

Assembly of Binuclear, Tetranuclear, and Multinuclear Complexes from Pincer-Like Mononuclear Metallotectons: Structural Diversity Dependent on Precursors

Sheng-Run Zheng,^{†,§} Mei Pan,^{*,†,‡} Kai Wu,[†] Ling Chen,[†] Ji-Jun Jiang,^{*,†} Da-Wei Wang,[†] Jian-Ying Shi,[†] and Cheng-Yong Su[†]

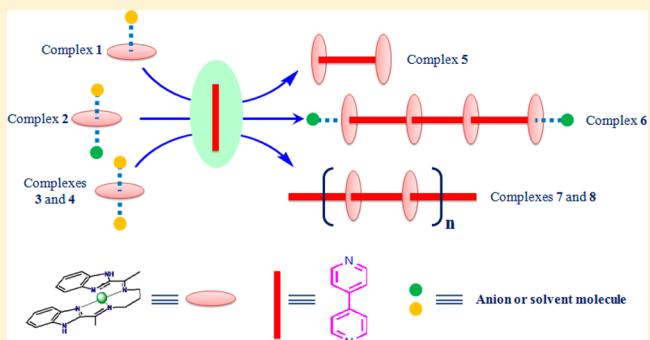
[†] MOE Laboratory of Bioinorganic and Synthetic Chemistry, Lehn Institute of Functional Materials, State Key Laboratory of Optoelectronic Materials and Technologies, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

[‡] State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, CAS, Fuzhou, 350002, China

[§] School of Chemistry and Environment, South China Normal University, Guangzhou, 510006, China

Supporting Information

ABSTRACT: Reactions of Cu(II), Cd(II), and Ni(II) with a new tetradeятate ligand N^1,N^3 -bis(1-(1H-benzimidazol-2-yl)-ethylidene)propane-1,3-diamine (H_2bbepd) afforded four mononuclear pincer-like complexes of $[Cu(H_2bbepd)(ClO_4)] \cdot CH_3OH \cdot ClO_4$ (**1**), $[Cd(H_2bbepd)(CH_3OH)(ClO_4)] \cdot CH_3OH \cdot ClO_4$ (**2**), $[Ni(H_2bbepd)(H_2O)_2] \cdot 2ClO_4$ (**3**), and $[Ni(H_2bbepd)(NO_3)_2]$ (**4**), respectively. The labile small coordinated components (anions or solvent molecules) on the apical coordination site of metal ions in complexes **1–4** display three different modes, which can be substituted by 4,4'-bipyridine (bpy) to obtain four new multinuclear complexes of $[Cu_2(H_2bbepd)_2(bpy)]_2 \cdot 2ClO_4$ (**5**), $[Cd_4(H_2bbepd)_4(bpy)_3 \cdot (ClO_4)_2] \cdot 6ClO_4 \cdot (bpy) \cdot 2CH_3OH \cdot 6H_2O$ (**6**), $\{[Ni(H_2bbepd) \cdot (bpy)] \cdot 2ClO_4 \cdot CH_3OH\}_n$ (**7**), and $\{[Ni(H_2bbepd) \cdot (bpy)] \cdot 2NO_3 \cdot CH_3OH \cdot H_2O\}_n$ (**8**), respectively. Complex **5** is a binuclear dumbbell-like molecule, complex **6** is a rare example of discrete linear tetranuclear molecule, while complexes **7** and **8** are one-dimensional chains formed by an alternate arrangement of bpy molecules and mononuclear subunits. The differences in complexes **5–8** are largely dependent on the structure of the mononuclear precursors of complexes **1–4**. All eight complexes are assembled into higher dimensional supramolecular frameworks by diverse noncovalent interactions including unusual anion- π interactions between perchlorate and five-membered benzimidazole rings.



INTRODUCTION

Small metal-organic coordination molecular units with special structures are important in crystal engineering mainly in two facets: (i) they act as metallotectons to construct diverse frameworks via noncovalent contacts such as hydrogen bond, $\pi \cdots \pi$ interaction, $CH \cdots \pi$ interaction, cation- π interaction, and so on;^{1–12} (ii) they act as a precursor to construct more complicated (higher dimensional or containing more nuclear) supramolecular assemblies via a substitution reaction taking on the labile coordination sites of the metallotectons, which can be seen as a stepwise bottom-up strategy.^{13–21} Recently, coordination compounds based on this strategy are becoming interesting because the conditions for the assembly from structure-known subunits are more unambiguous than one-step synthesis, and thus it may lead to a more controllable system.²⁰ Obviously, the final assembly structures are largely dependent on the inferences of the precursors, whose structures may provide an important message for predicting the possible productions. Therefore, it is important to systematically

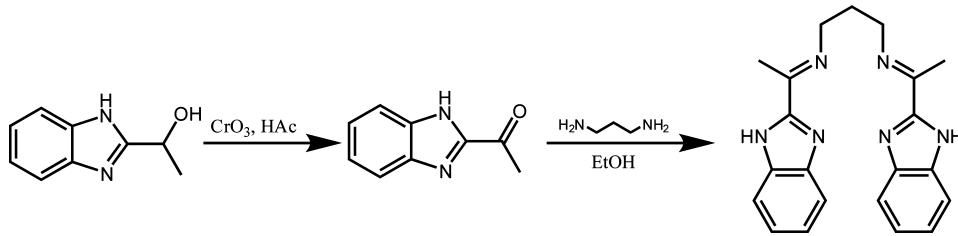
illustrate the relationship between the precursors and the products.

A stable mononuclear pincer-like complex can be constructed easily from tetradeятate ligands with planar four-chelated coordination sites. When the equatorial plane of tetragonal pyramid or octahedral coordination sphere around the metal center is occupied by such tetradeятate ligands, the resulting mononuclear complex will leave one or two labile coordination site(s) in the apex position which is suitable for substitution reaction, thus becoming a building block that can act as a precursor to be assembled into coordination polymers in higher dimension or more complicated assemblies.^{22–33} Obviously, the competition coordination of anions, solvent molecules, and secondary ligand will tune up the final architectures. On the basis of such considerations, herein, we chose a tetradeyatate

Received: September 2, 2014

Revised: December 7, 2014

Published: January 8, 2015

Scheme 1. Synthetic Route of H₂bbepd

double Schiff base ligand containing a benzimidazolyl group, namely, *N*¹,*N*³-bis(1-(1*H*-benzimidazol-2-yl)ethylidene)-propane-1,3-diamine (H₂bbepd), as a ligand to synthesize four mononuclear complexes based on Cu(II), Cd(II), and Ni(II), and then the mononuclear complexes were used as precursors to generate binuclear, tetranuclear, and one-dimensional (1D) linear infinite complexes by addition of 4,4'-bipyridine (bpy). Interestingly, the labile small coordinated components (anions or solvent molecules) in the mononuclear complexes show three different modes depending on central metal ions. This further determines the structures of the multinuclear complexes which can be seen as the conglomerates of mononuclear precursors by the linkage of bpy at the original sites of small coordinated components in the mononuclear counterparts. In addition, anion- π interactions^{34–53} between perchlorate anion and five-membered benzimidazole ring are found in the assembled complexes, which is relatively less discussed, since most of the reported cases are involved with anions and electron-deficient six-membered aromatic rings such as hexafluorobenzene, *s*-triazine, *s*-tetrazine, and so on.^{52,53}

EXPERIMENTAL SECTION

Materials and Methods. All chemicals were of reagent grade obtained from commercial sources and used without further purification. The C, H, N elemental analyses were performed on a PerkinElmer 240 elemental analyzer. IR spectra were recorded on a Nicolet/Nexus-670 FT-IR spectrometer with KBr pellets in the 4000–400 cm⁻¹ region. The X-ray powder diffraction was recorded on a Bruker D8 Advance diffractometer at 40 kV, 40 mA with a Cu-target tube and a graphite monochromator.

