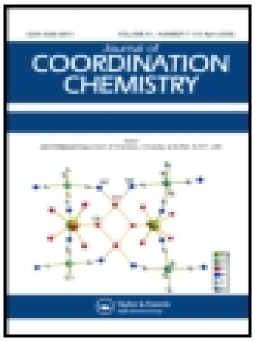

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A mesitylene-bridged bis-benzimidazolyl ligand and six metal coordination compounds

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ABSTRACT

The mesitylene-bridged bis-benzimidazolyl ligand 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (**L**) and six metal complexes, $[Cu_9L_6(OH)_7Cl_8]$ (**1**), $[Co_2L_4(NO_3)(H_2O)_2](NO_3)_3$ (**2**), $[Zn_2L_2Cl_4]$ (**3**), $[CdL_2(NO_3)_2]_n$ (**4**), $[MnL(L_A)(CH_3OH)]_n$ (**5**), and $[CoLCl_2]_n$ (**6**) ($\mathbf{L_A}$ = terephthalate), have been prepared and characterized. Complex **1** is a football-like cluster formed by six **L**s, nine Cu(II) ions, eight chlorides, and seven hydroxides, in which the size of the football is about 13.9 × 15.4 Å. Complex **2** contains a cage-like ball formed by four **L**s and two Co(II) ions, in which the external and internal sizes of the ball are about 12.2 × 14.6 Å and 6.5 × 10.7 Å, respectively. In this complex, one nitrate is fixed in the middle of the cage through two Co–O bonds. The 24-membered metallomacrocycle of **3** is formed by two **L**s and two Zn(II) ions. In **4**, 2-D layers with 48-membered metallomacrocycles are formed via **L**s and Cd(II) ions. In **5**, **L** and terephthalate ions ($\mathbf{L_A}$) participate in coordination with Mn(II) to afford 2-D network layers. The 1-D polymeric chain of **6** is formed via **L** and Co(II) chloride moieties. In the crystal packing of **1**–**6**, 2-D supramolecular layers and 3-D supramolecular frameworks are formed via intermolecular weak interactions, including hydrogen bonds, π–π interactions, and C–H···π contacts. The conformations of metal complexes from **L** are described. Additionally, the fluorescence emission spectra of **L** and **1**–**6** are reported.

Software of Graphics: Ligand **L**, $\mathbf{H_2L_A}$ and Schemes 1–3: Chem Draw 8.0
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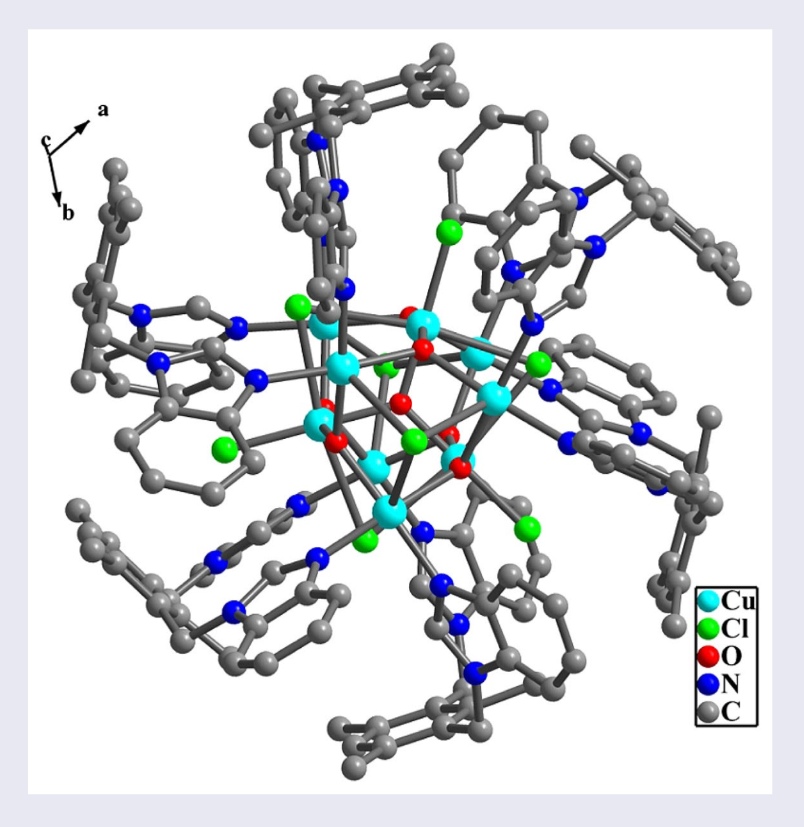
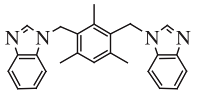


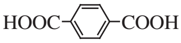
1. Introduction

Polynuclear metal complexes attract attention due to potential applications in ion-exchange resins [1], biological probes [2], and host–guest chemistry [3]. These complexes are generally formed by organic ligands and transition metals via coordination bonds, in which the metal centers are connecting nodes and the organic ligands are building blocks. Discrete low-dimensional metal complexes can be further connected into high-dimensional supramolecular architectures via intermolecular weak interactions (such as hydrogen bonds [4], aromatic $\pi\cdots\pi$ interactions [5], and C–H$\cdots\pi$ contacts [6]).

In construction of polynuclear metal complexes, the ligands have important influence on the sizes and shapes of the architectures formed. Bis-benzimidazolyl compounds with different linkers (such as polyether chains [7] and alkyl chains [8]) are important bidentate ligands, and they can coordinate with a number of metal ions to form coordination architectures with variable cavities or channels [9]. Additionally, the benzimidazole ring is a structural component of many compounds in living organisms [10]. Therefore, investigating the structure of metal complexes from benzimidazolyl ligands and metal ions has significance toward knowing the coordinating process in life science. We are interested in coordination behavior of bis-benzimidazolyl ligands bearing different linkers. Herein, we report the preparation of 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (**L**), as well as the preparation, structures, and weak interactions of six of its metal complexes. The conformations of the metal complexes from **L**, and the fluorescence emission spectra of **L** and **1–6** are reported.



L



H_2L_A

2. Experimental

2.1. General procedures

Commercially available reagents and chemicals were of analytical grade purity and used without purification. 1,3-bis(bromomethyl)mesitylene and 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene were prepared with analogous methods to the literature [11, 12]. Melting points were determined with a Boetius Block apparatus. ^{1}H NMR spectra were recorded on a Varian Mercury Vx 400 spectrometer at 400 MHz. Chemical shifts, δ, were reported in ppm relative to the internal standard TMS for ^{1}H NMR, and J values were given in Hz. Elemental analyses of all compounds were obtained from powder compounds recrystallized and measured using a Perkin-Elmer 2400C Elemental Analyzer. The fluorescence spectra were performed using a Cary Eclipse fluorescence spectrophotometer.

2.2. Preparation of 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (L)

To a mixture of mesitylene (12.000 g, 99.8 mmol), paraformaldehyde (6.000 g, 199.8 mmol), and glacial acetic acid (100 mL), hydrogen bromide gas was introduced for 5 h at 50 °C and a massive precipitate formed. A white powder of 1,3-bis(bromomethyl)mesitylene was obtained after filtration. Yield: 28.496 g (93%). M.p.: 140–142 °C.

A CH_3CN (100 mL) suspension of benzimidazole (1.699 g, 14.4 mmol), KOH (1.467 g, 26.3 mmol), and tetrabutylammonium bromide (0.211 g, 0.6 mmol) was stirred for 2 h under reflux and then 1,3-bis(bromomethyl)mesitylene (2.000 g, 6.5 mmol) was slowly added and stirred continually for 72 h at 80 °C. A pale yellow powder was obtained after removing the solvent. The powder was dissolved in CH_2Cl_2 (100 mL) and washed with water (3 × 100 mL), and the organic layer was dried over anhydrous $MgSO_4$. After removing the CH_2Cl_2, a white powder of 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (**L**) was obtained. Yield: 2.215 g (89%). M.p.: 258–260 °C. Anal. Calcd for $C_{25}H_{24}N_4$: C, 79.91; H, 6.35; N, 14.72%. Found: C, 79.55; H, 6.47; N, 14.89%. ^{1}H NMR (400 MHz, DMSO-d_6): δ 2.13 (s, 3H, CH_3), 2.30 (s, 6H, CH_3), 5.46 (s, 4H, PhCH_2), 7.15 (s, 1H, Ph*H*), 7.20–7.23 (q, J = 3.1 Hz, 4H, bimi*H*), 7.45–7.47 (t, J = 4.4 Hz, 2H, bimi*H*), 7.65–7.67 (q, J = 3.1 Hz, 2H, bimi*H*), 7.78 (s, 2H, 2-bimi*H*) (bimi = benzimidazole).

