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鑭(Ⅲ)金屬在含吡啶-3, 5-雙羧酸根自我組裝三維配位結構：合成及結構

Self-assembly of 3-D Lanthanum(Ⅲ) coordination frameworks based on pyridine-3,5-dicarboxylate: synthesis and structure

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摘　要：高分子聚合物 $[La_2(C_7H_3NO_4)_3(H_2O)_3]_n$ ，包含兩個獨立 La(Ⅲ)離子，三個吡啶-3,5-雙羧酸根陰離子及配位三個水分子，兩個 La(Ⅲ)離子使用吡啶雙羧酸根陰離子當橋鍵形成雙核單元體。每個吡啶-3,5-雙羧酸根陰離子顯示四種連結模式。La1 離子連接九個氧原子分別來自六個吡啶-3,5-雙羧酸根陰離子及兩個水分子，形成九配位四面平方帽四方稜柱形的幾何結構。另一個 La2 離子連接七個氧原子分別來自六個吡啶-3,5-雙羧酸根陰離子及一個水分子，形成七配位 4,4'-雙帽三角錐形的幾何結構。結構中含有典型氫鍵(O—H⋯O、O—H⋯N)作用力及非典型的分子(內)間氫鍵作用(C—H⋯O)，以及吡啶環之間的π–π吸引力，[其中心最近距離為 3.7749 (15)Å ，兩芳香環的雙面角為 5.78 (12)°]。

關鍵詞：水熱合成、吡啶-3,5-雙羧酸、鑭(Ⅲ)-錯合物、氫鍵

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Abstract：The polymer compound, $[La_2(C_7H_3NO_4)_3(H_2O)_3]_n$, contains two independent La^{III} ions, three pyridine-3,5-dicarboxylate anions and three coordinated water molecules in which two La(Ⅲ) ions are bridged by carboxylate and forms dinuclear unit. Each pyridine-3,5-dicarboxylate anion affords a four-connecting nodes. Around nine-coordinated La^{III} cation (La1) is completed by nine oxygen atoms from six pyridine-3,5-dicarboxylate and two aqua, forming a square-face capped square antiprism. Other seven-coordinated La^{III} cation (La2) is coordinated with seven oxygen atoms from six pyridine-3,5-dicarboxylate and one aqua, forming a 4,4'-bicapped trigonal prism. There are classical hydrogen bondings (O—H···O and O—H···N) and weak non-classical hydrogen bondings (C—H···O) is observed in the crystal structure. The crystal structure is further consolidated by π···π stacking between nearly parallel pyridine rings of adjacent pyridine-3,5-dicarboxylate ligands [shortest centroid–centroid distance between π···π is 3.7749 (15)Å, dihedral angle = 5.78 (12)°].

Keywords：Hydrothermal synthesis, Pyridine-3,5-dicarboxylate, Lanthanum(Ⅲ) Complexes, Hydrogen bonding

Ⅰ. Introduction

In recent years, metal-organic compounds with open framework or micro porous structures are widely studied because of their potential applications in molecular recognition, separation and catalysis[1–8]. Several studies have used rigid, multifunctional ligands to bridge metal ions into two- or three-dimensional structures. Among these ligands, the aromatic carboxylates such as pyridine-2,4-dicarboxylic acid[9,10], pyridine-3,4-dicarboxylic acid[11], pyridine-2,5-dicarboxylic acid[13,14], pyridine-2,3-dicarboxylic acid[12] and pyridine-2,6-dicarboxylic acid[15,16] have been used to synthesize such materials. Pyridine-3,5-dicarboxylic acids(3,5-pydH_2) ligand is a good candidate ligand due to its flexible and various coordination donor containing either N- or O- atom donors. Some examples of coordination polymers with 3,5-pydH_2 have been reported[17-22]. As continuation of our investigations[23], we pay attention to 3,5-pydH_2 as functional ligand to build linkers to $La(NO_3)_3$ and synthesis the high-dimensional coordination polymer compound, $[La_2(C_7H_3NO_4)_3(H_2O)_3]_n$.

