

## 6,7-二氰基联吡啶啉喹啉的 $\text{Eu}^{\text{III}}$ 、 $\text{Tb}^{\text{III}}$ 配合物的合成和晶体结构

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**摘要:** 6,7-二氰基联吡啶啉喹啉(DICNQ)分别与  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ 、 $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  水热反应产生两个新的三价稀土金属-有机配合物  $[\text{Eu}(\text{DICNQ})_2(\text{NO}_3)_3] \cdot (\text{CH}_3\text{CN})_2$  (**1**) 和  $[\text{Tb}(\text{DICNQ})(\text{NO}_3)_3]_2$  (**2**)。X 射线单晶衍射研究表明化合物 **1** 结晶于单斜晶系,  $Cc$  无心空间群, 晶胞参数  $a=1.157\ 7(6)$  nm,  $b=3.193\ 4(2)$  nm,  $c=1.106\ 6(6)$  nm,  $\beta=97.633(2)^\circ$ ,  $V=4.055(4)$  nm<sup>3</sup>,  $Z=4$ ,  $M_r=984.63$ ,  $D_c=1.613$  g·cm<sup>-3</sup>,  $\mu=1.623$  mm<sup>-1</sup>,  $F(000)=1\ 952$ ,  $S=1.035$ ,  $T=293(2)$  K。最终精修结果为:  $R=0.033\ 5$ ,  $wR=0.078\ 1$ ,  $I>2\sigma(I)$  的点为 6 467 个。化合物 **2** 结晶于三斜晶系,  $P\bar{1}$  空间群, 晶胞参数  $a=0.871\ 1(3)$  nm,  $b=0.890\ 8(3)$  nm,  $c=1.544\ 9(5)$  nm,  $\alpha=80.852(9)^\circ$ ,  $\beta=84.217(9)^\circ$ ,  $\gamma=65.475(7)^\circ$ ,  $V=1.076\ 0(6)$  nm<sup>3</sup>,  $Z=1$ ,  $M_r=1\ 254.44$ ,  $D_c=1.936$  g·cm<sup>-3</sup>,  $\mu=3.356$  mm<sup>-1</sup>,  $F(000)=604$ ,  $S=1.026$ ,  $T=293(2)$  K。最终精修结果为:  $R=0.036\ 8$ ,  $wR=0.095\ 6$ ,  $I>2\sigma(I)$  的点为 3 697 个。化合物 **1** 中孤立中性分子之间具有 C-H $\cdots$ O 氢键作用, 而化合物 **2** 的晶体结构既包含配体间的  $\pi\cdots\pi$  堆积作用又有分子间 C-H $\cdots$ N 和分子内 C-H $\cdots$ O 氢键作用。

**关键词:** 晶体结构; 氢键; 金属-有机配合物;  $\pi\cdots\pi$  堆积作用

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## Syntheses and Crystal Structures of Two Europium(III) and Terbium(III) Complexes with 6,7-Dicyanodipyridoquinoline

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**Abstract:** Two lanthanide<sup>III</sup> metal-organic complexes,  $[\text{Eu}(\text{DICNQ})_2(\text{NO}_3)_3] \cdot (\text{CH}_3\text{CN})_2$  (**1**) and  $[\text{Tb}(\text{DICNQ})(\text{NO}_3)_3]_2$  (**2**), were prepared from  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and  $\text{Tb}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with 6,7-dicyanodipyridoquinoline (DICNQ) by solvothermal reactions, respectively, and characterized by single-crystal X-ray diffraction analyses. Compound **1** crystallizes in the monoclinic noncentrosymmetric space group  $Cc$ , with  $a=1.157\ 7(6)$  nm,  $b=3.193\ 4(2)$  nm,  $c=1.106\ 6(6)$  nm,  $\beta=97.633(2)^\circ$ ,  $V=4.055(4)$  nm<sup>3</sup>,  $Z=4$ ,  $M_r=984.63$ ,  $D_c=1.613$  g·cm<sup>-3</sup>,  $\mu=1.623$  mm<sup>-1</sup>,  $F(000)=1\ 952$ ,  $S=1.035$  and  $T=293(2)$  K. The final  $R=0.033\ 5$  and  $wR=0.078\ 1$  for 6 467 observed reflections with  $I>2\sigma(I)$ . Compound **2** crystallizes in the triclinic centrosymmetric space group  $P\bar{1}$ , with  $a=0.871\ 1(3)$  nm,  $b=0.890\ 8(3)$  nm,  $c=1.544\ 9(5)$  nm,  $\alpha=80.852(9)^\circ$ ,  $\beta=84.217(9)^\circ$ ,  $\gamma=65.475(7)^\circ$ ,  $V=1.076\ 0(6)$  nm<sup>3</sup>,  $Z=1$ ,  $M_r=1\ 254.44$ ,  $D_c=1.936$  g·cm<sup>-3</sup>,  $\mu=3.356$  mm<sup>-1</sup>,  $F(000)=604$ ,  $S=1.026$  and  $T=293(2)$  K. The final  $R=0.036\ 8$  and  $wR=0.095\ 6$  for 3 697 observed reflections with  $I>2\sigma(I)$ . Compound **1** is built upon isolated neutral molecules, which are connected by C-H $\cdots$ O hydrogen-bonding interactions, while compound **2** forms a packing structure by  $\pi\cdots\pi$  stacking interactions as well as intermolecular C-H $\cdots$ N and intramolecular C-H $\cdots$ O hydrogen-bonding interactions. CCDC: 857317, **1**; 857318, **2**.