2.3. Preparation of {[1,3-bis(benzimidazol-1′-yl-methyl)mesitylene]$_6$Cu$_9$(OH)$_7$Cl$_8$} (1)

A DMF (5 mL) solution of 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (**L**) (0.050 g, 0.1 mmol) was added to a methanol solution (15 mL) of $CuCl_2\cdot 2H_2O$ (0.051 g, 0.3 mmol). The mixture was stirred for 1 h at 40 °C. The filtrate was allowed to evaporate slowly under ambient conditions, and blue single crystals suitable for X-ray analysis were obtained within two weeks. Yield: 0.034 g (63%). M.p.: 180–182 °C. Anal. Calcd for $C_{150}H_{151}N_{24}Cu_9O_7Cl_8$: C, 55.30; H, 4.67; N, 10.31%. Found: C, 55.43; H, 4.65; N, 10.53%.

2.4. Preparation of {[1,3-bis(benzimidazol-1′-yl-methyl)mesitylene]$_4$Co$_2$(NO$_3$)(H$_2$O)$_2$}(NO$_3$)$_3$ (2)

This complex was prepared in a manner analogous to that of **1**, only $Co(NO_3)_2\cdot 6H_2O$ (0.087 g, 0.3 mmol) was used instead of $CuCl_2\cdot 2H_2O$, and red single crystals suitable for X-ray analysis were obtained after three weeks. Yield: 0.020 g (42%). M.p.: 210–212 °C. Anal. Calcd for $C_{50}H_{50}CoN_{10}O_7$: C, 62.43; H, 5.23; N, 14.56%. Found: C, 62.80; H, 5.45; N, 14.32%.

2.5. Preparation of {[1,3-bis(benzimidazol-1′-yl-methyl)mesitylene]$_2$Zn$_2$Cl$_4$} (3)

This complex was prepared in a manner analogous to that of **1**, only $ZnCl_2$ (0.039 g, 0.3 mmol) was used instead of $CuCl_2\cdot 2H_2O$, and colorless single crystals suitable for X-ray analysis were obtained after three weeks. Yield: 0.031 g (60%). M.p.: 280–282 °C. Anal. Calcd for $C_{50}H_{48}N_8Zn_2Cl_4$: C, 58.10; H, 4.68; N, 10.84%. Found: C, 58.41; H, 4.76; N, 10.64%.

2.6. *Preparation of {[1,3-bis(benzimidazol-1′-yl-methyl)mesitylene]$_2$Cd(NO$_3$)$_2$}$_n$* (4)

This complex was prepared in a manner analogous to that of **1**, only $Cd(NO_3)_2{\cdot}4H_2O$ (0.092 g, 0.3 mmol) was used instead of $CuCl_2{\cdot}2H_2O$, and colorless single crystals suitable for X-ray analysis were obtained after two weeks. Yield: 0.030 g (62%). M.p.: 262–264 °C. Anal. Calcd for $C_{25}H_{24}N_5Cd_{0.5}O_3$: C, 60.21; H, 4.85; N, 14.04%. Found: C, 60.42; H, 4.72; N, 14.35%.

2.7. *Preparation of {[1,3-bis(benzimidazol-1′-yl-methyl)mesitylene](terephthalate) Mn(CH$_3$OH)}$_n$* (5)

A DMF (5 mL) solution of terephthalic acid ($\mathbf{H_2L_A}$) (0.049 g, 0.3 mmol) was added to a DMF (5 mL) solution of **L** (0.050 g, 0.1 mmol). The mixture was stirred for 3 min. Then a methanol solution (15 mL) of $Mn(ClO_4)_2{\cdot}6H_2O$ (0.108 g, 0.3 mmol) was added and the pH of the solution was adjusted to 7 with triethylamine. The mixture was stirred for 2 h at 40 °C. The filtrate was allowed to evaporate slowly under ambient conditions, and colorless single crystals suitable for X-ray analysis were obtained within two weeks. Yield: 0.038 g (61%). M.p.: 310–312 °C. Anal. Calcd for $C_{34}H_{32}N_4MnO_5$: C, 64.65; H, 5.10; N, 8.87%. Found: C, 64.89; H, 4.93; N, 8.74%.

2.8. *Preparation of {[1,3-bis(benzimidazol-1′-yl-methyl)mesitylene]CoCl$_2$}$_n$* (6)

This complex was prepared in a manner analogous to that of **1**, only $CoCl_2{\cdot}2H_2O$ (0.049 g, 0.3 mmol) was used instead of $CuCl_2{\cdot}2H_2O$, and blue single crystals suitable for X-ray analysis were obtained after three weeks. Yield: 0.031 g (62%). M.p.:>320 °C. Anal. Calcd for $C_{50}H_{48}N_8Co_2Cl_4$: C, 58.83; H, 4.74; N, 8.87%. Found: C, 58.77; H, 4.94; N, 8.63%.

2.9. *X-ray data collection and structure determinations*

X-ray single-crystal diffraction data for **1**–**6** were collected using a Bruker Apex II CCD diffractometer at 296(2) K for **1**, **2**, and **5** and 173(2) K for **3**, **4**, and **6** with Mo-Kα radiation ($\lambda = 0.71073$ Å) by ω scan mode. There was no evidence of crystal decay during data collection in all cases. Semiempirical absorption corrections were applied using SADABS and SAINT was used for integration of the diffraction profiles [13]. All structures were solved by direct methods using SHELXS of the SHELXTL package and refined with SHELXL [14] by full-matrix least-squares methods with anisotropic thermal parameters for all non-hydrogen atoms on F^2. Hydrogens bonded to C were placed geometrically and solvent hydrogens were first located in difference Fourier maps and then fixed in the calculated sites. Further details for crystallographic data and structural analysis are listed in tables 1 and 2, which were generated using Crystal-Maker [15]. Bond distances and angles of **1**–**6** are given in tables 3 and 4.

3. Results and discussion

3.1. *Synthesis and characterization of 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (L) and metal complexes* 1–6

The 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (**L**) was prepared through reaction of benzimidazole with 1,3-bis(bromomethyl)mesitylene (scheme 1). **L** is stable to air and moisture and soluble in CH_3OH, CH_3CN, and DMF, but scarcely soluble in water, petroleum ether, and diethyl ether.

$[Cu_9L_6(OH)_7Cl_8]$ (**1**), $[Co_2L_4(NO_3)(H_2O)_2](NO_3)_2$ (**2**), $[Zn_2L_2Cl_4]$ (**3**), $[CdL_2(NO_3)_2]_n$ (**4**) and $[CoLCl_2]_n$ (**6**) were prepared via reaction of **L** with metal salts in DMF/CH_3OH ($CuCl_2{\cdot}2H_2O$ for **1**, $Co(NO_3)_2{\cdot}6H_2O$ for **2**, $ZnCl_2$ for **3**, $CoCl_2{\cdot}2H_2O$ for **4**, and $Cd(NO_3)_2{\cdot}4H_2O$ for **6**). $[MnL(L_A)(CH_3OH)]_n$ (**5**) was prepared via the reaction of a mixture of **L** and terephthalic acid ($\mathbf{H_2L_A}$) with $Mn(ClO_4)_2{\cdot}6H_2O$ in the presence of triethylamine in DMF/CH_3OH. Crystals of **1**–**6** suitable for X-ray diffraction were grown by slow evaporation at room temperature. Complexes **1-6** are stable to air and moisture, and their structural integrity can

Table 1. Summary of crystallographic data for **1**–**3**.

	1	**2**·$2H_2O·CH_3OH$	**3**·DMF
Chemical formula	$C_{150}H_{151}Cl_8Cu_9N_{24}O_7$	$C_{50}H_{50}CoN_{10}O_7·2H_2O·CH_3OH$	$C_{50}H_{48}Cl_4N_8Zn_2·DMF$
Formula weight	3257.40	1030.00	1106.60
Crystal system	Hexagonal	Monoclinic	Triclinic
Space group	$P6_3/m$	$P2_1/n$	$P\bar{1}$
a (Å)	20.8473(9)	14.5539(18)	10.516(4)
b (Å)	20.8473(9)	18.471(2)	11.786(5)
c (Å)	26.0224(10)	18.809(2)	21.521(9)
α (°)	90	90	82.654(8)
β (°)	90	92.766(2)	79.702(9)
γ (°)	120	90	69.589(7)
V (Å^3)	9794.4(9)	5050.4(11)	2453.4(18)
Z	2	4	2
D_{Calcd} (Mg m^{-3})	1.105	1.355	1.498
Abs. coeff. (mm^{-1})	1.114	0.408	1.246
F(0 0 0)	3344	2164	1144
Crystal size (mm)	0.19 × 0.18 × 0.17	0.14 × 0.13 × 0.12	0.15 × 0.14 × 0.13
θ_{min}, θ_{max} (°)	1.128, 24.590	1.546, 25.010	0.964, 25.009
T (K)	296.15	296.15	173.15
No. of data collected	48,778	25,409	12,624
No. of unique data	5621	8880	8618
No. of refined params.	303	693	648
Reflns. number gt	3822	7205	4510
R (int)	0.0606	0.0378	0.0748
Goodness-of-fit on F^2 [a]	1.039	1.049	1.011
Final R indices [b] [$I > 2\sigma(I)$]			
R_1	0.0752	0.0453	0.0633
wR_2	0.2336	0.1231	0.1034
R indices (all data)			
R_1	0.0970	0.0589	0.1591
wR_2	0.2493	0.1358	0.1348

[a] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n is the number of reflection and p is the number of parameters refined.

