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# Syntheses and characterizations of four metal coordination polymers constructed by the pyridine-3,5-dicarboxylate ligand

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# Abstract

A series of metal-organic frameworks, namely  $[Ni(PDB)(H_2O)]_n$  (1),  $[Pb(PDB)(H_2O)] \cdot (H_2O)$  (2),  $[Co_2(PDB)_2(bpy)_2(H_2O)_4] \cdot 4H_2O$ (3) and  $[Co_2(PDB)_2(phen)_2]_n$  (4)  $(H_2PDB = pyridine-3,5-dicarboxylic acid, bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline), have$ been synthesized based on pyridine-3,5-dicarboxylate acid and two neutral chelate ligands, with different metal ions such as Ni<sup>II</sup>, Co<sup>II</sup>and Pb<sup>II</sup>, under hydrothermal conditions. The framework structures of these polymeric complexes have been determined by the Xray single crystal diffraction technique. In the four complexes, the pyridine-3,5-dicarboxylate acid ligand exhibits diverse coordinationmodes, which play an important role in the construction of metal-organic frameworks. The thermal analyses of these four complexeshave been measured and discussed. In addition, complex**2**shows strong phosphorescent emission at room temperature and the magneticmeasurement of the polymer of**4**reveals a typical antiferromagnetic exchange.© 2007 Elsevier Ltd. All rights reserved.

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Keywords: Coordination polymer; Pyridine-3,5-dicarboxylate acid; Crystal structure; Phosphorescence; Magnetic property

# 1. Introduction

The construction of metal-organic framework (MOF) structures is receiving increasing attention because of the potential applications of novel functional materials such as magnetism, gas storage, molecular sieves, size- and shape-selective catalysis and electric conductivity [1,2]. However, rational design and synthesis of MOFs with unique structures and functions is still hard work. Therefore, the rational exploitation of the knowledge of the coordination geometry of a metal and ligand structure continues to be an important synthetic strategy widely used in the construction of metal-organic framework structures [3]. Organic aromatic polycarboxylate ligands as an important family of multidentate O-donors have been employed

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in the preparation of such metal-organic compounds [4]. Pyridyl dicarboxylic acids containing N- and O-donors are also particularly attractive as excellent building blocks with charge and multi-connecting ability [5]. In particular, pyridine-2,4-dicarboxylate acid, pyridine-3,4-dicarboxylate acid, pyridine-2,5-dicarboxylate acid and pyridine-2,6dicarboxylate acid have been widely used by Kitagawa, Wang, Cao, Zhu and their co-workers in the construction of high-dimensional structures with large pores or undulated layers [5-8]. In contrast, pyridine-3,5-dicarboxylic acid [9], as a member of the multicarboxylate ligands containing N-donors, is rarely used. In this context, the majority of this research focuses on the synthesis, structural elements and properties of complexes constructed from different divalent metal ions and pyridine-3,5-dicarboxylic acid as well as two chelate bpy-liked ligands, and the utility of these versatile ligands in the fabrication of functional organic-inorganic hybrid materials is contemplated. In this paper, four new coordination complexes, namely,

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 $[Ni(PDB)(H_2O)] (1), [Pb(PDB)(H_2O)] \cdot (H_2O) (2), \\ [Co_2(PDB)_2(bpy)_2(H_2O)_4] \cdot 4H_2O (3) and [Co_2(PDB)_2-(phen)_2] (4) (H_2PDB = pyridine-3,5-dicarboxylic acid, \\ bpy = 2,2'-bipyridine, phen = 1,10-phenanthroline), were \\ prepared and investigated to determine the influence of metal ions and chelate ligands on the formation of such metal-organic frameworks. In addition, the photoluminescent property of complex$ **2**and the magnetic property of complex**4**were measured and discussed.

# 2. Experimental

## 2.1. Materials and analyses

All chemicals were commercially purchased and used without further purification. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400CHN Elemental Analyzer. FT-IR spectra were recorded in the range 400–4000 cm<sup>-1</sup> on an Alpha Centaurt FT/IR spectrophotometer as KBr pellets. The emission/excitation spectra were recorded on a Varian Cary Eclipse spectrometer. TG analyses were performed on a Perkin–Elmer TGA7 instrument in flowing N<sub>2</sub> with a heating rate of 10 °C min<sup>-1</sup>. Variable-temperature magnetic susceptibility data were obtained on a SQUID magnetometer (Quantum Design, MPMS-5) in the temperature range 5–300 K with an applied field of 1000 Oe.

