

## 3,4-吡啶二甲酸根钙配合物的合成、结构和性质

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**摘要:** 配体 3,4-吡啶二酸( $H_2pdc$ )和  $CaCO_3$  反应合成了配合物  $[Ca_2(pdc)_2(H_2O)_7]$  (**1**), 用单晶 X-射线、FTIR 和元素分析对生成的晶体进行了表征。 $Ca(II)$  采取八配位扭曲四方反棱柱几何构型, 整个  $pdc^{2-}$  作为三齿桥联配体连结 3 个不同的  $Ca(II)$  原子形成一维链结构, 一维链由  $\pi-\pi$  相互作用和  $O-H\cdots N$  氢键连结形成二维层, 二维层再进一步由  $O-H\cdots O$  氢键连结形成三维结构。还研究了配合物 **1** 的荧光和热重性质。CCDC: 806131。

**关键词:** 钙配合物; 羧基; 荧光性质; 热重

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## Synthesis, Structure, Properties of 3,4-Pyridinedicarboxylate Calcium Complex

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**Abstract:** The title complex  $[Ca_2(pdc)_2(H_2O)_7]$  (**1**), where  $H_2pdc$  is 3,4-pyridinedicarboxylic acid, was obtained by using  $H_2pdc$  and  $CaCO_3$  under evaporation process. Its structure was determined by single-crystal X-ray diffraction analyses and further characterized by IR spectrum and elemental analyses. Complex **1** is one-dimensional chain structure, in which the  $Ca(II)$  takes eight-coordinated distorted square antiprism geometry. Each  $pdc^{2-}$  anion acts as a  $\mu_3$ -bridge to form one-dimensional structure. The two-dimensional layers are constructed through  $\pi-\pi$  interactions and  $O-H\cdots N$  hydrogen bond. The three-dimensional structure is formed by  $O-H\cdots O$  hydrogen bonding interactions. Luminescent property and thermogravimetry analyses of complex **1** were investigated. CCDC: 806131.

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

The rational design and syntheses of novel coordination polymers have achieved considerable progress in the field of supramolecular chemistry and crystal engineering, owing to their potential applications in gas storage, sensor technology, separation processes, ion exchange, luminescence, magnetism, catalysis, nonlinear optics (NLO), and optical limiting capability<sup>[1-2]</sup>, as well as their intriguing variety of architectures and topologies<sup>[3-6]</sup>. The self-assembly of supramolecular coordination compound is the result of combina-

tion of various forces including not only strong and highly directional interactions (for example metal-ligand coordination bond), but also weak interactions like hydrogen bonds and  $\pi-\pi$  stacking interactions<sup>[7]</sup>. Many factors can influence the synthesis of coordination frameworks, such as the character of ligands, the coordination geometry of metal ions, and the reaction conditions for the construction of new supramolecular or polymeric complexes. So, it is very significant to select befitting ligands and metal ions in the assembly

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of coordination polymers. Carboxylate-containing ligands have particularly aroused much more attention because of diverse coordination modes of carboxylate groups to the metal ions. Among these ligands, benzene multicarboxylate ligands, such as benzenedicarboxylic acid (1,2-, 1,3-), benzenetricarboxylic acid and even benzenetetracarboxylic acid, benzenehexacarboxylic acid have been extendedly used. Owing to containing oxygen and nitrogen donors, containing-nitrogen aromatic multicarboxylate ligands like pyridinedicarboxylic acids (2,3-, 2,4-, 2,5-, 2,6-, 3,4-, 3,5-), and so on, have been investigated widely<sup>[8]</sup>. However, much of the work has so far been focused on the coordination polymers containing transition and lanthanide metal elements<sup>[9]</sup>. The studies of alkali earth metal complexes are still rare. Because alkali earth elements have high coordination number along with luminescent properties, the MOFs containing alkali earth metal elements are likely to provide new materials with desirable properties. We have initiated research in building MOFs with alkali earth elements and different multidentate ligands. In the present work, we have obtained a new calcium complex  $[\text{Ca}_2(\text{pdc})_2(\text{H}_2\text{O})_7]$ , which crystal structure is described herein and luminescent property was investigated.

