Syntheses, crystal structures and properties of Co(II) complexes with N,N′-bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine (bpb), and Cd(II), Hg(II) complexes with reduced bpb ☆

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Abstract

Five novel coordination polymers, $[Co(bpb)_2Cl_2]$ (**1**), $[Co(bpb)_2(SCN)_2]$ (**2**), $[Cd(H_4bpb)_{0.5}(dmf)(NO_3)_2]$ (**3**), $[Cd_2(H_4bpb)Br_4]$ (**4**), and $[Hg_2(H_4bpb)I_4]$ (**5**) [bpb = N,N′-bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine, H_4bpb = N,N′-bis(3-pyridylmethyl)-1,4-benzenedimethylamine], were synthesized and their structures were determined by X-ray crystallography. In the solid state, complex **1** is a 1D hinged chain, while **2** has 2D network structure with the ligand bpb serving as a bridging ligand using its two pyridyl N atoms. The imine N atoms keep free of coordination and bpb acts as a bidentate ligand in both **1** and **2**. Complexes **3**, **4**, and **5** with reduced bpb ligand, i.e. H_4bpb, show similar 2D network structure, in which ligand H_4bpb serves as a tetradentate ligand. Thermogravimetric analyses for complexes **1–5** were carried out and found that they have high thermal stability. The magnetic susceptibilities of compounds **1**, **2** were measured over a temperature range of 75–300 K.
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1. Introduction

In recent years, the construction of various coordination polymers and hydrogen-bonded networks has attracted considerable attention [1]. The main attractions of such compounds are due to their interesting structures such as rotaxanes [2], catenanes [3], helicate and knots [4], infinite 1D chains, 2D networks, and 3D frameworks [5], as well as their potential application in many fields, for example magnetism, spectroscopy, catalysis, and non-linear optical activity [6]. However, it is still difficult to design and synthesize architectures with predicted structure and properties when the ligands have more than two donors. Because the formation of architecture depends on factors such as the nature of the ligand, the coordination geometry of the metal centers,

the ratio of the ligand and metal ion, the counter ions, the solvent system, and even the pH value of the solution and crystallization conditions [7]. Recently, extensive studies have been carried out to give many new 1D, 2D, and 3D frameworks through the coordination of metal atoms with pyridone- or pyridine-based bridge ligands for example 4,4′-bipyridine and its derivatives like 1,2-bis(4-pyridyl)ethane, 1,2-bis(4-pyridyl)ethylene, and 1,3-bis(4-pyridyl)propane [8].

We focused our attentions on the reactions of metal salts with flexible multidentate ligands containing pyridyl groups since they can adopt diverse coordination modes when they react with different metal salts [9]. In our previous studies, we synthesized di-Schiff base and reduced di-Schiff base ligands with flexible ($-CH_2CH_2-$) and rigid ($1,4-C_6H_4-$) spacers, e.g. 1,2-bis(4-pyridylmethylamino)ethane (L1), 1,2-bis(3-pyridylmethyleneimino)ethane (L2), N,N′-bis(3-pyridylmethyl)-1,4-benzenedimethyleneimine (bpb), and its reduced derivative (H_4bpb) (Scheme 1). The results demonstrate that these compounds are versatile ligands
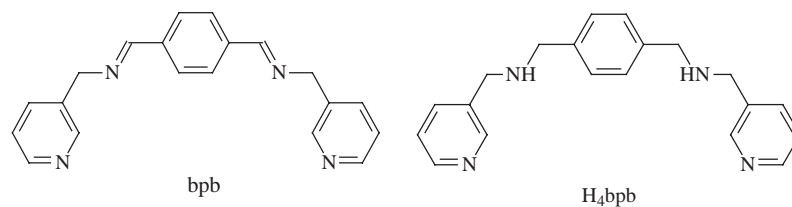
Scheme 1.

and can coordinate with various metal atoms to give 1D chains and 2D networks [10]. To further probe the influence of metal ions and the counter ions on the formation of supramolecular architectures, reactions of ligands bpb and H$_4$bpb with various metal salts were carried out. Here we reported the synthesis, structural characterizations, and properties of five new coordination polymers, namely [Co(bpb)$_2$Cl$_2$] (**1**), [Co(bpb)$_2$(SCN)$_2$] (**2**), [Cd(H$_4$bpb)$_{0.5}$(dmf)(NO$_3$)$_2$] (**3**), [dmf = coordinated *N,N*-dimethylformamide (DMF)], [Cd$_2$(H$_4$bpb)Br$_4$] (**4**), and [Hg$_2$(H$_4$bpb)I$_4$] (**5**) obtained by reactions of bpb with CoCl$_2$, Co(SCN)$_2$, and H$_4$bpb with Cd(NO$_3$)$_2$, CdBr$_2$, HgI$_2$, respectively.

2. Experimental section

All commercially available chemicals are of reagent grade and used as received without further purification. Ligands bpb and H$_4$bpb were prepared by the previously reported method [10d,e]. Solvents were purified according to standard methods. Elemental analyses for C, H, and N were made on a Perkin-Elmer 240C elemental analyzer at the Analysis Center of Nanjing University. Magnetic measurements on polycrystalline sample of complexes **1** and **2** were carried out using a CHAN-2000 Faraday magnetometer in the 75–300 K temperature range. The apparatus was calibrated with [Ni(en)$_3$]S$_2$O$_3$ (en = ethylenediamine). Diamagnetic corrections were made using Pascal's constants. Thermogravimetric analysis (TGA) was performed on a simultaneous SDT 2960 thermal analyzer. Powder samples of complexes **1–5** were heated from room temperature to 600°C under flowing N$_2$ at a heating rate of 5°C/min.