# 2.2. Syntheses of the complexes

# 2.2.1. $[Ni(PDB)(H_2O)]$ (1)

A mixture of NiCl<sub>2</sub> · 6H<sub>2</sub>O (0.072 g, 0.3 mmol), pyridine 3,5-dicarboxylate acid (0.05 g, 0.3 mmol), NaOH (0.024 g, 0.6 mmol) and H<sub>2</sub>O (10 ml) was heated at 150 °C for 3 days in a 25 ml Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled down to room temperature, green block crystals were produced in a yield of 60%. Elem. *Anal.* Calc. for complex C<sub>7</sub>H<sub>5</sub>NiNO<sub>5</sub> (1) (241.83): C, 34.77; H, 2.07; N, 5.79. Found: C, 34.80; H, 2.11; N, 5.71%. IR (cm<sup>-1</sup>, KBr): 3398 (br), 1607 (s), 1560 (s), 1432 (m), 1377 (s), 1302 (m), 1124 (m), 1035 (w), 936 (w), 835 (m), 775 (m), 697 (m), 564 (sm), 437 (m).

## 2.2.2. $[Pb(PDB)(H_2O)] \cdot (H_2O)$ (2)

An identical procedure to **1** was followed to prepare **2** except NiCl<sub>2</sub> · 6 H<sub>2</sub>O was replaced by Pb(NO<sub>3</sub>)<sub>2</sub> (0.099 g, 0.3 mmol), yield 65%. Elem. *Anal.* Calc. for complex C<sub>7</sub>H<sub>7</sub>PbNO<sub>6</sub> (**2**) (408.33): C, 20.59; H, 1.71; N, 3.43. Found: C, 20.50; H, 1.75; N, 3.40%. IR (cm<sup>-1</sup>, KBr): 3396 (br), 3080 (m), 1603 (s), 1557 (s), 1361 (vs), 1261 (m), 1147 (ms), 1208 (w), 958 (w), 911 (w), 821 (m), 767 (m), 725 (s), 681 (m), 669 (w), 573 (w), 515 (w), 430 (w).

#### 2.2.3. $[Co_2(PDB)_2(bpy)_2(H_2O)_4] \cdot 4H_2O(3)$

A mixture of  $Co(OAc)_2 \cdot 4H_2O$  (0.075 g, 0.3 mmol), pyridine 3,5-dicarboxylate acid (0.05 g, 0.3 mmol), 2,2'-

bipyridine (0.031 g, 0.02 mmol), NaOH (0.024 g, 0.6 mmol) and H<sub>2</sub>O (10 ml) was heated at 150 °C for 3 days in a 25 ml Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was slowly cooled down to room temperature, pink block crystals were produced in a yield of 70%. Elem. *Anal.* Calc. for complex  $C_{34}H_{38}Co_2N_6O_{16}$  (3) (904.56): C, 45.15; H, 4.20; N, 9.29. Found: C, 45.10; H, 4.27; N, 9.31%. IR (cm<sup>-1</sup>, KBr): 3420 (br), 1608 (vs), 1566 (s), 1489 (w), 1478 (w), 1438 (m), 1397 (m), 1375 (s), 1282 (w), 1151 (w), 1125 (w), 932 (w), 771 (s), 736 (mm), 695 (m), 529 (m), 439 (m).

## 2.2.4. $[Co_2(PDB)_2(phen)_2]$ (4)

An identical procedure to **3** was followed to prepare **4** except 2,2'-bipyridine was replaced by 1,10-phenanthroline (0.031 g, 0.02 mmol), yield 50%. Elem. *Anal.* Calc. for complex  $C_{38}H_{22}Co_2N_6O_8$  (**4**) (808.48): C, 56.45; H, 2.72; N, 10.39. Found: C, 56.38; H, 2.81; N, 10.32%. IR (cm<sup>-1</sup>, KBr): 3420 (br), 3056 (m), 2359 (w), 1663 (s), 1610 (s), 1576 (s), 1516 (m), 1496 (w), 1442 (m), 1404 (s), 1354 (s), 1311 (s), 1284 (s), 1226 (w), 1144 (w), 1125 (m), 1104 (w), 1047 (w), 1031 (w), 936 (w), 918 (w), 866 (w), 846 (s), 818 (w), 771 (s), 725 (s), 715 (m), 696 (m), 641(w), 610(w), 564 (w), 438 (w).

# 2.3. X-ray crystallography analysis

Crystal data, data collection and refinement details for 1-4 are given in Table 1. X-ray diffraction measurements were performed using a Bruker APXII CCD diffractometer with graphite monochromated Mo K $\alpha$  ( $\lambda = 0.71073$  Å) radiation. An empirical absorption correction was applied using the sadabs computer program [10]. The coordinates of the heavy atoms were determined by direct methods with the SHELXS program [11]. The coordinates and anisotropic thermal displacement parameters for all non-hydrogen atoms were refined by the least squares methods based on  $F^2$  using the SHELXL97 program [12]. The H atoms attached to C atoms were positioned geometrically, with  $U_{\rm iso}$  values derived from  $U_{\rm eq}$  values of the corresponding C atom. The hydrogen atoms from water molecules were directly located from successive Fourier differences syntheses and were included in the calculation with estimated isotropic displacement parameters without refinement, with O-H distances restrained (DFIX) to 0.85(2) Å, in order to ensure a chemically reasonable geometry for these molecules.