## 1 Experimental

### 1.1 Reagents and physical measurements

All commercially available chemicals are of reagent grade and were used as received without further purified. Samples for C, H, N elemental analyses were performed on a Perkin-Elmer 240C Elemental Analyzer. The fluorescence spectra were recorded on a Cary Eclipse 300 spectrofluorimeter at room temperature with a xenon arc lamp as the light source in DMF (*N,N*-dimethylformamide). In the measurements of the emission and excitation spectra, the pass width is 5.0 nm. Infrared (IR) spectra were recorded on a Nicolett 6700 FTIR spectrophotometer by using KBr discs.

Thermogravimetry analyses (TGA) was performed on a simultaneous SDT thermal analyzer (SDT Q600) under a flow of  $\text{N}_2$  at a heating rate of  $20.00\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  between ambient temperature and  $1\ 000\text{ }^\circ\text{C}$ .

### 1.2 Synthesis of complex 1

$\text{CaCO}_3$  (10.0 mg, 0.1 mmol), 3,4-Pyridinedicarboxylic acid ( $\text{H}_2\text{pdc}$ ) (16.7 mg, 0.1 mmol), water (3 mL) were mixed with stirring for 0.5 h, and 3 mL  $\text{CH}_3\text{OH}$  was added. The mixture was sealed in a 25 mL Teflon-lined stainless-steel reactor with heating at  $150\text{ }^\circ\text{C}$  for 72 h under autogenous pressure. After the reaction mixture was slowly cooled to room temperature, colorless clear filtrate stood at ambient temperature for eight days. Colorless rod crystals (7.2 mg) of the title complex was collected by filtration and dried in air. The C, H, N contents were determined by elemental analysis: Calcd. for  $\text{C}_{14}\text{H}_{20}\text{Ca}_2\text{N}_2\text{O}_{15}$  (%): C, 31.34; H, 3.76; N, 5.22. Found (%): C, 31.39; H, 3.82; N, 5.29. IR (KBr,  $\text{cm}^{-1}$ ): 3 511s, 1 606s, 1 576s, 1 547s, 1 489m, 1 415s, 1 385s, 1 371s, 1 161w, 1 053w, 867w, 834m, 820m, 790m, 710m, 678m.

### 1.3 Crystal structure determination

A colorless single crystal of the title complex (0.32 mm×0.21 mm×0.18 mm) was put on a Bruker SMART APEX II CCD diffractometer equipped with a graphite-monochromatic Mo  $K\alpha$  radiation ( $\lambda=0.071\ 073\text{ nm}$ ) at  $296(2)\text{ K}$ . The data were collected at room temperature by using  $\varphi$ - $\omega$  scan mode in the range of  $2.70^\circ\leq\theta\leq 29.70^\circ$ . An empirical absorption correction was made by a multi-scan type. The structure was solved by direct methods and refined by full-matrix least-squares techniques with SHELX -97 programs<sup>[10-11]</sup>. Anisotropic displacement parameters were refined for all non-hydrogen atoms. The hydrogen atoms were added in the riding model. The crystal data and refinement details for the complex are listed in Table 1, and the selected bond lengths and bond angles are given in Table 2.

CCDC: 806131.

Table 1 Crystallographic data for complex 1

Empirical formula	$\text{C}_{14}\text{H}_{20}\text{Ca}_2\text{N}_2\text{O}_{15}$	Crystal color	Colorless
Formula weight	536.48	$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.674
Crystal system	Monoclinic	$\mu / \text{mm}^{-1}$	0.616

Continued Table 1

Space group	<i>P2<sub>1</sub>/c</i>	Crystal dimension / mm	0.32×0.21×0.18
<i>a</i> / nm	1.074 76(9)	$\theta$ range / (°)	2.70~29.70
<i>b</i> / nm	0.755 15(6)	<i>F</i> (000)	556
<i>c</i> / nm	1.314 57(11)	Goodness of fit	1.07
$\gamma$ / (°)	90	Reflections collected	2 855
<i>V</i> / nm <sup>3</sup>	1.064 18(15)	Independent reflns. ( <i>R</i> <sub>int</sub> )	0.021
<i>Z</i>	2	Obsd. reflns. ( <i>I</i> >2 $\sigma$ ( <i>I</i> ))	2 571
Temperature / K	296(2)	Parameters refined	150
<i>R</i> , <i>wR</i> ( <i>I</i> >2 $\sigma$ ( <i>I</i> ))	0.045 9, 0.110 4	<i>R</i> , <i>wR</i> (all reflections)	0.050 0, 0.112 6

