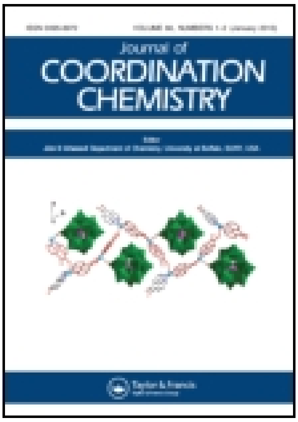
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:35
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Synthesis and characterization of Pb(II) compounds constructed from N-tosyl-L-glutamic acid

Li-Li Wu [a] & Hui-Hua Song [a]
[a] College of Chemistry and Material Sciences , Hebei Normal University , Shijiazhuang 050016 , P.R. China

Published online: 17 May 2012.

To cite this article: Li-Li Wu & Hui-Hua Song (2012) Synthesis and characterization of Pb(II) compounds constructed from N-tosyl-L-glutamic acid, Journal of Coordination Chemistry, 65:12, 2135-2146, DOI: 10.1080/00958972.2012.685166

To link to this article: http://dx.doi.org/10.1080/00958972.2012.685166

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 & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Journal of Coordination Chemistry
Vol. 65, No. 12, 20 June 2012, 2135–2146

Synthesis and characterization of Pb(II) compounds constructed from *N*-tosyl-L-glutamic acid

LI-LI WU and HUI-HUA SONG*

College of Chemistry and Material Sciences, Hebei Normal University,
Shijiazhuang 050016, P.R. China

(*Received 15 December 2011; in final form 8 February 2012*)

$\{[Pb(tsgluo)] \cdot H_2O\}_n$ (**1**), $[Pb_2(tsgluo)_2(phen)_2]$ (**2**), and $[Pb_2(tsgluo)_2(bipy)_2]$ (**3**) (H_2tsgluo = *N*-p-tolylsulfonyl-L-glutamate, phen = 1,10-phenanthroline, bipy = 2,2′-pyridine) have been synthesized in the absence or presence of phen or 2,2′-bipy and structurally characterized by elemental analysis, IR, and X-ray crystallography. Single-crystal X-ray analyses reveal that tsgluo exhibits two coordination modes to link lead ions. Complex **1** gives a 2-D layer structure while **2** and **3** exhibit monomolecular structures; **3** is further connected into a double-chain structure by hydrogen bonds. Phen and 2,2′-bipy are very important for the crystal structure. Fluorescence of the compounds is also discussed.

Keywords: Pb^{II} compounds; Crystal structure; Fluorescent properties

1. Introduction

Attention has been paid to the synthesis of coordination polymers for their interesting structures and potential applications in luminescence [1–6], adsorption [7–12], and heterogeneous catalysis. Even though a variety of complexes with intriguing structures have been prepared, complexes with desired topologies and specific properties are still a challenging task [13]. Structures of coordination polymers are influenced by the coordination number of metal ions, the nature of ligands, temperature, and the pH of solution [14, 15].

Metal and nature of ligands take a crucial role in the formation of different frameworks with tailored properties and functions. Focus is mainly on the incorporation of d and f block metal ions as coordination centers, while less consideration has been given to the p block metal ions. Lead(II), as a heavy p block metal, possesses 6 s lone-pair electrons which can be either stereochemically active or inactive. Lead(II) offers coordination numbers ranging from 2 to 12 and exhibits flexible coordination modes [16–20]. According to coordination number and disposition of ligands around lead, hemidirected and holodirected structures are possible. These features of lead provide particular framework construction and play an important role in the application of lead complexes. Lead compounds are widely used in industrial processes,

---

*Corresponding author. Email: songhuihua@hebtu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.685166

batteries, and environmental chemistry. Lead complexes are also applied in biology due to their toxicity and biological activities. *N*-*p*-tolylsulfonyl-L-glutamate is an ideal candidate to assemble compounds because it contains multiple N- and O-donors, and exhibits excellent coordination with various coordination modes. Some complexes containing this ligand have been reported [21, 22], but there is no example of lead compound. Based on this, we designed three $Pb^{(II)}$ compounds, $\{[Pb(tsgluo)]\cdot H_2O\}_n$ (**1**), $[Pb_2(tsgluo)_2(phen)_2]$ (**2**), and $[Pb_2(tsgluo)_2(bipy)_2]$ (**3**). Furthermore, we discuss the influence of 2,2′-bipy or phen for the synthesis and final crystal structure. We also study fluorescence properties of the compounds.

2. Experimental

2.1. *Materials and methods*

All reagents were commercially available and used as-received. Elemental analyses (C, H, and N) were performed with an Elemental Vario EL elemental analyzer. Infrared (IR) spectra were (KBr pellets) measured on an FTIR-8900 spectrometer from 4000 to 400 cm^{-1}. Fluorescence spectra were recorded on a Hitachi F-4600 luminescence spectrometer.

2.2. *Syntheses of the complexes*

2.2.1. $\{[Pb(tsgluo)]\cdot H_2O\}_n$. $Pb(NO_3)_2\cdot 6H_2O$ (0.0331 g, 0.1 mmol) and H_2tsgluo (0.0301 g, 0.1 mmol) were mixed in a solution containing H_2O (15.0 mL), placed in a 23 mL Teflon reactor, and then heated to 120°C for 7 days. The resulting solution was left to cool slowly to room temperature. Colorless crystals of **1** suitable for X-ray determination were collected by filtration and washed with water in 44.9% yield (based on Pb). Anal. Calcd for $C_{12}H_{15}NO_7PbS$ (%): C, 27.48; H, 2.86; N, 2.67. Found (%): C, 27.69; H, 2.87; N, 2.66. IR data (KBr, cm^{-1}): 3535 (b), 3256 (m), 1598 (s), 1521 (w), 1426 (s), 1334 (w), 1319 (m), 1159 (s), 1085 (s), 963 (m), 906 (m), 821 (s), 714 (m), 681 (s), 573 (m).