2.1. Preparation of [Co(bpb)$_2$Cl$_2$] **1**

The title complex was synthesized by layering method. A methanol solution (15 mL) of bpb (31.4 mg, 0.1 mmol) was carefully layered over a solution of CoCl$_2$ (6.5 mg, 0.05 mmol) also in methanol (10 mL). Pink block crystals were obtained after about 7 days. Yield: 65%. Compound **1** can also be obtained in methanol/H$_2$O mixed-solvents system. Cacl. elem. anal. for C$_{40}$H$_{36}$Cl$_2$CoN$_8$: C 63.33; H 4.78; N 14.77. Found: C 63.16; H 4.60; N 14.81.

2.2. Preparation of [Co(bpb)$_2$(SCN)$_2$] **2**

Complex **2** was also obtained by a layering method using bpb (31.4 mg, 0.1 mmol) in methanol (15 mL) and Co(SCN)$_2$ (8.75 mg, 0.05 mmol) in methanol (10 mL) in a test tube. High-quality pink platelet crystals formed on the 3rd day. Yield: 75%. Cacl. elem. anal. for C$_{42}$H$_{36}$CoN$_{10}$S$_2$: C 62.75; H 4.51; N 17.42. Found: C 62.72; H 4.51; N 17.39.

2.3. Preparation of [Cd(H$_4$bpb)$_2$(dmf)(NO$_3$)$_2$] **3**

A mixture of Cd(NO$_3$)$_2$ (23.6 mg, 0.1 mmol) and H$_4$bpb (63.6 mg, 0.2 mmol) in DMF (15 mL) was stirred for half an hour, then the solution was filtered. Colorless platelet crystals were obtained by slow diffusion of diethyl ether into the filtrate after about 6 days. Yield: 80%. Cacl. elem. anal. for C$_{13}$H$_{18}$CdN$_5$O$_7$: C 33.31; H 3.87; N 14.94. Found: C 33.32; H 3.85; N 14.75.

2.4. Preparation of [Cd$_2$(H$_4$bpb)Br$_4$] **4**

This compound was also prepared by a layering method by using a methanol solution (10 mL) of H$_4$bpb (15.9 mg, 0.05 mmol) and an aqueous solution (10 mL) of CdBr$_2 \cdot$4H$_2$O (34.4 mg, 0.1 mmol). Colorless block crystals were obtained after about 5 days. Yield: 55%. Cacl. elem. anal. for C$_{20}$H$_{22}$Br$_4$Cd$_2$N$_4$: C 27.84; H 2.57; N 6.49. Found: C 27.77; H 2.53; N 6.44.

2.5. Preparation of [Hg$_2$(H$_4$bpb)I$_4$] **5**

A methanol solution (10 mL) of H$_4$bpb (15.9 mg, 0.05 mmol) was carefully layered over a DMF solution (10 mL) of HgI$_2$ (45.4 mg, 0.1 mmol) in a test tube. Colorless platelet single-crystals were obtained on the 4th day. Yield: 70%. Cacl. elem. anal. for C$_{20}$H$_{22}$I$_4$Hg$_2$N$_4$: C 23.79; H 1.68; N 4.26. Found: C 23.88; H 1.74; N 4.46.

2.6. X-ray crystal structure determinations

The data collections for complexes **1–5** were carried out on a Rigaku RAXIS-RAPID Imaging Plate diffractometer using graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å) at 200 K. The structures were solved by direct method with SIR92 [11] and expanded

Table 1
Crystallographic data for complexes **1–5**

Complex	**1**	**2**
Empirical formula	$C_{40}H_{36}Cl_2CoN_8$	$C_{42}H_{36}CoN_{10}S_2$
Formula weight	758.60	803.86
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.676(5)	9.458(4)
b (Å)	9.217(6)	10.143(4)
c (Å)	12.851(9)	10.547(4)
α (deg)	100.70(5)	92.54(3)
β (deg)	103.16(6)	99.39(3)
γ (deg)	94.15(6)	108.47(3)
V (Å^3)	863.7(10)	941.9(6)
Z	1	1
Crystal size (mm)	$0.30 \times 0.20 \times 0.20$	$0.35 \times 0.30 \times 0.10$
D_c (g cm^{-3})	1.459	1.417
μ (mm^{-1})	0.695	0.613
2θ max (deg)	55.0	55.0
Reflns. collected	8557	9256
Independent reflns.	3918	4280
Obsd. reflns. ($I > 2\sigma(I)$)	2879	3077
Parameters refined	232	250
R_{int}	0.0646	0.0487
R (obsd. data)	0.0354	0.0393
wR (obsd. data)	0.0831[a]	0.0834[b]
R (all data)	0.0478	0.0576
wR_2 (all data)	0.0852	0.0873
Residual electron density (eÅ^{-3})	0.38; −0.40	0.44; −0.28

	3	**4**	**5**
Empirical formula	$C_{13}H_{18}CdN_5O_7$	$C_{20}H_{22}Br_4Cd_2N_4$	$C_{20}H_{22}I_4Hg_2N_4$
Formula weight	468.72	862.86	1227.20
Crystal system	Monoclinic	Orthorhombic	Orthorhombic
Space group	$P2_1/a$	$Pbca$	$Pbca$
a (Å)	11.538(11)	13.222(5)	13.605(6)
b (Å)	13.511(11)	12.892(4)	13.129(6)
c (Å)	12.384(11)	14.366(5)	14.887(6)
α (deg)	90.00	90.00	90.00
β (deg)	108.00(7)	90.00	90.00
γ (deg)	90.00	90.00	90.00
V (Å^3)	1836(3)	2448.7(14)	2659(2)
Z	4	4	4
Crystal size (mm)	$0.20 \times 0.15 \times 0.05$	$0.25 \times 0.20 \times 0.08$	$0.10 \times 0.10 \times 0.08$
D_c (g cm^{-3})	1.696	2.340	3.065
μ (mm^{-1})	1.234	8.279	16.192
2θ max (deg)	55.0	55.0	55.0
Reflns. collected	17595	24243	24343
Independent reflns.	4202	2807	3041
Obsd. reflns. ($I > 2\sigma(I)$)	3098	2151	1813
Parameters refined	237	136	136
R_{int}	0.0663	0.0632	0.0952
R (obsd. data)	0.0300	0.0237	0.0226
wR (obsd. data)	0.0545[c]	0.0431[d]	0.0416[e]
R (all data)	0.0509	0.0389	0.0514
wR_2 (all data)	0.0573	0.0453	0.0446
Residual electron density (eÅ^{-3})	0.58; −0.49	0.43; −0.61	0.61; −0.98

