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兩個鑭(Ⅲ)系金屬一維配位聚合物 含吡啶-2-羧酸根合成及結構分析

Synthesis, structure and of two new 1-D Lanthanide(Ⅲ) Coordination polymers based on the ligand Pyridine-2-carboxylate

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Synthesis, structure and of two new 1-D Lanthanide(Ⅲ) Coordination polymers based on the ligand Pyridine-2-carboxylate

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摘要:利用水熱合成反應,得到兩個含吡啶-2-羧酸根的鑭(Ⅲ)系金屬配位化合物 [Ln₂(pya)₆]_n (Ln = Pr (1) 及 Nd (2); pya = 吡啶-2-羧酸根)。利用 X-Ray 晶體繞射儀測定產物晶體結構, 兩個配位錯合物的結構相類似。錯合物以三配位羧酸根為橋鍵(μ₂-η²:η¹-橋鍵配位模式)形成一 維鏈狀聚合物。晶體結構中含有分子間 C—H…O 氫鍵,連結錯合物分子形成超分子網狀聚合物。金屬間最近距離 Ln…Ln 分別為 3.956 (1) Å 化合物 1 及 3.946 (2) Å 化合物 2。

關鍵詞:晶體結構、鑭(Ⅲ)系錯合物、配位聚合物、吡啶-2-羧酸

Abstract : Two lanthanide(III) coordination complexes $[Ln_2(pya)_6]_n$ (Ln = Pr (1) and Nd (2); pya = pyridine-2-carboxylate) were prepared by hydrothermal reaction. The crystal structures were determined by X-ray crystal diffraction and both of two coordination complexes are isostructures. The complexes form a one-dimensional chain polymer with a tridentate carboxylato-bridged



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 $(\mu_2 - \eta^2: \eta^1$ -bridging coordination mode). In both structures, intermolecular C—H…O hydrogen bonds link the molecules, forming a supramoleular network structure. The nearest Ln…Ln is 3.956(1) Å of 1 and 3.946(2) Å of 2, respectively.

Keywords: Crystal Structure, Lanthanide(III) Complex, Coordination Polymer, pyridine-2-carboxylate.

I. Introduction

Lanthanide complexes containing organic ligand with aromatic carboxylato ligand have been widely studied as luminescence properties, biomedical, sensing and industrial¹⁻³. Among these ligands, the aromatic carboxylates can be coordinated to the metal ion in various ways. These ligands such as pyridine-2-carboxylic acid⁴⁻⁷ (picolinic acid), pyridine-3-carboxylic acid⁸⁻¹⁰ (nicotinic acid) and pyridine-4-carboxylic acid¹¹ (isonicotinic acid) can bind as neutral molecular ligands or as anionic ligands in monodentate, bidentate or bridging manner. In general, the pyridine-2-carboxylate can coordinate to metal ion in a N,O-chelation mode through the nitrogen atom of the pyridine ring and an oxygen atom of the carboxylate to give discrete complexes. To the best of our knowledge, only a few lanthanide-pyridine-2-carboxylate¹²⁻¹⁴ complexes possess a polymeric structure. As continuation of our investigations^{10,11}, we pay attention to pyridine-2-carboxylic acid as functional ligand to build linkers to Ln(III) ion and synthesis the high-dimensional coordination polymer compounds, $[Ln_2(pya)_6]_n$ (Ln = Pr (1) and Nd (2); pya = pyridine-2-carboxylate).

II. Experimental Section

Materials and methods

All chemical reagents were used as purchased without further purification. ($Pr(NO_3)_3 \cdot 6H_2O$ 98.8%, NdCl₃·6H₂O 98.8%, N,N-dimethylethylenediamine 95.0%, pyridine-2-carboxylic acid 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 Lanthanide was determined by Perkin Elmer Optima 2100 inductively coupled plasma (ICP-OES) Emission Spectrometer. 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.

X-ray Crystallographic Analysis

Diffraction datas of the compound were collected on a Bruker SMART CCD area detector



diffractometer with graphite-monochromatized Mo K α 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^{15,16}. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. The crystallographic datas and experimental details for complexes **1**, **2** analyses are summarized in **Table 1**. Selected bond lengths and bond angles for the complexes are listed in **Table 2-3**.

