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由联苯三羧酸和含氮配体构筑的钴(Ⅱ)、铅(Ⅱ)和锌(Ⅱ)配合物的合成、晶体结构及荧光性质

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摘要: 采用水热方法,用联苯三羧酸配体(H_3btc)和菲咯啉(phen)或 2,2′-联吡啶(2,2′-bipy)分别与 $CoCl_2·6H_2O$、$PbCl_2$ 和 $ZnCl_2$ 反应,合成了一个单核配合物$[Co(Hbtc)(phen)_2(H_2O)]·3H_2O$ (**1**)以及 2 个一维链状配位聚合物$[Pb(\mu_3\text{-}Hbtc)(2,2'\text{-}bipy)]_n$ (**2**)和$\{[Zn_3(\mu_2\text{-}btc)_2(\mu_2\text{-}H_2O)(2,2'\text{-}bipy)_3(H_2O)_5]·8H_2O\}_n$ (**3**),并对其结构和荧光性质进行了研究。结构分析结果表明 3 个配合物分别属于正交和三斜晶系,$Pna2_1$ 和 $P\bar{1}$ 空间群。配合物 **1** 具有零维单核结构,而且这些单核钴单元通过 O–H···O 氢键作用进一步形成了三维超分子框架。而配合物 **2** 和 **3** 具有基于双核单元的一维链结构。研究表明,配合物 **2** 和 **3** 在室温下能发出蓝色荧光。

关键词: 配位聚合物; 氢键; 三羧酸配体; 荧光
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Syntheses, Crystal Structures, and Luminescent Properties of Three Cobalt(Ⅱ), Lead(Ⅱ) and Zinc(Ⅱ) Complexes Constructed from Mixed Biphenyl Tricarboxylic Acid and N-Donor Ligands

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Abstract: Zero-dimensional mononuclear cobalt(Ⅱ) complex, 1D lead(Ⅱ) and 1D zinc(Ⅱ) coordination polymers, namely $[Co(Hbtc)(phen)_2(H_2O)]·3H_2O$ (**1**), $[Pb(\mu_3\text{-}Hbtc)(2,2'\text{-}bipy)]_n$ (**2**) and $\{[Zn_3(\mu_2\text{-}btc)_2(\mu_2\text{-}H_2O)(2,2'\text{-}bipy)_3(H_2O)_5]·8H_2O\}_n$ (**3**), have been constructed hydrothermally using H_3btc (H_3btc=biphenyl-2,4,4′-tricarboxylic acid), phen (phen=1,10-phenanthroline), 2,2′-bipy (2,2′-bipy=2,2′-bipyridine), and cobalt, lead or zinc chlorides. Single-crystal X-ray diffraction analyses revealed that three complexes crystallize in the orthorhombic or triclinic systems, space groups $Pna2_1$ or $P\bar{1}$. Complex **1** has a discrete monomeric structure, which is assembled to a 3D supramolecular framework through O–H···O hydrogen bond. Complexes **2** and **3** show a 1D chain based on binuclear units. Luminescent properties of all complexes have been studied. CCDC: 1835223, **1**; 1835224, **2**; 1835225, **3**.

Keywords: coordination polymer; hydrogen bonding; tricarboxylic acid; luminescent properties

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0 Introduction

In recent years, the design and hydrothermal syntheses of metal-organic coordination polymers have attracted great interest in the field of coordination chemistry and organic chemistry owing to their intriguing architectures and topologies, as well as potential applications in catalysis, magnetism, luminescence and gas absorption[1-5]. There are many factors, such as the coordination geometry of the metal centers, type and connectivity of organic ligands, stoichiometry, reaction conditions, template effect, presence of auxiliary ligands, and pH values influencing the structures of target coordination polymers during self-assembly[6-11]. Among these factors, organic ligands play a very important role in constructing coordination polymers.

As we known, the multi-carboxylate biphenyl ligands have been certified to be of great significance as constructors due to their abundant coordination modes, which could satisfy different geometric requirements of metal centers[12-17]. In order to extend our research in this field, we have selected biphenyl-2,4,4′-tricarboxylic acid (H_3btc) as a functional building block on account of the following considerations: (a) H_3btc possesses three carboxyl groups that may be completely or partially deprotonated, depending on the pH value; (b) it is a flexible ligand allowing the rotation of two phenyl rings around the C-C single bond; (c) it can act as hydrogen-bond acceptor as well as donor, depending upon the degree of deprotonation.