2.2.2. $[Pb_2(tsgluo)_2(phen)_2]$. $Pb(NO_3)_2\cdot 6H_2O$ (0.0661 g, 0.2 mmol), H_2tsgluo (0.0602 g, 0.2 mmol), and phen (0.0396 g, 0.2 mmol) were mixed in a solution containing H_2O (10.0 mL) and the mixture was placed in a 23 mL Teflon reactor, which was heated to 140°C for 3 days. The resulting solution was left to cool slowly to room temperature. Yellow block-shaped crystals of **2** suitable for X-ray determination were collected by filtration and washed with water in 45.8% yield (based on Pb). Anal. Calcd for $C_{24}H_{21}N_3O_6PbS$ (%): C, 41.98; H, 3.06; N, 6.12. Found (%): C, 41.76; H, 3.01; N, 6.06. IR data (KBr, cm^{-1}): 3446 (b), 3199 (m), 1582 (s), 1509 (s), 1496 (w), 1409 (s), 1346 (w), 1321 (m), 1160 (s), 973 (m), 917 (m), 858 (s), 811 (s), 731 (s), 715 (m), 659 (s).

2.2.3. $[Pb_2(tsgluo)_2(bipy)_2]$. $Pb(NO_3)_2\cdot 6H_2O$ (0.0661 g, 0.2 mmol), H_2tsgluo (0.2408 g, 0.8 mmol), and 2,2′-bipy (0.0624 g, 0.4 mmol) in H_2O (10.0 mL) were mixed. The mixture was placed in a 23 mL Teflon reactor after adjusting to pH = 5.0 with the addition of a dilute aqueous 2 mol L$^-$ NaOH solution, which was then heated to 130°C for 6 days. The resulting solution was left to cool slowly to room temperature. White block-shaped crystals suitable for X-ray analysis were collected by filtration and washed with water in 45.1% yield (based on Pb). Anal. Calcd for $C_{44}H_{42}N_6O_{12}Pb_2S_2$ (%): C, 41.38; H, 3.29; N, 6.58. Found (%): C, 41.56; H, 3.25; N, 6.56. IR data (KBr, cm^{-1}): 3427 (b), 3211 (m), 1581 (s), 1541 (s), 1496 (w), 1409 (s), 1346 (w), 1325 (m), 1161 (s), 974 (m), 918 (m), 823 (s), 812 (s), 738 (s), 705 (m), 667 (s).

2.3. *X-ray crystallography*

Colorless plate-shaped crystals of **1** of dimensions 0.41 × 0.37 × 0.04 mm^3, yellow block-shaped crystals of **2** (0.35 × 0.31 × 0.25 mm) and colorless block-shaped crystals of **3** (0.42 × 0.38 × 0.10 mm) were subjected to single-crystal X-ray diffraction analysis on a Bruker SMART-CCD area detector diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 298(2) K by the ω–φ scan technique. The structure was solved by direct methods using SHELXS-97. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2 using SHELXL-97 [23]. Hydrogen atoms were added in geometrical positions and were not refined. A semi-empirical absorption correction was applied to the intensity data using SADABS [24]. A summary of the crystallographic data and refinement parameters is given in table 1. Selected bond lengths and angles are given in table 2; hydrogen bond lengths and angles are given in table 3.

3. Results and discussion

3.1. *Synthesis*

Factors such as initial reagent ratio, pH, temperature, and reaction time influence the growth of crystals. To obtain complexes based on lead, we attempted experiments under hydrothermal conditions. Complex **1** was obtained by the reaction of lead nitrate and tsgluo in 1 : 1 molar ratio and heated to 120°C for 7 days. We tried at this reactant ratio and temperature to get crystals which contain phen or 2,2′-bipy, but failed. In these experimental conditions, we get crystals similar to **1** every time with the second ligands not coordinated. So we explored new condition such as increased temperature and changed pH. The synthesis of **2** was as follows: mixture of metal salt, tsgluo, and phen in 1 : 1 : 1 mole ratio heated to 140°C for 3 days and **3** was obtained in 1 : 2 : 4 (metal: tsgluo: bipy) molar ratio at 130°C for 6 days. The IR spectrum suggests that the crystal structures of **2** and **3** were similar, confirmed by X-ray diffraction studies. The carboxylate is a multifunction ligand with various binding geometries, monodentate, bidentate either by chelating or by bridging in **1**–**3**.

3.2. *Crystal structure*

3.2.1. Crystal structure of {Pb(tsgluo) · H_2O}$_n$. The structure determination of **1** by single-crystal X-ray analysis showed that the complex crystallizes in the monoclinic

Table 1. Summary of crystal data and details of intensity collection and refinement.

