

### 3,4-吡啶二酸钡配合物的合成、结构、荧光和热稳定性研究

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**摘要:** BaCl<sub>2</sub>·2H<sub>2</sub>O 和配体 3,4-吡啶二酸在溶剂热条件下反应生成了配合物[Ba<sub>2</sub>(pdc)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**1**)(H<sub>2</sub>pdc=3,4-吡啶二酸), 用单晶 X-射线、元素分析和 FT-IR 对生成的晶体进行了表征。Ba1 和 Ba2 分别采取了八配位扭曲四方反棱柱和十配位的双帽四棱柱几何构型, 整个 pdc<sup>2-</sup>作为四齿桥联配体连结 4 个不同的 Ba(II)原子形成二维网结构, O-H...N 氢键将二维网结合在一起形成三维结构。还研究了配合物 **1** 的荧光和热重性质。

**关键词:** Ba(II)配合物; 羧基; 荧光性质; 热重

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### Synthesis, Structure, Luminescent and Thermal Stable Properties of 3,4-Pyridinedicarboxylic Acid Barium Complex

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**Abstract:** Solvothermal reaction of BaCl<sub>2</sub>·2H<sub>2</sub>O with 3,4-pyridinedicarboxylic acid afforded a new inorganic-organic hybrid framework, [Ba<sub>2</sub>(pdc)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub> (**1**) (H<sub>2</sub>pdc=3,4-pyridinedicarboxylic acid). This complex has been fully characterized by single crystal X-ray diffraction, elemental analysis, and IR spectrum. X-ray analysis shows that complex **1** features a two-dimensional network (2D). Ba1 takes eight-coordinated distorted square antiprism geometry. Ba2 takes ten-coordinate distorted dicapped square prism coordination geometry. The whole pdc<sup>2-</sup> anion connects four different Ba(II) atoms, giving rise to a 2D network structure. The three-dimensional structure is formed by O-H...N hydrogen bonding interactions. Thermal stability and luminescent property of compound **1** have also been investigated. CCDC: 887479.

**Key words:** Ba(II) complex; carboxylate group; luminescent property; thermogravimetry

The rational design and syntheses of metal-organic frameworks have been of increasing interest in the crystal engineering of coordination polymers owing to their ability to provide with fascinating topological structures and material properties, which may render them for potential applications in non-linear optical,

magnetic, and luminescent materials<sup>[1-4]</sup>. However, to predict and further control the framework array of a given crystalline product still remain a considerable challenge at this stage. This mainly arises from the fact that the subtle assembled progress may be influenced by many intrinsic and external parameters,

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such as solvent<sup>[5-6]</sup>, concentration<sup>[7]</sup>, counteranion<sup>[8]</sup>, temperature<sup>[9]</sup>, pH value of the solution<sup>[10]</sup>, and so on. However, it is very significant to select befitting ligands and metal ions in the assembly of coordination polymers. Carboxylate-containing ligands have particularly aroused much more attention because of diverse coordination modes of carboxylate groups to the metal ions, which can adopt a variety of bonding modes to metals, including (i) terminal monodentate, (ii) chelating to a single metal, (iii) bridging bidentate (iv) bridging tridentate and so on. Generally, multi-carboxyl acids can be utilized in the formation of different dimensional coordination polymers<sup>[11-14]</sup>.

On the other hand, most of the research works so far are mainly focused on the incorporation of transition metal ions and rare-earth ions as coordination centers. Relatively less attention has been paid to the alkaline earth metal-based compounds<sup>[15]</sup>. However, compared with divalent transition metal ions, alkaline earth metal ions, for example, strontium(II) and barium(II), have larger ionic radius and therefore could adopt a higher coordination number, leading to an interesting topological arrangement. In addition, the main group alkaline-earth metals, owing to their low polarizability and various coordination models for the construction of polymer materials featuring robust structures and interesting properties, are receiving more and more research attention recently<sup>[16-17]</sup>. In this manuscript, we describe syntheses, structure, properties of an alkaline earth metal barium coordination polymer  $[\text{Ba}_2(\text{pdc})_2(\text{H}_2\text{O})_3]_n$  (**1**) of 3,4-pyridinedicarboxylic acid ( $\text{H}_2\text{pdc}$ ).

