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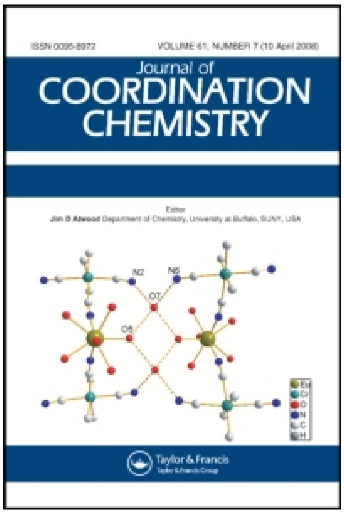

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Zinc(II) and lead(II) coordination polymers built by 3-(4-carboxyphenylhydrazono)pentane-2,4-dione

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Zinc(II) and lead(II) coordination polymers built by 3-(4-carboxyphenylhydrazono)pentane-2,4-dione

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Two coordination polymers $[Zn(L)_2(4,4'\text{-bipy})_2]_n$ (4,4′-bipy = 4,4′-bipyridine) (**1**) and $[Pb(\eta^2\text{-}L)(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ (**2**) have been prepared by the reaction of 3-(4-carboxy phenylhydrazono)pentane-2,4-diketone (HL) with zinc(II) or lead(II) in solution. Polymer **1** shows an infinite zigzag chain, in which Zn(II) are linked by 4,4′-bipy bridges with carboxylate of L^- monodentate to Zn(II). In **2**, Pb(II) are bridged by tetradentate $\mu_3\text{-}\eta^2\text{-}CH_3COO^-$ to form a linear 1-D chain, and each Pb(II) is chelated by carboxylate of L^-. Their molecular structures have been characterized by elemental analysis, infrared, and single-crystal X-ray diffraction. Thermal and fluorescent properties of the two complexes have been investigated.

Keywords: Coordination polymer; Crystal structure; Thermal properties; Fluorescence properties

1. Introduction

Preparations of interesting coordination polymeric networks and explorations of novel functional materials are the two main directions in coordination chemistry [1, 2]. Diverse structures directly affect the properties and applications of such complexes. Therefore, crystal engineering is drawing much attention to both the synthetic routes and the art of structural design [3–9].

In this context, the design and selection of ligand play important roles in directing the structural outcome of complexes [10]. 3-(4-Carboxyphenylhydrazono)pentane-2,4-diketone (HL) containing carboxylate, *β*-diketone, and two phenyl hydrazone nitrogens (scheme 1) is a very useful ligand. These functional groups have strong coordination abilities. However, reported complexes with HL are limited [11–13], mostly characterized by elemental analysis, infrared (IR) spectra, etc.; crystal data for these complexes are rare. Indeed, there are only a few examples of coordination polymers bearing HL recently reported by us [14].

We want to obtain a series of new complexes with novel structures and desired properties. In this article, we use the strong coordination abilities of HL to

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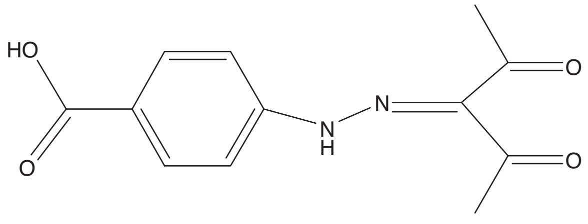

Scheme 1. The molecular sketch map of HL.

prepare complexes. The ligand NaL reacted with Zn(II) or Pb(II) and two 1-D coordination polymers, $[Zn(L)_2(4,4'\text{-bipy})_2]_n$ (4,4′-bipy = 4,4′-bipyridine) (**1**) and $[Pb(\eta^2\text{-L})(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ (**2**), were obtained. Thermal and fluorescent properties of **1** and **2** were determined.

2. Experimental

2.1. *Materials and physical techniques*

All chemicals were of reagent grade quality, obtained from commercial sources and used without purification. HL was prepared according to the literature method [11]. Its sodium salt NaL was prepared by the reaction of HL with sodium methoxide.

