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Layered zinc (II) and cadmium (II) dicarboxylates with aromatic chelate ligand-syntheses, crystal structures and luminescent properties

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Abstract

Two new two-dimensional (2D) layered d^{10} metal coordination polymers, $[M(PDB)(2,2'\text{-bpy})]_n$ ($M = Zn^{2+}$ (**1**) and Cd^{2+} (**2**), PDB = pyridine-3,4-dicarboxylate), have been prepared by hydrothermal reaction and characterized by IR, TGA, and single-crystal X-ray diffraction analysis. Compounds **1** and **2** both exhibit puckered hexagonal (6,3) sheets and represent the first examples of 2D structures formed by PDB and chelate heterocyclic ligand. Furthermore, both of them show intense luminescent properties at room temperature.

Keywords: Coordination polymer; Carboxylate; Hydrothermal synthesis; Puckered layer; Luminescent property

1. Introduction

The versatility of metal-organic chemistry offers a unique opportunity to construct multifunctional materials based on the assembly of molecular building blocks. Such an approach can lead to the design of coordination polymers with intriguing architectures and potential applications [1]. Particular attractive is the ability of organic moiety to diversify structural arrangements associated with the wide-ranging properties of transition metals (e.g. magnetic and optical properties, electronic conductivity and ferroelectricity) [2]. In this regard, much attention has been devoted to the deliberate design and control of self-assembly infinite coordination networks via selecting the chemistry structures of ligands [3]. Among these, the employment of symmetrical ligands is a successful paradigm owing to their high symmetry and structural predictability [4]. Nevertheless, incorporation of unsymmetrical ligands in such a system is relatively recent. Although important progress has been made in the construction of coordination polymers by applying unsymmetrical ligands [5], further research for them is still an especially attractive target, thus allowing the construction of an almost infinite number of new molecule-based entities.

Pyridine-3,4-dicarboxylic acid (H_2PDB), as a member of them, has been less studied up to now. Of the relatively few structurally characterized complexes which exit to date [6], all are constructed from PDB and linear ligands, such as 4,4′-bipyridine. No frameworks constructed by PDB and aromatic chelate ligands have been observed hitherto. Furthermore, the preparation of this type of species can provide some meaningful information for the effect of coligand on the resulting structure.

On the other hand, polynuclear d^{10} metal (Cu^I, Ag^I, Au^I, Zn^{II} or Cd^{II}) complexes have attracted extensive interest in recent years in that they not only exhibit appealing structures but also possess photoluminescent properties [7].

On the basis of the aforementioned points, we chose PDB and 2,2′-bipyridine as organic building blocks to synthesize new coordination polymers by hydrothermal synthesis and study their luminescent properties. In this paper we report two new d^{10} metal coordination polymers $[M(PDB)(2,2'\text{-bpy})]_n$ ($M = Zn^{2+}$ (**1**) and Cd^{2+} (**2**)). Compounds **1** and **2** exhibit two-dimensional (2D) puckered (6,3) sheets, whose 3-connecting nodes are provided by both PDB^{2-} and M^{2+}. To the best of our knowledge, they represent the first examples of metal-based frameworks constructed by PDB

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and chelate heterocyclic ligand. Furthermore, both of them show intense luminescent properties at room temperature.

2. Experimental section

2.1. General methods and materials

All organic solvents and materials used for the synthesis were of regent grade and were used without purification. Element analyses (C, H, N) were performed on a Perkin-Elmer 2400 CHN elemental analyzer. FTIR spectrum was recorded in the range 400–4000 cm^{-1} on an Alpha Centaurt FTIR spectrophotometer using a KBr pellet. TG analysis was performed on a Perkin-Elmer TGA7 instrument in flowing N_2 with a heating rate of 10 °C min^{-1}. Excitation and emission spectra were obtained on a SPEX FL-2T2 spectrofluorometer equipped with a 450 W xenon lamp as the excitation source. All measurements were performed at room temperature. X-ray powder diffraction (XRPD) patterns were recorded on a Siemens D5005 diffractometer with Cu Kα (λ = 1.5418 Å) radiation.

2.2. Syntheses of compounds 1 and 2

[Zn(PDB)(2,2′-bpy)]$_n$ (**1**): Compound **1** was synthesized from the reaction mixture of $Zn(NO_3)_2\cdot 6H_2O$ (1 mmol, 0.2975 g), H_2PDB (1 mmol, 0.1671 g), bpy (1 mmol, 0.1562 g) and water (10 ml) in a 23 ml Teflon reactor, under autogenous pressure at 140 °C for 5 days and then cooled to room temperature at a rate of 10 °C/h. Colorless crystals of **1** were obtained (yield: 72% based on Zn). Elemental analysis found: C, 52.4%; H, 2.5%; N, 11.2%. Calcd. For $C_{17}H_{11}N_3ZnO_4$: C, 52.80%; H, 2.87%; N, 10.87%. IR spectrum (cm^{-1}): 1614(s), 1564(s), 1493(w), 1449 (s), 1442(s), 1420(w), 1397(s), 1294(w), 1218(m), 1172(m), 1018(m), 947(w), 890(m), 852(s), 775(m), 741(s), 687(m), 576(m).

