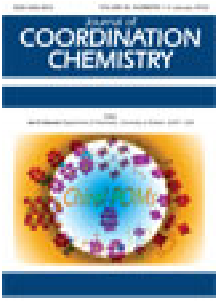
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:40
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Hydrothermal synthesis, structure, and properties of lead(II)-based coordination compounds with R-isophthalic acid (R=OH, CH_3)

Zhen Wang [a], Qing Wei [a], Gang Xie [a], Qi Yang [a], Sanping Chen [a] & Shengli Gao [a]

[a] Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, China

Published online: 20 Jan 2012.

To cite this article: Zhen Wang, Qing Wei, Gang Xie, Qi Yang, Sanping Chen & Shengli Gao (2012) Hydrothermal synthesis, structure, and properties of lead(II)-based coordination compounds with R-isophthalic acid (R=OH, CH_3), Journal of Coordination Chemistry, 65:2, 286-297, DOI: 10.1080/00958972.2011.648628

To link to this article: http://dx.doi.org/10.1080/00958972.2011.648628

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 65, No. 2, 20 January 2012, 286–297

Taylor & Francis
Taylor & Francis Group

Hydrothermal synthesis, structure, and properties of lead(II)-based coordination compounds with *R*-isophthalic acid ($R = \mathrm{OH}, \mathrm{CH_3}$)

ZHEN WANG, QING WEI, GANG XIE, QI YANG, SANPING CHEN* and SHENGLI GAO

Key Laboratory of Synthetic and Natural Functional Molecule Chemistry of Ministry of Education, College of Chemistry and Materials Science, Northwest University, Xi'an 710069, China

(*Received 25 August 2011; in final form 27 October 2011*)

Three new lead(II)-based coordination polymers, $[\mathrm{Pb(5\text{-}OH\text{-}BDC)}]_n \cdot n\mathrm{H_2O}$ (**1**) (5-OH-BDC = 5-hydroxyisophthalate), $[\mathrm{Pb_2(5\text{-}CH_3\text{-}BDC)_2}]_n$ (**2**), and $[\mathrm{Pb_2(5\text{-}CH_3\text{-}BDC)_2(phen)_2}]_n \cdot 2n\mathrm{H_2O}$ (**3**) ($5\text{-}\mathrm{CH_3}$-BDC = 5-methylisophthalate, phen = 1,10-phenanthroline), have been hydrothermally synthesized, structurally determined by single-crystal X-ray diffraction, and characterized by elemental analyses, IR spectra, and thermogravimetric analyses. Both **1** and **2** exhibit 2-D double-layer network structures, while **3** possesses 1-D chain structure bridged by $5\text{-}\mathrm{CH_3}$-BDC. The coordination sphere of Pb(II) in **1** is holodirected, whereas in **2** and **3** the spheres feature hemidirected structures. Fluorescence properties of **1**–**3** have been investigated in the crystalline state at room temperature.

Keywords: Pb(II)-based coordination compound; Isophthalate; Hydrothermal synthesis; Structural analysis; Fluorescence spectrum

1. Introduction

Lead(II) coordination compounds have been involved in a range of applications, including fuel additives, batteries, solder, photovoltaic conversion, fluorescent sensors, electroluminescent devices, and organic light-emitting diode (OLED) technology [1–3]. According to the electronic configuration ($[\mathrm{Xe}]4f^{14}5d^{10}6s^2$) and size, the lone pair electron in Pb(II) has influence on both coordination numbers and geometries, with the absence of crystal field stabilization energy allowing Pb(II) to adopt varied coordination geometries that can lead to interesting and novel topological arrangements.

Compared with transitional metal ions, however, relatively little attention has been paid to p-block lead ions [4–10]. Pb(II) ion has a large radius and flexible coordination environment making it extremely difficult to predict topologies and geometries of networks and as a toxic metal, the ion is often present as a contaminant in the

---

*Corresponding author. Email: sanpingchen@126.com

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2011.648628

environment [11–13]. Therefore, it is still necessary to perform systematic research on Pb(II) coordination compounds that relate to lone pair of electrons, coordination number, coordination geometry, and such compounds in the environment to understand roles of those factors in the formation of metal coordination frameworks [14–17]. In view of the steady increase in the amount of lead released into the environment by human activity, a possible method for the removal of this toxic metal might be introduction of chelating agents.

As an important organic polycarboxylate, isophthalic acid and derivatives have been employed in the preparation of lead(II)-based coordination compounds [18–22]. Extending the above research, we have focused on Pb(II) coordination compounds with isophthalates attached with different 5-position substituents in order to explore the effects of 5-position substituents on the formation of extended networks (MOFs).