Synthesis of *N*¹,*N*³-Bis(1-(1*H*-benzimidazol-2-yl)ethylidene)-propane-1,3-diamine (H₂bbepd). The ligand H₂bbepd was initiated by the precursor of 2-acetylbenzimidazole⁵⁴ (3.20 g, 20.0 mmol) which was dissolved in EtOH (30 mL), and then propane-1,3-diamine (0.74 g, 10.0 mmol) was added, and the mixture was stirred and refluxed for 24 h. The yellow precipitation was filtered and washed with EtOH for several times. Yield: 80%. ESI⁺-MS: *m/z* = 359.1972. EA for C₂₁H₂₂N₆: Calcd (%): C, 70.37; H, 6.19; N, 23.45. Found (%): C, 69.57; H, 6.25; N 22.90. ¹H NMR (300 MHz, DMSO-*d*₆, 25 °C): δ (ppm): 7.66 (d, 2H, *J* = 8.7 Hz), 7.48 (d, 1H, *J* = 7.5 Hz), 7.21 (m, 4H), 3.73 (t, 4H, *J* = 6.9 Hz), 2.39 (s, 6H), 2.17 (m, 2H, *J* = 6.9 Hz). ¹³C NMR (101 MHz, DMSO) δ 159.45 (s), 152.22 (s), 136.92 (s), 124.05 (s), 114.28 (s), 49.94 (s), 31.90 (s), 14.85 (s). IR (KBr, cm⁻¹): 3168s, 2940m, 1637s, 1415s, 783s.

Synthesis of [Cu(H₂bbepd)(ClO₄)₂]·CH₃OH·ClO₄ (1). A solution of Cu(ClO₄)₂·6H₂O (37.1 mg, 0.1 mmol) and H₂bbepd (35.8 mg, 0.1 mmol) in MeOH (5 mL) was stirred for 10 min and filtered out. The clear filtrate was left in a test tube, and slow evaporation of the Et₂O resulted in precipitation of blue crystals. Yield: 70%. Anal. Calc. for C₂₂H₂₆Cl₂CuN₆O₉: C, 40.47; H, 4.01; N, 12.87%; Found: C, 40.20; H, 4.12; N, 12.63%. IR (KBr, cm⁻¹): 3435m, 3055m, 1628w, 1144s, 1086s, 752m. Phase purity was verified by powder X-ray diffraction (XRD) (Figure S1, Supporting Information).

Synthesis of [Cd(H₂bbepd)(CH₃OH)(ClO₄)₂]·CH₃OH·ClO₄ (2). Complex 2 was obtained by a similar procedure as for 1 except for using Cd(ClO₄)₂·6H₂O (38.9 mg, 0.1 mmol) instead of Cu(ClO₄)₂·6H₂O. Yield: 50%. Anal. Calc. for C₂₃H₃₀CdCl₂N₆O₁₀: C, 37.64; H, 4.12; N, 11.45%. Found: C, 37.52; H, 4.20; N, 11.71%. IR (KBr, cm⁻¹): 3181m, 2928m, 1632m, 1145s, 1116s, 1089s, 747m. Phase purity was verified by powder XRD (Figure S2, Supporting Information).

Synthesis of [Ni(H₂bbepd)(H₂O)₂]·2ClO₄ (3). Complex 3 was obtained by a similar procedure as for 1 except for using Ni(ClO₄)₂·6H₂O (35.6 mg, 0.1 mmol) instead of Cu(ClO₄)₂·6H₂O. Yield: 65%. Anal. Calc. for C₂₁H₂₄Cl₂N₆NiO₉: C, 39.78; H, 3.82; N, 13.25%. Found: C, 39.64; H, 3.86; N, 13.00%. IR (KBr, cm⁻¹): 3181m, 2928m, 1632m, 1145s, 1116s, 1089s, 747m. Phase purity was verified by powder XRD (Figure S3, Supporting Information).

Synthesis of [Ni(H₂bbepd)(NO₃)₂] (4). A solution of Ni(NO₃)₂·6H₂O (29.1 mg, 0.1 mmol) and H₂bbepd (35.8 mg, 0.1 mmol) in MeOH (5 mL) was stirred for 10 min and filtered out. The clear filtrate was left at room temperature for several days resulting in green crystals. Yield: 65%. Anal. Calc. for C₂₁H₂₂N₈NiO₆: C, 46.61; H, 4.10; N, 20.71%; Found: C, 46.80; H, 4.35; N, 21.54%. IR (KBr, cm⁻¹): 3374s, 2940, 1633m, 1438s, 1293s, 802w. Phase purity was verified by powder XRD (Figure S4, Supporting Information).

Synthesis of [Cu₂(H₂bbepd)₂(bpy)]·4ClO₄ (5). A solution of Cu(ClO₄)₂·6H₂O (37.1 mg, 0.1 mmol) and H₂bbepd (35.8 mg, 0.1 mmol) in MeOH (5 mL) was stirred for 30 min, then bpy (15.6 mg, 0.1 mmol) was added to the solution and the precipitate was filtered out. The clear filtrate was left in a test tube, and slow evaporation of the Et₂O resulted in precipitation of green crystals. Yield: 75%. Anal. Calc. for C₅₂H₅₂Cl₂Cu₂N₁₄O₁₆: C, 44.68; H, 3.75; N, 14.03%; Found: C, 44.49; H, 4.02; N, 13.87%. IR (KBr, cm⁻¹): 3435m, 3055m, 1628w, 1144s, 1117s, 1086s, 752m. Phase purity was verified by powder XRD (Figure S5, Supporting Information).

Synthesis of [Cd₄(H₂bbepd)₄(bpy)]·6ClO₄·(bpy)·2CH₃OH·6H₂O (6). Complex 6 was obtained by a similar procedure as for 5 except for using Cd(ClO₄)₂·6H₂O instead of Cu(ClO₄)₂·6H₂O. Yield: 30%. IR (KBr, cm⁻¹): 3055m, 1601s, 1144s, 1117s, 1088s, 748m. Phase purity was verified by powder XRD (Figure S6, Supporting Information).

Synthesis of {[Ni(H₂bbepd)(bpy)]·2ClO₄·CH₃OH}_n (7). Complex 7 was obtained by a similar procedure as for 5 except for using Ni(ClO₄)₂·6H₂O instead of Cu(ClO₄)₂·6H₂O. Yield: 55%. Anal. Calc. for C₃₂H₃₄Cl₂N₈NiO₉: C, 47.79; H, 4.26; N, 13.93%; Found: C 48.09; H 4.22; N 14.26%. IR (KBr, cm⁻¹): 3055m, 1601s, 1144s, 1117s, 1088s, 748m. Phase purity was verified by powder XRD (Figure S7, Supporting Information).

