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Synthesis, Crystal Structure, and Porosity Calculation of Novel Lanthanide Coordination Polymers Involving Naphthalene-1,4,5,8-Tetra-Carboxylate as Ligand[1]

W. Tao, J. M. Liu*, Y. J. Zheng, and C. Y. Sun

The School of Chemical and Biological Engineering, University of Science and Technology Beijing, Beijing, 100083 P.R. China

**e-mail: liujm@ustb.edu.cn*

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Abstract—Two isostructural microporous coordination polymers of 1,4,5,8-naphthalenetetracarboxylic acid (H_4Ntc) with rare earth metals were obtained in gel diffusion method, with chemical formulae $[Y_2(Ntc)_{1.5}(H_2O)_5] \cdot 6H_2O$) (**I**) and $[Er_2(Ntc)_{1.5}(H_2O)_5] \cdot 6H_2O$ (**II**). They crystallized in the monoclinic system, space group $P2_1/c$. The crystal structure study revealed two crystallographically independent La^{3+} ions, and two crystallographically independent ligands were in the structure of the compounds **I** and **II**. Their crystal structure were 3D and exhibited some large channels with rectangular sections spreading along the *x* axis. The porosity has been calculated using Connolly's algorithm after the crystallization water molecules were formally removed.

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INTRODUCTION

Coordination polymers, also known as metal-organic coordination networks (MOCNs) or metal-organic frameworks (MOFs), extend "infinitely" into one, two or three dimensions (1D, 2D or 3D) via metal-ligand bonding [1–5]. For a few years, there is a considerably interest in this field because of its potential applications in many fields including ion exchange, adsorption catalysis, fluorescence, magnetism, and gas storage [6–13]. Consequently, numerous new compounds have been produced mostly by using appropriate organic ligands, especially bridging ligands containing multi-dentate oxygen with the metal centers. As functional metal centers, rare earth metals are attracting more and more attention from synthesis chemists for their fantastic coordination properties and special chemical characteristics arising from 4*f* electrons and the propensity to form isostructural complexes [14–18].

1,4,5,8-Naphthalenetetracarboxylic acid (H_4Ntc) is a rigid ligand with multiple coordination sites and thus it can be certainly a candidate for providing novel coordination polymer structures. So far, there are just a few reports on metal-organic compounds containing ligand H_4Ntc [19, 20]. The first two lanthanide based coordination polymers involving Ntc^{4-}, namely $Gd(HNtc)(H_2O)_4 \cdot 9H_2O$ and $Er_4(Ntc)_3(H_2O)_{10} \cdot 12H_2O$, have been reported in [21]. Two new compounds with respective chemical formulae $La_2(Ntc)(C_2O_4)(H_2O)_6 \cdot 4H_2O$ and $LaNa(Ntc)(H_2O)_7 \cdot 4H_2O$ have also been synthesized [22].

Two microporous coordination polymers of H_4Ntc with rare earth metals have been reported in this paper, with chemical formulae $[Y_2(Ntc)_{1.5}(H_2O)_5] \cdot 6H_2O$ (**I**) and $[Er_2(Ntc)_{1.5}(H_2O)_5] \cdot 6H_2O$ (**II**). As far as we know, **II** has been reported in [21], and **I** is the first rare earth containing coordination polymers involving this ligand. The synthesis, crystal structures and the estimated porosity of the compound **I** have been described in detail.

EXPERIMENTAL

All reagents, 1,4,5,8-naphtalene-tetra-carboxylic acid (H_4Ntc) and lanthanide oxides were reagent grade and used without further purification. Tetra-sodium naphtalenetetra-carboxylate salt and both lanthanide chlorides were prepared by the similar methods according to literature reported [23, 24]. Both yields of the synthesis were close to 100%. The productions were stored in a desiccator.

