009(5) 11.7865(5) 70.7230(10) 78.2360(10) 68.6200(10) 1017.57(7) 2 1.674	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18) 79.403(3) 80.933(3) 66.993(2) 1650.0(3) 2 1.625	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/n 296(2) 10.434(5) 18.729(9) 12.619(6) 90 110.996(14) 90 2302.3(19) 4 1.505
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å α/deg β/deg γ/deg γ/deg γ/deg $D/g \text{ cm}^{-3}$ μ/mm^{-1}	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic P-1 293(2) 8.5791(3) 11.5009(5) 11.7865(5) 70.7230(10) 78.2360(10) 68.6200(10) 1017.57(7) 2 1.674 1.129	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18) 79.403(3) 80.933(3) 66.993(2) 1650.0(3) 2 1.625 0.663	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5) 18.729(9) 12.619(6) 90 110.996(14) 90 2302.3(19) 4 1.505 1.327
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å a/deg β/deg γ/deg $V/Å^3$ Z $D/g \text{ cm}^{-3}$ μ/mm^{-1} F(000)	4 C ₂₁ H ₂₀ N ₆ O ₆ Cu 515.96 Triclinic <i>P</i> -1 293(2) 8.5791(3) 11.5009(5) 11.7865(5) 70.7230(10) 78.2360(10) 68.6200(10) 1017.57(7) 2 1.674 1.129 524	5 C ₃₆ H ₂₄ N ₁₄ O ₆ Ni 807.38 Triclinic <i>P</i> -1 293(2) 10.2072(11) 11.0572(12) 16.2310(18) 79.403(3) 80.933(3) 66.993(2) 1650.0(3) 2 1.625 0.663 828	6 C ₂₁ H ₁₉ N ₇ OCl ₂ Zn 521.70 Monoclinic <i>P</i> 21/ <i>n</i> 296(2) 10.434(5) 18.729(9) 12.619(6) 90 110.996(14) 90 2302.3(19) 4 1.505 1.327 1064
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å a/deg β/deg γ/deg $V/Å^3$ Z D/g cm ⁻³ μ/mm^{-1} F(000) Crystal size (mm ³)	$\begin{array}{c} 4\\ \hline \\ C_{21}H_{20}N_6O_6Cu\\ 515.96\\ Triclinic\\ P-1\\ 293(2)\\ 8.5791(3)\\ 11.5009(5)\\ 11.7865(5)\\ 70.7230(10)\\ 78.2360(10)\\ 68.6200(10)\\ 1017.57(7)\\ 2\\ 1.674\\ 1.129\\ 524\\ 0.22\times 0.20\times 0.18 \end{array}$	$\frac{5}{C_{36}H_{24}N_{14}O_6Ni}\\807.38}\\Triclinic\\P-1\\293(2)\\10.2072(11)\\11.0572(12)\\16.2310(18)\\79.403(3)\\80.933(3)\\66.993(2)\\1650.0(3)\\2\\1.625\\0.663\\828\\0.22\times0.20\times0.18$	$\begin{array}{c} 6 \\ \\ \hline \\ C_{21}H_{19}N_7OCl_2Zn \\ 521.70 \\ \\ Monoclinic \\ P21/n \\ 296(2) \\ 10.434(5) \\ 18.729(9) \\ 12.619(6) \\ 90 \\ 110.996(14) \\ 90 \\ 2302.3(19) \\ 4 \\ 1.505 \\ 1.327 \\ 1064 \\ 0.22 \times 0.20 \times 0.18 \\ \end{array}$
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å α/deg β/deg γ/deg $V/Å^3$ Z $D/g \text{ cm}^{-3}$ μ/mm^{-1} F(000) Crystal size (mm ³) Theta range (deg)	$\begin{array}{c} 4\\ \hline \\ C_{21}H_{20}N_6O_6Cu\\ 515.96\\ Triclinic\\ P-1\\ 293(2)\\ 8.5791(3)\\ 11.5009(5)\\ 11.7865(5)\\ 70.7230(10)\\ 78.2360(10)\\ 68.6200(10)\\ 1017.57(7)\\ 2\\ 1.674\\ 1.129\\ 524\\ 0.22\times 0.20\times 0.18\\ 1.98-28.92\\ \end{array}$	$\frac{5}{C_{36}H_{24}N_{14}O_6Ni}\\807.38}\\Triclinic\\P-1\\293(2)\\10.2072(11)\\11.0572(12)\\16.2310(18)\\79.403(3)\\80.933(3)\\66.993(2)\\1650.0(3)\\2\\1.625\\0.663\\828\\0.22\times0.20\times0.18\\1.28-25.36$	$\begin{array}{c} 6 \\ \\ \hline \\ C_{21}H_{19}N_7OCl_2Zn \\ 521.70 \\ \\ Monoclinic \\ P21/n \\ 296(2) \\ 10.434(5) \\ 18.729(9) \\ 12.619(6) \\ 90 \\ 110.996(14) \\ 90 \\ 2302.3(19) \\ 4 \\ 1.505 \\ 1.327 \\ 1064 \\ 0.22 \times 0.20 \times 0.18 \\ 2.04-25.00 \\ \end{array}$