Synthesis of {[Ni(H₂bbepd)(bpy)]·2NO₃·CH₃OH·H₂O}_n (8). Complex 8 was obtained by a similar procedure as for 5 except for using Ni(NO₃)₂·6H₂O instead of Cu(ClO₄)₂·6H₂O. Yield: 50%. IR (KBr, cm⁻¹): 3181m, 2928m, 1632m, 1145s, 1116s, 1089s, 747m. Phase purity was verified by powder XRD (Figure S8, Supporting Information).

Caution! Perchlorate metal salt and its complex in the presence of organic ligands are potentially explosive. Only a small amount of material should be used and handled with care.

X-ray Crystallography. The diffraction data were collected on an Oxford Gemini S Ultra diffractometer equipped with Mo-K α radiation (λ = 0.71073 Å) for complexes 2, 4–6, and 8 at 150 K by using φ and ω scans, a Bruker Smart 1000 CCD diffractometer for

Table 1. Crystallographic Data and Structure Refinement Summary for Complexes 1–8

complex	1	2	3	4
chemical formula	C ₂₂ H ₂₆ Cl ₂ CuN ₆ O ₉	C ₂₃ H ₃₀ CdCl ₂ N ₆ O ₁₀	C ₂₁ H ₂₆ Cl ₂ N ₆ NiO ₁₀	C ₂₁ H ₂₂ N ₈ NiO ₆
formula weight	652.93	733.83	652.09	541.18
space group	P $\bar{1}$	P $\bar{1}$	P $\bar{1}$	C ₂ /c
<i>a</i> /Å	9.9049(6)	9.1591(16)	20.955(14)	14.888(3)
<i>b</i> /Å	10.7803(8)	10.5151(13)	15.726(11)	11.648(2)
<i>c</i> /Å	13.9607(9)	15.692(3)	8.128(7)	14.253(3)
$\alpha/^\circ$	107.848(6)	81.424(13)	90	90
$\beta/^\circ$	101.550(5)	73.713(15)	97.420(15)	114.83(3)
$\gamma/^\circ$	104.173(6)	87.394(13)	90	90
<i>V</i> /Å ³	1313.14(15)	1434.4(4)	2656(3)	2243.1(8)
<i>Z</i>	2	2	4	4
<i>D/g cm</i> ⁻³	1.651	1.699	1.631	1.602
μ/mm^{-1}	1.099	1.013	0.998	0.923
<i>T/K</i>	150	150	293	150
<i>R/wR</i>	0.0570/0.1391	0.0408/0.0911	0.1096/0.2637	0.0347/0.1023
total/unique/ <i>R</i> _{int}	5625/2591/0.0660	4830/2842/0.0462	6719/2591/0.0896	2437/2137/0.0168
complex	5	6	7	8
chemical formula	C ₅₂ H ₅₂ Cl ₄ Cu ₂ N ₁₄ O ₁₆	C ₁₂₈ H ₁₄₀ Cd ₄ Cl ₈ N ₃₂ O ₄₀	C ₃₂ H ₃₄ Cl ₂ N ₈ NiO ₉	C ₃₂ H ₃₆ N ₁₀ NiO ₈
formula weight	1397.96	3475.90	804.28	761.43
space group	<i>Pbca</i>	P $\bar{1}$	P2(1)/ <i>n</i>	P2(1)/ <i>n</i>
<i>a</i> /Å	14.5503(5)	14.1870(10)	11.5631	12.0107(4)
<i>b</i> /Å	11.3288(3)	14.5672(9)	17.4706(6)	16.2421(8)
<i>c</i> /Å	34.7850(13)	19.9189(9)	17.6941(6)	17.5907(6)
$\alpha/^\circ$	90	111.146(5)	90	90
$\beta/^\circ$	90	96.060(5)	99.307(3)	98.536(4)
$\gamma/^\circ$	90	91.536(5)	90	90
<i>V</i> /Å ³	5733.9(3)	3808.5(4)	3527.4(2)	3393.6(2)
<i>Z</i>	4	1	4	4
<i>D/g cm</i> ⁻³	1.619	1.516	1.514	1.459
μ/mm^{-1}	1.011	0.777	0.767	0.638
<i>T/K</i>	150	150	293	150
<i>R/wR</i>	0.0840/0.2259	0.0762/0.2416	0.0558/0.1682	0.0860/0.2557
total/unique/ <i>R</i> _{int}	5604/4591/0.0427	14593/8986/0.0459	13536/6830/0.0234	6495/3845/0.0384

complexes **1** and **3** with graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å) at 150 and 293 K, respectively, and a Bruker FRAMBO diffractometer equipped with Mo–K α radiation for complex **7** at 293 K by using φ and ω scans, using program SMART,⁵⁵ and the data were processed by SAINT+.⁵⁶ Multiscan adsorption corrections were applied for all complexes. The structures were solved by the direct methods (SHELXS) and refined by the full matrix least-squares method against F_o^2 using the SHELXTL software.⁵⁷ The coordinates of the non-hydrogen atoms were refined anisotropically except solvent molecules in complex **6**. Most of hydrogen atoms were introduced in calculated positions and refined with fixed geometry with respect to their carrier atoms. The hydrogen atoms of the O atom of coordinated MeOH molecules in complex **2**, and the C atom of methylene group in complex **4** were located from electronic map and refined isotropically. One ClO₄⁻ anion in complex **2** is distributed over two positions and partial refinement was applied. H atoms of non-coordinating water molecules and solvent molecules in complex **6** are not included. The methylene group in complex **8** is also disordered over two positions. Partial refinement was applied and H atoms were not included. Experimental details of the X-ray structural analyses as well as the crystallographic data are provided in Table 1. Selected bond distances and angles are listed in Tables S1. CCDC reference numbers CCDC 1022226–1022231. For crystallographic data in CIF or other electronic format see DOI: xxxxxxxxx.

RESULTS AND DISCUSSION

Mononuclear Units and Their Dimensional Increase in Complexes 1–4. The mononuclear units in complexes 1–4

are shown in Figure 1, in which the four N atoms from the ligand occupy four equatorial coordination sites of the metal ions, while one or two axial site(s) are occupied by anion(s) or solvent molecule(s), forming either a tetragonal pyramid or octahedron coordination sphere. According to the number and type of labile coordination ligand(s) in the mononuclear units, the structure of mononuclear units can be classified as three types. Specifically, the coordination geometry of Cu(II) in complex **1** can be described as tetragonal pyramid, thus only leaving one labile coordination site that is occupied by a ClO₄⁻ anion (Figure 1, type I). In complex **2**, the Cd(II) ion adopts a distorted octahedral geometry, in which the two axial sites are coordinated by two different components, MeOH and ClO₄⁻, respectively (Figure 1, type II). While in complexes **3–4**, the two axial sites of the octahedral sphere around Ni(II) ion are coordinated by two same ligands, NO₃⁻ anions in **3** and H₂O in **4** (Figure 1, Type III). The differences in these four compounds may be due to both the coordination tendency of metal centers and the competing coordination between anions and solvent molecules. Furthermore, all the above anions or solvent molecules can be potentially substituted by other secondary ligands with stronger coordination abilities such as bpy. From this aspect, the basic structure of complex **1** can be regarded as a monodentate secondary building unit (SBU), while those of complexes **2–4** can be seen as potential heterobidentate or homobidentate SBUs, respectively. Because