Based on the above considerations, 5-hydroxyisophthalic acid (5-OH-H_2BDC) and 5-methylisophthalic acid (5-CH_3-H_2BDC) were chosen as ligands in this work. Three supramolecular architectures, $[Pb(5\text{-OH-BDC})]_n \cdot nH_2O$ (**1**) (5-OH-BDC = 5-hydroxyisophthalate), $[Pb_2(5\text{-}CH_3\text{-BDC})_2]_n$ (**2**), and $[Pb_2(5\text{-}CH_3\text{-BDC})_2(\text{phen})_2]_n \cdot 2nH_2O$ (**3**) (5-CH_3-BDC = 5-methylisophthalate, phen = 1,10-phenanthroline), have been obtained and characterized by single-crystal X-ray diffraction, elemental analysis, IR spectroscopy, and thermogravimetric analysis (TGA). Moreover, fluorescence properties of **1**–**3** have also been investigated in the solid state at room temperature.

2. Experimental

2.1. *Materials and instruments*

All chemicals were of analytical grade and used without purification. Hydrothermal reactions were performed in a 10 mL Teflon-lined stainless steel autoclave under autogenous pressure. Elemental analyses (C, N, and H) were carried out on a Perkin–Elmer elemental analyzer. IR spectra were recorded as KBr pellets from 400 to 4000 cm^{-1}. TGAs were performed on a NETZSCH TG 209 instrument with a heating rate of 10°C min^{-1} in a dynamic nitrogen flow. Photoluminescence studies were carried out on crystalline samples at room temperature.

2.2. *Synthesis*

2.2.1. Synthesis of $[Pb(5\text{-OH-BDC})(H_2O)]_n \cdot nH_2O$ (1). A mixture of $PbCl_2$ (0.1 mmol, 0.0278 g), 5-OH-H_2BDC (0.1 mmol, 0.0182 g), and deionized water (6 mL) was introduced into a Parr Teflon-lined stainless steel vessel. The vessel was sealed and heated at 170°C for 3 days and cooled naturally. Colorless crystalline **1** suitable for X-ray diffraction analysis was collected from the reaction system by filtration, washed with distilled water, and dried at ambient temperature. Yield: 28% based on Pb(II). Anal. Calcd for $C_8H_5O_6Pb$ ($Mr = 404.31$): C, 23.76; H, 1.24. Found: C, 23.96; H, 1.17. IR (solid KBr pellet, ν (cm^{-1})) for **1**: 3395 (s), 2319 (w), 1595 (vs), 1540 (vs), 1432 (s), 1142 (m), 872 (w), 771 (m), 719 (s), 575 (w).

2.2.2. Synthesis of [$Pb_2(5\text{-}CH_3\text{-}BDC)_2]_n$ (2). *Method A*: A mixture of $Pb(CH_3COO)_2 \cdot 3H_2O$ (0.1 mmol, 0.0379 g), 5-CH_3-H_2BDC (0.1 mmol, 0.0180 g), and deionized water (6 mL) was introduced into a Parr Teflon-lined stainless steel vessel. The vessel was sealed and heated at 180°C for 3 days and cooled naturally. Colorless crystalline **2** suitable for X-ray diffraction analysis was collected from the final reaction system by filtration, washed with distilled water, and dried at ambient temperature. Yield: 23% based on Pb(II). Anal. Calcd for $C_{18}H_{12}O_8Pb_2$ ($Mr = 770.66$): C, 28.05; H, 1.57. Found: C, 28.43; H, 1.45. IR (solid KBr pellet, ν (cm^{-1})) for **2**: 3390 (s), 1597 (vs), 1540 (vs), 1436 (vs), 1361 (vs), 982 (m), 865 (m), 824 (w), 796 (s), 732 (m), 683 (w), 633 (w), 542 (m).

Method B: A mixture of $PbCl_2$ (0.1 mmol, 0.0278 g) and 5-CH_3-H_2BDC (0.1 mmol, 0.0180 g) in deionized water (6 mL), with pH adjusted to 5–6 by aqueous sodium hydroxide, was introduced into a Parr Teflon-lined stainless steel vessel. The sealed vessel was heated at 180°C for 3 days and allowed to cool. Single crystals of **2** suitable for X-ray diffraction analysis were collected from the final reaction system by filtration, washed with distilled water, and dried at ambient temperature. Yield: 21% based on Pb(II).

2.2.3. Synthesis of [$Pb_2(5\text{-}CH_3\text{-}BDC)_2(phen)_2]_n \cdot 2nH_2O$ (3). A system involving $PbCl_2$ (0.1 mmol, 0.0278 g) or $Pb(NO_3)_2$ (0.1 mmol, 0.0331 g), 5-CH_3-H_2BDC (0.1 mmol, 0.0180 g), phen (0.1 mmol, 0.0198 g), and deionized water (6 mL) was hydrothermally treated at 160°C for 3 days in a Parr Teflon-lined stainless steel vessel. Upon cooling, light yellow crystalline product of **3** suitable for X-ray diffraction analysis was collected from the final reaction system by filtration, washed with distilled water, and dried at ambient temperature. Yield: 32% based on Pb(II). Anal. Calcd for $C_{42}H_{32}N_4O_{10}Pb_2$ ($Mr = 1167.10$): C, 43.22; H, 2.76; N, 4.80. Found: C, 43.37; H, 2.68; N, 4.86. IR (solid KBr pellet, ν (cm^{-1})) for **3**: 3420 (s), 1628 (m), 1582 (s), 1495 (m), 1360 (m), 1076 (m), 800 (m), 709 (s), 638 (m).