Ⅱ. Experimental Section

Materials and methods

All chemical reagents were used as purchased without further purification. ($La(NO_3)_3{\cdot}6H_2O$ 99.9%, $Mn(NO_3)_2{\cdot}4H_2O$ 98.8%, 3,5-pydH_2 99.0%) were purchased from Aldrich or similar companies. Elemental analysis (C, H and N) was performed on a Heraeus CHN-O-Rapid elemental analyzer. The content of lanthanum was determined by Perkin Elmer Optima 2100 inductively

coupled plasma (ICP-OES) Emission Spectrometer. Elemental analysis calcd. for $C_{21}H_{15}La_2N_3O_{15}$ (Mr = 827.18)： La, 33.59；C, 30.47; N,5.08; H, 1.83 %. Found：La, 34.05；C, 31.18; N,5.15；H, 1.87 %. FT-IR spectra were recorded in the range 400-4000 cm^{-1} on a ***JASCO* 6200 Micro-FT -IR** spectrophotometer using a KBr pellet. All measurements were performed at room temperature. IR(KBr)（cm^{-1}）：3443(m)、1661(s)、1581(s)、1553(s)、1495(m)、1432(s)、1362(s)、1148(m)、1090(w)、760(s)、691(m)、651(w)、565(w).

X-ray Crystallographic Analysis

Diffraction datas of the compound were collected on a Bruker SMART CCD area detector diffractometer with graphite-monochromatized Mo Kα radiation (λ= 0.71073 Å) in ψ and ω scan modes. The structure was solved by direct method using the program SHELXS 97 and refined by full-matrix least-square method on F^2 using the program SHELXL 97[24,25]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic datas and experimental details for structural analyses are summarized in **Table 1**. Selected bond lengths and bond angles for the compound are listed in **Table 2.**

Table 1. Crystal data, experimental details and refinement parameters for the structure of $[La_2(C_7H_3NO_4)_3(H_2O)_3]_n$.

Chemical formula	$C_{21}H_{15}La_2N_3O_{15}$
Molecular weight	827.18
Temperature, K	295(2)
Wavelength, Å	0.71073
Crystal system	Triclinic
Crystal description color	Columnar, colorless
Space group	*P* -1 (no. 2)
Unit cell parameters, a, b, c, Å	8.9803(5), 9.4818(5) , 14.5713(8)
Volume, $Å^3$	1173.93(11)
α, β , γ (deg)	98.23(0), 95.44(0) , 105.14(0)
Z	2
dx, g/cm^3	2.3401
Extinction coefficient, mm^{-1}	3.68
F(000)	792
Crystal size, mm	0.38 x 0.28 x 0.11

h, k, l limits	$-11 \le h \le 11$, $-12 \le k \le 12$, $-19 \le l \le 19$
Data completeness on θ, %	2.5-25.0, 99.8%
Measured/independent reflections	5099/5788 [R(int) = 0.033]
Reflections with I > 2σ(I)	5416
Number of parameters	371
Transmission	0.98517-1.00000
Refinement	Full-matrix least squares against F^2
Final R factor [I > 2σ(I)]	R1 = 0.0217 , *wR2* = 0.0532
R factor (all data)	R1 = 0.0239 , *wR2* = 0.0543
Residual electron density, e. $Å^{-3}$	-0.71 and 1.07

Table 2. selected geometric parameters (Å , °)