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

Ca1-O11	0.237 7(2)	Ca1-O8	0.240 3(2)	Ca1-O2#1	0.241 94(15)
Ca1-O1	0.242 35(15)	Ca1-O6	0.243 23(17)	Ca1-O1#2	0.243 61(15)
Ca1-O5	0.256 95(16)	Ca1-O2	0.277 13(17)		
O11-Ca1-O8	103.38(12)	O11-Ca1-O2#1	86.20(8)	O8-Ca1-O2#1	76.08(7)
O11-Ca1-O1	149.34(9)	O8-Ca1-O1	97.28(8)	O2#1-Ca1-O1	121.01(5)
O11-Ca1-O6	95.36(9)	O8-Ca1-O6	144.81(7)	O2#1-Ca1-O6	75.75(6)
O1-Ca1-O6	79.76(6)	O11-Ca1-O1#2	87.58(7)	O8-Ca1-O1#2	72.34(6)
O2#1-Ca1-O1#2	145.39(6)	O1-Ca1-O1#2	77.31(6)	O6-Ca1-O1#2	138.78(6)
O11-Ca1-O5	83.40(9)	O8-Ca1-O5	137.43(6)	O2#1-Ca1-O5	146.42(6)
O1-Ca1-O5	66.12(5)	O6-Ca1-O5	73.57(5)	O1#2-Ca1-O5	65.94(5)
O11-Ca1-O2	157.59(7)	O8-Ca1-O2	77.33(8)	O2-Ca1-O2#1	72.12(6)
O1-Ca1-O2	49.70(5)	O6-Ca1-O2	74.26(6)	O1#2-Ca1-O2	113.44(5)
O5-Ca1-O2	111.54(4)				

Symmetry codes: #1: 2-*x*, -*y*, -*z*; #2: 2-*x*, *y*, -*z*+1/2.

## 2 Results and discussion

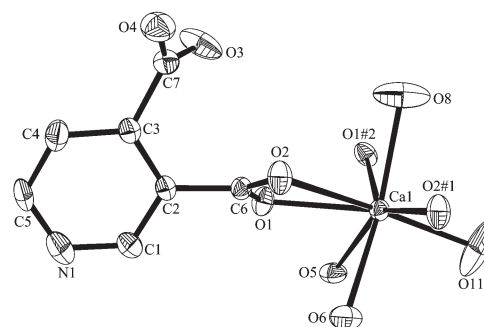
### 2.1 IR spectrum

The strong and broad absorption bands in the range of 3 000~3 600 cm<sup>-1</sup> for **1** is assigned as the characteristic peaks of OH vibration. The strong vibrations around 1 635 and 1 571 cm<sup>-1</sup> for **1** correspond to the asymmetric and symmetric stretching vibrations of carboxylate group, respectively. The absence of strong bands ranging from 1 690 to 1 750 cm<sup>-1</sup> indicates the deprotonation of ligands.

### 2.2 Crystal structure of 1

X-ray single-crystal diffraction study reveals that complex **1** crystallizes in the monoclinic space group *P2<sub>1</sub>/c*. The asymmetric unit consists of one crystallographic independent Ca<sup>2+</sup> ions, one ligand anion pdc<sup>2-</sup> and three and a half coordinated water molecules (Fig.1). As shown in Fig.1, Ca(1) in [Ca<sub>2</sub>(pdc)<sub>2</sub>(H<sub>2</sub>O)<sub>7</sub>] is eight-

coordinate with O8 donor set. Among of them, four O atoms are from water molecules, in which one water molecule takes a  $\mu_2$ -bridge to coordinate two Ca (II) atoms, and four from three different ligand pdc<sup>2-</sup>. The bond lengths of Ca-O are in the range of 0.237 7(2) to 0.277 13(17) nm. The O-Ca-O angles vary from 49.70(5)