2.3. *X-ray crystallography*

Single crystals of **1**–**3** were collected on a Bruker SMART APEXIICCD area detector diffractometer with graphite monochromated Mo-Kα radiation (0.071073 nm). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using SHELXL97 [23, 24]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystal data and structure refinements of **1**–**3** are summarized in table 1. Selected bond lengths and angles for **1**–**3** are listed in tables S1–S3.

3. Results and discussion

3.1. *Synthesis*

The three compounds were obtained from hydrothermal reactions of Pb(II) salts and an organic acid. The reactions were carried out at different temperatures, 170°C, 180°C,

Table 1. Crystal data and structure refinement parameters for **1–3**.

Compound	**1**	**2**	**3**
Empirical formula	$C_8H_5O_6Pb$	$C_{18}H_{12}O_8Pb_2$	$C_{42}H_{32}N_4O_{10}Pb_2$
Formula weight	404.31	770.66	1167.10
Space group	$P\bar{1}$	$C2/c$	$P\bar{1}$
Unit cell dimensions (Å, °)			
a	6.7714(4)	21.155(3)	8.8921(9)
b	7.9006(5)	8.0158(11)	9.7626(9)
c	8.2156(5)	25.536(4)	12.5916(12)
α	78.6390(10)	90	70.7250(10)
β	82.3940(10)	111.187(2)	87.703(2)
γ	86.1780(10)	90	65.9510(10)
Volume (Å^3), Z	426.74(5), 2	4037.6(10), 8	936.57(16), 1
Calculated density (Mg m^{-3})	3.146	2.536	2.069
Absorption coefficient (mm^{-1})	19.773	16.698	9.044
$F(000)$	366	2784	556
θ range for data collection (°)	2.55 to 25.99	1.71 to 25.10	1.72 to 26.49
Reflections collected	2341	9783	5235
Independent reflection R(int)	1638 [R(int) = 0.0125]	3603 [R(int) = 0.0544]	3720 [R(int) = 0.0297]
Data/restraints/parameters	1638/0/137	3603/168/255	3720/0/263
Goodness-of-fit on F^2	1.007	1.095	0.734
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0204$, $wR_2 = 0.0533$	$R_1 = 0.0477$, $wR_2 = 0.1230$	$R_1 = 0.0332$, $wR_2 = 0.0915$
R indices (all data)	$R_1 = 0.0212$, $wR_2 = 0.0541$	$R_1 = 0.0582$, $wR_2 = 0.1296$	$R_1 = 0.0375$, $wR_2 = 0.0958$

and 160°C. Compound **1** was achieved through a facile reaction of $PbCl_2$ with 5-OH-H_2BDC in aqueous solutions. When $Pb(CH_3COO)_2 \cdot 3H_2O$ or $Pb(NO_3)_2$ was used as a lead source, only a small quantity of microcrystals unsuitable for single-crystal X-ray diffraction was obtained. Compound **2** was obtained through the reaction of $Pb(CH_3COO)_2 \cdot 3H_2O$ with 5-methylisophthalic acid in water or using $PbCl_2$ as the lead source at pH 5–6. Compound **3** was the product of the aqueous reaction between $PbCl_2$ or $Pb(NO_3)_2$ and 5-methylisophthalic acid in the presence of phen at 160°C.

3.2. *Crystal structure analysis*

3.2.1. [Pb(5-OH-BDC)]$_n$·nH$_2$O (1). Single crystal X-ray diffraction analysis reveals that **1** is a 2-D coordination polymer with 1-D inorganic lead(II) oxygen chains. As shown in figure 1, the asymmetric unit consists of one Pb^{2+}, one 5-hydroxyisophthalate (5-OH-BDC) ligand, and one solvent water molecule.

The Pb(II) ion in **1** is holodirected, coordinating to six carboxylate oxygen atoms from four carboxylates of 5-OH-BDC and one hydroxyl oxygen from the fifth 5-OH-BDC, with Pb-O distances of 2.413(4)–2.972(4) Å. The coordination polyhedron around Pb1 can be attributed to a distorted mono-capped trigonal prism wherein the capped position is occupied by O4 while O1, O2, O5 and O3, O1A, O3A complete the two triangular planes of the prism. As shown in scheme 1(a), 5-OH-BDC is a pentadentate ligand with monodentate hydroxyl and two $\mu 2$–$\eta 1$: $\eta 2$ carboxylates in **1**. These PbO_7 polyhedra share edges with each other while adjacent lead ions are linked by $\mu 2$–$\eta 1$: $\eta 2$ coordination of carboxylate so as to form two independent infinite Pb–O–Pb double helical chains along the c axis (figure 2).