Formula Formular wt Crystal system Space group T/K a/\dot{A} b/\dot{A} c/\dot{A} α/deg β/deg γ/deg V/\dot{A}^3 Z D/g cm ⁻³ μ/mm^{-1} F(000) Crystal size (mm ³) Theta range (deg) GOOF(F ²)	$\begin{array}{c} 4\\ \hline \\ C_{21}H_{20}N_6O_6Cu\\ 515.96\\ Triclinic\\ P-1\\ 293(2)\\ 8.5791(3)\\ 11.5009(5)\\ 11.7865(5)\\ 70.7230(10)\\ 78.2360(10)\\ 68.6200(10)\\ 1017.57(7)\\ 2\\ 1.674\\ 1.129\\ 524\\ 0.22 \times 0.20 \times 0.18\\ 1.98-28.92\\ 0.982\\ \end{array}$	$\frac{5}{C_{36}H_{24}N_{14}O_6Ni}\\807.38}\\Triclinic\\P-1\\293(2)\\10.2072(11)\\11.0572(12)\\16.2310(18)\\79.403(3)\\80.933(3)\\66.993(2)\\1650.0(3)\\2\\1.625\\0.663\\828\\0.22\times0.20\times0.18\\1.28-25.36\\1.232$	$\begin{array}{c} 6 \\ \\ \hline \\ C_{21}H_{19}N_7OCl_2Zn \\ 521.70 \\ \\ Monoclinic \\ P21/n \\ 296(2) \\ 10.434(5) \\ 18.729(9) \\ 12.619(6) \\ 90 \\ 110.996(14) \\ 90 \\ 2302.3(19) \\ 4 \\ 1.505 \\ 1.327 \\ 1064 \\ 0.22 \times 0.20 \times 0.18 \\ 2.04-25.00 \\ 0.869 \\ \end{array}$
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å a/deg β/deg γ/deg γ/deg $V/Å^3$ Z D/g cm ⁻³ μ/mm^{-1} F(000) Crystal size (mm ³) Theta range (deg) GOOF(F ²) Messured refins	$\begin{array}{c} 4\\ \hline \\ C_{21}H_{20}N_6O_6Cu\\ 515.96\\ Triclinic\\ P-1\\ 293(2)\\ 8.5791(3)\\ 11.5009(5)\\ 11.7865(5)\\ 70.7230(10)\\ 78.2360(10)\\ 68.6200(10)\\ 1017.57(7)\\ 2\\ 1.674\\ 1.129\\ 524\\ 0.22\times 0.20\times 0.18\\ 1.98-28.92\\ 0.982\\ 8784\\ \end{array}$	$\frac{5}{C_{36}H_{24}N_{14}O_6Ni}\\807.38}\\Triclinic\\P-1\\293(2)\\10.2072(11)\\11.0572(12)\\16.2310(18)\\79.403(3)\\80.933(3)\\66.993(2)\\1650.0(3)\\2\\1.625\\0.663\\828\\0.22\times0.20\times0.18\\1.28-25.36\\1.232\\10768\\$	$\begin{array}{c} 6 \\ \\ \hline \\ C_{21}H_{19}N_7OCl_2Zn \\ 521.70 \\ \\ Monoclinic \\ P21/n \\ 296(2) \\ 10.434(5) \\ 18.729(9) \\ 12.619(6) \\ 90 \\ 110.996(14) \\ 90 \\ 2302.3(19) \\ 4 \\ 1.505 \\ 1.327 \\ 1064 \\ 0.22 \times 0.20 \times 0.18 \\ 2.04-25.00 \\ 0.869 \\ 12337 \\ \end{array}$
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å α/deg β/deg γ/deg	$\begin{array}{c} 4\\ \hline \\ C_{21}H_{20}N_6O_6Cu\\ 515.96\\ Triclinic\\ P-1\\ 293(2)\\ 8.5791(3)\\ 11.5009(5)\\ 11.7865(5)\\ 70.7230(10)\\ 78.2360(10)\\ 68.6200(10)\\ 1017.57(7)\\ 2\\ 1.674\\ 1.129\\ 524\\ 0.22\times 0.20\times 0.18\\ 1.98-28.92\\ 0.982\\ 8784\\ 5253\\ \end{array}$	$\frac{5}{C_{36}H_{24}N_{14}O_6Ni}\\807.38}\\Triclinic\\P-1\\293(2)\\10.2072(11)\\11.0572(12)\\16.2310(18)\\79.403(3)\\80.933(3)\\66.993(2)\\1650.0(3)\\2\\1.625\\0.663\\828\\0.22\times0.20\times0.18\\1.28-25.36\\1.232\\10768\\5923$	$\begin{array}{c} 6 \\ \\\hline\\ C_{21}H_{19}N_7OCl_2Zn \\ 521.70 \\\\ Monoclinic \\P21/n \\296(2) \\10.434(5) \\18.729(9) \\12.619(6) \\90 \\110.996(14) \\90 \\2302.3(19) \\4 \\1.505 \\1.327 \\1064 \\0.22 \times 0.20 \times 0.18 \\2.04-25.00 \\0.869 \\12337 \\3942 \\\end{array}$
Formula Formular wt Crystal system Space group T/K a/Å b/Å c/Å a/deg β/deg γ/deg	$\begin{array}{c} 4\\ \\ \hline C_{21}H_{20}N_6O_6Cu\\ 515.96\\ \\ Triclinic\\ P^{-1}\\ 293(2)\\ 8.5791(3)\\ 11.5009(5)\\ 11.7865(5)\\ 70.7230(10)\\ 78.2360(10)\\ 68.6200(10)\\ 1017.57(7)\\ 2\\ 1.674\\ 1.129\\ 524\\ 0.22\times0.20\times0.18\\ 1.98-28.92\\ 0.982\\ 8784\\ 5253\\ 0.0176\\ \end{array}$	$\frac{5}{C_{36}H_{24}N_{14}O_6Ni}\\807.38}\\Triclinic\\P-1\\293(2)\\10.2072(11)\\11.0572(12)\\16.23100(18)\\79.403(3)\\80.933(3)\\66.993(2)\\1650.0(3)\\2\\1.625\\0.663\\828\\0.22\times0.20\times0.18\\1.28-25.36\\1.232\\10768\\5923\\0.0215$	$\begin{array}{c} 6 \\ \\ \hline \\ C_{21}H_{19}N_7OCl_2Zn \\ 521.70 \\ \\ Monoclinic \\ P21/n \\ 296(2) \\ 10.434(5) \\ 18.729(9) \\ 12.619(6) \\ 90 \\ 110.996(14) \\ 90 \\ 2302.3(19) \\ 4 \\ 1.505 \\ 1.327 \\ 1064 \\ 0.22 \times 0.20 \times 0.18 \\ 2.04-25.00 \\ 0.869 \\ 12337 \\ 3942 \\ 0.1901 \\ \end{array}$