Table 2. Selected Details of the Hydrogen Bonds in Complexes 1–8

	symmetry code	$d(D-H)/\text{\AA}$	$d(H\cdots A)/\text{\AA}$	$d(D\cdots A)/\text{\AA}$	$\angle D-H\cdots A/\text{ }^\circ$
1					
N(6)–H(6A)…O(6)	$-x + 2, -y + 1, -z + 1$	0.86	1.95	2.791(6)	164.0
N(2)–H(2B)…O(9)		0.86	1.81	2.671(5)	174.0
O(9)–H(9)…O(4)	$-x + 3, -y + 2, -z + 2$	0.82	1.98	2.792(5)	170.4
2					
O(5)–H(5B)…O(6)		0.93(5)	1.79(6)	2.708(6)	173(6)
N(6)–H(6A)…O(3)	$-x + 2, -y, -z$	0.86	2.06	2.904(5)	165.8
N(2)–H(2B)…O(10)	$x - 1, y + 1, z$	0.86	1.97	2.811(5)	166.8
O(10)–H(10)…O(9)		0.82	2.20	2.922(6)	147.2
3					
O(1W)–H(1)…O(2)	$-x, y, -z + 1/2$	0.85	2.19	2.988(18)	157.6
O(1W)–H(2)…O(3)		0.85	2.30	3.14(3)	166.9
N(2)–H(2B)…O(4)	$-x + 1/2, -y + 1/2, -z + 1$	0.86	2.12	2.968(13)	169.0
4					
N(1)–H(1A)…O(1)	$-x + 3/2, -y - 1/2, -z + 2$	0.86	1.95	2.798(3)	170.2
N(1)–H(1A)…N(4)	$-x + 3/2, -y - 1/2, -z + 2$	0.86	2.63	3.387(3)	147.4
5					
N(2)–H(2A)…O		0.86	2.09	2.927(10)	165.3
N(6)–H(6A)…O(7)	$-x + 3/2, y + 1/2, z$	0.86	2.09	2.910(8)	160.3
6					
N(14)–H(14A)…N(16)	$x, y + 1, z + 1$	0.86	1.91	2.768(11)	174.6
7					
N(2)–H(2B)…O(7)	$-x + 1, -y + 2, -z + 1$	0.86	2.01	2.861(4)	168.4
N(6)–H(6A)…O(3)	$-x + 2, -y + 1, -z + 1$	0.86	1.92	2.749(4)	161.7
O(9)–H(9)…O(6)		0.82	1.95	2.734(8)	159.9
8					
N(2)–H(2B)…O(2)	$x + 1, y, z + 1$	0.86	2.12	2.929(9)	156.8
N(6)–H(6A)…O(5)		0.86	1.97	2.799(16)	160.3
O(7)–H(7)…O(6)	$-x + 1/2, y + 1/2, -z + 1/2$	0.82	1.93	2.694(12)	154.6

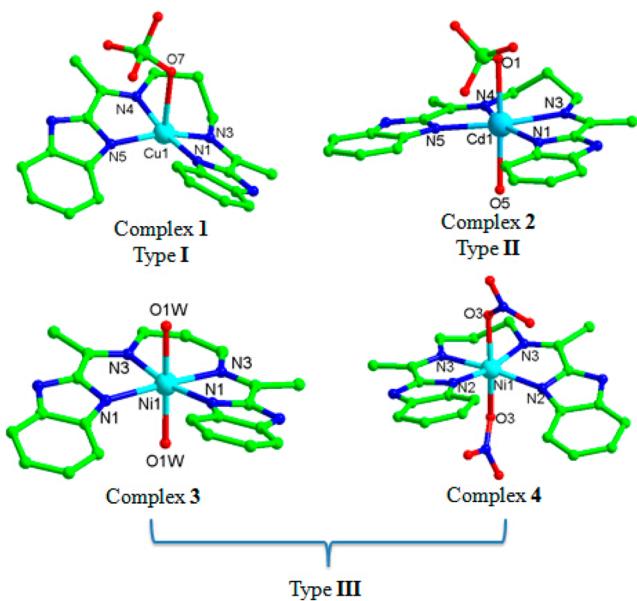


Figure 1. Mononuclear coordination structure in complexes 1–4.

the $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ spacer between the two benzimidazolyl groups is very flexible, the conformation of H_2bbepd ligand is switchable in complexes 1–4, in which the dihedral angle between two benzimidazolyl rings is 36.72° for 1, 4.46° for 2, 25.86° for 3, and 24.76° for 4. The angles are largely dependent on ionic radius ($65, 95$, and 69 pm for $\text{Cu}^{2+}, \text{Cd}^{2+}$, and Ni^{2+} , respectively), which are decreased with the increase in

ionic radius. Thus, it means the conformation of the ligand and the mononuclear unit can be partly controlled by the metal centers.

The NH group in the benzimidazolyl ring is a strong hydrogen donor; thus discrete complexes based on the benzimidazole ligand can usually be considered as effective building blocks with the potency to form hydrogen bond, as well as other important weak interactions during crystal packing, such as $\pi\cdots\pi$ and anion… π contacts. By choosing suitable metal ions, the interaction sites on the ligand can be regulated to arrange in designed orientations, which can lead to more predictable results.^{58,59} However, due to the coparticipation of other substances, such as solvent molecules and anions, in the process of hydrogen bonding, the prediction of the final product will usually become much more difficult.⁶⁰ It had been proven that the analyses of dimensional increase from the packing of structural units via suitable weak interactions will help to understand the rule of crystal engineering and the compensatory effects between various kinds of noncovalent interactions.⁶¹

In the crystal packing of complex 1, the NH groups on H_2bbepd ligand can serve as hydrogen bond donors and solvated MeOH or ClO_4^- as hydrogen acceptors, so two mononuclear units are linked together by N–H…O hydrogen bonds between benzimidazolyl groups, MeOH , and ClO_4^- , leading to an M_2L_2 ring (Figure 2a). In addition, the ring is further stabilized by $\pi\cdots\pi$ interaction between two parallel benzimidazolyl groups. The $\text{Cu}(\text{II})\cdots\text{Cu}(\text{II})$ separation in the ring is 14.72 Å. It is interesting to note that an unambiguous supramolecular contact was found between ClO_4^- and the

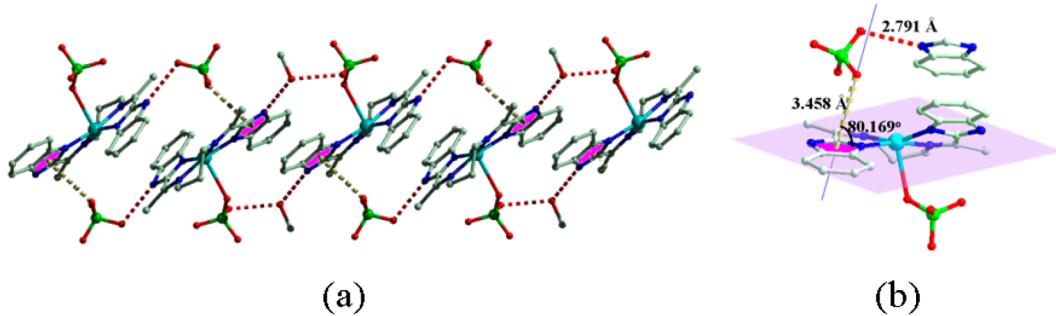


Figure 2. (a) 1D hydrogen bond chain and (b) distance and angle between ClO_4^- and imidazole ring in complex 1.

