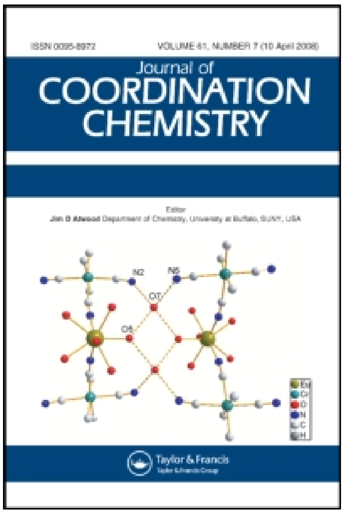

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Hydrothermal synthesis and crystal structure of a new neodymium(III) coordination polymer with fumaric acid

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To cite this Article Li, Xia and Zou, Ying-Quan(2006) 'Hydrothermal synthesis and crystal structure of a new neodymium(III) coordination polymer with fumaric acid', Journal of Coordination Chemistry, 59: 10, 1131 — 1138
To link to this Article: DOI: 10.1080/00958970500453234
URL: http://dx.doi.org/10.1080/00958970500453234

Journal of Coordination Chemistry
Vol. 59, No. 10, 10 July 2006, 1131–1138

Hydrothermal synthesis and crystal structure of a new neodymium(III) coordination polymer with fumaric acid

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(*Received 7 March 2005; in final form 25 July 2005*)

The coordination polymer $[Nd(C_4H_2O_4)(C_4H_3O_4)H_2O]_n$ ($C_4H_4O_4$ = Fumaric acid) has been synthesized by hydrothermal reactions and structurally characterized by single crystal X-ray diffration methods. The Nd(III) center is a distorted tricapped trigonal prism coordinated by nine oxygen atoms, seven from six fumarate dianions ($C_4H_2O_4^{2-}$), one from fumarate anion ($C_4H_3O_4^-$) and one a water molecule. Nd(III) ions are connected into a framework structure by the oxygen atoms of the carboxyl groups.

Keywords: Neodymium; Fumaric acid; Coordination polymer

1. Introduction

Coordination polymers of metal cations with organic multifunctional ligands have been received increasing interest, for these coordination polymers have one-, two-, three-dimensional structures as well as potential applications as catalysts, magnetic and porous materials [1–4]. Multi-carboxyle ligands are useful to construct unique architectures of metal-coordination polymers. The synthesis of novel lanthanide polymers and studies on luminescent, electric and magnetic properties of the compounds are of interest. Some metal coordination polymers using fumaric acid as ligand have been reported in the literature containing transition metals Cu [5], Zn [6], and Mn [7]. A series of rare earth fumarate complexes have also been previously reported [8–10]. Hydrothermal synthesis has some advantages over conventional methods for the formation of a polymer framework with higher dimensions. Fumaric acid was used to synthesize a new neodymium(III) coordination polymer, $[Nd(C_4H_2O_4)(C_4H_3O_4)H_2O]_n$ ($C_4H_4O_4$ = fumaric acid) by using hydrothermal synthesis method and the crystal structure is reported in the present article.

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Journal of Coordination Chemistry
ISSN 0095-8972 print: ISSN 1029-0389 online © 2006 Taylor & Francis
DOI: 10.1080/00958970500453234

2. Experimental

2.1. *Synthesis of complex*

1.2 mmol fumaric acid was dissolved in 6 mL water and its pH was controlled in a range 4–5 with 2 mol dm^{-3} NaOH solution. $NdCl_3 \cdot 6H_2O$, 0.4 mmol, dissolved in water (5 mL) was added. The mixture was placed in a Teflon-lined stainless-steel vessel (25 mL) and heated at 150°C for 24 h. Purple crystals were obtained in 41.6% yield (0.0651 g). Elemental analysis: found C, 24.58%; H, 1.78%; Calcd for $Nd(C_4H_2O_4)(C_4H_3O_4)H_2O$, C, 24.55%; H, 1.80%.

