

## 以草酸、碳酸根构筑的一个钕(III)配位聚合物的晶体结构和荧光性质

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**摘要:** 水热条件下采用  $\text{Nd}_2(\text{CO}_3)_3$  和草酸钠作为反应物合成出一个新的三维钕(III)配位聚合物  $\{[\text{Nd}_2(\text{ox})(\text{cb})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}\}_n$  (**1**) (ox=草酸, cb=碳酸), 并分别用元素分析、红外光谱、差热分析、X-射线粉末衍射和 X-射线单晶衍射等表征了该结构。晶体结构分析结果表明:  $\mu_2$  桥联的草酸根离子与  $\mu_4$  桥联的碳酸根离子将钕离子连接成三维微孔结构, 沿  $b$  轴和  $c$  轴方向分别具有孔径大小为  $0.53 \text{ nm} \times 0.41 \text{ nm}$  和  $0.59 \text{ nm} \times 0.84 \text{ nm}$  的通道。拓扑分析结果表明化合物 **1** 为 (4,5) 连接类型。荧光分析表明常温固态下配合物 **1** 发射近红外荧光。

**关键词:** 钕(III)配位聚合物; 晶体结构; 碳酸; 草酸; 荧光性质

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## A Neodymium(III) Coordination Polymer Based on Oxalate and Carbonate Ligands: Synthesis, Structure and Luminescence

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**Abstract:** A neodymium(III) coordination polymer, namely,  $\{[\text{Nd}_2(\text{ox})(\text{cb})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}\}_n$  (**1**) (ox=oxalate, cb=carbonate) (**1**), has been hydrothermally synthesized and characterized by elemental analysis, IR, TGA, powder X-ray diffraction, and single-crystal X-ray diffraction. Structural determination reveals that the neodymium ions are bridged by  $\mu_2$ -ox and  $\mu_4$ -cb ligands to give a 3D framework including 2D channels of  $0.53 \text{ nm} \times 0.41 \text{ nm}$  along the  $b$  axis and  $0.59 \text{ nm} \times 0.84 \text{ nm}$  along the  $c$  axis, respectively. It can also be described as a (4,5)-connected  $\{4^4.6^2\}$   $\{4^4.6^6\}$  topological 3D framework. Solid-state **1** emits the intensely NIR characteristic luminescence of  $\text{Nd}^{3+}$  ion at room temperature. CCDC: 917863.

**Key words:** neodymium(III) coordination polymer; crystal structure; oxalate; carbonate; luminescent

The study of microporous lanthanide-organic frameworks (MLOFs) has gained increasing recognition over the last decade due to their superior functional properties and wide variety of potential applications, i.e. sensor<sup>[1]</sup>, luminescence<sup>[2]</sup>, ionic conductors<sup>[3]</sup>, biomedical analyses and imaging<sup>[4-5]</sup>. Compared to first-row metals, lanthanide ions have a large coordination sphere and more flexible coordination geometry, which

make it even more difficult to predict and control their structures. Thus, to be able to rationally design and construct lanthanide-organic framework with a desired geometry is still a great challenge, as many factors can affect the overall structural formation. In addition to the choice of ligands and metal ions, reaction conditions such as solvent, pH and temperature can also affect the final structure. Investigations

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on how these factors affect structure will help us understand which reaction conditions afford lanthanide complexes with the desired structures. Complex **1** is isostructural with gadolinium compound reported by Rom ero<sup>[6]</sup>. However, the crystals were impure and small in size by using  $\text{Gd}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$  and  $\text{Ag}_2\text{C}_2\text{O}_4$  as starting materials. In addition, the yield is much lower than that achieved by using the sodium oxalate and  $\text{Nd}_2(\text{CO}_3)_3$ . In this work, we used sodium oxalate and  $\text{Nd}_2(\text{CO}_3)_3$  as starting materials to construct the title three-dimensional neodymium(III) coordination polymer,  $[\{\text{Nd}_2(\text{ox})(\text{cb})_2(\text{H}_2\text{O})_2\} \cdot 3\text{H}_2\text{O}]_n$  (**1**), under hydrothermal conditions. The crystal structure and photoluminescent properties of **1** are reported here.