IR spectra were recorded on a Nicolet NEXUS 470 FT-IR spectrophotometer as KBr pellets from 400 to 4000 cm^{-1}. Elemental analyses (C, H, and N) were carried out on a FLASH EA1112 Elemental Analyzer. Fluorescence spectra of the complexes were obtained at room temperature by an F-4500 fluorescence spectrophotometer (240 nm min^{-1}). Thermogravimetry–differential scanning calorimetry (TG–DSC) measurements were performed by heating the sample from 20°C to 750°C at a rate of 10°C min^{-1} in air on a Netzsch STA 409PC differential thermal analyzer.

2.2. *Preparation of $[Zn(L)_2(4,4'\text{-bipy})_2]_n$ (1)*

A solution of NaL (12.5 mg, 0.05 mmol) and 4,4′-bipy (15.6 mg, 0.1 mmol) in methanol (7 mL) was slowly added to the solution of $ZnSO_4 \cdot 7H_2O$ (16.1 mg, 0.1 mmol) in methanol (3 mL). The resulting mixture was filtered and the pale yellow filtrate was allowed to stand at room temperature. Good quality flaxen crystals of **1** were obtained after 1 month. Yield: 55.4% based on $ZnSO_4$. Anal. Calcd for $C_{34}H_{29}N_6O_8Zn$: C, 57.11; H, 4.09; and N, 11.75%. Found: C, 57.01; H, 3.99; and N, 11.80%. IR (cm^{-1}, KBr): 3395(m), 2975(m), 1678(s), 1632(m), 1160(s), 1511(s), 1422(s), 1363(m), 1292(s), 1161(s), 1112(w), 1023(w), 983(m), 932(s), 855(m), 797(w), 768(m), 647(m), 615(s), 546(m), and 510(w).

2.3. *Preparation of $[Pb(\eta^2\text{-L})(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ (2)*

A solution of NaL (12.5 mg, 0.05 mmol) in methanol (3 mL) was slowly added to the solution of $Pb(OAc)_2 \cdot 2H_2O$ (37.9 mg, 0.1 mmol) in methanol (5 mL). The resulting mixture was filtered and the yellow filtrate was allowed to stand at room temperature.

Table 1. Crystallographic data for **1** and **2**.

Compound	**1**	**2**
Empirical formula	$C_{34}H_{29}N_6O_8Zn$	$C_{28}H_{32}N_4O_{14}Pb_2$
Formula weight	715.00	1062.96
Temperature (K)	293(2)	293(2)
Crystal system	Monoclinic	Triclinic
Space group	$P2/c$	$P\bar{1}$
Crystal size (mm^3)	$0.20 \times 0.18 \times 0.15$	$0.23 \times 0.19 \times 0.18$
Unit cell dimensions (Å, °)		
a	14.227(3)	7.5171(15)
b	7.9061(16)	7.7188(15)
c	32.366(9)	15.521(3)
α	90.00	90.02(3)
β	114.51(3)	91.75(3)
γ	90.00	114.57(3)
Volume ($Å^3$), Z	3312.5(13), 4	818.6(3), 2
Calculated density ($Mg\,m^{-3}$)	1.434	2.156
Absorption coefficient (mm^{-1})	0.803	1.344
$F(0\ 0\ 0)$	1476	504
Reflections collected	29,668	8288
Unique reflections	5640 [$R(\text{int}) = 0.0886$]	2868 [$R(\text{int}) = 0.0349$]
Data/restraints/parameters	5640/0/449	2868/0/228
Goodness-of-fit on F^2	1.200	1.079
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.1486$, $wR_2 = 0.2993$	$R_1 = 0.0235$, $wR_2 = 0.0540$
R indices (all data)	$R_1 = 0.1630$, $wR_2 = 0.3081$	$R_1 = 0.0248$, $wR_2 = 0.0548$

Good quality yellow block crystals of **2** were obtained after 2 weeks. Yield: 58.5% based on NaL. Anal. Calcd for $C_{28}H_{32}O_{14}N_4Pb_2$ (%): C, 31.64; H, 3.03; and N, 5.27. Found (%): C, 31.72; H, 3.14; and N, 5.31. IR (cm^{-1}, KBr): 3429(m), 2362(m), 1678(s), 1631(w), 1599(s), 1521(s), 1378(s), 1317(s), 1271(w), 1204(w), 1164(s), 1024(w), 984(w), 835(w), 1026(m), 781(s), 655(s), 613(w), and 444(s).