[a] $w = 1/[\sigma^2(F_o)^2 + (0.0462P)^2]$, where $P = (F_o^2 + F_c^2)/3$.
[b] $w = 1/[\sigma^2(F_o)^2 + (0.0438P)^2]$, where $P = (F_o^2 + F_c^2)/3$.
[c] $w = 1/[\sigma^2(F_o)^2 + (0.0172P)^2]$, where $P = (F_o^2 + F_c^2)/3$.
[d] $w = 1/[\sigma^2(F_o)^2 + (0.0155P)^2]$, where $P = (F_o^2 + F_c^2)/3$.
[e] $w = 1/[\sigma^2(F_o)^2]$.

Table 2
Selected bond distances (Å) and angle (deg) for complexes **1–5**

[Co(bpb)$_2$Cl$_2$] (1)			
Co1–N11	2.165(2)	Co1–Cl1	2.4456(15)
Co1–N21[a]	2.304(2)		
N11–Co1–N11[b]	180.0	N21[a]–Co1–Cl1	89.50(7)
N11–Co1–N21[a]	91.10(8)	N11–Co1–Cl1	89.75(7)
N21[a]–Co1–N21[c]	180.0	Cl1–Co1–Cl1[b]	180.0
[Co(bpb)$_2$(SCN)$_2$] (2)			
Co1–N01	2.090(2)	Co1–N111	2.180(2)
Co1–N11	2.244(2)		
N01–Co1–N01[d]	180.0	N01–Co1–N11	89.48(7)
N111–Co1–N111[d]	180.0	N11–Co1–N111	88.69(6)
N11–Co1–N11[d]	180.0	N01–C01–S01	178.6(2)
N01–Co1–N111	91.01(7)	C01–N01–Co1	163.7(2)
[Cd(H$_4$bpb)$_{0.5}$(dmf)(NO$_3$)$_2$] (3)			
Cd1–O21	2.280(3)	Cd1–O42	2.433(3)
Cd1–N11[e]	2.298(3)	Cd1–O31	2.455(3)
Cd1–N1	2.331(3)	Cd1–O32	2.492(3)
Cd1–O41	2.399(3)		
O21–Cd1–N1	170.79(7)	O41–Cd1–O42	53.00(8)
O21–Cd1–N11[e]	84.43(9)	O21–Cd1–O31	82.05(10)
O21–Cd1–O41	84.29(10)	N11[e]–Cd1–O31	133.43(7)
N11[e]–Cd1–O41	139.47(9)	N1–Cd1–O31	90.49(10)
N1–Cd1–O41	89.47(10)	O41–Cd1–O31	82.97(9)
O21–Cd1–O42	83.21(12)	O42–Cd1–O31	134.66(9)
N11[e]–Cd1–O42	87.05(9)	O21–Cd1–O32	85.98(11)
N1–Cd1–O42	98.44(11)	N11[e]–Cd1–O32	82.90(9)
N1–Cd1–O32	93.67(10)	O41–Cd1–O32	134.75(8)
O31–Cd1–O32	51.91(8)	O42–Cd1–O32	165.90(8)
C21–O21–Cd1	127.8(2)	N11–Cd1–N1[e]	104.67(9)
[Cd$_2$(H$_4$bpb)Br$_4$] (4)			
Cd1–N11	2.277(2)	Cd1–Br1	2.5361(7)
Cd1–N1	2.287(2)	Cd1–Br2	2.5589(8)
N11–Cd1–N1	103.67(8)	N11–Cd1–Br2	96.54(6)
N11–Cd1–Br1	111.40(6)	N1–Cd1–Br2	103.59(6)
N1–Cd1–Br1	114.97(6)	Br1–Cd1–Br2	123.629(16)
[Hg$_2$(H$_4$bpb)I$_4$] (5)			
Hg1–N11	2.366(4)	Hg1–I1	2.6741(9)
Hg1–N1	2.382(5)	Hg1–I2	2.6992(9)
N11–Hg1–N1	98.06(16)	N11–Hg1–I2	95.10(11)
N11–Hg1–I1	110.14(12)	N1–Hg1–I2	105.22(11)
N1–Hg1–I1	109.33(11)	I1–Hg1–I2	133.070(19)

Symmetry transformations are used to generate equivalent atoms:
[a] $-2 + x$, $-1 + y$, $-1 + z$.
[b] $2 - x$, $1 - y$, $1 - z$.
[c] $4 - x$, $2 - y$, $2 - z$.
[d] $1 - x$, $-y$, $1 - z$.
[e] $1.5 - x$, $0.5 + y$, $1 - z$.

using Fourier techniques [12]. The absorption correction for all complexes was carried out by multiscan method. All non-hydrogen atoms were refined anisotropically by the full-matrix least-squares method on F^2. The hydrogen atoms were generated geometrically. All calculations were carried out on SGI workstation using the teXsan crystallographic software package of Molecular Structure Corporation [13]. Details of the crystal

parameters, data collection and refinements for complexes **1–5** are summarized in Table 1, and selected bond lengths and angles with their estimated standard deviations are given in Table 2. Further details are provided in the Supporting Information. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-223541 (**1**), CCDC-223542 (**2**), CCDC-223543 (**3**), CCDC-223544 (**4**), and CCDC-223545 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