Taking into consideration the above discussion, we herein report the syntheses, crystal structures, and luminescent properties of three Co(Ⅱ), Pb(Ⅱ) and Zinc (Ⅱ) complexes constructed from biphenyl tricarboxylic acid ligands.

1 Experimental

1.1 Reagents and physical measurements

All chemicals and solvents were of AR grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TGA) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of 10 ℃·min^{-1}. Excitation and emission spectra were recorded for the solid samples on an Edinburgh FLS920 fluorescence spectrometer at room temperature.

1.2 Synthesis of [Co(Hbtc)(phen)$_2$(H_2O)]·3H_2O (1)

A mixture of $CoCl_2·6H_2O$ (0.071 g, 0.30 mmol), H_3btc (0.086 g, 0.30 mmol), phen (0.060 g, 0.3 mmol), NaOH (0.024 g, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 ℃ for 3 days, followed by cooling to room temperature at a rate of 10 ℃·h^{-1}. Yellow block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 35% (based on H_3btc). Anal. Calcd. for $C_{39}H_{32}CoN_4O_{10}$(%): C 60.39, H 4.16, N 7.22; Found(%): C 60.24, H 4.17, N 7.16. IR (KBr, cm^{-1}): 3 318w, 2 921m, 1 691w, 1 546s, 1 516m, 1 417s, 1 364m, 1 335w, 1 295w, 1 218w, 1 137w, 1 102 w, 1 050w, 898w, 869w, 846m, 770m, 723s, 676w, 636w, 548w.

1.3 Synthesis of [Pb(μ_3-Hbtc)(2,2′-bipy)]$_n$ (2)

A mixture of $PbCl_2$ (0.083 g, 0.30 mmol), H_3btc (0.086 g, 0.3 mmol), 2,2′-bipy (0.047 g, 0.3 mmol), NaOH (0.024 g, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 ℃ for 3 days, followed by cooling to room temperature at a rate of 10 ℃·h^{-1}. Colorless block-shaped crystals of **2** were isolated manually, and washed with distilled water. Yield: 60% (based on H_3btc). Anal. Calcd. for $C_{25}H_{16}PbN_2O_6$ (%): C 46.37, H 2.49, N 4.33; Found(%): C 46.51, H 3.51, N 4.30. IR (KBr, cm^{-1}): 3 656w, 2 979w, 1 679w, 1 586s, 1 540s, 1 475w, 1 417w, 1 353s, 1 312w, 1 283w, 1 178w, 1 125 w, 1 056w, 1 003w, 852w, 822w, 770m, 693w, 642w.

1.4 Synthesis of {[Zn_3(μ_2-btc)$_2$(μ_2-H_2O)(2,2′-bipy)$_3$(H_2O)$_5$]·8H_2O}$_n$ (3)

A mixture of $ZnCl_2$ (0.041 g, 0.30 mmol), H_3btc (0.057 g, 0.2 mmol), 2,2′-bipy (0.047 g, 0.3 mmol), NaOH (0.024 g, 0.60 mmol), and H_2O (10 mL) was stirred at room temperature for 15 min, and then

sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 ℃ for 3 days, followed by cooling to room temperature at a rate of 10 ℃·h^{-1}. Colorless block-shaped crystals of **3** were isolated manually, and washed with distilled water. Yield: 65% (based on H_3btc). Anal. Calcd. for $C_{60}H_{64}Zn_3N_6O_{26}$(%): C 48.65, H 4.35, N 5.67; Found(%): C 48.74, H 4.31, N 5.63. IR (KBr, cm^{-1}): 3 685w, 2 927w, 1 597m, 1 574s, 1 528m, 1 475w, 1 446m, 1 376s, 1 312w, 1 248w, 1 172w, 1 097 w, 1 061w, 1 020w, 932w, 875w, 822w, 770m, 735w, 653w. The complexes are insoluble in water and common organic solvents, such as methanol, ethanol, acetone and DMF.

1.4 Structure determinations

Three single crystals with dimensions of 0.28 mm×0.21 mm×0.20 mm (**1**), 0.27 mm×0.20 mm×0.18 mm (**2**), and 0.27 mm×0.24 mm×0.23 mm (**3**) were collected at 293(2) K on a Bruker SMART APEX Ⅱ CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm). The structures were solved by direct methods and refined by full matrix least-square on F^2 using the SHELXTL-2014 program[18]. All non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were positioned geometrically and refined using a riding model. A summary of the crystallography data and structure refinements for **1**~**3** is given in Table 1. The selected bond lengths and angles for complexes **1**~**3** are listed in Table 2. Hydrogen bond parameters of complexes **1**~**3** are given in Table 3.