## 1 Experimental

### 1.1 Reagents and physical measurements

All reagents commercially available were of reagent grade and used without further purification. Solvents were purified according to the standard methods. C, H and N element analyses were carried out on a Perkin-Elmer 240C elemental analyzer. IR spectra were recorded on a Nicolet 6700 FT-IR spectrophotometer by using KBr pellet in the range of 4 000~400  $\text{cm}^{-1}$ . Thermogravimetric analyses (TGA)

were carried out with a SDT Q600 instrument under 100.0  $\text{mL} \cdot \text{min}^{-1}$  flowing nitrogen, and ramp rate of 20.00  $^{\circ}\text{C} \cdot \text{min}^{-1}$  from 26 to 900  $^{\circ}\text{C}$ . The luminescent spectra of the solid samples were recorded at room temperature on a CaryEclipse 300 spectrophotometer with a xenon arc lamp as the light source. In the measurements of the emission and excitation spectra, the passage width is 10.0 nm. Powder X-ray diffraction patterns were performed with a Bruker D8 ADVANCE X-ray diffractometer with  $\text{Cu } K\alpha_1$  radiation at 40 kV and 40 mA.

### 1.2 Synthesis of the title complex

#### $[\text{Ba}_2(\text{pdc})_2(\text{H}_2\text{O})_3]_n$ (**1**)

The mixture of 3,4-pyridinedicarboxylic acid 16.7 mg (0.1 mmol) and  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  24.4 mg (0.1 mmol) in mixture solution of 3 mL distilled  $\text{H}_2\text{O}$  and 5 mL DMF (*N,N*-dimethylformamide) was stirred about 30 min at room temperature. Then the mixture was sealed in a 25 mL Teflon-lined stainless steel container and heated at 160  $^{\circ}\text{C}$  for 3 d. The colorless block crystals were obtained (15.1 mg). Anal. Calcd. for  $\text{C}_{14}\text{H}_{12}\text{Ba}_2\text{N}_2\text{O}_{11}$  (658.94)(%): C, 25.52; H, 1.84; N, 4.25. Found(%): C, 25.49; H, 1.88; N, 4.26. FT-IR spectrum was recorded as KBr pellets on a 6700 FT-IR spectrophotometer (KBr pellet,  $\text{cm}^{-1}$ ): 3 410(bs), 1 608(s), 1 566(s), 1 524(w), 1 459(s), 1 443(m), 1 162(m), 1 066(w), 888(m), 850(m), 793(m), 726(w).

### 1.3 Crystal structure determination

The crystallographic data collections for complex **1** with dimensions of 0.34 mm  $\times$  0.29 mm  $\times$  0.24 mm were carried out on a Bruker Smart Apex II CCD with graphite monochromated  $\text{Mo } K\alpha$  radiation ( $\lambda=0.071\ 073$  nm) at 296(2) K using the  $\omega$ -scan technique. The structure was solved by direct methods using the SHELXS-97 program; and all non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares technique using the SHELXL-97 crystallographic software package<sup>[18-19]</sup>. The hydrogen atoms were generated geometrically. The details of the crystal parameters, data collection and refinement for this compound are summarized in Table 1. Selected bond lengths and bond angles for complex **1** are listed in Table 2.

CCDC: 887479.