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

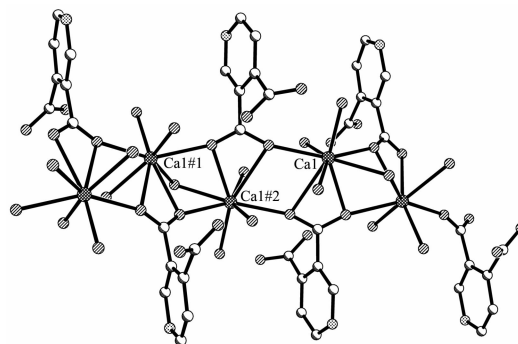
Fig.1 Coordination environment around the Ca(II) atom of **1** with 50% probability displacement

to  $157.59(7)^\circ$  (Table 2). As a result, the coordination geometry of  $\text{Ca}^{2+}$  ion is best described as highly distorted square antiprism geometry (Fig.1).

It is worth noting that two carboxylate groups of  $\text{pdc}^{2-}$  are not coplanar with the central pyridine ring. The angles of pyridine ring plane C(1)-C(2)-C(3)-C(4)-C(5)-N(1) between carboxylate groups O(3)-C(7)-O(4) and O(1)-C(6)-O(2) are  $125.6, 57.9^\circ$ , respectively. In each  $\text{pdc}^{2-}$  ion, two carboxylate groups take different coordination mode. One carboxylate group does not coordinate with  $\text{Ca}(\text{II})$  ion, the other one take a  $\mu_3\text{-}\eta^2\text{:}\eta^2$  coordination mode (Fig.2). The N atom of pyridine also does not coordinate with a  $\text{Ca}^{2+}$  ion, which takes part in forming  $\text{O-H}\cdots\text{N}$  hydrogen bond. So whole ligand  $\text{pdc}^{2-}$  adopts a tridentate coordination mode to connect three calcium ions to generate a 1D chain with  $\text{Ca}\cdots\text{Ca}$  distances of 0.420 1 and 0.367 7 nm (Fig.2).

There are  $\pi\text{-}\pi$  interactions between pyridine cycles from neighbor chains since the separation of centroid-to-centroid is 0.371 7 and 0.365 5 nm with the dihedral angles of  $7.7$  and  $0$  between pyridine cycles planes. These one-dimensional chains are first extended into a 2D layer in the  $ac$  plane through  $\pi\text{-}\pi$  interactions and  $\text{O11-H11A}\cdots\text{N1\#6}$  hydrogen bond. And then 2D layers further are linked together to give rise to 3D structure by  $\text{O-H}\cdots\text{O}$  hydrogen bonds ( $\text{O6-H6C}\cdots\text{O4\#3}$ , 0.271 1 (3) nm,  $145^\circ$ ;  $\text{O5-H5B}\cdots\text{O3\#4}$ ,

0.271 4(3) nm,  $176^\circ$  (Fig.3, Table 3).



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

Fig.2 One-dimensional chain of **1**

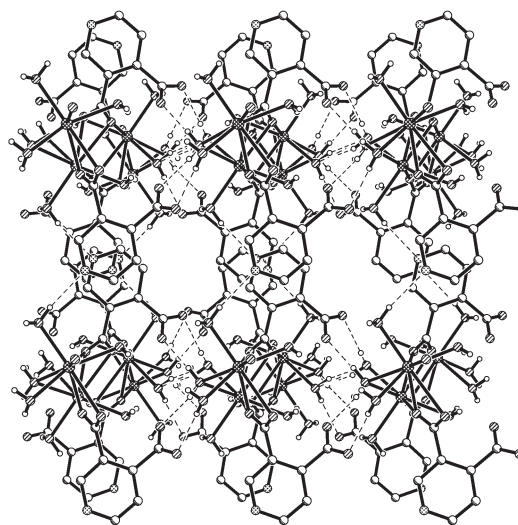


Fig.3 Three-dimensional structure of **1** stabilized by  $\text{O-H}\cdots\text{O}$  hydrogen bonding interactions

