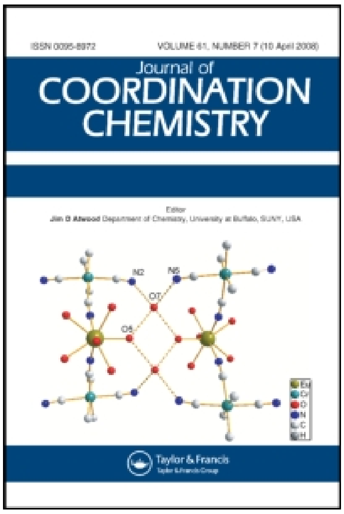

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Syntheses, crystal structures, and characterization of three metal-organic complexes with 2,2'-biphenyldicarboxylic acid and phenanthroline ligands

Chun-Bo Liu[ab]; Jian Wang[a]; Xiao-Lin Zha[a]; Xing-Jing Zhang[a]; Xiu-Ying Li[a]; Guang-Bo Che[ab]; Yong-Sheng Yan[b]
[a] Department of Chemistry, Jilin Normal University, Siping 136000, People's Republic of China [b] School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, People's Republic of China

To cite this Article Liu, Chun-Bo , Wang, Jian , Zha, Xiao-Lin , Zhang, Xing-Jing , Li, Xiu-Ying , Che, Guang-Bo and Yan, Yong-Sheng(2011) 'Syntheses, crystal structures, and characterization of three metal-organic complexes with 2,2'-biphenyldicarboxylic acid and phenanthroline ligands', Journal of Coordination Chemistry, 64: 2, 232 — 243, First published on: 08 December 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.540650

URL: http://dx.doi.org/10.1080/00958972.2010.540650

Journal of Coordination Chemistry
Vol. 64, No. 2, 20 January 2011, 232–243

Syntheses, crystal structures, and characterization of three metal–organic complexes with 2,2′-biphenyldicarboxylic acid and phenanthroline ligands

CHUN-BO LIU†‡, JIAN WANG†, XIAO-LIN ZHA†, XING-JING ZHANG†,
XIU-YING LI†, GUANG-BO CHE*†‡ and YONG-SHENG YAN‡

†Department of Chemistry, Jilin Normal University, Siping 136000,
People's Republic of China
‡School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013,
People's Republic of China

(*Received 26 February 2010; in final form 19 October 2010*)

Three complexes constructed with 2,2′-biphenyldicarboxylic acid, multidentate nitrogen donors, and metal salts, $\{[Cd(2,2'\text{-dpdc})(tppp)(H_2O)]_2 \cdot 2H_2O\}_n$ (**1**), $\{[Pb(2,2'\text{-dpdc})(pyphen)]_2\}_n$ (**2**), and $\{[Pb(2,2'\text{-dpdc})(dppz)]\}_n$ (**3**) (H_2dpdc = 2,2′-diphenyldicarboxylic acid; tppp = 4-(1H-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)phenol; pyphen = pyrazino[2,3-f]-[1,10]phenanthroline; and dppz = dipyrido[3,2-a:2′,3′-c]phenazine), are synthesized under hydrothermal conditions. These complexes are characterized by single-crystal X-ray diffraction, elemental analysis, IR, TGA, and photoluminescence. In **1**, two 2,2′-dpdc ions bridge two Cd(II) ions to form an isolated cluster with Cd···Cd distance of 5.023(4) Å. These clusters are further linked by intermolecular hydrogen bonds, yielding a 2-D supramolecular structure. Complex **2** contains two crystallographically independent Pb(II) ions in the asymmetric unit. Pb1 ions are bridged by 2,2′-dpdc anions to form a chain along the *x*-axis. Two Pb2 ions are coordinated by two 2,2′-dpdc anions and two pyphen ligands to form a cluster. These clusters are linked by π–π interactions to yield a 1-D supramolecular chain along the *y*-axis. In **3**, neighboring Pb(II) atoms are bridged by 2,2′-dpdc anions to form a 1-D chain structure. Further, the chains are linked into a 3-D supramolecular network through aromatic π–π interactions.

Keywords: 2,2′-Diphenyldicarboxylic acid; Cadmium; Lead; Crystal structure; Photoluminescence

1. Introduction

Rational design and construction of metal organic frameworks (MOFs) through coordination of metal ions with multifunctional organic multicarboxylic acid ligands and multidentate nitrogen donors have received much attention [1–5] from their intriguing topological structures and potential applications as functional materials [6–12] applied in luminescence, gas storage, separation, catalysis, etc. [13–20]. In these complexes, weak intermolecular forces, such as hydrogen bonding, π–π stacking, dipole–dipole attractions, and van der Waals interactions, can be used in design of