Bond	*d*(Å)	Angle	Deg(°)
La1—O3	2.6190(18)	$O1^{i}$—La1—$O7^{ii}$	84.96(6)
La1—O5	2.6764(19)	$O1^{i}$—La1—$O9^{iii}$	158.86(6)
La1—O6	2.8466(19)	$O11^{iv}$—La1—O3	142.70(6)
La1—O13	2.6260(3)	$O7^{ii}$—La1—O13	129.53(7)
La1—O14	2.6520(2)	$O9^{iii}$—La1—O13	129.53(7)
La1—$O7^{i}$	2.4635(18)	O3—La1—O13	143.32(7)
La1—$O11^{ii}$	2.5450(2)	$O1^{i}$—La1—O14	130.35(7)
La1—$O1^{iii}$	2.4240(19)	$O7^{ii}$—La1—O14	131.01(7)
La1—$O9^{iv}$	2.4662(19)	$O11^{iv}$—La1—O5	141.27(7)
La2—O3	2.7953(19)	$O2^{v}$—La2—$O8^{vi}$	93.27(6)
La2—O4	2.5893(19)	$O2^{v}$—La2—$O10^{iii}$	150.59(6)
La2—O6	2.5804(18)	$O8^{vi}$—La2—O6	148.05(6)
La2—O12	2.5662(18)	$O8^{vi}$—La2—O4	132.56(6)
La2—O15	2.6043(19)	$O10^{iii}$—La2—O4	130.00(6)
La2—$O8^{v}$	2.4212(18)	O12—La2—O4	138.00(6)
La2—$O10^{iv}$	2.4385(19)	$O2^{v}$—La2—O15	126.55(6)
La2—$O2^{vi}$	2.3791(19)	O12—La2—O15	135.27(6)

Symmetry code: (i) x-1, y-1, z；(ii)x-1, y,z；(iii) –x, -y+1, -z；(iv) –x+1, -y,-z+1；
(v) x, y-1, z；(vi) –x+1, -y+1, -z.

Table 3. Hydrogen bonds and Angles for title compound (Å ,°)

D–H···A	*d*(D–H)	*d*(H···A)	*d*(D···A)	∠D–H···A
O13—H13A···N2^{vii}	0.86	2.00	2.805(4)	157
O13—H14A···N3	0.84	1.97	2.803(4)	169
O15—H15B···O4^{viii}	0.91	2.20	2.877(3)	130
O15—H15C···N1^{v}	0.90	1.77	2.660(3)	171
C8—H8A···O12	0.95	2.57	3.385(3)	144
C9—H9A···O7^{ix}	1.00	2.43	2.784(3)	100
C9—H9A···O9^{ix}	1.00	2.37	3.363(3)	171
C15—H15A···O6	0.98	2.32	3.246(3)	157
C16—H15A···O10^{iv}	1.02	2.36	2.762(3)	102

Symmetry code: (vii)-1+x, −y, z;.(viii) 1−x, −y, −z; (ix)1+x, 1+y, z.

Synthesis

A mixture of $La(NO_3)_3{\cdot}6H_2O$ (0.2595 g, 0.60 mmole), 3,5-pydH_2 (0.1006 g, 0.60 mmole), $Mn(NO_3)_2{\cdot}4H_2O$ (0.1004 g, 0.40 mmole) and distillated water(10 mL) under nearly neutral condition (the pH value adjusted to 6.8~7.0) was sealed in a 23 mL Teflon-lined stainless autoclave and heated to 453 K under autogenous pressure for 72 h, then allowed to cool slowly to room temperature. The resulting reaction mixture was washed with 5 mL of acetone and colorless single crystals were isolated by suction filtration (yield 38.58 % based on La). The crystalline was air-stable and not soluble in water and common organic solvents such as 1,2-dichloroethane, acetone, ethanol, acetonitrile, DMF and THF.

Results and discussion

Structure of the polymer compound, $[La_2(C_7H_3NO_4)_3(H_2O)_3]_n$, is shown in Fig1.Two independent lanthanum centers which are connected through two carboxylate O atoms into a binuclear unit. The two La^{III} cations (La1 and La2) are arranged in a circular fashion through bridging carboxylate group, where La1 is nine-coordinated by seven oxygen atoms from six 3,5-pyd ligands and two aqua, forming a square-face capped square antiprism. La2 is coordinated with seven oxygen atoms from six 3,5-pyd ligands and only one aqua, forming a 4,4'-bicapped trigonal prism. Each binuclear unit is linked to symmetry-related units by four μ_4-pyd (Chart 1) ligands to form a two-dimensional layer structure parallel to the ac plane. These 2-D layers are, in turn, linked into a three-dimensional network via shared carboxylate O atoms. The compound is isomorphous to the recently reported $[Dy_2(C_7H_3NO_4)_3(H_2O)_3]_n$[19] and $[Pr_2(C_7H_3NO_4)_3(H_2O)_3]_n$[22].

