

3-羧基苯氧乙酸根及邻菲咯啉构筑的钕(III) 配位聚合物的合成、晶体结构及磁性质

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摘要: 在水热反应条件下,采用 3-羧基苯氧乙酸(3-H₂CPOA=3-carboxyphenoxyacetic acid)和 phen (phen=1,10-phenanthroline)与 NdCl₃·6H₂O 反应,合成了 1 个具有三维结构的配位聚合物[Nd(3-CPOA)_{1.5}(phen)]_n (**1**),并对其结构和磁性质进行了研究。结构分析结果表明该聚合物的晶体属于单斜晶系, *P*2₁/*c* 空间群。2 个钕(III)离子、3 个 3-CPOA²⁻配体和 2 个 phen 配体形成了 1 个 [Nd₂(3-CPOA)₃(phen)₂]双核轮状结构单元,这些双核单元通过钕(III)离子与 3-CPOA²⁻配体的配位作用形成了 1 个三维框架结构。磁性研究表明,该聚合物中相邻的钕(III)离子之间存在很强的反铁磁相互作用。

关键词: 钕(III)配位聚合物; 3-羧基苯氧乙酸; 磁性质

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Synthesis, Crystal Structure and Magnetic Properties of a Nd(III) Coordination Polymer Constructed by 3-Carboxyphenoxyacetate and 1,10-Phenanthroline

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Abstract: Under hydrothermal conditions, NdCl₃·6H₂O reacts with 3-H₂CPOA (3-H₂CPOA=3-carboxyphenoxyacetic acid) and phen (phen=1,10-phenanthroline), producing a novel coordination polymer [Nd(3-CPOA)_{1.5}(phen)]_n (**1**). Complex **1** crystallizes in monoclinic space group *P*2₁/*c*, with *a*=0.982 7(8), *b*=1.140 6(10), *c*=2.115 8(19) nm, *β*=90.574(9)°, *V*=2.371(4) nm³, and *Z*=4. X-ray diffraction studies show that complex **1** possesses a three-dimensional framework structure based on a binuclear unit. Magnetic studies for complex **1** indicate the presence of stronger antiferromagnetic coupling between the adjacent Nd(III) ions. CCDC: 888765.

Key words: neodymium(III) coordination polymer; 3-carboxyphenoxyacetic acid; magnetic properties

0 Introduction

The rational design and syntheses of lanthanide coordination polymers have attracted great interests not only for their intriguing architectures and topologies^[1-4] but also for their potential applications in areas of catalysis^[5-6], sorption and separation^[7-9],

luminescence^[10-12], and magnetism^[13-15]. However, it is a great challenge to control structures with desired properties because many factors affect the result, such as central metal ions, organic ligands, solvents, pH value, and so on. The most effective approach to overcome this problem is the appropriate choice of the well-designed organic bridging ligands. Many multi-

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carboxylate or heterocyclic carboxylic acids are used for this purpose^[1-15]. In order to extend our investigation in this field, we chose 3-H₂CPOA (3-carboxyphenoxyacetic acid) as a functional ligand, which based on the following considerations: (1) 3-H₂CPOA is a flexible ligand that not only includes rigid carboxylate groups but also bearing a flexible -OCH₂-spacer, which allows more flexibility and may result in rich topologies, including coordination modes, packing fashions, and dimensionalities of supramolecular coordination compounds^[16-17]. (2) It can act not only as hydrogen-bond acceptor but also as hydrogen-bond donor which depend upon the number of deprotonated carboxy group, which is beneficial for the construction of coordination polymers. (3) To our knowledge, 3-H₂CPOA has not been adequately explored in the construction of lanthanide coordination polymers.

Taking into account these factors, we herein report the synthesis, crystal structure, magnetic properties of Nd(III) compound with 3-CPOA ligands.

1 Experimental

1.1 Reagents and physical measurements

The 3-carboxyphenoxyacetic acid was prepared by the reaction of chloroacetic acid with 3-hydroxybenzoic acid^[18], and all other chemicals were of analytical reagent grade and used without further purification. Carbon, hydrogen and nitrogen were determined using an Elementar Vario EL elemental analyzer. IR spectra

were recorded using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermogravimetric analysis (TG) data were collected on a LINSEIS STA PT1600 thermal analyzer with a heating rate of 10 °C · min⁻¹. Powder X-ray diffraction patterns (PXRD) were determined with a Rigaku-Dmax 2400 diffractometer using Cu K α radiation. Magnetic susceptibility data were collected in the 2~300 K temperature range with a Quantum Design SQUID Magnetometer MPMS XL-7 with a field of 0.1 T. A correction was made for the diamagnetic contribution prior to data analysis.

