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# Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/gcoo20

# Syntheses, crystal structures, and photophysical properties of two 2-D coordination polymers

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Accepted author version posted online: 15 Oct 2012. Published online: 30 Oct 2012.

To cite this article: Li Yan & Chuan-Bi Li (2012) Syntheses, crystal structures, and photophysical properties of two 2-D coordination polymers, Journal of Coordination Chemistry, 65:24, 4288-4298, DOI: <u>10.1080/00958972.2012.740022</u>

To link to this article: <u>http://dx.doi.org/10.1080/00958972.2012.740022</u>

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## Syntheses, crystal structures, and photophysical properties of two 2-D coordination polymers

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(Received 1 June 2012; in final form 27 August 2012)

Two coordination polymers,  $[Mn(dipt)(m-BDC)_3]_n$  (1) and  $[Pb(mip)(1,4-NDC)]_n$  (2) [dipt = 2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline, mip = 2-(3-methoxyphenyl)-1H-imidazo[4,5-f][1,10]phenanthroline, m-BDC = isophthalic acid, 1,4-NDC = naphthalene-1,4-dicarboxylic acid], have been synthesized by hydrothermal reactions and characterizedby elemental analysis, thermogravimetric analysis, infrared spectrum, and single-crystal X-raydiffraction. Single-crystal X-ray diffraction reveals that 1 and 2 have 1-D chain architecture. $Complex 1 has a 2-D-layered structure constructed from C-H···O hydrogen bonds and <math>\pi$ - $\pi$  interactions. TG analyses suggest 1 and 2 have excellent thermal stabilities from hydrogen bonds and  $\pi$ - $\pi$ interactions. Mn(II) in 1 has trigonal bipyramidal geometry surrounded by three carboxylate oxygen atoms from three monodentate bridging m-BDC and two nitrogen atoms from one dipt. Pb(II) has [:PbN2O4] pentagonal bipyramidal geometry in 2. The luminescent properties for dipt, mip, 1, and 2 are also presented.

Keywords: Manganese; Lead; Crystal structures; Thermal stability analysis; Fluorescence

#### 1. Introduction

Construction of metal–organic frameworks (MOFs) is an active area of materials research, driven by interesting network topologies and potential applications in catalysis, porosity, sensors, magnetism, luminescence, molecular recognition, nonlinear optics, and electrical conductivity [1–7]. Ligands and metals can be organized by non-covalent interactions in MOFs. Hydrothermal synthesis is widely used to obtain crystal structures, addressing problems of ligand solubility and possibilities for enhanced reactivity of molecules in crystallization. Progress has been made in theoretical predictions [8–10]. However, it is still a challenge to predict the exact structures and composition of target products in crystal engineering because formation of MOFs is determined by coordination nature of metal ions, ligand structures, pH, temperature, etc. [11]. Multidentate ligands such as poly-carboxylates and *N*-heterocycles give structures with desired properties. Among poly-carboxylates, the best studied are

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Scheme 1. Syntheses of dipt and mip ligands.

dicarboxylates, tricarboxylates, and biphenyldicarboxylates. 2-(Pyridin-2-yl)pyridine, 4-(pyridin-4-yl)pyridine, and 1,10-phenanthroline can act as terminal ligands and provide supramolecular interaction sites for molecular recognition. Our strategy is to employ long-conjugated unsymmetrical ligands dipt (2-(2,4-dichlorophenyl)-1H-imidazo[4,5-f][1,10]phenanthroline) and mip (2-(3-methoxyphenyl)-1H-imidazo[4,5-f][1,10] phenanthroline) (as shown in scheme 1) because they (1) possess extended conjugated unsymmetrical aromatic system to provide supramolecular interactions; (2) possess two nitrogen atoms for bidentate chelating molecules; (3) possess strong and rigid coordination to metals [12]. Combining *N*-heterocyclic ligands and anionic O-donor is an attractive design strategy [13, 14]; investigation of similar *N*-heterocyclic ligands is lacking [15–18], with few reports using dipt, mip, isophthalic acid (m-BDC), and naphthalene-1,4-dicarboxylic acid (1,4-NDC) as mixed ligands to construct coordination polymers.