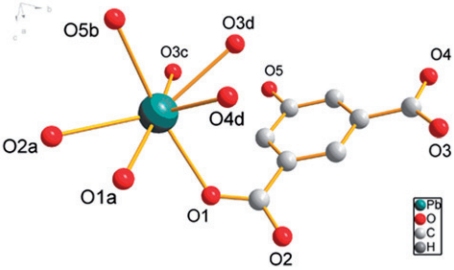
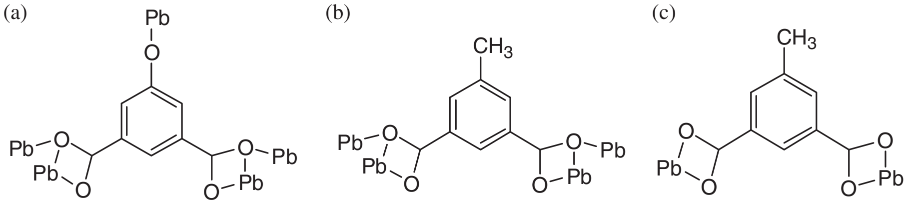


Figure 1. Coordination environments of Pb(II). Symmetry codes: a: $1-x$, $1-y$, $2-z$; b: $1-x$, $1-y$, $2-z$; c: x, $-1+y$, z; d: $1-x$, $2-y$, $1-z$.



Scheme 1. Coordination modes of 5-OH-BDC and 5-CH_3-BDC.

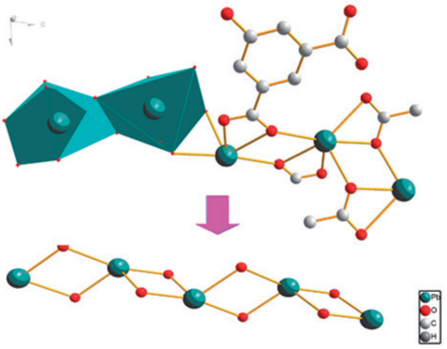


Figure 2. The 1D infinite Pb–O–Pb double helical chains along the *c* axis.

As illustrated in figure 3, all the 1-D Pb–O–Pb chains are interconnected by 5-OH-BDC to form a 2-D bilayer structure. Hydrogen bonding interactions further extend the structure into a 3-D supramolecular framework.

3.2.2. $[Pb_2(5\text{-}CH_3\text{-}BDC)_2]_n$ (2). Compound **2** crystallizes in the monoclinic space group *C*2/*c* and also is a 2-D bilayer structure with 1-D Pb(II) oxygen chains. As shown in figure 4, the asymmetric unit of **2** consists of two crystallographically independent Pb^{2+} ions (Pb1 and Pb2) and two 5-CH_3-BDC ligands. Pb1 is hemidirected and coordinated by six oxygen atoms from four 5-CH_3-BDC ligands, forming a PbO_6 polyhedron.

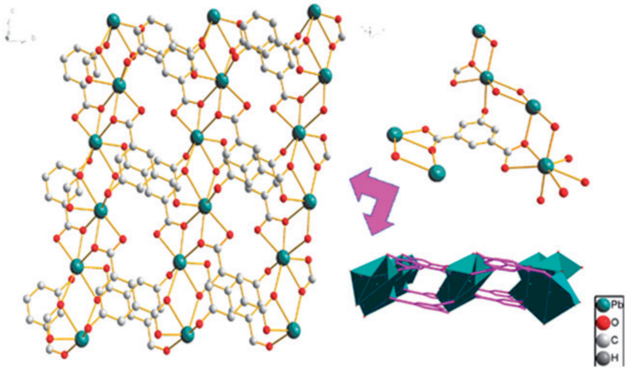


Figure 3. The 2-D bilayer structure in **1**.

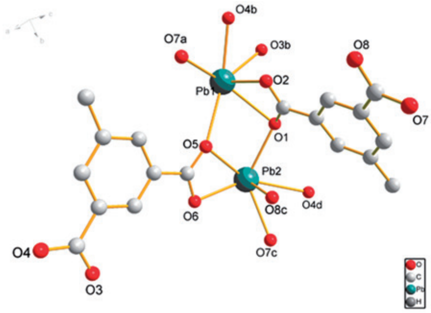


Figure 4. The coordination environments of Pb1 and Pb2 in **2**. Symmetry codes: a: $0.5-x$, $-0.5+y$, $1.5-z$; b: $-0.5+x$, $-0.5+y$, z; c: $0.5-x$, $0.5+y$, $1.5-z$; d: $-0.5+x$, $0.5+y$, z.