**Key words:** crystal structure; hydrogen-bonding interactions; metal-organic complexes;  $\pi\cdots\pi$  stacking interactions

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## 0 Introduction

One of the most significant achievements in the inorganic and material science community over the past two decades is the emergence of functional coordination polymers (CPs)<sup>[1-3]</sup>. CPs are experiencing great growth in crystal engineering owing to their fascinating molecular structures and rich electronic, optical, catalytic, and magnetic properties<sup>[4-7]</sup>. Metal-ligand coordination may lead to the formation of discrete or extended coordination structures based on the coordination preferences of ligands and metal ions<sup>[8-9]</sup>. Additional supramolecular interactions, such as hydrogen bonding and  $\pi \cdots \pi$  stacking, can be also able to interlink discrete or low-dimensional coordination motifs into higher-dimensional architectures<sup>[10]</sup>. Thus, selection of suitable ligands is very important for the design and syntheses of functional CPs with particular structures. The 6,7-dicyanodipyridoquinaxaline (DICNQ) ligand containing aromatic nitrogen heterocycles is a good candidate for assembling coordination polymers due to its multi-coordination sites and potentials to form  $\pi \cdots \pi$  interactions and hydrogen bonds. To the best of our knowledge, only a few DICNQ metal complexes have been reported to date<sup>[10-18]</sup>. Furthermore, only two DICNQ lanthanide<sup>III</sup> complexes have been reported in our previous work<sup>[19]</sup>. Here we report syntheses and crystal structures of another two new lanthanide<sup>III</sup> complexes: [Eu(DICNQ)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] · (CH<sub>3</sub>CN)<sub>2</sub> (**1**), where discrete neutral mononuclear [Eu(DICNQ)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] moieties and CH<sub>3</sub>CN molecules are connected into a supramolecular network by hydrogen bonding interactions, and [Tb(DICNQ)(NO<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (**2**), in which isolated binuclear neutral [Tb(DICNQ)(NO<sub>3</sub>)<sub>3</sub>]<sub>2</sub> complexes are connected into a supramolecular structure by hydrogen bonding interactions and  $\pi \cdots \pi$  stacking interactions.

## 1 Experimental

### 1.1 Materials and instruments

All reagents were commercially purchased and used without further purification. IR spectra were measured in the range of 4 000~400 cm<sup>-1</sup> on a Perkin

Elmer Spectrum One FT-IR spectrometer using KBr pellets.

### 1.2 Preparation of [Eu(DICNQ)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] · (CH<sub>3</sub>CN)<sub>2</sub> (**1**)

A mixture of Eu(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (0.1 mmol, 45.0 mg), DICNQ (0.1 mmol, 28.2 mg), acetonitrile (5 mL) and methanol (2 mL) was sealed into a 25 mL polytetrafluoroethylene-lined stainless steel container under autogenous pressure and then heated at 110 °C for 3 d and cooled to 30 °C at 1.7 °C · h<sup>-1</sup>. Lightpink prismatic crystals of **1** were isolated in 28% yield based on DICNQ. IR (KBr, cm<sup>-1</sup>): 3 072 (w), 2 340 (w), 2 230 (w), 1 985 (w), 1 930 (w), 1 580 (s), 1 507 (s), 1 463 (s), 1 375 (vs), 1 330 (w), 1 305 (w), 1 260 (w), 1 223 (m), 1 140 (s), 1 110 (w), 1 071 (m), 1 027 (w), 825 (m), 743 (s), 687 (w), 617 (m), 568 (w), 440 (w), 415 (w).