CCDC: 1835223, **1**; 1835224, **2**; 1835225, **3**.

Table 1　Crystal data for complexes 1~3

Complex	1	2	3
Chemical formula	$C_{39}H_{32}CoN_4O_{10}$	$C_{25}H_{16}PbN_2O_6$	$C_{60}H_{64}Zn_3N_6O_{26}$
Molecular weight	775.61	647.59	1 481.28
Crystal system	Orthorhombic	Triclinic	Triclinic
Space group	$Pna2_1$	$P\bar{1}$	$P\bar{1}$
a / nm	1.453 11(12)	0.834 75(3)	0.854 71(4)
b / nm	1.391 53(7)	1.058 08(5)	1.074 73(8)
c / nm	1.716 80(10)	1.255 20(7)	1.906 40(10)
α / (°)		84.056(4)	77.622(5)
β / (°)		77.249(4)	79.700(4)
γ / (°)		86.958(3)	77.012(5)
V / nm^3	3.471 5(4)	1.074 96(9)	1.650 95(17)
Z	4	2	1
F(000)	1 604	620	764
Crystal size / mm	0.25×0.20×0.18	0.27×0.20×0.18	0.27×0.24×0.23
θ range for data collection / (°)	3.375~25.045	3.294~25.047	3.798~23.023
Limiting indices	$-17 \leqslant h \leqslant 11$, $-15 \leqslant k \leqslant 16$, $-20 \leqslant l \leqslant 20$	$-9 \leqslant h \leqslant 9$, $-12 \leqslant k \leqslant 8$, $-14 \leqslant l \leqslant 14$	$-9 \leqslant h \leqslant 10$, $-8 \leqslant k \leqslant 12$, $-20 \leqslant l \leqslant 22$
Reflection collected, unique (R_{int})	12 373, 6 036 (0.055 3)	6 264, 3 799 (0.035 3)	10 069, 5 838 (0.049 9)
D_c / (g·cm^{-3})	1.484	2.001	1.490
μ / mm^{-1}	0.563	7.895	1.167
Data, restraint, parameter	6 036, 1, 483	3 799, 0, 307	5 838, 0, 443
Goodness-of-fit on F^2	1.026	1.026	1.094
Final R indices [($I \geqslant 2\sigma(I)$)] R_1, wR_2	0.056 3, 0.113 8	0.031 4, 0.057 7	0.106 5, 0.217 7
R indices (all data) R_1, wR_2	0.084 7, 0.132 1	0.037 7, 0.061 7	0.134 2, 0.232 8
Largest diff. peak and hole / (e·nm^{-3})	421 and −364	976 and −909	537 and −1 395