Complex	1	2
Empirical formula	$C_{36}H_{24}N_6O_{12}Pr_2$	$C_{36}H_{24}N_6O_{12}Nd_2$
Molecular weight	1014.43	1021.09
Temperature, K	295(2)	295(2)
Wavelength, Å	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Crystal description color	columnar, green	columnar, purple
Space group	<i>P</i> 1 21/n 1 (no. 14)	P 1 21 1 (no. 4)
a, Å	11.6305(5)	11.0321(4)
b, Å	7.7133(3)	7.6937(4)
c, Å	19.2051(12)	11.3893(6)
Volume, Å ³	1721.74(15)	856.28(7)
β (deg)	92.08(0)	117.65(0)
Z	2	1
dx, g/cm ³	1.957	1.980
Extinction coefficient, mm ⁻¹	3.68	3.07
Data completeness on θ , %	2.5-25.0, 99.8%	2.5-25.0, 99.8%
R _{all}	0.080	0.077
R ₁	0.0455	0.0556
wR ₂	0.1183	0.1232

Table 1. Crystal and Structure Refinement Data for Complexes 1 and 2.

Table 2. Selected bond distances (${\rm \AA}\,$) and bond angles ($^{\circ}$) for complex 1.

Bond	$d(\text{\AA})$	Angle	Deg(°)
Pr1—O3	2.475(7)	O3—Pr1—O5	66.98(23)
Pr1—O5	2.480(7)	O3—Pr1—O1 ⁱ	67.14(22)
Pr1—O1 ⁱ	2.488(7)	O5—Pr1—O1 ⁱ	63.19(21)



Pr1—O1	2.534(7)	O5 ⁱⁱ —Pr1—O3 ⁱⁱ	64.50(21)
Pr1—O5 ⁱⁱ	2.542(7)	O3—Pr1—N2	62.86(21)
Pr1—O3 ⁱⁱ	2.581(6)	O5—Pr1—N2	120.09(22)
Pr1—N2	2.634(8)	O3—Pr1—N3 ⁱⁱ	76.90(21)
Pr1—N3 ⁱⁱ	2.698(8)	O1—Pr1—N3 ⁱⁱ	116.75(22)
Pr1—N1	2.700(8)	N2—Pr1—N3 ⁱⁱ	66.02(24)
Pr1—Pr1 ⁱⁱ	3.956(1)	O5—Pr1—N1	71.85(22)
Pr1—Pr1 ⁱ	3.956(1)	O1—Pr1—N1	60.95(22)
O1—Pr1 ⁱⁱ	2.488(7)	N3 ⁱⁱ —Pr1—N1	133.23(24)

Symmetry code: (i) 0.5-x, -0.5+y, 0.5-z; (ii) 0.5-x, 0.5+y, 0.5-z.

Table 3 Selected bond distances (${\rm \AA}$) and bond angles ($^{\circ}$) for complex 2.

Bond	$d(\text{\AA})$	Angle	Deg(°)
Nd1—O5 ⁱ	2.339(9)	O2 ⁱ —Nd1—O5	93.74(31)
Nd1—O4	2.376(11)	N3—Nd1—O5	134.71(33)
Nd1—O2 ⁱ	2.39(1)	O4 ⁱ —Nd1—O5	134.00(28)
Nd1—N3	2.624(14)	O5 ⁱ —Nd1—N2	78.86(43)
Nd1—O4 ⁱ	2.625(9)	O4—Nd1—N2	134.65(37)
Nd1—O2	2.631(10)	O2 ⁱ —Nd1—N2	73.23(34)
Nd1—O5	2.664(11)	N3—Nd1—N2	68.07(36)
Nd1—N2	2.679(10)	O4 ⁱ —Nd1—N2	60.27(37)
Nd1—N1	2.675(9)	O2—Nd1—N2	113.85(36)
Nd1—Nd1 ⁱ	3.946(2)	O5—Nd1—N2	107.97(36)
Nd1—Nd1 ⁱⁱ	3.946(2)	O5 ⁱ —Nd1—N1	79.09(39)
O2—Nd1 ⁱⁱ	2.39(1)	O4—Nd1—N1	73.86(37)
O4—Nd1 ⁱⁱ	2.625(9)	O2 ⁱ —Nd1—N1	133.53(31)
O5—Nd1 ⁱⁱ	2.339(9)	N3—Nd1—N1	65.81(30)
		N2—Nd1—N1	133.74(29)

Symmetry code: (i) 1-x, 0.5+y, 1-z; (ii) 1-x, -0.5+y, 1-z.