### 1.3 Preparation of [Tb(DICNQ)(NO<sub>3</sub>)<sub>3</sub>]<sub>2</sub> (**2**)

A mixture of Tb(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O (0.1 mmol, 45.3 mg), DICNQ (0.1 mmol, 28.2 mg) and acetonitrile (5 mL) was sealed into a 25 mL polytetrafluoroethylene-lined stainless steel container under autogenous pressure and then heated at 110 °C for 5 d and cooled to 30 °C at 1.1 °C · h<sup>-1</sup>. Pale yellow blocky crystals of **2** were isolated in 40% yield based on Tb(NO<sub>3</sub>)<sub>3</sub> · 6H<sub>2</sub>O. IR (KBr, cm<sup>-1</sup>): 3 065 (w), 2 240 (w), 1 985 (w), 1 930 (w), 1 583 (s), 1 507 (s), 1 464 (s), 1 442 (m), 1 385 (s), 1 377 (vs), 1 328 (w), 1 301 (w), 1 263 (w), 1 219 (m), 1 138 (s), 1 110 (w), 1 073 (m), 1 024 (w), 829 (m), 812 (m), 747 (s), 687 (w), 611 (m), 579 (w), 520 (w).

### 1.4 Structure determination

Single-crystal X-ray diffraction measurements of **1** and **2** were performed on a Rigaku Mercury CCD diffractometer, using graphite-monochromatic Mo K $\alpha$  radiation ( $\lambda$ =0.071 073 nm). In **1**, a total of 14 903 reflections were collected, of which 6 831 were independent ( $R_{\text{int}}$ =0.046 7). The final  $R$ =0.033 5 and  $wR$ =0.078 1 for 6 467 observed reflections with  $I > 2\sigma(I)$ . The intensity data set was collected with an  $\omega$  scan mode at 293(2) K in the range of  $3.06^\circ < \theta < 25.50^\circ$  and reduced by the Crystal Clear software<sup>[20]</sup>. The final refinement gave  $R$ =0.036 1,  $wR$ =0.080 0 ( $w=1/[\sigma^2(F_o^2) + (0.034\ 5P)^2]$ , where  $P=(F_o^2 + 2F_c^2)/3$ ),  $S=1.035$ ,  $(\Delta/\sigma)_{\text{max}}=0.001$ ,  $(\Delta\rho)_{\text{max}}=969\ \text{e} \cdot \text{nm}^{-3}$  and  $(\Delta\rho)_{\text{min}}=-746\ \text{e} \cdot \text{nm}^{-3}$ .

In **2**, a total of 7 182 reflections were collected, of which 3 987 were independent ( $R_{\text{int}}=0.029\ 6$ ). The final  $R=0.036\ 8$  and  $wR=0.095\ 6$  for 3 697 observed reflections with  $I>2\sigma(I)$ . The intensity data set was collected with an  $\omega$  scan mode at 293(2) K in the range of  $3.27^\circ<\theta<25.50^\circ$  and reduced by the Crystal Clear software. The final refinement gave  $R=0.039\ 8$ ,  $wR=0.098\ 0$  ( $w=1/[\sigma^2(F_o^2)+(0.063\ 0P)^2+1.753\ 5P]$ ),  $S=1.026$ ,  $(\Delta/\sigma)_{\text{max}}=0.005$ ,  $(\Delta\rho)_{\text{max}}=1\ 356\ \text{e}\cdot\text{nm}^{-3}$  and  $(\Delta\rho)_{\text{min}}=-1\ 936\ \text{e}\cdot\text{nm}^{-3}$ . All structures were solved by the direct method and refined by full-matrix least-squares techniques on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were added according to theoretical models. All of the calculations were performed with Siemens SHELXTL™ version 5 package of crystallographic software<sup>[21]</sup>.

CCDC: 857317, **1**; 857318, **2**.

## 2 Results and discussion

### 2.1 Structure description and discussion

Selected bond distances and bond angles of **1** and **2** are listed in Table 1. As shown in Fig.1a, the

crystallographically asymmetric unit of **1** has two uncoordinated  $\text{CH}_3\text{CN}$  molecules and one  $[\text{Eu}(\text{DICNQ})_2(\text{NO}_3)_3]$  neutral moiety. The central  $\text{Eu}^{\text{III}}$  atom of **1** is ten-coordinated by six O atoms from three  $\eta^2\text{-O,O'}$ -chelating nitrate groups and four N atoms from two chelating DICNQ ligands. The coordination geometry around the  $\text{Eu}^{\text{III}}$  atom may be described as a distorted bicapped square antiprism with two oxygen atoms (O13, O22) in the capped positions. The Eu-O bond distances, ranging from 0.247 4(2) to 0.255 3(2) nm, are similar to those of typical  $\text{Eu}^{\text{III}}$ -nitrate compounds<sup>[22]</sup>. The Eu-N bond distances from 0.257 0(3) to 0.261 4(3) nm are in common values, and obviously longer than the Eu-O bond lengths. The Flack  $x$  parameter of **1** is 0.018(11), indicating a correct absolute structure.