### 3. Results and discussion

#### 3.1. Description of the structures

Crystallographic and structural refinement data for the compounds are given in Table 1. Selected bond distances and angles for 1, 2, 3 and 4 are shown in Tables 2–5, respectively.

Table 1 Crystal data and structure refinement for 1–4

	1	2	3	4	
Empirical formula	C7H5NiNO5	C <sub>7</sub> H <sub>7</sub> PbNO <sub>6</sub>	C <sub>34</sub> H <sub>38</sub> Co <sub>2</sub> N <sub>6</sub> O <sub>16</sub>	C <sub>38</sub> H <sub>22</sub> Co <sub>2</sub> N <sub>6</sub> O <sub>8</sub>	
Formula weight	241.83	408.33	904.56	808.48	
<i>T</i> (K)	293(2)	293(2)	293(2)	293(2)	
$\lambda(\dot{A})$	0.71069	0.71069	0.71069	0.71069	
Crystal system	monoclinic	monoclinic	triclinic	monoclinic	
Space group	$P2_1/c$	$P2_1/n$	$P\overline{1}$	$P2_1/c$	
a (Å)	7.751(5)	10.3826(6)	9.542(5)	9.677(5)	
b (Å)	15.049(5)	6.8387(4)	12.351(5)	31.194(5)	
c (Å)	6.435(5)	12.7710(8)	16.654(5)	11.181(5)	
α (°)	90	90	84.766(5)	90	
$\beta$ (°)	108.440(5)	92.277(1)	73.737(5)	108.069(5)	
γ (°)	90	90	86.728(5)	90	
$V(Å^3)$	712.1(8)	906.07(9)	1875.3(14)	3029(2)	
Ζ	4	4	2	4	
$D_{\text{calc}} (\text{g cm}^{-3})$	2.256	2.993	1.602	1.674	
$\mu (\mathrm{mm}^{-1})$	2.716	18.630	0.968	1.103	
<i>F</i> (000)	488	744	932	1640	
Reflections collected	4335	5039	11709	19926	
Independent reflections $[R_{int}]$	1654	2132	8435	7628	
Data/restraints/parameters	1654/0/135	2132/0/152	8435/24/587	7628/0/487	
Goodness-of-fit on $F^2$	1.039	1.004	0.985	0.940	
$R_1^{\mathrm{a}}$	0.0290	0.0222	0.0366	0.0393	
$wR_2^{\rm b}$	0.0752	0.0492	0.1148	0.1064	

$${}^{b}wR_{2} = \sum [w(F_{0}^{2} - F_{c}^{2})^{2}] / \sum [w(F_{0}^{2})^{2}]^{1/2}.$$

- - - -

Table 2			
Salastad hand h	angths (Å) and a	nalas (°) fan aan	mound 1

Sciected bolid length	its (A) and angles		
Ni(1)-O(4)	2.005(2)	Ni(1)–N(2)	2.064(2)
Ni(1)–O(3)	2.094(3)	Ni(1)-O(1)	2.115(2)
Ni(1)-O(5)	2.120(3)	Ni(1)-O(2)	2.143(2)
O(4)-Ni(1)-N(2)	109.67(8)	O(4)-Ni(1)-O(3)	87.39(9)
N(2)-Ni(1)-O(3)	89.0(1)	O(4) - Ni(1) - O(1)	92.35(7)
N(2)-Ni(1)-O(1)	157.85(8)	O(3)-Ni(1)-O(1)	89.7(1)
O(4)-Ni(1)-O(5)	92.37(7)	N(2)-Ni(1)-O(5)	91.35(8)
O(3)-Ni(1)-O(5)	179.64(9)	O(1)-Ni(1)-O(5)	90.07(8)
O(4)-Ni(1)-O(2)	153.80(7)	N(2)-Ni(1)-O(2)	96.17(8)
O(3)-Ni(1)-O(2)	88.88(8)	O(1)-Ni(1)-O(2)	61.70(7)
O(5)-Ni(1)-O(2)	91.22(7)		

