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Hydrothermal synthesis, crystal structure and magnetism of $[Nd(C_7H_6NO_2)_3 \cdot H_2O]_n$, a novel coordination polymer with three-dimensional network

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Abstract

A novel coordination polymer with three-dimensional network, $[Nd(C_7H_6NO_2)_3 \cdot H_2O]_n$, has been hydrothermally synthesized and characterized by X-ray diffraction of the single-crystal, IR and UV–vis–NIR spectra as well as by the measurement of the magnetic susceptibility. The polymer crystallizes in the monoclinic, space group $P2(1)/n$ with $a = 9.8069(5)$ Å, $b = 22.736(2)$ Å, $c = 9.8254(8)$ Å, $\beta = 100.053(5)°$, $V = 2157.1(3)$ Å^3, $Z = 4$, and $R(Rw) = 0.038(0.0924)$. Cryomagnetic investigations (4.5–300 K) reveal that the polymer possesses weak antiferromagnetic property. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nd(III) coordination polymer; Three-dimensional network; Hydrothermal synthesis; Crystal structure; Magnetism

1. Introduction

In recent years, the study of metal-coordination polymer has drawn more and more attention. Especially, the investigation on spontaneous self-assembly of metal-coordination provides a solid foundation for exploring the relationship between the structural framework and function and for researching the interactions between the metals and metals of the polymer [1–5].

We have an interest in the self-assembling of lanthanide coordination ions. The coordinating capacity of lanthanide elements is powerful and the coordination number is larger. Especially the configuration of their 4f electrons possesses specific properties of spectrum and magnetism. All of these provide particular structures and functions for the coordination compounds and polymers with Ln(III) ions. Therefore, these complexes have great potential of applications to optics, electronics, magnetics, biology as well as medicine, etc. [6–10]. Although the study of mononuclear and binuclear complexes as well as polymers is very extensive, the report for Ln(III) coordination polymer having three-dimensional network is rarely seen [11–17].

This paper reports a novel Nd(III) coordination polymer having three-dimensional network structure and varied H-bonds with *p*-aminobenzoate ligands. We study the hydrothermal synthesis, structural characterization and magnetism of the polymer.

2. Experimental

2.1. Physical measurements

The element contents were measured using a

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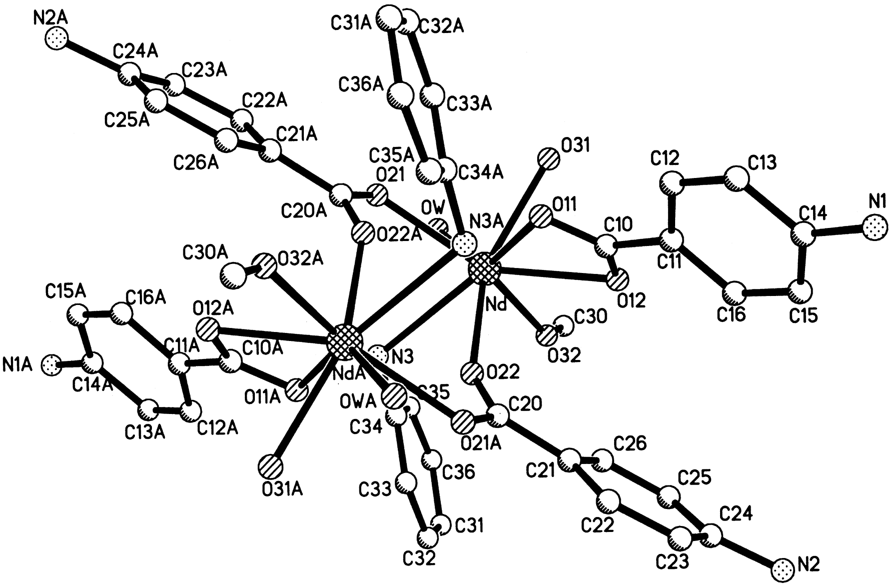


Fig. 1. The structure diagram of [Nd($C_7H_6NO_2$)$_3$·H_2O] unit.

