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# 兩個鑭（III）系金屬—維配位聚合物 <br> 含吡啶－2－羧酸根合成及結構分析 <br> Synthesis，structure and of two new 1－D <br> Lanthanide（III）Coordination polymers based on the ligand Pyridine－2－carboxylate 

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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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#### Abstract

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 $\left[\mathrm{Ln}_{2}(\mathrm{pya})_{6}\right]_{n}$ $(\operatorname{Ln}=\operatorname{Pr}(1)$ 及 $N d(2) ; p y a=$ 吡啶－2－羧酸根）$\circ$ 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 $\left(\mu_{2}-\eta^{2}: \eta^{1}-\right.$ 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… 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 $\cdots \operatorname{Ln}$ 分別為 3.956 （1）$\AA$ 化合物 1 及 3.946 （2）$\AA$ 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 $\left[\mathrm{Ln}_{2}(\mathrm{pya})_{6}\right]_{\mathrm{n}}(\mathrm{Ln}=\operatorname{Pr}(1)$ and $\mathrm{Nd}(2)$ ；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


( $\mu_{2}-\eta^{2}: \eta^{1}$-bridging coordination mode). In both structures, intermolecular $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ hydrogen bonds link the molecules, forming a supramoleular network structure. The nearest Ln $\cdots \mathrm{Ln}$ is 3.956 (1) $\AA$ of 1 and 3.946(2) $\AA$ 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 industrial ${ }^{1-3}$. Among these ligands, the aromatic carboxylates can be coordinated to the metal ion in various ways. These ligands such as pyridine-2-carboxylic acid ${ }^{4-7}$ (picolinic acid), pyridine-3-carboxylic acid ${ }^{8-10}$ (nicotinic acid) and pyridine-4-carboxylic acid ${ }^{11}$ (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 $\mathrm{N}, \mathrm{O}$-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-carboxylate ${ }^{12-14}$ 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 $\operatorname{Ln}$ (III) ion and synthesis the high-dimensional coordination polymer compounds, $\left[\operatorname{Ln}_{2}(\text { pya })_{6}\right]_{\mathrm{n}}(\mathrm{Ln}=\operatorname{Pr}(1)$ and $\mathrm{Nd}(2)$; pya $=$ pyridine-2-carboxylate).

## II. Experimental Section

## Materials and methods

All chemical reagents were used as purchased without further purification. $\left(\operatorname{Pr}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}\right.$ $98.8 \%, \mathrm{NdCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O} 98.8 \%$, 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 $400-4000 \mathrm{~cm}^{-1}$ 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 Karadiation ( $\lambda=0.71073 \AA$ ) in $\psi$ and $\omega$ 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.

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

| Complex | 1 | 2 |
| :---: | :---: | :---: |
| Empirical formula | $\mathrm{C}_{36} \mathrm{H}_{24} \mathrm{~N}_{6} \mathrm{O}_{12} \mathrm{Pr}_{2}$ | $\mathrm{C}_{36} \mathrm{H}_{24} \mathrm{~N}_{6} \mathrm{O}_{12} \mathrm{Nd}_{2}$ |
| Molecular weight | 1014.43 | 1021.09 |
| Temperature, K | $295(2)$ | $295(2)$ |
| Wavelength, $\AA$ | 0.71073 | 0.71073 |
| Crystal system | monoclinic | monoclinic |
| Crystal description color | columnar, green | columnar, purple |
| Space group | $P 121 / \mathrm{n} 1$ (no. 14) | $P 1211$ (no. 4$)$ |
| $\mathrm{a}, \AA$ | $11.6305(5)$ | $11.0321(4)$ |
| $\mathrm{b}, \AA$ | $7.7133(3)$ | $7.6937(4)$ |
| $\mathrm{c}, \AA$ | $19.2051(12)$ | $11.3893(6)$ |
| Volume, $\AA{ }^{3}$ | $1721.74(15)$ | $856.28(7)$ |
| $\beta($ deg $)$ | $92.08(0)$ | $117.65(0)$ |
| Z | 2 | 1 |
| $\mathrm{dx}, \mathrm{g} / \mathrm{cm}^{3}$ | 1.957 | 1.980 |
| Extinction coefficient, $\mathrm{mm}^{-1}$ | 3.68 | 3.07 |
| Data completeness on $\theta, \%$ | $2.5-25.0,99.8 \%$ | $2.5-25.0,99.8 \%$ |
| $\mathrm{R}_{\text {all }}$ | 0.080 | 0.077 |
| $\mathrm{R}_{1}$ | 0.0455 | 0.0556 |
| $\mathrm{wR}_{2}$ | 0.1183 | 0.1232 |
|  |  |  |