using ZnCl₂ (0.013 g, 0.1 mmol) instead of Cu(NO₃)₂·3H₂O. The mixture was dissolved in 15 mL mixed solvent (EtOH: DMF = 1: 1). Colorless crystals were obtained with a yield of 39% (based on L²). Anal. Calcd (%) for C₂₁H₁₉N₇OCl₂Zn (%): C, 48.34; H, 3.67; N, 18.79. Found: C, 49.30; H, 3.78; N, 18.62. IR (KBr pellets, cm⁻¹): 3094(m), 3057(m), 3011(w), 2924(w), 2851(w), 1925(w), 1773(w), 1718(w), 1665(s), 1610(m), 1587(m), 1559(m), 1515(s), 1469(s), 1403(w), 1384(m), 1351(w), 1325(m), 1014(m), 983(m), 955(w), 914(m), 887(w), 853(m), 784(m), 764(m), 755(m), 680(w), 657(w), 621(w), 596(w).

2.4. X-ray crystallography

A suitable single crystal was carefully selected under a polarizing microscope. Single-crystal data were collected with a Bruker APEX2 Smart CCD diffractometer using Mo-K α (λ = 0.71073 Å) radiation. The program SAINT [18] was used for integration of the diffraction profiles and an empirical absorption correction was applied using the SADABS program [19]. The structures of **1–6** were solved by the direct methods and refined on F² by the full-matrix least squares, using the SHELXTL [20]. Metal atoms in each complex were located from the E-maps. All non-hydrogen atoms were refined with anisotropic displacement parameters. Most of hydrogen atoms were assigned to calculate positions and refined with fixed geometry with respect to their carrier atoms, and the water hydrogen atoms were located from difference maps. Crystallographic datas and experimental details for structure determination are presented in Table 1. Selected bond lengths and bond angles are listed in Table S1 of Supplementary 1.

3. Results and discussion

3.1. Syntheses and general characterization

A series of experiments were carried out in order to get the suitable reaction temperature and solvents for single crystal growth. Single crystals of **1** and **5** were obtained through hydro-thermal method with different solvents. Complexes **2** and **3** were obtained in the same organic solvent by interface diffusion process at room temperature. Complexes **4** and **6** were obtained in different mixed solvents by refluxing.

The infrared spectra of **1**–**6** exhibit characteristic absorptions for corresponding ligands with a slight shift due to coordination. In the IR spectra of **1** and **2**, the broad band observed at 3389 cm⁻¹ is due to the stretching vibrations of coordinated O–H. The characteristic bands of the free perchlorate ion appear at 1097 cm⁻¹ and 620 cm⁻¹ in **1**. The absorption bands at about 1382 cm⁻¹ and 1384 cm⁻¹ indicate the existence of the NO₃ anions in **4** and **5**. The bands at 1054 cm⁻¹ and 970 cm⁻¹ in **6** can be assigned to the solvent DMF molecule, while that at 1743 cm⁻¹ may be ascribed to the existence of the HCOO⁻ anion in **4**. Ligands **L**¹, **L**² and complexes **1**–**6** all exhibit absorptions corresponding to the framework vibrations of aromatic rings at about 1600–1450 cm⁻¹.

3.2. Description of the crystal structure

3.2.1. Structure of $[Ni(L^1)_4(OH)_2]$ (1) and $[Cu(L^1)_4(OH)_2]$ (2)

Structural analyses were carried out and similar cell parameters of complexes **1** and **2** (Table 1) indicate that they have similar structures, just with different metal ions in the molecular structures. Therefore, we just describe later the structure of complex **1** in detail.