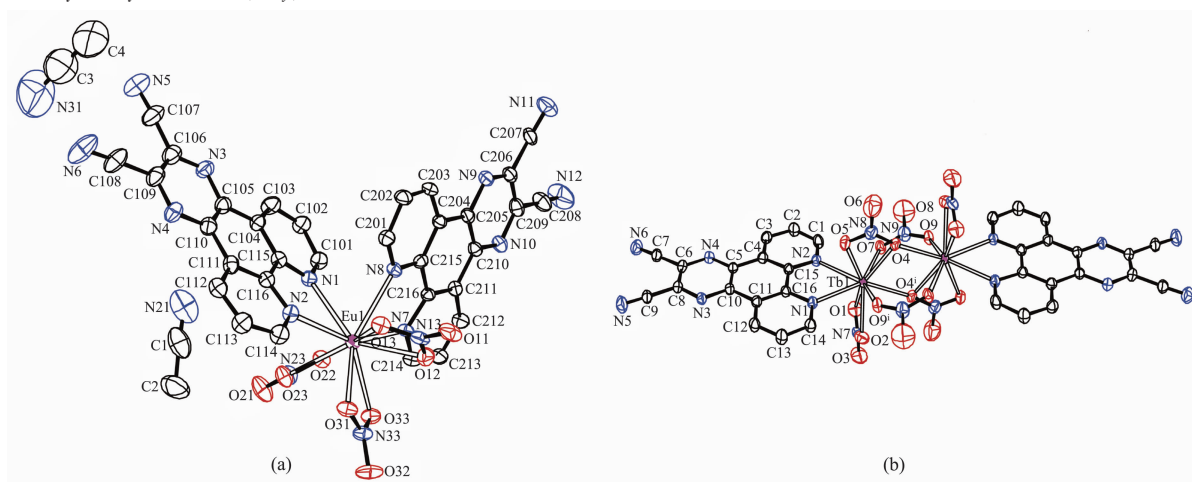
As shown in Fig.1b, the central  $\text{Tb}^{\text{III}}$  atom of compound **2** assumes a distorted monocapped square antiprism geometry with one oxygen atom (O4) in the capped position, and is ligated by two nitrogen atoms from a DICNQ ligand and seven O atoms from five nitrate groups. The mean Tb-N bond distance of 0.253 7(5) nm is comparable to those found in

Table 1 Selected bond lengths (nm) and bond angles ( $^\circ$ ) for **1** and **2**

1					
Eu(1)-O(33)	0.247 4(2)	Eu(1)-O(31)	0.251 4(2)	Eu(1)-N(2)	0.259 6(3)
Eu(1)-O(12)	0.248 6(3)	Eu(1)-O(22)	0.255 3(2)	Eu(1)-N(8)	0.261 4(3)
Eu(1)-O(23)	0.249 0(2)	Eu(1)-N(7)	0.257 0(3)		
Eu(1)-O(13)	0.249 2(2)	Eu(1)-N(1)	0.258 6(3)		
O(33)-Eu(1)-O(12)	72.77(7)	O(33)-Eu(1)-N(7)	78.80(7)	O(23)-Eu(1)-N(2)	68.74(8)
O(33)-Eu(1)-O(23)	74.71(8)	O(12)-Eu(1)-N(7)	72.33(8)	O(13)-Eu(1)-N(2)	69.50(8)
O(12)-Eu(1)-O(23)	142.70(8)	O(23)-Eu(1)-N(7)	118.32(7)	O(31)-Eu(1)-N(2)	83.96(8)
O(33)-Eu(1)-O(13)	109.20(8)	O(13)-Eu(1)-N(7)	114.55(7)	O(22)-Eu(1)-N(2)	107.95(8)
O(12)-Eu(1)-O(13)	51.84(8)	O(31)-Eu(1)-N(7)	125.38(7)	N(7)-Eu(1)-N(2)	150.55(8)
O(23)-Eu(1)-O(13)	126.54(8)	O(22)-Eu(1)-N(7)	68.41(7)	N(1)-Eu(1)-N(2)	62.93(8)
O(33)-Eu(1)-O(31)	51.42(7)	O(33)-Eu(1)-N(1)	140.61(7)	O(33)-Eu(1)-N(8)	134.39(8)
O(12)-Eu(1)-O(31)	72.56(8)	O(12)-Eu(1)-N(1)	139.00(8)	O(12)-Eu(1)-N(8)	72.48(8)
O(23)-Eu(1)-O(31)	73.08(8)	O(23)-Eu(1)-N(1)	78.29(9)	O(23)-Eu(1)-N(8)	144.82(8)
O(13)-Eu(1)-O(31)	70.76(8)	O(13)-Eu(1)-N(1)	109.86(9)	O(13)-Eu(1)-N(8)	69.26(8)
O(33)-Eu(1)-O(22)	71.07(8)	O(31)-Eu(1)-N(1)	142.38(8)	O(31)-Eu(1)-N(8)	137.78(7)
O(12)-Eu(1)-O(22)	130.49(8)	O(22)-Eu(1)-N(1)	69.66(8)	O(22)-Eu(1)-N(8)	112.78(8)
O(23)-Eu(1)-O(22)	50.54(8)	N(7)-Eu(1)-N(1)	89.60(8)	N(7)-Eu(1)-N(8)	63.08(7)
O(13)-Eu(1)-O(22)	177.03(8)	O(33)-Eu(1)-N(2)	128.95(8)	N(1)-Eu(1)-N(8)	66.53(8)
O(31)-Eu(1)-O(22)	107.73(8)	O(12)-Eu(1)-N(2)	121.00(8)	N(2)-Eu(1)-N(8)	94.36(8)