2.4. *X-ray crystallography*

Crystal data and experimental details of **1** and **2** are presented in table 1. All measurements were made on a Bruker Smart 1000 diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). All data were collected at 291(2) K using the ω–2θ scan technique and corrected for Lorenz-polarization effects. A correction for secondary extinction was applied. The structures were solved by direct methods and expanded using the Fourier technique. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogens were generated theoretically onto the specific carbons and refined isotropically with fixed thermal factors. All calculations were performed using the SHELX-97 crystallographic software package [15]. Selected bond lengths and angles are given in table 2.

3. Results and discussion

3.1. *Synthesis*

As mentioned in section 1, complexes bearing HL or relative organic ligands are limited. Indeed, there are only several examples of such complexes [11–13, 16, 17]. For example,

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

1			
Zn(1)–O(1)$^{\#1}$	1.901(8)	Zn(2)–O(7)$^{\#2}$	1.924(8)
Zn(1)–N(1)$^{\#1}$	2.071(8)	Zn(2)–N(2)$^{\#2}$	2.049(9)
Zn(2)–N(2)	2.049(8)	N(3)–N(4)	1.287(14)
N(5)–N(6)	1.304(12)	N(1)$^{\#1}$–Zn(1)–N(1)	96.4(5)
O(1)$^{\#1}$–Zn(1)–O(1)	97.9(6)	O(1)$^{\#1}$–Zn(1)–N(1)	123.3(4)
O(1)$^{\#1}$–Zn(1)–N(1)$^{\#1}$	109.1(4)	O(7)$^{\#2}$–Zn(2)–O(7)	100.5(5)
O(7)$^{\#2}$–Zn(2)–N(2)$^{\#2}$	111.9(4)	O(7)–Zn(2)–N(2)$^{\#2}$	119.9(4)
N(2)$^{\#2}$–Zn(2)–N(2)	94.1(6)		
2			
Pb(1)–O(1)	2.444(3)	Pb(1)–O(5)	2.479(3)
Pb(1)–O(6)	2.551(3)	Pb(1)–O(6)$^{\#1}$	2.691(3)
Pb(1)–O(7)	2.728(5)	Pb(1)–O(2)	2.734(4)
N(1)–N(2)	1.307(6)	O(5)–Pb(1)–O(2)	95.39(13)
O(1)–Pb(1)–O(5)	82.42(12)	O(6)–Pb(1)–O(2)	122.08(12)
O(1)–Pb(1)–O(6)$^{\#1}$	80.82(11)	O(7)–Pb(1)–O(2)	164.52(14)
O(5)–Pb(1)–O(6)$^{\#1}$	117.10(11)	O(6)–Pb(1)–O(6)$^{\#1}$	65.99(12)
O(1)–Pb(1)–O(7)	144.84(13)	O(6)$^{\#1}$–Pb(1)–O(7)	71.09(16)
O(6)$^{\#1}$–Pb(1)–O(2)	117.04(11)		

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

Weber *et al.* [11] reported four Cu(II) and Ni(II) complexes with HL or corresponding derivatives. Moustafa [12] has studied several Cu(II), Co(II), and Ni(II) mononuclear complexes bearing L$^-$. El-Shetary and Zidan [13] have described the synthesis and characterizations of Zn(II), Cd(II), Mn(II), Co(II), and Ni(II) mononuclear complexes from L$^-$. Hao *et al.* [16] have recently reported a Cu(II) polymer constructed by a similar ligand 4-[*N′*-(2,4-dioxo-3-pentylidene)hydrazino]benzoate. Basu Baul and Tiekink [17] prepared a polymeric [*p*-(2-hydroxy-5-methylphenylazo)benzoato]-trimethyltin by another similar ligand.