[b] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

be retained at room temperature for a considerable length of time. The solubility of these complexes is poor in most organic solvents; however, they can be dissolved in DMSO.

3.2. *Crystal structure of* 1–6

The football-like **1** lies about a center of *-6* symmetry and is formed by six bis-benzimidazolyl ligands **L**, nine Cu(II) ions, eight chlorides, and seven hydroxide ions as shown in figure 1(a), in which the size of the football is about 13.9 × 15.4 Å. In each ligand, the dihedral angle of two benzimidazole rings is 72.4(5)°, and the dihedral angles between the mesitylene moiety and the two benzimidazole rings are 84.0(9)° and 86.3(1)°. The dihedral angle between two benzimidazole rings connected to the same Cu(II) is 75.6(1)°. In the football, two adjacent mesitylene rings form the dihedral angle of 58.8(1)°, two interval mesitylene rings form the dihedral angle of 60.0(8)°, and two opposing mesitylene rings are parallel. The core of this complex is a bipyramidal cylinder as shown in figure 1(b), in which nine Cu(II) ions are divided into two groups according to different coordination numbers. Six Cu(II) ions in the first group lie at both ends of the bipyramidal cylinder, and they are five-coordinate by one chloride, two oxygens, and two nitrogens from two benzimidazole rings of two **L**s to adopt a distorted square pyramidal geometry. Three Cu(II) ions in the second group lie in the middle of the bipyramidal cylinder, and they are six-coordinate with three oxygens and three chlorides to adopt a slightly distorted octahedral coordination. Seven oxygens in the bipyramidal cylinder are three-coordinate, and each oxygen is bonded to three Cu(II) ions to form a O–Cu_3 unit. In the central O-Cu_3 unit of the bipyramidal cylinder, four atoms are coplanar. The other six O–Cu_3 units have a shallow trigonal pyramidal shape. The eight chlorides in the bipyramidal cylinder contain three types of coordination models, two chlorides which are placed at

Table 2. Summary of crystallographic data for **4**–**6**.

	4·2DMF	**5**·CH_3OH	**6**·CH_3OH
Chemical formula	$C_{50}H_{48}CdN_{10}O_6$·2DMF	$C_{34}H_{32}MnN_4O_5$·CH_3OH	$C_{50}H_{48}Cl_4Co_2N_8$·CH_3OH
Formula weight	1143.59	663.62	1052.67
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	*C*2/*c*	$P2_1/n$	*Pbca*
a (Å)	21.0093(19)	13.290(3)	18.1766(17)
b (Å)	13.2687(12)	18.050(4)	18.5808(19)
c (Å)	20.1632(19)	13.903(3)	29.801(3)
α (°)	90	90	90
β (°)	108.4360(10)	105.749(18)	90
γ (°)	90	90	90
V (Å^3)	5332.3(8)	3209.9(13)	10,064.9(17)
Z	4	4	8
D_{Calcd} (Mg m^{-3})	1.424	1.373	1.389
Abs. coeff. (mm^{-1})	0.477	0.463	0.917
F(0 0 0)	2376	1388	4352
Crystal size (mm)	0.15 × 0.14 × 0.13	0.12 × 0.11 × 0.10	0.13 × 0.12 × 0.10
θ_{min}, θ_{max} (°)	1.84, 25.01	1.880, 28.493	1.37, 25.01
T (K)	173(2)	296.15	173(2)
No. of data collected	13,222	20,078	49,516
No. of unique data	4708	7893	8867
No. of refined params.	353	420	602
Reflns. number gt	4411	4728	5736
R (int)	0.0231	0.0249	0.1137
Goodness-of-fit on F^2 [a]	1.027	1.031	1.016
Final *R* indices[b] [$I > 2\sigma(I)$]			
R_1	0.0229	0.0401	0.0471
wR_2	0.0552	0.1143	0.0903
R indices (all data)			
R_1	0.0250	0.0565	0.0931
wR_2	0.0563	0.1252	0.1090

[a] GOF = $[\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where *n* is the number of reflection and *p* is the number of parameters refined.

[b] $R_1 = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}$.

the ends of the bipyramidal cylinder are coordinated by three Cu(II) ions, three chlorides (Cl(1), Cl(1A) and Cl(1B)) are coordinated by two Cu(II) ions, and three other chlorides (Cl(2), Cl(2A) and Cl(2B)) are coordinated by one Cu(II). In the middle of the bipyramidal cylinder, six chlorides and one O–Cu_3 unit are coplanar, and this plane is the symmetric plane of the bipyramidal cylinder and the football. The values of bond distances and angles in this complex are similar to those of known Cu(II) complexes [16].

Complex **2** contains a cage-like ball formed by four **L** and two Co(II) ions as shown in figure2(a). The external and internal sizes of the ball are about 12.2 × 14.6 Å and 6.5 × 10.7 Å, respectively. The Co···Co distance is 6.557(7) Å. In the same ligand, the dihedral angle of two benzimidazole rings is 87.1(9)°, and the dihedral angles between the mesitylene ring and two benzimidazole rings are 83.2(2)° and 88.9(2)°. Among the four benzimidazole rings connected to each Co(II), the dihedral angles of two adjacent benzimidazole rings are 54.2(4)–68.5(8)° (table S1), and two opposing benzimidazole rings form dihedral angles of 88.5(6)–87.2(9)°. The opposing mesitylene rings are symmetry-related, and the distances between two groups of opposing mesitylene rings are *ca.* 10.94 and 11.11 Å. One nitrate in **2** is fixed in the cage through two Co–O bonds and is disordered about a center of symmetry at the center of the cage. Each Co(II) is six-coordinate with four nitrogens from four benzimidazole rings of four **L**s, and two oxygens (one from a nitrate and another from a water) to afford slightly distorted octahedral coordination. An equatorial plane of the octahedron may be defined by the four nitrogens (N(1), N(4A), N(5) and N(8A)), and the two oxygens (O(1) and O(2)) lie in the axial positions. The values of bond distances and angles in this complex are similar to those of known Co(II) complexes [17].

In **3** (figure 3(a)), there are two independent, but essentially identical 24-membered macrocyclic molecules; *π*···*π* interactions between mesitylene and benzimidazole rings from both molecules are

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

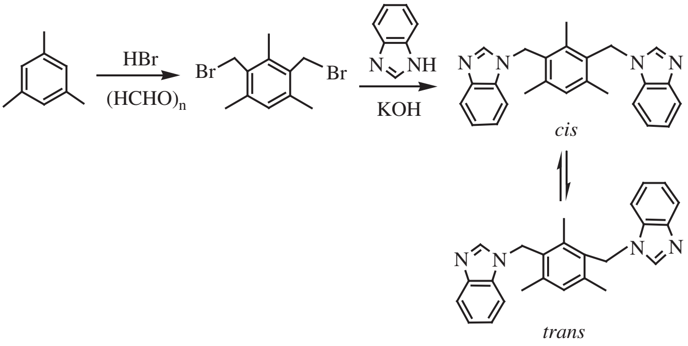
*Complex **1***			
Cu(1)–Cl(3)	2.7835(18)	Cu(1)–O(2B)	2.009(3)
Cu(1)–O(2)	1.986(3)	Cu(1)–N(1)	2.031(4)
Cu(1)–N(3)	1.974(4)	Cu(2)–Cl(1)	2.721(2)
Cu(2)–Cl(2)	2.196(3)	Cu(2)–O(1)	1.8347(12)
Cu(2)–O(2)	2.033(4)	Cu(2)–O(2D)	2.033(4)
O(2)–Cu(1)–O(2B)	90.24(18)	N(3)–Cu(1)–N(1)	90.92(19)
O(2)–Cu(1)–Cl(3)	81.52(10)	O(2B)–Cu(1)–Cl(3)	81.13(10)
N(3)–Cu(1)–Cl(3)	105.70(14)	N(1)–Cu(1)–Cl(3)	107.25(14)
O(2)–Cu(1)–N(1)	88.40(16)	O(2)–Cu(1)–N(3)	172.60(18)
Cl(2)–Cu(2)–Cl(1)	94.17(9)	O(1)–Cu(2)–Cl(1)	86.30(6)
O(1)–Cu(2)–Cl(2)	179.53(10)	O(2)–Cu(2)–Cl(1)	92.08(9)
O(2)–Cu(2)–Cl(2)	95.70(9)	O(1)–Cu(2)–O(2)	84.28(9)
O(2)–Cu(2)–O(2D)	167.54(19)	Cu(2)–O(1)–Cu(2A)	120.0
Cu(1)–O(2)–Cu(1A)	119.63(18)	Cu(1)–O(2)–Cu(2)	112.18(15)
Cu(1A)–O(2)–Cu(2)	117.19(15)		
*Complex **2***			
Co(1)–N(1)	2.125(2)	Co(1)–N(4A)	2.124(2)
Co(1)–N(5)	2.121(2)	Co(1)–N(8A)	2.129(2)
Co(1)–O(1)	2.1081(19)	Co(1)–O(2)	2.223(5)
N(1)–Co(1)–N(8A)	92.00(8)	N(4A)–Co(1)–N(8A)	89.13(9)
N(1)–Co(1)–N(5)	89.42(8)	N(1)–Co(1)–N(4A)	175.55(9)
N(5)–Co(1)–N(4A)	89.81(8)	N(5)–Co(1)–N(8A)	175.03(8)
N(1)–Co(1)–O(1)	87.44(8)	N(1)–Co(1)–O(2)	83.17(14)
N(4A)–Co(1)–O(1)	88.20(8)	N(4A)–Co(1)–O(2)	101.15(14)
N(5)–Co(1)–O(1)	91.52(8)	N(5)–Co(1)–O(2)	86.00(16)
N(8A)–Co(1)–O(1)	93.30(8)	N(8A)–Co(1)–O(2)	89.45(16)
O(1)–Co(1)–O(2)	170.30(13)		
*Complex **3***			
Zn(1)–Cl(1)	2.192(2)	Zn(1)–Cl(2)	2.2382(19)
Zn(1)–N(1)	2.017(5)	Zn(1)–N(4A)	2.034(5)
Zn(2)–Cl(3)	2.2164(18)	Zn(2)–Cl(4)	2.2056(19)
Zn(2)–N(5)	2.017(5)	Zn(2)–N(8A)	1.998(6)
Cl(1)–Zn(1)–Cl(2)	118.75(8)	N(1)–Zn(1)–Cl(1)	110.34(16)
N(1)–Zn(1)–Cl(2)	108.68(14)	N(1)–Zn(1)–N(4A)	99.2(2)
Cl(3)–Zn(2)–Cl(4)	119.28(8)	N(5)–Zn(2)–Cl(3)	108.05(14)
N(5)–Zn(2)–Cl(4)	106.05(16)	N(8A)–Zn(2)–Cl(3)	107.95(17)