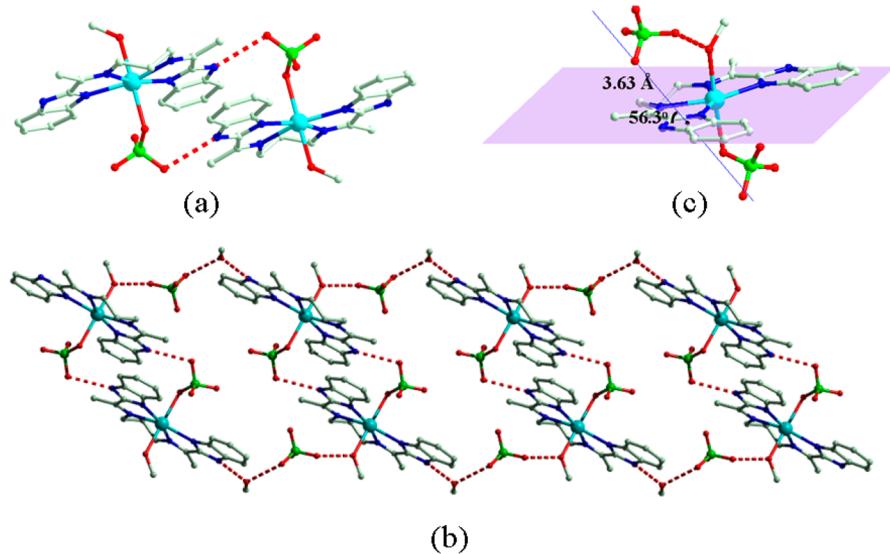


Figure 3. (a) Hydrogen bonded M_2L_2 ring, (b) 1D hydrogen bond chain, and (c) distance and angle between ClO_4^- and imidazole ring in complex 2.

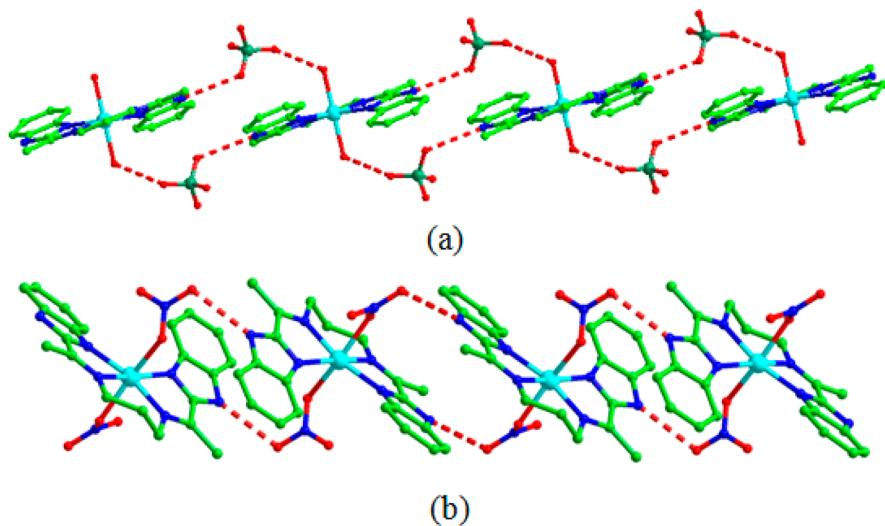


Figure 4. (a) 1D hydrogen bond chain in complex 3 and (b) 1D hydrogen bond chain in complex 4.

benzimidazolyl group in the complex. As shown in Figure 2b, the distance between O3 and the center of imidazole ring is 3.458 Å, and the angle for the O3–ring centroid–aromatic plane is 80.169°, which indicates the existence of a weak anion– π interaction.³⁸ Therefore, both anion– π interactions and hydrogen bonds connect the units into a 1D looplike chain.

As stated in the introduction part, this observation affords a rare example of anion– π interactions between anion and five-membered heterocycle.

In complex 2, the coordinated ClO_4^- is a hydrogen bond acceptor, and MeOH serves as a hydrogen bond donor besides two NH donors from the ligand; thus the unit can be seen as a

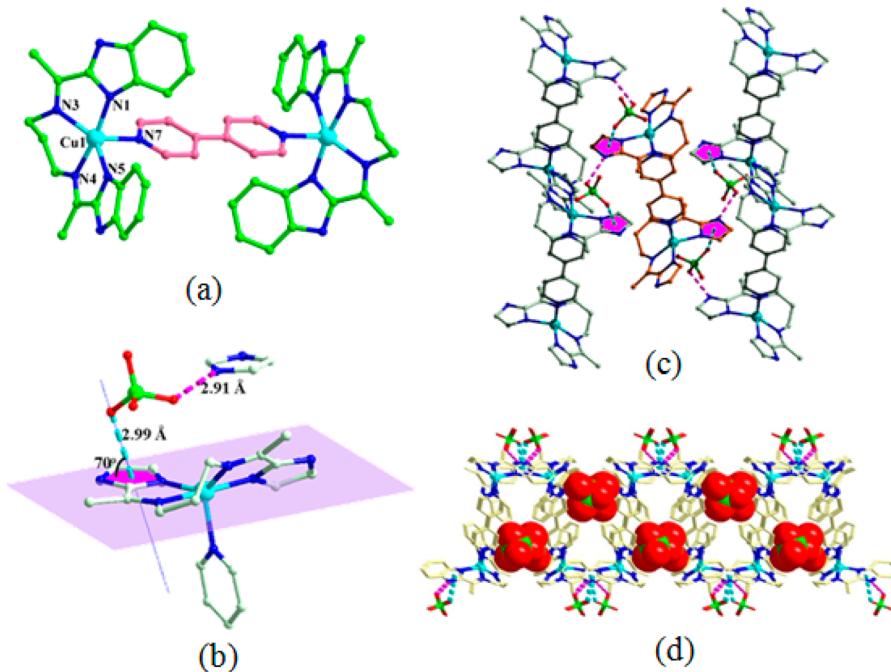


Figure 5. (a) The linear dinuclear structure of complex 5. (b) Anion- π interactions and N-H...O hydrogen bonds between binuclear units. (c) Distance and angle between ClO₄⁻ and imidazole ring. (d) The 1D channels occupied by ClO₄⁻ anions in complex 5.

hydrogen bond building block with three donors and one acceptor. Two adjacent mononuclear units are connected by a couple of complementary NH...O hydrogen bonds formed between NH donors and ClO₄⁻ acceptors, as shown in Figure 3a, also resulting in an M₂L₂ ring. Furthermore, the M₂L₂ rings are assembled into a ladder-like 1D chain by various hydrogen bonds involving the mononuclear units (including the coordinated ClO₄⁻ and MeOH) and uncoordinated ClO₄⁻ anions and MeOH molecules in the crystal lattice (NH...O hydrogen bond between coordinated MeOH and uncoordinated ClO₄⁻, OH...O hydrogen bond between uncoordinated ClO₄⁻ and uncoordinated MeOH and NH...O hydrogen bond between uncoordinated MeOH and NH as shown in Figure 3b, respectively). Unlike the situation in complex 1, the anion- π interaction between ClO₄⁻ and benzimidazolyl ring in complex 2 is weaker, with the distance and angle displayed in Figure 3c.