Table 2 Selected bond distances (nm) and bond angles (°) for complexes 1~3

1					
Co(1)-O(2)	0.209 6(5)	Co(1)-O(7)	0.209 3(5)	Co(1)-N(1)	0.212 9(6)
Co(1)-N(2)	0.214 3(6)	Co(1)-N(3)	0.214 7(6)	Co(1)-N(4)	0.215 7(7)
O(2)-Co(1)-O(7)	91.0(2)	O(2)-Co(1)-N(4)	87.9(2)	O(7)-Co(1)-N(4)	167.3(2)
O(2)-Co(1)-N(3)	91.4(2)	O(7)-Co(1)-N(3)	90.0(2)	N(4)-Co(1)-N(3)	77.3(3)
O(2)-Co(1)-N(2)	171.6(2)	O(7)-Co(1)-N(2)	90.3(2)	N(4)-Co(1)-N(2)	92.6(2)
N(3)-Co(1)-N(2)	96.9(2)	O(2)-Co(1)-N(1)	94.1(2)	O(7)-Co(1)-N(1)	100.7(2)
N(4)-Co(1)-N(1)	92.0(3)	N(3)-Co(1)-N(1)	167.8(3)	N(2)-Co(1)-N(1)	77.6(3)
2					
Pb(1)-O(1)	0.230 2(4)	Pb(1)-O(2)	0.280 7(4)	Pb(1)-O(3)A	0.244 4(3)
Pb(1)-O(2)B	0.283 8(3)	Pb(1)-N(1)	0.256 4(4)	Pb(1)-N(2)	0.262 4(5)
O(1)-Pb(1)-O(2)	50.07(1)	O(1)-Pb(1)-N(1)	74.74(1)	O(1)-Pb(1)-N(2)	81.32(1)
O(1)-Pb(1)-O(3)A	80.59(1)	O(1)-Pb(1)-O(2)B	95.79(1)	O(2)-Pb(1)-N(1)	122.64(1)
O(2)-Pb(1)-N(2)	114.49(1)	O(2)-Pb(1)-O(3)A	74.94(1)	O(2)-Pb(1)-O(2)B	67.39(1)
N(1)-Pb(1)-N(2)	63.06(1)	N(1)-Pb(1)-O(3)A	82.83(1)	N(1)-Pb(1)-O(2)B	142.31(1)
N(2)-Pb(1)-O(3)A	144.55(1)	N(2)-Pb(1)-O(2)B	79.59(1)	O(3)A-Pb(1)-O(2)B	132.42(1)
3					
Zn(1)-O(1)	0.199 7(6)	Zn(1)-O(7)	0.202 6(6)	Zn(1)-O(8)	0.207 4(7)
Zn(1)-N(1)	0.209 2(8)	Zn(1)-N(2)	0.214 6(8)	Zn(2)-O(3)	0.204 2(7)
Zn(2)-O(9)	0.200 3(17)	Zn(2)-O(9)A	0.242 8(15)	Zn(2)-O(10)A	0.202 5(16)
Zn(2)-N(3)	0.214 2(11)				
O(1)-Zn(1)-O(7)	102.0(3)	O(1)-Zn(1)-O(8)	95.1(3)	O(7)-Zn(1)-O(8)	90.2(3)
O(1)-Zn(1)-N(1)	141.2(3)	O(7)-Zn(1)-N(1)	116.3(3)	O(8)-Zn(1)-N(1)	90.6(3)
O(1)-Zn(1)-N(2)	92.4(3)	O(7)-Zn(1)-N(2)	97.9(3)	O(8)-Zn(1)-N(2)	167.6(3)
N(1)-Zn(1)-N(2)	77.4(3)	O(10)A-Zn(2)-O(9)	112.2(6)	O(10)A-Zn(2)-O(3)	90.6(5)
O(9)-Zn(2)-O(3)	85.5(4)	O(10)A-Zn(2)-N(3)	90.2(5)	O(9)-Zn(2)-N(3)	106.4(5)
O(3)-Zn(2)-N(3)	166.3(4)	O(10)A-Zn(2)-O(9)A	31.3(6)	O(9)-Zn(2)-O(9)A	81.1(6)
O(3)-Zn(2)-O(9)A	85.5(4)	N(3)-Zn(2)-O(9)A	102.1(5)	Zn(2)-O(9)-Zn(2)A	98.9(6)

Symmetry codes: A: $-x+1, -y, -z+1$; B: $-x+2, -y, -z+1$ for **2**; A: $-x, -y+2, -z+1$ for **3**.

Table 3 Hydrogen bond parameters for complexes 1~3

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠DHA / (°)
1				
O(5)–H(5) ···O(3)A	0.082	0.169	0.249 8	165.7
O(7)–H(1W)···O(4)B	0.082	0.192	0.263 5	145.2
O(7)–H(2W)···O(1)	0.084	0.196	0.270 5	147.4
O(8)–H(3W)···O(3)C	0.087	0.192	0.279 3	177.6
O(8)–H(4W)···O(9)	0.075	0.200	0.272 9	166.6
O(9)–H(5W)···O(6)D	0.085	0.209	0.294 0	179.5
O(9)–H(6W)···O(1)	0.085	0.197	0.282 4	179.8
O(10)–H(7W)···O(4)B	0.085	0.207	0.291 8	179.6
2				
O(5)–H(1)···O(6)A	0.082	0.187	0.267 0	163.3