Continued Table 1

2					
Tb(1)-O(7)	0.227 3(4)	Tb(1)-O(5)	0.233 7(4)	Tb(1)-O(4)	0.252 0(4)
Tb(1)-O(4) <sup>i</sup>	0.228 1(3)	Tb(1)-O(1)	0.237 5(4)	Tb(1)-N(1)	0.250 7(4)
Tb(1)-O(9) <sup>i</sup>	0.227 9(4)	Tb(1)-O(2)	0.245 3(4)	Tb(1)-N(2)	0.256 2(4)
O(7)-Tb(1)-O(4) <sup>i</sup>	75.69(13)	O(9) <sup>i</sup> -Tb(1)-O(2)	72.39(15)	O(5)-Tb(1)-O(4)	52.91(12)
O(7)-Tb(1)-O(9) <sup>i</sup>	138.42(13)	O(5)-Tb(1)-O(2)	141.87(15)	O(1)-Tb(1)-O(4)	148.90(15)
O(4) <sup>i</sup> -Tb(1)-O(9) <sup>i</sup>	77.20(13)	O(1)-Tb(1)-O(2)	52.38(17)	O(2)-Tb(1)-O(4)	136.30(14)
O(7)-Tb(1)-O(5)	89.73(15)	O(7)-Tb(1)-N(1)	139.17(13)	N(1)-Tb(1)-O(4)	122.38(13)
O(4) <sup>i</sup> -Tb(1)-O(5)	127.34(14)	O(4) <sup>i</sup> -Tb(1)-N(1)	142.52(13)	O(7)-Tb(1)-N(2)	74.96(13)
O(9) <sup>i</sup> -Tb(1)-O(5)	82.31(14)	O(9) <sup>i</sup> -Tb(1)-N(1)	78.10(13)	O(4) <sup>i</sup> -Tb(1)-N(2)	143.40(13)
O(7)-Tb(1)-O(1)	82.41(17)	O(5)-Tb(1)-N(1)	76.00(14)	O(9) <sup>i</sup> -Tb(1)-N(2)	139.14(13)
O(4) <sup>i</sup> -Tb(1)-O(1)	82.78(15)	O(1)-Tb(1)-N(1)	88.49(16)	O(5)-Tb(1)-N(2)	73.78(14)
O(9) <sup>i</sup> -Tb(1)-O(1)	124.46(16)	O(2)-Tb(1)-N(1)	71.27(14)	O(1)-Tb(1)-N(2)	72.12(15)
O(5)-Tb(1)-O(1)	145.89(15)	O(7)-Tb(1)-O(4)	71.64(13)	O(2)-Tb(1)-N(2)	107.79(15)
O(7)-Tb(1)-O(2)	128.04(15)	O(4) <sup>i</sup> -Tb(1)-O(4)	74.56(13)	N(1)-Tb(1)-N(2)	64.38(13)
O(4) <sup>i</sup> -Tb(1)-O(2)	74.63(14)	O(9) <sup>i</sup> -Tb(1)-O(4)	71.12(13)	O(4)-Tb(1)-N(2)	115.46(13)

Symmetry code: 2: <sup>i</sup> -x, 2-y, -z.H atoms are omitted for clarity; Symmetry code: <sup>i</sup> -x, 2-y, -z.Fig.1 (a) Molecular structures of **1** and (b) **2** with 30% thermal ellipsoids

[Tb(terpy)(acac)(NO<sub>3</sub>)<sub>2</sub>]<sup>[23]</sup>, and the Tb-O bond distances from 0.227 7(3) to 0.252 2(3) nm are in common values. Two [Tb(DICNQ)(NO<sub>3</sub>)<sub>3</sub>] components form a neutral binuclear molecule, where each Tb<sup>III</sup> atom is  $\eta^2$ -O,O'-chelated by one nitrato group. Two Tb<sup>III</sup> centers in the same molecule, with a separation of 0.382 28(1) nm, are bridged by four nitrato groups, two of which are in a  $\mu$ , $\eta^2$ -O,O'-bridging mode and the others in a  $\mu$ , $\eta^2$ -O,O,O'-bridging one. To our best knowledge, there was only one reported binuclear lanthanide compound with such two bridging nitrato

groups in the same molecule<sup>[24]</sup>.