Synthesis I and II. The coordination polymers were obtained by the slow diffusion of de-ionized aqueous solutions of lanthanum chloride and naphthalene-tetra-carboxylate sodium salts, through an agarose gel bridge, in a U-shaped tube. Compounds **I** and **II** were

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Table 1. Crystal data and structure refinement for compounds **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	826.24	982.95
Crystal system; space group	Monoclinic; $P2_1/c$	Monoclinic; $P2_1/c$
Unit cell dimensions:		
a, Å	9.8475(8)	9.8605(6)
b, Å	29.058(2)	29.210(16)
c, Å	10.8151(9)	10.8652(6)
β, deg	92.3110(10)	92.203(10)
Volume, Å^3	3092.2(4)	
Z	4	4
ρ_{calcd}, mg/m^3	1.772	2.129
F(000)	1680	1912
Absorption coefficient, mm^{-1}	3.789	5.488
Crystal size, mm	0.20 × 0.16 × 0.14	0.27 × 0.13 × 0.08
θ Range for data collection, deg	2.00–27.63	2.07–27.59
Limiting indices	$-12 \le h \le 10$, $-38 \le k \le 33$, $-11 \le l \le 14$	$-12 \le h \le 9$, $-37 \le k \le 36$, $-13 \le l \le 14$
Reflections collected/unique (R_{int})	18634/7201 (0.0589)	18676/7094 (0.0486)
Completeness to θ = 27.57°, %	98.9	99.1
Absorption correction	Semi-empirical from equivalents	
Max and min transmission	0.6190 and 0.5178	0.6679 and 0.3189
Data/restraints/parameters	7201/33/483	7094/57/483
Goodness-of-fit on F^2	1.055	1.047
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0474$, $wR_2 = 0.1003$	$R_1 = 0.0366$, $wR_2 = 0.0813$
R indices (all data)	$R_1 = 0.0856$, $wR_2 = 0.1112$	$R_1 = 0.0520$, $wR_2 = 0.0879$
Largest diff. peak and hole, e Å^{-3}	0.810 and –0.567	1.828 and –1.121

obtained in a 0.3% agarose gel. After several weeks, yellow transparent single crystals were obtained.

For $C_{21}H_{28}O_{23}Y_2$ (**I**)

anal. calcd., %:	C, 30.50;	H, 3.39;	O, 44.54.
Found, %:	C, 30.52;	H, 4.00;	O, 44.51.

For $C_{21}H_{28}O_{23}Er_2$ (**II**)

anal. calcd., %:	C, 26.64;	H, 2.85;	O, 37.44.
Found, %:	C, 26.67;	H, 2.86;	O, 37.40.

The IR spectrum had been observed for compounds **I** and **II**. It clearly showed vibration bands characteristic of the –(O–C–O)– groups around 1566 and 1447 cm^{-1} confirming the presence of carboxylate groups.

X-ray structure determination. Single-crystal X-ray diffraction studies of complexes **I** and **II** were performed on a Bruker Smart Apex II CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam. The data collections were performed with MoK_α radiation ($\lambda = 0.71073$ Å). The crystal data collection were performed at 296(2) (**I**) and 150(2) K (**II**), respectively. The crystallographic data and experimental details for the structural analyses of compounds **I** and **II** were summarized in Table 1. All structures were solved by the direct methods using SHELXS program and were refined with SHELXL of the SHELXTL-97 package [23]. The final refinements were performed by full-matrix least-squares methods on F^2 with anisotropic thermal parameters for non-hydrogen atoms. All hydrogen atoms were included in calculated positions and were refined with isotropic thermal parameters riding on those of the parent atoms. The

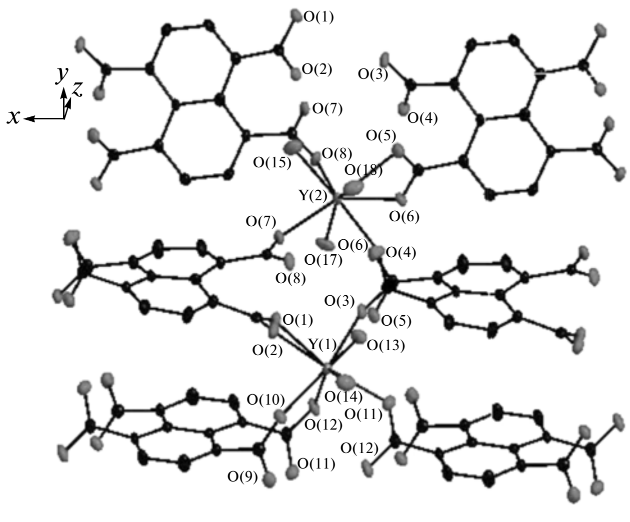
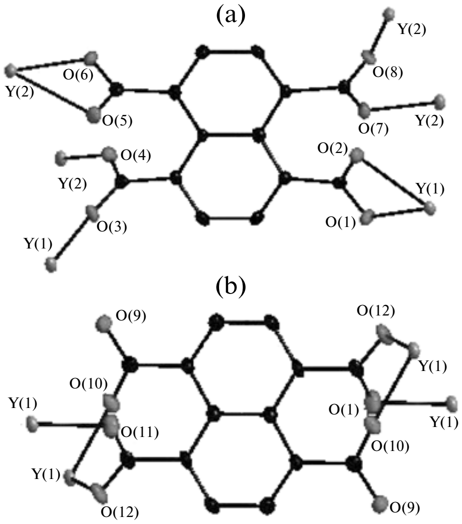