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*Corresponding author. Email: guangbochejl@yahoo.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958972.2010.540650

molecular solids with specific supramolecular structures and functions [21–23]. Self-assemblies of supramolecular complexes can be achieved by controlling non-covalent interactions among the ligands [24, 25]. So in synthesis, appropriate choice of well-designed multidentate nitrogen and oxygen donors are the outstanding challenges. Some O-donors can act as bridging ligands like 2,2′-diphenyldicarboxylic acid (2,2′-H_2dpdc) [26, 27]. 1,10-Phenanthroline (phen) and its derivatives have numerous uses in crystal engineering of MOFs [28–33]. Recently, we selected derivatives of phen, 4-(1H-1,3,7,8-tetraazacyclopenta[*l*]phenanthren-2-yl)phenol (tppp), pyrazino[2,3-f]-[1, 10]phenanthroline (pyphen) and bridging 2,2′-H_2dpdc with a hydrothermal technique and synthesized $\{[Cd(2,2'\text{-dpdc})(tppp)(H_2O)]_2 \cdot 2H_2O\}_n$ (**1**) and $\{[Pb(2,2'\text{-dpdc})(pyphen)]_2\}_n$ (**2**). The structural, thermal, and photophysical properties of **1** and **2** are compared to those of the related Pb(II) complex $\{[Pb(2,2'\text{-dpdc})(dppz)]\}_n$ (**3**) (dppz = dipyrido[3,2-a:2′,3′-c]phenazine) [34].

2. Experimental

2.1. *Materials*

All analytical grade chemicals and solvents were purchased commercially and used without purification. The ligands were synthesized by the literature method [35].

2.2. *Syntheses*

2.2.1. Synthesis of $\{[Cd(2,2'\text{-dpdc})(tppp)(H_2O)]_2 \cdot 2H_2O\}_n$ (1). A mixture of $CdCl_2 \cdot 2H_2O$ (0.110 g, 0.5 mmol), 2,2′-H_2dpdc (0.121 g, 0.5 mmol), tppp (0.186 g, 0.5 mmol), and water (15 mL) was sealed in a 23 mL Teflon-lined stainless autoclave. The autoclave was allowed to stay at 160°C for 4 days, followed by cooling to room temperature over 48 h. Yellow single crystals of **1** suitable for X-ray single-crystal diffraction analysis were obtained (yield 71%). Anal. Calcd for **1** $C_{66}H_{48}O_{14}N_8Cd_2$: C 56.54; H 3.45; and N 7.99; found: C 56.51; H 3.46; and N 8.01.

2.2.2. Synthesis of $\{[Pb(2,2'\text{-dpdc})(pyphen)]_2\}_n$ (2). A mixture of $Pb(NO_3)_2$ (0.166 g, 0.5 mmol), 2,2′-H_2dpdc (0.121 g, 0.5 mmol), pyphen (0.116 g, 0.5 mmol), and water (15 mL) was sealed in a 23 mL Teflon-lined stainless autoclave and allowed to stay at 160°C for 4 days, followed by cooling to room temperature over 48 h. Yellow crystals of **2** suitable for X-ray single-crystal diffraction analysis were obtained (yield 65%). For **2** $C_{56}H_{34}N_8O_8Pb_2$: C 49.41; H 2.52; N 8.23; found: C 49.36; H 2.55; and N 8.25.

2.2.3. Synthesis of $\{[Pb(2,2'\text{-dpdc})(dppz)]\}_n$ (3). Complex **3** was synthesized by a method similar to that of **2** using dppz (0.141 g, 0.5 mmol) instead of pyphen as the chelate ligand. Yellow crystals of **3** suitable for X-ray single-crystal diffraction analysis were obtained (yield 76%). Anal. Calcd for **3** C_{32} $H_{18}N_4O_4Pb$: C 52.60; H 2.51; N 7.71; found: C 52.63; H 2.47; and N 7.67.

2.3. *General characterization and physical measurements*

Elemental analysis was carried out with a Perkin Elmer 240°C analyzer; thermal gravimetric (TG) measurements were performed on a NETZSCH STA 449°C analyzer; visible luminescence properties of the ligands and complexes were measured on a Perkin Elmer LS55 spectrometer. Crystallographic data of the three complexes were collected at room temperature on a Bruker Smart Apex CCD diffractometer equipped with a normal-focus. In this study, a 2.4 kW X-ray source (graphite-monochromated Mo-Kα radiation with $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA with increasing ω (width of 0.3° and exposure time 30 s per frame) was used. The structures were solved by direct methods using SHELXS-97 [36] and refined by full-matrix least-squares against F^2 using the SHELXTL-97 crystallographic software package [37]. All non-hydrogen atoms were easily found from the difference Fourier map and refined anisotropically, whereas hydrogens of the complexes were placed by geometrical considerations and added to the structure factor calculation. The crystallographic data and details of refinement for the three complexes are summarized in table 1, and selected bond lengths and angles of **1**–**3** are listed in table 2.