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

| Bond | $d(\AA)$ | Angle | $\operatorname{Deg}\left({ }^{\circ}\right)$ |
| :---: | :---: | :---: | :---: |
| $\operatorname{Pr} 1-\mathrm{O} 3$ | $2.475(7)$ | $\mathrm{O} 3-\operatorname{Pr} 1-\mathrm{O} 5$ | $66.98(23)$ |
| $\operatorname{Pr} 1-\mathrm{O} 5$ | $2.480(7)$ | $\mathrm{O} 3-\operatorname{Pr} 1-\mathrm{O} 1^{\mathrm{i}}$ | $67.14(22)$ |
| $\operatorname{Pr}-\mathrm{O1}^{\mathrm{i}}$ | $2.488(7)$ | $\mathrm{O} 5-\operatorname{Pr} 1-\mathrm{O1}^{\mathrm{i}}$ | $63.19(21)$ |


| Pr1-O1 | 2.534(7) | $\mathrm{O} 5{ }^{\mathrm{ii}}-\mathrm{Pr} 1-\mathrm{O} 3^{\mathrm{ii}}$ | 64.50(21) |
| :---: | :---: | :---: | :---: |
| $\operatorname{Pr} 1-\mathrm{O} 5^{\text {ii }}$ | 2.542(7) | $\mathrm{O} 3-\mathrm{Pr} 1-\mathrm{N} 2$ | 62.86(21) |
| Pr1-O3 $3^{\text {ii }}$ | 2.581(6) | O5-Pr1-N2 | 120.09(22) |
| Pr1-N2 | 2.634(8) | $\mathrm{O} 3-\mathrm{Pr} 1-\mathrm{N} 3{ }^{\text {ii }}$ | 76.90(21) |
| $\operatorname{Pr} 1-\mathrm{N} 3{ }^{\text {ii }}$ | 2.698(8) | $\mathrm{O} 1-\mathrm{Pr} 1-\mathrm{N} 3{ }^{\text {ii }}$ | 116.75(22) |
| Pr1-N1 | 2.700 (8) | $\mathrm{N} 2-\mathrm{Pr} 1-\mathrm{N} 3{ }^{\text {ii }}$ | 66.02(24) |
| $\operatorname{Pr} 1-\operatorname{Pr} 1^{1 i}$ | 3.956(1) | O5-Pr1-N1 | 71.85(22) |
| $\operatorname{Pr} 1-\operatorname{Pr} 1^{1}$ | 3.956(1) | $\mathrm{O} 1-\mathrm{Pr} 1-\mathrm{N} 1$ | 60.95(22) |
| $\mathrm{O} 1-\mathrm{Pr} 1^{\text {ii }}$ | 2.488(7) | N3 ${ }^{\text {iii }}$ - Pr1—N1 | 133.23(24) |

Symmetry code: (i) $0.5-\mathrm{x},-0.5+\mathrm{y}, 0.5-\mathrm{z}$; (ii) $0.5-\mathrm{x}, 0.5+\mathrm{y}, 0.5-\mathrm{z}$.