Table 3 Selected bond lengths (Å) and angles (°) for compound  ${\bf 2}$ 

Pb(1) = O(1W)	2.392(4)	Pb(1) - O(2)	2,463(3)
Pb(1)-O(5)	2.492(3)	Pb(1) - O(1)	2.685(3)
Pb(1)–N(1)	2.824(3)		
O(1W)–Pb(1)–O(2)	77.9(1)	O(1W)–Pb(1)–O(5)	74.8(1)
O(2)–Pb(1)–O(5)	83.1(1)	O(1W)-Pb(1)-O(1)	74.4(1)
O(2)–Pb(1)–O(1)	50.7(1)	O(5)-Pb(1)-O(1)	128.5(1)

# $3.1.1. [Ni(PDB)(H_2O)] (1)$

Single crystal X-ray diffraction analysis shows that the asymmetric unit of compound 1 contains one Ni<sup>II</sup> ion, one PDB ligand and one coordinated water molecule. As shown in Fig. 1, each Ni<sup>II</sup> ion adopts distorted octahedral coordination geometry supplied by one N atom and five O atoms. Three carboxylate oxygen atoms (O1,O2,O4) and the nitrogen atom (N2) (Ni1–N2 2.064(2) Å) comprise the

Table 4								
Selected	bond	lengths (Å	() and	angles	(°)	for	compou	nd 3

$\begin{array}{c cccc} \hline Co(1) - O(1) & 2.039(2) & Co(2) \\ \hline Co(1) - O(2W) & 2.075(3) & Co(2) \\ \hline Co(1) - O(1W) & 2.136(3) & Co(2) \\ \hline Co(1) - N(1) & 2.102(3) & Co(2) \\ \hline Co(1) - N(2) & 2.128(3) & Co(2) \\ \hline Co(1) - N(6) & 2.186(3) & Co(2) \\ \hline O(1) - Co(1) - (1W) & 90.5(1) & O(3W) \\ \hline N(1) - Co(1) - O(1W) & 176.5(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 93.0(1) & N(4) \\ \hline O(1) - Co(1) - N(1) & 96.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 96.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 96.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - Co(1) - N(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) & 0.8(1) & O(8) \\ \hline O(1) - O(1) & O(1) & O(8) \\ \hline O(1) - O(1) & O(1) & O(8) \\ \hline O(1) - O(1) & O(1) & O(8) \\ \hline O(1) - O(1) & O(1) & O(8) \\ \hline O(1) - O(1) & O(1) & O(8) \\ \hline O(1) - O(1) & O(1) & O(8) \\ \hline O(1) - O(1) & O(1) & O(1) \\ \hline O(1) - O(1) & O(1) & O(1) \\ \hline O(1) - O(1) & O(1) & O(1) \\ \hline O(1) - O(1) & O(1) & O(1) \\ \hline O(1) - O(1) & O(1) & O(1) \\ \hline O(1) - O(1) & O(1) & O(1) \\ \hline O(1) - O(1) & O(1) & O(1) \\ \hline O(1) - O(1) & O(1) & O(1) \\ \hline O(1) - O(1) & O(1) \\ \hline O(1) & $	$\begin{array}{c c} -O(8) & 2.069(2) \\ -O(3W) & 2.079(3) \\ -O(4W) & 2.093(3) \\ -N(4) & 2.123(3) \\ -N(3) & 2.147(3) \\ N(5^{3}) & 2.147(3) \end{array}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{c} -O(3W) & 2.079(3) \\ -O(4W) & 2.093(3) \\ -N(4) & 2.123(3) \\ -N(3) & 2.147(3) \\ N(5\%) & 2.147(3) \end{array}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$\begin{array}{c} -O(4W) & 2.093(3) \\ -N(4) & 2.123(3) \\ -N(3) & 2.147(3) \\ N(5)^8 & 2.197(3) \end{array}$
$\begin{array}{llllllllllllllllllllllllllllllllllll$	-N(4) 2.123(3) -N(3) 2.147(3) $N(5)^{3}$ 2.10(2)
$\begin{array}{cccc} Co(1)-N(2) & 2.128(3) & Co(2) \\ Co(1)-N(6) & 2.186(3) & Co(2) \\ O(1)-Co(1)-(1W) & 90.5(1) & O(3W) \\ N(1)-Co(1)-O(1W) & 176.5(1) & O(8) \\ O(1)-Co(1)-N(1) & 93.0(1) & N(4) \\ O(1)-Co(1)-N(2) & 169.8(1) & O(8) \\ O(1)-Co(1)-N(2) & O(8) \\ O(1)-N$	-N(3) 2.147(3)
Co(1)-N(6)2.186(3) $Co(2)$ $O(1)-Co(1)-(1W)$ 90.5(1) $O(3W)$ $N(1)-Co(1)-O(1W)$ 176.5(1) $O(8)$ - $O(1)-Co(1)-N(1)$ 93.0(1) $N(4)$ - $O(1)-Co(1)-N(2)$ 160.8(1) $O(8)$	NI(5)8 0 10((2)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	$-IN(3)^{-1}$ 2.196(3)
$\begin{array}{llllllllllllllllllllllllllllllllllll$	V)-Co(2)-N(3) 94.5(1)
O(1)-Co(1)-N(1) 93.0(1) N(4) O(1) $Co(1)$ N(2) 160.8(1) $O(8)$	Co(2)–N(4) 93.6(1)
$O(1)$ $C_{0}(1)$ $N(2)$ 160.8(1) $O(8)$	-Co(2)-N(3) 77.0(1)
O(1) - O(1) - In(2) 109.0(1) $O(0)$	Co(2)–O(3W) 94.8(1)
N(1)-Co(1)-N(2) 76.9(1) O(3V	$V_{\rm O} = Co(2) = N(4)$ 171.6(1)
N(2)-Co(1)-O(1W) 99.6(1) O(8)-	Co(2)–N(3) 169.3(1)
O(2W)-Co(1)-N(6) 172.9(1) O(4W	