PE-240C elemental analyzer and TLASMA-II ICP. The IR spectrum was recorded on a NICOLET NEXUS 470 FT/IR spectrometer (CsI pellet) and UV–vis–NIR spectrum (diffuse reflectance spectrum) was obtained on a UV-3100 spectrophotometer by using $BaSO_4$ pellet as a reference. The magnetic susceptibilities were measured with a MPMS-7 superconducting quantum magnetometer in the temperature range of 4.5–300 K and in the magnetic field of 1 T.

2.2. Synthesis

The polymer was prepared by hydrothermal reaction. $Nd(NO_3)_3 \cdot 6H_2O$ (0.44 g, 1.0 mmol) and $NH_2C_6H_4COOH$ (0.68 g, 5.0 mmol) was dissolved in water (30 ml, 50 °C), after addition of ethanol (5 ml), the solution was heated and stirred. The dissolution was over, and the liquid was sealed in a 50 ml teflon-lined autoclave and heated at 125 °C for 96 h. Then the autoclave was cooled to room temperature. Flesh-colored crystals were observed after several days. The product was collected by filtration. Anal. found (%): C, 43.56; H, 3.45; N, 7.31; Nd, 25.63; calcd for $C_{21}H_{20}N_3O_7Nd$: C, 44.21; H, 3.53; N, 7.36; Nd, 25.28. The IR spectrum (CsI pellet, cm^{-1}): 3397(m), 3312(m) (ν_{N-H}); 3280(m) ($\nu_{O-H\cdots O}$); 3125(m) (ν_{C-H}, Ar); 1608 (vs) ($\nu_{C=C}$, Ar); 1510 (vs) ($\nu_{as\ coo}$); 1392 (vs) ($\nu_{s\ coo}$); 395(s) (ν_{Nd-O}); 290(m) (ν_{Nd-N}). The UV–vis–NIR spectrum (diffuse reflectance, $BaSO_4$ pellets as reference, nm) has 11 bands: 870, 802, 748, 740, 638, 630, 584, 526, 515, 470, 365, which correspond to the transitions of Nd(III) ion, respectively: $^4I_{9/2} \rightarrow {}^4F_J$ ($J = 3/2, 5/2, 7/2, 9/2$), $^4S_{3/2}$, ^4G_J ($J = 5/2, 7/2, 9/2, 11/2$) and ^4D_J ($J = 1/2, 3/2$) [20].

2.3. X-ray crystallography

Crystal data: $C_{21}H_{20}N_3O_7Nd$, $M = 570.625(3)$, monoclinic, space group $P2(1)/n$ $a = 9.8069(5)$ Å, $b = 22.736(2)$ Å, $c = 9.8254(8)$ Å, $\beta = 100.053(5)°$, $V = 2157.1(3)$ Å^3, $Z = 4$, $\lambda = 0.71073$ Å, $T = 293$ K. A single-crystal with dimensions $0.24 \times 0.32 \times 0.38$ mm^3 was fixed inside a glass capillary. Data were collected on a Siemens R_3 four-circle diffractometer with the ω-scan mode in the range of $3.5 < 2\theta < 48°$. A total of 4286 (3386 independent) reflections were measured. The structure was solved by heavy atom method and refined with a full-matrix least-squares program. All the reflection data were corrected for the L–P factor and empirical absorption. In refinement, the function minimized was $\sum W(F_0 - F_c)^2$, where weighing scheme $W^{-1} = [\sigma^2(F_0)^2 + (0.0570P)^2 + 3.0949P]$, $(P = (F_0^2 + 2F_c^2)/3)$ was used. Final $R = 0.038$, $Rw = 0.092[I > 2\sigma(I)]$,