Complex 1 reveals a mononuclear structure belonging to



Fig. 1. View of (a) the coordination environment of M(II) (Ni and Cu) ions in **1** and **2** (hydrogen atoms have been omitted for clarity); (b) The 2D supramolecular sheet formed via hydrogen bonding interactions in **2**.

orthorhombic space group *Aba*² and the selected bond distances and angles are listed in Table S1 of Supplementary 1. The complex **1** contains one Ni(II) ion, four **L**¹ ligands and two OH⁻ anions. As shown in Fig. 1(a), the Ni(II) center shows a distorted octahedral coordination geometry and is coordinated by four nitrogen atoms from four distinct **L**¹ ligands and two oxygen atoms from two OH⁻ anions. The best equatorial plane is formed by four nitrogen atoms (N1, N4, N1^{#1} and N4^{#1}, symmetry code: #1 -x,-y+1, z), and the axial positions are occupied by O1 and O1^{#1} (symmetry code: #1 -x,-y+1). The Ni–N distances are 2.089(7) and 2.110(7) Å, respectively. And the Ni–O lengths are 2.084(5) Å, which are in the normal range of those observed in nickel complexes.

Complex **2** belongs to the monoclinic space group *Pc*. There are four **L**¹ ligands, one Cu(II) ion, and two OH⁻ anions in complex **2**. The **L**¹ acts as a monodentate ligand in complexes **1** and **2**, and two-coordinated OH⁻ anions not only participated in coordination but also were used to balance the charge. Furthermore, the mononuclear $[Cu(L^1)_4(OH)_2]$ units are connected into 2D layer by hydrogen bonding interaction between coordinated OH⁻ anions and N-atoms from imidazole with O···N separations being 2.806 Å. In the crystal packing diagram, the 2D layers pack together via O–H···N hydrogen bonds (show in Fig. 1(b)). The related hydrogenbonding geometries are given in Table S2 of Supplementary 1. In such a 2D supramolecular framework, the dimensions of intralayer incipient voids are 13.874(71) × 13.8820(73) Å, as measured by through-space Cu–Cu distances.



Fig. 2. View of (a) the coordination environment of Cu(II) atom in complex **3**; (b) the 2D sheet of **3**; (c) the three-dimensional supramolecular framework of **3** along the *c* axis (hydrogen atoms have been omitted for clarity); (d) the 6-connected net topology with the Schläfli symbol of $(4^{12} \cdot 6^3)$.

3.2.2. Structure of $[Cu(L^1)_2(SiF_6)]_n$ (3)

Single crystal X-ray diffraction analysis reveals that complex **3** shows a 3D framework structure that crystallizes in monoclinic space group *P*21/*c*. As depicted in Fig. 2(a), the crystallographically independent Cu(II) with distorted octahedral coordination geometry is six-coordinated by four nitrogen atoms from four different L¹ ligands, and two fluorine atoms from different SiF₆²⁻ anions. The Cu–N lengths are in the range of 1.981(4) – 1.998(3) Å and Cu–F lengths are 2.426(3) – 2.518(3) Å. The Cu–N and Cu–F bond distances are in the normal ranges.

The dihedral angle between two imidazole rings in the same L^1 is 5.78°. As shown in Fig. 2(b), the bridging L^1 ligands link neighboring Cu(II) to form a ladder-like 2D sheet. Furthermore, the SiF₆²⁻ anions further link the neutral layers to form a 3D framework, which contains a larger channel, and the size is about 11.2807 × 12.5774 Å² (Fig. 2(c)). The Cu···Cu distance separated by



Fig. 3. View of (a) the coordination environment of the Cu(II) center in 4; (b) the one dimensional chain of 4 (hydrogen atoms have been omitted for clarity).

the SiF₆²⁻ anions is 6.3320(41) Å, and the distances by **L**¹ are 11.2807(70) Å and 12.5774(75) Å. From the viewpoint of structural topology, the Cu(II) atoms can be as six-connected nodes with all crystallographically independent **L**¹ ligands and SiF₆²⁻ anions as linkers. Therefore, the whole structure of complex **3** can be defined as a 6-connected net topology with the Schläfli symbol of (4¹²·6³) (Fig. 2(d)).

3.2.3. Structure of $\{[Cu(L^2)(HCOO)_2] \cdot H_2 \cup CH_3 \cup H_n(4)\}$

Complex 4 exhibits 1D ladder chain structure. Single-crystal structure analysis reveals that 4 crystallized in the triclinic system space group P-1. The complex 4 which contains one crystallographically independent Cu(II) ions, two L^2 ligands, two coordinating HCOO⁻ anions, one CH₃OH molecule and one H₂O molecule. As shown in Fig. 3(a), Cu(II) center adopts trigonal bipyramidal geometry with [CuN2O3] coordination environment, in which the value of τ parameter is 0.02. The Cu(II) center is five coordinated by three O atoms from three HCOO⁻ anions [Cu-O1 = 2.3962(16) Å, $Cu-O1^{#2} = 1.9693(16)$ Å and Cu-O3 = 1.9451(17) Å, symmetry code: #2 - x + 1 - y - z + 2 and two nitrogen atoms from two different ligands L^{2} [Cu(1)–N(4) = 2.0060(17) Å and Cu(1)–N(5) = 2.0155(17)]. The equatorial plane is occupied by three oxygen atoms (O1, O1^{#2}, O3), N4 and N5 atoms are located at two sides of the plane. In complex 4, two Cu(II) are connected through two HCOO⁻ anions to form dinuclear structure unit, which is arranged into a 1D ladder-like structure by μ_2 -L² spacers (Fig. 3(b)). Complex 4 exhibits a pair of oxygen atoms bridging mode with the shorter Cu--Cu separation of 3.4530(3) Å. The Cu···Cu separations across L^2 (for 4) are 13.0878(5) Å. The two benzimidazole rings of L^2 moieties are not coplanar with the dihedral angles between the two planar benzimidazole rings of 7.34° for 4.