2.2. *Crystal structure determination*

X-ray diffraction data of the single crystal were collected on a crystal of approximate dimensions $0.22 \times 0.18 \times 0.16$ mm^3 by using a Bruker Smart 1000 CCD diffractometer with monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 293 K. Semi-empirical absorption corrections were applied using the SADABS program. All calculations were carried out on a computer with use of SHELXS-97 and SHELXL-97 programs [11, 12]. The structures were solved by direct methods and refinement on $|F|^2$ used the full-matrix least-squares methods. A summary of the crystallographic data and details of the structure refinements are listed in table 1.

3. Results and discussion

Selected bond lengths and bond angles are listed in table 2. Figure 1 shows the coordination environment of one Nd(III) ion. Among the nine oxygen atoms coordinated

Table 1. Crystal data and structure refinement for $[Nd(C_4H_2O_4)(C_4H_3O_4)H_2O]_n$.

Empirical formula	$C_8H_7NdO_9$
Formula weight	391.38
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system, space group	Monoclinic, $P2(1)/c$
Unit cell dimensions (Å, °)	$a = 8.360(2)$, $\alpha = 90$ $b = 14.553(4)$, $\beta = 103.028(4)$ $c = 8.741(3)$, $\gamma = 90$
Volume (Å^3)	1036.1(5)
Z	4
Calculated density (Mg m^{-3})	2.509
Absorption coefficient (mm^{-1})	5.053
$F(000)$	748
Crystal size (mm^3)	$0.22 \times 0.18 \times 0.16$
Theta range for data collection (°)	2.50 to 25.01
Limiting indices	$-7 \le h \le 9$, $-14 \le k \le 17$, $-10 \le l \le 9$
Reflections collected/unique	5251/1824 [R(int) = 0.0251]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1824/0/165
Goodness-of-fit on F^2	1.097
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0184$, $wR_2 = 0.0432$
R indices (all data)	$R_1 = 0.0209$, $wR_2 = 0.0441$
Extinction coefficient	0.0386(8)
Largest diff. peak and hole (e Å^{-3})	0.514 and −0.884

Table 2. Bond lengths [Å] and bond angles [°] for $[Nd(C_4H_2O_4)(C_4H_3O_4)H_2O]_n$.

Nd(1)–O(7)#1	2.390(2)	Nd(1)–O(5)	2.438(2)
Nd(1)–O(6)#2	2.441(2)	Nd(1)–O(4)#3	2.459(2)
Nd(1)–O(8)#4	2.504(2)	Nd(1)–O(3)	2.507(2)
Nd(1)–O(1)	2.543(2)	Nd(1)–O(9)	2.564(2)
Nd(1)–O(4)	2.771(2)		
O(7)#1–Nd(1)–O(5)	145.80(8)	O(7)#1–Nd(1)–O(6)#2	91.50(8)
O(5)–Nd(1)–O(6)#2	79.66(7)	O(7)#1–Nd(1)–O(4)#3	75.41(8)
O(5)–Nd(1)–O(4)#3	70.39(8)	O(6)#2–Nd(1)–O(4)#3	75.23(8)
O(7)#1–Nd(1)–O(8)#4	77.26(8)	O(5)–Nd(1)–O(8)#4	95.93(8)
O(6)#2–Nd(1)–O(8)#4	153.17(8)	O(4)#3–Nd(1)–O(8)#4	78.36(8)
O(7)#1–Nd(1)–O(3)	124.63(8)	O(5)–Nd(1)–O(3)	85.83(7)
O(6)#2–Nd(1)–O(3)	77.26(8)	O(4)#3–Nd(1)–O(3)	146.27(8)
O(8)#4–Nd(1)–O(3)	129.13(8)	O(7)#1–Nd(1)–O(1)	72.39(8)
O(5)–Nd(1)–O(1)	137.46(8)	O(6)#2–Nd(1)–O(1)	129.31(8)
O(4)#3–Nd(1)–O(1)	139.23(8)	O(8)#4–Nd(1)–O(1)	70.74(8)
O(3)–Nd(1)–O(1)	74.21(8)	O(7)#1–Nd(1)–O(9)	132.38(8)
O(5)–Nd(1)–O(9)	69.89(8)	O(6)#2–Nd(1)–O(9)	134.16(8)
O(4)#3–Nd(1)–O(9)	122.08(7)	O(8)#4–Nd(1)–O(9)	65.85(8)
O(3)–Nd(1)–O(9)	67.34(8)	O(1)–Nd(1)–O(9)	67.81(8)
O(7)#1–Nd(1)–O(4)	76.58(7)	O(5)–Nd(1)–O(4)	127.49(7)
O(6)#2–Nd(1)–O(4)	67.06(7)	O(4)#3–Nd(1)–O(4)	131.74(5)
O(8)#4–Nd(1)–O(4)	131.36(7)	O(3)–Nd(1)–O(4)	48.90(6)
O(1)–Nd(1)–O(4)	62.54(7)	O(9)–Nd(1)–O(4)	105.85(6)