## 1 Experimental

### 1.1 Materials and measurements

All chemicals purchased were of reagent grade and used without further purification. All syntheses were carried out in 23 mL Teflon-lined autoclaves under autogenous pressure. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Infrared spectra were recorded ( $4\,000\sim 400\text{ cm}^{-1}$ ) as KBr disks on Shimadzu IR-440 spectrometer. Powder XRD investigations were carried out on a Bruker AXS D8-Advanced diffractometer at 40 kV and 40 mA with  $\text{Cu K}\alpha$  ( $\lambda=0.154\,06\text{ nm}$ ) radiation. Luminescence spectra for crystal solid samples were recorded at room temperature on an Edinburgh FLS920 phosphorimeter. Thermogravimetry analyses (TGA) were performed on an automatic simultaneous thermal analyzer (DTG-60, Shimadzu) under a flow of  $\text{N}_2$  at a heating rate of  $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$  between ambient temperature and  $800\text{ }^\circ\text{C}$ .

### 1.2 Synthesis of complex 1

A mixture of  $\text{Nd}_2(\text{CO}_3)_3$  (0.234 g, 0.5 mmol), sodium oxalate (0.067 g, 0.5 mmol) and  $\text{H}_2\text{O}$  (10 mL) to was stirred for 30 min in air and then sealed in a 23 mL Teflon reactor and kept under autogenous pressure at  $180\text{ }^\circ\text{C}$  for 72 h. The mixture was cooled to room temperature at a rate of  $5\text{ }^\circ\text{C} \cdot \text{h}^{-1}$ , and block colorless crystals were obtained in a yield of 68% based on Nd. Elemental analysis (%) calcd. for **1**

( $\text{C}_4\text{H}_{10}\text{Nd}_2\text{O}_{15}$ ), C, 8.18; H, 1.70; N, 2.39. Found(%): C, 8.23; H, 1.66; N, 2.41. Main IR frequencies (KBr,  $\text{cm}^{-1}$ ): 3 418(vs), 1 610(vs), 1 513(w), 1 479(m), 1 403(s), 1 318(s), 1 175(m), 1 043(s), 929(w), 845(m), 771(m), 692(w), 573(w), 518(w), 477(w), 422(w).

### 1.3 Crystal structure determination

A single crystal with dimensions of  $0.30\text{ mm} \times 0.28\text{ mm} \times 0.27\text{ mm}$  was mounted on a glass fiber for data collection which was performed on a Bruker Smart Apex II CCD diffractometer operating at 50 kV and 30 mA using  $\text{Mo K}\alpha$  radiation ( $\lambda=0.071\,073\text{ nm}$ ) at room temperature. In the range of  $2.77^\circ < \theta < 26.10^\circ$ , a total of 2868 reflections were collected, of which 662 were unique ( $R_{\text{int}}=0.121\,5$ ) and 450 observed ones ( $I>2\sigma(I)$ ) were used in the succeeding structure calculations. Data collection and reduction were performed using the APEX II software<sup>[7]</sup>. Multi-scan absorption corrections were applied for all the data sets using the SADABS<sup>[7]</sup>. The structure was solved by direct methods and refined by full matrix least squares on  $F^2$  using the SHELXTL program package<sup>[8]</sup>. All non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms attached to carbon were placed in geometrically idealized positions and refined using a riding model. O2W is disordered and it is split into two sets of positions, with occupancy ratios of 0.5:0.5. Water H atoms were tentatively located in difference Fourier maps and were refined with distance restraints of  $\text{O-H}=0.085\text{ nm}$  and  $\text{H}\cdots\text{H}=0.138\text{ nm}$ , with an standard deviation of  $0.001\text{ nm}$ , and with  $U_{\text{iso}}(\text{H})=1.5U_{\text{eq}}(\text{O})$ . The final  $R=0.054\,4$  and  $wR=0.222\,1$  ( $w=1/[\sigma^2(F_o^2)+(0.164\,9P)^2+1.680\,1P]$ , where  $P=(F_o^2+2F_c^2)/3$ ) for 450 observed reflections with  $I>2\sigma(I)$ .  $S=1.059$ ,  $(\Delta/\sigma)_{\text{max}}=0.000$ . Crystal parameters and details of the data collection and refinement are given in Table 1. Selected bond lengths and angles are given in Table 2. H-bonding parameters are given in Table 3.

CCDC: 917863.

