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研究简报

基于 3,4-吡啶二羧酸的二维层状聚合物的合成和晶体结构

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关键词:镧(Ⅲ)配位聚合物;水热合成;晶体结构
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Synthesis and Crystal Structure of 2D Layer Lanthanum Polymer Constructed from Pyridine-3,4-dicarboxylate Ligand

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Abstract: A metal-organic coordination polymer $\{[La(PDC)(N\text{-}HPDC)]\cdot H_2O\}_n$ (**1**) (H_2PDC=pyridine-3,4-dicarboxylic acid) has been hydrothermally synthesized and structurally characterized by X-ray diffraction single-crystal structure determination, elemental analyses and IR spectroscopy. The complex crystallizes in the monoclinic system, space group $P2_1/c$ with a=1.452 8(2) nm, b=0.681 59(11) nm, c=1.464 0(2) nm, β=94.270(2)°, V=1.445 6(4) nm^3, D_c=2.243 Mg·m^{-3}, Z=4, M_r=488.14, F (000)=944, μ (Mo $K\alpha$)=3.015 mm^{-1}, R=0.031 0 and wR=0.076 2 for 2 424 observed reflections ($I>2\sigma(I)$). There are La-O-C-O-C-La double chains in the complex. The chelating carboxylate O atoms and pyridyl N atoms lead the compound to 2D layers structure, which is extended to 3D supramolecular architecture through intermolecular hydrogen bonds. It is interesting that the polymer containing one-dimensional channels. CCDC: 708868.

Key words: La(Ⅲ) coordination polymer; hydrothermal synthesis; crystal structure

0 Introduction

The construction of metal-organic frameworks (MOFs) is now of great interest, not only because of their potential applications in catalysis, photochemistry and electromagnetism[1~5], but also owing to their intriguing architectures and topologies[6~12]. Among the most extensively studied metal-organic frameworks are those based on carboxylate ligands for exhibiting various coordination modes to finish various structures with honeycomb, brickwall, rectangular grid, bilayer, ladder, diamonds and open frameworks[13,14]. However, much work on MOFs has been focusing on the metal and symmetrical multicarboxylate ligands system, such as 1,2-benzenedicarboxylate[15] and pyridine-2,6-dicarboxylic acid[16]. Recently, studies have shed some light on asymmetrical multicarboxylate ligands[17]. As a member of asymmetric ligands, pyridine-3,4-dicarboxylic acid

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(H_2PDC) containi ng *p*-pyridinecarboxylic acid and *m*-pyridinecarboxylic acid, showing an excellent building block with charge and multi-connecting ability[18,19] has also attracted more and more attention in recent years due to their unique structure features[20,21]. On the other hand, the lanthanide ions generally adopt higher than six coordination and, therefore, can become important building blocks in designing different MOF structures[22]. To the best of knowledge, there has been only a few reports on polymers constructed by lanthanide metal and PDC ligand up to now[22,23]. In this paper, we report a novel lanthanide metal complex $\{[La(PDC)(N\text{-}HPDC)]\cdot H_2O\}_n$.

1 Experimental

1.1 General

$LaCl_3\cdot 6H_2O$ was prepared by dissolving their respective oxides in concentrated hydrochloric acid followed by drying. All the other reagents are of commercially available and were used as received without further purification. Elemental analyses (C, H, N) were determined with an Elemental Vario EL elemental analyzer. IR spectra were (KBr pellets) recorded in the 4 000~400 cm^{-1} range with a FTIR-8900 spectrometer.

1.2 Preparation of $\{[La(PDC)(N\text{-}HPDC)]\cdot H_2O\}_n$ (1)

A mixture of $LaCl_3\cdot 7H_2O$ (0.125 mmol), pyridine-3,4-dicarboxylic acid (0.15 mmol), Sebacic acid (0.062 5 mmol), triethylamine (0.25 mmol) and H_2O (6.5 mL) was mixed in a 23 mL Teflon reactor, which was heated to 180 ℃ for 7 days, and then was cooled to room temperature at a rate of 10 ℃·h^{-1}, colorless needle-like crystals of compound 1 suitable for X-ray determination were obtained in ca. 47.8% yield (based on La). The final pH value was 4. Elemental anal.(%) calcd. for $C_{14}H_9LaN_2O_9$: C, 34.45; N, 5.739; H,1.858, found(%): C, 34.05; N, 5.623; H, 1.536. IR data (KBr pellet, ν/cm^{-1}): 3 446(m), 1 569(s), 1 494(s), 1 419(s), 1 282(m), 1 173(m), 1 121(m), 1 061(s), 879(s), 839(s), 435(s).