In this study, we use m-BDC and 1,4-NDC to obtain  $[Mn(dipt)(m-BDC)_3]_n$  (1) and  $[Pb(mip)(1,4-NDC)]_n$  (2). Complexes 1 and 2 exhibit 1-D chain structures, with 2-D layer structures *via* hydrogen bonds and inter-chain  $\pi$ - $\pi$  stacking interactions.

#### 2. Experimental

#### 2.1. Materials and physical measurements

The dipt and mip were prepared by literature procedures [19]. All other chemicals from commercial sources were of AR grade and used without purification. The FT-IR spectra were recorded on an Alpha Centauri FT-IR spectrophotometer using KBr discs from 400 to 4000 cm<sup>-1</sup>. Thermogravimetric (TG) analysis was performed with a Diamond DSC thermal analyzer at 10°C min<sup>-1</sup> in nitrogen. Crystal structures were determined on a Bruker SMART APEX II CCD X-ray diffractometer. Elemental analyses (C, H, and N) were performed on a PE-2400 elemental analyzer. Fluorescence spectra were recorded on an FLSP 920 Edinburgh fluorescence spectrometer.

#### 2.2. Syntheses of 1 and 2

**2.2.1.** Synthesis of  $[Mn(dipt)(m-BDC)_3]_n$  (1). A mixture of  $MnSO_4 \cdot H_2O$  (0.051 g, 0.3 mmol), dipt (0.120 g, 0.3 mmol), m-BDC (0.100 g, 0.3 mmol), and  $H_2O$  (18 mL) was stirred at room temperature and the pH adjusted to 7.0 with NaOH. The cloudy solution was placed in a 30-mL Teflon-lined stainless vessel under autogenous pressure at 443 K for 72 h and afterwards cooled to room temperature at 5°Ch<sup>-1</sup>. Yellow crystals of 1 were collected in 78% yield based on Mn. Calcd for  $C_{27}H_{14}Cl_2MnN_4O_4$  (%): C, 55.50; H, 2.41; N, 9.58. Found (%): C, 55.45; H, 2.39; N, 9.51. Infrared (IR) (KBr, cm<sup>-1</sup>): 3418(s), 2362(s), 1613(vs), 1383(vs), 1072(s), 731(s), 706(m), 627(m).

**2.2.2.** Synthesis of  $[Pb(mip)(1,4-NDC)]_n$  (2). A mixture of  $Pb(Ac)_2 \cdot 3H_2O$  (0.114 g, 0.3 mmol), 1,4-NDC (0.130 g, 0.6 mmol), mip (0.099 g, 0.3 mmol), and H<sub>2</sub>O (18 mL) was stirred at room temperature and the pH was adjusted to 7.0 with NaOH. The cloudy solution was placed into a 30-mL Teflon-lined stainless vessel under autogenous pressure at 443 K for 72 h and afterwards cooled to room temperature at 5°C h<sup>-1</sup>. Small yellow crystals of **2** were collected in 85% yield based on Pb. Calcd for  $C_{32}H_{21}N_4O_{5.50}Pb$  (%): C, 50.78; H, 2.79; N, 7.40. Found (%): C, 50.75; H, 2.66; N, 7.52. IR (KBr, cm<sup>-1</sup>): 3476(s), 3406(s), 2369(s), 1530(vs), 1403(vs), 1251(s), 837(s), 706(m).

#### 2.3. X-ray crystallography

Single-crystal X-ray diffraction data were collected at room temperature with a Bruker SMART APEX II CCD diffractometer equipped with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293(2) K from  $1.65 \le \theta \le 26.06^{\circ}$  for 1 and  $1.68 \le \theta \le 26.07^{\circ}$  for 2. Absorption corrections were applied using the multi-scan technique and all structures were solved by direct methods with SHELXS-97 [20] and refined with SHELXL-97 [21] by full-matrix least-squares on  $F^2$ . Non-hydrogen atoms were refined with anisotropic temperature parameters. Experimental details for crystallographic data and structure refinement parameters for 1 and 2 are listed in table 1.