## 2 Results and discussion

### 2.1 IR spectra

The IR spectra of complex **1** shows broad bands in the  $3\,418\text{ cm}^{-1}$ , which may be assigned to the  $\nu(\text{O-H})$

**Table 1** Crystal data and structure refinements of complex **1**

Empirical formula	C <sub>4</sub> H <sub>10</sub> Nd <sub>2</sub> O <sub>15</sub>	<i>Z</i>	4
Formula weight	586.60	$\mu$ / mm <sup>-1</sup>	8.604
Temperature / K	298(2)	<i>D<sub>c</sub></i> / (g·cm <sup>-3</sup> )	3.231
Size / mm	0.30×0.28×0.27	<i>F</i> (000)	1 096
$\theta$ range for data collection / (°)	2.77 to 26.10	Reflections collected	2 868
Crystal system	Orthorhombic	Independent reflections ( <i>R<sub>int</sub></i> )	662 (0.121 5)
Space group	<i>Cmcm</i>	Goodness of fit on <i>F</i> <sup>2</sup>	1.062
<i>a</i> / nm	1.469 02(15)	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> ( <i>I</i> > 2σ( <i>I</i> ))	0.054 4, 0.222 1
<i>b</i> / nm	0.848 00(10)	<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> (all data)	0.072 4, 0.246 1
<i>c</i> / nm	0.968 01(11)	(Δρ) <sub>max</sub> , (Δρ) <sub>min</sub> / (e·nm <sup>-3</sup> )	231.3, -183.9
<i>V</i> / nm <sup>3</sup>	1.205 9(2)		

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

Nd1-O1W	0.241(2)	Nd1-O1	0.245 1(9)	Nd1-O2	0.248 6(8)
Nd1-O3 <sup>ii</sup>	0.251 1(4)	Nd1-O2 <sup>i</sup>	0.262 0(8)		
O1W-Nd1-O1	146.1(6)	O1W-Nd1-O1 <sup>i</sup>	142.8(5)	O1-Nd1-O1 <sup>i</sup>	67.5(4)
O1-Nd1-O2 <sup>i</sup>	139.9(3)	O1W-Nd1-O2	70.2(6)	O2 <sup>ii</sup> -Nd1-O2	143.3(5)
O1W-Nd1-O3 <sup>iii</sup>	112.5(6)	O1-Nd1-O3 <sup>ii</sup>	83.6(4)	O2-Nd1-O2 <sup>iii</sup>	113.5(3)
O3 <sup>iii</sup> -Nd1-O2 <sup>iii</sup>	51.6(3)	O1-Nd1-O2 <sup>iii</sup>	72.53(3)	O2-Nd1-O2 <sup>ii</sup>	62.3(3)
O3 <sup>iii</sup> -Nd1-O2 <sup>ii</sup>	131.3(3)	O2 <sup>iii</sup> -Nd1-O2 <sup>i</sup>	167.9(4)	O1 <sup>i</sup> -Nd1-O2 <sup>ii</sup>	118.4(3)

Symmetry codes: <sup>i</sup> *x*, 1-*y*, -*z*; <sup>ii</sup> 0.5-*x*, 0.5-*y*, -*z*; <sup>iii</sup> 0.5-*x*, 0.5+*y*, *z*.

**Table 3** Hydrogen bond lengths and angles for complex **1**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
O(1W)-H(1W)···O(1) <sup>iii</sup>	0.085	0.199	0.283(4)	169
O(1W)-H(2W)···O(3W) <sup>i</sup>	0.085	0.222	0.306 3(3)	176
O(2W)-H(3W)···O(1W) <sup>iii</sup>	0.085	0.223	0.304(3)	160
O(2W)-H(4W)···O(1W) <sup>iii</sup>	0.085	0.223	0.304(3)	160
O(3W)-H(5W)···O(1) <sup>ix</sup>	0.085	0.219	0.301(3)	164
O(3W)-H(6W)···O(1) <sup>iii</sup>	0.085	0.219	0.301(3)	164