The valence sum calculation give the average value of 3.06 for La atom, suggesting that all La centers are in the **+3** oxidation state **(**[Xe]$5d^0 6s^0$**)** [26,27]. The FT-IR spectrum of the title compound showing strong absorption bands at 1654, 1599, and 1557 cm^{-1} that are diagnostic of coordinated carboxylate group and coordinated water (3088 cm^{-1}, 3487 cm^{-1}). The absence of the strong carbonyl absorption band at 1724 cm^{-1} for pyridine-3,5-dicarboxylic acid (3,5-pydH_2) indicates complete deprotonation of 3,5-pyd^{-2} (Fig 2)[28].

In the polymer compound, there are classical hydrogen bonding interactions (O—H···O and O—H···N) and non-classical hydrogen-bondings[29] (C—H···O) are observed in the crystal structure (Fig 3, Table 3). In addition, π···π stacking interactions are also observed, the centroid-centroid betweenCg3$^{(iii)}$(N1/C1—C5)···Cg3, Cg3···Cg4$^{(vi)}$(N2/C8—C12) and Cg5$^{(iv)}$(N3/C15—C18)···Cg5 are 3.8519(15)Å , 3.7749 (15)Å and 3.5139(16)Å (Fig 4), [symmetry codes: (iii) = -X, 1-Y,-Z , (iv) =1-X, -Y, 1-Z, (vi) = 1-X, 1-Y,-Z.], respectively[30].

Ⅲ. Conclusions

In this study, a La^{III} polymer has been synthesized and structurally characterized. The synthesis of the title compound not only proves that the hydrothermal reaction in preparing new metal-organic hybrid materials is successful but also shows that strong intermolecular interactions (O—H···O and O—H···N) hydrogen-bonding and weak no-classical hydrogen-bonding (C—H···O) and π···π stacking interactions contribute to the formation of higher-dimensional network.

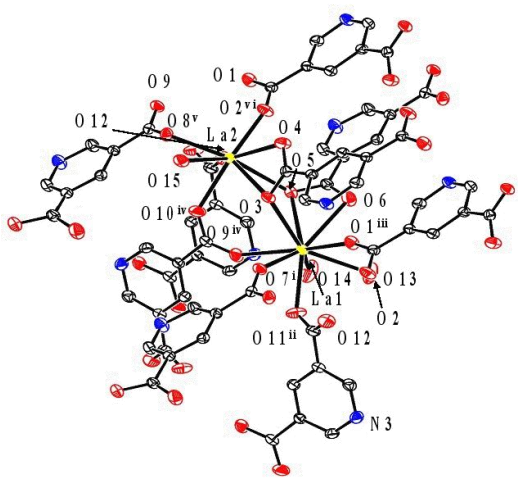

Fig 1. View of the title compound with the atom numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 50% probability level. Symmetry codes: (i)x-1,y-1,z,(ii)x-1,y,z,(iii)-x,-y+1,-z,(iv)-x+1,-y,-z+1,(v)x,y-1,z,(vi)-x+1,-y+1,z.

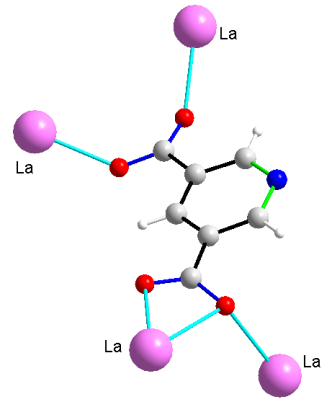

Chart 1.