Continued Table 3

		3		
O(7)–H(1W)···O(12)A	0.075	0.195	0.268 3	167.0
O(7)–H(2W)···O(5)B	0.085	0.187	0.272 4	179.4
O(8)–H(3W)···O(14)	0.070	0.209	0.277 4	167.8
O(8)–H(4W)···O(6)B	0.085	0.175	0.260 0	179.4
O(9)–H(5W)···O(4)C	0.085	0.1866	0.271 6	179.7
O(9)–H(6W)···O(9)C	0.114	0.1804	0.289 8	160.1
O(10)–H(7W)···O(4)C	0.102	0.1576	0.256 4	163.1
O(10)–H(8W)···O(3)C	0.103	0.1870	0.289 6	174.2
O(11)–H(9W)···O(1)D	0.085	0.194	0.278 6	179.8
O(11)–H(10W)···O(4)E	0.085	0.191	0.276 2	179.5
O(12)–H(11W)···O(11)	0.070	0.199	0.267 3	168.7
O(12)–H(12W)···O(2)	0.085	0.188	0.272 9	179.2
O(13)–H(13W)···O(6)B	0.085	0.188	0.272 8	179.5
O(13)–H(14W)···O(9)	0.066	0.199	0.263 5	167.2
O(14)–H(15W)···O(5)E	0.085	0.196	0.281 4	178.2
O(14)–H(16W)···O(13)	0.085	0.215	0.300 4	178.8

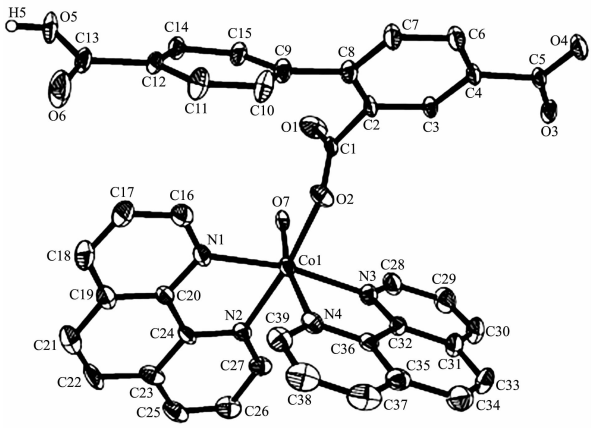
Symmetry codes: A: x, y−1, z; B: −x+1/2, y−1/2, z+1/2; C: x+1/2, −y+3/2, z; D: x+1/2, −y+1/2, z for **1**; A: −x−1, −y+1, −z+2 for **2**; A: x−1, y, z; B: x−1, y+1, z; C: −x, −y+2, −z+1; D: x+1, y, z; E: −x+1, −y+1, −z+1; F: x, y+1, z for **3**.

2 Results and discussion

2.1 Description of the structure

2.1.1 [Co(Hbtc)(phen)$_2$(H_2O)]·3H_2O (**1**)

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in the orthorhombic space group *Pna*2$_1$. This complex has a discrete monomeric structure with the asymmetric unit containing of one crystallographically unique Co(Ⅱ) ion, one $Hbtc^{2-}$ block, two phen moieties, one H_2O ligand, and three lattice water molecules. As depicted in Fig.1, the six-coordinated Co(Ⅱ) ion is surrounded by one carboxylate O atom from one $Hbtc^{2-}$ block, one O atom from H_2O ligand, and four N atoms from two phen moieties, thus forming a distorted octahedral {CoO_2N_4} environment. The lengths of Co-O bonds range from 0.209 3(5) to 0.209 6(5) nm, whereas the Co-N distances vary from 0.212 9(6) to 0.215 7(7) nm; these bonding parameters are comparable to those found in other reported Co(Ⅱ) complexes[11-12,14]. In **1**, the $Hbtc^{2-}$ ligand adopts terminal coordination mode (mode Ⅰ, Scheme 1), in which the deprotonated carboxylate groups exhibit the monodentate or uncoordinated modes. The dihedral angle between two phenyl rings in the $Hbtc^{2-}$ is 56.32°. The discrete units of **1** are connected by means of O–H···O hydrogen bond to give rise to a 3D supramolecular framework (Fig.2 and Table 3).

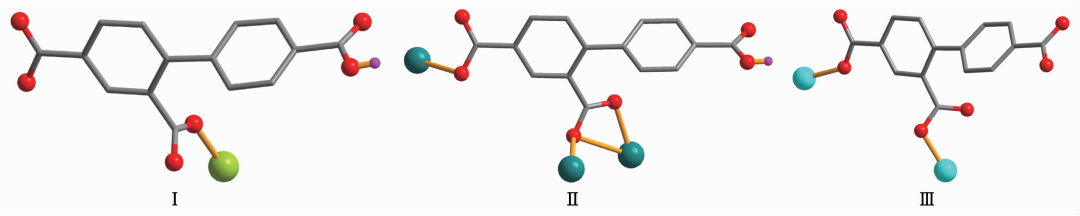


H atoms and lattice water molecules were omitted for clarity except H of COOH group