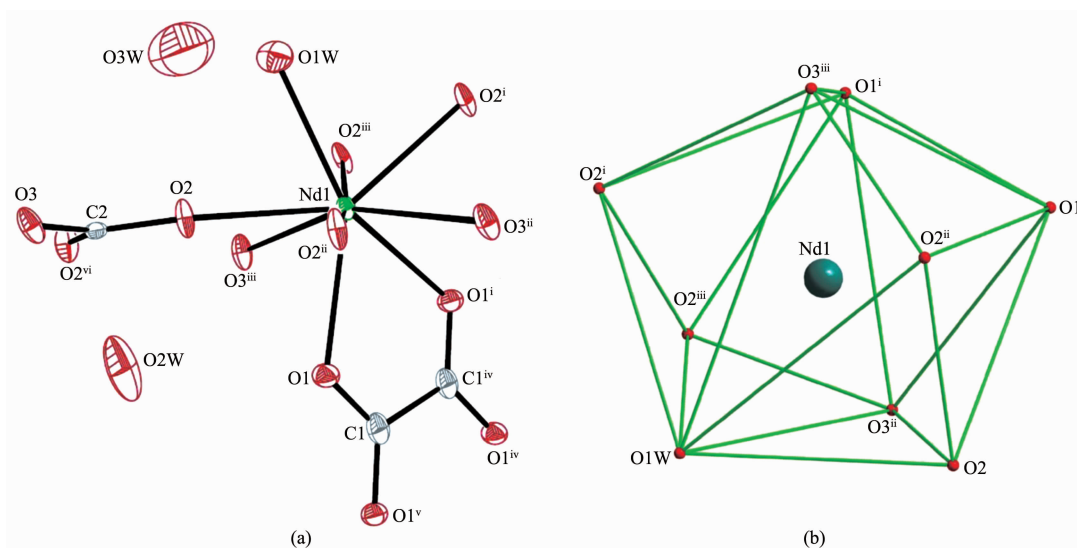
Symmetry codes: <sup>i</sup> *x*, 1-*y*, -*z*; <sup>iii</sup> 0.5-*x*, 0.5+*y*, *z*; <sup>vii</sup> 0.5-*x*, 0.5-*y*, 1-*z*; <sup>viii</sup> 0.5-*x*, 0.5-*y*, 0.5+*z*; <sup>ix</sup> 0.5-*x*, 0.5+*y*, 0.5-*z*.

stretching vibrations of the coordinated and uncoordinated water molecules. The features at 1610 and 1 479 cm<sup>-1</sup> are associated with the asymmetric (COO<sup>-</sup>) and symmetric (COO<sup>-</sup>) stretching vibrations.

## 2.2 Structure description

Complex **1** is a 3D coordination framework constructed by Nd-cb layers and ox pillars. As illustrated in Fig.1a, each Nd<sup>III</sup> center is nine-coordinated, forming a distorted tricapped trigonal-prism coordination geometry, in which six oxygen atoms from four cb ligands, two from one ox ligand and one from a water molecule to result in a [Nd10<sub>9</sub>] unit (Fig.1b). The Nd-O distances and O-Nd-O bond

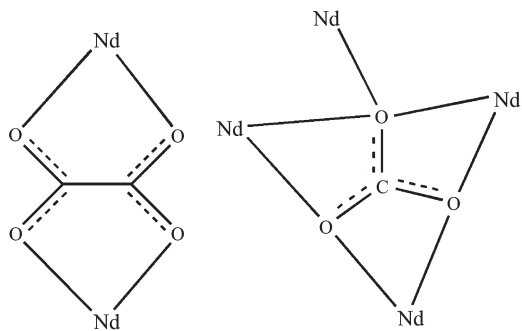
angles ranging from 0.240 (2) to 0.262 2 (8) nm and from 51.7(3)° to 167.7(4)°, respectively, all of which are within the range of those reported in other nine-coordinated Nd(III) compounds with oxygen donating ligands<sup>[9-10]</sup>. In the polymeric structure of **1**, the ox ligands adopt a μ<sub>2</sub> linear bridging and chelating mode to link two Nd(III) ions, and the cb ligands exhibit the same μ<sub>4</sub> bridging mode to link four Nd(III) ions (scheme 1). On the based on of the connection of μ<sub>4</sub> bridging cb ligands, Nd(III) centers were connected together to form a neodymium-cb layer in the *a* axis direction (Fig.2). The neodymium-cb layers are further pillared by ox struts to construct a three-dimensional



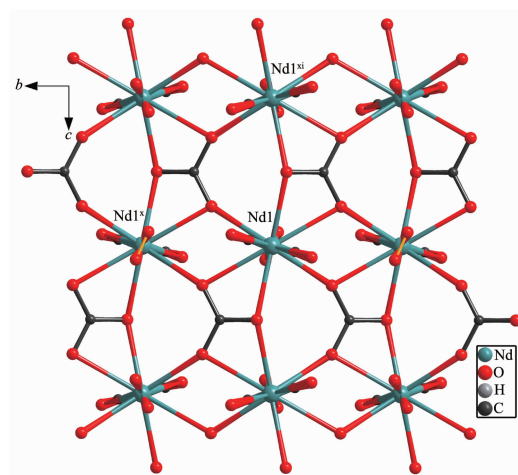
H atoms are omitted for clarity in (a); Symmetry codes: <sup>i</sup>  $x, 1-y, -z$ ; <sup>ii</sup>  $0.5-x, 0.5-y, -z$ ; <sup>iii</sup>  $0.5-x, 0.5+y, z$ ; <sup>iv</sup>  $-x, 1-y, -z$ ; <sup>v</sup>  $-x, y, z$ ; <sup>vi</sup>  $x, y, 0.5-z$