Table 4. Hydrogen bonds and Angles for complex 1 ($\rm \mathring{A}$ $^{, o}$).

D–H…A	d(D–H)	$d(\mathbf{H}\cdots\mathbf{A})$	$d(D \cdots A)$	∠(D–H…A)
C1—H1···O2 ⁱⁱⁱ	0.96	2.18	3.028(11)	146
C3—H3…O4 ^{iv}	0.96	2.44	3.376(14)	165



$C7$ — $H7 \cdots O4^{v}$	0.96	2.24	3.119(12)	152
C9—H9…O6 ^{vi}	0.96	2.46	3.410(14)	169
C13—H13…O6 ⁱⁱⁱ	0.96	2.25	3.028(11)	138
intraC13—13···O3 ^{vi}	0.96	2.60	3.219(12)	123

Symmetry code:(i) 0.5 -x, -0.5+y, 0.5-z; (ii) 0.5 -x, 0.5+y, 0.5-z; (iii) x, -1+y, z; (iv) -x, -y,-z; (v) x, 1+y,z; (vi) 0.5+x, 0.5-y, -0.5+z.

D–H···A	d(D-H)	$d(\mathbf{H}\cdots\mathbf{A})$	$d(D \cdots A)$	\angle (D–H···A)
$C1$ — $H1 \cdots O1^{iii}$	0.93	1.97	2.74(5)	139
intraC1—H1…O2	0.93	1.62	2.32(2)	129
intraC7—H7…O3 ⁱⁱ	0.93	2.06	2.87(2)	144
C9—H9…O6 ^{iv}	0.93	2.44	3.35(4)	166
intraC13—H13…O6 ⁱⁱ	0.93	2.26	3.115(19)	152
$C15-15\cdots O1^{v}$	0.93	2.50	3.431(18)	179

Table 5. Hydrogen bonds and Angles for complex 2 (Å $^{,\circ}$).

Symmetry code: (i)1-x, 0.5+y, 1-z; (ii)1-x, -0.5+y, 1-z; (iii) x, -1+y, z; (iv) 1+x, y, z; (v)1-x, -0.5+y, -z.

Synthesis

Complex 1. An aqueous solution (5 mL) containing $Pr(NO_3)_3 \cdot 6H_2O$ (0.0871 g, 0.20 mmole) and 0.10 mL N,N-dimethylethylenediamine was added to an aqueous solution (5 mL) with pyaH (0.0418g, 0.20 mmole), and the mixture was stirred for 30 minutes and then filtered. The mixture was placed in 23 mL Teflon-lined reactor. After heating for two days at 423 K and then cooling to room-temperature in air. Green transparent single crystals were isolated in 35.12 % yield. (based on Pr). Elemental analysis: Calculated for $C_{36}H_{24}N_6O_{12}Pr_2$: Pr, 27.78 C, 42.59; H, 2.37; N, 8.28%. Found: Pr, 27.60; C, 41.95; H, 2.28; N, 8.13%. IR data (cm⁻¹): 1661(s), 1593(m), 1570(w), 1483(w),1447(w),1346(s), 1295(w), 1239(m), 1162(m), 1097(w),1059(w),1012(w), 843(w), 765(m), 697(s), 633(m).

Complex 2. Synthesis procedure is similar to **1** except that $NdCl_3 6H_2O$ (0.0717 g, 0.20 mmole) was used instead of Pr salt. Purple transparent single crystals were obtained in 36.26 % yield (based on Nd). Elemental analysis: Calculated for $C_{36}H_{24}N_6O_{12}Nd_2$: Nd, 28.24 C, 42.31; H, 2.35; N, 8.23%. Found: Nd, 27.82; C, 41.52; H, 2.30; N, 8.01%. IR data (cm⁻¹): 1661(s), 1593(m), 1570(w), 1483(w), 1447(w), 1346(s), 1295(w), 1239(m), 1162(m), 1097(w),1059(w),1012(w), 843(w), 765(m), 697(s), 633(m).



Results and discussion

Complexes, **1** and **2** have been prepared by hydrothermal reactions under nearly neutral conditions (the pH value was adjusted to $6.8\sim7.0$). Pr(III) or Nd(III) salts reacts with pyridine-2-carboxylic acid and N,N-dimethylethylenediamine at 423 K. The products are stable in air and insoluble in water and common organic solvents such as ethanol, acetonitrile, tetrahydrofuran, 1,2-dichloroethane, acetone and DMF. In the absence of N,N-dimethylethylenediamine, only poor crystalline product was obtained which lacked of further characterizations.