Fig. 1. A view of the environment of Y^{3+} ions in $Y_2(Ntc)_{1.5}(H_2O)_5 \cdot 6H_2O$ (**I**).


(a)

(b)

Fig. 2. Coordination modes of the Ntc ligand in $Er_2(Ntc)_{1.5}(H_2O)_5 \cdot 6H_2O$ (**II**).

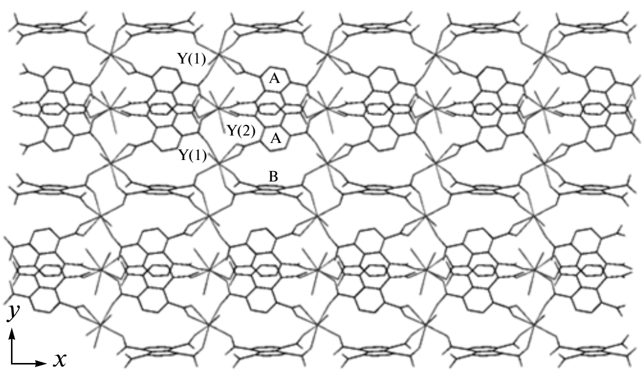


Fig. 3. View along the *z* axis of compound **I**.

crystal structures of compounds **I** and **II** have been deposited at the Cambridge Crystallographic Data Centre (nos. 800394 (**I**) and 800391 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

Single crystal X-ray structural analysis shows that there are two crystallographically independent Y^{3+} ions in structure of **I** (Fig. 1). The first one (Y(1)) is eight coordinated by two oxygen atoms from coordination water molecules and six oxygen atoms of four carboxylate groups (a bidentate one and three unidentate) from four different ligands. Its coordination polyhedron can be described as a slightly distorted bicapped trigonal-prizm. The second Y^{3+} ion (Y(2)) is also eight-coordinated. Three of the oxygen atoms are from coordination water molecules, and the five others are belonging to four carboxylate groups from four different ligands (one chelating bidentate, one of bridging bidentate and two monodentate). The coordination polyhedron is also best described by a distorted bicapped trigonal-prizm.

There are also two crystallographically independent ligands. The first Ntc ligand (type A) acts as a μ_6-bridge linking six Y^{3+} ions (Fig. 2a). For type A, each of two carboxylate groups adopts a bidentate chelating mode, chelating one Y^{3+} ion, whereas each of the other two adopts a bidentate bridging mode, coordinating to two Y^{3+} ions. The second ligand (type B) has its four carboxylate groups bound to four different Y^{3+} ions (Fig. 2b). For type B, each of two carboxylate groups adopts a bidentate bridging mode, coordinating to two Y^{3+} ions (O(12) and O(11)), whereas each of the other two adopts a monodentate bridging mode, coordinating to one Y^{3+} ion. In type B, Ntc ligand offers a chelating mode via the oxygen atoms of two neighboring carboxylate groups. The carboxylic O–Y bond distances range from 2.240 to 2.476 Å and those of the water's O–Y bonds from 2.355 to 2.402 Å. More data on selected bond lengths and angles are presented in Table 2.