Fig.1 (a) Perspective view of the asymmetric unit of **1**; (b) Tricapped trigonal-prism (TTP) geometry surrounding the Nd(III) atom

coordination frameworks with channels of about 0.53 nm×0.41 nm along the *b* axis (Fig.3a) and 0.59 nm×0.84 nm along the *c* axis (Fig.3b), respectively. The



Scheme 1 Coordination mode of ox and cb ligands in the structure of complex **1**



Symmetry codes: <sup>x</sup>  $0.5+x, 0.5+y, z$ ; <sup>xi</sup>  $1-x, 1-y, -0.5+z$

Fig.2 View of the 2D Nd-cb layer in the *a* axis

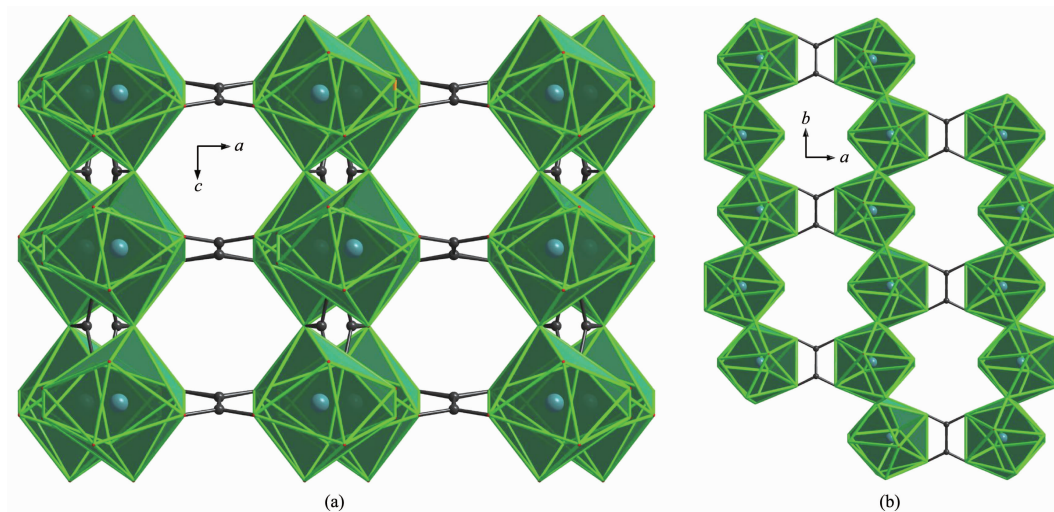


Fig.3 View of the channels in the *b* axis (a) and *c* axis (b)

solvent water molecules are located in cavities of the metal-organic framework, allowing them to participate in various  $O-H \cdots O$  hydrogen bonds with the coordinated water molecules and oxygen atoms, which help to stabilize the packing structure (Table 3). The size of the total void created by the formal removal of the coordinated and uncoordinated water molecules is  $0.284\ 2\ \text{nm}^3$ , which is about 23.6% of the unit cell volume<sup>[11]</sup>.

Better insight into this framework can be achieved by topology analysis. In this structure, if each  $\text{Nd(III)}$  cation can be regarded as a 5-connected node,  $\text{CO}_3^{2-}$  anion as a 4-connected node and  $\text{C}_2\text{O}_4^{2-}$  as a line linker, topological mode of **1** can be described as a (4,5)-connected  $\{4^4.6^2\}\{4^4.6^6\}$  topological 3D framework (Fig.4).

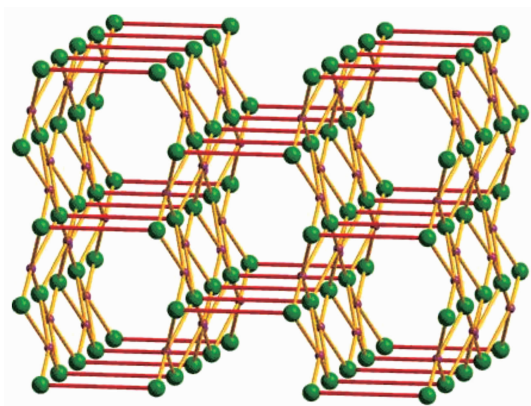


Fig.4 Topological perspective of titile compound  
Sea green balls, plum balls and red lines stand for  $\text{Nd}^{\text{III}}$  cations,  $\text{CO}_3^{2-}$  and  $\text{C}_2\text{O}_4^{2-}$  anions, respectively