#1: $x+1$, $-y+1/2$, $z+1/2$; #2: x, $-y+1/2$, $z+1/2$; #3: x, $-y+1/2$, $z-1/2$; #4: $x+1$, y, z.

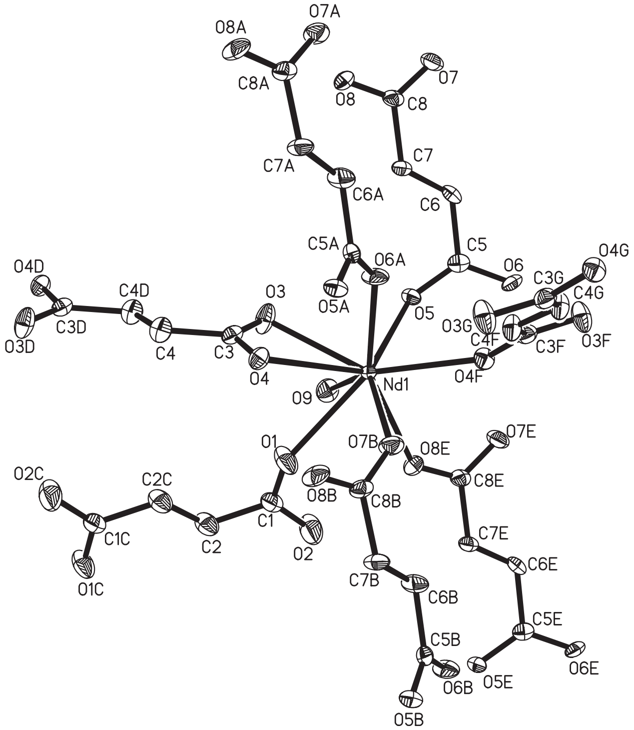


Figure 1. The coordination environment of Nd(III) in $[Nd(C_4H_2O_4)(C_4H_3O_4)H_2O]_n$ at the 70% probability level (all the hydrogen are omitted for clarity).