Compound	**1**	**2**	**3**
Empirical formula	$C_{12}H_{15}NO_7SPb$	$C_{24}H_{21}N_3O_6SPb$	$C_{44}H_{42}N_6O_{12}S_2Pb_2$
Formula weight	524.50	686.69	1325.34
Temperature (K)	298(2)	298(2)	298(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2(1)/c$	$P2(1)/c$	$P2(1)/c$
Unit cell dimensions (Å,°)			
a	19.188(4)	12.212(3)	11.524(3)
b	4.9851(10)	19.976(5)	20.337(5)
c	16.215(3)	10.034(3)	9.955(3)
α	90	90	90
β	102.050(3)	104.884(4)	102.188(3)
γ	90	90	90
Volume (Å^3), Z	1516.8(5), 4	2365.6(11), 4	2280.4(10), 2
Calculated density (Mg m^{-3})	2.297	1.928	1.930
Absorption coefficient (mm^{-1})	11.294	7.267	7.534
$F(000)$	992	1328	1280
θ range for data collection (°)	2.17–25.02	1.73–25.03	1.81–25.02
Limiting indices	$-22 \le h \le 11$; $-5 \le k \le 5$; $-17 \le l \le 19$	$-10 \le h \le 14$; $-23 \le k \le 23$; $-11 \le l \le 11$	$-13 \le h \le 13$; $-24 \le k \le 17$; $-11 \le l \le 11$
Reflections collected	5823	9829	9479
Independent reflection	2645 [R(int) = 0.0423]	4167 [R(int) = 0.0261]	4008 [R(int) = 0.0300]
Completeness to $\theta = 25.02$ (%)	99.2	99.7	99.7
Max. and min. transmission	0.6608 and 0.0904	0.2638 and 0.1853	0.5196 and 0.1440
Data/restraints/parameters	2645/0/200	4167/0/317	4008/0/299
Goodness-of-fit on F^2	1.115	1.031	1.019
Final R^a indices [$I > 2\sigma(I)$]	$R_1 = 0.0530$, $wR_2 = 0.1210$	$R_1 = 0.0275$, $wR_2 = 0.0647$	$R_1 = 0.0281$, $wR_2 = 0.0624$
R^a indices (all data)	$R_1 = 0.0652$, $wR_2 = 0.1290$	$R_1 = 0.0323$, $wR_2 = 0.0666$	$R_1 = 0.0458$, $wR_2 = 0.0688$
Largest difference peak and hole (e Å^{-3})	3.262 and −2.108	1.704 and −1.219	0.639 and −0.681

$^{a}R_1 = |F_o - F_c|/\Sigma F_o$, $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)]^{1/2}$.

system with a space group $P2(1)/c$. As shown in figure 1(a), **1** consists of one tsgluo, one Pb^{II,} and one water molecule. Each Pb^{II} is seven-coordinate by six oxygen atoms from four different tsgluo ligands (three α-carboxylate oxygen atoms (O1, O2, O2#3) and three γ-carboxylate oxygen atoms (O3#1, O4#1, O4#2)), and one water molecule. The Pb–O (tsgluO) distances range from 2.333(7) to 2.718(8) Å, while Pb–O(H_2O) distance is 2.842(11) Å. The distances of Pb–O are close to those previously reported for other Pb^{II} complex [25, 26]. Compound **1** exhibits a distorted heart face octagonal geometry. The tsgluo in **1** (scheme 1) has two α-carboxylate oxygen atoms linked to a Pb and two γ-carboxylate oxygen atoms linked to the adjacent Pb; two Pb's and two tsgluo generate a non-planar 16-membered ring (figure 1b) (Pb1···Pb1#1 distance = 8.992 Å). In addition, one α-carboxylate oxygen also connects another Pb, as does the γ-carboxylate oxygen. Every Pb links four tsgluo ligands and every tsgluo joins four Pb ions to form a 2-D layer structure (figure 1c). There are two kinds of hydrogen-bonding interactions

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

1					
Pb(1)–O(3)#1	2.333(7)	Pb(1)–O(1)	2.479(7)	Pb(1)–O(4)#2	2.514(7)
Pb(1)–O(2)	2.618(6)	Pb(1)–O(4)#1	2.718(8)	Pb(1)–O(7)	2.842(11)
O(3)#1–Pb(1)–O(1)	74.5(3)	O(3)#1–Pb(1)–O(4)#2	82.4(3)	O(1)–Pb(1)–O(4)#2	125.7(2)
O(3)#1–Pb(1)–O(2)	73.2(2)	O(1)–Pb(1)–O(2)	51.1(2)	O(4)#2–Pb(1)–O(2)	75.5(2)
O(3)#1–Pb(1)–O(4)#1	50.1(2)	O(1)–Pb(1)–O(4)#1	119.4(2)	O(4)#2–Pb(1)–O(4)#1	74.37(16)
O(2)–Pb(1)–O(4)#1	118.0(2)	O(3)#1–Pb(1)–O(7)	143.2(3)	O(1)–Pb(1)–O(7)	73.4(3)
O(4)#2–Pb(1)–O(7)	102.2(3)	O(2)–Pb(1)–O(7)	72.8(3)	O(4)#1–Pb(1)–O(7)	166.4(2)
2					
N(2)–Pb(1)	2.724(4)	N(3)–Pb(1)	2.638(4)	O(1)–Pb(1)	2.753(3)
O(2)–Pb(1)	2.283(3)	Pb(1)–O(3)#1	2.489(3)	Pb(1)–O(4)#1	2.490(4)
O(2)–Pb(1)–O(3)#1	79.89(12)	O(2)–Pb(1)–O(4)#1	80.13(12)	O(3)#1–Pb(1)–O(4)#1	52.53(10)
O(2)–Pb(1)–N(3)	77.50(11)	O(3)#1–Pb(1)–N(3)	129.72(11)	O(4)#1–Pb(1)–N(3)	79.56(11)
O(2)–Pb(1)–N(2)	81.76(13)	O(3)#1–Pb(1)–N(2)	154.61(12)	O(4)#1–Pb(1)–N(2)	140.03(11)
N(3)–Pb(1)–N(2)	61.83(11)	O(2)–Pb(1)–O(1)	50.97(10)	O(3)#1–Pb(1)–O(1)	79.04(11)
O(4)#1–Pb(1)–O(1)	117.11(11)	N(3)–Pb(1)–O(1)	117.04(10)	N(2)–Pb(1)–O(1)	75.78(11)
O(4)#1–Pb(1)–O(1)	117.11(11)	N(3)–Pb(1)–O(1)	117.04(10)	N(2)–Pb(1)–O(1)	75.78(11)
3					
N(2)–Pb(1)	2.722(4)	N(3)–Pb(1)	2.619(4)	O(1)–Pb(1)	2.720(4)
O(2)–Pb(1)	2.292(3)	Pb(1)–O(4)#1	2.468(4)	Pb(1)–O(3)#1	2.505(3)
O(2)–Pb(1)–O(4)#1	80.00(12)	O(2)–Pb(1)–O(3)#1	77.99(12)	O(4)#1–Pb(1)–O(3)#1	52.48(11)
O(2)–Pb(1)–N(3)	79.36(12)	O(4)#1–Pb(1)–N(3	79.38(12)	O(3)#1–Pb(1)–N(3)	129.41(12)
O(2)–Pb(1)–O(1)	51.30(11)	O(4)#1–Pb(1)–O(1)	117.92(12)	O(3)#1–Pb(1)–O(1)	78.77(12)
N(3)–Pb(1)–O(1)	118.40(12)	O(2)–Pb(1)–N(2)	81.67(13)	O(4)#1–Pb(1)–N(2)	138.36(13)
O(3)#1–Pb(1)–N(2)	154.21(13)	N(3)–Pb(1)–N(2)	60.60(13)	O(1)–Pb(1)–N(2)	76.17(12)

