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Two novel Pb(II)-based heterometallic coordination polymers assembled from 1,3,5-benzenetricarboxylic acid: Syntheses, structures and luminescent properties

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HIGHLIGHTS

- Two heterometallic complexes have been synthesized and characterized.
- Complex 1 shows a two-dimensional bilayer structure containing (3,6) networks. Complex 2 holds a three-dimensional heterometallic framework.
- The fluorescence spectra of the complexes have also been investigated.

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ABSTRACT

Two new heterometallic coordination polymers: $[Pb_2Zn(btc)_2(H_2O)_6]$ (**1**), $[Pb_2Cd(btc)_2(H_2O)_2]\cdot 2H_2O$ (**2**) (H_3btc = 1,3,5-benzenetricarboxylic acid) have been synthesized under hydrothermal condition and characterized by elemental analysis, IR, PXRD and single crystal X-ray diffraction. Complex **1** crystallizes in the triclinic space group *P*-1, showing a two-dimensional (2D) bilayer structure containing (3,6) networks with the binuclear $[Pb_2O_8]$ units acting as six-connected nodes. Complex **2** crystallizes in the monoclinic space group $P2_1/a$ and features a heterometallic 3D framework. Solid state emission spectra of both the two compounds have also been studied at room temperature.

1. Introduction

Coordination polymers (CPs) assembled from metal ions and organic linkers are an important class of materials and have been attracting tremendous interest from chemists during the past decade [1–4]. To date, many examples of CPs showing diverse novel structures and intriguing properties in the fields of magnetism, photoluminescence, gas storage, catalysis and so on have been reported [5–9]. As well known, advantages that CPs show as structure adjustability or property novelty originate from the central metal ions and the organic ligands. However, most of current research works on the synthesis of CPs are focus on single metal or single ligand systems. Therefore, it is significant to involve different types of metal ions and organic ligands in the construction of CPs. Several CPs assembled from mixed ligands have been reported by our group [10–11]. Now, we expand work to the construction of CPs based on multiple types of metal ions. Employing different kinds of metal ions in the construction of CPs will not only tune the complex's structure but also increase the chance to obtain new heterometallic CPs with interesting properties [12–15]. Pb(II) cation is an important heavy metal ion of main group with large radius, rich coordination numbers and good coordination ability with oxygen atom, but less research work has been done about it. On the other hand, among organic ligands, 1,3,5-benzenetricarboxylic acid is one of the most popular functional linker, due to the rigidity of the aromatic part and the various coordination modes of carboxylate groups, which favors the formation of coordination complexes with interesting topological structures and novel properties. Taking account of these, recently we began to assemble CPs based on Pb(II) ion, H_3btc and different transition metal ions. In this paper, we report the synthesis, structure, and luminescence properties of two new heterometallic coordination polymers: $[Pb_2Zn(btc)_2(H_2O)_6]$ (**1**) and $[Pb_2Cd(btc)_2(H_2O)_2]\cdot 2H_2O$ (**2**).

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2. Experimental section

2.1. Materials required and general methods

All the starting materials and solvents were commercially purchased and used as received without further purification. Elemental analysis (C, H, N) was carried out on an Elementar Vario EL III analyzer. Infrared (IR) spectrum was recorded on PerkinElmer Spectrum One with a sample prepared as KBr pellet in the range 4000–400 cm^{-1}. The thermogravimetric analysis (TGA) was carried out with a NETZSCH STA 449C unit, at a heating rate of 10 °C/min under a nitrogen atmosphere. Fluorescence spectroscopy of the compound was performed on an Edinburgh Analytical instrument FLS920. This instrument is equipped with an Edinburgh Xe900 xenon arc lamp as exciting light source. X-ray Powder diffraction (XRPD) pattern of the sample was recorded by an X-ray diffractometer (MiniFlex2 goniometer).

2.2. Synthesis of compounds **1**–**2**

2.2.1. $[Pb_2Zn(btc)_2(H_2O)_6]$ (**1**)

A mixture of $Pb(NO_3)_2$ (0.2 mmol), $Zn(NO_3)_2{\cdot}6H_2O$ (0.2 mmol), H_3btc (0.3 mmol) and $NH_3{\cdot}H_2O$ (0.5 mmol) in 10 ml H_2O are stirred for 10 min at room temperature. The mixture was then transferred to and sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 130 °C for 3 day and then slowly cooled to room temperature. Colorless block crystals were collected by filtration and washed with distilled water in 60% yield based on Pb. Anal. Calcd. for $C_{18}H_{18}O_{18}Pb_2Zn$ (%): C, 21.57; H, 1.81. Found (%): C, 21.62; H, 1.79. IR (KBr, cm^{-1}): 3436(m), 2920(w), 1610(s), 1550(s), 1517(s), 1436(s), 1357(s), 1199(w), 714(m).

2.2.2. $[Pb_2Cd(btc)_2(H_2O)_2]{\cdot}2H_2O$ (**2**)

A mixture of $Pb(NO_3)_2$ (0.2 mmol), $Cd(NO_3)_2{\cdot}6H_2O$ (0.2 mmol), H_3btc (0.3 mmol) and NaOH (0.6 mmol) in 10 ml H_2O/DMF (1:1 volume ratio) are stirred for 10 min at room temperature. The mixture was then transferred to and sealed in a 25 mL Teflon-lined stainless steel autoclave and heated at 130 °C for 3 day and then slowly cooled to room temperature. Colorless block crystals were collected by filtration and washed with distilled water in 55% yield based on Pb. Anal. Calcd. for $C_{18}H_{14}O_{16}Pb_2Cd$ (%): C, 21.34; H, 1.39. Found (%): C, 21.38; H, 1.42. IR (KBr, cm^{-1}): 3432(m), 2925(w), 1614(s), 1558(m), 1435(s), 1369(s), 1107(w), 729(m).