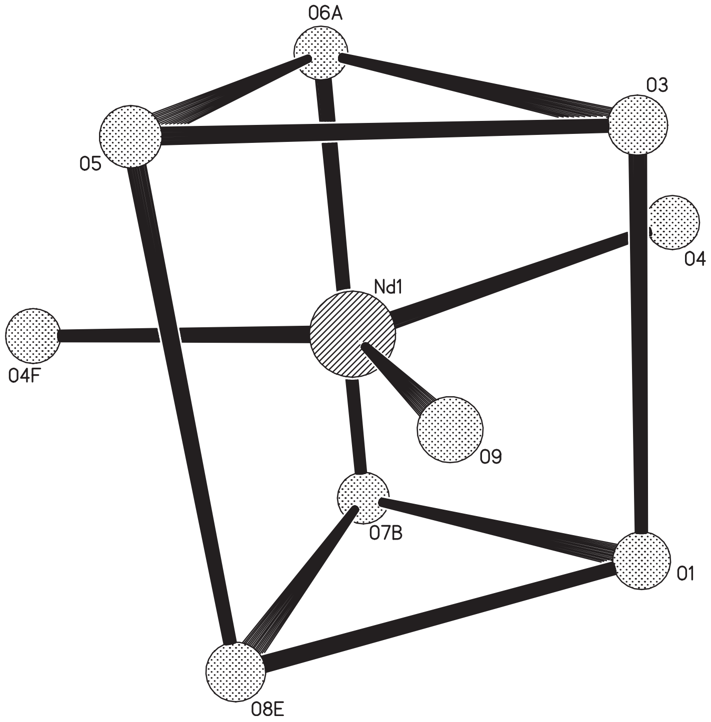
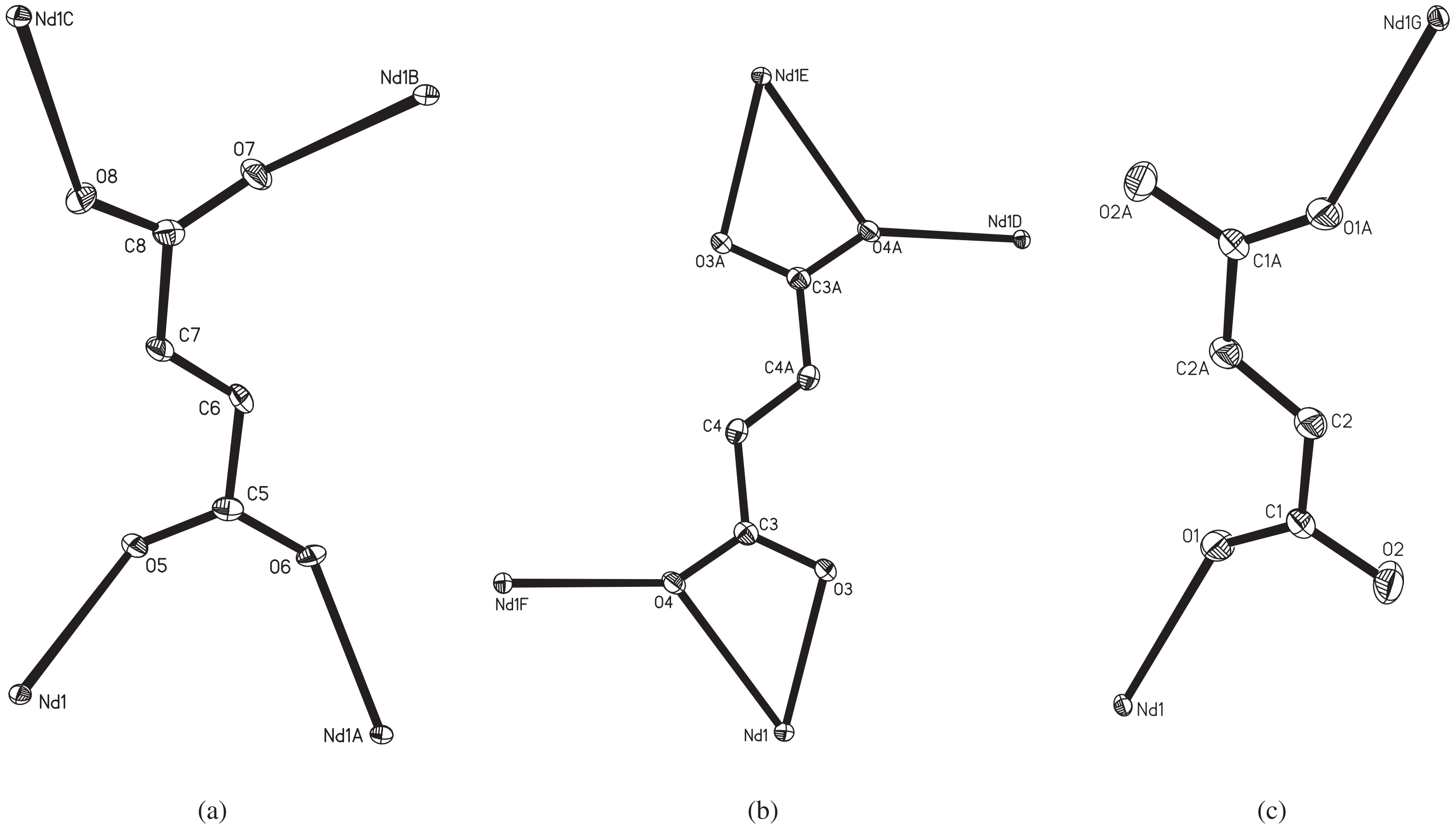


Figure 2. The coordination polyhedron of Nd1(III).