1.3 Crystal structure determination

A single crystal with dimensions of 0.48 mm×0.43 mm×0.04 mm was selected for structure determination. Diffration data was collected on a Bruker smart CCD area detector diffractometer with graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 298(2) K using ω-ϕ scan technique. A total of 7 267 reflections were collected in the range of $2.79° \leqslant \theta \leqslant 25.50°$, of which 2 690 were unique with R_{int}=0.032 9 and 2 424 observed reflections [$I>2\sigma(I)$] were used in the succeeding structure solution and refinements. A semi-empirical absorption correction with the SADABS was applied. All non-H atoms and the hydrogen atoms of water molecules are found from the different Fourier maps and refined anisotropically. The structure was solved by direct methods using SHELXS-97[24] program and refined by full-matrix least-squares on F^2 using SHELXL-97[25] program. A summary of the crystallographic data and refinement parameters are given in Table 1. The selected important bond parameters are given in Table 2.

CCDC: 708868.

Table 1 Crystallographic data for compound 1

Empirical formula	$C_{14}H_9LaN_2O_9$	D_c / (Mg·m^{-3})	2.243
Formula weight	488.14	μ / mm^{-1}	3.015
Temperature / K	298(2)	F(000)	944
Wavelength / nm	0.071 073	Crystal size / mm	0.48×0.43×0.04
Crystal system	Monoclinic	θ range / (°)	2.79~25.50
Space group	$P2_1/c$	Reflections collected / unique	7 267 / 2 690 (R_{int}=0.032 9)
a / nm	1.452 8(2)	Completeness to θ=27.48°	99.6%
b / nm	0.681 59(11)	Data / restraints / parameters	2 690 / 3 / 235
c / nm	1.464 0(2)	Goodness-of-fit on F^2	1.071
β / (°)	94.270(2)	Final R indices [$I>2\sigma(I)$]	R_1=0.031 0, wR_2=0.076 2
V / nm^3	1.445 6(4)	R indices (all data)	R_1=0.0463, wR_2=0.0644
Z	4	Largest diff. peak and hole / (e·nm^{-3})	979 and −646

Table 2　Selected bond lengths (nm) and bond angles (°)

La(1)-O(8)	0.243 7(3)	La(1)-O(7)ii	0.249 8(3)	La(1)-O(5)iii	0.250 0(3)
La(1)-O(6)ii	0.251 2(3)	La(1)-O(4)iv	0.261 9(3)	La(1)-O(3)iv	0.262 5(3)
La(1)-O(1)	0.264 1(3)	La(1)-O(2)	0.267 7(3)	La(1)-N(2)iv	0.271 4(4)
O(8)-La(1)-O(7)ii	72.42(11)	O(8)-La(1)-O(5)iii	75.61(11)	O(7)ii-La(1)-O(5)iii	142.15(10)
O(8)-La(1)-O(6)ii	140.96(10)	O(7)ii-La(1)-O(6)ii	68.59(10)	O(5)iii-La(1)-O(6)ii	140.77(11)
O(8)-La(1)-O(4)iv	143.92(10)	O(7)ii-La(1)-O(4)iv	138.20(10)	O(5)iii-La(1)-O(4)iv	79.27(10)
O(7)ii-La(1)-N(2)iv	72.29(11)	O(5)iii-La(1)-N(2)iv	84.59(10)	O(6)ii-La(1)-N(2)iv	86.54(10)
O(4)iv-La(1)-N(2)iv	119.46(11)	O(3)iv-La(1)-N(2)iv	69.64(11)	O(1)-La(1)-N(2)iv	152.56(10)

Symmetry modes: i: x, $-y+3/2$, $z-1/2$; ii: $-x+1$, $y-1/2$, $-z+3/2$; iii: $-x+1$, $y+1/2$, $-z+3/2$; iv: x, $-y+3/2$, $z+1/2$.