Symmetry codes: For **1**: #1: $-x+2, -y, -z+1$; #2: $x, -y+1/2, z-1/2$. For **2**: #1: $-x+1, -y+2, -z+1$. For **3**: #1: $-x+1, -y+2, -z+2$.

Table 3. Hydrogen bond lengths (Å) and angles (°) for **1** and **3**.

Compound	D–H···A	d(D–H)	d(H···A)	d(D···A)	∠DHA
1	O(7)–H(7B)···O(5)#2	0.96	2.37	3.178(13)	141.7
	O(7)–H(7 A)···O(6)#4	0.96	2.21	3.058(13)	147.1
	N(1)–H(1)···O(5)#5	0.86	2.58	3.115(10)	121.3
3	N(1)–H(1)···O(1)#2	0.87	2.18	2.975(5)	152.2
	N(1)–H(1)···O(1)	0.87	2.27	2.717(5)	111.7

Symmetry codes: For **1**: #2: $x, -y+1/2, z-1/2$; #4: $x, -y-1/2, z-1/2$. For **3**: #2: $-x+1, -y+2, -z+1$.

between coordinated water (O7) and oxygen (O5#2, O6#4) of tsgluo and coordinated oxygen (O5#5) and nitrogen (N1) of tsgluo. The hydrogen-bonding interactions further stabilize the complex. Parameters of hydrogen bonds are given in table 3. The coordination sphere of Pb in **1** is holodirected (figure 1d) and the $6s^2$ lone pair electrons around Pb are stereochemically inactive.

3.2.2. Crystal structure of [$Pb_2(tsgluo)_2(phen)_2$].

The structure determination of **2** by single-crystal X-ray analysis showed that the complex crystallizes in the monoclinic system with a space group *P*2(1)/*c*. As shown in figure 2(a), the symmetric unit of **2** consists of two tsgluo ligands, two Pb^{II} ions, and two phens. The complex of **2** is

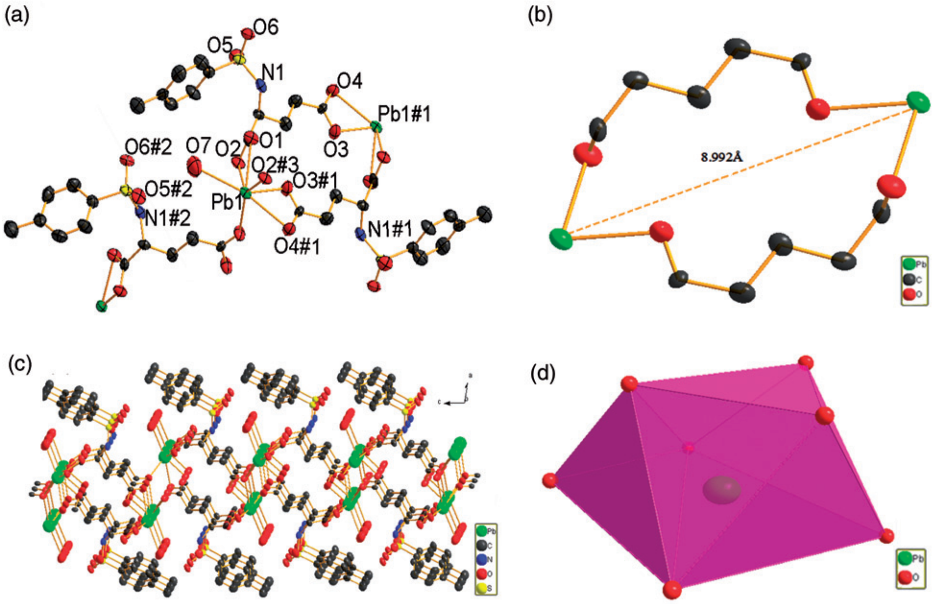
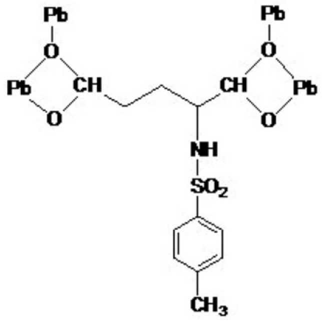


Figure 1. (a) The coordination environment of Pb(II) for **1**; (b) the 16-membered ring for **1**; (c) the 2-D layer structure for **1**; (d) the coordination sphere of Pb^{II} in **1**.