An interesting feature of the complexes is the carboxylato coordination mode of L$^-$. In **1** and **2**, L$^-$ is terminal monodentate (in **1**), or chelating to a single metal (in **2**) with only the carboxylate of L coordinating to the metal. This is different from the reported complexes bearing L$^-$ [11–13] where the chelating β-diketone group [12] or oxygen of carbonyl and nitrogen of hydrazone of L$^-$ [13] coordinate.

Single crystals suitable for X-ray crystallography for **1** and **2** were collected by slow evaporation of methanol solutions. Polymers **1** and **2** are not soluble in common organic solvents, such as MeOH, EtOH, MeCN, and tetrahydrofuran (THF), but soluble in DMSO or DMF.

3.2. *Crystal structure of [Zn(L)$_2$(4,4′-bipy)$_2$]$_n$ (1)*

X-ray diffraction analysis of **1** shows that it crystallizes in the space group *P2/c*. The structure consists of zigzag polymeric chains in which adjacent [Zn(L)$_2$] units are linked by 4,4′-bipy. A view of the chain structure of **1** is depicted in figure 1.

In this compound, there are two kinds of Zn(II) ions with very similar coordination; we will restrict our description to Zn1 and only mention pertinent points for Zn2, wherever appropriate.

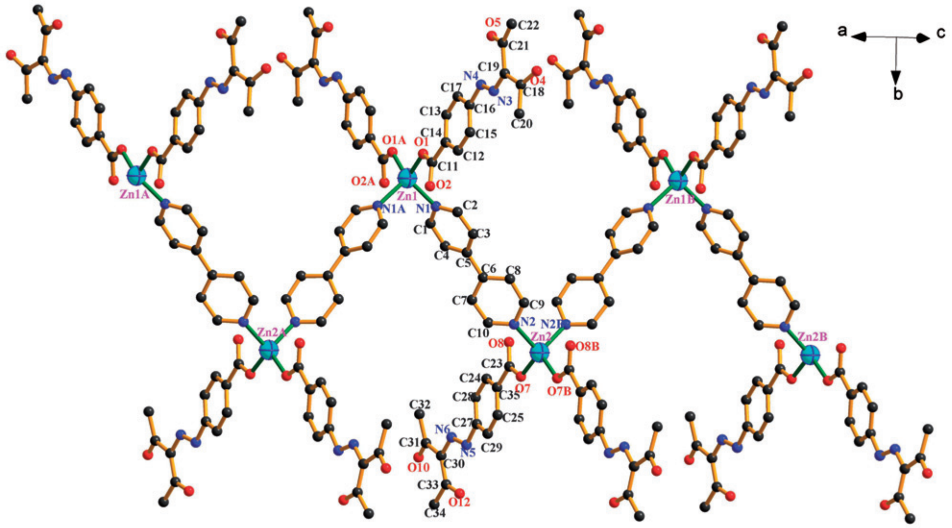

Figure 1. The 1-D zigzag chain of **1** (H atoms omitted for clarity).

Zn(II) ions are coordinated by two carboxylato oxygens from two L^- and two nitrogens from two 4,4′-bipy. The Zn1–O1 and Zn1–N1 distances are 1.901 and 2.071 Å, respectively, while the Zn2–O7 and Zn2–N2 distances are 1.924 and 2.049 Å, respectively. The Zn–O and Zn–N distances can be compared to those found in the Zn-4,4′-bipy carboxylate coordination polymer, $\{[Zn(o\text{-}OOCC_6H_4COFc)_2(4,4'\text{-bipy})(H_2O)_2]\cdot 2MeOH\cdot 2H_2O\}_n$ ($Fc = (\eta^5\text{-}C_5H_5)Fe(\eta^5\text{-}C_5H_4)$) (Zn–O: 2.079(4)–2.150(4) Å; Zn–N: 2.007(2)–2.154(2) Å) [18]. Bond angles around Zn1 range from 96.4° to 123.3° and the bond angles around Zn2 are between 94.1° and 119.9° in a distorted tetrahedral coordination sphere.

The dihedral angle between the two pyridine rings of the same 4,4′-bipy is 24.3°, indicating a slight twist. The dihedral angle between the two pyridine rings of two 4,4′-bipy coordinated to Zn1 is 61.7°, showing a large twist.