3. Results and discussion

3.1. *Description of crystal structures*

3.1.1. The crystal structure of $\{[Cd(2,2'\text{-dpdc})(tppp)(H_2O)]_2\cdot 2H_2O\}_n$ (1). Structural analysis shows one cadmium ion, one 2,2′-dpdc, one tppp, one coordinated water, and one lattice water per asymmetric unit cell in **1**. The cadmium, shown in figure 1, is coordinated with two tppp nitrogens (Cd–N1 = 2.302(4) and Cd–N2 = 2.335(4) Å), and three oxygens from two 2,2′-dpdc (Cd–O2 = 2.194(3) and Cd–O3A = 2.212(3) Å), and one water (Cd–O6 = 2.253(4) Å) to form a distorted square pyramid. Cd–O distances ranging from 2.194(3) to 2.253(4) Å are similar to those in a related compound [38]. In **1**, two 2,2′-dpdc bridge two Cd(II) ions to form an isolated unit with Cd ··· Cd distance of 5.023(4) Å (figure 2a). In the *xz* plane, these clusters are linked to form a 2-D supramolecular structure through intermolecular hydrogen bonds (O5–H5 ··· O1 $[-x+1, -y+1, -z+1]$, O6–H6A ··· O5 $[-x+1, -y+1, -z+1]$, O6–H6A ··· O5 $[-x+1, -y+1, -z+1]$, O7–H7B ··· O4 $[x, y, z+1]$, O7–H7A ··· N3 $[-x+1, -y+1, -z+1]$, and N4–H4 ··· O4 $[x, y, z+1]$) as shown in figure 2(b). Selected hydrogen bond distances and angles are given in table 3.

3.1.2. The crystal structure of $\{[Pb(2,2'\text{-dpdc})(pyphen)]_2\}_n$ (2). X-ray analysis reveals that **2** contains two crystallographically independent Pb(II) ions in the asymmetric unit. As shown in figure 3, Pb1 is coordinated with two nitrogens (N1 and N2) from one pyphen and four oxygens (O1, O2, O3, and O4) from two bridging 2,2′-dpdc ligands (figure 3a). The distances of Pb–O bonds (2.367(5)–2.700(5) Å) and Pb–N bonds (2.665(5)–2.697(6) Å) are little different from those reported [39]. The coordination environment of Pb2 is the same as Pb1 in figure 3(b). As shown in figure 4(a) and (b), although the coordination modes of Pb1 and Pb2 are the same, their linking modes with ligands are different. Neighboring Pb1 ions are bridged by 2,2′-dpdc to form a 1-D

Table 1. Crystallographic data for **1–3**.

	1	**2**	**3**
Empirical formula	$C_{66}H_{48}O_{14}N_8Cd_2$	$C_{56}H_{34}N_8O_8Pb_2$	$C_{32}H_{18}N_4O_4Pb$
M ($g\,mol^{-1}$)	1401.94	1361.29	729.69
Crystal system	Triclinic	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	*P2(1)/c*
Unit cell dimensions (Å, °)			
a	10.067(9)	8.2902(7)	7.787(2)
b	12.107(11)	12.1185(10)	24.639(7)
c	13.103(11)	24.661(2)	13.950(4)
α	68.199(10)	98.7240(10)	90
β	74.338(11)	91.4080(10)	103.829(3)
γ	77.420(11)	106.4740(10)	90
Volume ($Å^3$), Z	1415(2), 1	2342.4(3), 2	2599.0(13), 4
Calculated density ($g\,cm^{-3}$)	1.645	1.930	1.865
$F(000)$	708	1308	1408
Crystal size (mm^3)	0.246 × 0.181 × 0.142	0.308 × 0.181 × 0.161	0.021 × 0.029 × 0.459
μ(Mo-Kα, mm^{-1})	0.831	7.247	6.539
θ range for data collection (°)	2.43–26.08	2.09–26.09	2.23–26.07
Reflections collected	12090	20247	22158
Independent reflection [$I > 2\sigma(I)$]	5550	9200	5129
Parameters	430	667	370
Goodness-of-fit F^2	0.990	1.020	1.020
R^a	0.0477 (0.0957)[b]	0.0393 (0.0762)[b]	0.0262 (0.0493)[b]
$wR_2{}^a$	0.0786 (0.1095)[b]	0.0680 (0.0853)[b]	0.0390 (0.0530)[b]
$\Delta(\rho)$ (e $Å^{-3}$)	0.730 and −0.684	2.349 and −1.057	0.421 and −0.553

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2/[\Sigma(w(F_o^2)^2]^{1/2}$; [$F_o > 4\sigma(F_o)$].
[b] Based on all data.

Table 2. Selected bond lengths (Å) and angles (°) for **1–3**.