In complex 3, the coordinated H₂O molecules and NH groups in the mononuclear units both serve as hydrogen bond donors; therefore, hydrogen acceptors are needed to connect them together. Indeed, ClO₄⁻ anion use two O atoms forming OH...N hydrogen bonds with NH groups and OH...O hydrogen bonds with H₂O molecules, giving rise to a 1D beaded chain (Figure 4a). The mononuclear unit in complex 4 can be seen as a hydrogen bond building block with two donors and two acceptors, and they are arranged in an alternative fashion. Because the number of donors and acceptors are the same, the formation of a hydrogen bonding chain can be finished without the aid of other substances such as uncoordinated anions and MeOH molecules in complexes 1–3. As shown in Figure 4b, every two mononuclear units in complex 4 are linked by two N-H...O hydrogen bonds formed between benzimidazolyl N atoms and O atoms of the coordinated NO₃⁻ anions, thus generating a 1D chain comprised of a series of M₂L₂ rings. The Ni(II)...Ni(II) separation in each ring is 14.72 Å.

Multinuclear Structure of Complexes 5–8 Based on Mononuclear Building Blocks. By adding bpy into the reaction systems, we obtained multinuclear compounds based on the mononuclear units. Complexes 5 and 6 can be seen as a fragment of a 1D chain. The molecular structure in complex 5 is binuclear comprising two Cu(II) ions, two H₂bbepd and one bpy (Figure 5a). The coordination geometry of the Cu(II) ion is similar to complex 1 except the ClO₄⁻ is replaced by bpy. The asymmetric unit contains one H₂bbepd, half of a bpy which is located on an inversion center, one Cu(II) ion, and two ClO₄⁻ anions. The Cu-N bond distances and bond angles around the Cu(II) center are normal as listed in Table S1, Supporting Information. Compared with complex 1, the dihedral angle between two benzimidazolyl groups in complex 5 becomes larger (46.51°), which may be due to the larger steric hindrance induced by bigger bpy molecule. Because of the coordination geometry of the Cu(II) ion, it only leaves one labile coordination site in the mononuclear motif and hence cannot construct a complex with more than two Cu(II) basic units. Similar to complex 1, we found anion- π interaction between ClO₄⁻ and benzimidazolyl group in complex 5. As shown in Figure 5b, the distance from O atom of ClO₄⁻ to the center of imidazole ring is shorter than that in complex 1, but the angle between them is also smaller. One ClO₄⁻ connects two binuclear units via anion- π interaction and N-H...O hydrogen bond between ClO₄⁻ and NH. Each binuclear unit is connected to other four binuclear units via ClO₄⁻ (Figure 5c), so the 2D network can be denoted as (4, 4) net considering each binuclear unit as a nod. The 2D network is undulating, and a small channel exists in parallel with the net, by which ClO₄⁻ anions are occupied (Figure 5d).

Complex 6 is constructed by Cd(II) basic unit, which is a tetramer containing four Cd(II) ions, four H₂bbepd ligands, three bpy ligands, and two ClO₄⁻ anions. All the Cd(II) ions adopt a distorted octahedral coordination sphere but with two different coordination environments; one is defined by four N

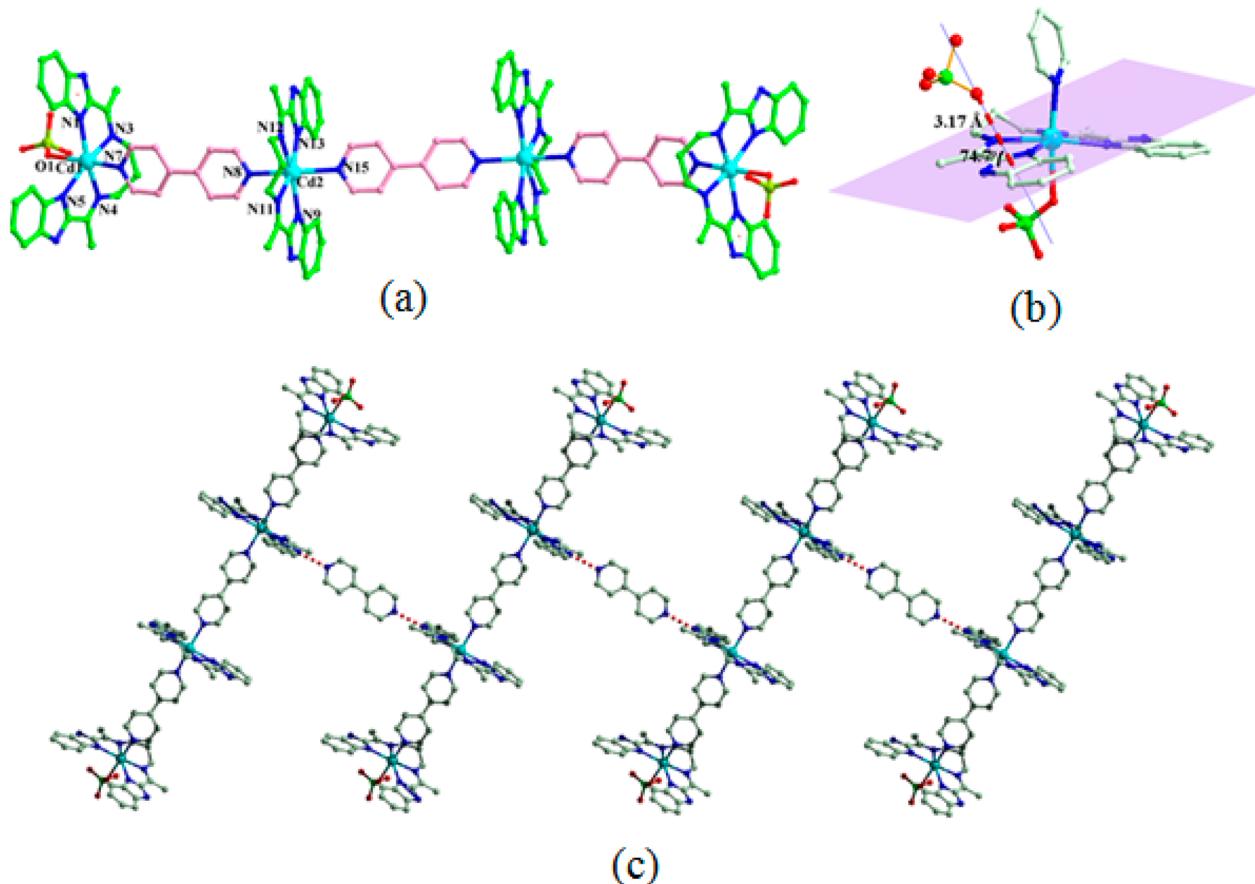


Figure 6. (a) The linear tetranuclear structure of complex 6. (b) 1D hydrogen bond ribbon, and (c) distance and angle between ClO_4^- and imidazole ring in complex 6.