2.3. X-ray crystallography

Suitable single crystal with a approximate dimensions (0.25 mm × 0.18 mm × 0.18 mm for **1** and 0.20 mm × 0.16 mm × 0.13 mm for **2)** were mounted on a Xcalibur Eos Gemini diffractometer with graphite-monochromated Mo Kα (λ) 0.71073 Å) radiation at room temperature. Data reduction was performed with the CrysAlisPro program [16]. Empirical absorption corrections were applied to the data using the SADABS program [17]. The structures were solved by direct methods and refined by the full-matrix leastsquares on F^2 using the SHELXTL-97 program [18]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The positions of hydrogen atoms attached to carbon atoms were generated geometrically and refined with isotropic thermal parameters. Crystallographic data and structure determination summaries are listed in Table 1, and the selected bond lengths and angles for the complexes are listed in Tables 2 and 3.

Table 1
Crystal data collection and refinement parameter for **1** and **2**.

	1	**2**
Formula	$C_{18}H_{18}O_{18}Pb_2Zn$	$C_{18}H_{14}O_{16}$ Pb_2Cd
Fw	1002.13	1013.11
Crystal system	Triclinic	Monoclinic
Space group	*P*-1	$P2_1/a$
a/Å	7.0760(11)	6.5478(3)
b/Å	9.7609(12)	16.1021(6)
c/Å	9.8297(9)	10.2812(5)
α/°	63.661(11)	90
β/°	73.793(11)	105.351(5)
γ/°	71.727(13)	90
V/Å^3	569.88(12)	1045.31(8)
Z	1	2
D_c/g cm^{-3}	1.443	1.597
F(000)	452	908
T/K	298(2)	298(2)
λ(Mo Kα)/Å	0.71073	0.71073
θ_{min} (°)	3.27	2.53
θ_{max} (°)	26.37	26.36
Reflections collected	5924	5445
Unique reflections	2310	2130
Observed reflections	2164	1875
R_{int}	0.0395	0.0532
Data/restraints/parameters	2310/0/191	2130/0/164
S on F^2	1.042	1.050
R_1 ($I > 2\sigma(I)$)[a]	0.0242	0.0488
wR_2 ($I > 2\sigma(I)$)[b]	0.0517	0.1197
R_1 (all data)[a]	0.0267	0.0551
wR_2 (all data)[b]	0.0527	0.1262
$\Delta\rho_{max\ and\ min}$ [e/Å^3]	1.097 and −1.549	4.023 and −3.771

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

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

Bond	Dist.	Bond	Dist.
Pb(1)–O(1)	2.565(4)	Pb(1)–O(2)	2.524(4)
Pb(1)–O(4)#2	2.552(4)	Pb(1)–O(6)#1	2.359(4)
Pb(1)–O(6)#3	2.700(4)	Zn(1)–O(7)	2.088(4)
Zn(1)–O(7)#4	2.088(4)	Zn(1)–O(8)	2.089(4)
Zn(1)–O(8)#4	2.089(4)	Zn(1)–O(9)	2.134(4)
Zn(1)–O(9)#4	2.134(4)		
Angle	(°)	Angle	(°)
O(2)–Pb(1)–O(1)	50.82(12)	O(2)–Pb(1)–O(4)#2	127.61(12)
O(6)#1–Pb(1)–O(1)	86.04(13)	O(6)#1–Pb(1)–O(4)#2	90.44(13)
O(4)#2–Pb(1)–O(1)	76.99(12)	O(1)–Pb(1)–O(6)#3	147.93(12)
O(7)#4–Zn(1)–O(7)	180.0(2)	O(7)–Zn(1)–O(8)	91.73(17)
O(7)–Zn(1)–O(9)	90.16(16)	O(8)–Zn(1)–O(9)	89.71(17)

Symmetry transformation used to generate the equivalent atoms: #1: $-x+2$, $-y$, $-z+2$; #2: x, $y+1$, $z-1$; #3: $x-1$, $y+1$, z; #4: $-x$, $-y+2$, $-z+1$.

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

Bond	Dist.	Bond	Dist.
Pb(1)–O(1)	2.369(8)	Pb(1)–O(2)	2.7732(1)
Pb(1)–O(3)#3	2.8531(2)	Pb(1)–O(5)#1	2.360(7)
Pb(1)–O(6)#2	2.428(7)	Cd(1)–O(2)#4	2.308(7)
Cd(1)–O(4)	2.208(7)	Cd(1)–O(7)	2.372(8)
Angle	(°)	Angle	(°)
O(1)–Pb(1)–O(2)	49.855(1)	O(1)–Pb(1)–O(6)#2	86.3(3)
O(5)#1–Pb(1)–O(1)	73.8(3)	O(5)#1–Pb(1)–O(6)#2	80.700(1)
O(4)–Cd(1)–O(7)	88.2(3)	O(4)–Cd(1)–O(2)#4	89.0(3)
O(2)#4–Cd(1)–O(7)	93.0(3)		

Symmetry transformation used to generate the equivalent atoms: #1: $-x+1/2$, $y-1/2$, $-z+2$; #2: $-x$, $-y$, $-z+2$; #3: $-x$, $-y+1$, $-z+1$; #4: $-x-1/2$, $y+1/2$, $-z+1$.