Complex **1**					
Cd–O2	2.194(3)	Cd–O3A	2.212(3)	Cd–O6	2.253(4)
Cd–N1	2.302(4)	Cd–N2	2.335(4)		
O2–Cd–O3A	95.04(14)	O2–Cd–O6	98.89(11)	O3A–Cd–O6	84.42(10)
O2–Cd–N1	168.62(9)	O3A–Cd–N1	93.01(11)	O6–Cd–N1	89.87(8)
O2–Cd–N2	98.02(11)	O3A–Cd–N2	145.84(10)	O6–Cd–N2	124.10(8)
N1–Cd–N2	70.9				
Complex **2**					
Pb1–O1	2.367(5)	Pb1–O3	2.499(4)	Pb1–O2	2.646(4)
Pb1–N2	2.665(5)	Pb1–N1	2.697(6)	Pb1–O4	2.700(5)
Pb2–O8	2.286(4)	Pb2–O5	2.494(5)	Pb2–N5	2.570(5)
Pb2–O6	2.620(5)	Pb2–N6	2.674(6)	Pb2–O7	2.683(5)
O1–Pb1–O3	86.30(17)	O1–Pb1–O2	51.53(15)	O3–Pb1–O2	122.39(16)
O1–Pb1–N2	75.28(17)	O3–Pb1–N2	136.19(16)	O2–Pb1–N2	75.22(15)
O1–Pb1–N1	71.77(17)	O3–Pb1–N1	75.66(16)	O2–Pb1–N1	115.14(16)
N2–Pb1–N1	60.95(16)	O1–Pb1–O4	83.08(18)	O3–Pb1–O4	49.57(15)
O2–Pb1–O4	83.98(16)	N2–Pb1–O4	156.37(18)	N1–Pb1–O4	120.93(16)
Complex **3**					
Pb–O3	2.305(3)	Pb–O4	2.630(3)	Pb–N1	2.622(3)
Pb–N2	2.686(3)	Pb–O1	2.640(3)	Pb–O2	2.389(3)
O3–Pb–O2	83.20(10)	O3–Pb–N1	81.28(10)	O2–Pb–N1	76.68(10)
O3–Pb–O4	52.52(8)	O2–Pb–O4	120.43(10)	N1–Pb–O4	123.52(9)
O3–Pb–O1	88.03(11)	O2–Pb–O1	51.36(9)	N1–Pb–O1	127.88(9)
O4–Pb–O1	85.56(10)	O3–Pb–N2	78.55(10)	O2–Pb–N2	136.37(9)
N1–Pb–N2	61.64(9)	O4–Pb–N2	77.23(9)	O1–Pb–N2	162.38(10)

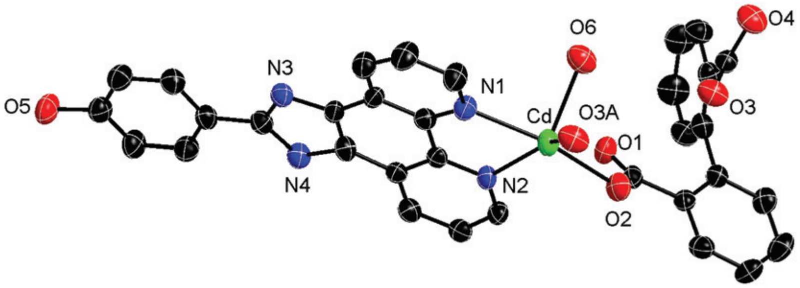

Figure 1. Crystal structure of **1** with 50% probability displacement ellipsoids with hydrogens omitted for clarity.

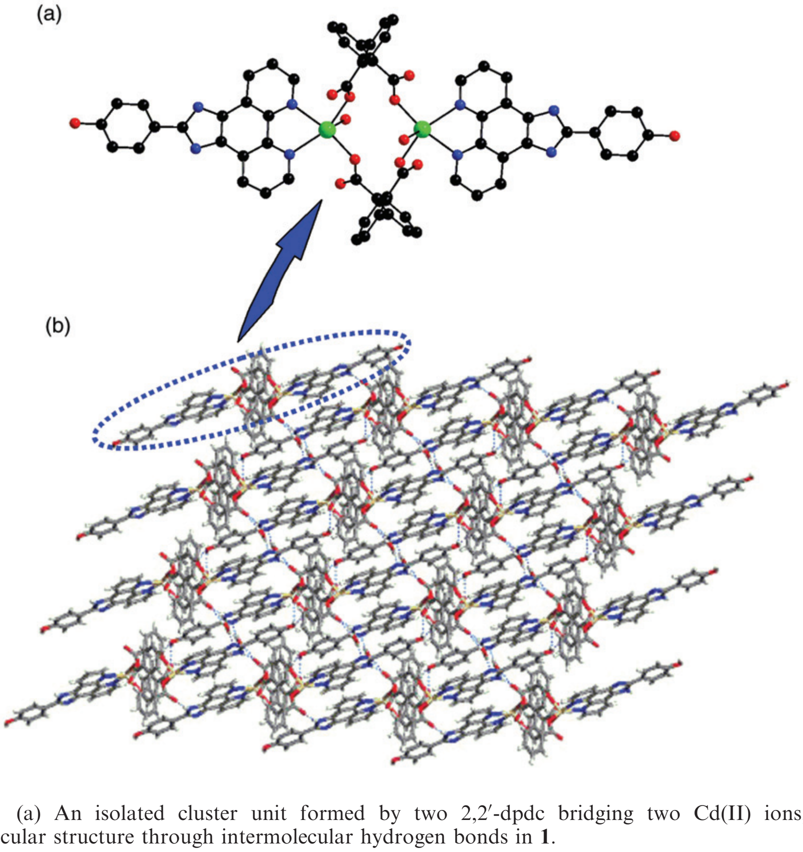

Figure 2. (a) An isolated cluster unit formed by two 2,2′-dpdc bridging two Cd(II) ions; (b) 2-D supramolecular structure through intermolecular hydrogen bonds in **1**.