Scheme 1. The observed coordination modes of H_2tsgluo ligand for **1**.

six-coordinate and the coordination geometry can be described as a distorted pentagonal pyramid. Each Pb^{II} is coordinated by two α-carboxylate oxygen atoms (O1, O2) from one tsgluo with Pb–O distances of 2.753(3), 2.283(3) Å, two γ-carboxylate oxygen atoms (O3#1, O4#1) from the other tsgluo with Pb–O distances of 2.489(3), 2.490(4), and two nitrogen atoms (N2, N3) belonging to one phen with Pb–N distances of 2.724(4) and 2.638(4). All bond lengths are within the normal range [27, 28]. From figure 1(a), two different tsgluo ligands display the same configuration (scheme 2), with four oxygen atoms from a tsgluo (two α-carboxylate and two γ-carboxylate oxygen atoms) adopt chelate tetradentate coordination as $\mu^2\text{–}\eta^1:\eta^1:\eta^1:\eta^1$ to bridge Pb1 and Pb1#1 forming a 16-membered ring (figure 2b) which is central

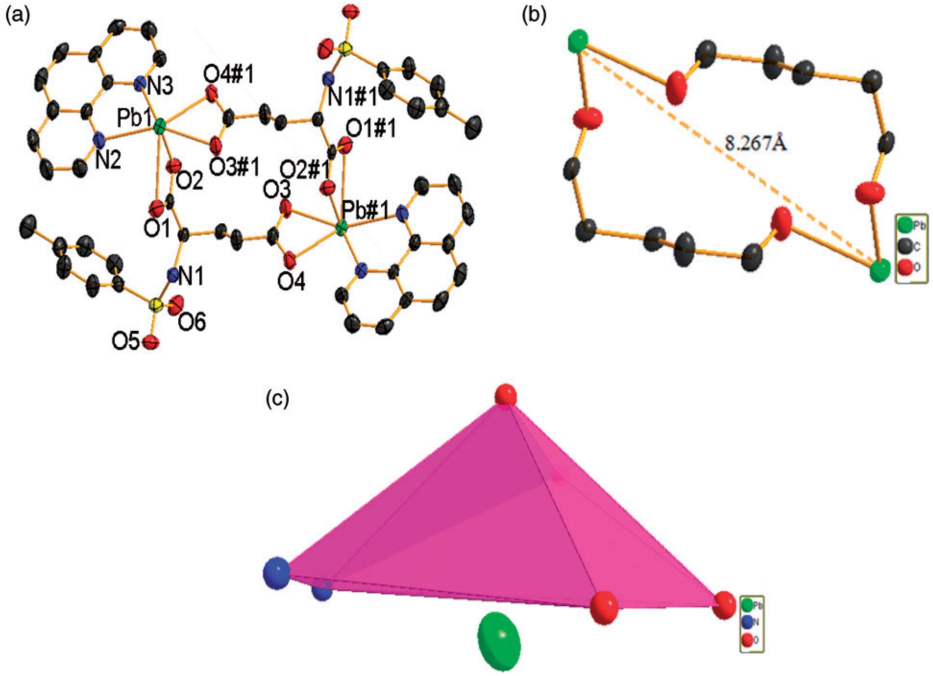
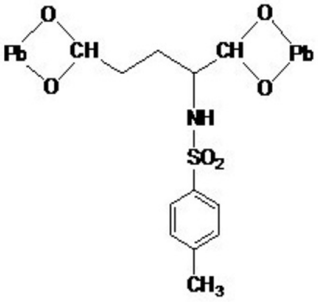


Figure 2. (a) The coordination environment of Pb(II) for **2**; (b) the 16-membered ring for **2**; (c) the coordination sphere of Pb^{II} in **2**.



Scheme 2. The observed coordination modes of H_2tsgluo ligand for **2**.

symmetric ($Pb1\cdots Pb1\#1$ distance = 8.267 Å). As shown in figure 2(c), compound **2** exhibits a hemidirected sphere with the six donors located on one side of the Pb. Therefore, the $6s^2$ lone pair electrons are stereochemically active.

3.2.3. Crystal structure of [$Pb_2(tsgluo)_2(bipy)_2$].

The structure determination of **3** showed that the complex crystallizes in the monoclinic system with a space group *P*2(1)/*c*. The structure of **3** is similar to **2**. The symmetric unit of **3** contains two

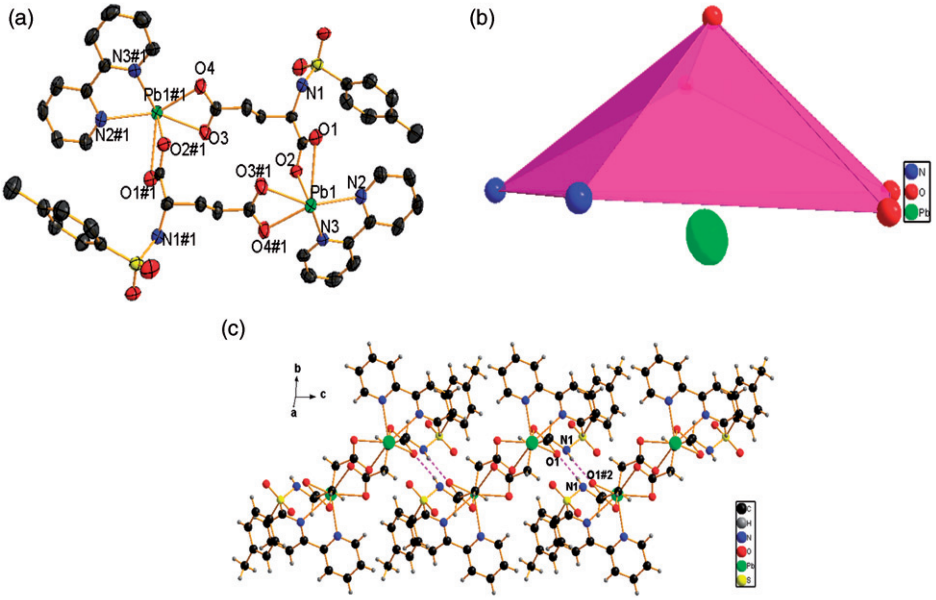


Figure 3. (a) The coordination environment of Pb(II) for **3**; (b) the coordination sphere of Pb^{II} in **3**; (c) the 1-D chain structure for **3**.