The general arrangement (Fig. 3) consists of a succession, along the *x* axis, of yttrium atoms planes and organic planes. The nearest yttrium–yttrium interplane distance (Y(1)–Y(1)) is 4.8826 Å. The yttrium–yttrium interplane distance is 9.8475 Å. As shown in Fig. 3, there is one crystallographically independent organic molecule in the general position (labeled "A") and one-half located in an inversion center (labeled "B"). The coordination modes of these two organic molecules are different. The angle between the "A" and "B" Ntc naphthyl plane is about 50°. The Ntc^{4-} ligand links the Y atoms with different coordination mode to afford a 2D layer (Fig. 4) and adjacent 2D layers are further connected by the Ntc^{4-} ligands to form a 3D metal-organic framework. A view of the 3D network along the *x* axis is shown in Fig. 5. Its crystal structure presents some large channels with rectangular sections spreading along the *x* axis. The channels are full of crystallization water molecules which have been removed. As far as metallic ions are concerned, the section of the channels can be described as a slightly distorted irregular octagon. The longest side of this irregular octagon is roughly 5.7 Å long and the smallest side is 4.9 Å.

In order to evaluate the porosity of $Y_2(Ntc)_{1.5}(H_2O)_5$, we have formally removed the crystallization water molecules from the crystal structure of **I** and applied a computational method based on Connolly's algorithm which has already been described and successfully used elsewhere [21, 22, 24]. The porosity of a partially dehydrated material can be calculated on the basis of its crystal structure. Furthermore, this method allows obtaining the maximal kinetic radius a guest molecule can present for being hosted by the structure. The porosity profile (Fig. 6) reveals that the porosity radius along the *x* axis of compound $Y_2(Ntc)_{1.5}(H_2O)_5 \cdot 6H_2O$ is 2.3 Å. In this case (Fig. 6), it appears that the compound can host molecules with a kinetic radius as big as 2.3 Å. This is in perfect agreement with what could be anticipated from the crystallographic data.

Thus, we have reported here novel rare earth coordination polymers involving 1,4,5,8-naphthalenetetracarboxylate as ligand, namely $[Y_2(Ntc)_{1.5}(H_2O)_5] \cdot 6H_2O$ and $[Er_2(Ntc)_{1.5}(H_2O)_5] \cdot 6H_2O$. Two crystallographically independent La^{3+} ions and two crystallographically independent ligands were in the structure of the compound $[Y_2(Ntc)_{1.5}(H_2O)_5] \cdot 6H_2O$ and $[Er_2(Ntc)_{1.5}(H_2O)_5] \cdot 6H_2O$. Their potential porosity has been estimated using Connolly's approach.

However, they are not available for technical applications or even for further physical measurements because we have obtained them only as single crystal in gel media. We are currently working for obtaining them as microcrystalline powders. Up to now, 1,4,5,8-naphthalene-tetra-carboxylate-based coordination polymers have been only obtained with Y^{3+} and Er^{3+} ions. It would be very interesting to extend the families to other rare earth ions and exhibiting catalytic or optical properties.

Table 2. Selected bond lengths (Å) and angles (deg) for **I***

Bond	*d*, Å	Bond	*d*, Å
O(1)–Y(1)	2.422(3)	O(10)–Y(1)	2.261(3)
O(2)–Y(1)	2.480(3)	O(11)–Y(1)$^{\#6}$	2.272(3)
O(3)–Y(1)$^{\#2}$	2.246(3)	O(12)–Y(1)	2.319(3)
O(4)–Y(2)$^{\#3}$	2.298(3)	O(13)–Y(1)	2.414(3)
O(5)–Y(2)	2.485(3)	O(14)–Y(1)	2.382(3)
O(6)–Y(2)	2.463(3)	O(15)–Y(2)	2.373(3)
O(7)–Y(2)$^{\#4}$	2.311(3)	O(16)–Y(2)	2.367(3)
O(8)–Y(2)$^{\#5}$	2.249(3)	O(17)–Y(2)	2.375(3)
Angle	ω, deg	Angle	ω, deg
O(3)$^{\#5}$Y(1)O(10)	144.27(11)	O(10)Y(1)O(2)	73.56(10)
O(3)$^{\#5}$Y(1)O(11)$^{\#6}$	89.32(11)	O(11)$^{\#6}$Y(1)O(2)	150.60(10)
O(10)Y(1)O(11)$^{\#6}$	104.79(11)	O(12)Y(1)O(2)	124.36(10)
O(3)$^{\#5}$Y(1)O(12)	141.38(11)	O(1)Y(1)O(2)	52.91(9)
O(10)Y(1)O(12)	74.01(10)	O(8)$^{\#2}$Y(2)O(6)	80.64(10)
O(11)$^{\#6}$Y(1)O(12)	81.44(11)	O(4)$^{\#7}$Y(2)O(6)	73.13(10)
O(3)$^{\#5}$Y(1)O(1)	86.49(10)	O(7)$^{\#8}$Y(2)O(6)	142.15(10)
O(10)Y(1)O(1)	93.50(10)	O(8)$^{\#2}$Y(2)O(5)	86.41(10)
O(11)$^{\#6}$Y(1)O(1)	153.68(11)	O(4)$^{\#7}$Y(2)O(5)	89.43(10)
O(12)Y(1)O(1)	85.74(10)	O(7)$^{\#8}$Y(2)O(5)	163.67(10)
O(3)$^{\#5}$Y(1)O(2)	78.22(10)	O(6)Y(2)O(5)	52.28(9)

* Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y + 1, -z$; $^{\#2}$ $x - 1, y, z$; $^{\#3}$ $x, -y + 1/2, z - 1/2$; $^{\#4}$ $x + 1, -y + 1/2, z - 1/2$; $^{\#5}$ $x + 1, y, z$; $^{\#6}$ $-x + 1, -y + 1, -z$; $^{\#7}$ $x, -y + 1/2, z + 1/2$; $^{\#8}$ $x - 1, -y + 1/2, z + 1/2$.

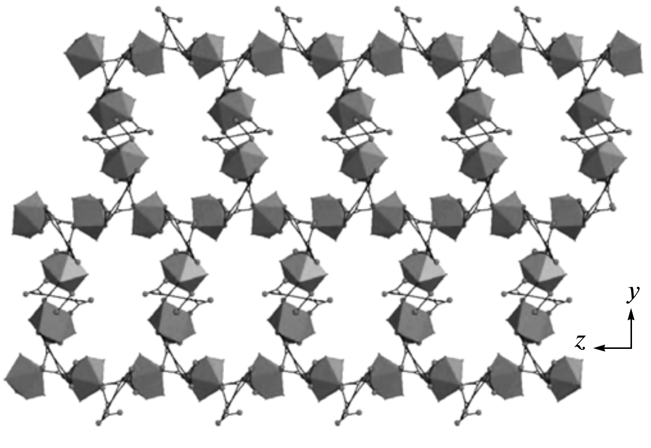


Fig. 4. View along the *x* axis of compound **I**. The coordination polyhedron of the Y^{3+} ions has been drawn.

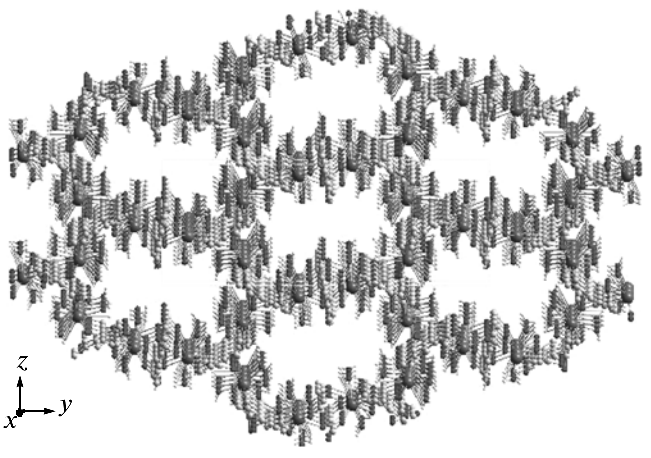


Fig. 5. View along the *x* axis of compound **II**. The coordination water molecules have been removed.

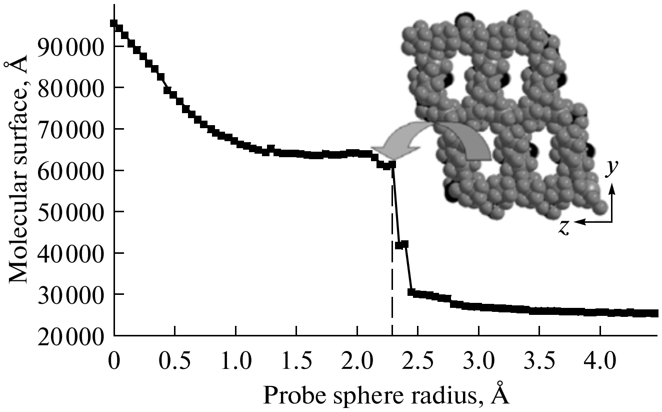


Fig. 6. Porosity profile of compound **I**.

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