chain structure along the *x*-axis with pyphen arranged in the same side of the chain. However, two 2,2′-dpdc ligands bridge two Pb2 ions to form an isolated cluster unit. These isolated cluster units are stacked to a 1-D infinite chain *via* aromatic π–π stacking interactions ($d_{\pi-\pi} = 3.615$ Å) along the *y*-axis. In the *xz* plane, cluster units are arranged

Table 3. Distances (Å) and angles (°) of selected hydrogen bonding for **1**.

D–H···A	d(D···A)	∠(D–H···A)
O5–H5···O1 $[-x+1, -y+1, -z+1]$	2.662	124.21
O6–H6B···O2 $[-x, -y+1, -z]$	2.749	176.28
O6–H6A···O5 $[-x+1, -y+1, -z+1]$	2.729	155.82
O7–H7B···O4 $[x, y, z+1]$	2.939	157.98
O7–H7A···N3 $[-x+1, -y+1, -z+1]$	2.918	174.50
N4–H4···O4 $[x, y, z+1]$	2.799	168.37

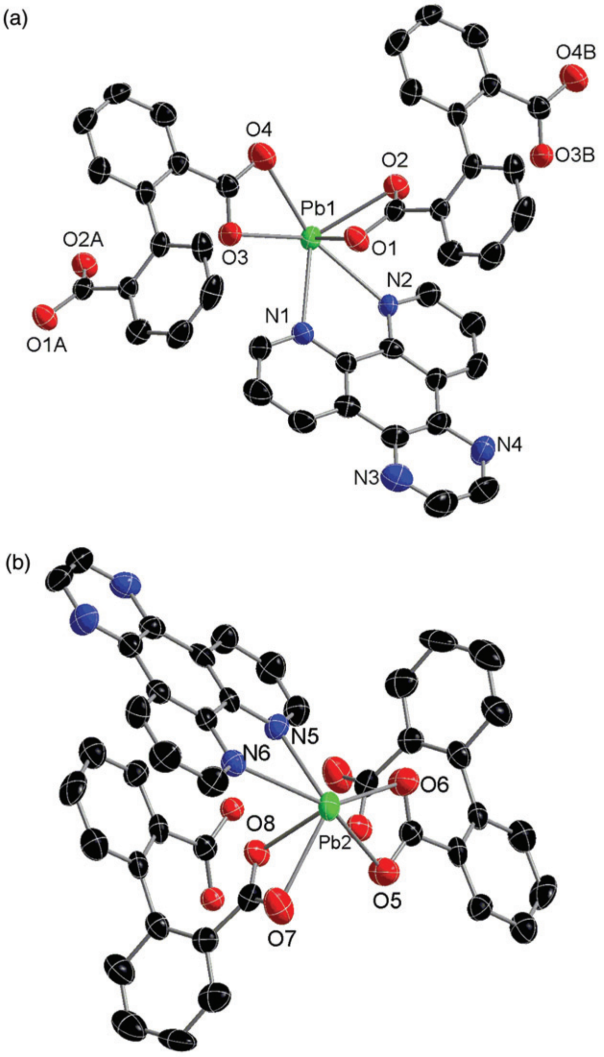

Figure 3. Crystal structure of **2** (a) Pb1 and (b) Pb2 with 50% probability displacement ellipsoids with hydrogens omitted for clarity.