Pb^{II} ions, two tsgluo, and two 2,2′-bipy (figure 3a). Compound **3** is six-coordinate by four oxygen atoms and two nitrogen atoms, revealing a distorted pentagonal pyramid. The $6s^2$ lone pair electrons are stereochemically active, presenting a hemidirected sphere (figure 3b). However, different from **2**, there are hydrogen-bonding interactions in **3** which exist between O1 of tsgluo and N1 from another tsgluo (figure 3c); the compound is further connected into a double chain structure.

The (+)-*N*-tosyl-L-glutamic acid are chiral ligands, but the three compounds synthesized are achiral. This may be caused by the hydrothermal conditions or flexibility of lead. During the synthetic procedure, half of the ligands undergo inversion and were present as the D enantiomer, so $tsgluO^{2-}$ racemized and the compounds are achiral. Racemization of amino acids has been reported previously [29]. X-ray structure analysis reveals that **1** is a 2-D layer structure while **2** and **3** with phen or 2,2′-bipy give monomolecular structures; **3** further formed a 1-D chain by hydrogen bond interactions, indicating that bipyridine or phen play roles in determining the final crystal structure.

3.3. *Powder XRD pattern*

Figure 4 shows simulated X-ray diffraction (XRD) patterns from single crystal X-ray data of **1**–**3** compared to the powder XRD patterns. Acceptable matches, with slight differences in 2θ, were observed between the simulated and experimental powder X-ray diffraction patterns, suggesting they are single crystalline phase and that these phases are identical to those obtained by single crystal diffraction.

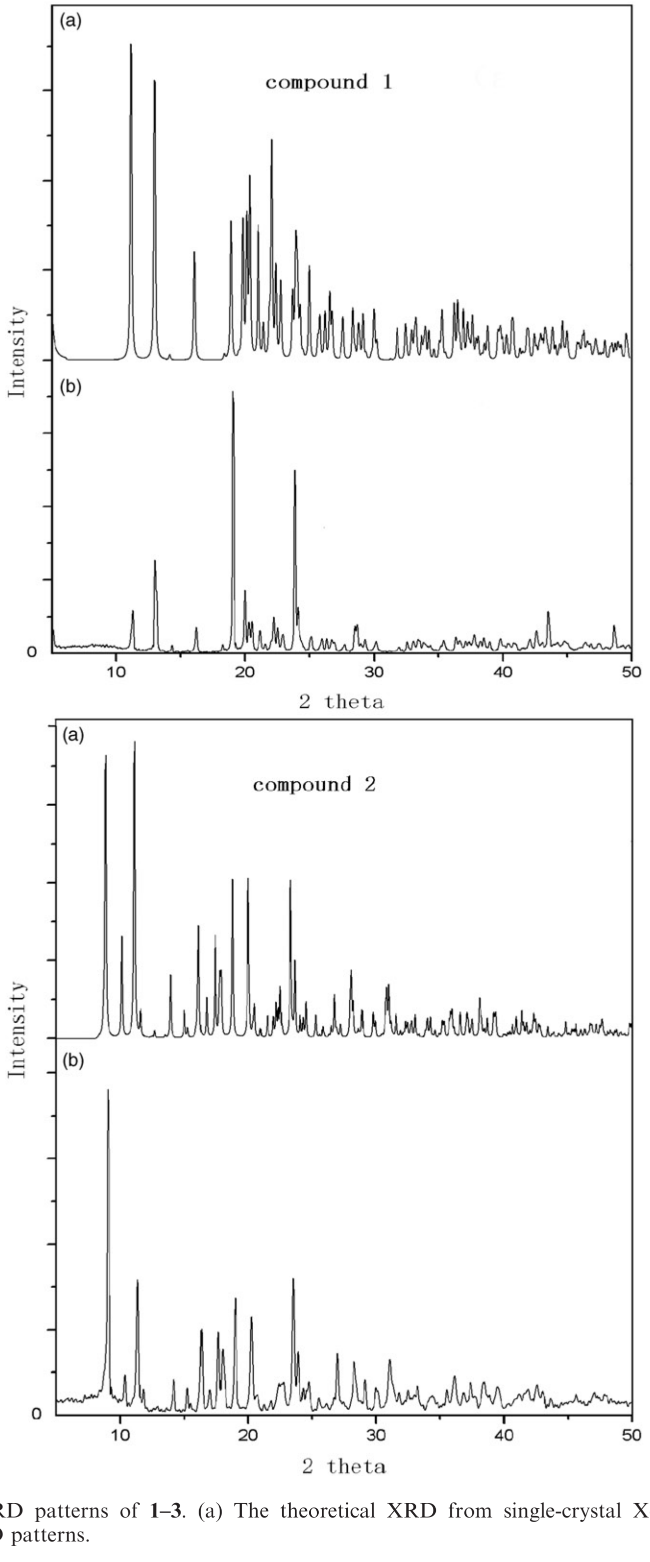


Figure 4. The XRD patterns of **1–3**. (a) The theoretical XRD from single-crystal X-ray data; (b) the experimental XRD patterns.