3. Results and discussion

3.1. Crystal structure of [Co(bpb)$_2$Cl$_2$] **1**

The crystal structure of compound **1** is shown in Fig. 1a, in which the Co(II) atom sites on the inversion center. Each Co(II) atom is six coordinated by four N atoms of the pyridyl units from four different bpb ligands with Co–N bond lengths of 2.165(2) and 2.304(2) Å (Table 2), and the additional two coordination positions are occupied by two chloride anions with the *trans* fashion (Cl1–Co–Cl1 = 180.0°). Thus the Co(II) atom in **1** adopts a slight distorted octahedral geometry with a N$_4$Cl$_2$ donor set. The two pyridyl units in each bpb ligand are nearly perpendicular to each other with a dihedral angle of 92.2°. It is noteworthy that each bpb connects two metal atoms using its two pyridyl N atoms, while the imine N atoms are free of coordination with the metal atoms in **1**. Such coordination mode makes complex **1** an infinite 1D hinged chain structure (Fig. 1a). Similar hinged chain structures have been observed in the Zn(II), Mn(II) complexes with bpb ligand [10d], and the silver(I) complex with L1 ligand [10b]. Each linker of the chain can be regarded as a ring, which is enclosed by two equivalent bpb ligands and two Co(II) atoms. The intra-ring Co···Co distance is 18.21 Å, which is similar as that in [ZnCl$_2$(bpb)$_2$] (18.10 Å), and [MnCl$_2$(bpb)$_2$] (18.28 Å) [10d]. There are intra- and inter-chain hydrogen bonds in **1**, which are summarized in Table 3. The 1D chains are connected together by inter-chain C–H···Cl hydrogen bonds between methylene C(21)–H(14) from one chain and coordinated Cl$^-$ from adjacent chain to form 2D layer structure (Fig. 1b).

3.2. Crystal structure of [Co(bpb)$_2$(SCN)$_2$] **2**

In order to investigate the influence of anion on the structure of framework, reaction of bpb ligand with Co(SCN)$_2$, instead of CoCl$_2$, was carried out and
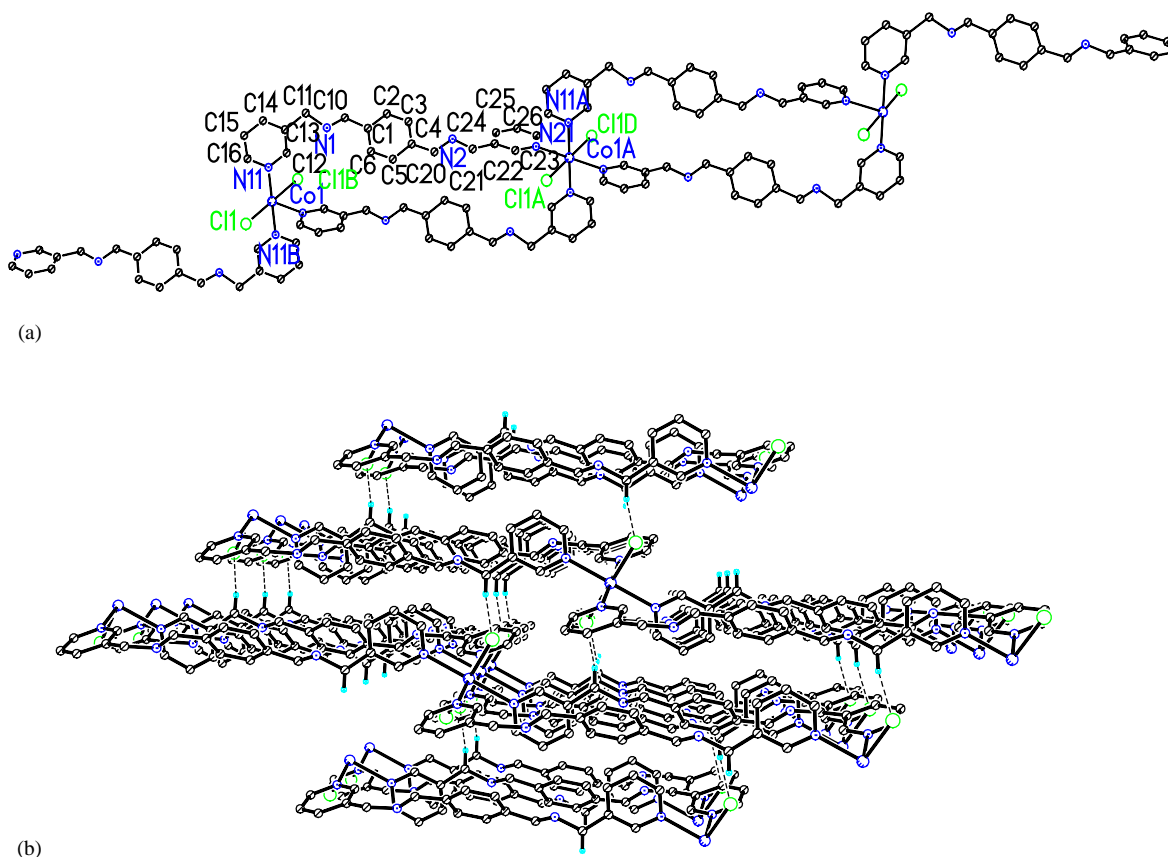
Fig. 1. (a) ORTEP view of 1D infinite chain structure of **1** with hydrogen atoms omitted for clarity. (b) Crystal packing diagram of **1** with inter-chain hydrogen bonds indicated by dashed lines.

complex **2** was isolated. Single-crystal X-ray analysis reveals that the Co(II) atom in **2** is also located at the inversion center and has similar distorted octahedral geometry with that in **1**, only the two Cl$^-$ in **1** was replaced by two SCN$^-$ in **2** (Fig. 2a). The Co–N (bpb) [2.180(2)–2.244(2) Å] and Co–N (SCN$^-$) [2.090(2) Å (Table 2)] distances in **2** are similar to the corresponding distances in [Co(SCN)$_2$(1,2-bis(4-pyridylmethyl)disulfenyl)$_2$]: Co–N (ligand) distances of 2.187(8)–2.249(6) Å and Co–N (SCN$^-$) distance of 2.085(6) Å [14]. The SCN$^-$ anion in **2** is nearly linear with a S–C–N angle of 178.6(2)°, while the connection between Co(II) atom and the SCN$^-$ group is bent since the C01–N01–Co1 angle is 163.7(2)°. Similar coordination mode of SCN$^-$ to metal atom has been observed in the complex [Zn(SCN)$_2$(piperazine)] [15]. In **2** each bpb links two Co(II) atoms using its two pyridyl N atoms and the imine N atoms do not take part in the coordination as same as those in **1**.