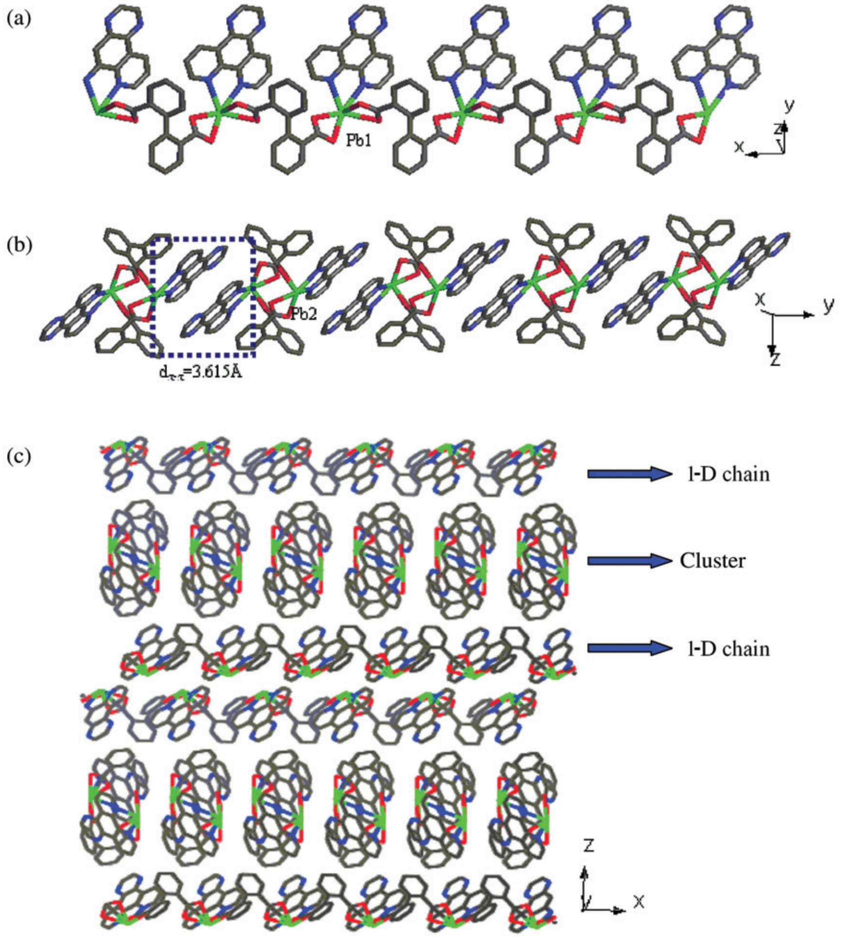

Figure 4. (a) 1-D chain structure along the *x* direction formed by Pb1 ions and linked ligands. (b) 1-D chain structure along the *y* direction formed by Pb2 and linked ligands *via* aromatic π–π stacking interactions. (c) The stacking structure of **2**.

between two parallel chains, as shown in figure 4(c). The structures are repeated infinitely in the *z*-axis direction.

Crystal structures containing two distinct and crystallographically independent polymeric motifs can be found in some silver coordination polymers [40, 41], but few reported on Cd(II)- or Pb(II)-based compounds. A related Cd(II) compound, $[Cd_3(bbtz)_6(H_2O)_6](BF_4)_6 \cdot 1.75H_2O$ (bbtz = 1,4-*bis*(1,2,4-triazol-1-ylmethyl)benzene), affords a 3-D coordination network containing two motifs; one consists of a planar 2-D (4,4) network and another is composed of a ribbon [42].

3.1.3. The crystal structure of $\{[Pb(2,2'\text{-dpdc})(dppz)]\}_n$ (3). X-ray analysis revealed that the asymmetric unit of **3** contains one lead, one dppz, and one 2,2′-dpdc. As shown in figure 5, Pb is coordinated with two nitrogens of one dppz ligand, and four oxygens

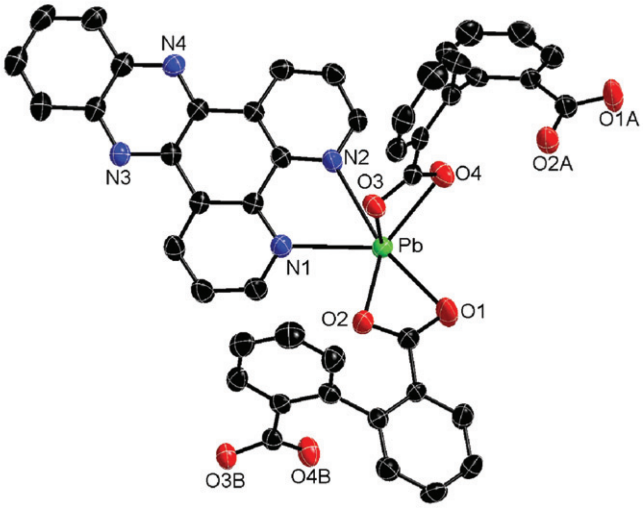

Figure 5. Crystal structure of **3** with 50% probability displacement ellipsoids with hydrogens omitted for clarity.

from two 2,2′-dpdc ligands. Along the *z*-axis, neighboring leads are bridged by 2,2′-dpdc into a 1-D chain as shown in figure 6(a). Along the *y*-axis, aromatic π–π stacking interactions ($d_{\pi-\pi} = 3.633$ Å) between ligands link the 1-D chains together, leading to a 2-D layer structure (figure 6b). These 2-D layer structures were connected *via* aromatic π–π stacking interactions ($d_{\pi-\pi} = 3.538$ and 3.632 Å) to form a 3-D supramolecular network, as shown in figure 6(c).