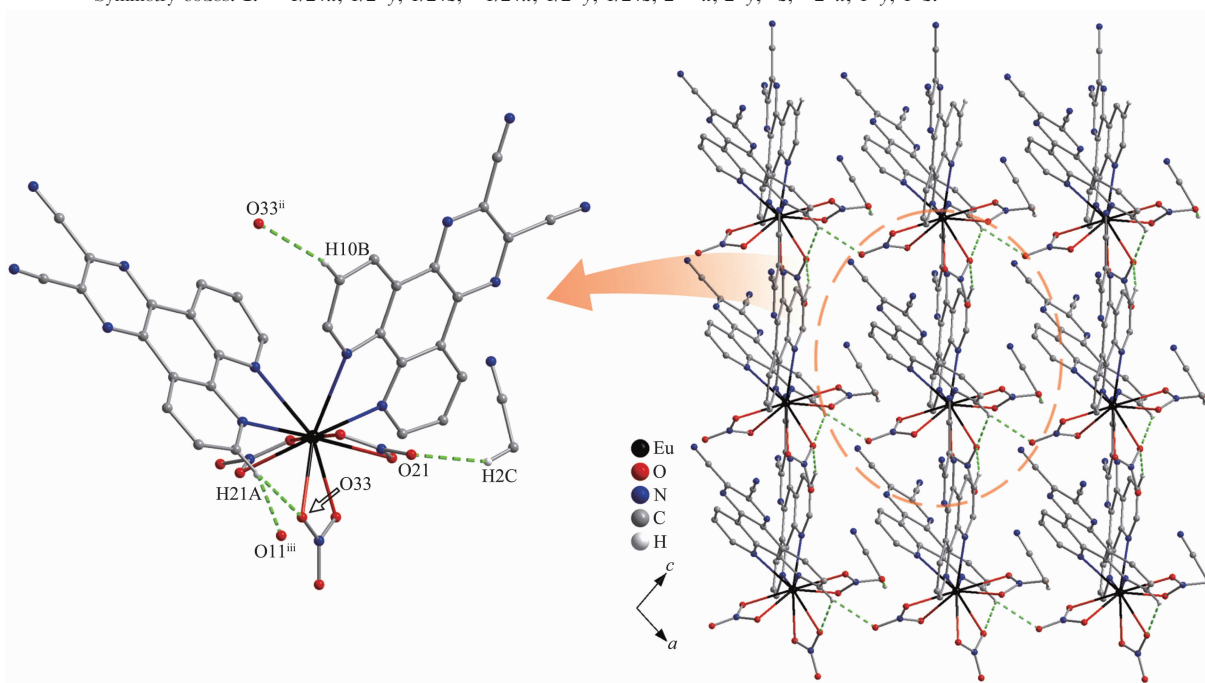
In both structures of **1** and **2**, the cyano groups of each DICNQ ligand remain uncoordinated and the 2,9-dimethyl-1,10-phenanthroline parts adopt a chelating fashion, which is similar to the case found in reported DICNQ compounds<sup>[12]</sup>. The atoms of each DICNQ ligand are nearly coplanar with a maximum deviation of atom being about 0.030 7 nm in **1** and 0.010 9 nm in **2**.

The crystal structure of **1** involves three kinds of intermolecular and one kind of intramolecular C-H...

Table 2 Hydrogen-bond geometry for **1** and **2**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠D-H...A / (°)
<b>1</b>				
C(2)-H(2C)···O(21)	0.096	0.247	0.332 9(7)	150
C(102)-H(10B)···O(33) <sup>ii</sup>	0.093	0.251	0.338 8(4)	158
C(214)-H(21A)···O(11) <sup>iii</sup>	0.093	0.235	0.315 6(4)	146
Intra C(214)-H(21A)···O(33)	0.093	0.250	0.312 3(4)	125
<b>2</b>				
C(12)-H(12A)···N(5) <sup>iv</sup>	0.093	0.255	0.346 6(9)	170
Intra C(1)-H(1A)···O(7)	0.093	0.229	0.291 6(8)	124
Intra C(14)-H(14A)···O(9) <sup>i</sup>	0.093	0.241	0.299 5(7)	121

Symmetry codes: **1**: <sup>i</sup> -1/2+x, 1/2-y, 1/2+z; <sup>iii</sup> 1/2+x, 1/2-y, 1/2+z; <sup>i</sup> -x, 2-y, -z; <sup>iv</sup> 2-x, 1-y, 1-z.