observed (table S2) [5]. Each molecule is formed by two **L** and two Zn(II) ions, with each Zn(II) surrounded by two chlorides and two nitrogens from two benzimidazole rings of two **L** in a tetrahedral coordination. In each molecule, an inversion center is observed. The Zn(1)···Zn(1A) and Zn(2)···Zn(2A) distances are 10.964(4) and 10.609(4) Å. Two pairs of opposing benzimidazole rings in each molecule are parallel to each other, and the face-to-face distances between them are 4.965(1) and 9.705(2) Å (or 4.962(3) and 9.735(7) Å). One pair of opposing mesitylene rings in each molecule is also parallel with face-to-face distance of 7.504(9) Å (or 8.501(8) Å). In the same ligand of each molecule, the dihedral angle between two benzimidazole rings is 68.4(1)° (or 77.8(8)°), and the dihedral angles between the mesitylene and two benzimidazole rings are 83.0(4) and 84.6(9)° (or 87.6(9) and 89.6(7)°). The values of bond distances and angles in this complex are consistent with those from published Zn(II) complexes [18].

Complex **4** is a 2-D network layer containing 48-membered metallomacrocyclic rings (figure 4(a)). Each metallomacrocycle is constructed from four **L** and four Cd(II) ions (figure 4(b)), in which two pairs of opposing mesitylene rings are parallel to each other, the distance between two adjacent Cd(II) ions is 12.424(3) Å, and the distances between two pairs of opposing Cd(II) ions are 13.268(1) and 21.009(1) Å. In the same ligand, the dihedral angle between two benzimidazole rings is 77.5(1)°, and the dihedral angles between the mesitylene and two benzimidazole rings are 87.6(4) and 87.8(1)°. Among the four benzimidazole rings connected to the same Cd(II), the dihedral angles between two benzimidazole rings range from 58.7(5) to 79.1(1)°. Each Cd(II) is surrounded by four nitrogens from four benzimidazole

Table 4. Selected bond lengths (Å) and angles (°) for **4**–**6**.

*Complex **4***			
Cd(1)–N(1)	2.3051(14)	Cd(1)–N(4A)	2.3228(14)
Cd(1)–O(1)	2.4087(12)	N(4A)–Cd(1)–N(4B)	81.04(7)
N(1)–Cd(1)–N(1A)	104.65(7)	N(1)–Cd(1)–N(4B)	87.50(5)
N(1)–Cd(1)–N(4A)	166.60(5)	N(1)–Cd(1)–O(1)	86.36(5)
N(1)–Cd(1)–O(1A)	84.88(5)	N(4A)–Cd(1)–O(1A)	90.38(5)
N(4B)–Cd(1)–O(1A)	100.55(5)	O(1)–Cd(1)–O(1A)	165.66(7)
*Complex **5***			
Mn(1)–O(4A)	2.0939(13)	Mn(1)–O(5)	2.1742(16)
Mn(1)–O(1)	2.2242(14)	Mn(1)–N(4A)	2.2454(17)
Mn(1)–N(1)	2.2678(17)	Mn(1)–O(2)	2.3244(15)
O(1)–Mn(1)–O(2)	57.79(5)	O(1)–Mn(1)–O(5)	89.27(6)
O(2)–Mn(1)–O(5)	146.99(6)	O(2)–Mn(1)–O(4A)	119.11(6)
O(4A)–Mn(1)–O(1)	176.70(6)	O(4A)–Mn(1)–O(2)	119.11(6
O(4A)–Mn(1)–O(5)	93.86(6)	N(1)–Mn(1)–N(4A)	174.00(6)
O(1)–Mn(1)–N(1)	92.35(5)	O(1)–Mn(1)–N(4A)	93.27(6)
O(2)–Mn(1)–N(1)	91.60(6)	O(2)–Mn(1)–N(4A)	89.61(6)
O(4A)–Mn(1)–N(1)	86.50(6)	O(4A)–Mn(1)–N(4A)	87.78(6)
O(5)–Mn(1)–N(1)	92.00(6)	O(5)–Mn(1)–N(4A)	90.18(7)
*Complex **6***			
Co(1)–N(1)	2.009(3)	Co(1)–N(8A)	2.009(3)
Co(1)–Cl(1)	2.2776(11)	Co(1)–Cl(2)	2.2357(11)
Co(2)–N(4)	2.029(3)	Co(2)–N(5)	2.017(3)
Co(2)–Cl(3)	2.2612(11)	Co(2)–Cl(4)	2.2295(11)
N(1)–Co(1)–N(8A)	109.61(13)	Cl(1)–Co(1)–Cl(2)	111.29(4)
Cl(1)–Co(1)–Cl(8A)	104.57(9)	Cl(2)–Co(1)–Cl(8A)	112.39(9)
N(1)–Co(1)–Cl(1)	100.09(10)	N(1)–Co(1)–Cl(2)	117.50(10)
N(4)–Co(2)–N(5)	102.39(13)	Cl(3)–Co(2)–Cl(4)	116.52(4)
N(4)–Co(2)–Cl(3)	113.20(10)	N(4)–Co(2)–Cl(4)	102.91(10)
N(5)–Co(2)–Cl(3)	107.25(9)	N(5)–Co(2)–Cl(4)	113.74(9)



Scheme 1. Preparation of ligand **L**.

rings of four **L** and two oxygens from two nitrates in an octahedral coordination. The equatorial plane of the octahedron is occupied by four nitrogens (N(1), N(1A), N(4) and N(4A)), and two oxygens (O(1) and O(1A)) are axial. The values of bond distances and angles in this complex compare favorably with analogous ones from known Cd(II) complexes [19].

In **5**, **L** and **L**$_{\mathbf{A}}$ (terephthalate) participate in coordination with the Mn(II) to afford 2-D network layers with 42-membered metallomacrocyclic rings (figure 5(a)). Each metallomacrocycle is constructed by two **L**, two **L**$_{\mathbf{A},}$ and four Mn(II) ions around a center of symmetry at the center of the ring (figure 5(b)). In each metallomacrocycle, two pairs of opposing benzimidazole rings and two pairs of opposing benzene rings are parallel to each other, and π–π interactions [5] between two benzimidazole rings