### 2.3 Thermal analysis

Thermal gravimetric analyses (TGA) were carried out to examine the thermal stability of complex **1**. The samples were heated up in flowing  $\text{N}_2$  with a heating rate of  $10\ ^\circ\text{C} \cdot \text{min}^{-1}$ . The  $\text{Nd(III)}$  complex decomposed through intermediates to give the neodymium oxide as an end product ( $\text{Nd}_2\text{O}_3$ ). The TG curve of **1** shows three weight loss steps. The first corresponding the release of three free water molecules is observed from 50 to  $120\ ^\circ\text{C}$  (Obsd. 9.17%, Calcd. 9.21%). The second corresponding the escape of two coordinated water molecules is observed from 140 to  $180\ ^\circ\text{C}$  (Obsd. 6.15%, Calcd. 6.13%). The sharp weight loss above  $400\ ^\circ\text{C}$  corresponds to the decomposition of framework

structure. Finally, **1** was completely degraded into  $\text{Nd}_2\text{O}_3$  with total loss of 42.93% (Calcd. 42.66%).

### 2.4 Powder X-ray diffraction analysis

Samples of complex **1** were measured by X-ray powder diffraction at room temperature. As shown in Fig.5, the peak positions of the experimental patterns are in a good agreement with the simulated patterns, which clearly indicates the good purity of the complex.

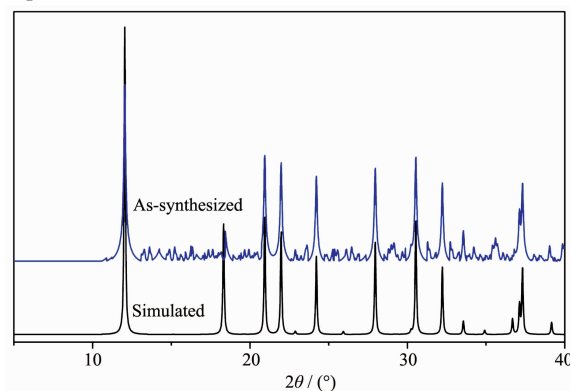


Fig.5 PXRD patterns of complex **1**

### 2.5 Luminescent properties

The emission spectrum of complex **1** in the solid state at room temperature in the NIR range upon excitation of the 325 nm depict the typical  $\text{Nd}^{\text{III}}\ 4f^3-4f^3$  transitions which have been assigned to emission from the excited  $^4F_{3/2}$  state to  $^4I_{9/2}$  (889 nm),  $^4I_{11/2}$  (1 066 nm), and  $^4I_{13/2}$  (1 382 nm) ground states (Fig.6). Compared to the pure inorganic Nd compounds, the bands are relatively broad and no crystal field splitting is resolved<sup>[12]</sup>. The clear spectrum is typical for an “antenna effect”, resulting in an energy transfer from the ligand to the lanthanide centre<sup>[13]</sup>. This demonstrates that ox and cb ligands can sensitize the  $\text{Nd}^{3+}$  luminescence in the near-IR. No ligand emission bands could be

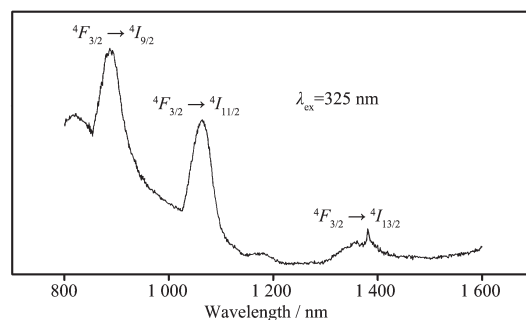


Fig.6 NIR solid-state emission spectra at room temperature for complex **1**



detected in the visible region of the spectrum leading to the assumption of relatively efficient energy transfer processes.

### 3 Conclusions

In summary, a neodymium(III) coordination polymer involving ox and cb ligands has been synthesized with the crystal products of good pure and yield and structurally characterized. The  $\text{Nd}^{3+}$  ions are bridged by  $\mu_2$ -ox and  $\mu_4$ -cb ligands to give a 3D framework including two channels. Complex **1** emits the intensely NIR luminescence in the solid state at room temperature, which may have potential applications as luminescent materials in NIR light-emitting devices.

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