Symmetry transformations used to generate equivalent atoms: (a) x, y + 1, z.

equatorial plane, and the other carboxyl oxygen atom (O5C) and the oxygen atom (O3) from a coordinated water molecule occupy the axial positions (O3–Ni–O5C =  $179.64(2)^{\circ}$ ), the Ni–O (2.005(2)–2.143(2) Å) and Ni–N (2.064(2) Å) bond distances are similar to those found in related Ni(II) complexes [13] (see Figs. 2a and 2b).

The coordination modes of PDB in this work are summarized in Scheme 1. As can be seen in Scheme 1c, one carboxylate bridges two metal atoms in a carboxylate O,O'mode, and the other links to the third Ni atom in bidentate-chelate mode. The pyridyl N atom bonds to the fourth Ni center, and thus, each pydc ligand acts as a tetra-connector. Interestingly, one carboxylate group is roughly coplanar with the adjacent pyridine ring and the other is

Table 5 Selected bond lengths  $(\text{\AA})$  and angles (°) for compound **4** 

	. ()	· ( ) · · · · · · · · · · · ·	
Co(1)-O(1)	2.076(2)	Co(2)–O(3)	2.226(2)
$Co(1) - O(3)^{a}$	2.089(2)	Co(2)–O(5)	1.985(2)
$Co(1) - O(7)^{b}$	2.107(2)	$Co(2)-O(8)^d$	2.079(2)
Co(1)–N(5)	2.141(3)	$Co(2)-O(1)^e$	2.082(2)
$Co(1) - N(1)^{c}$	2.163(3)	Co(2) - N(2)	2.137(3)
Co(1)–N(6)	2.166(3)	Co(2)–N(3)	2.102(3)
N(5)-Co(1)-N(6)	77.0(1)	N(3)-Co(2)-N(2)	78.0(1)
$O(7)^{b}$ -Co(1)-N(6)	165.6(1)	$O(8)^{d}$ -Co(2)-N(2)	89.7(1)
$O(3)^{a}$ -Co(1)-O(7) <sup>b</sup>	84.23(8)	$O(8)^{d}$ -Co(2)-O(1) <sup>e</sup>	88.08(9)
$O(3)^{a}-Co(1)-N(5)$	171.38(9)	$O(1)^{e}-Co(2)-N(2)$	176.77(9)
$O(3)^{a}-Co(1)-N(6)$	109.6(1)	$O(8)^{d}$ -Co(2)-N(3)	163.3(1)
$O(7)^{b}-Co(1)-N(5)$	88.87(9)	$O(1)^{e}-Co(2)-N(3)$	103.7(1)
$O(1)-Co(1)-N(1)^{c}$	174.75(9)	O(5)–Co(2)–O(3)	165.60(9)

Symmetry transformations used to generate equivalent atoms: (a) x + 1, y, z; (b) x + 1, -y + 1/2, z - 1/2; (c) x + 1, y, z - 1; (d) x, -y + 1/2, z - 1/2; (e) x - 1, y, z.



Fig. 1. ORTEP diagram showing the coordination environment for the Ni atoms in 1. Symmetry code A: x - 1, y, z; B: x, -y + 1/2, z + 1/2; C: -x, -y + 1, -z.



Fig. 3. ORTEP diagram showing the coordination environment of the Pb atom in **2**. Symmetry code A: x + 1, y, z.

deviated from the plane with a dihedral angle of 21.55°, nipping two Ni atoms located in adjacent single layers. Such a regular crossing-plane coordination fashion is still rare in the system of multi-carboxylates, and it plays an important role in the construction of the 3D metal-organic framework (see Fig. 4b). Moreover, the hydrogen bondings between the water molecule and carboxylic O atoms  $(O3\cdots O1i = 2.708(3) \text{ Å}, i: 1 - x, 1 - y, 1 - z; O3\cdots O5ii = 3.143(4) \text{ Å}, ii: x, y, 1 + z)$  further stabilize the framework.