2　Results and discussion

2.1　Crystal structure of compound 1

The single-crystal structure shows that the title compound is a two-dimensional layer structure as well in which the asymmetric unit contains one lanthanum atoms, two 3,4-pyda ligands and one lattice water molecule. As illustrated in Fig.1, lanthanum atom is coordinatated with two pairs of oxygen atoms [O(1), O(2), O(3)iv, O(4)iv] from two chelating carboxylates of N-HPDC$^-$ ligands, one oxygen atom from each of four bridging carboxylates [O(5)iii, O(7)ii, O(6)ii, O8)]and one pyridyl nitrogen [N(2)iv] from PDC^{2-} ligands, showing a distorted triply capped trigonal prism geometry. The four carboxylate O atoms of PDC^{2-} ligands are coordinated to three La atoms to form an triangle in which two O atoms coordinated to the same La atom becoming the apex of the triangle. These triangles are in an edge-sharing mode of which bottom edge makes the formation of La-O-C-O-C-La double chains. The N-HPDC$^-$ ligands are coordinated to adjacent La atoms by the chelating carboxylate O atoms which are located at both sides of the chain as wings which enlarged the width of the chain into *ca.* 1.713 nm. The chelating carboxylate O atoms and pyridyl N atoms lead the compound to 2D layer, which is shown in Fig.2. The 4-carboxylate oxygen atoms of PDC^{2-} ligands and uncoordinated N atoms provide the hydrogen-bonding donor and acceptor to form hydrogen bonds. The hydrogen bond between chains is N(1)-H(1)⋯O(6)v, whose length is 0.284 0(5) nm and bond angle is 142.5° (Table 3). There are also π-π stacking interactions of the aromatic ring of N-HPDC$^-$ ligands with face-to-face distances of *ca.* 0.339 2 nm. The intermolecular hydrogen bonds lead the complex to the formation of 3D supramolecular architecture as shown in Fig.3. It is interesting that the three-dimensional network contains one-dimensional channels (Fig.4). The approximate dimensions of the channel are 0.55 nm × 0.57 nm. Free water molecules are located in the channels.

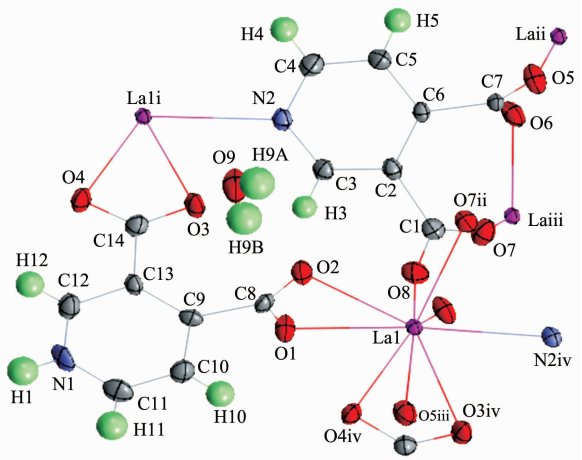


Fig.1　Coordination environment of La atom in the complex with non-hydrogen atoms

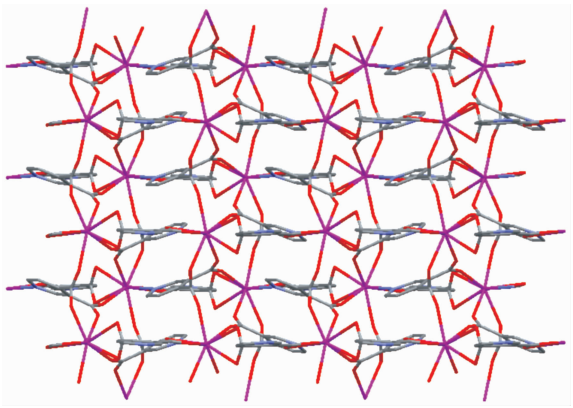


Fig.2　Two-dimensional framework viewed from *a* axis

Table 3 Hydrogen bonds and angles for the compound

D–H···A	*d*(D-H) / nm	*d*(H···A) / nm	*d*(D···A) / nm	∠(DHA) / (°)
O(9)–H(9B)···O(2)	0.085	0.206	0.285 2(5)	155.1
N(1)–H(1)···O(6)v	0.086	0.211	0.284 0(5)	142.5
N(1)–H(1)···O(5)v	0.086	0.258	0.316 8(5)	126.6
N(1)–H(1)···O(9)vi	0.086	0.253	0.305 9(6)	120.3
O(9)–H(9A)···O(1)vii	0.085	0.206	0.285 2(5)	155.3

Symmetry codes: v: $x+1, y, z$; vi: $-x+2, -y+1, -z+1$; vii: $x, y-1, z$.