Within the same L^-, the dihedral angle between the phenyl ring and carboxylate plane is 6.4° (or 5.8°), which is significantly narrower than 14.7° in the corresponding free HL [11]. The nitrogen–nitrogen bond in **1** (N3–N4: 1.287(14) Å or N5–N6: 1.304(12) Å) is slightly shorter than, or close to, that found in free HL (1.307(3) Å). The C–O bond lengths of the carboxylate of **1** [C11–O1 1.284(15), C11–O2 1.233(15) Å, C23–O7 1.287(14) Å, and C23–O8 1.239(14) Å] are longer than those in free HL [C–O 1.209–1.214 Å]. Apparently, this is due to carboxylate coordination. The C–O bond lengths of the pentane-2,4-dione fragment of **1** [O4–C19 1.222(19), O5–C21 1.229(18) Å, O10–C31 1.225(13) Å, and O12–C33 1.271 (14) Å] are near to those in free HL [C–O 1.220(3) to 1.213(3) Å].

Terminal monodentate L^- coordinates with Zn and hang from the main chain, $[Zn(4,4'\text{-bipy})]_n$. There exist the weak intermolecular hydrogen bonds between O of diketone from one $[Zn(L)_2(4,4'\text{-bipy})_2]_n$ chain and CH of phenyl from a neighboring $[Zn(L)_2(4,4'\text{-bipy})_2]_n$ chain, O···H–C. These weak H bonds supply additional stability for the solid state structure of **1**.

As mentioned in section 1, there are two examples, $[Zn(L)(\mu_2\text{-}OOCCH_3)(H_2O)]_n$ and $[Zn(L)_2(MeOH)_4]$ [14], of Zn(II) coordination polymers with L^-; however, **1** is the first example of coordination polymer built by L^- and 4,4′-bipy.

3.3. *Crystal structure of* $[Pb(\eta^2\text{-}L)(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ *(2)*

Single-crystal structural determination reveals that **2** crystallizes in the triclinic space group $P\bar{1}$ and assumes an infinite 1-D chain in which neutral asymmetric $[Pb(\eta^2\text{-}L)(H_2O)]$ bridges by $\mu_3\text{-}\eta^2\text{-}CH_3COO^-$ (figure 2).

As shown in figure 2(a), the geometry around each Pb(II) ion is seven-coordinate, formed by four oxygens from four $\mu_3\text{-}\eta^2\text{-}CH_3COO^-$, two oxygens from one chelating $\eta^2\text{-}L^-$, and one oxygen from coordinated water. The Pb–O distances vary from 2.444(3) to 2.734(4) Å, close to those in $[Pb(\mu_2\text{-}\eta^2\text{-}C_6H_{13}COO)(\eta^2\text{-}C_6H_{13}COO)]_n$ [19] (Pb–O: 2.411–2.567 Å). The bond angles around the central Pb(II) range from 50.15° to 164.52°. The intrachain distance between metallic cations Pb1 ··· Pb1A of 4.397 Å is slightly longer than that in $\{[Pb(\mu_2\text{-}\eta^2\text{-}OOCCH{=}(CH_3)CFc)_2]\cdot MeOH\}_n$ (4.044 Å) [18].