# 3.1.2. $[Pb(PDB)(H_2O)] \cdot (H_2O)$ (2)

The structural analysis of complex **2** reveals that it is a 2D layer structure containing (6,3) topology. The Pb atom is in a square-pyramidal coordinated geometry with four O atoms and one N atom from three separated PDB ligands and one aqua ligand (Fig. 3). Three oxygen atoms (Pb1–O2 = 2.463(3) Å, Pb1–O5 = 2.492(3) Å, Pb1–O1 = 2.685(3) Å) from two carboxylic groups of the PDB ligands and one pyridyl N atom (Pb1–N1 = 2.824(3) Å) are ligated to the Pb<sup>II</sup> ion in the quasi-plane, with another oxygen atom belonging to a water molecule (Pb1–O1W =



Fig. 2. Views of the 2D layer structure of 1 viewed down along the (a) c-axis; (b) a-axis.



Scheme 1. Coordination modes of the PDB ligand in compounds 1-4.



Fig. 4. (a) 2D layer structure of **2** viewed along the *b*-axis; (b) undulated along the *c*-axis; (c) projection of **2** showing the (6, 3) net based on the Pb atoms and PDB ligands.

2.392(4) Å) located in the axial position, as displayed in Fig. 4a. Longer distances are observed between Pb and O4 (2.781(4) Å); some long Pb–O weak bonds have also been reported in other lead complexes [14].

Different from that of complex 1, each PDB ligand acts as a tri-connector linking three Pb atoms in complex 2 (Scheme 1b), one of carboxylate groups connects with one Pb atom through a mono-dentate O atom, the other bonds with the second Pb atom; the pyridyl N atom binds to the third Pb atom, consequently resulting in the formation of a 2D layer. In compound 2, two carboxylate groups and the pyridine ring of the ligand are both distorted. The twist angles between the two  $-CO_2$  planes and the pyridyl ring plane of PDB are  $9.39^{\circ}$  (O4,O5) and  $14.51^{\circ}$ (O1,O2), so the 2D layer is developed in an undulated layer pattern parallel to the *ab*-plane. By treating the Pb atom as a single node and connecting the nodes according to the connectivity defined by the geometrical centers of the benzene rings of the BTC ligands, a distorted 2D (6,3) network sustained by 3-connected nodes is then yielded, as illustrated in Fig. 4c. The multipoint hydrogen-bonding interactions among free water molecules, coordinated water molecules and carboxylic O atoms extend the 2D layer into a 3D supramolecular net.

# 3.1.3. $[Co_2(PDB)_2(bpy)_2(H_2O)_4] \cdot 4H_2O(3)$

When the chelate neutral ligand 2,2'-bpy is introduced, and simultaneously replacing the divalent lead salt with a divalent cobalt salt, complex **3** is obtained. Single-crystal X-ray diffraction analysis reveals that complex **3** crystallizes in a triclinic space group  $P\bar{1}$  and there are two crystallographically independent cobalt atoms, two PDB, two bpy, four aqua ligands and four free water molecules in the asymmetric unit. The Co atom, in a distorted octahedral geometry (Fig. 5), is bounded by two N atoms from one bpy molecule, two O atoms from coordinated water



Fig. 5. ORTEP diagram showing the coordination environment of two Co atoms in 3. Symmetry code A: x, y + 1, z.

molecules (Co–O(water) 2.075(3)–2.136(3) Å), one pyridyl N atom and one carboxylic O atom from two PDB ligands.

Each PDB ligand acts as a bridge to connect with between Co<sup>II</sup> centers through one carboxyl O atom and the pyridyl N atom (Scheme 1a), and thus a one-dimensional zig-zag chain is generated, as shown in Fig. 6. Two types of supramolecular interactions,  $\pi \cdots \pi$  stacking interactions between bpys of adjacent layer (3.375 Å) and multipoint hydrogen-bonding interactions between lattice water molecules, and coordinated water molecules, as well as uncoordinated carboxylate O atoms, contribute to the formation of the three-dimensional supramolecular architecture.