3.1.4. Comparison of structures 1–3. In **1** and **2**, the two 2,2′-dpdc ligands, in *cis*-conformations, bridge two Cd(II) ions and two Pb(II) ions, respectively, generating two similar clusters. Further, pyphen and dppz, in similar modes, are attached on both sides of the clusters. The Cd ⋯ Cd and Pb ⋯ Pb distances in the two clusters are 5.023 and 6.194 Å, respectively. In **2** and **3**, the dpdc ligands, in similar *trans*-conformations, link the central Pb(II) ions to form similar chain structures. To the best of our knowledge, similar chains have not been observed in Pb(II) compounds. Compared with the pyphen ligand of **2**, the dppz ligand of **3** has an additional phenyl group. Although the N-donors show small differences in their structures, the π–π stacking distance that links clusters in **2** is near to those which link the chains in **3**. It should be noted that although the chain motifs in **2** and **3** are very similar, a small difference exists. The Pb ⋯ Pb distances (8.290 Å for **2** and 7.724 Å for **3**) bridged by dpdc ligands in the chains are slightly different, arising from slightly different twists in the dpdc of **2** and **3**. In **2**, the pyphen ligands are attached on one side of the chain, while in **3** the dppz ligands are located on both sides of the chain.

3.2. *IR spectra*

IR spectra of the three compounds were recorded from 4000 to 400 cm^{-1} on a Perkin Elmer 2400LSII spectrometer. The broad peak at 3402 cm^{-1} can be attributed to O–H

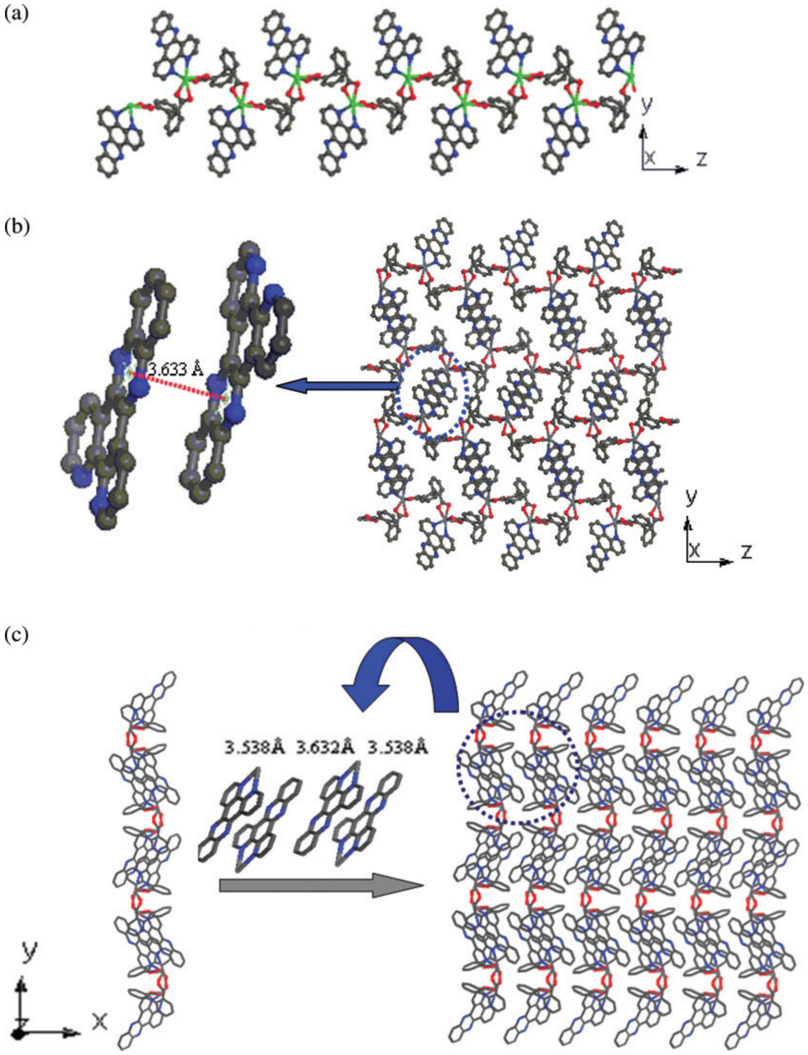

Figure 6. (a) A 1-D chain structure along the *z* direction. (b) A 2-D layer structure *via* aromatic π–π stacking interactions in the *y*-*z* plane. (c) A 3-D supramolecular network.

stretching of water in **1**. The peak at 1390 cm^{-1} for **1**, 1382 cm^{-1} for **2**, and 1361 cm^{-1} for **3** are ascribed to ν(C=N) vibrations of the phen ligands. For all three complexes, the C–H stretching mode for the phenyl or pyridine rings is relatively weak at 3100 cm^{-1}. Peaks at about 1617, 1546, and 1534 cm^{-1} could be attributed to ν(C=O) of carboxylate. The signals at 1638 cm^{-1} for **1**, 1617 cm^{-1} for **2,** and 1596 cm^{-1} for **3** can be assigned to ν(C=C) of the aromatic ring. Broad peaks at 3380 cm^{-1} for **2** and 3442 cm^{-1} for **3** may be due to O–H stretching of water affected by hygroscopic potassium bromide.