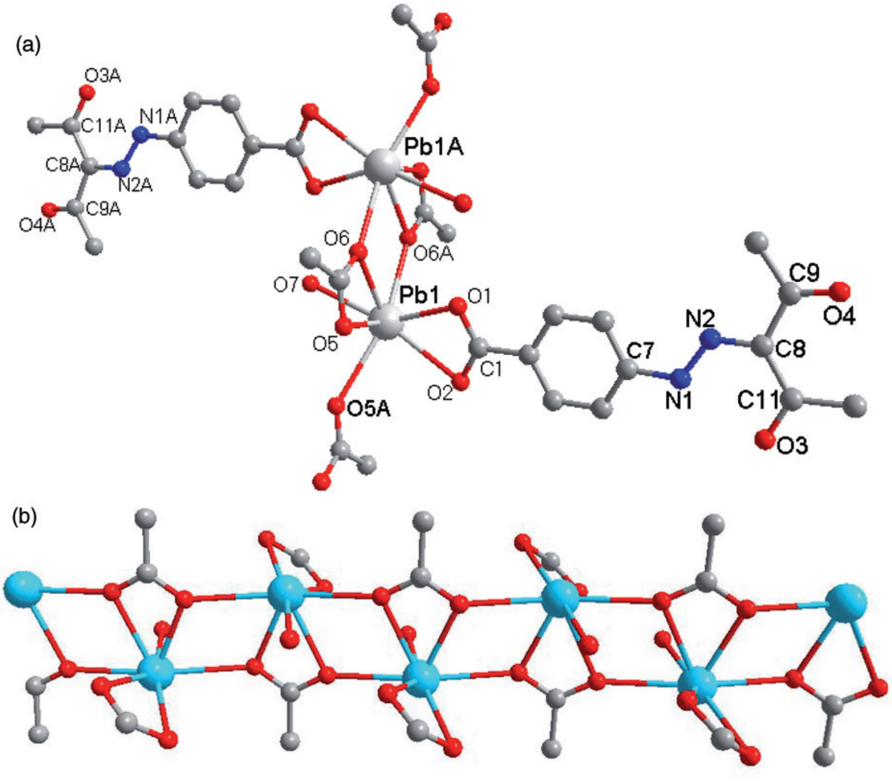

Figure 2. (a) Perspective view of **2** (H atoms omitted for clarity). (b) The 1-D structure of **2** (the partial unit of L omitted for clarity).

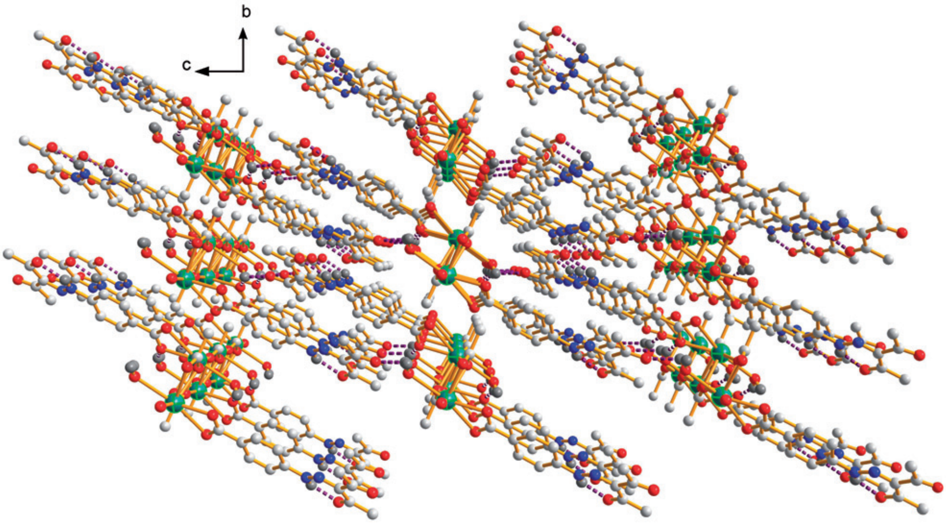

Figure 3. 3-D solid state structure supported by hydrogen bonding of **2**.

In this complex, the intramolecular hydrogen bond between N1H1 and O3 [N1–H1 ··· O3 1.891 Å, 131.12°] can be found in the same L^-. At the same time, intermolecular hydrogen bond between OH of $[Pb(\eta^2\text{-}L)(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ and O from the ketone group of $[Pb(\eta^2\text{-}L)(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ [O7–H7A ··· O5 3.678 Å, 87.63°] links $[Pb(\eta^2\text{-}L)(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ chains to form a 2-D sheet (figure 3). Furthermore, another kind of intermolecular hydrogen bond between OH of $[Pb(\eta^2\text{-}L)(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ and O from carboxylate of another $[Pb(\eta^2\text{-}L)(\mu_3\text{-}\eta^2\text{-}CH_3COO)(H_2O)]_n$ chain [O7A–H7B ··· O1A 2.031 Å, 154.50°] joined these sheets into a 3-D supramolecular structure (figure 3).