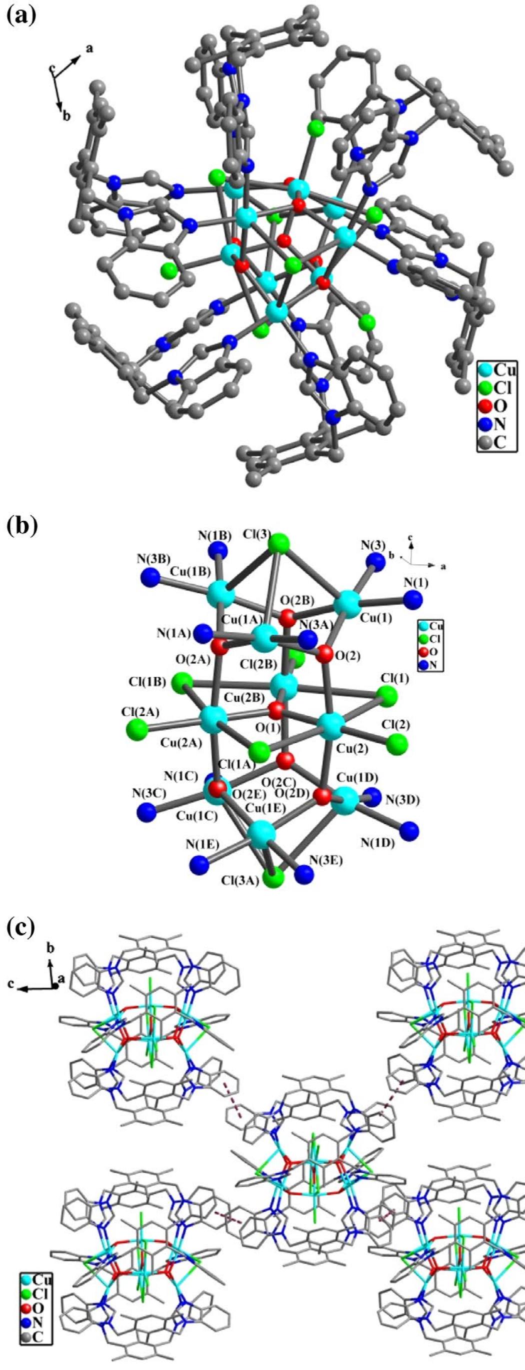


Figure 1. (a) Perspective view of **1**. (b) The coordination environment of Cu(II). Symmetry code: A = 1 − x + y, 1 − x, z, B = 1 − y, x − y, z, C = 1 − y, x − y, 0.5 − z, D = x, y, 0.5 − z, E = 1 − x + y, 1 − x, 0.5 − z. (c) 2-D layer of **1** via π–π interactions.

are observed (table S2). The Mn···Mn distance between the two ends of a terephthalate is 10.855(3) Å and between the ends of **L** is 12.336(3) Å. In each **L**, the dihedral angle between two benzimidazole rings is 31.9(7)°, and the dihedral angles between the mesitylene and two benzimidazole rings are 74.2(2) and 85.3(3)°. The dihedral angle between two benzimidazole rings connected to the same

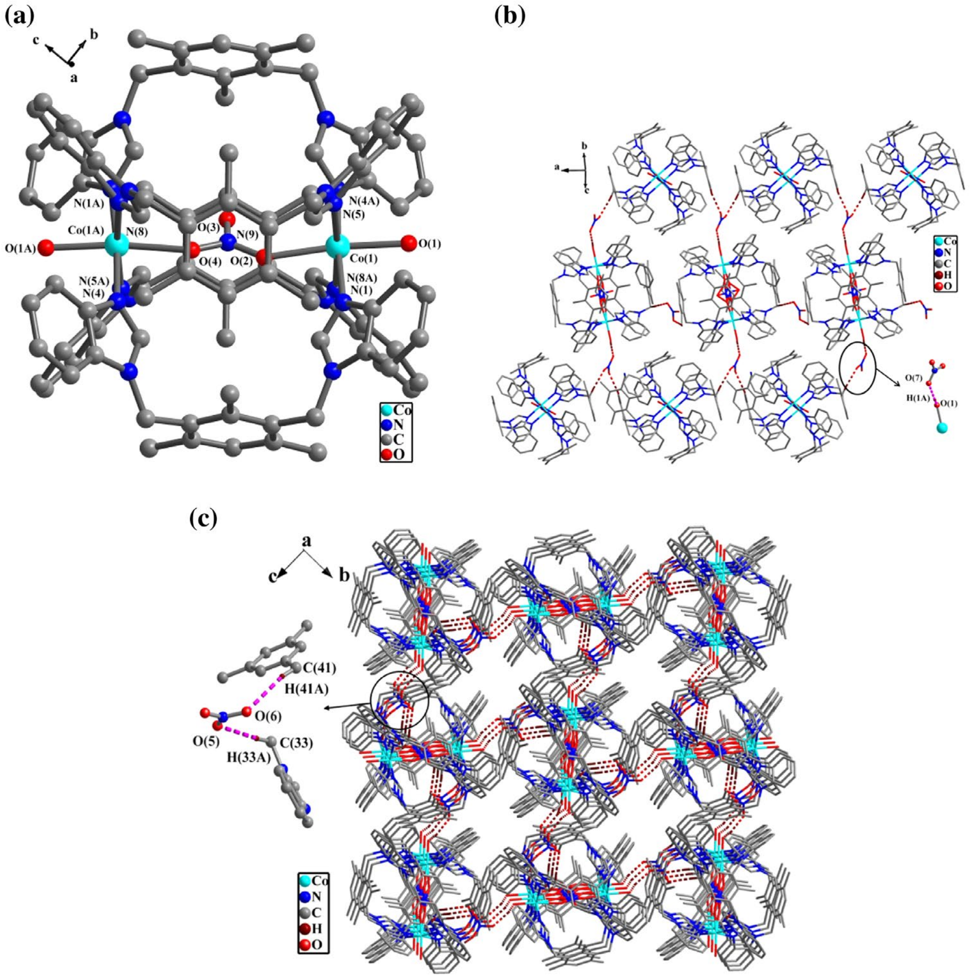


Figure 2. (a) Perspective view of **2**. All hydrogens were omitted for clarity, and the alternative site of the disordered nitrate has been omitted; Symmetry code: A = 1 − *x*, 2 − *y*, 2 − *z*. (b) 2-D supramolecular layer of **2** formed via C–H···O hydrogen bonds. (c) 3-D supramolecular architecture of **2** formed via O–H···O hydrogen bonds. In (b) and (c), all hydrogens except those participating in the C–H···O and O–H···O hydrogen bonds were omitted for clarity.

Mn(II) is 31.9(7)°. In the two carboxyl groups of each terephthalate, one is mono-coordinated and the other is di-coordinated. Each Mn(II) is six-coordinate with two nitrogens from two benzimidazole rings of two **L** and four oxygen donors (two from one chelating carboxyl group, the third oxygen from another carboxyl group, and the fourth from a methanol) in octahedral coordination. The equatorial plane of the octahedron is occupied by four oxygens (O(1), O(2), O(4A) and O(5)), with N(1) and N(4A) axial. The values of bond distances and angles in this complex are similar to those from reported Mn(II) complexes [20].

The 1-D zigzag polymeric chains of **6** are formed via **L**s and Co(II) ions (figure 6(a)). In the polymer chain, both ligands connected to the same Co(II) are very similar, but independent, and the dihedral angle between the two mesitylene rings from both ligands is 88.2(7)°. The dihedral angle between two benzimidazole rings connected to the same Co(II) is 89.2(7)°. In each ligand, the dihedral angle between two benzimidazole rings is 26.4(4)° (or 46.0(5)°), and the dihedral angles between the mesitylene and two benzimidazole rings are 79.2(8) and 82.3(2)° (or 79.8(6) and 83.4(0)°). The Co···Co separations between the two ends of **L** are 11.947(5) and 12.132(5) Å, and the angles between neighboring