Even though complexes **1** and **2** have similar coordination behavior of Co(II) and bpb ligand, the framework structures of these two complexes are entirely different. As illustrated in Fig. 2b, complex **2** has a 2D grid network structure, rather than 1D chain structure in **1**. The results showed that the anion plays important role in determining the structure of frameworks in this system. In the 2D sheet of **2**, each grid with dimensions of 14.95 × 15.27 Å consists of four Co(II) atoms and four bpb ligands. Thus the 2D sheet can be regarded as a (4,4) topology if the Co(II) atoms and bpb ligands are considered as nodes and spacers, respectively. The 2D sheets are further linked together through C–H⋯N hydrogen bond (Table 3) between methylene C(111)–H(13) from one layer and uncoordinated imine N(101) atom from adjacent layer to give a 3D framework (Fig. 2c). In addition, there are three intra-layer C–H⋯N hydrogen bonds as listed in Table 3.

It should be noticed that the conformations of bpb ligand in complexes **1** and **2** are different. The ligand has "L" shape in complex **1**, while in complex **2** the conformation of bpb is a "Z" shape (Scheme 2). The dihedral angle between two terminal pyridyl groups of bpb in **2** is 22.6°, which is much smaller than that in **1** (92.2°). Such difference in the conformation of the bpb ligand cause different metal–metal distances in **1** (18.21 Å) and **2** (14.95 and 15.27 Å).

Table 3
Hydrogen bonds data for the complexes **1–5**

D–H$\cdots A$	Distance of $D\cdots A$ (Å)	Angle of D–H–A (deg)
[Co(bpb)$_2$Cl$_2$] (1)		
C21–H14$\cdots$Cl1[a]	3.749(3)	164
C22–H15$\cdots$Cl1[b]	3.277(3)	130
C26–H18$\cdots$Cl1[c]	3.309(3)	129
[Co(bpb)$_2$(SCN)$_2$] (2)		
C12–H6$\cdots$N01[d]	3.088(3)	124
C16–H9$\cdots$N01	3.124(3)	121
C111–H13$\cdots$N101[e]	3.173(3)	121
C112–H15$\cdots$N101	2.773(3)	135
[Cd(H$_4$bpb)$_{0.5}$(dmf)(NO$_3$)$_2$] (3)		
N1–H1$\cdots$O33[f]	3.033(4)	169
C11–H6$\cdots$O31	3.177(5)	132
C12–H8$\cdots$O33[g]	3.437(5)	174
C14–H9$\cdots$O32[f]	3.375(5)	162
C21–H12$\cdots$O43[h]	3.396(6)	146
C23–H16$\cdots$O43[h]	3.281(9)	149
[Cd$_2$(H$_4$bpb)Br$_4$] (4)		
N1–H1$\cdots$Br1[i]	3.503(3)	161
[Hg$_2$(H$_4$bpb)I$_4$] (5)		
N1–H1$\cdots$I1[j]	3.749(5)	155

Symmetry transformations are used to generate equivalent atoms:
[a] $3-x, 2-y, 2-z$.
[b] $2+x, 1+y, 1+z$.
[c] $4-x, 2-y, 2-z$.
[d] $1-x, -y, 1-z$.
[e] $1-x, -y, 2-z$.
[f] $1-x, 1-y, 1-z$.
[g] $0.5+x, 0.5-y, z$.
[h] $-0.5+x, 0.5-y, z$.
[i] $-x, -0.5+y, 0.5-z$.
[j] $-x, 0.5+y, 1.5-z$.

3.3. Crystal structure of [Cd(H$_4$bpb)$_{0.5}$(dmf)(NO$_3$)$_2$] 3

To elucidate the effect of organic ligand on formation and structure of framework, reduced form of bpb, namely H$_4$bpb (Scheme 1), was employed to react with metal salts, and complexes **3**, **4**, and **5** were obtained. As clearly shown in Fig. 3a, each Cd(II) center is hepta-coordinated with distorted pentagonal bipyramid geometry. The equatorial plane defined by pyridyl N(11A) atom from H$_4$bpb ligand and four O atoms (O31, O32, O41, O42) from two nitrate anions which both act as bidentate ligands has deviations less than 0.05 Å, and the Cd(II) atom lies 0.25 Å below the plane towards the N(1) atom. The axial positions are occupied by an amine N(1) atom from another H$_4$bpb ligand and one O(21) atom from coordinated dmf molecule with O(21)–Cd(1)–N(1) angle of 170.79(7)° (Table 2). Thus each Cd(II) atom connects two H$_4$bpb ligands, rather than four in **1** and **2**. The Cd–N bond lengths are 2.331(3) and
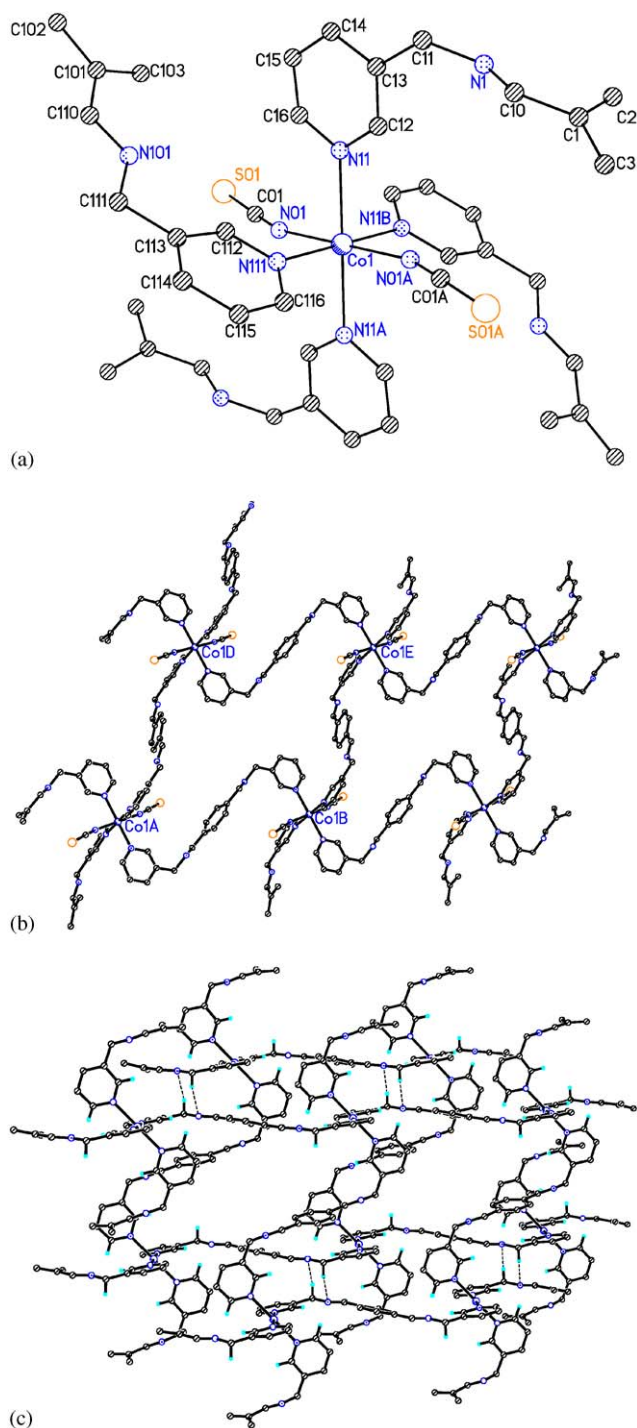