Green lines denote the C-H...O hydrogen bonds; H atoms without hydrogen-bonding interactions are omitted; There are no obviously intermolecular  $\pi$ -stacking interactions; Symmetry code: <sup>ii</sup> -1/2+x, 1/2-y, 1/2+z; <sup>iii</sup> 1/2+x, 1/2-y, 1/2+z

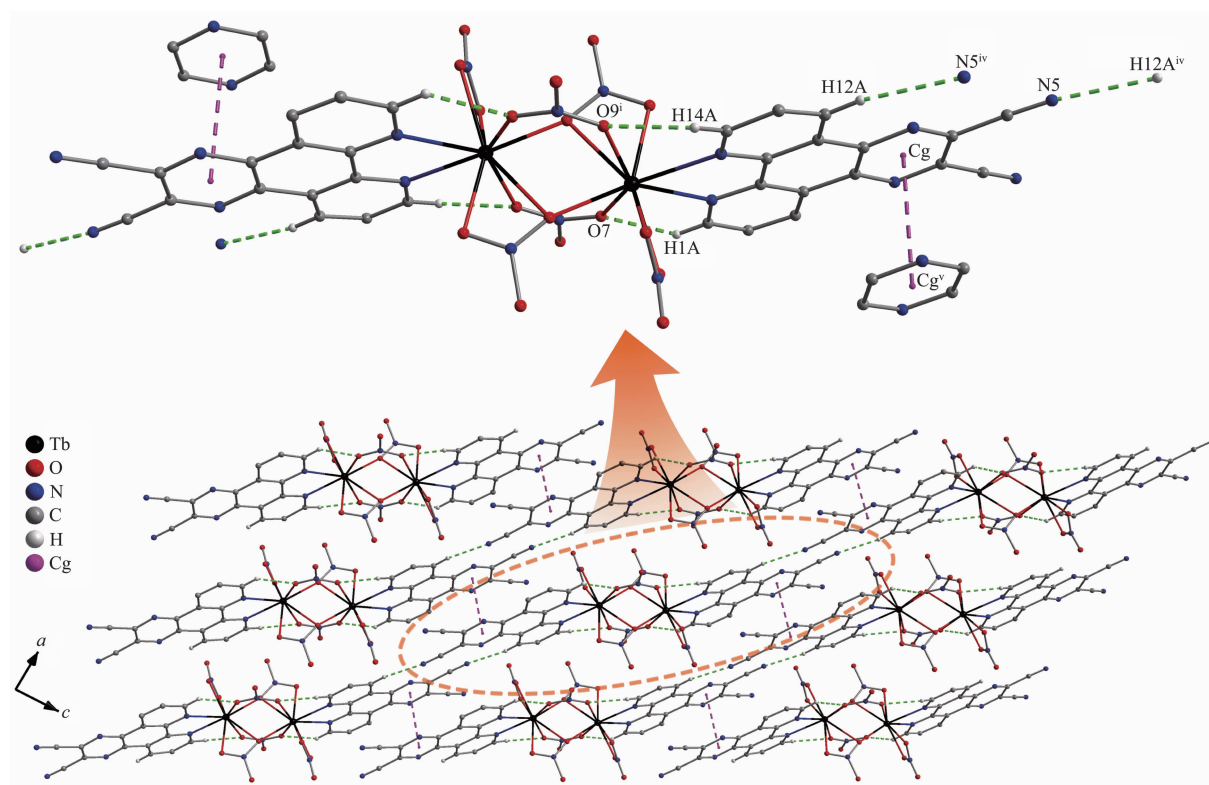
Fig.2 A 2D hydrogen-bonding sheet of **1** viewed along the *b* direction

O hydrogen bonds (Table 2 and Fig.2). The [Eu(DICNQ)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] units of **1** connect to each other via three intermolecular C-H...O hydrogen bonds, with two H21A...O11<sup>iii</sup> distances of about 0.235 nm and one H10B...O33<sup>ii</sup> distance of about 0.251 nm. The angles of these hydrogen bonds range from ~146° to 158°. Each [Eu(DICNQ)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] unit of **1** hydrogen-bonds to one CH<sub>3</sub>CN unit, with the H2C...O21 distance of about 0.247 nm and a corresponding angle at the H atom of about 150°. The third component of the supramolecular interaction in this structure is intramolecular C-H...O hydrogen bonds in the

[Eu(DICNQ)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] moieties, with the H21A...O33 distance of about 0.250 nm and a corresponding angle at the H atom of about 125° (Table 2). There is no obviously intermolecular  $\pi$ -stacking interactions. The discrete mononuclear [Eu(DICNQ)<sub>2</sub>(NO<sub>3</sub>)<sub>3</sub>] moieties and CH<sub>3</sub>CN molecules in **1** are connected through these hydrogen bonding interactions into a 2D supramolecular sheet in the *ac* plane. Such sheets are further stacked along the *b* direction to yield the whole crystal structure of **1**.