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

| Bond | $d(\mathrm{~A})$ | Angle | $\operatorname{Deg}\left({ }^{\circ}\right)$ |
| :---: | :---: | :---: | :---: |
| Nd1-O5 ${ }^{\text {i }}$ | $2.339(9)$ | O 2 - ${ }^{\text {i }}$ Nd1-O5 | 93.74(31) |
| Nd1-O4 | 2.376(11) | N3-Nd1-O5 | 134.71(33) |
| $\mathrm{Nd} 1-\mathrm{O} 2{ }^{\text {i }}$ | 2.39(1) | $\mathrm{O} 4{ }^{\text {i }} \mathrm{-Nd1}-\mathrm{O} 5$ | 134.00(28) |
| Nd1-N3 | 2.624(14) | $\mathrm{O} 5^{\mathrm{i}}-\mathrm{Nd} 1-\mathrm{N} 2$ | 78.86(43) |
| $\mathrm{Nd} 1-\mathrm{O} 4{ }^{\text {i }}$ | $2.625(9)$ | $\mathrm{O} 4-\mathrm{Nd} 1-\mathrm{N} 2$ | 134.65(37) |
| Nd1-O2 | 2.631(10) | $\mathrm{O} 2{ }^{\text {i }}-\mathrm{Nd} 1-\mathrm{N} 2$ | 73.23(34) |
| Nd1-O5 | 2.664(11) | N3-Nd1-N2 | 68.07(36) |
| Nd1-N2 | 2.679(10) | $\mathrm{O} 4{ }^{\mathrm{i}}-\mathrm{Nd} 1-\mathrm{N} 2$ | 60.27(37) |
| Nd1-N1 | 2.675(9) | $\mathrm{O} 2-\mathrm{Nd} 1-\mathrm{N} 2$ | 113.85(36) |
| $\mathrm{Nd} 1-\mathrm{Nd} 1{ }^{\text {i }}$ | $3.946(2)$ | O5-Nd1-N2 | 107.97(36) |
| $\mathrm{Nd} 1-\mathrm{Nd} 1{ }^{\text {ii }}$ | 3.946(2) | $\mathrm{O} 5{ }^{\mathrm{i}}-\mathrm{Nd} 1-\mathrm{N} 1$ | 79.09(39) |
| $\mathrm{O} 2-\mathrm{Nd} 1{ }^{\text {ii }}$ | 2.39(1) | $\mathrm{O} 4-\mathrm{Nd} 1-\mathrm{N} 1$ | 73.86(37) |
| $\mathrm{O} 4-\mathrm{Nd} 1{ }^{\text {ii }}$ | $2.625(9)$ | $\mathrm{O} 2{ }^{\text {i }}-\mathrm{Nd} 1-\mathrm{N} 1$ | 133.53(31) |
| $\mathrm{O} 5-\mathrm{Nd} 1{ }^{\text {ii }}$ | 2.339(9) | N3-Nd1-N1 | 65.81(30) |
|  |  | $\mathrm{N} 2-\mathrm{Nd} 1-\mathrm{N} 1$ | 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 $1\left(\AA^{\circ}{ }^{\circ}\right)$.

| $\mathrm{D}-\mathrm{H} \cdots \mathrm{A}$ | $d(\mathrm{D}-\mathrm{H})$ | $d(\mathrm{H} \cdots \mathrm{A})$ | $d(\mathrm{D} \cdots \mathrm{A})$ | $\angle(\mathrm{D}-\mathrm{H} \cdots \mathrm{A})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C} 1-\mathrm{H} 1 \cdots \mathrm{O} 2^{\mathrm{iii}}$ | 0.96 | 2.18 | $3.028(11)$ | 146 |
| $\mathrm{C} 3-\mathrm{H} 3 \cdots 4^{\text {iv }}$ | 0.96 | 2.44 | $3.376(14)$ | 165 |


| C7—H7 $\cdots \mathrm{O}^{\mathrm{v}}$ | 0.96 | 2.24 | $3.119(12)$ | 152 |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C} 9 — \mathrm{H} 9 \cdots \mathrm{O}^{\mathrm{vi}}$ | 0.96 | 2.46 | $3.410(14)$ | 169 |
| $\mathrm{C} 13 — \mathrm{H} 13 \cdots \mathrm{O}^{\mathrm{iii}}$ | 0.96 | 2.25 | $3.028(11)$ | 138 |
| intraC13—13 $^{\mathrm{iin}} \mathrm{O}^{\mathrm{vi}}$ | 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) $0.5+x, 0.5-y,-0.5+z$.

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

| D-H $\cdots \mathrm{A}$ | $d(\mathrm{D}-\mathrm{H})$ | $d(\mathrm{H} \cdots \mathrm{A})$ | $d(\mathrm{D} \cdots \mathrm{A})$ | $\angle(\mathrm{D}-\mathrm{H} \cdots \mathrm{A})$ |
| :---: | :---: | :---: | :---: | :---: |
| $\mathrm{C} 1-\mathrm{H} 1 \cdots \mathrm{O} 1^{\text {iii }}$ | 0.93 | 1.97 | 2.74(5) | 139 |
| intraC1- $\mathrm{H} 1 \cdots \mathrm{O} 2$ | 0.93 | 1.62 | 2.32(2) | 129 |
| intraC7-H7...O3 ${ }^{\text {ii }}$ | 0.93 | 2.06 | 2.87(2) | 144 |
| C9-H9...O6 ${ }^{\text {iv }}$ | 0.93 | 2.44 | 3.35(4) | 166 |
| intraC13-H13...O6 ${ }^{\text {ii }}$ | 0.93 | 2.26 | 3.115(19) | 152 |
| $\mathrm{C} 15-15 \cdots \mathrm{O} 1^{\mathrm{v}}$ | 0.93 | 2.50 | 3.431(18) | 179 |