3.2.4. Structure of $[Ni(L^2)_2(NO_3)_2]_n$ (5)

When the reaction of L^2 with Ni(NO₃)₂·6H₂O was carried out, complex **5** was obtained. Complex **5** crystallizes in the triclinic

space group P-1. As shown in Fig. 4(b), complex 5 displays 1D zigzag chain structure. Complex 5 consists of one Ni(II) ion, two L² ligands and two coordinated NO_3^- anions (Fig. 4(a)). Each Ni(II) ion adopts a distorted octahedral coordination geometry [NiN₃O₃], in which the value of τ parameter is 0.13. The equatorial plane is occupied by three O atoms from two NO_3^- anions and one coordinated N atom from one ligand L^2 , as well as two axial N atoms from two individual L² ligands. In complex 5, adjacent Ni(II) ions are bridged by ligands in *cis*-trans conformation to form a zigzag chain. In 5, one ligand L^2 adopt bidentate and the other adopt monodentate coordination modes. A part of L^2 ligands display a bidentate mode linking neighboring two Ni(II) ions with the Ni…Ni distance of 13.1359 Å and 13.2523 Å, respectively. The angle of Ni…Ni…Ni through the ligand L^2 is 52.913(7)°. The Ni–N bond lengths [Ni(1) -N(7) = 2.058(6) Å, Ni(1)-N(6) = 2.122(6) Å, Ni(1)-N(9) = Ni(1)-N(6) = 2.122(6) Å]. The Ni–O bond lengths [Ni(1) -O(1) = 2.172(6) Å, Ni(1)–O(2) = 2.109(6) Å, Ni(1) -O(4) = 2.014(5) Å]. The dihedral angle between two benzimidazole rings in the same L^2 is 8.97°. The NO₃ anions not only participate in coordination but also are used as counter anions.

3.2.5. Structure of $\{[Zn(L^2)Cl_2] \cdot DMF\}_n$ (6)

The one-dimensional zigzag chain of **6** is depicted in Fig. 5(b). The complex crystallizes in the monoclinic space group, P21/n. In complex **6**, there is one Zn(II) atom, two **L**² ligands, two Cl⁻ anions, and one DMF molecule. As shown in Fig. 5(a), each Zn(II) atom is four-coordinated by two nitrogen atoms [N(1)] $-Zn(1)^{\#1} = 2.026(4)$ Å, N(6)-Zn(1) = 2.031(5) Å, symmetry code: #1 -x-1/2,y-1/2,-z+1/2] from distinct ligands and two Cl^{-} anions [Zn(1)-Cl(1) = 2.233(2) Å, Zn(1)-Cl(2) = 2.214(2) Å], forming aslightly distorted [ZnN₂Cl₂] tetrahedral geometry, in which the value of τ parameter is 0.19. The distance between two Zn(II) atoms separated by the bridging ligands along the chain is 12.8317(41) Å. The ligands are almost coplanar in the complex, thus resulting in weaving gulfs as depicted in Fig. 5(c). Such gulfs are important



Fig. 4. View of (a) the coordination environment of the Ni(II) center in **5**; (b) the 1D zigzag chain of **5** (hydrogen atoms have been omitted for clarity).

because potential cavity could be formed depending on arrangement of the 1D zig-zag chains in the crystal lattice. The size of the gulfs can be estimated by its opening width and triangle depth. The opening width is defined as d_{width} (18.7890) and the triangle depth as d_{depth} (12.8317) by metal-metal distances.

3.3. Powder X-ray diffraction (PXRD)

The bulk materials of **1–6** were verified via a comparison of the X-ray powder diffraction (PXRD). The PXRD of **1–6** show that the diffraction patterns are most the same as the computer-simulated patterns of the corresponding complexes (Fig. S1 of Supplementary 2). The peak positions of the experimental and simulated PXRD are in good consistency with each other. The result suggests that the crystal structures are truly representative of the bulk crystal materials. Although the experimental patterns have a few unindexed diffraction lines and some are slightly broadened in comparison with those simulated from the single crystal materials and the as-grown crystals were homogeneous for **1–6**.

3.4. Luminescent properties

Luminescent Zn(II) complexes possessing closed d¹⁰ transition



Fig. 5. View of (a) the coordination environment of the Zn(II) center in **6**; (b) the 1D zigzag chain of **6**; (c) the zigzag chain structures in space-filling mode showing weaving gulfs in complex (hydrogen atoms have been omitted for clarity).

metal are superior potential candidates as valuable luminescent materials [21]. We investigated the solid state luminescence of ligand L^2 along with complex 6 at room temperature. Upon excitation with 370 nm light, the ligand L^2 displays fluorescence spectra with an emission maxima at 470 nm. which could be attributed to intraligand $\pi - \pi^*$ emission. However, complex **6**exhibites an intense blue luminescent property with emission maxima at 480 nm ($\lambda_{ex} = 370$ nm). Compared with that of the free ligand, complexes in the solid state have a slight blue shift, which can be generally ascribed to the ligand-centered nature of the emission [22]. The emission bands for **6** are neither ligand-to-metal charge transfer (LMCT) nor metal-to-ligand charge transfer (MLCT) in nature, due to the fact that the d^{10} Zn(II) is very difficult to oxidize and reduce [23]. Fig. S2 of Supplementary 2 illustrares fluorescence enhancement of complexes 6 compared to free ligand L². This could be attributed to the d¹⁰ metal Zn(II) that does not facilitate any lowenergy metal-centered or charge-separated excited states in to the molecule. Thus, the energy transfer or electron transfer process cannot occur easily [24].