Nitrato groups are useful building blocks for the construction of lanthanide compounds through





$\pi$ - $\pi$  stacking interactions (Cg is the center of the pyrazine ring in the DICNQ ligand) being shown as purple lines and intermolecular C-H $\cdots$ N (cyano) and intramolecular C-H $\cdots$ O hydrogen bonds being shown as green lines; H atoms without hydrogen bonding interactions are omitted for clarity; Symmetry codes: <sup>i</sup>  $-x, 2-y, -z$ ; <sup>iv</sup>  $2-x, 1-y, 1-z$ ; <sup>v</sup>  $1-x, 1-y, 1-z$

Fig.3 An interaction scheme of **2** viewed along the  $b$  direction

bridging the metal cations. The most intriguing feature in the structure of complex **2** is the success in using nitrate groups as  $\mu, \eta^2\text{-O, O'}$ - and  $\mu, \eta^2\text{-O, O, O'}$ -bridging ligands and a hydrogen-bond acceptor, simultaneously. The 3D supramolecular network in **2** is stabilized by  $\pi \cdots \pi$  stacking interactions, intermolecular C-H $\cdots$ N (cyano) hydrogen bonds and intramolecular C-H $\cdots$ O hydrogen-bonding interactions. As shown in Fig.3, significant overlap occurs between the adjacent quinoxaline groups of DICNQ ligands with a dihedral angle of  $0.000(3)^\circ$ . The  $\pi_{\text{Cg}} \cdots \pi_{\text{Cg}}^{\text{v}}$  distance of pyrazine rings from the antiparallel DICNQ ligands is about  $0.350\ 9\ \text{nm}$ . There are two different intramolecular C-H $\cdots$ O hydrogen bonds in each  $[\text{Tb}(\text{DICNQ})(\text{NO}_3)_3]$  neutral component, with one H14A $\cdots$ O9<sup>i</sup> distance of about  $0.241\ \text{nm}$  and the other H1A $\cdots$ O7 distance of about  $0.229\ \text{nm}$ . The angles at the H atom of these hydrogen bonds range from  $\sim 121^\circ$  to  $124^\circ$ . The third component of the supramolecular interaction in this

structure is intermolecular C-H $\cdots$ N (cyano) hydrogen bonds, with the H12A $\cdots$ N5<sup>iv</sup> distance of about  $0.255\ \text{nm}$  and a corresponding angle at the H atom of about  $170^\circ$ . The hydrogen-bond data of **2** are shown in Table 2.

Compound **1** and **2** were produced with the same ratio of lanthanide nitrate and DICNQ (1:1), but they have very different structural features, shown as below Table 3. This should be due to the different mineralization of reaction solvents.

In conclusion, we have successfully synthesized and structurally characterized one  $\text{Eu}^{\text{III}}$  and one  $\text{Tb}^{\text{III}}$  complexes with DICNQ ligands. Single-crystal X-ray diffraction analyses reveal that these two compounds have very different structural characteristics in numbers of metal nuclear in each metal complex, coordination spheres of the lanthanide centers, bridging modes of coordinated nitrate groups, and supramolecular interactions. Our work presents again

Table 3 Different structural features of 1 and 2

	Compound 1	Compound 2
Molecular structure	Acentric; Mononuclear	Central; Binuclear
Coordination sphere of metal atom (s)	Distorted bicapped square antiprism	Distorted monocapped square antiprism
Coordination modes of nitrate groups (numbers per mol)	$\eta^2-O,O'$ -chelating (3)	$\eta^2-O,O'$ -chelating (1); $\mu,\eta^2-O,O'$ -bridging (2); $\mu,\eta^2-O,O,O'$ -bridging (2)
Supramolecular interactions	Intramolecular C-H $\cdots$ O; Intermolecular C-H $\cdots$ O	Intramolecular C-H $\cdots$ O; Intermolecular C-H $\cdots$ N; $\pi\cdots\pi$ stacking interactions

another example, which shows the important influence of reaction solvents on the coordination structure.

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