Fig.1 Drawing of the asymmetric unit of complex **1** with 30% probability thermal ellipsoids

2.1.2 [Pb(μ_3-Hbtc)(2,2′-bipy)]$_n$ (**2**)

Complex **2** shows a 1D chain structure. The asymmetric unit of **2** consists of one crystallographically distinct Pb(Ⅱ) ion, one μ_3-$Hbtc^{2-}$ block, and one 2,2′-bipy ligand. As shown in Fig.3, six-coordinate Pb1 center displays a distorted octahedral {PbO_4N_2}



Scheme 1 Coordination modes of $Hbtc^{2-}$/btc^{3-} ligands in complexes **1~3**

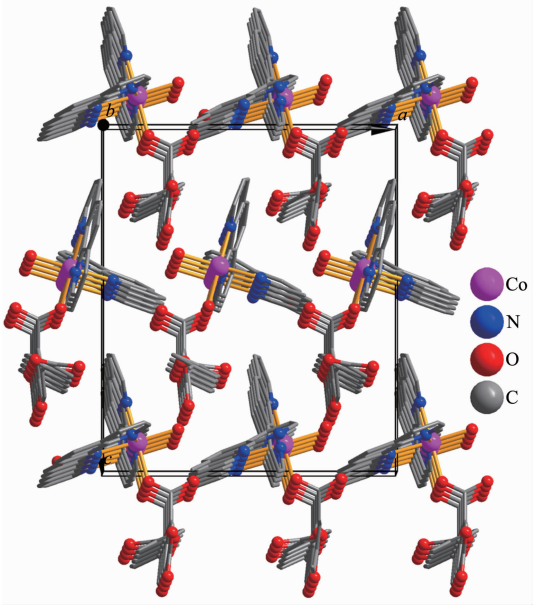
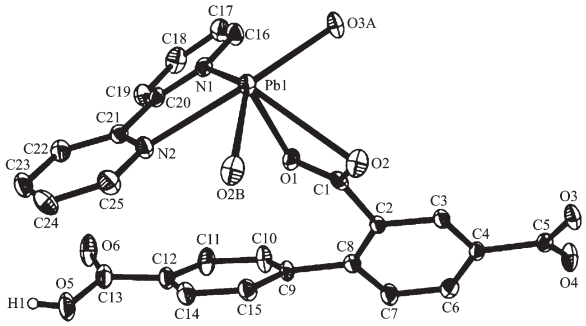


Fig.2 Perspective of 3D supramolecular framework parallel to the ac plane in **1**

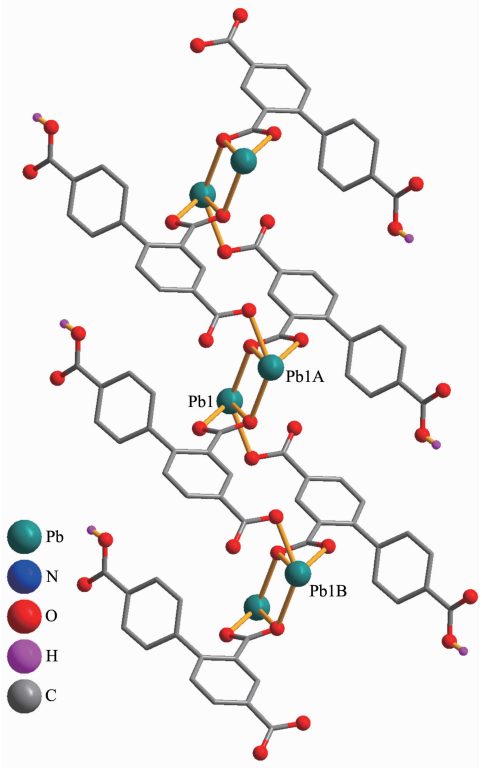
environment, filled by four carboxylate O atoms from three individual μ_3-$Hbtc^{2-}$ blocks and two N atoms from one 2,2′-bipy ligand. The Pb-O distances range from 0.230 2(4) to 0.283 8(3) nm, whereas the Pb-N distances vary from 0.256 4(4) to 0.262 4(5) nm; these bonding parameters agree with those observed in other Pb(Ⅱ) complexes[12,14]. In **2**, the $Hbtc^{2-}$ block acts as a