3.5. Luminescence lifetimes

The luminescence properties of **6** were probed further using time-resolved experiments. The luminescence decay curve of complex **6** was obtained at room temperature. The decay curve is well fitted into a triple exponential function: $I = I_0 + A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + A_3 \exp(-t/\tau_3)$, $\tau = (A_1\tau_1^2 + A_2\tau_2^2 + A_3\tau_3^2)/(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)$ where *I* and I_0 are the luminescent intensities

at time t = t and t = 0, respectively, whereas τ , τ_1 , τ_2 and τ_3 are defined as the luminescent lifetimes (Fig. S3 of Supplementary 2). Emission lifetime data determined from TCSPC measurements for crystal samples are summarized in Table S3 of Supplementary 1. The following luminescence lifetimes result from the optimum matching of the experimental luminescence intensities to the above equation ($\tau_1 = 5.02$ ns, $\tau_2 = 96.58$ ns, $\tau_3 = 0.66$ ns and $\tau = 20.03$ ns), which indicates that complex **6** may be an excellent candidate for potential light-sensitive materias.

3.6. UV-visible (UV-vis) diffuse reflection spectrum

One of major factors that influence the rate of the photocatalysis degradation process of the organic dye was the optical band gap [25]. Diffuse reflectance spectroscopy (Fig. S4 of Supplementary 2) was applied to judge the energy band gap of the complex. The solid-state complex **6** with a band gap of 3.49 eV manifests that this sample can be activated by blue light and acted as an underlying semiconductive material [26]. Strikingly, the charge-transfer transition of **6** occurs in the UV region showing a higher photocatalytic activity with UV-light. Therefore, it might represent the well performance in photocatalytic degradation of the organic dye in water because of the small band gap.

4. Conclusion

In summary, we have synthesized and characterized six new complexes based on two flexible bridging bis(imidazole/ benzimidazole-1-vl)pvridazine ligands through varving measures. Single-crystal analyses reveal that these complexes exhibit rich structural variation including 0D, 1D and 3D architectures. Complexes 1 and 2 have a similar structure except different metal ions. Complex 3 has a three-dimensional (3D) structure with the Schläfli symbol of $(4^{12} \cdot 6^3)$. Complex **4** exhibits 1D ladder-like structure. Complexes **5** and **6** are 1D zigzag chains with different geometrical configurations of metal ions. In addition, the X-ray powder diffraction (PXRD) investigation of the complexes 1-6 demonstrates that they have high phase purity. The luminescence experiment illustrates that L^2 and complex **6** could be emission blue luminescence. Emission lifetime experiment indicates that complex 6 may be an excellent candidate for potential light-sensitvie materias. The UV-vis diffuse reflection of 6 shows a higher photocatalytic activity with UV-light.

Acknowledgements

This work was financially supported by the National Natural Science Foundation of China (No. 21361026).

Appendix A. Supplementary data

CCDC 1436587-1436588, 1484855-1484857 and 1484859 contains the supplementary crystallographic data for complexes $1 \cdot [Ni(L^1)_4(OH)_2]$, $2 \cdot [Cu(L^1)_4(OH)_2]$, $3 \cdot [Cu(L^1)_2(SiF_6)]_n$, $4 \cdot [Cu(L^2)(HCOO)_2] \cdot H_2O \cdot CH_3OH]_n$, $5 \cdot [Ni(L^2)_2(NO_3)_2]_n$ and $6 \cdot [[Zn(L^2)Cl_2] \cdot DMF]_n$ respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.molstruc.2016.08.051.

References

- [1] (a) F. Sun, Z. Yin, Q.Q. Wang, D. Sun, M.H. Zeng, M. Kurmoo, Angew. Chem. Int. Ed. 52 (2013) 4538;
 (b) Y.J. Mu, J.H. Fu, Y.J. Song, Z. Li, H.W. Hou, Y.T. Fan, Cryst. Growth Des. 11
 - (c) Y.X. Guo, X. Feng, T.Y. Han, S. Wang, Z.G. Lin, Y.P. Dong, B. Wang, J. Am.

(d) Y.L. Wang, J.H. Fu, J.J. Wei, X. Xu, X.F. Li, Q.Y. Liu, Cryst. Growth Des. 12

(2012) 4663;

(e) Z.B. Han, R.Y. Lu, Y.F. Liang, Y.L. Zhou, Q. Chen, M.H. Zeng, Inorg. Chem. 51 (2012) 674;

(f) T. Kundu, S. Mitra, P. Patra, A. Goswami, D. Díaz Díaz, R. Banerjee, Chem. Eur. J. 20 (2014) 10514.