3.4. *IR spectroscopy*

The IR spectral data (400–4000 cm^{-1}) of the two complexes are in agreement with their single-crystal X-ray analyses. The carbonyl stretching vibration of HL is at 1697 cm^{-1} [11] and moves to a lower wave number after coordination. The strong absorptions at 1660 and 1400 cm^{-1} are assigned to $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$, respectively (**1**: 1678 and 1423 cm^{-1} and **2**: 1678 and 1378 cm^{-1}), close to the reported values [11–13]. In free HL, bands around 3300 and 1587–1606 cm^{-1} can be attributed to the $\nu(NH)$ and $\nu(C{=}N)$, which can be found in the two complexes (for **1**, 3395 and 1512–1607 cm^{-1}; for **2**, 3429 and 1521–1600 cm^{-1}). The characteristic $\delta(CO\text{–}CH_3)$ is found at 1293 cm^{-1} for **1** and at 1318 cm^{-1} for **2**.

3.5. *Fluorescence spectrum*

Fluorescence of free NaL and **1** and **2** were examined in solid state at room temperature.

Similar emission of NaL and complexes **1** and **2** can be observed at 485–506 nm under excitation at 295 nm (Supplementary material). The NaL and **1** and **2** show a peak with a maximum emission at 354 nm with fluorescence intensities of the two complexes weakened. The fluorescence emission of the two complexes might be attributed to ligand-to-ligand charge transfer ($L^* \rightarrow L$) [20, 21], and the introduction of metal ions (Zn^{2+} or Pb^{2+}) to the complexes may weaken the intraligand transitions of NaL.

3.6. *Thermogravimetric analysis*

The TG–DSC of the two complexes from 20°C to750°C in air (Supplementary material) show that **1** loses weight from 85.3°C to 198.8°C and keeps losing weight from 198.8°C to 486.6°C. The two-step weight loss corresponds to decomposition of 4,4′-bipy and a small part of L^-. It keeps losing weight from 486.6°C to 680°C corresponding to the decomposition of L^-, then shows a plateau from 680°C to 750°C. A white amorphous residue of ZnO remained (observed 10.93%, Calcd 11.29%). There are two weak endothermic peaks at 111.5°C and 267.6°C, one strong exothermic peak at 525.9°C and one weak exothermic peak at 566.7°C on the DSC curve of **1**.

TG data (Supplementary material) show that **2** loses coordinated water at 133.6°C to 191.5°C, then loses weight from 191.5°C to 457.3°C and 457.3°C to 521.5°C corresponding to decomposition of acetate and L^-, with a plateau from 521.5°C to 625°C. A yellow amorphous residue of PbO (observed 42.39%, Calcd 42.00%) remained. There are two weak endothermic peaks at 152.3°C and 436.4°C and one strong exothermic peak at 515.7°C on the DSC curve of **2**.

4. Conclusion

By the reaction of NaL with metal ions under mild conditions, two crystalline polymeric products have been prepared. The X-ray diffraction results indicate that L^- coordinates through carboxylate. IR data are consistent with the X-ray analysis results.

Zn-containing coordination polymers have attracted much attention due to their potential applications in the preparation of luminescent and non-linear optical materials. In 2003, Erxleben [22] gave a detailed description on the structures and properties of Zn(II) coordination polymers. Recently, there are still a large number of Zn(II) polymers [23–32], most of them constructed by carboxylate ligands. Reported Zn(II) polymers built by HL are rare with only two examples found in the literature [14]. Polymer **1** is the third example of a Zn-containing polymer with HL.

Pb(II) coordination polymers exhibit potential applications in biological systems and removal of lead by chelating agents through coordination [33–40]. By utilizing various multifunctional ligands, solvent or synthetic methods, a remarkable variety of polymeric Pb(II) frameworks with intriguing topologies have been prepared. To the best of our knowledge, **2** is the first example of a coordination polymer built by HL.

Supplementary material

Crystallographic data for these structures reported in this article in the form of CIF files have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos CCDC nos 687362 and 687363 for **1** and **2**, respectively. Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 IEZ, UK [Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk].

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