(a)

(b)

(c)

Fig. 2. (a) ORTEP representation of **2** showing the coordination of Co(II), hydrogen atoms were omitted for clarity. (b) The 2D grid structure of **2**. (c) Crystal packing diagram of **2** with inter-layer hydrogen bonds indicated by dashed lines.

2.298(3) Å. And the Cd–O (from dmf) bond distance is 2.280(3) Å, which is shorter than those of Cd–O (from NO$_3^-$ group) ranging from 2.399(3) to 2.492(3) Å as listed in Table 2. The bond lengths are similar to those observed in the reported complex [Cd(NO$_3$)$_2$(4,4′-bipy)$_2$]$\cdot$2C$_6$H$_4$Br$_2$ [16]. It is interesting that in **3** with
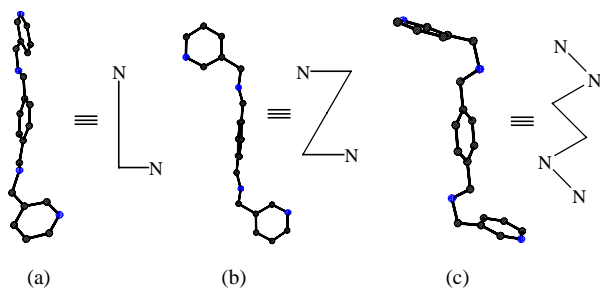
Scheme 2. (a) L shape, (b) Z shape, and (c) zigzag shape.

the reduced H_4bpb ligand, all four N atoms of each ligand with a zigzag shape (Scheme 2) coordinate with metal atoms, which may probably be ascribed to the flexibility of H_4bpb. Two pyridyl units within the same H_4bpb ligand are parallel to each other and the dihedral angle between the pyridyl ring and the benzene ring planes is 66.9°. Thus, each H_4bpb ligand links four Cd(II) atoms with its four N atoms and each Cd(II) connects two different H_4bpb ligands to generate a 38-membered rings, which are further expanded through Cd–N coordination bonds to generate a undulant 2D grid network (Fig. 3b). The 2D network structure in **3** is different from that of **2**, which can be seen more clearly from a simplified 2D network shown in Fig. 3c where only the amine N atoms are presented. Each of the grids is a hexagon defined by six N atoms in a chair conformation. The N···N edge distances are 7.49 Å for N(1C)···N(1BC) and N(1B)···N(BB), 6.82 Å for N(1C)···N(1AB), N(1AB)···N(1B), N(1BC)···N(1CD), and N(1CD)···N(1BB) (Fig. 3b). The coordinated NO_3^- anions and dmf molecules are towards outside of the layer as shown in Fig. S1.

In the 2D network of **3**, the two parallel pyridine rings in head-to-end fashion sandwiched a benzene ring as exhibited in Fig. 3b with dashed line and there are π–π staking interactions between them. The dihedral angle between the benzene ring and the pyridine ring is 10.9° and the centroid–centroid distance between them is 3.74 Å. Furthermore, there are C–H···O and N–H···O hydrogen bonds in complex **3** with the N···O distance of 3.033(4) Å, the N(1)–H(1)–O(33) angle of 169°, and the C···O distances ranging from 3.177(5) to 3.437(5) Å, C–H–O angles ranging from 132° to 174° (Table 3) [17]. The hydrogen bonds give rise to a 3D framework in the crystalline state of **3** (Fig. S1). The existence and structural importance of such weak hydrogen bonds have been discussed [17,18].