Table 1 Crystallographic data for complex 1

|  |  |   |                  |
|--|--|---|------------------|
| Empirical formula                                | C <sub>14</sub> H <sub>12</sub> Ba <sub>2</sub> N <sub>2</sub> O <sub>11</sub> | Crystal color                                   | Colorless        |
| Formula weight                                   | 658.94   | $D_c / (\text{g} \cdot \text{cm}^{-3})$         | 2.400            |
| Crystal system                                   | Orthorhombic   | $\mu / \text{mm}^{-1}$                          | 4.357            |
| Space group                                      | <i>Pnna</i>  | Crystal dimension / mm                          | 0.34×0.29×0.24   |
| <i>a</i> / nm                                    | 2.175 59(19)   | $\theta$ range / (°)                            | 1.87~27.55       |
| <i>b</i> / nm                                    | 0.973 09(9)  | <i>F</i> (000)                                  | 1 240            |
| <i>c</i> / nm                                    | 0.861 48(8)  | Goodness of fit                                 | 1.070            |
| <i>V</i> / nm <sup>3</sup>                       | 1.823 8(3)   | Reflections collected                           | 2 106            |
| <i>Z</i>   | 4  | Independent reflns. ( <i>R</i> <sub>int</sub> ) | 0.038 7          |
| Parameters refined                               | 133  | Obsd. reflns. ( <i>I</i> >2σ( <i>I</i> ))       | 1 775            |
| <i>R</i> , <i>wR</i> ( <i>I</i> >2σ( <i>I</i> )) | 0.023 3, 0.064 5   | <i>R</i> , <i>wR</i> (all reflections)          | 0.030 0, 0.068 5 |