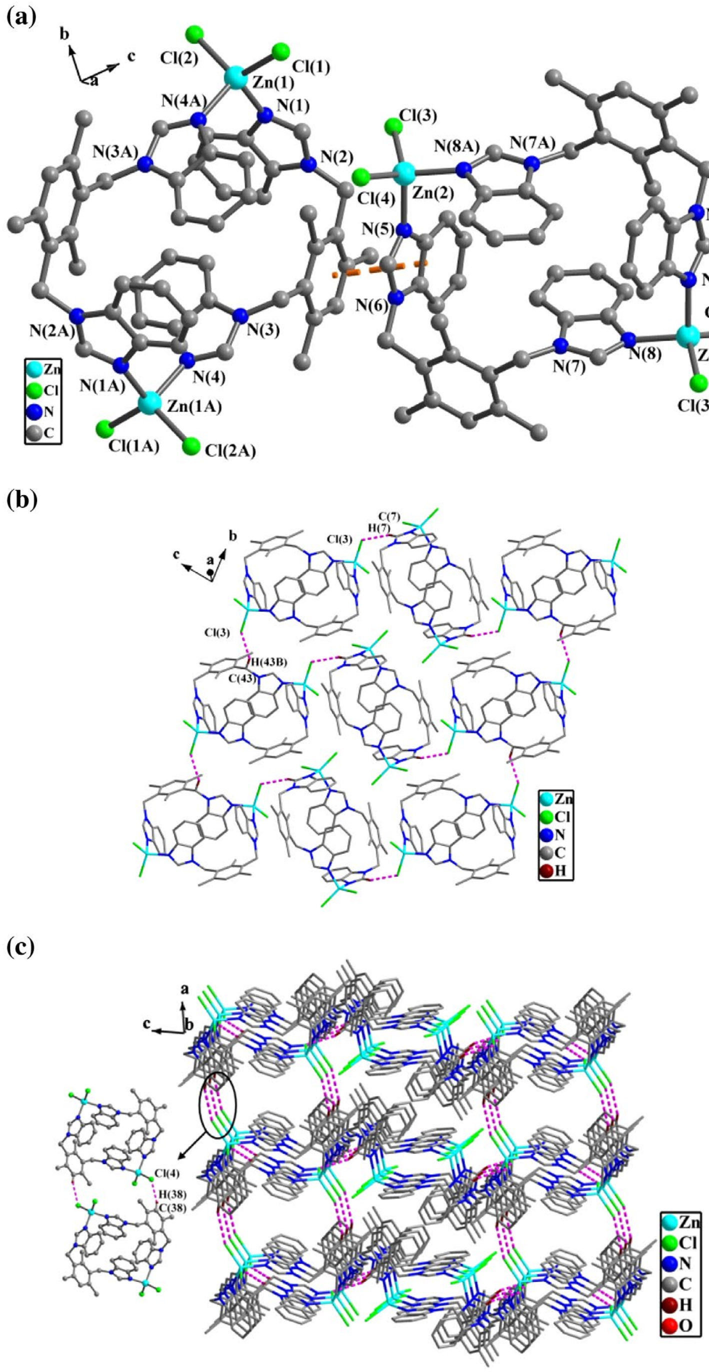


Figure 3. (a) Perspective view of **3**. All hydrogens were omitted for clarity. Symmetry code: $A = -x, 2 - y, -z$. (b) 2-D supramolecular layer of **3** formed via C–H···Cl hydrogen bond interactions. (c) 3-D supramolecular architecture of **3** formed via new C–H···Cl hydrogen bond interactions. In (b) and (c), all hydrogens except those participating in the C–H···Cl hydrogen bonds were omitted for clarity.

Co···Co···Co are 59.8(3) and 108.0(1)°. Each Co(II) has two nitrogens from two benzimidazole rings of two **L** and two chlorides in tetrahedral coordination. The values of bond distances and angles in this complex are similar to those of **2** and reported Co(II) complexes [17].

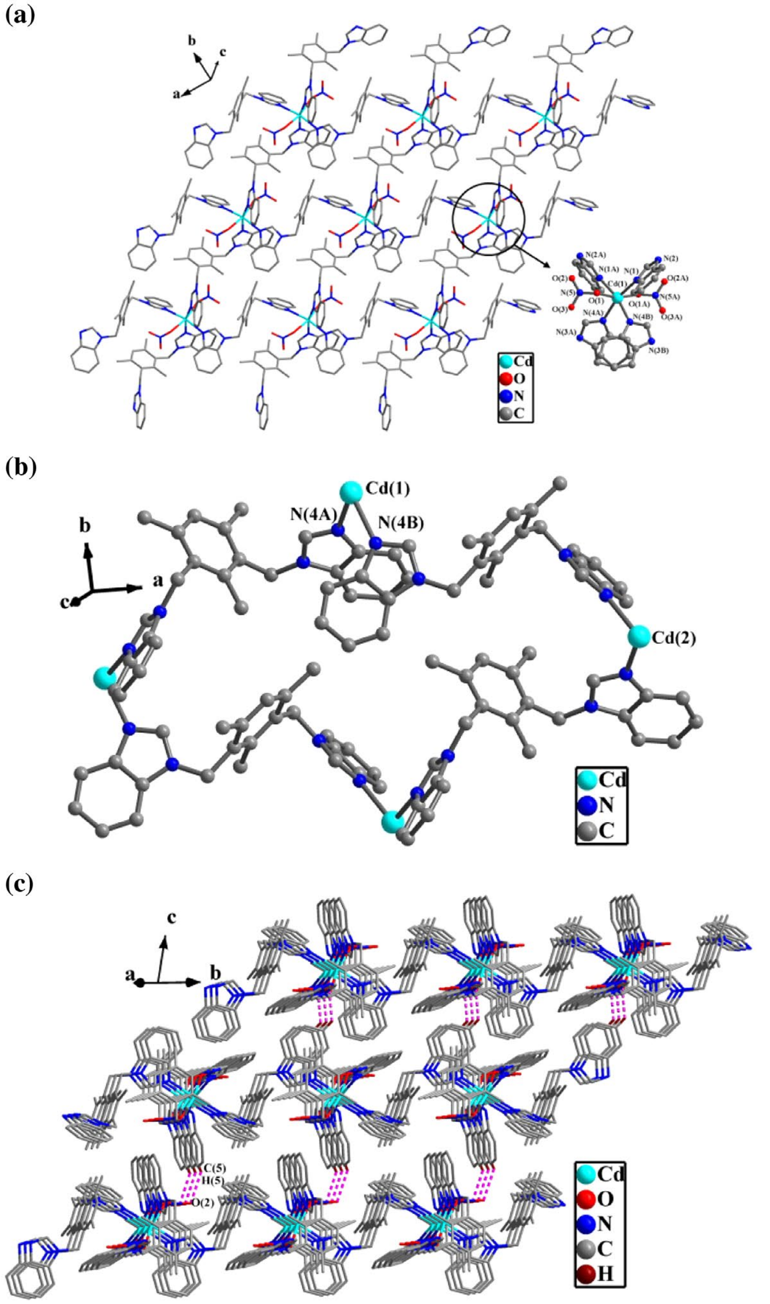


Figure 4. (a) Perspective view of **4**. All hydrogens were omitted for clarity. Symmetry code: A = -0.5 + *x*, 0.5 + *y*, *z*, B = 1.5 − *x*, 0.5 + *y*, 1.5 − *z*. (b) The 48-membered metallomacrocycle in **4**. (c) 3-D supramolecular architecture of **4** formed via C–H···O hydrogen bonds. All hydrogens except those participating in the C–H···O hydrogen bonds were omitted for clarity.

3.3. The crystal packing of **1–6**

As shown in figure 1(c), the 2-D supramolecular layer of **1** is formed via $\pi\cdots\pi$ interactions [5] from benzimidazole rings (table S2).

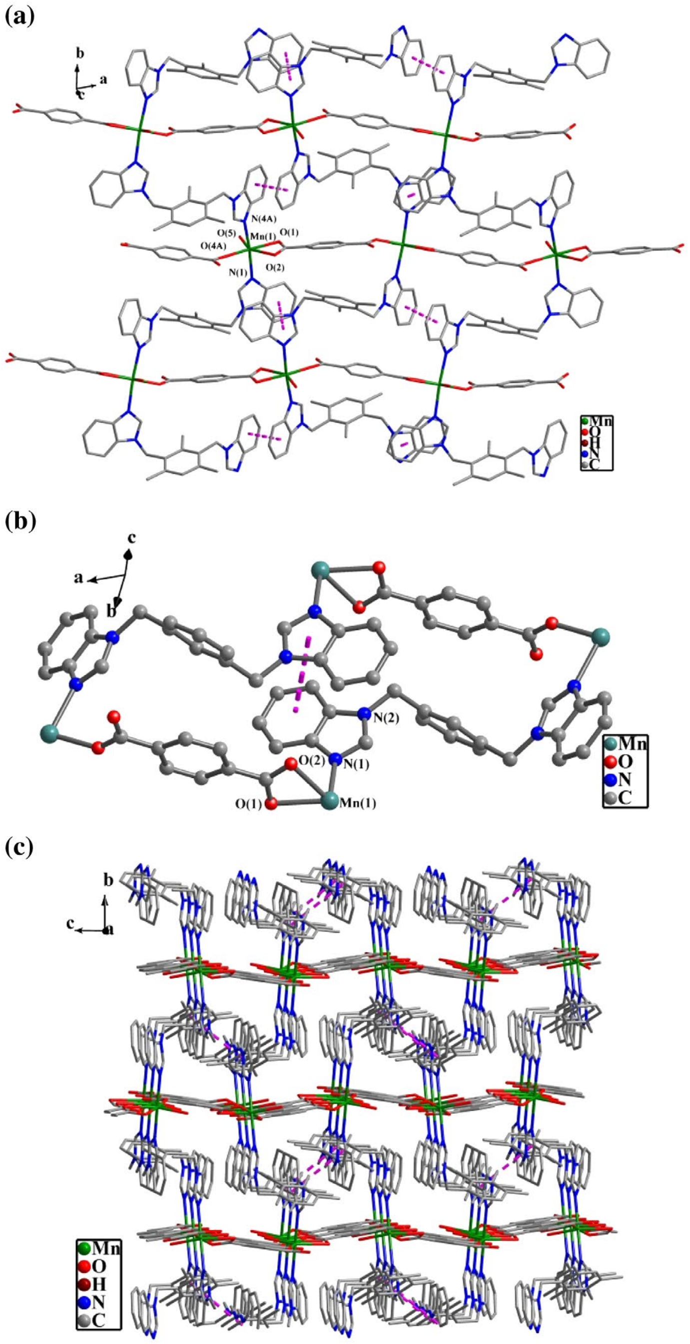


Figure 5. (a) Perspective view of **5**. (b) The 42-membered metallomacrocycle in **5**. (c) 3-D supramolecular frameworks of **5** formed via π–π interactions. In (a)–(c), all hydrogens were omitted for clarity.