[Cd(PDB)(2,2′-bpy)]$_n$ (**2**): compound **2** was prepared using a similar method to that employed for the synthesis of **1**, with $Cd(NO_3)_2\cdot 4H_2O$ (1 mmol, 0.3084 g) in place of $Zn(NO_3)_2\cdot 6H_2O$. Light-yellow crystals were obtained (yield: 65% based on Cd). Elemental analysis found: C, 46.7%; H, 2.3%; N, 9.3%. Calcd. For $C_{17}H_{11}N_3CdO_4$: C, 47.08%; H, 2.56%; N, 9.69%. IR spectrum (cm^{-1}): 1655(w), 1607(s), 1557(s), 1431(s), 1418(w), 1383(s), 1287(w), 1222(m), 1171(m), 1074(m), 946(w), 884(m), 816(m), 745(s), 734(m), 689(m), 575(m).

2.3. X-ray crystallography

Single crystals of **1** and **2** were carefully selected under a polarizing microscope and glued at the tip of thin glass fibers with cyanoacrylate (super glue) adhesive, respectively. Single-crystal structure determinations by XRD were performed on a *R*-axis RAPID IP diffractometer equipped with a normal focus, 18 kW sealed tube X-ray source (Mo Kα radiation, λ = 0.71073 Å) operating at 50 kV and 200 mA. Empirical absorption correction was applied. The structures were solved by the direct method and refined by the full-matrix least-squares method on F^2 using the SHELXTL crystallographic software package [8]. Anisotropic thermal parameters were used to refine all non-hydrogen atoms. Hydrogen atoms were located from difference Fourier maps. Further details of the X-ray structural analysis are given in Table 1. Selected bond lengths and angles are listed in Table 2.

Table 1
Crystal data and structure refinement of **1** and **2**

Molecular formula	$C_{17}H_{11}N_3ZnO_4$	$C_{17}H_{11}N_3CdO_4$
F_w	386.66	433.69
Crystal system	Monoclinic	Monoclinic
Space group	Pn	$P2_1/n$
a (Å)	7.7210(15)	7.0294(14)
b (Å)	9.2375(18)	17.733(4)
c (Å)	10.602(2)	12.420(3)
β	96.10(3)	102.78(3)
V (Å^3)	751.9(3)	1718.5(6)
Z	2	4
D_{calcd} (g/cm^3)	1.708	1.876
T/K	293(2)	293(2)
μ/mm^{-1}	1.663	1.452
F(000)	392	856
Reflections collected/unique	3268/3258	6646/3477
Final *R1*,[a] *wR2*[b] [$I > 2\sigma(I)$]	0.0290, 0.0695	0.0338, 0.0497
Final *R1*,[a] *wR2*[b] (all data)	0.0313, 0.0704	0.0591, 0.0528

[a] $R_1 = \sum ||F_0| - |F_c||/S|F_0|$.
[b] $wR_2 = \sum[w(F_0^2 - F_c^2)^2]/\sum[w(F_0^2)^2]^{1/2}$.

Table 2
Selected Bond lengths [Å] and angles [°] for **1** and **2**

1			
Zn(1)–O(3)#1	1.974(2)	Zn(1)–N(1)	2.183(2)
Zn(1)–O(2)#2	2.108(2)	Zn(1)–N(2)	2.145(3)
Zn(1)–O(1)#2	2.429(2)	Zn(1)–N(3)	2.121(2)
O(3)#1–Zn(1)–O(2)#2	103.31(8)	O(3)#1–Zn(1)–N(2)	92.11(10)
O(3)#1–Zn(1)–N(3)	107.70(10)	O(2)#2–Zn(1)–N(2)	92.20(9)
O(2)#2–Zn(1)–N(3)	147.39(9)	N(3)–Zn(1)–N(2)	77.00(9)
O(3)#1–Zn(1)–N(1)	98.80(10)	O(2)#2–Zn(1)–N(1)	89.50(8)
N(2)–Zn(1)–N(1)	168.26(9)	N(3)–Zn(1)–N(1)	95.44(9)
2			
Cd(1)–O(3)#1	2.211(2)	Cd(1)–N(1)	2.348(3)
Cd(1)–O(1)#2	2.277(2)	Cd(1)–N(2)	2.367(3)
Cd(1)–N(3)	2.313(2)		
O(3)#1–Cd(1)–O(1)#2	102.36(8)	N(3)–Cd(1)–N(1)	106.24(9)
O(3)#1–Cd(1)–N(3)	131.85(8)	O(3)#1–Cd(1)–N(2)	97.31(9)
O(1)#2–Cd(1)–N(3)	91.32(9)	O(1)#2–Cd(1)–N(2)	152.11(8)
O(3)#1–Cd(1)–N(1)	120.96(9)	N(3)–Cd(1)–N(2)	90.08(10)
O(1)#2–Cd(1)–N(1)	83.32(9)	N(1)–Cd(1)–N(2)	69.59(10)