Table 2 Selected bond lengths (nm) and bond angles (°) for complex 1

|                     |            |                     |            |                     |            |
|---------------------|------------|---------------------|------------|---------------------|------------|
| Ba(1)-O(1)          | 0.273 8(3) | Ba(1)-O(1)#1        | 0.273 8(3) | Ba(1)-O(3)          | 0.281 6(2) |
| Ba(1)-O(3)#1        | 0.281 6(2) | Ba(1)-O(4)          | 0.270 6(3) | Ba(1)-O(4)#1        | 0.270 6(3) |
| Ba(1)-O(5)#1        | 0.292 3(2) | Ba(1)-O(5)          | 0.292 3(2) | Ba(2)-O(2)#2        | 0.273 8(3) |
| Ba(2)-O(2)#1        | 0.273 8(3) | Ba(2)-O(6)#3        | 0.282 8(3) | Ba(2)-O(6)          | 0.282 8(3) |
| Ba(2)-O(1)          | 0.283 3(2) | Ba(2)-O(1)#3        | 0.283 3(2) | Ba(2)-O(3)#1        | 0.291 0(3) |
| Ba(2)-O(3)#2        | 0.291 0(3) | Ba(2)-O(2)          | 0.320 9(3) | Ba(2)-O(2)#3        | 0.320 9(3) |
| O(4)-Ba(1)-O(4)#1   | 111.07(13) | O(4)-Ba(1)-O(1)     | 148.27(8)  | O(4)-Ba(1)-O(1)#1   | 89.74(8)   |
| O(4)#3-Ba(1)-O(1)   | 89.74(8)   | O(4)#1-Ba(1)-O(1)#1 | 148.27(8)  | O(1)-Ba(1)-O(1)#1   | 83.26(11)  |
| O(4)-Ba(1)-O(3)     | 139.77(7)  | O(4)-Ba(1)-O(3)#1   | 76.94(8)   | O(1)-Ba(1)-O(3)     | 66.50(7)   |
| O(1)-Ba(1)-O(3)#1   | 71.87(7)   | O(4)#1-Ba(1)-O(3)   | 76.94(8)   | O(1)-Ba(1)-O(3)#1   | 71.87(7)   |
| O(4)#1-Ba(1)-O(3)#1 | 139.77(7)  | O(1)#1-Ba(1)-O(3)#1 | 66.50(7)   | O(3)-Ba(1)-O(3)#1   | 123.29(11) |
| O(4)-Ba(1)-O(5)#1   | 75.88(8)   | O(4)#1-Ba(1)-O(5)#1 | 93.13(8)   | O(1)-Ba(1)-O(5)#1   | 128.42(6)  |
| O(1)#1-Ba(1)-O(5)#1 | 68.21(7)   | O(3)-Ba(1)-O(5)#1   | 64.17(7)   | O(3)#1-Ba(1)-O(5)#1 | 126.49(8)  |
| O(4)-Ba(1)-O(5)     | 93.13(8)   | O(4)#1-Ba(1)-O(5)   | 75.88(8)   | O(1)-Ba(1)-O(5)     | 68.21(7)   |
| O(1)-Ba(1)-O(5)#1   | 128.42(6)  | O(3)-Ba(1)-O(5)     | 126.49(8)  | O(3)-Ba(1)-O(5)#1   | 64.17(7)   |
| O(5)-Ba(1)-O(5)#1   | 160.74(2)  | O(2)#2-Ba(2)-O(2)#1 | 80.68(11)  | O(2)#2-Ba(2)-O(6)#3 | 140.41(8)  |
| O(2)#1-Ba(2)-O(6)#3 | 107.86(8)  | O(2)#2-Ba(2)-O(6)   | 107.86(8)  | O(2)#1-Ba(2)-O(6)   | 140.41(8)  |
| O(6)-Ba(2)-O(6)#3   | 90.06(13)  | O(2)#2-Ba(2)-O(1)   | 135.79(8)  | O(2)-Ba(2)-O(1)#1   | 83.43(8)   |
| O(6)-Ba(2)-O(1)#3   | 83.76(8)   | O(2)#2-Ba(2)-O(1)#3 | 83.43(8)   | O(6)-Ba(2)-O(1)     | 63.26(7)   |
| O(2)#1-Ba(2)-O(1)#3 | 135.79(8)  | O(6)#3-Ba(2)-O(1)#3 | 63.26(7)   | O(6)-Ba(2)-O(1)#3   | 83.76(8)   |
| O(1)-Ba(2)-O(1)#3   | 133.45(10) | O(2)#2-Ba(2)-O(3)#1 | 66.65(7)   | O(2)#1-Ba(2)-O(3)#1 | 66.57(7)   |
| O(6)#3-Ba(2)-O(3)#1 | 152.68(7)  | O(6)-Ba(2)-O(3)#1   | 81.24(8)   | O(1)-Ba(2)-O(3)#1   | 69.17(7)   |
| O(1)#3-Ba(2)-O(3)#1 | 140.11(7)  | O(2)#2-Ba(2)-O(3)#2 | 66.57(7)   | O(2)#1-Ba(2)-O(3)#2 | 66.65(7)   |
| O(6)#3-Ba(2)-O(3)#2 | 1.24(8)    | O(6)-Ba(2)-O(3)#2   | 152.68(7)  | O(1)-Ba(2)-O(3)#2   | 140.11(7)  |
| O(1)#3-Ba(2)-O(3)#2 | 69.17(7)   | O(3)#1-Ba(2)-O(3)#2 | 117.22(10) | O(2)-Ba(2)-O(2)#2   | 145.59(6)  |
| O(2)-Ba(2)-O(2)#1   | 64.93(8)   | O(6)-Ba(2)-O(2)#3   | 58.69(7)   | O(6)-Ba(2)-O(2)     | 98.49(7)   |
| O(1)-Ba(2)-O(2)     | 42.59(7)   | O(1)-Ba(2)-O(2)#3   | 121.88(7)  | O(3)-Ba(2)-O(2)#1   | 96.85(6)   |
| O(3)-Ba(2)-O(2)#2   | 98.91(6)   | O(2)#2-Ba(2)-O(2)#3 | 64.93(8)   | O(2)#1-Ba(2)-O(2)#3 | 145.59(6)  |
| O(6)#3-Ba(2)-O(2)#3 | 98.49(7)   | O(6)-Ba(2)-O(2)#3   | 58.69(7)   | O(1)-Ba(2)-O(2)#3   | 121.88(7)  |
| O(1)#3-Ba(2)-O(2)#3 | 42.59(7)   | O(3)#1-Ba(2)-O(2)#3 | 98.91(6)   | O(3)#2-Ba(2)-O(2)#3 | 96.85(6)   |
| O(2)-Ba(2)-O(2)#3   | 149.48(9)  |                     |            |                     |            |