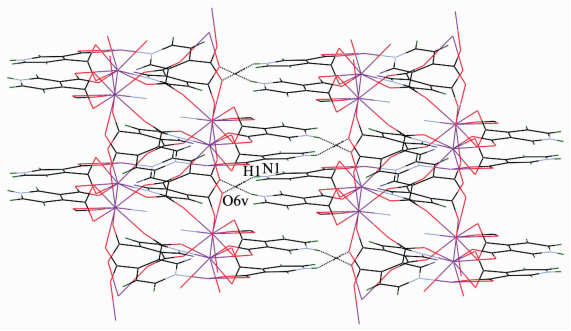
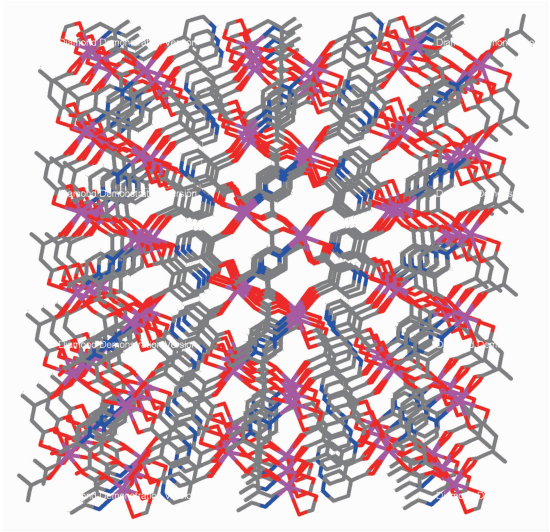


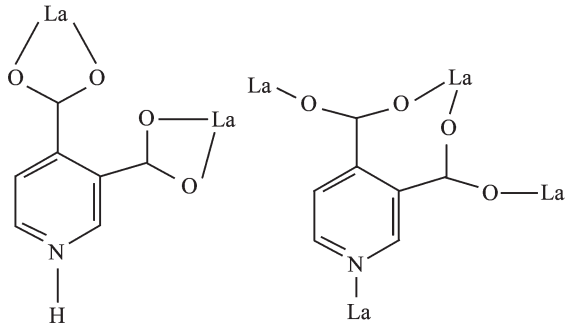
Fig.3 Hydrogen bonds interactions linking layers into a 3D supramolecular network



Guest water molecules included in the channels are omitted for clarity

Fig.4 Regular parallelogram channels of complex viewed along *b* axis

As can be seen from Scheme 1, it should be noteworthy that carboxylate groups of 3,4-PDC ligands adopt two kinds of coordination modes: (1) The *N*-HPDC$^-$ anion acts as cheating tetradentate ligand towards two La(Ⅲ) cations (Scheme 1(a)), with four carboxylic oxygen; (2) The PDC^{2-} anion acts as bridging-cheating-bridging-bridging pentadentate ligand towards the four La(Ⅲ) cation (Scheme 1 (b)), with four carboxylic oxygen and one nitrogen atom. Interestingly, in three cases pyridine nitrogen atom participate in coordination. The two types of H_2PDC ligands play a key role in extending the chains.



N-HPDC$^-$ (a) PDC^{2-} (b)

Scheme 1 Coordination modes of two pyridine-3,4-dicarboxylate ligands

2.2 IR Spectra

The IR spectrum of the title complex shows characteristic bands of carboxylate groups of the pydc ligand at 1 569 cm^{-1} for asymmetric vibration and 1 419 and 1 399 cm^{-1} for symmetric vibration. The separations between $\nu_{asym(COO)}$ and $\nu_{sym(COO)}$ bands show that the carboxylate groups coordinate to the metal atoms in a bridging fashion[26]. The absence of the characteristic bands at around 1 700 cm^{-1} in compounds **1** attributed to the protonated carboxylic group indicates that the complete deprotonation of PDC ligand upon reaction with La ion. A new strong characteristic absorption peak at 3 446 cm^{-1} confirm the presence of the water. The ν(La-O) vibration is also observed at 435 cm^{-1}. These assignments are consistent with the structur al analysis results.

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