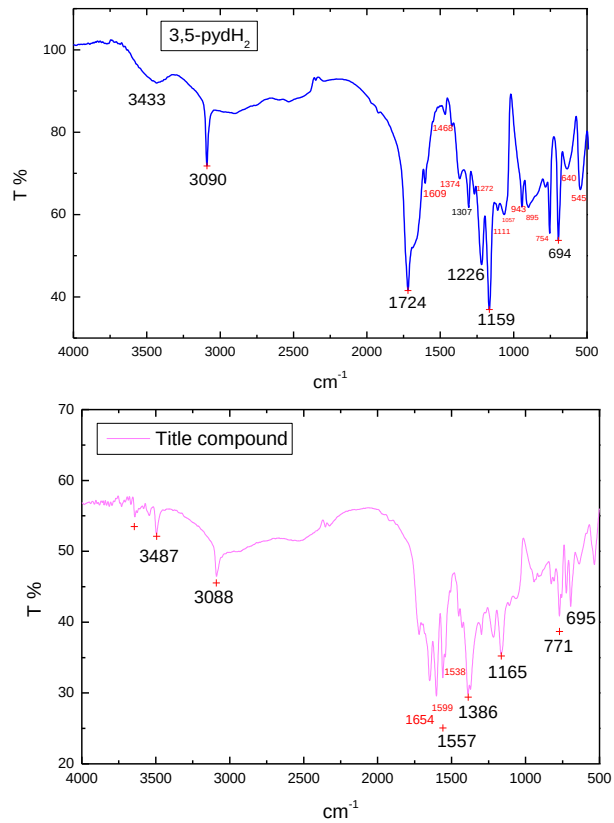

Fig 2. The FT-IR spectrum of the title compound and ligand.

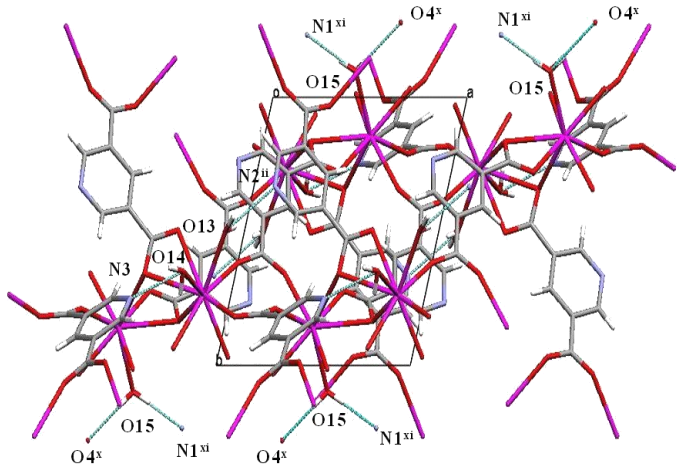

Fig 3. The molecular packing for the title compound. Hydrogen bonds are shown as dashed lines.

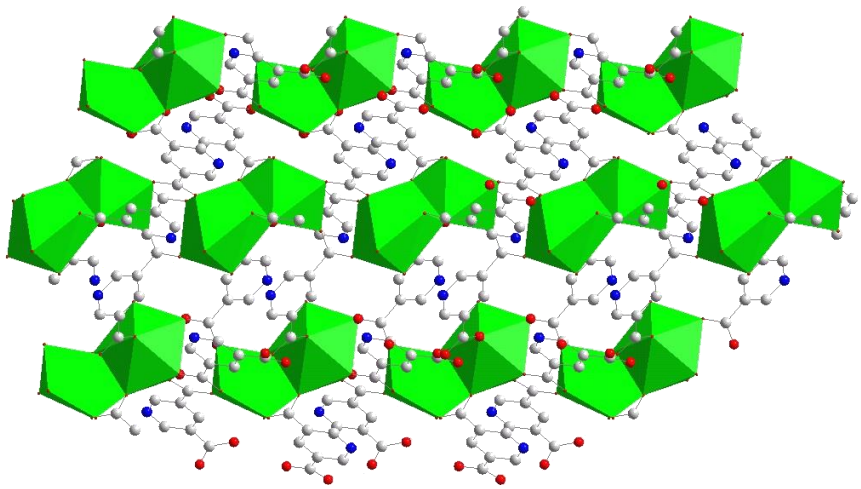

Fig 4. View of the stacking arrangement of title compound showing strong Hydrogen-bonding and π···π stacking interactions.

Ⅳ. Acknowledgments

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