# 3.1.4. $[Co_2(PDB)_2(phen)_2]$ (4)

When another chelate ligand, phen, is used, we obtained complex **4** under similar reaction conditions. The asymmetry unit of complex **4** contains two Co ions, two phen ligands and two PDB ligands. As shown in Fig. 7, the two crystallographically unique cobalt atoms exhibit two different coordination geometries. The Co1 site shows a distorted-octahedral geometry, being chelated by two N atoms from one phen ligand. The remaining four coordination sites are occupied by one N atom and three oxygen atoms from three pydc ligands. The Co1-O bond lengths are in the range 2.076(2)-2.107(2) Å and the Co1-N bond lengths are 2.141(3) and 2.166(3) Å. The Co2 ion is also six-coordinated in a more distorted octahedral symmetry with a N2O4 donor set. The equatorial plane is occupied by two N-donors from a phen molecule and two O-donors from carboxylate groups of two PDB ligands, and the axial positions are completed by two oxygen atoms from another two PDB ligands. The Co2–O bond lengths are in the range 1.985(2)–2.226(2) Å and Co2–N bond lengths are 2.102(3) and 2.137(3) Å.

In complex 4, PDB ligands adopt two coordination modes different from those in complexes 1–3: one acts as



Fig. 6. View of the 1D zigzag chain highlighting the  $\pi$ - $\pi$  interactions between pyridine rings in adjacent chains in 3.



Fig. 7. ORTEP diagram showing the coordination environment for the two Co atoms in 4. Symmetry code A: x + 1, y, z; B: x + 1, -y + 1/2, z - 1/2; C: x + 1, y, z - 1; D: x, -y + 1/2, z - 1/2; E: x - 1, y, z.

a tetra-connector to link four Co atoms through two monodentate carboxylic O atoms from two carboxylic groups in the  $\mu$ -O mode, containing an uncoordinated pyridyl N atom; the other, also being a tetra-connector, bonds with four Co atoms through one pyridyl N atom, one monodentate carboxylic O atom from one carboxylate group and two bis-monodentate carboxylic O atom from the other carboxylate group, as depicted in Scheme 1d–e.

A pair of  $\mu$ -O atoms link to two adjacent Co atoms, generating a  $[Co_2O_2]$  unit with a  $Co1 \cdots Co2$  separation of 3.202 Å, in which the distances are in the normal range compared with those reported (3.076–3.393 Å) in the literature [15]. As shown in Fig. 8, firstly, one kind of PDB ligand bridges to two  $[Co_2O_2]$  units to form a 2D net. Interestingly, when viewed along the *b*-axis, the two-dimensional layer contains rectangular windows with a dimensions of ca.  $9.129 \times 10.557$  Å<sup>2</sup> that are occupied by phen ligands. Secondly, the other kind of PDB ligand



Fig. 8. View of the 2D net showing the rectangular window in 4.

connects with three  $[Co_2O_2]$  units in two layers, consequently resulting in the formation of a bilayer structure (see Fig. 9).

## 3.2. Properties

#### 3.2.1. Luminescent properties

Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry and electroluminescent (EL) displays [16]. Recently, the luminescent properties of complexes containing Pb<sup>II</sup> have been reported [17]. In this work, we investigated the photoluminescent property of compound 2 in the solid-state at room temperature. The free pyridine-3,5-dicarboxylic acid ligand only shows a fluorescent emission band at  $\lambda_{max} = 378$  nm under 320 nm excitation (see Fig. 1S), whereas, the complex exhibits an emission peak located at about 475 nm (upon excitation at 330 nm), and undergoes a red shift by 97 nm compared to the acid ligand, as shown in Fig. 10. Hence, the emissions of compound 2 in this work might be assigned to be derived from a ligand to metal charge transition (LMCT). The lowenergy emissions associated with large Stokes shifts for complex 2 have been commonly observed for other  $s^2$ metal complexes [18]. The heavy-atom effect of lead(II) increases the spin-orbit coupling and facilitates intersystem crossing, so the phosphorescence is fast enough to successfully compete with radiationless deactivations [18d]. The observation indicates that complex 2 may be an excellent candidate for potential photoactive materials.

# 3.2.2. Magnetic properties

The magnetic property of polymer 4 has been investigated over the temperature range 5–300 K at 1000 Oe. The temperature dependence of the molar magnetic susceptibility is illustrated in Fig. 11. The  $\chi_m T$  value of 4 remains almost constant from 300 to 115 K (5.659 cm<sup>3</sup> K mol<sup>-1</sup>), and then decreases on further cooling, reaching a value of 0.793 cm<sup>3</sup> K mol<sup>-1</sup> at 5 K. This behavior indicates a dominant weak antiferromagnetic interaction between the Co<sup>II</sup> ions in the structure. In 4, the Co…Co distance



Fig. 9. View of the bilayer structure in 4.



Fig. 10. Absorption (left) and phosphorescence (right) spectra of complex **2** in the solid state.