#### 3. Results and discussion

#### 3.1. Description of crystal structures

**3.1.1.** [Mn(dipt)(m-BDC)<sub>3]n</sub> (1). The molecular structure of 1 is shown in figure 1. The 1-D binuclear double-chain structure is shown in figure 2 and the 2-D layer structure linked by C–H···O hydrogen bonds is suggested in figure 3. Selected bond lengths and angles are given in table 2.

As shown in figure 1, the asymmetric unit contains one Mn(II), one dipt, and three m-BDC. In general, Mn(II) exhibits five-, six-, or seven-coordination with six- or seven-coordinate more common; five-coordinate Mn(II) complexes are rare [22–25]. In 1, Mn(II) is five-coordinate with three carboxylate oxygen atoms from three distinct

Table 1. Crystal data and details of structure refinement parameters for 1 and 2.

Complex	1	2
Empirical formula	C <sub>27</sub> H <sub>14</sub> Cl <sub>2</sub> MnN <sub>4</sub> O <sub>4</sub>	C <sub>32</sub> H <sub>21</sub> N <sub>4</sub> O <sub>5.50</sub> Pb
Formula weight	584.26	756.72
Crystal system	Monoclinic	Monoclinic
Space group	C2/c	C2/c
Unit cell dimensions (Å, °)	,	,
a	18.9697(1)	15.531(2)
b	17.5113(1)	19.833(3)
С	15.6937(1)	17.188(2)
β	113.228(2)	99.098(2)
Volume (Å <sup>3</sup> ), Z	4790.6(8), 8	5227.8(1), 8
Calculated density $(Mg m^{-3})$	1.620	1.923
Absorption coefficient $(mm^{-1})$	0.819	6.510
F(000)	2360	2936
Crystal size (mm <sup>3</sup> )	$0.433 \times 0.371 \times 0.308$	$0.747 \times 0.420 \times 0.338$
$\theta$ range for data collection (°)	1.65-26.06	1.68-26.07
Reflections collected	15,175	13,827
Unique reflections	4725 [R(int) = 0.0513]	5178 [R(int) = 0.0306]
Goodness-of-fit on $F^2$	1.031	1.028
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0612, wR_2 = 0.1384$	$R_1 = 0.0247, wR_2 = 0.0524$
R indices (all data)	$R_1 = 0.0967, wR_2 = 0.1578$	$R_1 = 0.0405, wR_2 = 0.0572$
Largest difference peak and hole $(e \text{ Å}^{-3})$	1114 and -285	683 and -1242



Figure 1. The molecular structure of 1 (hydrogen atoms were omitted).

bridging m-BDC and two nitrogen atoms from one chelating dipt, forming a distorted trigonal bipyramidal geometry. The O(1)–Mn(1)–O(4)<sup>#1</sup> (<sup>#1</sup>: x, -y, z+1/2), O(1)–Mn(1)–N(1), and O(4)<sup>#1</sup>–Mn(1)–N(1) angles are 105.91°, 120.56°, and 132.60°, and the sum is 359.07°. Mn(1), O(4)<sup>#1</sup>, O(1), and N(1) define the basal plane, and N(2) and O(3)<sup>#2</sup> (<sup>#2</sup>: -x, -y, -z+1) occupy axial positions. The equation of a plane is: -14.3474 (0.0219) x - 10.8300 (0.0147) y + 7.7566 (0.0190) z = 2.0934 (0.0110). The deviation of Mn1, O(4)<sup>#1</sup>, O(1), N(1), N(2), and O(3)<sup>#2</sup> to the plane is 0.3868, -0.0795, -0.3964, -0.0699, -1.3453, and 1.4768 Å, respectively.

The Mn–O bond distances in 1 are 2.023(3) to 2.117(3)Å and Mn–N distances are 2.241(3)–2.283(3)Å, similar to values reported [26–31]. The average Mn–O bond is 2.059Å, smaller than the average Mn–N bond (2.262Å), which suggests that



Figure 2. 1-D binuclear double chain structure of 1 (hydrogen atoms were omitted).