atoms from H₂bbepd ligands in the equatorial plane, together with two N donors from two bpy in axial positions, and the other is defined by four N atoms from H₂bbepd ligands in the equatorial plane, together with one N donor from bpy and one O donor from ClO₄⁻ in axial positions. Three bpy join four mononuclear units to form a tetramer. The mononuclear unit in the tail is quite similar to complex 2 except MeOH is replaced by bpy. As we know, only a few examples of discrete linear complexes with more than three metal ions have been reported.⁶²⁻⁶⁵ In complex 6, ClO₄⁻ anion forms an anion···π interaction with the benzimidazolyl group, and the distance and angle are shown in Figure 6b. The anion···π interaction seems stronger in complexes 5 and 6 than in their corresponding mononuclear analogues complexes 1 and 2, which may be due to the enhancement of electron-deficiency of the benzimidazolyl ring by coordination of bpy. Furthermore, the tetranuclear units are connected by N–H···N hydrogen bonds between uncoordinated bpy and NH groups to generate a 1D ribbon, as shown in Figure 6c.

The coordination backbones of complexes 7 and 8 are almost identical 1D polymeric chains (Figure 7a,b), but with different uncoordinated anions and solvent molecules in the crystal lattice. Each Ni(II) atom is coordinated by four N donors from the tetradentate chelating ligand and two N donors from two bpy. The coordination environment around Ni(II) can be described as an octahedron. The repeating unit along the chain comprises two Ni(II) mononuclear units, which is similar to complexes 3 and 4 except that the coordinated water molecules or NO₃⁻ anions are replaced by bpy. A variety of weak

interactions exist in these two complexes. Taking complex 8 as an example, every 1D chain is connected to four chains via two series of hydrogen bonds. The first series include N–H···O hydrogen bonds formed between NH and NO₃⁻ anions, C–H···O hydrogen bond between NO₃⁻ and benzene ring of benzimidazolyl groups. The second series involve N–H···O hydrogen bond between NH and NO₃⁻, O–H···O hydrogen bond between NO₃⁻ and MeOH, and C–H···O hydrogen bond between MeOH and bpy. The 1D chains are arranged in pcu topology if we consider each mononuclear unit as a node, as shown in Figure 7c. For close packing, the overall network is a pcu net with 3-fold interpenetration (Figure 7d).

Structural Relationship and Possible Assembly Mechanism. As we discussed above, the potential labile substitution site(s) around the metal ions in the mononuclear building blocks are arranged in a line because the equatorial coordination sites have been occupied by cheating donors from the ligand H₂bbepd, leaving only the opposite axial position(s). Considering that the coordination donors in bpy are also in line, the combination of the mononuclear building blocks and bpy may result in segment- or chain-like structures as expected. The types of mononuclear units (complexes 1–4) played a significant role in the structural diversity of polynuclear compounds 5–8. The structural relationship among them is depicted in Scheme 2 as a topological view. The type I mononuclear unit leads to binuclear complex, the type II mononuclear unit leads to discrete multinuclear complex, while the type III mononuclear unit leads to an infinite chain based on countless nodes and rods.

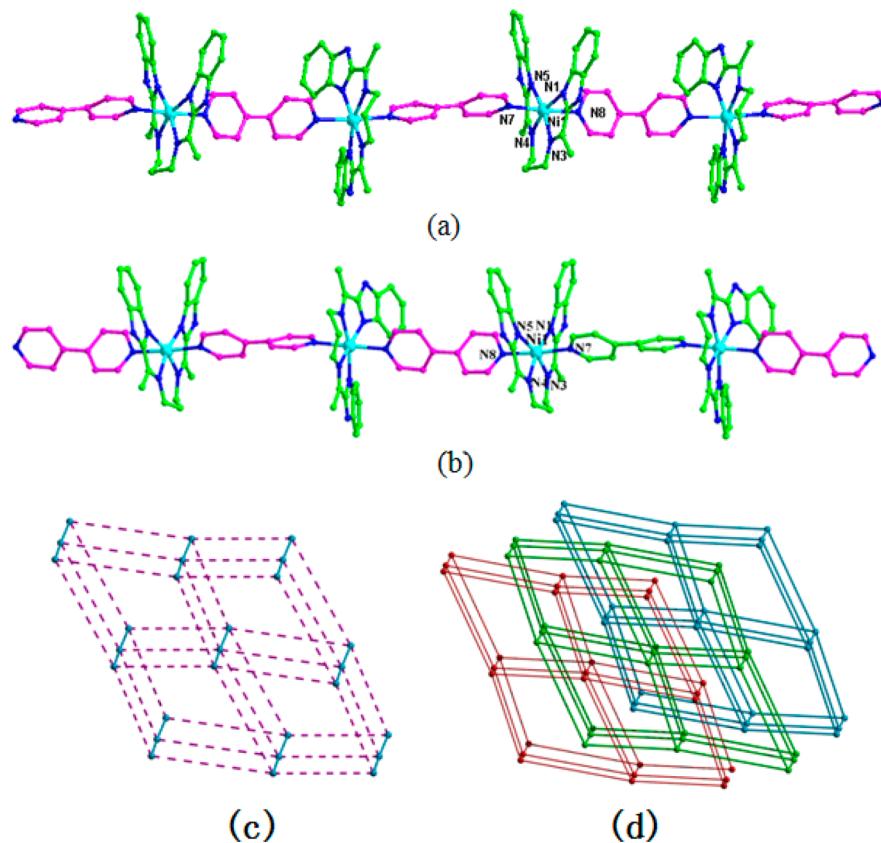
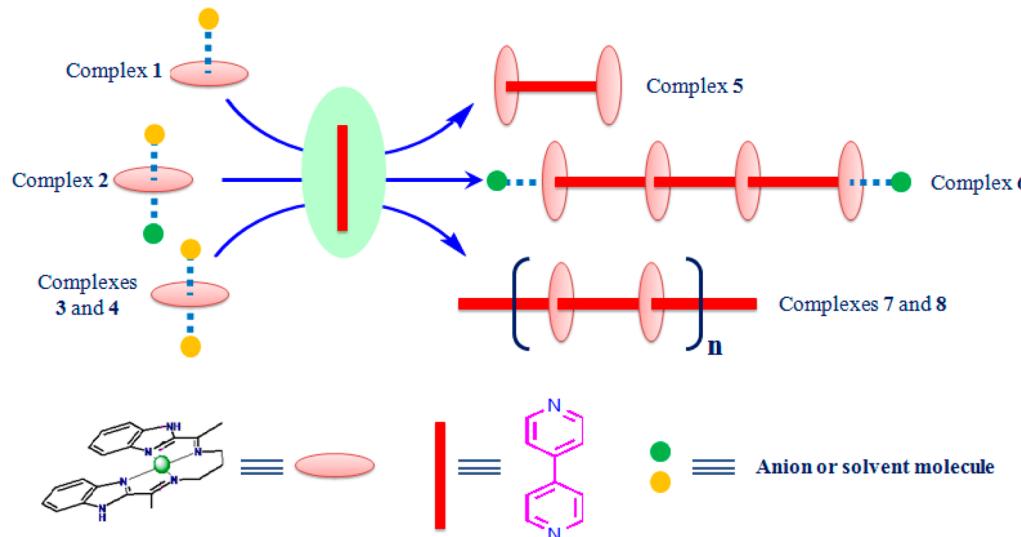


Figure 7. (a) The 1D chain structure of complex 7. (b) The 1D chain structure, (c) pcu net, and (d) 3-fold interpenetration in complex 8.