[2] (a) W.J. Zhuang, X.J. Zheng, L.L. Li, D.Z. Liao, H. Ma, L.P. Jin, CrystEngComm 9 (2007) 653;

(b) Z.P. Deng, L.H. Huo, H.L. Qi, L.N. Zhu, H. Zhao, S. Gao, CrystEngComm 13 (2011) 4218;

(c) X.J. Li, Z.J. Yu, T.N. Guan, X.X. Li, G.C. Ma, X.F. Guo, Cryst. Growth Des. 15 (2015) 278;

(d) L. Liu, C. Huang, L. Zhang, R. Ding, X.N. Xue, H.W. Hou, Y.T. Fan, Cryst. Growth Des. 15 (2015) 2712;

(e) S.J. Liu, J.P. Zhao, W.C. Song, S.D. Han, Z.Y. Liu, X.H. Bu, Inorg. Chem. 52 (2013) 2103.

- [3] (a) Y. Wang, P. Cheng, Y. Song, D.Z. Liao, S.P. Yan, Chemistry 13 (2007) 8131;
 (b) L. Chen, G.J. Xu, K.Z. Shao, Y.H. Zhao, G.S. Yang, Y.Q. Lan, X.L. Wang, H.B. Xu, Z.M. Su, CrystEngComm 12 (2010) 2157.
- [4] (a) I. Kuźniarska-Biernacka, M.M.M. Raposo, R. Batista, P. Parpot, K. Biernacki, A.L. Magalhães, A.M. Fonseca, I.C. Neves, Microporous Mesoporous Mater. 227 (2016) 272;
 - (b) J.G. Deng, Y. Gou, W. Chen, X. Fu, H. Deng, Biorgan. Med. Chem. 24 (2016) 2190.
- [5] (a) H. Chen, M. Yu, G.X. Liu, Synth. React. Inorg. M. 46 (2016) 1455;
 (b) H. Chen, X.Q. Ma, Y.Y. Lv, L. Jia, J. Xu, Y. Wang, Z.J. Ge, J. Mol. Struct. 1109 (2015) 146.

 [6] (a) J.J. Huang, X. Zhang, Q.S. Huo, J.H. Yu, J.Q. Xu, Inorg. Chem. 3 (2016) 406;
 (b) I.M.L. Rosa, M.C.S. Costa, B.S. Vitto, L. Amorim, C.C. Correa, C.B. Pinheiro, A.C. Doriguetto, Cryst. Growth Des. 16 (2016) 1606;
 (c) D. M. H. Karaki, M. W.Y. F. Margar, M. Yang, Chem. 55

(c) R. An, H. Zhao, H.M. Hu, X.F. Wang, M.L. Yang, G.L. Xue, Inorg. Chem. 55 (2016) 871.

[7] (a) T. Huang, Y.L. Wang, Q. Yin, B. Karadeniz, H.F. Li, J. Lü, R. Cao, CrystEngComm 18 (2016) 2742;
(b) L.M. Fan, W.L. Fan, B. Li, X.Z. Liu, X. Zhao, X.T. Zhang, CrystEngComm 17 (2015) 4669;
(c) X.Y. Li, X.X. Liu, K.F. Yue, Y.P. Wu, T. He, N. Yan, Y.Y. Wang, RSC Adv. 5

(c) X.Y. LI, X.X. LIU, K.F. YUE, Y.P. WU, T. HE, N. Yali, Y.Y. Walig, KSC AGV. 5 (2015) 81689;

- (d) H.Q. Huang, X.Y. Cheng, T. Zhang, R.B. Huang, Inorg. Chem. Commun. 68 (2016) 21.
- [8] (a) M. Roy, S. Sengupta, S. Bala, S. Bhattacharya, R. Mondal, Cryst. Growth Des. 16 (2016) 3170;
- (b) H.L. Sung, C.H. Lee, J.E. Wu, Y.S. Wen, T.W. Tseng, Z.J. Hu, T.M. Her, Polyhedron 115 (2016) 54.
- [9] (a) S. Mukherjee, P.S. Mukherjee, Acc. Chem. Res. 11 (2013) 2556;
- (b) D. Skomski, C.D. Tempas, K.A. Smith, S.L. Tait, J. Am. Chem. Soc. 136 (2014) 9862.
- (a) J. Fan, G.T. Yee, G.B. Wang, B.E. Hanson, Inorg. Chem. 45 (2006) 599;
 (b) J. Fan, C. Slebodnick, Ross Angel, B.E. Hanson, Inorg. Chem. 44 (2005) 2719;
 (c) J. Liang, Y. Wang, J.H. Yu, Y. Li, R.R. Xu, Chem. Commun. 7 (2003) 882.
- [11] (a) N.N. Adarsh, F. Novio, D. Ruiz-Molina, Dalton Trans. (2016), http:// dx.doi.org/10.1039/C6DT01157H;
 (b) H.J. Cheng, X.Y. Tang, R.X. Yuan, J.P. Lang, CrystEngComm (2016), http://

 (b) H.J. Cheng, X.Y. Tang, R.X. Yuan, J.P. Lang, CrystEngComm (2016), http:// dx.doi.org/10.1039/C6CE00768F.
 [12] (a) J. Fan, G.T. Yee, G.B. Wang, B.E. Hanson, Inorg. Chem. 45 (2) (2006) 599;

[12] (a) J. Fan, G.I. Yee, G.B. Wang, B.E. Hanson, Inorg. Chem. 45 (2) (2006) 599;
 (b) L.M. Fan, X.T. Zhang, Z. Sun, W. Zhang, Y.S. Ding, W.L. Fan, L.M. Sun, X. Zhao, H. Lei, Cryst. Growth Des. 13 (2013) 2462.