3.4. Crystal structure of $[Cd_2(H_4bpb)Br_4]$ **4** and $[Hg_2(H_4bpb)I_4]$ **5**

Single-crystal X-ray analysis reveals that complexes **4** and **5** are isomorphous and isostructural since they crystallize in the same space group with similar cell
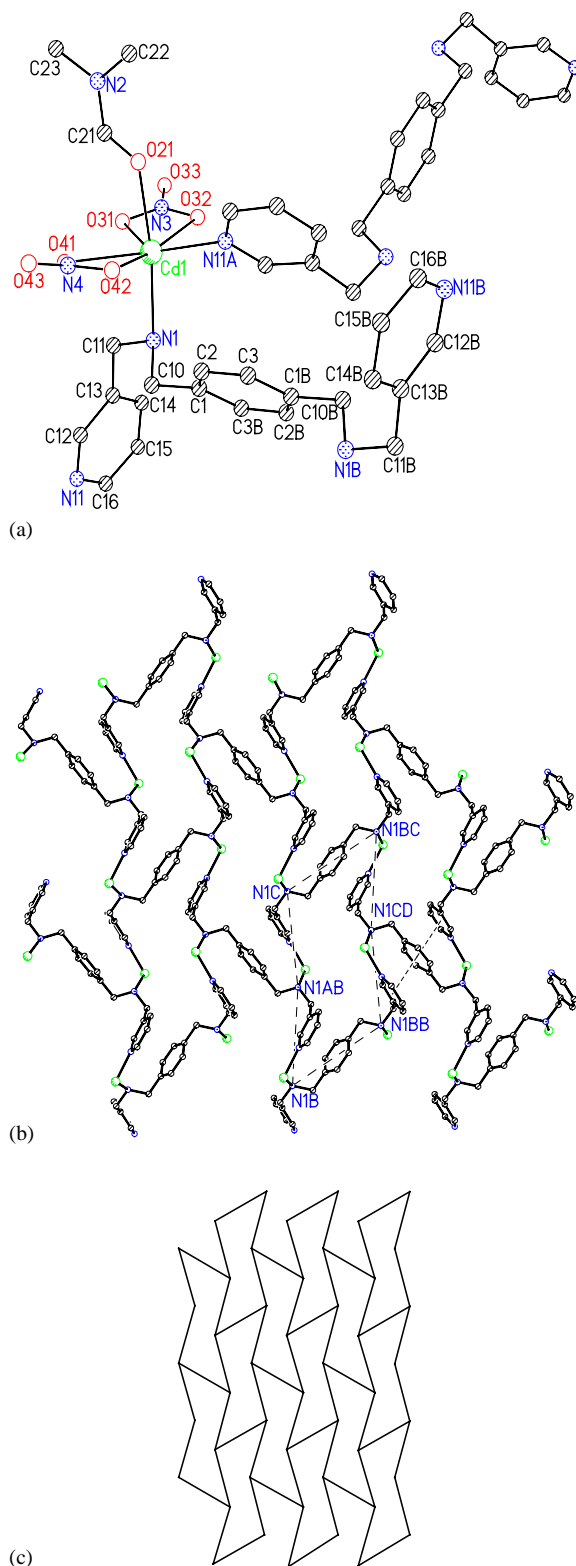

(a)

(b)

(c)

Fig. 3. (a) Coordination environment of Cd(II) in **3**, hydrogen atoms were omitted for clarity. (b) 2D grid network structure of **3**; π–π staking interactions are indicated by dashed lines (hydrogen atoms and nitrate anions, DMF were omitted for clarity). (c) Schematic 2D sheet consists of six-membered rings and only the amine N atoms are presented.
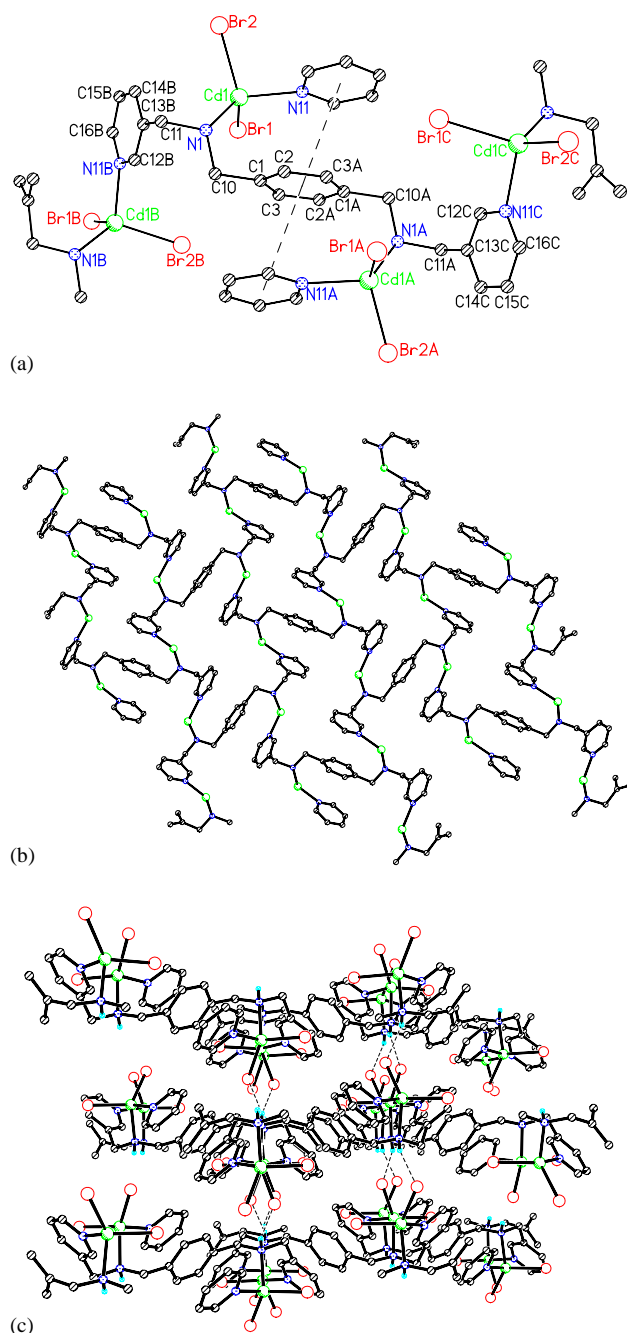
Fig. 4. (a) ORTEP representation of **4**, hydrogen atoms were omitted for clarity. (b) 2D network of **4** in which bromide and hydrogen atoms were omitted for clarity. (c) 3D network of compound **4** linked by hydrogen bonds indicated by dashed lines.