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 $\operatorname{Pr}\left(\mathrm{NO}_{3}\right)_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}(0.0871 \mathrm{~g}, 0.20$ mmole) and $0.10 \mathrm{~mL} \mathrm{~N}, \mathrm{~N}$-dimethylethylenediamine was added to an aqueous solution ( 5 mL ) with pyaH ( $0.0418 \mathrm{~g}, 0.20 \mathrm{mmole}$ ) , 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 $\mathrm{C}_{36} \mathrm{H}_{24} \mathrm{~N}_{6} \mathrm{O}_{12} \mathrm{Pr}_{2}$ : $\mathrm{Pr}, 27.78 \mathrm{C}, 42.59 ; \mathrm{H}, 2.37 ; \mathrm{N}, 8.28 \%$. Found: $\operatorname{Pr}, 27.60 ; \mathrm{C}, 41.95 ; \mathrm{H}, 2.28 ; \mathrm{N}, 8.13 \%$. IR data $\left(\mathrm{cm}^{-1}\right): 1661(\mathrm{~s}), 1593(\mathrm{~m}), 1570(\mathrm{w})$, 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 $\mathrm{NdCl}_{3} \cdot 6 \mathrm{H}_{2} \mathrm{O}$ ( $0.0717 \mathrm{~g}, 0.20 \mathrm{mmole}$ ) was used instead of Pr salt. Purple transparent single crystals were obtained in 36.26 \% yield (based on Nd ). Elemental analysis: Calculated for $\mathrm{C}_{36} \mathrm{H}_{24} \mathrm{~N}_{6} \mathrm{O}_{12} \mathrm{Nd}_{2}$ : Nd, $28.24 \mathrm{C}, 42.31 ; \mathrm{H}, 2.35 ; \mathrm{N}, 8.23 \%$. Found: Nd, 27.82; C, 41.52; H, 2.30; N, $8.01 \%$. IR data $\left(\mathrm{cm}^{-1}\right): 1661(\mathrm{~s}), 1593(\mathrm{~m}), 1570(\mathrm{w})$, 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, $\mathbf{1}$ and 2 have been prepared by hydrothermal reactions under nearly neutral conditions (the pH value was adjusted to $6.8 \sim 7.0$ ). Pr (III) or Nd (III) salts reacts with pyridine-2-carboxylic acid and $\mathrm{N}, \mathrm{N}$-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 $3.25(\mathrm{Pr})$ and $3.39(\mathrm{Nd})$ atom, respectively. Suggesting that all Ln centers are in the $\mathbf{+ 3}$ oxidation state (Pr: $[\mathrm{Xe}] 4 \mathrm{f}^{2} 6 \mathrm{~s}^{0}$, Nd: $[\mathrm{Xe}] 4 \mathrm{f}$ $\left.{ }^{3} 6 \mathrm{~s}^{0}\right)^{17,18}$. 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 $247 \mathrm{~cm}^{-1}$ between the is symmetric ( $1593 \mathrm{~cm}^{-1}$ ) and symmetric ( $1346 \mathrm{~cm}^{-1}$ ) stretching vibration of the carboxylate group is in line with a monodentate type of coordination ${ }^{19-21}$. The FT-IR spectra of pyridine-2-carboxylic acid contain broad absorption bands at $2607 \mathrm{~cm}^{-1}$ and $2152 \mathrm{~cm}^{-1}$ and indicate the existence of $\mathrm{O}-\mathrm{H} \cdots \mathrm{N}$ type of intermolecular hydrogen bonding, but it disappears in the complexes whose phenomenon confirms that the nitrogen atom is coordinated to the $\operatorname{Pr}($ III $)$ ion. The absorption peak found in the $438 \mathrm{~cm}^{-1}$ region is assigned to the $\operatorname{Pr}-\mathrm{N}$ bond and in the $412 \mathrm{~cm}^{-1}$ region is assigned to the $\mathrm{Pr}-\mathrm{O}$ bond ${ }^{6,22}$.