3.3. *Thermal stability analysis*

To examine the thermal stability of **1**, **2**, and **3**, TG analyses were carried out. Thermal decomposition of **1** shows that the degradation occurs in four steps (figure S1, Supporting information). The first step, in the 90–130°C range, is assigned to loss of free water (found 2.62%, Calcd 2.57%). The second step, 170–220°C, comprises the elimination of coordinated water (found 2.59%, Calcd 2.57%) and the third step, 255–360°C, suggests elimination of tppp (found 44.53%, Calcd 44.56%). Finally, the last step, 375–520°C, corresponds to the elimination of $dpdc^{2-}$ (found 34.25%, Calcd 34.27%). The final residue is suggested to be CdO. The TG curve of **2** exhibits three weight losses (figure S2, Supporting information). The first is 1.50% in the temperature range 47–200°C, which may correspond to loss of non-coordinated water. The second with an endothermic process centered at 360°C is 34.80% at 200–380°C, and the last step with an endothermic process centered at 380°C is 35.40% in the temperature range 380–530°C and with an exothermic process centered at 500°C, all assigned to decomposition of pyphen and $dpdc^{2-}$ (Calcd 69.51%). The remaining weight (29.80%) indicates that the final product was PbO (Calcd 32.85%). The TG curve of **3** exhibits two weight loss stages at 300–360°C (38.30%) and 360–550°C (33.04%) (figure S3, Supporting information), corresponding to release of dppz and $dpdc^{2-}$, with two endothermic processes centered at 370 and 445°C, and an exothermic center at 530°C. The residue is also PbO. The whole weight loss (71.34%) is in good agreement with the calculated value (71.58%). Complex **3** with dppz shows more thermal stability. The reason for different thermal stability of the three compounds was presumably owing to the differences of conjugation of ligands and coordination mode of complexes.

3.4. *Photoluminescent properties*

Cd(II) and Pb(II) can produce complexes with appealing structures and photoluminescence properties. The solid–state luminescence properties of **1**–**3**, as well as free ligands, were investigated at room temperature. The ligands exhibit emissions at 424 nm for 2,2′-H_2dpdc ($\lambda_{ex} = 344$ nm) [43], at 430 nm for tppp ($\lambda_{ex} = 267$ nm) [39], at 439 nm for pyphen ($\lambda_{ex} = 300$ nm) (figure S4, Supporting information), and at 444 nm for dppz

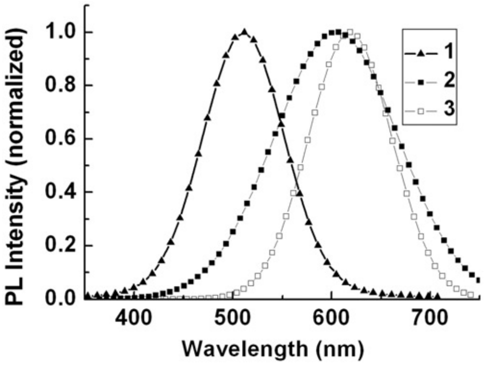

Figure 7. Normalized photoluminescence spectra of the complexes.

($\lambda_{ex} = 328$ nm) [44]. As shown in figure 7, **1** exhibits blue–green photoluminescence with an emission maximum at 511 nm upon excitation at 340 nm. Compounds **2** and **3** exhibit red emissions, maxima at 607 and 618 nm, upon excitation at 365 nm. Compared with the photoluminescence spectra, the emission spectra of the three complexes are obviously similar to those of the phen ligands, which might be attributable to coordination of the planar phen ligands in the complexes. The photoluminescent emissions of **1**, **2**, and **3** also mainly originate from intraligand fluorescent emissions [45]. In comparison to **2**, a slight red shift of 11 nm has been observed in **3** because of the change of coordination geometry of the metal centers and the increasing conjugation of dppz in contrast to pyphen.

4. Conclusion

Three complexes have been synthesized under hydrothermal conditions and structurally characterized by X-ray diffraction analyses. The structure variation of the three complexes depends primarily on the different linking modes of H_2dpdc. At the same time, the multidentate nitrogen donor played an important role in the formation of supramolecular structures. These results indicate that H_2dpdc can adopt different coordination modes to adapt to changes in multidentate nitrogen donor and metal ion. These changes have significant effect on the novel framework structures of the complexes.

Supplementary material

The crystallographic data have been deposited at the Cambridge Crystallographic Data Centre, CCDC nos. 767666 for **1** and 767667 for **2**. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Email: deposit@ccdc.cam.ac.uk; Fax: 44-1223-336-033; http://www.ccdc.cam.ac.uk).

Acknowledgments

The authors thank the Postdoctoral Foundation of Jiangsu Province (no. 0801010B) and the Natural Science Foundation Project of Jiangsu University (no. 09JDG001) of China.

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