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

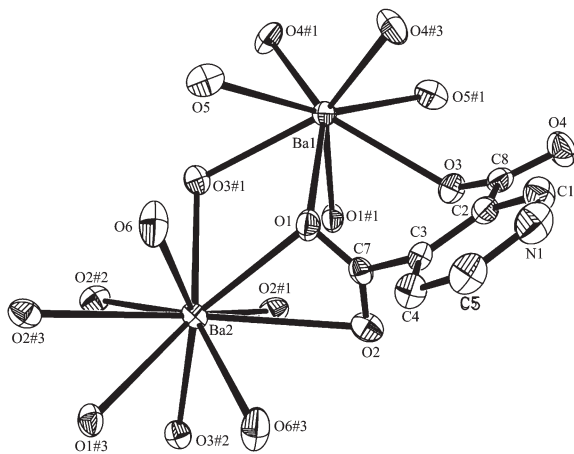
## 2 Results and discussion

### 2.1 IR spectra

The strong and broad absorption bands in the range of  $3\ 410\text{ cm}^{-1}$  for **1** is assigned as the characteristic peaks of OH vibration. The strong vibrations around  $1\ 608$  and  $1\ 566\text{ cm}^{-1}$  for **1** correspond to the asymmetric and symmetric stretching vibrations of carboxylate group, respectively. The absence of strong bands ranging from  $1\ 690$  to  $1\ 730\text{ cm}^{-1}$  indicates the deprotonation of ligand  $\text{H}_2\text{pdC}$ , which agrees with the structural results.

### 2.2 Crystal structure of **1**

Titled compound **1** crystallized in the orthorhombic space group  $\text{Pnna}$ , and has the 2D network structure. In complex **1**, there are two  $\text{Ba}(\text{II})$  ions, two  $\text{pdC}^{2-}$  anion and three coordinated water molecules per formula unit. Because the site occupation factor of  $\text{Ba1}$ ,  $\text{Ba2}$  is 0.5, respectively, asymmetric unit only contains one  $\text{Ba}(\text{II})$  atom and a  $\text{pdC}^{2-}$  anion. The  $\text{Ba1}$  center is coordinated by eight oxygen atoms of six carboxylate groups from four  $\text{pdC}^{3-}$  anions and two  $\mu_2$ -bridging coordinated water molecules to form a distorted square anti-prism (Fig.1). The distortion of the structure is clearly evident from the different  $\text{Ba1-O}$  bond lengths and  $\text{O-Ba1-O}$  bond angles, which can be divided into six shorter ( $0.270\ 6(3)\sim 0.281\ 6(2)\text{ nm}$ ) and two longer bonds ( $0.292\ 3(2)\text{ nm}$ ), and the  $\text{O-Ba1-O}$  bond angles



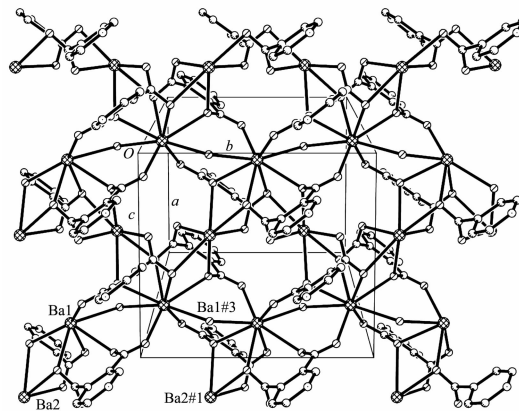
Hydrogen atoms are omitted for clarity; Symmetry codes: #1:  $-x+3/2, -y, z$ ; #2:  $-x+3/2, y+1/2, -z-1/2$ ; #3:  $x, -y+1/2, -z+1/2$

Fig.1 ORTEP view of coordination environment of  $\text{Ba}(\text{II})$  atom in **1** with 50% probability displacement

around the metal center range from  $64.17(7)^\circ$  to  $148.27(8)^\circ$ .