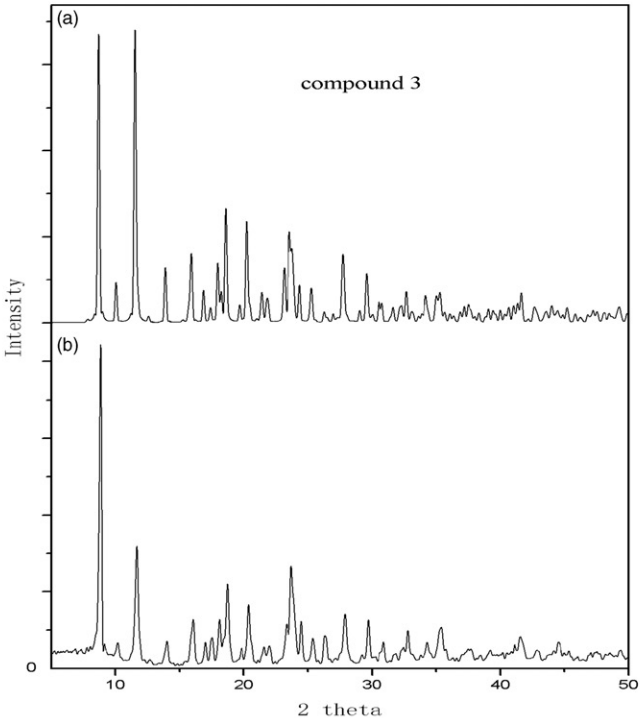


Figure 4. Continued.

3.4. *Fluorescence property*

Room-temperature solid-state fluorescence properties of **1**–**3** are shown in figure 5. We also investigated the fluorescence of H_2tsgluo and phen. Free H_2tsgluo shows a main emission at 597 nm by excitation at 275 nm. Upon the complexion of H_2tsgluo with lead(II), **1** displays a peak at $\lambda_{max} = 619$ nm when excited at 275 nm. A red shift of 22 nm for **1** is observed, which is considered to arise mainly from the coordination of Pb(II) [30]. For **2**, free phen shows two intense peaks at $\lambda_{max} = 363$, 380 nm and a shoulder at 402 nm by excitation at 275 nm, attributed to $\pi \cdots \pi$ transition [31]. Upon the coordination of both phen and H_2tsgluo with lead, **2** exhibits a fluorescent emission with a maximum at 468 and 564 nm ($\lambda_{max} = 275$ nm). The emissions for **2** is not metal-to-ligand charge transfer or ligand-to-metal charge transfer, which may be assigned to the intra-ligand emission state [32–34]. Compound **3** displays a strong peak at $\lambda_{max} = 475$ nm when excited at 340 nm; 2,2′-bipy displays a peak at 540 nm and H_2tsgluo has no obvious absorption peaks under excitation at 340 nm. As a result, the fluorescence of **3** can be assigned to $\pi \cdots \pi^*$ transition of 2,2′-bipy [35–38]. Obviously, lead plays an important role in the luminescent properties of **1**–**3**.

4. Conclusions

We synthesized three Pb(II) compounds with (+)-*N*-tosyl-L-glutamic acid using hydrothermal process. By comparing synthetic methods, the temperature and amount

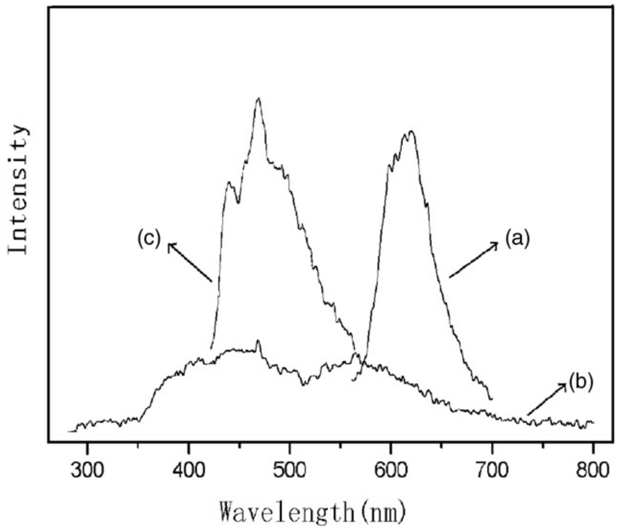


Figure 5. Emission spectra of **1**, **2**, and **3** in the solid-state at room temperature.

of reactants are different. Crystal structures of **1**, **2**, and **3** are different, with **2** and **3** containing phen or 2,2′-bipy giving monomers. Presence of phen or 2,2′-bipy plays a role in the synthesis conditions and structure of the lead complexes. The three compounds exhibit distinctly different fluorescence at room temperature, due to different structures. Building **1**–**3** with Pb(II) may provide a useful route for the design of metal–organic frameworks for further lead applications.

Supplementary material

CCDC-844428 (**1**), −844429 (**2**) and −844431 (**3**) contain the supplementary crystallographic data. Copies of the data can be obtained free of charge *via* the Internet at http://www.ccdc.cam.ac.uk/conts/retrieving.html or by post from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033, E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

This work was supported by the Natural Science Foundation of China (grant nos. 20601007, 21141002, 20772022, and 20971035), the Natural Science Foundation of Hebei Education Department (grant no. ZH2006002), the Natural Science Foundation of Hebei Province (grant no. B2008000143), and the Doctoral Foundation of Hebei Normal University (no. 130374).