Figure 3. 2-D layer structure of 1 linked by C–H $\cdots$ O hydrogen bonds (dotted lines represent hydrogen bonds).

coordination of carboxylate is stronger than dipt. The N(O)–Mn–O(N) angles range from  $88.40(13)^{\circ}$  to  $161.82(12)^{\circ}$ .

As shown in figure 2, one m-BDC coordinates to three Mn(II) ions through three carboxylate oxygen atoms in a mono-bridging fashion, giving a 1-D binuclear wave double-chain structure. In 1, two types of rings form, an eight-membered ring, in which

$\frac{1}{Mn(1)-O(1)} \\ Mn(1)-O(3)^{\#2} \\ Mn(1)-N(2) \\ \end{cases}$	2.023(3) 2.117(3) 2.283(3)	Mn(1)-O(4) <sup>#1</sup> Mn(1)-N(1)	2.037(3) 2.241(3)
$\begin{array}{l} O(1)-Mn(1)-O(4)^{\#1}\\ O(4)^{\#1}-Mn(1)-O(3)^{\#2}\\ O(4)^{\#1}-Mn(1)-N(1)\\ O(1)-Mn(1)-N(2)\\ O(3)^{\#2}-Mn(1)-N(2) \end{array}$	105.91(12) 98.48(13) 132.61(13) 103.67(12) 161.82(12)	$\begin{array}{c} O(1)-Mn(1)-O(3)^{\#2}\\ O(1)-Mn(1)-N(1)\\ O(3)^{\#2}-Mn(1)-N(1)\\ O(4)^{\#1}-Mn(1)-N(2)\\ N(1)-Mn(1)-N(2) \end{array}$	90.68(12) 120.56(12) 90.24(12) 88.40(13) 72.94(12)
<b>2</b> Pb(1)–O(3) <sup>#1</sup> Pb(1)–O(4) <sup>#1</sup> Pb(1)–N(1)	2.465(3) 2.583(3) 2.464(3)	Pb(1)–O(1) Pb(1)–O(2) Pb(1)–N(2)	2.505(3) 2.693(3) 2.554(3)
$\begin{array}{l} O(3)^{\#1} - Pb(1) - O(2) \\ O(3)^{\#1} - Pb(1) - O(4)^{\#1} \\ O(4)^{\#1} - Pb(1) - O(2) \\ N(2) - Pb(1) - O(4)^{\#1} \\ N(1) - Pb(1) - O(1) \\ O(1) - Pb(1) - N(2) \\ N(1) - Pb(1) - O(2) \\ N(1) - Pb(1) - N(2) \end{array}$	$\begin{array}{c} 131.71(9)\\ 51.14(9)\\ 155.44(11)\\ 79.83(10)\\ 76.71(10)\\ 124.86(9)\\ 73.35(10)\\ 65.11(10)\\ \end{array}$	$\begin{array}{l} O(1)-Pb(1)-O(2)\\ O(1)-Pb(1)-O(4)^{\#1}\\ O(3)^{\#1}-Pb(1)-O(1)\\ N(1)-Pb(1)-O(3)^{\#1}\\ O(3)^{\#1}-Pb(1)-N(2)\\ N(1)-Pb(1)-O(4)^{\#1}\\ N(2)-Pb(1)-O(2) \end{array}$	50.09(8) 135.93(9) 85.80(9) 78.70(10) 121.23(10) 84.90(11) 80.73(9)

Table 2. Selected bond lengths (Å) and angles (°) for 1 and 2.

the O(3)–Mn(1)–O(4) angle is 98.485° and the distance of Mn···Mn is 3.8592 Å, and a 16-membered ring with O(3)–Mn(1)–O(1) angle of 90.671° and Mn···Mn of 7.9453 Å (figure 3). *N*-heterocyclic ligands dipt attach to both sides of this chain and the ligands on the same side are nearly parallel.