Scheme 2. Structure Relationship between Mononuclear Complexes 1–4 and Multinuclear Complexes 5–8



The ESI-MS analyses of complexes 1–8 in solution were performed (Figures S9–16, Supporting Information). They all contain a peak attributed to the mononuclear unit $[M\text{-}(\text{H}_3\text{bbepd})]^+$. It means that the mononuclear units are stable in solution and indeed have a great influence on the assembly process. Furthermore, it means that the small ligands at the apex of metal centers are easily substituted. It is also interesting to note the message of the coordination number and geometry of metal ions, and the conformation of H_2bbepd ligands in the mononuclear complexes (indicated by dihedral angles between two benzimidazole planes from single crystal XRD data, see

Table 3) were preserved during the substitution reaction; thus the structural diversity of multinuclear complexes is strongly correlated with the mononuclear precursor unit. The possible assembly mechanism of the multinuclear complexes starting from mononuclear precursors is shown in Scheme 3. In complex 1, the mononuclear unit has only one labile coordination site in the axial position (occupied by ClO_4^-), and thus it undoubtedly forms a binuclear complex once this position is substituted by bpy as observed in complex 5 (ROUTE 1). In complex 2, the mononuclear unit has two different labile coordination sites in the axial positions, which

Table 3. Dihedral Angles between Two Benzimidazolyl Rings (\angle_{Bims}) in Mononuclear Units in Complexes 1–8

complex	$\angle_{\text{Bims}}/^\circ$	complex	$\angle_{\text{Bims}}/^\circ$
1	36.72	5	46.56
2	4.46	6	10.94
			16.45
3	25.86	7	27.15
4	24.76	8	25.46

means that the more labile coordination site may be substituted first. As shown in ROUTE 2 and ROUTE 3, when the more labile coordination site (denoted by yellow ball) on the type II mononuclear unit was substituted by bpy, a binuclear unit with two remaining less labile coordination sites (denoted by green ball) will be formed (intermediate A). Otherwise, a mononuclear unit which is substituted by a hanging bpy ligand can also be generated (intermediate B), which has one remaining less labile coordination site. Then, when the hanging bpy molecule further replaces the leaving labile coordination sites in binuclear intermediate A, a tetranuclear molecule may be formed. That is just the case obtained in complex 5. If the further substitution of leaving labile coordination sites on the tetranuclear unit or among units of intermediate B was continued, it may result in a polynuclear 1D chain, although no corresponding structures have been obtained in our present conditions. The reason may be that the tetranuclear compound is dynamically more favored and will be crystallized out directly once formed. In complexes 3 and 4, the mononuclear unit has two equal labile coordination sites in axial positions. It is hard to replace only one of the labile sites in type III mononuclear; therefore, the polymerization cannot be stopped and straightforwardly leads to a 1D polymer chain, which is observed in complexes 7–8 (ROUTE 4).

CONCLUSIONS

In summary, a double Schiff base ligand containing a benzimidazolyl group with tetradentate chelate coordination sites has been designed and synthesized. Assembly of Cu(II), Cd(II), and Ni(II) with the ligand affords three types of mononuclear complexes showing differences in the coordinated

axial positions. When the coordinated labile components (anions or solvent molecules) on these positions are replaced by bidentate bpy secondary ligands, corresponding Cu(II) binuclear, Cd(II) tetranuclear, and Ni(II) infinite 1D chain complexes are formed, respectively. It means that the construction of multinuclear complexes from suitable mononuclear precursors with labile coordination sites is possible. The coordination competition among anions, solvent molecules, and secondary ligands define the final molecular structures. Weak interactions between ClO_4^- and five-membered benzimidazolyl groups are observed in complexes 1, 5, and 6.

ASSOCIATED CONTENT

Supporting Information

Tables of selected bond lengths and angles, PXRD, ESI-MS as well as X-ray crystallographic files in CIF format for compounds 1–8. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Authors

*(M.P.) E-mail: panm@mail.sysu.edu.cn.

*(J.-J.J.) E-mail: jiangjij@mail.sysu.edu.cn.

Notes

The authors declare no competing financial interest.

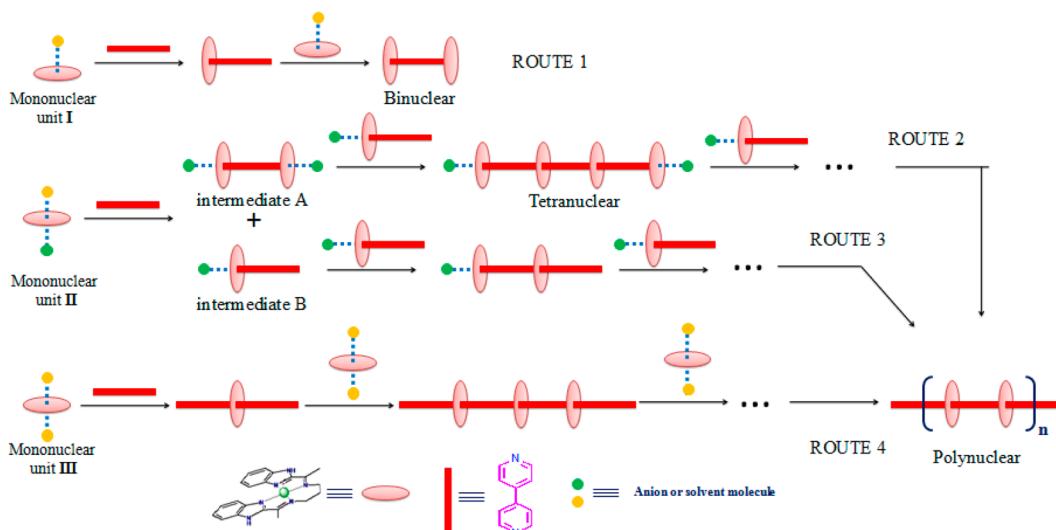
ACKNOWLEDGMENTS

We thank the 973 Program of China (2012CB821701), the NSFC projects (21373276, 21103233, 21121061, 21173272, 21303273), the NSF of Guangdong (S2013030013474), the FRF for the Central Universities (13lgpy12), and the RFDP of Higher Education of China for funding.

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Scheme 3. Tentative Assembly Mechanism of the Multinuclear Complexes Starting from Mononuclear Precursors



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