The 2-D supramolecular layer of **2** (figure 2(b)) is formed via C–H···O hydrogen bonds [4(c)] (table S3). In the hydrogen bonds, the hydrogens are from methyl groups of mesitylene rings and the oxygens are from nitrate. The 2-D layers are further extended into 3-D supramolecular frameworks via similar C–H···O hydrogen bonds (figure 2(c)).

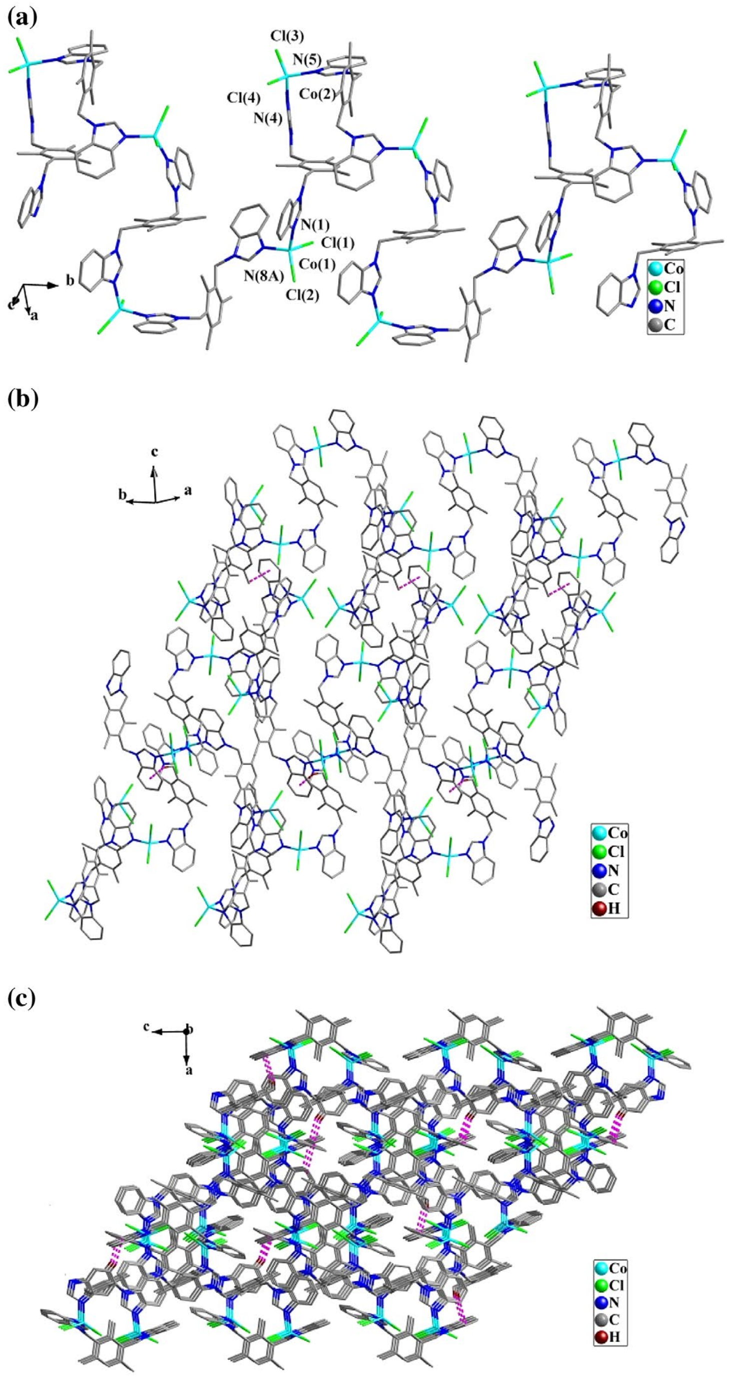


Figure 6. (a) Perspective view of **6**. All hydrogens were omitted for clarity. Symmetry code: A = $-x$, $-0.5 + y$, $0.5 - z$. (b) 2-D supramolecular layer of **6** formed via C–H···π contacts. (c) 3-D supramolecular architecture of **6** formed via new C–H···π contacts. In (b) and (c), all hydrogens except those participating in the C–H···π contacts were omitted for clarity.

The 2-D supramolecular layer of **3** is formed via C–H···Cl hydrogen bonds [4(a)] (figure 3(b)). In the hydrogen bonds, the hydrogens are from benzimidazole rings and methylene groups. The 2-D supramolecular layers are further extended into a 3-D architecture via additional C–H···Cl hydrogen bonds (figure 3(c)). In these hydrogen bonds, aromatic hydrogens from the mesitylene rings are involved.

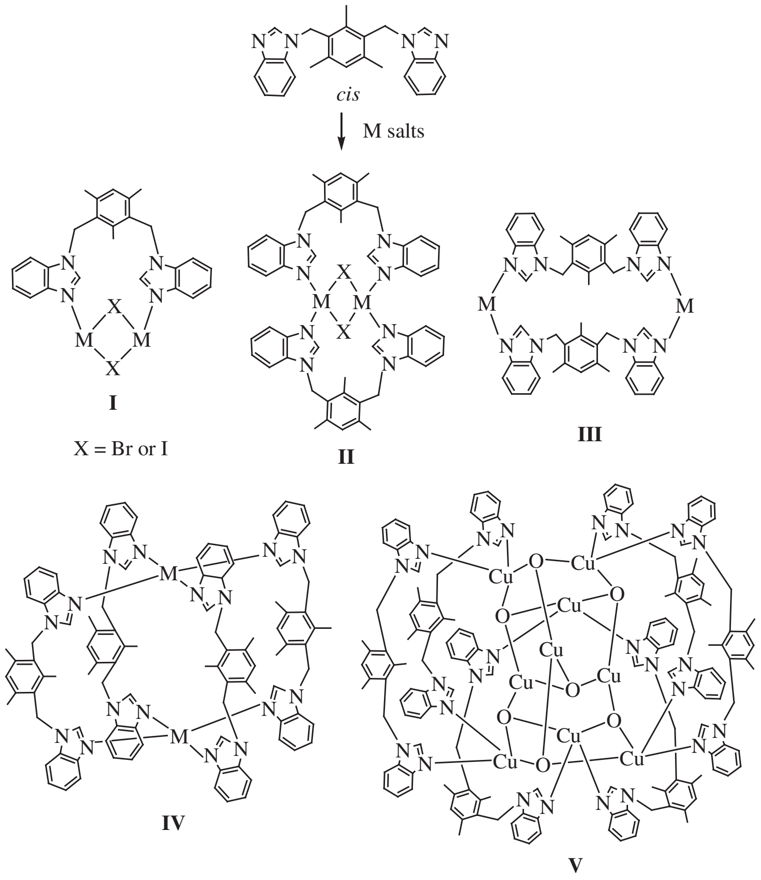
The 3-D supramolecular frameworks of **4** are formed via C–H···O hydrogen bonds (figure4(b)) between the benzimidazole rings and nitrates. The 3-D supramolecular frameworks of **5** (figure 5(c)) are formed via $\pi\cdots\pi$ interactions between benzene rings of the mesitylene units.

The 2-D supramolecular layer of **6** (figure 6(b)) is formed via C–H···π contacts [6] (table S2) between hydrogens from methyl groups and π systems from benzimidazole rings. In addition, the 2-D supramolecular layers are further extended into 3-D supramolecular networks via additional C-H···π contacts (figure 6(c)) between benzimidazole rings.

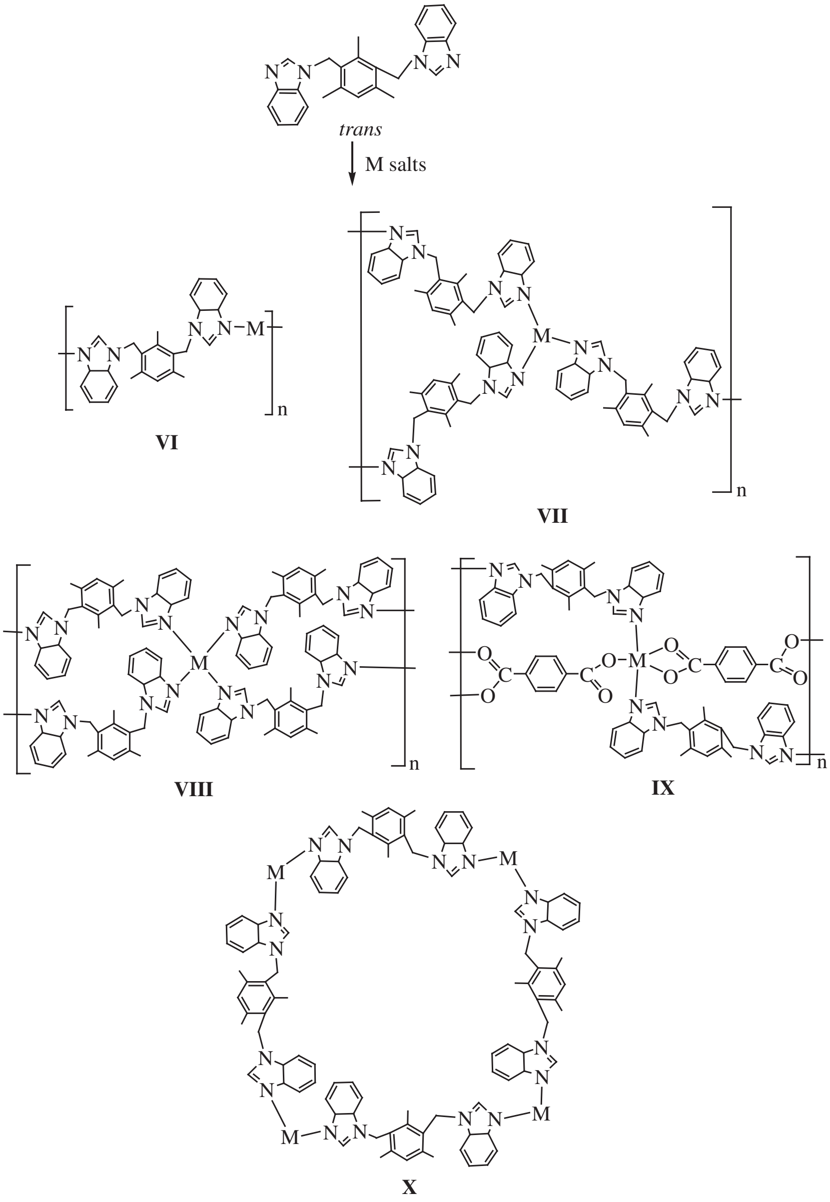
3.4. The conformations of 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (L) and its metal complexes