References

[1] P. Zhang, D.S. Li, J. Zhao, Y.P. Wu, C. Li, K. Zou, J.Y. Lu. *J. Coord. Chem.*, **64**, 2329 (2011).
[2] G.A. Farnum, C.Y. Wang, C.M. Gandolfo, R.L. LaDuca. *J. Mol. Struct.*, **998**, 62 (2011).
[3] C.J. Wang, K.F. Yue, Z.X. Tu, L.L. Xu, Y.L. Liu, Y.Y. Wang. *Cryst. Growth Des.*, **11**, 2897 (2011).
[4] X. Zhang, J.K. Cheng, F. Chen, M.L. Sun, Y.G. Yao. *Inorg. Chem. Commun.*, **14**, 358 (2011).
[5] 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).
[6] Y.H. Zhao, Z.M. Su, Y.M. Fu, K.Z. Shao, P. Li, Y. Wang, X.R. Hao, D.X. Zhu, S.D. Liu. *Polyhedron*, **27**, 583 (2008).
[7] Y. Hijikata, S. Horike, D. Tanaka, J. Groll, M. Mizuno, J. Kim, M. Takata, S. Kitagawa. *Chem. Commun.*, 7632 (2011).
[8] Y.C. Ou, J. Wang, J.D. Leng, Z.J. Lin, M.L. Tong. *Dalton Trans.*, 3592 (2011).
[9] A. Kondo, H. Kajiro, H. Noguchi, L. Carlucci, D.M. Proserpio, G. Ciani, K. Kato, M. Takata, H. Seki, M. Sakamoto, Y. Hattori, F. Okino, K. Maeda, T. Ohba, K. Kaneko, H. Kanoh. *J. Am. Chem. Soc.*, **133**, 10512 (2011).
[10] S. Galli, G. Tagliabue, N. Masciocchi, W.G. Wang, E. Barea, J. Navarro. *Inorg. Chim. Acta*, **371**, 79 (2011).
[11] L.L. Qu, Y.L. Zhu, Y.Z. Li, H.B. Du, X.Z. You. *Cryst. Growth Des.*, **11**, 2444 (2011).
[12] S. Noro, K. Fukuhara, K. Kubo, T. Nakamura. *Cryst. Growth Des.*, **11**, 2379 (2011).
[13] N.K. Al-Rasbi, I.S. Tidmarsh, S.P. Argent, H. Adams, L.P. Harding, M.D. Ward. *J. Am. Chem. Soc.*, **130**, 11641 (2008).
[14] P. Mahata, M. Prabu, S. Natarajan. *Inorg. Chem.*, **47**, 8451 (2008).
[15] L. Zhang, J. Zhang, Z.J. Li. *Chem. Eur. J.*, **15**, 989 (2009).
[16] X. Zhang, J.K. Cheng, F. Chen, M.L. Sun, Y.G. Yao. *Inorg. Chem. Commun.*, **14**, 358 (2011).
[17] M. Farzin, M. Ali. *Inorg. Chim. Acta*, **370**, 526 (2011).
[18] X.L. Wang, Q. Gao, Y.Q. Chen, G.C. Liu, A.X. Tian, Z.H. Kang. *Z. Anorg. Allg. Chem.*, **637**, 142 (2011).
[19] M.L. Hu, Y.P. Lu, H.M. Zhang, B. Tu, Z.M. Jin. *Inorg. Chem. Commun.*, **9**, 962 (2006).
[20] A. Alireza, M. Ali, T.Y. Veysel, K. Canan. *J. Mol. Struct.*, **929**, 187 (2009).
[21] R. He, H.H. Song, Z. Wei, J.J. Zhang, Y.Z. Gao. *J. Solid State Chem.*, **183**, 2021 (2010).
[22] A.B. Corradia, G. Lusvardia, L. Menabuea, M. Saladinia, P. Sgarabottob. *Polyhedron*, **18**, 1975 (1999).
[23] G.M. Sheldrick. *SHELXS-97, a Program for X-Ray Crystal Structure Solution, and SHELXL-97, a Program for X-ray Structure Refinement*, University of Göttingen, Germany (1997).
[24] G.M. Sheldrick. *SADABS, a Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Germany (1997).
[25] J. Jin, D. Wu, M.J. Jia, Y. Peng, J.H. Yu, Y.C. Wang, J.Q. Xu. *Solid State Chem.*, **184**, 667 (2011).
[26] Z.F. Chen, Z.L. Zhang, Y.H. Tan, Y.Z. Tang. *CrystEngComm*, **10**, 217 (2008).
[27] J. Shi, J.W. Ye, T.Y. Song, D.J. Zhang, K.R. Ma, J. Ha, J.N. Xu, P. Zhang. *Inorg. Chem. Commun.*, **10**, 1534 (2007).
[28] P. Singh, M.M. Richter. *Inorg. Chim. Acta*, **357**, 1589 (2004).
[29] I. Sasaji, M. Hara, S. Tatsumi, K. Seki, T. Akashi, K. Ohno. US Patent 3,213,106 (1965).
[30] R.R. Hu, H. Cai, J.H. Luo. *Inorg. Chem. Commun.*, **14**, 433 (2011).
[31] F.Y. Yi, T.H. Zhou, J.G. Mao. *J. Mol. Struct.*, **987**, 51 (2011).
[32] F.Y. Yi, J.L. Song, N. Zhao, J.G. Mao. *Solid State Chem.*, **181**, 1393 (2008).
[33] S.L. Zheng, J.M. Yang, X.L. Yu, X.M. Chen, W.T. Wong. *Inorg. Chem.*, **43**, 830 (2004).
[34] Y.Y. Liu, J.F. Ma, J. Yang. *CrystEngComm*, **10**, 894 (2008).
[35] X.M. Zhang, M.L. Tong, M.L. Gong, X.M. Chen. *Eur. J. Inorg. Chem.*, 138 (2003).
[36] H.Y. Bai, J.F. Ma, J. Yang, Y.Y. Liu, H. Wu, J.C. Ma. *Cryst. Growth Des.*, **2**, 10 (2010).
[37] L.L. Wen, Z. Lu, J. Lin, Z.F. Tian, H.Z. Zhu, Q.J. Meng. *Cryst. Growth Des.*, **1**, 7 (2007).
[38] K.Z. Shao, Y.H. Zhao, Y. Xing, Y.Q. Lan, X.L. Wang, Z.M. Su, R.S. Wang. *Cryst. Growth Des.*, **8**, 8 (2008).