to one Nd(III) ion, seven are from six fumarate dianions ($C_4H_2O_4^{2-}$), one from fumarate anion ($C_4H_3O_4^-$) and one from water. The polyhedral coordination geometry is a distorted tricapped trigonal prism (figure 2). Atoms O3, O5 and O6A, and atoms O1, O8E and O7B, take the tips of the upper and lower triangles of the prism, respectively. The dihedral angle between them is 11.4°. Atoms O9, O4, and O4F take the three cap positions. The distances of Nd–O(carboxyl) are in range from 2.390(2) to 2.771(2) Å with average distance of 2.507 Å. The Nd–O(water) distance is 2.564(2) Å. The fumarate dianions coordinate Nd(III) in two coordination modes. In the first, fumarate dianions adopt a tetradentate-bridging mode, namely, all COO^- of fumarate dianions bridge with four oxygen atoms coordinating four different Nd(III) ions (scheme 1a). Nd(III) ions are linked into two parallel 1-D chains along the *a*-axis with neighboring Nd(III) ions separated by 4.704 Å. In the second mode, fumarate dianions adopt hexadentate-bridging mode, namely, all COO^- of fumarate dianions are chelating-bridging, in which four oxygen atoms coordinate four different Nd(III) ions (scheme 1b). The fumarate anion coordinates two neodymium(III) ions through its two oxygen atoms in a monodentate mode to form a bidentate bridge (scheme 1c). It is not common for a carboxylic acid ligand to coordinate lanthanide ion in a monodentate mode. 1-D chains are connected into a layer structure along the ab plane by two coordination modes (scheme 1b and c) (figure 3). Viewed along the crystallographic *a*-axis, the Nd(III) ions are connected into a framework structure by the oxygen atoms of the carboxyl groups with an open channel structure containing a regular rhombus paralleling the [0, 1, 1] plane (figure 4). The short edge of the



Scheme 1. Coordination modes of fumarate in $[Nd(C_4H_2O_4)(C_4H_3O_4)H_2O]_n$.

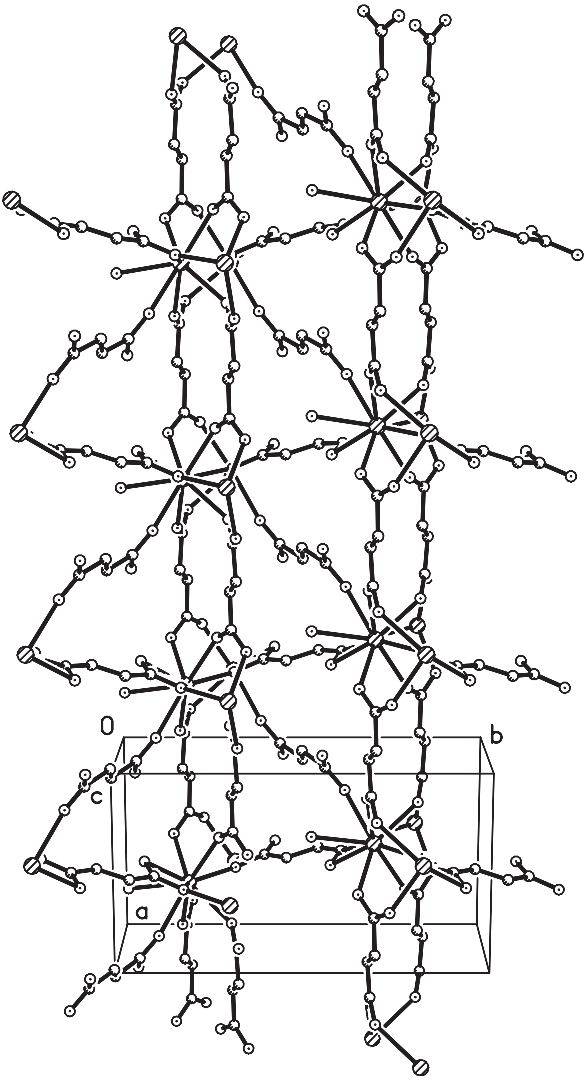


Figure 3. Projection down the *c*-axis showing the 2D layer structure (all the hydrogen are omitted for clarity).

rhombus has a dimeric unit of Nd $\cdots$ Nd ions separated at 4.704 Å, through a COO^- group. The long edge has a dimeric unit of Nd $\cdots$ Nd ions separated at 4.704 Å through COO^- and a dimeric unit through –OOCCHCHCOO– with Nd $\cdots$ Nd ions separated at 9.006 Å. The channel is 4.704 × 13.710 Å based on the Nd $\cdots$ Nd distance. The coordinated water molecules point into the channels. Several structural features are similar to the neodymium compound with sebacic acid, $[Nd(C_{10}H_{16}O_4)(C_{10}H_{17}O_4)(H_2O)]_n$ [13], synthesized also by hydrothermal synthesis. Its framework structure was constructed from the longest aliphatic ligand.