Among the six oxygen atoms, O1 and O2, O3b and O4b are from two chelating carboxylates of two ligands, and O5 and O7a are from another two different 5-CH$_3$-BDC ligands. The Pb–O bond lengths are 2.284(9)–2.695(2) Å with Pb1–O2 the shortest (2.2849 Å) while Pb1–O5 is the longest (2.5717 Å); therefore, the 6 s lone pair electrons may be opposite to Pb1–O2 and close to Pb1–O5. The coordination geometry of Pb1 can be described as a distorted mono-capped trigonal prism with the seventh coordination site occupied by its lone pair of electrons. The carboxylate O2 occupies the capped position, the lone pair of electrons, O5 and O7a complete one triangular plane of the prism, and the remaining three sites are occupied by O1, O3b, and O4b. The coordination environment of Pb2 is similar to that of Pb1 (figure 5a).

As shown in figure 5(b), two adjacent leads are linked by sharing two $\mu2$-oxygens to form a 1-D infinite Pb–O–Pb double chain with a Pb···Pb distance of 4.1 Å along the *b* axis. The 1-D chain contains an uncommon inorganic lead-oxide chain featuring four-membered rhombic-shaped rings, in which the O–Pb–O angles range from 51.8(2)° to 127.7(2)°.

As shown in scheme 1(b), 5-CH$_3$-H$_2$BDC is deprotonated to the 5-CH$_3$-BDC dianion in **2**, both carboxylate groups adopt $\mu2$–$\eta1$:$\eta2$-chelating/bridging coordination. As shown in figure 6, the lead carboxylate-oxygen chains are linked by the carboxylates to

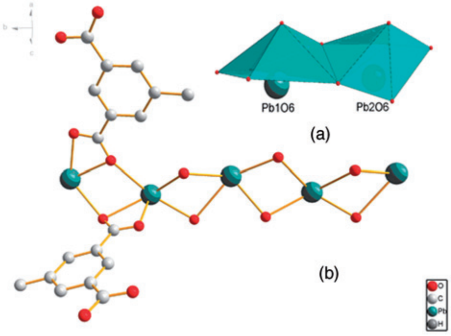


Figure 5. (a) PbO_6 polyhedron showing the coordination geometry of lead in **2**; (b) the 1-D infinite Pb–O–Pb double chains in **2**.

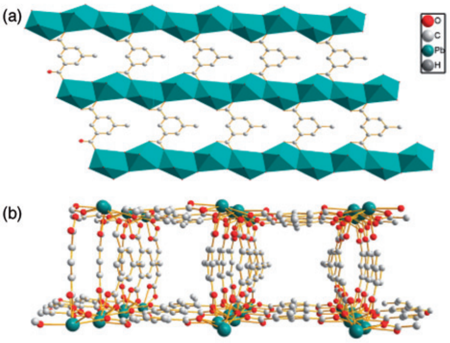


Figure 6. The 2-D double-layer in **2**.

form a 2-D-layered structure along the *ab* plane. Two adjacent layers are connected by 5-CH_3-BDC ligands to form a double-layer structure.

3.2.3. $[Pb_2(5\text{-}CH_3\text{-}BDC)_2(phen)_2]_n \cdot 2H_2O$ (3). Compound **3** crystallizes in the triclinic space group $P\bar{1}$ with two Pb(II) ions, two 5-CH_3-BDC ligands, two phen, and two lattice water molecules in the asymmetric unit. The Pb(II) in **3** is coordinated by four oxygen atoms from two bis-chelating 5-CH_3-BDC ligands and two nitrogen atoms from a chelating phen to furnish a highly distorted pentagonal bipyramidal coordination sphere (figure 7). The Pb–O distances range from 2.404(4) Å to 2.689(5) Å. Two carboxylates in 5-CH_3-H_2BDC are deprotonated and adopt $\mu2$–$\eta1$: $\eta1$-chelating coordination (scheme 1c). Each pair of adjacent Pb(II) atoms is bridged by 5-CH_3-BDC to give a zigzag chain along the [1,1,0] direction. The phen ligands in **3** are extended on one side of the zigzag chain in almost perpendicular fashion, the dihedral angle between phen and the benzene ring of 5-CH_3-BDC anion being 91.868° (figure 8). The chains are extended into a 1-D double-layer through π–π intercalations between phen's from adjacent chains with a face-to-face distance of about 3.55 Å. The corresponding phen ligands are almost parallel and participate in weak π–π stacking interactions, which further contribute to the stability of the compound (figure 9).

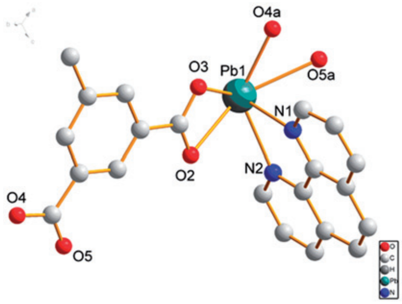


Figure 7. The coordination environment of Pb1 in **3**. Symmetry codes: a: $1+x$, $-1+y$, z.

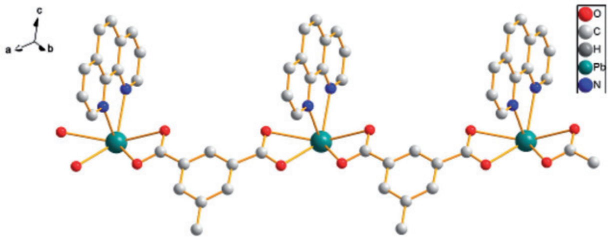


Figure 8. View of the 1-D chain of **3**.