[13] (a) Z.X. Li, T.L. Hu, H. Ma, Y.F. Zeng, C.J. Li, M.L. Tong, X.H. Bu, Cryst. Growth Des. 10 (2010) 1138;
(b) Z.X. Li, Y. Xu, Y. Zuo, L. Li, Q.H. Pan, T.L. Hu, X.H. Bu, Cryst. Growth Des. 9 (2009) 3904;
(c) Z.X. Li, H. Ma, S.L. Chen, Z.D. Pan, Y.F. Zeng, X.L. Wang, X.H. Bu, Dalton Trans. 40 (2011) 31.

[14] (a) Q.X. Liu, Q. Wei, X.J. Zhao, H. Wang, S.J. Li, X.G. Wang, Dalton Trans. 42 (2013) 5902;
 (b) W. Zhou, X.R. Meng, Y.N. Ding, W.Q. Li, H.W. Hou, Y.L. Song, Y.T. Fan, J. Mol.

Struct. 937 (2009) 100; (c) X.F. Guo, Z.F. Li, C. Yue, G. Li, Y.C. Gao, Y. Zhu, Polyhedron 29 (2010) 384; (d) X.L. Wang, J. Li, A.X. Tian, H.Y. Lin, G.C. Liu, H.L. Hu, Inorg. Chem. Commun. 14 (2011) 103.

[15] (a) Q. Hua, Y. Zhao, G.C. Xu, M.S. Chen, Z. Su, K. Cai, W.Y. Sun, Cryst. Growth Des. 10 (2010) 2553;

(b) Q. Hua, Z. Su, Y. Zhao, T.-a. Okamura, G.C. Xu, W.Y. Sun, N. Ueyama, Inorg. Chim. Acta 363 (2010) 3550.

[16] (a) J. Fan, B.E. Hanson, Inorg. Chem. 44 (2005) 6998;
 (b) C.Y. Li, C.S. Liu, J.R. Li, X.H. Bu, Cryst. Growth Des. 7 (2007) 286.

- [17] J.M. Pan, Q. Wei, J.X. Ju, B. Liu, S.W. Jin, Z.H. Lin, D.Q. Wang, J. Coord. Chem. 67 (2014) 3578.
- [18] A.X.S. Bruker, SAINT Software Reference Manual, 1998. Madison, WI.
- [19] G.M. Sheldrick, SADABS, Siemens Area Detestor Absorption Correction Program, University of Gottingen, Gottingen, Germany, 1994, p. 22. [20] G.M. Sheldrick, SHELXTL NT Version 5.1. Program for Solution and Refinement
- of Crystal Structures, University of Göttingen, Germany, 1997.
- [21] (a) R. Yi, Huang, H. Jiang, C.H. Zhu, H. Xu, RSC Adv. 6 (2016) 3341;
 (b) G. Cheng, G.K.M. So, W.P. To, Y. Chen, C.C. Kwok, C.S. Ma, X.G. Guan, X.Y. Chang, W.M. Kwok, C.M. Che, Chem. Sci. 6 (2015) 4623;
- (c) R. Gao, Y.B. Zhao, X.G. Yang, D.P. Yan, RSC Adv. 5 (2015) 56470.
 [22] (a) Y.W. Li, W.L. Chen, Y.H. Wang, Y.G. Li, E.B. Wang, J. Solid State Chem. 182 (2009) 736;
 - (b) X.L. Feng, W.P. Chen, B.L. Xiang, Synth. React. Inorg. M. 46 (2015) 1302.
- [23] (a) Q.Q. Li, W.Q. Zhang, C.Y. Ren, Y.P. Fan, J.L. Li, P. Liu, Y.Y. Wang, CrystEngComm 18 (2016) 3358; (b) M.S. Wang, S.P. Guo, Y. Li, L.Z. Cai, J.P. Zou, G. Xu, W.W. Zhou, F.K. Zheng, G.C. Guo, J. Am. Chem. Soc. 131 (2009) 13572.
- [24] B. Mohapatra, V. Venkatesh, S. Verma, Cryst. Growth Des. 14 (2014) 5042.
 [25] (a) J.M. Hao, B.Y. Yu, K.V. Heckeb, G.H. Cui, CrystEngComm 17 (2015) 2279; (b) LL. Wen, J.B. Zhao, K.L. LV, Y.H. Wu, K.J. Deng, X.K. Leng, D.F. Li, Cryst. Growth Des. 12 (2012) 1603; (c) S. Mosleh, M.R. Rahimi, M. Ghaedi, K. Dashtian, S. Hajati, RSC Adv. 6 (2016)
- 17204. [26] (a) L. Liu, J. Ding, C. Huang, M. Li, H.W. Hou, Y.T. Fan, Cryst. Growth Des. 14
- (2014) 3035; (b) J. Guo, J.F. Ma, B. Liu, W.Q. Kan, J. Yang, Cryst. Growth Des. 11 (2011) 3609.