H atoms were omitted for clarity except H of COOH group; Symmetry codes: A: $-x+1, -y, -z+1$; B: $-x+2, -y, -z+1$

Fig.3 Drawing of the asymmetric unit of complex **2** with 30% probability thermal ellipsoids

μ_3-spacer and its deprotonated COO^- groups take a monodentate or tridentate modes (mode Ⅱ, Scheme 1). In $Hbtc^{2-}$, the dihedral angle between two benzene rings is 57.62°. The carboxylate groups of $Hbtc^{2-}$ blocks link neighboring Pb(Ⅱ) ions to give a Pb_2 unit (Fig.4) with the Pb⋯Pb separation of 0.469 7(4) nm. Neighboring Pb_2 subunits are additionally interlinked by the $Hbtc^{2-}$ spacers to give a 1D chain (Fig.4).



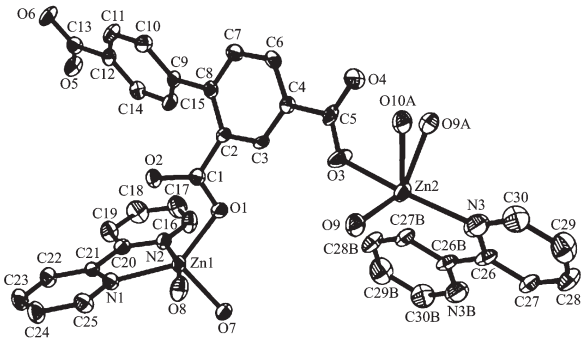
Symmetry codes: A: $-x, -y+2, -z+1$; B: $-x+1, -y+2, -z+1$

Fig.4 One-dimensional chain in complex **2**

2.1.3 $\{[Zn_3(\mu_2\text{-btc})_2(\mu_2\text{-}H_2O)(2,2'\text{-bipy})_3(H_2O)_5]\cdot 8H_2O\}_n$ (**3**)

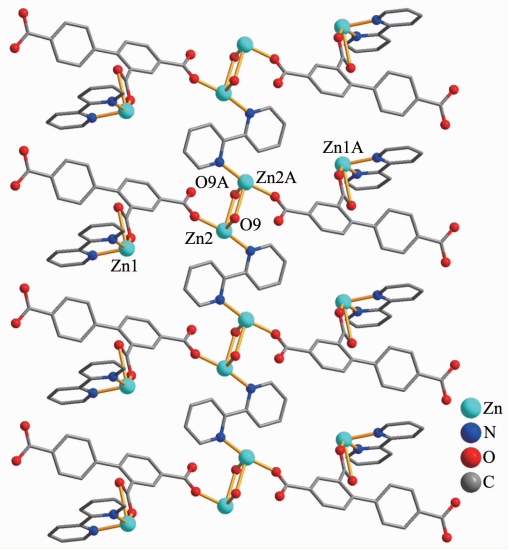
Complex **3** also exhibits a 1D chain structure. The asymmetric unit of **3** bears two crystallographically unique Zn (Ⅱ) ions (Zn1 with full occupancy; Zn2 with half occupancy), one μ_2-btc^{3-} block, a half of one μ_2-H_2O, two and a half of terminal

coordinated water molecules, one and a half of 2,2′-bipy ligands, and four lattice water molecules. As shown in Fig.5, both Zn1 and Zn2 centers are five-coordinated and feature distorted trigonal bipyramidal $\{ZnN_2O_3\}$ or $\{ZnNO_4\}$ environments, respectively. Zn1 atom is surrounded by one carboxylate O atom from one μ_2-btc^{3-} block, two O atoms from two H_2O ligands, and two N atoms from one 2,2′-bipy moiety. The Zn2 atom is bound by one carboxylate O atom from one btc^{3-} moiety, three O atoms from three water ligands, and one N atom from one 2,2′-bipy ligand. The Zn-O (0.199 7(6)~0.242 8(15) nm) and Zn-N (0.209 2(8)~0.214 6(8) nm) bond distances are in agreement with those reported for related zinc(Ⅱ) complexes[11,14,19]. In **3**, the btc^{3-} block behaves as a μ_2-spacer and its COO^- groups adopt a monodentate or uncoordinated mode



H atoms were omitted for clarity; Symmetry codes: A: $-x$, $-y+2$, $-z+1$

Fig.5　Drawing of the asymmetric unit of complex **3** with 30% probability thermal ellipsoids



Symmetry codes: A: $-x$, $-y+2$, $-z+1$

Fig.6　One-dimensional chain in complex **3**

(mode Ⅲ, Scheme 1). In btc^{3-}, a dihedral angle (between two aromatic rings) is 42.84°. Two O atoms from two water ligands bridge adjacent Zn2 atoms to form a dinuclear zinc unit (Fig.6) having a Zn⋯Zn distance of 0.338 1(7) nm. The Zn_2 units are linked by the 2,2′-bipy ligands to form a 1D chain (Fig.6).