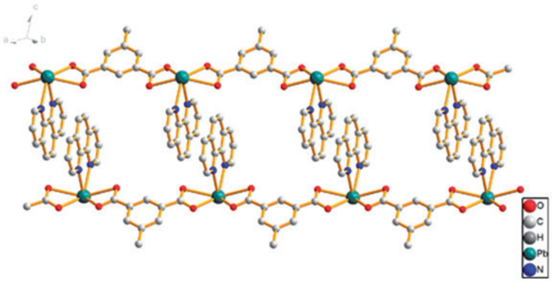


Figure 9. View of 1-D double-layer through π–π interactions between phen ligands in **3**.

3.3. *Effects of the organic-acid and N-donor on the structures*

The structures of coordination polymers are influenced by geometrical and electronic properties of metal ions and ligands [25, 26]. The role of organic carboxylates depend on differences in shape and flexibility [27–31]. Compounds **1** and **2** exhibit structural differences through varying 5-position substituent in isophthalic acid under similar synthetic conditions [26]. The hydroxyl in 5-OH-H_2BDC involved in coordination leads to a seven-coordinate lead wherein the coordination sphere of Pb(II) ion is holodirected. Pb(II) in **2** possesses a hemidirected coordination sphere, although the coordination number reduces to six while the gap between the layers increases.

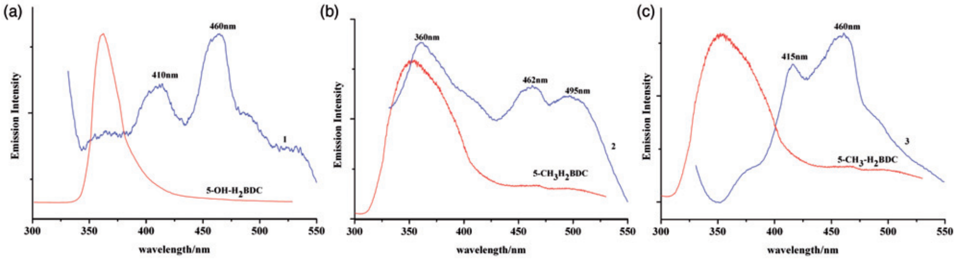


Figure 10. Emission and excitation spectra for 5-OH-H_2BDC and **1** (a), 5-CH_3-H_2BDC and **2** (b), 5-CH_3-H_2BDC and **3** (c) in the crystalline state at room temperature.

Compared with isophthalic acid, lower dimensional Pb-based compounds are formed with the introduction of 5-substituent groups [18–20]. The differences between **2** and **3** show the importance of N-donor chelating ligands on the construction of functional coordination compounds [32]. Compound **2** features a 2-D structure while **3** possesses a 1-D chain structure. The auxiliary ligand phen is beneficial to form lower dimensional compounds, observed in poly[[(1,10-phenanthroline)lead(II)]-μ_5-1,3-benzenedicarboxylato] [33].

3.4. *IR spectrum*

IR spectra of **1**–**3** are slightly different. Broad bands at 3395, 3390, and 3420 cm^{-1} for **1**–**3**, respectively, are attributed to water. For **1**, typical asymmetric and symmetric stretching bands of carboxylates are at 1595, 1540, and 1432 cm^{-1}. The respective values of [ν_{as}(COO)–ν_s(COO)] indicate the presence of chelating (55 cm^{-1}) and bridging (163 cm^{-1}) coordination of carboxylate in **1**. Similar to that of **1**, the strong bands at 1597, 1540, and 1436 cm^{-1}, respectively, correspond to the asymmetric and symmetric stretching bands of the carboxylates in **2**. For **3**, bands at 1582–1630 cm^{-1} and 1360–1495 cm^{-1} are ascribed to asymmetric and symmetric stretch of carboxylates with [ν_{as}(COO)–ν_s(COO)] of 56 cm^{-1}, suggesting that carboxylate in **3** chelate the metal centers. The absence of the characteristic band at *ca* 1700 cm^{-1} for a protonated carboxylate is consistent with all carboxylic acid groups being deprotonated.

3.5. *Photoluminescence property*

Pb(II) is a heavy metal with S^2 electron configuration, which may reduce the radiative lifetime of triplets by increasing spin–orbit coupling and promote emission from the triplet state under ambient conditions. Pb(II) coordination compounds are, thus, a potential class of functional materials with interesting photochemical and photophysical properties [34, 35]. However, compared with transition metals and lanthanide complexes, relatively little attention has been paid to photoluminescence of coordination complexes of lead. The fluorescence spectra of **1**–**3** were examined in the crystalline state at room temperature (figure 10).