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

D-H $\cdots$ A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
O8-H8A $\cdots$ O6#1	0.085	0.190	0.274 2(3)	173
O8-H8B $\cdots$ O3#2	0.085	0.206	0.277 7(3)	142
O5-H5A $\cdots$ O3#3	0.085	0.190	0.271 4(3)	160
O5-H5B $\cdots$ O3#4	0.085	0.187	0.271 4(3)	176
O6-H6A $\cdots$ O6#5	0.085	0.194	0.276 8(2)	163
O6-H6C $\cdots$ O4#3	0.085	0.197	0.271 1(3)	145
O11-H11A $\cdots$ N1#6	0.085	0.232	0.315 2(4)	166
O11-H11B $\cdots$ O4#5	0.085	0.199	0.283 5(3)	176
C5-H5 $\cdots$ O8#7	0.096	0.209	0.303 3(4)	166

Symmetry codes: #1:  $2-x, -y, -z$ ; #2:  $2-x, y, 1/2-z$ ; #3:  $x, 1+y, z$ ; #4:  $2-x, 1+y, 1/2-z$ ; #5:  $2-x, 1-y, -z$ ; #6:  $1+x, y, z$ ; #7:  $-1+x, y, z$ .

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

Coordination polymers have been reported to have ability to adjust the emission wavelength of organic ligands through incorporation of metal centers.

Therefore, it is important to investigate the luminescent properties of coordination polymers in view of potential applications as light-emitting diodes (LEDs)<sup>[12-13]</sup>. The luminescent of complex **1** was investigated at room

temperature in DMF (*N,N*-dimethylformide). The emission spectrum is shown in Fig.4. It can be seen that complex **1** exhibits narrow radiation emission maxima at 528 nm upon photoexcitation at 207 nm. To ascertain the adscription of emission spectra, the photoluminescence of pure H<sub>2</sub>pdc and solvent DMF were measured under the same conditions. However, the free H<sub>2</sub>pdc ligand displays weak emission maxima at 528 nm, DMF exhibit emission peak at 406 nm. Such fluorescent behavior of complex **1** suggests that the emission is mainly attributed to  $\pi$ - $\pi^*$  intraligand fluorescence.

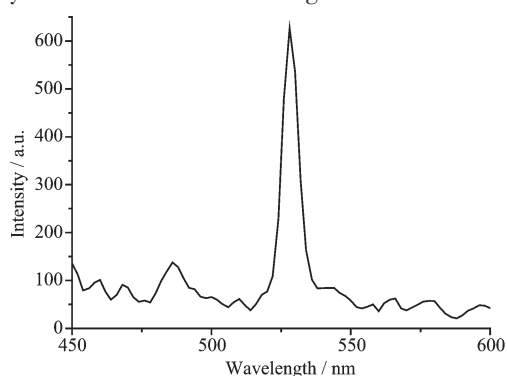


Fig.4 Emission spectrum of complex **1**

### 3.2 Thermal analysis

The thermal stability of complex **1** has been investigated by thermogravimetric analysis (TGA) technique and the TGA curves are shown in Fig.5. The

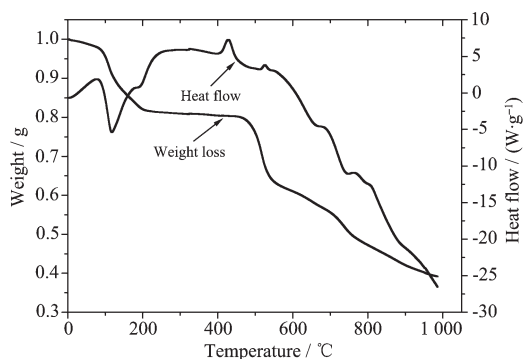


Fig.5 TGA curve of **1**

TG curve is depicted in Fig.5. The weight loss from room temperature to 480 °C (22.19%), corresponding to the escape of seven water molecules (calcd. 23.50%). The second weight loss of 28.85% from 480 to 760 °C results from the release of pyridine molecule, corresponding to the decomposition of the framework structure (calcd. 29.49%). Finally, the weight-loss step occurs above 760 °C, which corresponds to the decomposition of CaCO<sub>3</sub>.

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