parameters as summarized in Table 1. Thus we just describe the structure of **4** as an example. As shown in Fig. 4a, the Cd(II) center is four coordinated by two bromide anions [Cd–Br 2.5361(7)–2.5589(8) Å] and two N atoms [Cd1–N, 2.277(2)–2.287(2) Å] from the pyridyl group of one ligand and the amine group of another ligand with a distorted tetrahedron geometry since the coordination angles range from 96.54(6)° to

123.629(16)° (Table 2). Each H$_4$bpb ligand links four Cd(II) atoms with its four N atoms and each Cd(II) connects two H$_4$bpb ligands to generate a 38-membered ring which are same as those in complex **3**. Therefore, a similar undulant 2D rhombohedral grid network was achieved for **4** (Fig. 4b). The ligand H$_4$bpb also adopts a zigzag shape with the dihedral angle of 76.4° (71.3° in **5**) between the pyridyl group and the benzene ring, which is larger than that in **3** (66.9°), and the two terminal pyridyl groups are also parallel to each other in the *trans* position. In the 2D network, a benzene ring located in the middle of two parallel pyridyl rings from two ligands with the dihedral angle of 9.8° (9.5° for **5**) between the benzene ring and the pyridine ring (Figs. 4a and b). Thus, there are also π–π staking interactions between the two pyridine rings and the benzene ring with a distance of 3.69 Å (3.82 Å in the case of **5**), which is close to that in compound **3** (3.74 Å). As shown in Fig. 4c, the 2D networks are further connected by inter-layer N–H⋯Br hydrogen bonds to form 3D network with a distance of 3.503(3) Å for N⋯Br and an angle of 161° for N(1)–H(1)–Br(1) (Table 3).

Due to its flexibility, the ligands H$_4$bpb in the complexes **3**–**5** adopt a zigzag conformation (Scheme 2c) with all of the four N atoms coordinated with the metal atoms. While in the complexes **1** and **2**, the ligands bpb serve as bridging ligands with only two N atoms of the pyridyl units coordinating to the metal atoms. The non-coordination of the imine N atoms of the bpb ligand may be caused by the low electron density around the imine N atoms. Since the conjugation of the –C=N– groups with the central benzene ring group may decrease the electron density around the imine N atoms, so that the donation of the imine N atoms is weakened [10d]. While in the reduced ligand H$_4$bpb, the conjugations disappeared and thus the amine N atoms can coordinate with metal atoms.

3.5. Magnetic properties

The magnetic susceptibilities of polycrystalline powders of compounds **1** and **2** were measured over a temperature range of 75–300 K. The observed effective magnetic moments are 4.98 μ_B ($\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}) for **1** and 4.85 μ_B for **2** at 300 K, which are within the expected range (4.3–5.2 μ_B) for isolated d^7 high-spin, six-coordinated Co(II) complexes [19] and agree well with other observed effective magnetic moments of Co(II) complexes [20]. The plots of the observed effective magnetic moments vs. the temperature for the two compounds are shown in Fig. 5. The measured magnetic moments decreased to the values of 4.23 and 4.03 μ_B at 75 K for complexes **1** and **2**, respectively. These magnetic data show that no strong magnetic interactions between the Co(II) centers bridged by bpb ligands due to the long inter-metallic distances revealed by X-ray crystal
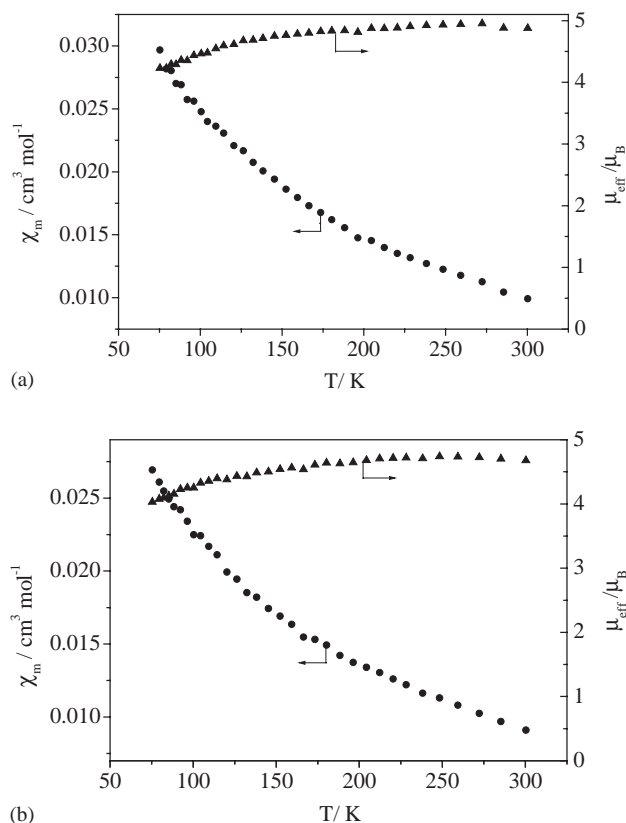
Fig. 5. (a) Temperature dependences of χ_M (●) and μ_B (▲) for complex **1**. (b) Temperature dependences of χ_M (●) and μ_B (▲) for complex **2**.

structures [18.21 Å (intra-chain) in complex **1**; 14.95 Å and 15.27 Å in complex **2**].

3.6. Thermogravimetric analyses

All the synthesized complexes are air stable. TGA for complexes **1–5** were carried out to exam their thermal stabilities by heating the samples up to 600°C. The TGA data of **1** show that the complex is stable up to 210°C. And **2** has similar thermal behavior. Decomposition of **2** begins from 205°C. The TGA data of **3** show that the first weight loss of 15.1% between 170°C and 212°C corresponds to the loss of one dmf molecule per formula unit (calculated 15.4%). After loss of dmf, the complex is stable up to 280°C. The TGA curve for **4** shows that the complex is stable up to 235°C. The TGA data show that **5** is stable up to 200°C, which has lower thermal stability than **4**.

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