To understand the nature of these emission bands, we also measured the luminescence of free ligands, which display emission at 360 nm ($\lambda_{ex} = 280$ nm) for 5-OH-H_2BDC and 350 nm ($\lambda_{ex} = 280$ nm) for 5-CH_3-H_2BDC. These emission bands of free ligands are assigned to the π–π^* transition. For **1**–**3**, the emission bands are 410 and 460 nm ($\lambda_{ex} = 280$ nm) for **1**, 415 and 460 nm for **3**, occurring at longer wavelengths than that of the free ligands. Emission bands can be attributed to ligand-to-metal charge transfer between delocalized π-bonds of these aromatic carboxylates and *p* orbitals of Pb(II). Compound **2** shows three emission peaks at 360, 462, 495 nm, respectively. The bands at 360 nm can be attributed to the intraligand emission from 5-CH_3-BDC and the bands at 462 and 495 nm are ascribed to the ligand-to-metal charge-transfer (LMCT).

The bathochromic shifts of emission bands between the ligands and the compounds are affected by either the substituent on 5-position or the N-donor chelating ligands in these compounds. Compound **1** gives only 50 and 100 nm bathochromic shifts, while **2** shows the increased bathochromic shifts 112 and 145 nm with different substituent on the 5-position. When phen is introduced in **3**, there is a bathochromic shift decrease to 65 and 110 nm. These differences might be associated with the metal ion and the coordination status of the ligand.

3.6. *Thermogravimetric analyses*

To study thermal stabilities, TGAs were performed under nitrogen flow at a heating rate of 10°C·min^{-1} from 30°C to 800°C (figures S1–S3).

TGA shows two steps of decomposition of **1**. First, the weight loss of 4.27% (Calcd 4.45%) from 180°C to 290°C corresponds to the release of lattice water molecules accompanied by an endothermic peak. The need for such an unusually high temperature for the removal of water is ascribed to hydrogen bonding with the carboxylate and hydroxyl oxygen atoms. The second step from 389°C to 500°C corresponds to the decomposition of 5-OH-BDC, the calculated and observed weight losses are 42.2% and 41.5%, respectively. The remaining fragment is stable upon further heating until it ends at 800°C, ascribed to PbO, which possesses a mass of 40.07% (Calcd: 40.34%).

Compound **2** shows no weight loss to 400°C, then starts to decompose at 420°C and is completely decomposed at 552°C, corresponding to PbO residue with the weight loss of 41.58% (Calcd 42.07%).

TGA curve of **3** exhibits two distinct weight loss steps. The first between 50°C and 150°C of 2.94% (Calcd: 3.08%) is due to the loss of water. The second weight loss at 250–420°C corresponds to decomposition of the organic ligand with a mass loss of 60.48% (Calcd: 65.56%).

4. Conclusions

We have obtained three MOF-based materials by assembly of Pb^{2+} and 5-*R*-H_2BDC (*R* = OH, CH_3) under hydrothermal conditions, $[Pb(5\text{-OH-BDC})]_n \cdot nH_2O$ (**1**), $[Pb_2(5\text{-}CH_3\text{-BDC})_2]_n$ (**2**), and $[Pb_2(5\text{-}CH_3\text{-BDC})_2(\text{phen})_2]_n \cdot 2nH_2O$ (**3**). The structures and physical properties were discussed. Based on the diversity of substituent on 5-position and the tuning of phen, the lower dimensional lead(II)-based coordination polymers were more inclined to form the above-mentioned compounds. TGA illustrates that the three compounds are rather stable. Emission bands of the compounds show prominent bathochromic shifts compared to the corresponding organic ligands, illustrating that the differences in structure result in interesting physical properties.

Acknowledgments

We gratefully acknowledge the financial support from the National Natural Science Foundation of China (Grant No. 20873100 and 21173168) and the Nature Science Foundation of Shaanxi Province (Grant Nos. FF10091 and SJ08B09).