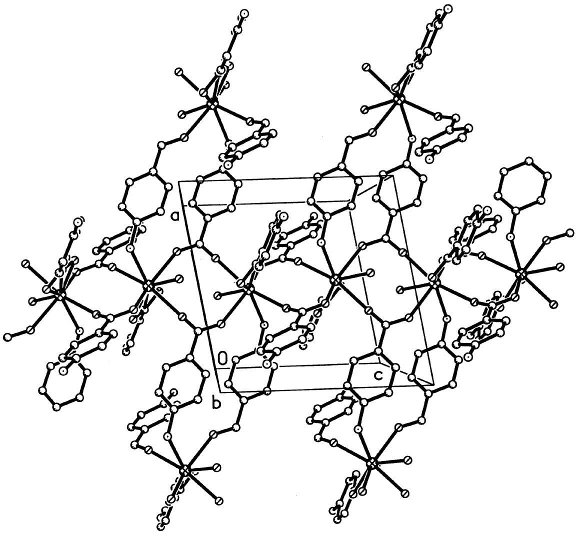


Fig. 2. Crystal packing diagram of [Nd($C_7H_6NO_2$)$_3$·H_2O] in the two-dimensional network.

$S = 1.013$, $\Delta/\sigma = 0.001$, $\Delta\rho_{\max} = 1.175$ eÅ^3, $\Delta\rho_{\min} = -1.058$ eÅ^3. The atomic coordinates of hydrogen atoms were found in the Fourier figure. All calculations were performed on a VMS computer by using SHELXTL programs. Further details of the crystallographic data and the crystal structure investigations can be obtained from Cambridge Crystallographic Data Center. The deposition number is CCDC 168176.

3. Results and discussion

3.1. Structure

The structural analysis shows that the polymer is prepared by self-assembly of [Nd($C_7H_6NO_2$)$_3$·H_2O] units. Each unit contains one Nd(III) ion and three independent p-aminobenzoate ligands. One (**A**) of three ligands coordinates to one Nd(III) ion with two carboxyl O atoms, while other two ligands (**B**, **C**) bond, respectively, to two Nd(III) ions and one (**C**) of them links to third Nd(III) ion with its amino N atom. Each Nd(III) ion is coordinated by six carboxyl O atoms, one amino N atom and one O atom of structure water molecule, forming eight-coordination irregular polyhedron. The distances of Nd–O range from 2.386 to 2.595 Å and Nd–N bond length is 2.713 Å (Fig. 1). In the polymer, the Nd(III) ions are bridged first by two carboxyl groups from two respective *p*-aminobenzoates, forming one-dimensional chain which is along the direction of the *c* axis. In the interchain, the Nd–Nd separation is 5.243 Å. Then the Nd(III) ions belonging to adjacent chains

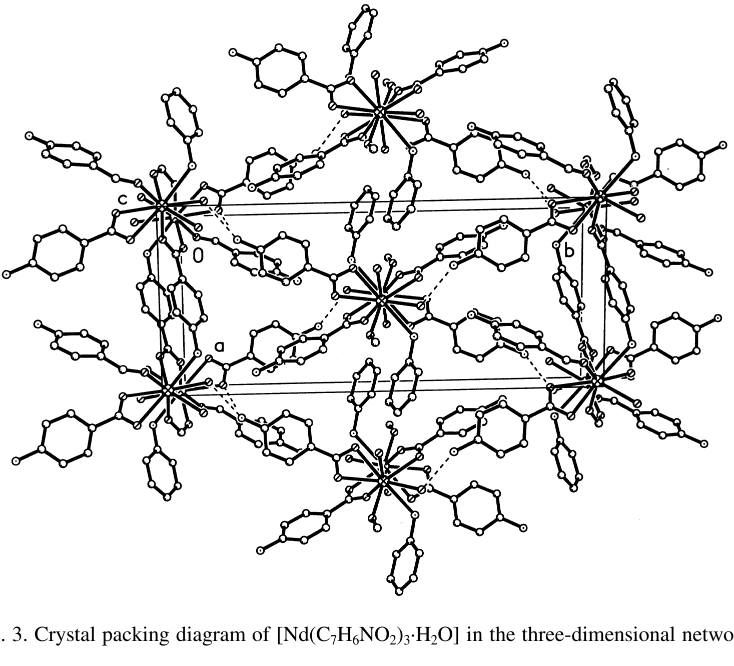


Fig. 3. Crystal packing diagram of [Nd($C_7H_6NO_2$)$_3$·H_2O] in the three-dimensional network.