Each  $\text{Ba2}$  atom is 10-coordinate and in a distorted dicapped square prism coordination geometry, coordinating to eight carboxyl O atoms from six different carboxyl groups of four different  $\text{pdC}^{2-}$  anions, two oxygen atoms from two coordinated molecules (Fig.1). The  $\text{Ba2-O}$  bond distances are in the range of  $0.273\ 8(3)\sim 0.320\ 9(3)\text{ nm}$ , and the  $\text{O-Ba2-O}$  bond angles around the metal center vary from  $42.59(7)^\circ$  to  $152.68(7)^\circ$ . The distortion of the structure is also clearly evident from the different  $\text{Ba2-O}$  bond lengths, which can be divided into six shorter ( $0.273\ 8(3)\sim 0.283\ 3(2)\text{ nm}$ ) and four longer bonds ( $0.291\ 0(3)\sim 0.320\ 9(3)\text{ nm}$ ). The  $\text{Ba-O}$  distances in compound **1** are of the same order of magnitude as in comparable complexes<sup>[20-22]</sup>. The N atom of pyridine does not coordinate with  $\text{Ba}^{2+}$  ion, which takes part in forming  $\text{O-H}\cdots\text{N}$  hydrogen bond, resulting in 3D structure.

In ligand  $\text{pdC}^{2-}$  anion, two carboxylate groups of  $\text{pdC}^{2-}$  are not coplanar with the central pyridine ring. The angles of pyridine ring plane between two carboxylate groups are  $87.8^\circ, 8.8^\circ$ , respectively. Two carboxylate groups of  $\text{pdC}^{2-}$  adopt two different coordination modes. One takes  $\mu_3\text{-}\eta^2\text{:}\eta^1$  bridging coordination mode, while the other takes  $\mu_3\text{-}\eta^2\text{:}\eta^2$  bridging coordination mode. The whole  $\text{pdC}^{2-}$  anion and  $\mu_2$ -bridged water molecules connect  $\text{Ba}(\text{II})$  atoms, giving rise to a 2D network structure (Fig.2). Then 2D layers further are



Hydrogen atoms omitted for clarity; Symmetry code: #1:  $-x+3/2, -y, z$ ; #3:  $x, -y+1/2, -z+1/2$

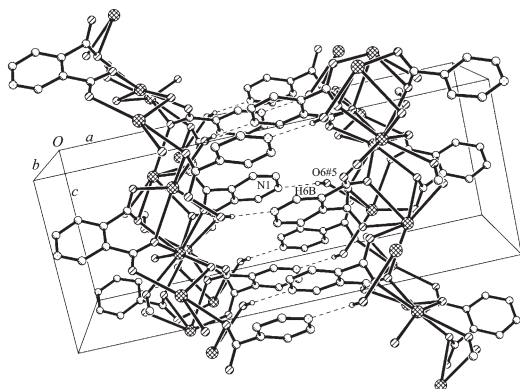
Fig.2 Two-dimensional layer of **1**

Table 3 Distances and angles of hydrogen bonds for complex **1**

| D-H...A              | <i>d</i> (D-H) / nm | <i>d</i> (H...A) / nm | <i>d</i> (D...A) / nm | ∠DHA / (°) |
|----------------------|---------------------|-----------------------|-----------------------|------------|
| O(5)-H(5B) ...O(6)#4 | 0.085               | 0.215                 | 0.290 7(4)            | 148        |
| O(5)-H(5D) ...O(6)   | 0.085               | 0.230                 | 0.290 7(4)            | 128        |
| O(6)-H(6B) ...N(1)#5 | 0.085               | 0.212                 | 0.278 9(5)            | 135        |

Symmetry transformations used to generate the equivalent atoms: #4:  $x, 1/2-y, 1/2-z$ ; #5:  $1-x, -y, -z$ .

linked together to give rise to 3D structure by O-H...N hydrogen bonds (Fig.3, Table 3).



Symmetry code: #5:  $1-x, -y, -z$

Fig.3 Three-dimensional structure of **1** stabilized by O-H...N hydrogen bonding interactions

### 3.1 Luminescent property of complex **1**

The fluorescent properties of the H<sub>2</sub>pdC ligand and its Ba(II) complex **1** were studied in the solid state at room temperature (Fig.4). The maximum of the emission for the complex **1** is located at 450 nm when excited with the light of 300 nm. To ascertain the ascription of emission spectra, the photoluminescence of pure H<sub>2</sub>pdC was measured under the same conditions. However, the free H<sub>2</sub>pdC ligand almost does not display emission at this condition. Such fluorescent behavior of complex **1** suggests that the emission may be mainly attributed to  $\pi$ - $\pi^*$  intraligand