References

[1] K.D. Subodh, W.P. Marc. *Inorg. Chem.*, **41**, 6838 (2002).
[2] X.-D. Zhu, X.-J. Li, Q.-Y. Liu, J. Lu, Z.-G. Guo, J.-R. He, Y.-F. Li, R. Cao. *J. Solid State Chem.*, **180**, 2386 (2007).
[3] P. Singh, M.M. Richter. *Inorg. Chim. Acta*, **357**, 1589 (2004).
[4] Y.-J. Shi, L.-H. Li, Y.-Z. Li, X.-T. Chen, Z.-L. Xue, X.-Z. You. *Polyhedron*, **22**, 917 (2003).
[5] A. Eichhofer. *Eur. J. Inorg. Chem.*, **9**, 1683 (2005).
[6] U.N. Nehete, V. Chandrasekhar, V. Jancik, H.W. Roesky, R. Herbst-Irmer. *Organometallics*, **23**, 5372 (2004).
[7] Y.-H. Zhao, H.-B. Xu, K.-Z. Shao, Y. Xing, Z.-M. Su. *Cryst. Growth Des.*, **7**, 513 (2007).
[8] L.-K. Li, Y.-L. Song, H.-W. Hou, Y.-T. Fan, Y. Zhu. *Eur. J. Inorg. Chem.*, **16**, 3238 (2005).
[9] Y.-J. Zhu, Z.-G. Ren, W.-H. Zhang, Y. Chen, H.-X. Li, Y. Zhang, J.-P. Lang. *Inorg. Chem. Commun.*, **10**, 485 (2007).
[10] J. Yang, J. Miao, J. Dai, L. Yang, L.-N. Zhang. *Chin. J. Inorg. Chem.*, **26**, 1992 (2010).
[11] L. Shimoni-Livny, J.P. Glusker, C.W. Bock. *Inorg. Chem.*, **37**, 1853 (1998).
[12] Z.-M. Shan, Y.-L. Wang, Q.-Y. Liu, N. Zhang, E.-L. Yang, J.-J. Wei. *Inorg. Chim. Acta*, **363**, 2269 (2010).
[13] B. Wu, Z.-G. Ren, H.-X. Li, M. Dai, D.-X. Li, Y. Zhang, J.-P. Lang. *Inorg. Chem. Commun.*, **12**, 1168 (2009).
[14] X.-C. Wang, C.-B. Liu, X.-Y. Li, C.-X. Li, Y.-S. Yan, G.-B. Che. *Chin. J. Inorg. Chem.*, **26**, 2126 (2010).
[15] J. Dai, J. Yang, J.-T. Li. *Chin. J. Inorg. Chem.*, **26**, 176 (2010).
[16] R.A. Varga, J.E. Drake, C. Silvestru. *J. Organomet. Chem.*, **675**, 48 (2003).
[17] S.-M. Ying, J.-G. Mao. *Eur. J. Inorg. Chem.*, 1270 (2004).
[18] L. Zhang, Y.-Y. Qin, Z.-J. Li, Q.-P. Lin, J.-K. Cheng, J. Zhang, Y.-G. Yao. *Inorg. Chem.*, **47**, 8286 (2008).
[19] E.-C. Yang, J. Li, B. Ding, Q.-Q. Liang, X.-G. Wang, X.-J. Zhao. *CrystEngComm*, **10**, 158 (2008).
[20] Z. Zhang, Y.-L. Zhou, H.-Y. He. *Acta Cryst.*, **E62**, m2591 (2006).
[21] Q.-Y. Liu, L. Xu. *Eur. J. Inorg. Chem.*, 3458 (2005).
[22] Q.-Y. Liu, L. Xu. *Eur. J. Inorg. Chem.*, 1620 (2006).
[23] G.M. Sheldrick. *SHELXTL, Crystallographic Software Package (Version 5.1)*, Bruker-AXS, Madison, WI (1998).
[24] X.-L. Wang, Y.-Q. Chen, Q. Gao, H.-Y. Lin, G.-C. Liu, J.-X. Zhang, A.-X. Tian. *Cryst. Growth Des.*, **10**, 2174 (2010).
[25] S.-R. Fan, L.-G. Zhu. *Inorg. Chem.*, **45**, 7935 (2006).
[26] J. Yang, J.-F. Ma, Y.-Y. Liu, J.-C. Ma, S.-R. Batten. *Inorg. Chem.*, **46**, 6542 (2007).
[27] H. Sadeghzadeh, A. Morsali. *J. Coord. Chem.*, **63**, 713 (2010).
[28] Y.-L. Chen, L. Wang, L.-X. Yu, Y. Fan, J. Shi, H. Yang, J.-H. Jiang, W. Wang, P. Zhang, L.-R. Zhang. *J. Coord. Chem.*, **63**, 2079 (2010).
[29] X.-X. Xu, X.-X. Liu, X.-G. Sang, E.-B. Wang. *J. Coord. Chem.*, **63**, 3060 (2010).
[30] Y.-C. Gao, X.-C. Yang, J. Zhang, G. Li, H.-F. Zhang. *J. Coord. Chem.*, **63**, 3413 (2010).

[31] H. Sadeghzadeh, A. Morsali, V.T. Yilmaz, O. Büyükgüngör. *J. Coord. Chem.*, **63**, 3423 (2010).
[32] X.-L. Wang, Y.-Q. Chen, J.-X. Zhang, G.-C. Liu, H.-Y. Lin, A.-X. Tian. *Z. Anorg. Allg. Chem.*, **636**, 830 (2010).
[33] H.-D. Wang, H.-Y. He, Y.-J. Wang, L.-G. Zhu, S.W. Ng. *Acta Cryst.*, **E61**, m531 (2005).
[34] S. Deo, H.A. Godwin. *J. Am. Chem. Soc.*, **122**, 174 (2000).
[35] Y.-Q. Xu, D.-Q. Yuan, L. Han, E. Ma, M.-Y. Wu, Z.-Z. Lin, M.-C. Hong. *Eur. J. Inorg. Chem.*, 2054 (2005).