Hydrogen bonds exist in the crystal. Hydrogen atoms of coordinated water form hydrogen bonds with oxygen atoms of fumarate anions, O9–H9B $\cdots$ O3 $[-x+1, -y, -z+1]$, 2.818 Å, 155.29° and O9–H9B $\cdots$ O5 $[-x+1, -y, -z+1]$, 2.912 Å, 161.02°.

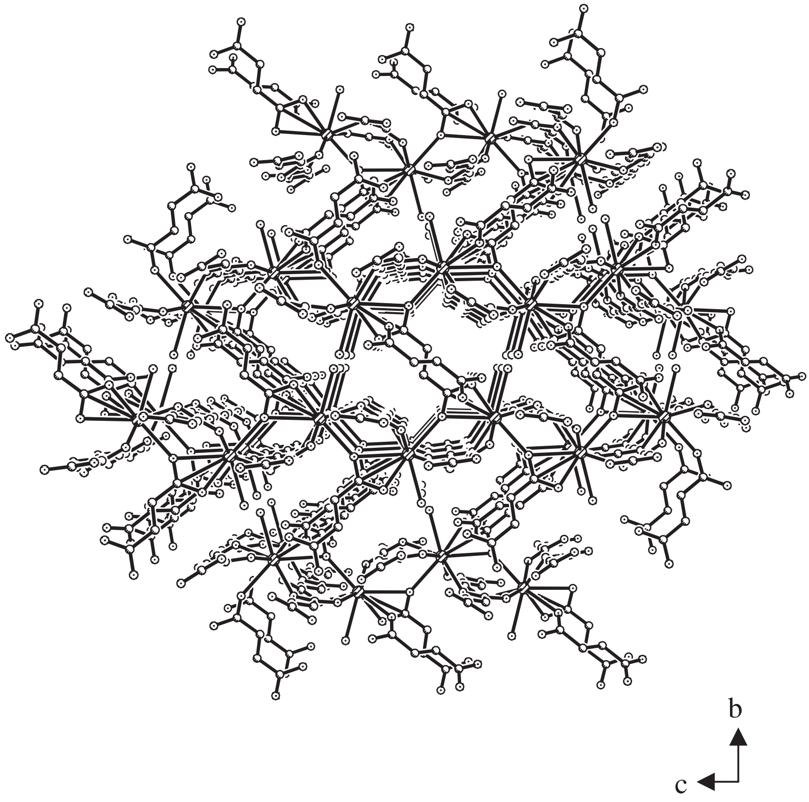


Figure 4. Packing diagram of $[Nd(C_4H_2O_4)(C_4H_3O_4)H_2O]_n$ with open channel structure along *a*-axis (all the hydrogen atoms have been omitted for clarity).

Hydrogens of fumarate anion form hydrogen bonds with oxygen atoms of fumarate dianion, $O1{=}C1{-}O2{-}H2 \cdots O8$ $[x+1, y, z]$, 2.663 Å, 164.91°. The complex is different from complexes $[M_2F_3{\cdot}12H_2O]_n$ reported in ref. [8], in which some uncoordinated water molecules exist in the crystal due to conventional solution reactions. $[Nd(C_4H_2O_4)(C_4H_3O_4)H_2O]_n$ does not contain lattice water molecules, because of the synthesis at higher temperature.

Supplementary material

CCDC-239484 contains the supplementary crystallographic data for this article. These data can be obtained free of charge from CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk.

Acknowledgements

We are grateful to the Natural Science Foundation of Beijing (No. 2022007). This project was also sponsored by the Science and Technology Program, Beijing Municipal Education Commission (KM200510028007) and the Scientific Research Foundation for Returned Overseas Chinese Scholars, Beijing Municipal Government.

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