The valence sum calculation give the average value of 3.25 (Pr) and 3.39 (Nd) atom, respectively. Suggesting that all Ln centers are in the +**3** oxidation state (**Pr:** [Xe]4f²6s⁰, Nd: [Xe]4f ${}^{3}6s^{0}$)^{17,18}. The FT-IR spectra of pyridine-2-carboxylic acid and the title complexes is given in Fig 1. Comparison of IR spectra of the free ligand reveals that considerable changes in frequencies have occurred which can determine the coordination sites in chelation. The difference value of 247 cm⁻¹ between the is symmetric (1593 cm⁻¹) and symmetric (1346 cm⁻¹) stretching vibration of the carboxylate group is in line with a monodentate type of coordination¹⁹⁻²¹. The FT-IR spectra of pyridine-2-carboxylic acid contain broad absorption bands at 2607 cm⁻¹ and 2152 cm⁻¹ and indicate the existence of O–H· · ·N type of intermolecular hydrogen bonding, but it disappears in the complexes whose phenomenon confirms that the nitrogen atom is coordinated to the Pr(III) ion. The absorption peak found in the 438 cm⁻¹ region is assigned to the Pr–N bond and in the 412cm⁻¹

The complexes **1** and **2** are isostructures, so we take **1** as an example for structural description. Selected bond lengths and angles are given in Table 2-3. Fig. 2 shows the structure and the numbering scheme for complex **1**. The asymmetric unit is composed of one Pr(III) atom and three pyridine-2-carboxylate ligands. Each Pr(III) center is nine-coordinated by three N atoms and six carboxylate O atoms from six different pyridine-2-carboxylate ligands (Fig.2). Each pyridine-2-carboxylate ion coordinates the Pr(III) ion via its nitrogen atom and one of its carboxyl oxygen atoms to form a five-membered ring (Chart 1), and the other carboxyl oxygen atom is free. Pr(1)O(1)C(6)C(5)N(1)] plane and the pyridine ring [C(1)C(2)C(3)C(4)C(5)N(1)] plane is 2.56(118)°, and those of the other two pyridine-2-carboxylate ions are -0.40(127)° and 0.65(122)°, respectively. The average Pr—O distance (2.52 Å) is shorter than that of Pr—N (2.68 Å). The coordination polyhedron of Pr(III) is best described as a distorted tricapped trigonal prism. That both of complexes are unique tridentate carboxylato-bridged one-dimensional chain structures (Fig 3)¹⁴. The nearest Ln…Ln separation is 3.956(1) Å of **1** and 3.946(2) Å of **2**, respectively.

In the polymer compound, there are non-classical hydrogen-bonding 23 interactions (C—H··O)



are observed in the crystal structure (Fig 4, Table 4-5). In addition, C—H… π stacking²⁴ interactions are also observed, the C—H… π contacts are 3.625(11) Å (C8—H8… π angle110°) and 3.728(10) Å (C10—H10… π angle 115°; π = centroid of the ring) in the crystal structure of **1** (Fig 5-6).

III. Conclusions

In this study, two Ln^{III} -pyridine-2-carboxylate polymers have been synthesized and structurally characterized. The synthesis of the not only proves that the hydrothermal reaction in preparing new metal-organic hybrid materials is successful but also shows that weak no-classical hydrogen-bonding (C—H··O) and C—H·· π stacking interactions contribute to the formation of higher-dimensional network.



Fig 1.The FT-IR spectrum of the pya and complexes 1-2.



Fig 2. The asymmetry unit of complex **1** showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level. (Symmetry code: (i) 0.5-X, -0.5+Y, 0.5-Z; (ii) 0.5-X, 0.5+Y, 0.5-Z).





Chart 1.



Fig 3.Chain structure of complex 1 (The hydrogen atoms are omitted for clarity).





Fig 4. The molecular packing for the complex **1**. Hydrogen bonds are shown as dashed lines.



Fig 5. Weak spatial C—H $\cdots\pi$ stacking interactions of the complex 1.





Fig 6.View of the stacking arrangement of complex 1 showing weak Non-classical(C—H··O) stacking interactions hydrogen-bonding and weak C—H·· π stacking interactions.

IV. Acknowledgments

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