Fig. 11. Thermal variations of  $\chi_M T$  and  $\chi_M^{-1}$  for complex 4.

through two  $\mu_2$ -O atoms is 3.202 Å. Even small changes in these parameters could lead to changes in the Co···Co interaction. For polymer **4**, Co–O bridge distances ranging from 2.076(2) to 2.226(2) Å are slightly longer than those in the literature [19], but the lengths of the pathways are

about 4.6 Å, which is a very short transmittance distance, helpful for magnetic coupling. The variation of  $\chi_{\rm M}^{-1}$  is well described by the Curie–Weiss law in the experimental temperature range 5–300 K with  $C = 5.86 \text{ cm}^3 \text{ K mol}^{-1}$  and  $\theta = -3.69 \text{ K}$ .

The experiment data of complex **4** was fitted using the theoretical expression of the magnetic susceptibility, (Eq. (1)) which was deduced from the Heisenberg spin Hamiltonian  $H = -JS_1 \cdot S_2$ , where J is the intradimer interaction parameter between the Co(II) ions [20].

$$\chi_{\rm dim} = \frac{2Ng^2\beta^2}{kT} \times \frac{e^{5x} + 5e^{3x} + 14}{7 + e^{6x} + 3e^{5x} + 5e^{3x}} \tag{1}$$

where x = -J/kT. Taking into consideration the possibility of an interdimer interaction in the crystal lattice, the following correction of the molecular field is made:

$$\chi_{\rm M} = \frac{\chi_{\rm dim}}{1 - \chi_{\rm dim} (zJ'/N^2\beta^2)} \tag{2}$$

The best fitting of the experimental magnetic data by Eq. (2) gives the following parameters: g = 2.52,  $J = -4.67 \text{ cm}^{-1}$ ,  $zJ' = 0.878 \text{ cm}^{-1}$  and  $R = 9.98 \times 10^{-4}$ , where  $R = \sum [(\chi_m T)_{obs} - (\chi_m T)_{calcd}]^2 / \sum [(\chi_m T)_{obs}]^2$ . The results suggest that the interlayer interactions are weak compared with the intralayer interaction. The negative J value suggests the occurrence of an obvious antiferromagnetic Co(II)–Co(II) interactions in **4**, being in good agreement with the  $\chi_m T$  versus T curve behavior in the temperature range 300–5 K. It is difficult to estimate the exchange interaction accurately within the Co(II) complexes because of the effect of spin–orbit coupling.

#### 3.2.3. Thermal properties

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stabilities of 1–4. The results show that complexes 1–4 are very stable in air at ambient temperature, which make them potential candidates for practical applications. The samples were heated up in air at 1 atm pressure with a heating rate of 10 °C min<sup>-1</sup>. The TGA curve shows that 1 is stable up to 127 °C. A weight loss of 7.6% occurred in the temperature range 127–226 °C, presumably due to the removal of a coordinated water molecule per formula unit (calcd. 7.4%). Another weight loss of 60.9% occurred in the temperature range 297–465 °C. corresponding to the removal of two PDB ligands per formula unit (calcd. 61.7%), no weight losses were observed up to 800 °C indicating the complete deposition of the complex with the formation of NiO as the final product. The TGA curve of 2 shows that the first weight loss of 4.2% between 46 and 90 °C corresponds to the loss of the lattice water molecules (calcd. 4.4%). A total weight loss of 41.2% occurred in the temperature range 215–513 °C, mainly corresponding to the removal of the one coordinated water molecule and one PDB ligand per formula unit (calcd. 40.9%), no weight losses were observed up to 800 °C indicating the complete deposition of the complex with the formation of PbO as the final product. The TGA curve of 3 shows that the first weight loss of 16.01% between 40 and 172 °C corresponds to the loss of the lattice water molecules and coordinated water molecules (calcd. 15.92%). and then it is stable up to 280 °C. The framework collapsed in the temperature range 280-800 °C before the final formation of a metal oxide. The TGA curve shows that 4 is stable up to 350 °C. The framework collapsed in the temperature range 350-800 °C, suggesting that the organic ligands decompose slowly over a wide temperature range. The results indicate that a 3D porous framework constrained by the N–H $\cdot$ ··N self-complementary hydrogen bonds is more stable than 2D sheets.

# 4. Conclusion

In summary, we have synthesized four novel metalorganic frameworks based on pyridine-3,5-dicarboxylic acid and two chelate ligands by hydrothermal reactions. The successful syntheses of the four compounds indicate that it is promising to build up unusual architectures via combining transition metals or main group elements and pyridine-carboxylate ligands, thus opening up a new field in the preparation of metal coordination polymers with potential magnetic and luminescent properties.

# 5. Supplementary material

CCDC 625481, 625482, 625483 and 625484 contain the supplementary crystallographic data for 1, 2, 3 and 4. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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