The complexes $\mathbf{1}$ and $\mathbf{2}$ are isostructures, so we take $\mathbf{1}$ 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 $\operatorname{Pr}($ III ) atom and three pyridine-2-carboxylate ligands. Each $\operatorname{Pr}(\mathrm{III})$ 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 $\operatorname{Pr}$ (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. $\operatorname{Pr}(1) \mathrm{O}(1) \mathrm{C}(6) \mathrm{C}(5) \mathrm{N}(1)$ ] plane and the pyridine ring $[\mathrm{C}(1) \mathrm{C}(2) \mathrm{C}(3) \mathrm{C}(4) \mathrm{C}(5) \mathrm{N}(1)$ ] plane is $2.56(118)^{\circ}$, and those of the other two pyridine-2-carboxylate ions are $-0.40(127)^{\circ}$ and $0.65(122)$ ${ }^{\circ}$, respectively. The average $\operatorname{Pr}-\mathrm{O}$ distance $(2.52 \AA)$ is shorter than that of $\operatorname{Pr}-\mathrm{N}(2.68 \AA)$. The coordination polyhedron of $\operatorname{Pr}($ 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 $\cdots \operatorname{Ln}$ separation is $3.956(1) \AA$ of $\mathbf{1}$ and 3.946(2) $\AA$ of $\mathbf{2}$, respectively.

In the polymer compound, there are non-classical hydrogen-bonding ${ }^{23}$ interactions ( $\mathrm{C}-\mathrm{H} \cdots \mathrm{O}$ )
are observed in the crystal structure (Fig 4, Table 4-5). In addition, $\mathrm{C}-\mathrm{H} \cdots \pi$ stacking $^{24}$ interactions are also observed, the $\mathrm{C}-\mathrm{H} \cdots \pi$ contacts are $3.625(11) \AA\left(\mathrm{C} 8-\mathrm{H} 8 \cdots \pi\right.$ angle $\left.110^{\circ}\right)$ and $3.728(10)$ $\AA\left(\mathrm{C} 10-\mathrm{H} 10 \cdots \pi\right.$ angle $115^{\circ} ; \pi=$ centroid of the ring $)$ in the crystal structure of $\mathbf{1}$ (Fig 5-6).

## III. Conclusions

In this study, two $\mathrm{Ln}^{\text {III }}$-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 $(\mathrm{C}-\mathrm{H} \cdots \mathrm{O})$ and $\mathrm{C}-\mathrm{H} \cdots \pi$ stacking interactions contribute to the formation of higher-dimensional network.


Fig 1.The FT-IR spectrum of the pya and complexes $\mathbf{1 - 2}$.


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) $0.5-\mathrm{X},-0.5+\mathrm{Y}$, $0.5-\mathrm{Z}$; (ii) $0.5-\mathrm{X}, 0.5+\mathrm{Y}, 0.5-\mathrm{Z}$ ).


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 $\mathrm{C}-\mathrm{H} \cdots \pi$ stacking interactions of the complex 1.


Fig 6.View of the stacking arrangement of complex 1 showing weak Non-classical(C-H $\cdots \mathrm{O})$ stacking interactions hydrogen-bonding and weak $\mathrm{C}-\mathrm{H} \cdots \pi$ stacking interactions.

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## References

1. Han, S. S., Furukawa, H., Yaghi, O. M., Goddard III, W. A. Covalent Organic Frameworks as Exceptional Hydrogen Storage Materials. J. Am. Chem. Soc, 130(35), 2008, pp. 1580-11581.
2. Uchida, S., Kawamoto, R., Tagami, H., Nakagawa, Y., Mizuno, N. Highly Selective Sorption of Small Unsaturated Hydrocarbons by Nonporous Flexible Framework with Silver Ion. J. Am. Chem. Soc, 130(37), 2008, pp. 12370-12376.
3. Pack, Y. J., Lee, H. H., Kim, W. H., Y. D. Investigation of Coordinational Properties of