Hydrogen-bonding interactions are prevalent in the synthesis of supramolecular architectures with the most interesting aspect of **1** the intermolecular C-H···O interactions. Every pair of molecules is linked by intermolecular C15–H15A···O2 hydrogen bonds. The existence of C15–H15A···O2 hydrogen-bond interactions  $[H(15A)\cdots O(2) = 2.52 \text{ Å}, C(15)\cdots O(2) = 3.265 \text{ Å} \text{ and } C(15)-H(15A)\cdots O(2) = 137^{\circ}]$  lead the 1-D zigzag chain to a 2-D layer structure (figure 3). The two parallel dipt in the same side have  $\pi - \pi$  stacking interactions with face to face distance of 3.693 Å. Hydrogen bonds and  $\pi - \pi$  stacking interactions reinforce the structure, giving thermal stability to **1**.

**3.1.2.** [Pb(mip)(1,4-NDC)]<sub>n</sub> (2). The molecular structure of 2 is shown in figure 4 and the 1-D arm-shaped chain is shown in figure 5. The 1-D ladder double-chain structure is illustrated in figure 6 and the 2-D structure is suggested in figure 7. Selected bond lengths and angles are listed in table 2.

As shown in figure 4, the asymmetric unit of **2** consists of one Pb(II), one mip, and one 1,4-NDC. Pb(II) is six-coordinate with two nitrogen atoms (N(1), N(2)) from one chelating mip ligand and four oxygen atoms from two chelating bidentate 1,4-NDC, furnishing a distorted [:PbN2O4] pentagonal bipyramidal geometry [32]. Pb(1), the Pb(1), O1, O2, O3, O4, N2 atoms define the basal plane and N1 and the lone pair of electrons occupy apical positions. The N(O)–Pb–O(N) angles range from 73.35° to

Symmetry transformations used to generate equivalent atoms: (1)  $^{\#1}x + 1/2$ , -y + 1/2, z + 1/2,  $^{\#2}x - 1/2$ , -y + 1/2, z - 1/2; (2)  $^{\#1}x$ , -y, z + 1/2.



Figure 4. The molecular structure of 2 (hydrogen atoms were omitted).



Figure 5. 1-D arm-shaped chain structure of 2 (hydrogen atoms were omitted).



Figure 6. 1-D ladder chain structure of 2 (hydrogen atoms were omitted).



Figure 7. 2-D layer structure of **2** linked by N-H···O hydrogen bonds and inter-chain  $\pi$ - $\pi$  stacking interactions (dotted lines represent hydrogen bonds).

124.86°. Pb–O bond distances in **2** are from 2.465(3) to 2.693(3) Å and Pb–N distances are 2.464(3) to 2.554(3) Å, similar to reported values [33–38]. The average Pb–O bond is similar to Pb–N (2.613 Å), suggesting that coordination ability of carboxylate is similar to mip. Lead geometries are holo-directed, in which the bonds to ligands are distributed throughout the surface of an encompassing globe, or hemi-directed, in which the bonds to ligands are directed throughout only part of an encompassing globe [39]. The coordination environment of Pb(II) in **2** is hemi-directed with identifiable gap (or void) in the distribution of bonds to the ligands.

Each pair of adjacent Pb(II) ions is bridged by 1,4-NDC (bis-chelating mode) to form an arm-shaped chain structure with Pb···Pb distance of 11.5400 Å. The mip are attached to the same side of this chain in a slanted fashion, in which the Pb–Pb–Pb angle, defined by the orientation of 1,4-NDC in the chain, is 134.257° (figure 5).

Intermolecular N–H···O [H(3B)···O(3) = 2.08 Å, N(3)···O(2) = 2.887 Å, and N(3)– H(3B)···O(2) = 157°] interactions help in construction of the 1-D ladder chain (figure 6). The effective length of each mip of 10.6277 Å provides the possibility for stacking. The double chains recognize each other through aromatic  $\pi$ – $\pi$  stacking interaction of mip ligands, resulting in a 2-D structure (figure 7). The existence of hydrogen bonds (N(3)–H(3B)···O(2)) and  $\pi$ – $\pi$  stacking interactions reinforces the structure.