2.2　TGA analysis

To determine the thermal stability of complexes **1**~**3**, their thermal behaviors were investigated under nitrogen atmosphere by thermogravimetric analysis (TGA). As shown in Fig.7, complex **1** lost its three lattice water molecules and one H_2O ligand in the range of 59~291 ℃ (Obsd. 8.9%; Calcd. 9.3%), followed by the decomposition at 371 ℃. For complex **2**, the TGA curve reveals that the sample is stable up to 339 ℃, followed by a decomposition on further heating. The TGA curve of **3** shows that eight lattice and six coordinated water molecules are released between 19~192 ℃ (Obsd. 16.8%; Calcd. 17.0%), and the dehydrated solid begins to decompose at 232 ℃.

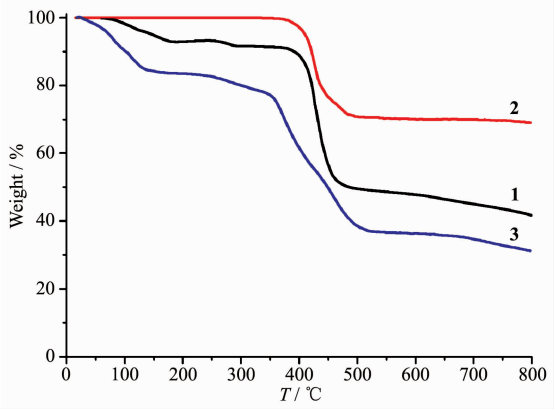


Fig.7　TGA curves of complexes **1**~**3**

2.3　Luminescence properties

The emission spectra of H_3btc and complexes **2** and **3** were measured in the solid state at room temperature, as depicted in Fig.8. The free H_3btc ligand displays a weak photoluminescence with an emission maximum at 372 nm. For complexes **2** and **3**, the more intense emission bands were observed with maximum at 369 nm for **2** and 415 nm (λ_{ex}=300 nm in all cases) for **3**. All bands can be assigned to an intraligand ($\pi^*\rightarrow n$ or $\pi^*\rightarrow\pi$) emission[10,12,14]. The enhancement of luminescence of complexes **2** and **3**

can be attributed to the binding of ligands to the metal centers, which effectively increases the rigidity of the ligand and reduces the loss of energy by radiationless decay[10-11,13].

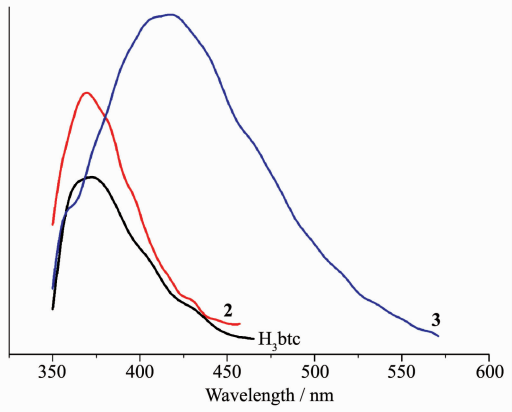


Fig.8 Solid state emission spectra of H_3btc and complexes **2** and **3**

3 Conclusions

In summary, three new complexes, namely $[Co(Hbtc)(phen)_2(H_2O)]\cdot 3H_2O$ (**1**), $[Pb(\mu_3\text{-}Hbtc)(2,2'\text{-bipy})]_n$ (**2**), and $\{[Zn_3(\mu_2\text{-}btc)_2(\mu_2\text{-}H_2O)(2,2'\text{-bipy})_3(H_2O)_5]\cdot 8H_2O\}_n$ (**3**), have been synthesized under hydrothermal conditions. The complexes feature the 0D mononuclear and 1D chain structures, respectively. Luminescent properties of complexes **2** and **3** have also been studied. For complexes **2** and **3**, the more intense emission bands were observed.

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