According to literature reports and our results reported here, the mesitylene-bridged bis-benzimidazolyl ligand **L** can form two different conformations when coordinating to metal ions, a *cis*-conformation (two benzimidazole rings lying on the same flank of the mesitylene plane) and a *trans*-conformation (two benzimidazole rings lying on the opposing flanks of the mesitylene plane) as shown in scheme 1.

When **L** adopts the *cis*-conformation, the metal complexes contain mainly five types of conformations (scheme 2): (1) the metallomacrocycle (**I**) formed by one ligand **L**, two metal ions and two halide



Scheme 2. The conformations of complexes formed by *cis*-ligand **L** and metal salts.



Scheme 3. The conformations of complexes formed by *trans*-ligand **L** and metal salts.

ions (such as [Hg_2LI_2]I_2 [21]); (2) the dimer with two metallomacrocycles (**II**) (such as [$Cd_2L_2Br_2$]Br_2 [22]), in which each metallomacrocycle is similar to that of **I**; (3) the metallomacrocycle (**III**), formed by two **L** and two metal ions; this type of complex contains an inversion center (such as **3**, [Hg_2L_2]I_4 [21], [Ag_2L_2](CF_3SO_3)$_2$ [12] and [Ag_2L_2](ClO_4)$_2$ [23]); (4) the cage-like ball (**IV**) formed by four **L** and two metal ions (such as **2** and [Cu_2L_4](ClO_4)$_4$ [12, 24]), in which an approximate symmetry plane is observed; (5) the football-like cluster (**V**) formed by six **L**, nine Cu(II) ions and seven hydroxide ions (such as **1**); this type of complex contains many symmetry planes.

When **L** is in the *trans*-conformation, the metal complexes also contain five types of conformations (scheme 3): (6) a 1-D zig-zag polymeric chain (**VI**) formed by **L** and metal ions (such as **6** and [HgLI$_2$] [21]); (7) an (M$_3$L$_2$)$_n$ type of 2-D network layer (**VII**) formed by **L** and metal ions (such as {[Ag$_3$L$_2$](ClO$_4$)$_3$}$_n$ [23]); (8) an (ML$_2$)$_n$ type of 2-D network layer (**VIII**) formed by **L** and metal ions (such as **4**); (9) the (MLL$_A$)$_n$ type of 2-D network layer (**IX**) formed by ligands and metal ions (such as **5**); (10) the M$_4$L$_4$ type of the metallomacrocycle (**X**) formed by four **L** and four metal ions (such as [Hg$_4$L$_4$]Cl$_8$ [25]).

The conformations of metal complexes based on bis-benzimidazolyl bidentate ligands with flexible linkers (such as alkanyl, oligoether and 1,2-bis(2′-ethoxy)phenyl) [7, 8, 17(f)] or semi-rigid linkers (such as –CH$_2$–benzene–CH$_2$–, –CH$_2$–trimethylbenzene–CH$_2$– and –CH$_2$–tetramethylbenzene–CH$_2$–) [16(a), 17(e)] have some differences. Their similar points are that these complexes contain some similar conformations, such as the metallomacrocycle, 1-D polymeric chain, and 2-D layer. Their main differences are that complexes from the bis-benzimidazolyl ligands with semi-rigid linkers can form cage-like conformations [2b, 12, 23, 24], and this may originate from the large steric hindrance of linkers and semi-rigidity of ligands. By contrast, metal complexes from ligands bearing flexible linkers do not easily form this type of complex.

On the whole, conformations of metal complexes based on bis-benzimidazolyl bidentate ligands are related mainly to steric hindrance and sizes of linkers, the conformation of **L**, and metal ions. The counter ions and the reaction conditions (such as the ratio of ligands with metal salts and solvents) also have influence on the conformations of complexes.

3.5. Fluorescence emission spectra of 1,3-bis(benzimidazol-1′-yl-methyl)mesitylene (L) and 1–6

As indicated in figure 7, the fluorescence emission spectra of **L** and **1**–**6** in acetonitrile at room temperature are obtained upon excitation at 245 nm (the fluorescence emission spectrum of **3** is similar to that of **1**, and the fluorescence emission spectrum of **5** is similar to that of **4**). **L** shows three weak emission bands from 280 to 320 nm, corresponding to intraligand transitions [26]. Complexes **1**–**6** exhibit analogous emission bands in same region, but they are stronger than that of **L**, which should originate from the metal perturbed intraligand processes. In **4** and **6**, a peak near 285 nm disappears and it may be ascribed to the incorporation of metal-ligand coordination interactions.

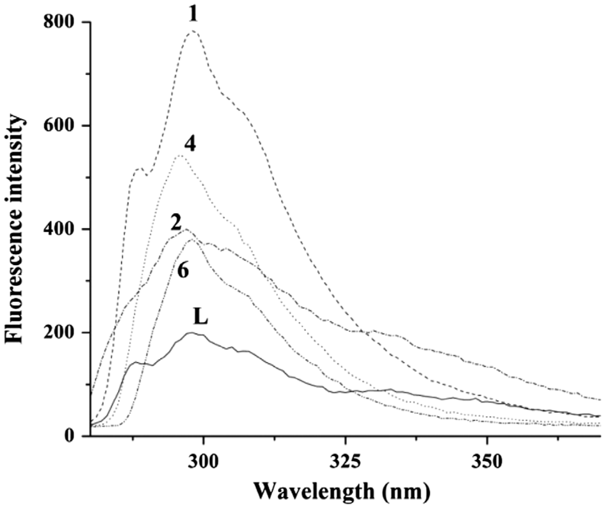


Figure 7. Emission spectra of **L**, **1**, **2**, **4** and **6** at room temperature in CH$_3$CN (5.0 × 10^{-6} mol L^{-1}) solution.

4. Conclusion

Six new copper(II), cobalt(II), zinc(II), cadmium(II), and manganese(II) complexes have been prepared and characterized. Complex **1** is a football-like cluster formed by six **L**, nine copper(II) ions, eight chlorides, and seven hydroxides. Complex **2** is a cage-like ball, in which one nitrate is in the middle of the cage through two Co-O bonds. Complex **3** is a 24-membered metallomacrocycle formed by two **L** and two Zn(II) ions. The 2-D layer with a 48-membered metallomacrocycle of **4** is formed via **L** and Cd(II) ions. In **5**, **L** and a terephthalate ion participate in coordination with Mn(II) ions to afford 2-D network layers. The 1-D polymeric chain of **6** is formed via **L** and Co(II). In the crystal packing of **1–6**, 2-D supramolecular layers or 3-D supramolecular frameworks are formed via intermolecular weak interactions, including hydrogen bonds, *π–π* interactions and C–H⋯*π* contacts. The mesitylene-bridged bis-benzimidazolyl ligand **L** exhibits two different conformations (*cis*- and *trans*-) upon coordinating to metal ions. The metal complexes based on *cis*- or *trans*- **L** each contain five types of conformations. The resultant structures of these complexes provide valuable experimental data for crystal engineering and supramolecular chemistry. Additionally, these cage-like or metallomacrocycle complexes suggest that they may have potential applications in host–guest chemistry. Further studies on new metal-organic compounds from these precursors and analogous ligands are underway.

Supplementary material

Tables of selected dihedral angles, *π–π* interactions, C–H⋯*π* contacts, and H-bonding geometry for **1**–**6**. CCDC 1407640-1407645 for **1**–**6** contain the supplementary crystallographic data for this article. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Disclosure statement

No potential conflict of interest was reported by the authors.

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