Different coordination modes of dicarboxylates result in different structures in 1 and 2. Coordination modes (chelating bis-bidentate or bis-monodentate) usually support 1-D chain or 1-D double-chain structures and diverse coordination modes (monodentate-bidentate or chelating/bridging bis-bidentate) usually support higher dimensional structures [40].

#### 3.2. IR spectra

In 1, peaks at 1613 and 1383 cm<sup>-1</sup> correspond to antisymmetric and symmetric stretching of carboxyl. The  $\Delta v$  ( $v_{as}(COO^{-})-v_{s}(COO^{-})$ ) is 230 cm<sup>-1</sup> (larger than 200 cm<sup>-1</sup>),

indicating that the carboxylates are monodentate with Mn(II). In **2**, the strong absorption peaks at  $1530 \text{ cm}^{-1}$  is the antisymmetric stretching of carboxylate and the absorption at  $1403 \text{ cm}^{-1}$  is the symmetric stretch. The separation is  $127 \text{ cm}^{-1}$ , indicating bidentate coordination. The IR results are in agreement with the results of their crystal structures.

#### 3.3. Thermal analyses

TG analyses were used to investigate the stabilities of 1 and 2 (Supplementary material). As expected, 1 exhibits good stability, stable at 360°C. First weight loss of 27.00% from 360°C to 480°C reveals loss of m-BDC (Calcd 28.42%). The second weight loss of 61.20% from 480°C to 670°C corresponds to loss of dipt (Calcd 62.50%); In 2, the first weight loss of 26.50% from 350°C to 380°C corresponds to loss of 1,4-NDC (Calcd 28.55%). The second weight loss at 380–620°C can be ascribed to release of mip (Obsd 39.20%, Calcd 43.10%). The final formation may be PbO. The analysis results indicate that 2 exhibits higher thermal stability than similar complexes [41–43]; the existence of hydrogen bonds and  $\pi$ - $\pi$  stacking interactions reinforce the structure, demonstrating thermal stability of 2.

#### 3.4. Photoluminescent properties

Luminescent complexes are currently of interest because of their applications in photochemistry and photophysics [44, 45]. Here, we studied the luminescence of the free



Figure 8. Luminescence spectrum of 1 and dipt in the solid state at room temperature.

4296



Figure 9. Luminescence spectrum of 2 and mip in the solid state at room temperature.

ligands, 1 and 2 (figures 8 and 9). Free dipt exhibits one emission band at 388 nm upon excitation at 325 nm and mip exhibits one emission band at 529 nm upon excitation at 320 nm. Complex 1 shows one strong emission band at 591 nm (excitation at 300 nm), which is red-shifted by 203 nm relative to that of free dipt. Complex 2 shows one strong emission at 595 nm (excitation at 320 nm), which is red-shifted by 66 nm relative to that of free mip. The emission of 1 and 2 can be attributed to a metal-centered transition involving s and p metal orbitals, as proposed by Vogler *et al* [46]. The luminescence results suggest emission bands of the complexes result from poly-carboxylate and N-heterocyclic ligands interacting on each other. Our complexes exhibit strong emissions, which may be attributed to rigidity, reducing the loss of energy through a radiationless pathway. However, the effect of the microenvironment between ligands and complexes on the luminescence properties still needs further investigations. Complexes 1 and 2 may be candidates for photoluminescence materials, highly thermally stable and insoluble in water and common organic solvents.

#### 4. Conclusion

Binuclear 1 and mononuclear 2 have been synthesized by using planar multifunctional ligands dipt, mip, m-BDC, and 1,4-NDC. Hydrogen bonds and  $\pi$ - $\pi$  interactions reinforce the stabilities of the complexes. TG analysis reveals that the frameworks of 1 and 2 are very stable and worthy of further study as potential photoluminescent materials.

#### Supplementary material

CCDC 745117 and 818553 contain the supplementary crystallographic data for 1 and 2, respectively. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk/data\_request/cif

#### Acknowledgments

We thank the National Natural Science Foundation of China (No. 20971019) and the Postdoctoral Science foundation of China (No. 2005038561) for financial support.

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