Table 1
The selected bond lengths (Å) and angles (°) (A: $-x + 1$, $-y + 1$, $-z + 1$; B: $-x + 1$, $-y + 1$, $-z + 2$)

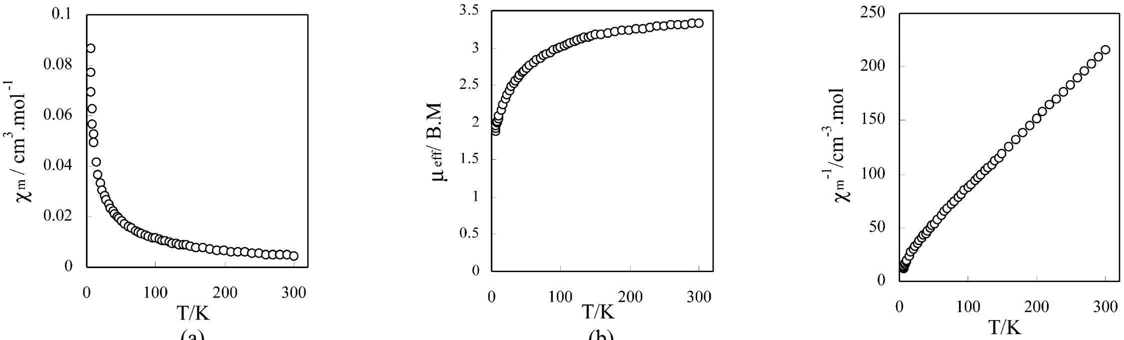
Bond lengths	
Nd–O(22)	2.386(5)
Nd–O(32)	2.398(5)
Nd–O(31)	2.406(5)
Nd–O(21)	2.409(5)
Nd–O(11)	2.487(5)
Nd–O(12)	2.523(5)
Nd–Ow	2.595(5)
Nd–N(3)	2.713(7)
Bond angle	
O(22)–Nd–O(32)	94.3(2)
O(22)–Nd–O(31)	147.3(2)
O(32)–Nd–O(31)	92.1(2)
O(22)–Nd–O(21)	107.6(2)
O(32)–Nd–O(21)	139.8(2)
O(31)–Nd–O(21)	87.1(2)
O(22)–Nd–O(11)	77.2(2)
O(32)–Nd–O(11)	125.7(2)
O(31)–Nd–O(11)	73.1(2)
O(21)–Nd–O(11)	92.5(2)
O(22)–Nd–O(12)	79.4(2)
O(32)–Nd–O(12)	73.6(2)
O(31)–Nd–O(12)	71.8(2)
O(21)–Nd–O(12)	142.3(2)
O(11)–Nd–O(12)	52.1(2)
O(22)–Nd–Ow	139.3(2)
O(32)–Nd–Ow	73.8(2)
O(31)–Nd–Ow	73.0(2)
O(21)–Nd–Ow	67.6(2)
O(11)–Nd–Ow	141.3(2)
O(12)–Nd–Ow	130.28(4)
O(22)–Nd–N(3)	71.4(2)
O(32)–Nd–N(3)	80.2(2)
O(31)–Nd–N(3)	141.2(2)
O(21)–Nd–N(3)	75.7(2)
O(11)–Nd–N(3)	140.7(2)
O(12)–Nd–N(3)	138.9(2)
Ow–Nd–N(3)	68.3(2)
C(34)–N(3)–Nd	118.9(5)
C(10)–O(11)–Nd	94.1(4)
C(10)–O(12)–Nd	92.8(4)
C(20A)–O(21)–Nd	116.5(5)
C(20)–O(22)–Nd	150.2(5)
C(30B)–O(31)–Nd	146.2(4)
C(30)–O(32)–Nd	137.2(4)

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for the polymer. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor

Atoms	*x*	*y*	*z*	*U*(eq)
Nd	5172(1)	4995(1)	7372(1)	19(1)
N(1)	1628(8)	1611(3)	5215(8)	38(2)
N(2)	8947(8)	2058(3)	7411(8)	54(2)
N(3)	7186(7)	5737(3)	6855(7)	26(2)
O(11)	3358(5)	4324(2)	6151(5)	27(1)
O(12)	4856(5)	3914(2)	7810(5)	27(1)
O(21)	3938(6)	5858(2)	6414(5)	39(1)
O(22)	6263(6)	4574(2)	5613(5)	36(1)
O(31)	3445(5)	4896(2)	8821(5)	27(1)
O(32)	6998(5)	4723(2)	9220(5)	26(1)
Ow	5490(5)	5876(2)	9076(5)	27(1)
C(10)	3858(8)	3870(3)	6817(7)	24(2)
C(11)	3248(8)	3276(3)	6405(7)	25(2)
C(12)	1961(9)	3216(3)	5633(9)	35(2)
C(13)	1444(9)	2674(4)	5237(8)	35(2)
C(14)	2216(8)	2168(3)	5628(8)	30(2)
C(15)	3510(10)	2224(4)	6412(10)	41(2)
C(16)	4031(9)	2772(4)	6788(9)	34(2)
C(20)	6470(7)	4140(3)	4874(8)	27(2)
C(21)	7195(8)	3613(3)	5517(7)	27(2)
C(22)	7240(8)	3096(3)	4747(8)	30(2)
C(23)	7812(10)	2587(4)	5365(10)	40(2)
C(24)	8388(8)	2578(3)	6761(8)	35(2)
C(25)	8387(9)	3096(4)	7517(8)	36(2)
C(26)	7784(9)	3600(4)	6903(8)	34(2)
C(30)	7352(7)	4839(3)	10,498(7)	20(2)
C(31)	11,241(7)	5335(3)	8801(7)	23(2)
C(32)	10,752(8)	5141(3)	7450(7)	27(2)
C(33)	9437(8)	5282(4)	6821(8)	32(2)
C(34)	8571(7)	5619(3)	7454(7)	20(2)
C(35)	9072(8)	5815(3)	8790(8)	26(2)
C(36)	10,377(8)	5667(3)	9446(8)	26(2)

are linked by the $-COO^-$ or $-NH_2$ group from different ligands forming two-dimensional infinite network in the *ac* plane with center height about *b*/2. The distance of Nd–Nd in the intrachain is 4.164 Å (Fig. 2). The two-dimensional network is bonded by various hydrogen bonds, N–H…O (2.930 Å) and N–H…Ow (2.846 Å)) assembling three-dimensional network structure (Fig. 3). The selected bond lengths and angles, non-hydrogen atomic coordinates and thermal parameters are listed in Tables 1 and 2, respectively.

Obviously, there are two characters in the structure of the polymer: (1) It has two kinds of direct coordinate atoms (N and O) from the $-NH_2$ and $-COO^-$ group of the same ligand. This Ln(III) coordination polymer is seldom seen. (2) The structure of the polymer possesses three-dimensional infinite network, which is favorable for electron and proton transfer between metal atoms or metals and ligands [18].



(a) (b) (c)

Fig. 4. Temperature dependence of (a) χ_m, (b) μ_{eff} and (c) χ_m^{-1}.

3.2. Magnetic properties

In light of variable temperature magnetic moments in 4.5–300 K, we obtained the molar magnetic susceptibility (χ_m) and effective magnetic moments (μ_{eff}) and studied the curves of χ_m–T, μ_{eff}–T and χ_m^{-1}–T (Fig. 4(a)–(c)). In Fig. 4(a), as the temperature (T) downs to 11 K, χ_m shows an obvious increase, which reveals a tendency of the magnetic coupling of Nd(III)–Nd(III) in the polymer. From Fig. 4(b) it can be seen that as T decreases, μ_{eff} decreases and drops quickly at 11 K, which demonstrates that there is an antiferromagnetic coupling between the Nd(III) ions. Furthermore, if we treat χ_m^{-1}–T curve (Fig. 4(c)) as linear and extrapolate it intersecting the T axis, the crossing is at the side of $-T$, which agrees with the $\chi_m = C/(T + \theta)$ [19]. These phenomena shows that this polymer possesses the character of weak antiferromagnetic material.

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