Europium(III) Complexes with Picolinic Acid Using Eu(III) Excitation Spectroscopy. J. Coll. Inter. Science, 209, 1999, pp. 268-270.
4. Fu, A. Y. \& Wang, D. Q. Tris(pyridine-2-carboxylato- $\mathrm{K}^{2} \mathrm{O}, \mathrm{N}$ )cobalt(III)monohydrate. Acta Cryst, E61, 2005, pp. m481-m482.
5. Hao, L. J. \&Liu, T. T. Poly[bis( $\mu_{3}$-pyridine-2-carboxylato)iron(II)]. Acta Cryst. E63, 2007, pp. m263-m264.
6. Li, D. \& Zhong, G. Q. Synthesis, Crystal Structure, and Thermal Decomposition of the Cobalt(II) Complex with 2-Picolinic Acid. The Scientific World Journal, 2014, pp.1-7.
7. Li, Y. Z.,Wang, M., Wang, L. F. \& Xia, C. G. Bis(pyridinecarboxylato-O,N) (pyridine carboxylic acid-O,N)manganese(III) hydroxide. Acta Cryst, C56, 2000, pp. e445-e446.
8. Hao, X., Wei, Y. G., Liu, Q. \& Zhang, S. W. Poly[trans- diaquamanganese(II) -l-(3-pyridine carboxylato-N:O)-1-(3-pyridinecarboxylato-O:N)]. Acta Cryst,C56,2000, pp. 296-298
9. Batten, S. R. \& Harris, A. R. trans-Tetraaquabis(pyridine-3-carboxylate-kN)-nickel(II). Acta Cryst, E57, 2001, pp. m9-m11
10. Shen, F. M., \& Lush, S. F. Synthesis and Crystal Structure of Cobalt ( II) Complex of trans-[Tetraaquabis(pyridine-3-picolinato-kN)-Cobalt(II)]. Chia-Nan Annual Bulletin, Vol. 37, 2011, pp. 14-18.
11. Shen, F. M. \& Lush, S. F. Synthesis and Crystal Structure of the Coordination Compound Trans-tetraaquabis (Pyridine-4-Carboxylate-кN)-Cobalt(II). Journal of Yuanpei University. No.19, 2012, pp. 33-42
12. Hong, J. H., Oh, Y., Kim,Y., Kang, S. K., Choi, J. K., Kim, W. S., Lee,J. I., Kim, S. J. \& Hur, N. H. Polymorph Selective Growth of Sodium Tetrakis(2-pyridinecarboxylato) Lanthanides and Their Structure Sensitive Properties. Crystal Growth \& Design, Vol. 8, No. 4, 2008, pp. 1364-1371.
13. Oh, Y., Kim, J. Y., Kim, H. J., Lee, T. \& Kang, S. K. Synthesis and Crystal Structure of Cerium(III) Picolinate Complex. Bull. Korean Chem. Soc, Vol. 31, No. 4. 2010, pp. 10581060.
14. Li, W., Wang, X. L., Song, X. Y., Li, L. C., Liao, D. Z. \& Jiang, Z. H. Crystal structures, magnetic and photoluminescent properties of one-dimensional lanthanide complexes with picolinate ligand. Journal of Molecular Structure, 885, 2008, pp. 1-6.
15. Bruker . SMART and SAINT. Bruker AXS Inc., Madison, Wisconsin, USA. 1997.
16. Bruker . SHELXTL. Version 5.1. Bruker AXS Inc., Madison, Wisconsin, USA. 1998.
17. Brese, N. E. \& Keeffe, M. O. Bond-valence parameters for solids. Acta Cryst, B47, 1991, pp. 192-197.
18. Brown, I. D. \& Altermatt, D. Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Data base. Acta Cryst, B41, 1985, pp. 244-247.
19. Vargová , Z ., Zeleòák, V., C'isaøová, I . \& Györyová, K. Correlation of thermal and spectral
properties of zinc(II) complexes of pyridinecarboxylic acids with their crystal structures. Thermo chimica Acta, 423, 2004, pp.149-157.
20. Martini, D., Pellei, M., Pettinari, C., Skelton, B.W. \& White, A.H. Synthesis, spectroscopic and structural characterization of $\mathrm{Cu}(\mathrm{II})$ derivatives of tris (pyrazol-1-yl)methanes. Inorg Chim Acta, 333, 2002, pp. 72-82.
21. Nara, M., Torii, H., Tasumi, M. Correlation between the Vibrational Frequencies of the Carboxylate Group and the Types of Its Coordination to a Metal Ion: An $a b$ Initio Molecular Orbital Study. J Phys Chem, 100(51), 1996, pp. 19812-19817.
22. Nakamoto, K. Infrared Spectra and Raman Spectra of Inorganic and Coordination Compounds, John Wiley\& Sons, New York, NY, USA, $4^{\text {th }}$ edition. 1986.
23. Steiner, T. The Hydrogen Bond in the Solid State. Angew Chem Int Ed, 41, 2002, pp. 48-76.
24. Meyer, E. A., Castellano, R. K. \& Diederich, F. Interactions with Aromatic Rings in Chemical and Biological Recognition. Angew Chem Int Ed, 42, 2003, pp. 1210-1250.