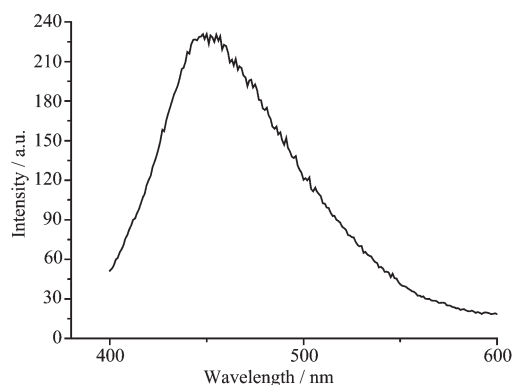


Fig.4 Emission spectrum of complex **1**

fluorescence.

### 3.2 Thermal analysis

Typical curve for **1** is presented in Fig.5. In the temperature range 26~218 °C, there is only one weight-loss of 7.73% with an endothermal peak that corresponds to the successive release of three coordinated water per formula, which is in good agreement with the theoretical weight-loss value (7.73%). The anhydrous product is stable between 218~477 °C. However, there is a weight-loss of 23.43% (theoretical, 24.01%) observed from 477 to 716 °C attributed to the release of the two pyridine molecules, resulting from decomposition of ligand. In this step, BaCO<sub>3</sub> is formed. Finally, there is exothermic peak at 733 °C, which is ascribed to the decomposition of the BaCO<sub>3</sub> to the metal oxide BaO. The TG curve of **1** is consistent with the formula, [Ba<sub>2</sub>(pdC)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sub>n</sub>, and in agreement with the single crystal X-ray analysis.

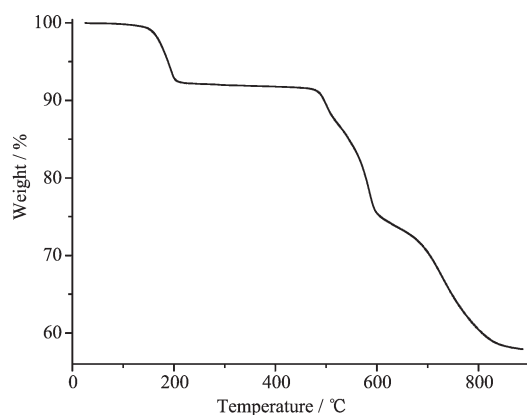


Fig.5 TG curve of **1**

Furthermore, dehydration and rehydration experiments were performed for **1** and powder X-ray diffraction (PXRD) was used to check the phases (Fig. 6). **1** was heated at about 218 °C for 1 h, to obtain complete loss of water. Then, the dehydrated phase was afterwards exposed to water vapor at room temperature for another 24 h. From the Fig.6, the

powdered dehydrated phase has a PXRD pattern different from that of complex **1** (Fig.6), indicating that the framework of **1** collapses after removal of coordinated water. Also from the Fig.6, we can see the PXRD pattern of rehydrated sample is different from the diffraction pattern of **1**, which shows that the dehydration and rehydration processes for **1** are irreversible.

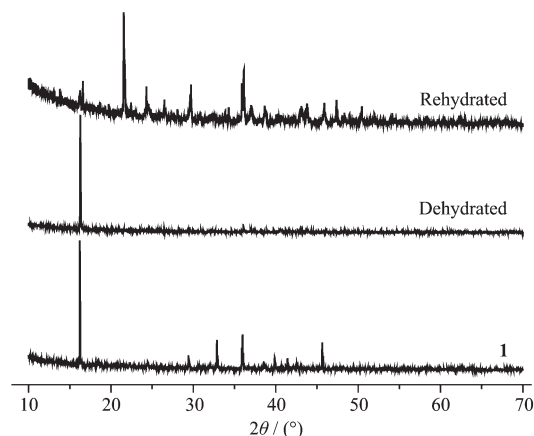


Fig.6 Powder X-ray diffraction patterns of **1**, the dehydrated and the rehydrated

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