1.2 Synthesis of [Nd(3-CPOA)_{1.5}(phen)]_n (1)

A mixture of NdCl₃·6H₂O (0.112 g, 0.3 mmol), 3-H₂CPOA (0.088 g, 0.45 mmol), phen (0.060 g, 0.3 mmol), NaOH (0.024 g, 0.6 mmol) and H₂O (10 mL) was stirred at room temperature for 15 min, and then sealed in a 25 mL Teflon-lined stainless steel vessel, and heated at 160 °C for 3 d, followed by cooling to room temperature at a rate of 10 °C · h⁻¹. Purple block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 70% (based on Nd). Anal. Calcd for C_{25.5}H₁₇NdN₂O_{7.5} (%): C 49.75, H 2.78, N 4.55; Found(%): C 50.06, H 2.47, N 4.28. IR (KBr, cm⁻¹): 3 423m, 1 634s, 1 586m, 1 540s, 1 406s, 1 339m, 1 278m, 1 233m, 1 071m, 848s, 769m, 726m, 670m. The compound is insoluble in water and common organic solvents, such as methanol, ethanol, acetone, and DMF.

1.3 Structure determinations

Single-crystal data of **1** were collected at 296(2)

Table 1 Crystal data for complex 1

Complex	1	Crystal size / mm	0.28×0.26×0.25
Chemical formula	C _{25.5} H ₁₇ N ₂ NdO _{7.5}	θ range for data collection	2.63~25.5
Molecular weight	615.65	Limiting indices	$-11 \leq h \leq 10, -13 \leq k \leq 10, -22 \leq l \leq 25$
Crystal system	Monoclinic	Reflections collected / unique (R_{int})	10 341 / 4 315 (0.047 5)
Space group	$P2_1/c$	D_c / (g · cm ⁻³)	1.724
a / nm	0.982 7(8)	μ / mm ⁻¹	2.241
b / nm	1.140 6(10)	Data / restraints / parameters	4 315 / 24 / 376
c / nm	2.1158(19)	Goodness-of-fit on F^2	1.046
β / (°)	90.574(9)	Final R indices ($(I \geq 2\sigma(I))$ R_1, wR_2	0.058 3, 0.111 5
V / nm ³	2.371(4)	R indices (all data) R_1, wR_2	0.103 3, 0.139 4
Z	4	Largest diff. peak and hole / (e · nm ⁻³)	1 993 and -2 164
$F(000)$	1 216		

Table 2 Selected bond distances (nm) and bond angles (°) for compound 1

Nd(1)-O(1)	0.251 0(6)	Nd(1)-O(2)	0.248 1(7)	Nd(1)-O(4)#3	0.241 3(7)
Nd(1)-O(5)#2	0.241 1(6)	Nd(1)-O(6)	0.226 4(12)	Nd(1)-O(6)#4	0.288 0(16)
Nd(1)-O(7)#4	0.269 3(12)	Nd(1)-O(9)#5	0.270 4(12)	Nd(1)-O(10)#1	0.223 6(16)
Nd(1)-N(1)	0.265 4(8)	Nd(1)-N(2)	0.263 4(8)		
O(10)#1-Nd(1)-O(6)	88.6(4)	O(10)#1-Nd(1)-O(5)#5	71.7(5)	O(6)-Nd(1)-O(5)#2	74.4(4)
O(10)#1-Nd(1)-O(4)#6	77.7(5)	O(6)-Nd(1)-O(4)#3	70.6(4)	O(5)#2-Nd(1)-O(4)#3	133.5(2)
O(10)#1-Nd(1)-O(2)	93.5(6)	O(6)-Nd(1)-O(2)	155.3(4)	O(5)#2-Nd(1)-O(2)	129.4(2)
O(4)#3-Nd(1)-O(2)	85.8(2)	O(10)#1-Nd(1)-O(1)	91.5(5)	O(6)-Nd(1)-O(1)	152.7(4)
O(5)#2-Nd(1)-O(1)	79.7(2)	O(4)#3-Nd(1)-O(1)	135.9(2)	O(2)-Nd(1)-O(1)	51.9(2)
O(10)#1-Nd(1)-N(2)	146.4(5)	O(6)-Nd(1)-N(2)	92.4(4)	O(5)#2-Nd(1)-N(2)	76.3(2)
O(4)#3-Nd(1)-N(2)	133.9(2)	O(2)-Nd(1)-N(2)	99.2(2)	O(1)-Nd(1)-N(2)	72.9(2)
O(10)#1-Nd(1)-N(1)	151.1(5)	O(6)-Nd(1)-N(1)	94.9(4)	O(5)#2-Nd(1)-N(1)	136.8(3)
O(4)#3-Nd(1)-N(1)	76.5(3)	O(2)-Nd(1)-N(1)	71.9(2)	O(1)-Nd(1)-N(1)	98.1(2)
N(2)-Nd(1)-N(1)	62.3(3)	O(10)#1-Nd(1)-O(7)#4	33.1(6)	O(6)-Nd(1)-O(7)#4	118.5(5)
O(5)#2-Nd(1)-O(7)#4	94.0(4)	O(4)#3-Nd(1)-O(7)#4	77.2(4)	O(2)-Nd(1)-O(7)#4	60.4(3)
O(1)-Nd(1)-O(7)#4	71.5(3)	N(2)-Nd(1)-O(7)#4	144.2(3)	N(1)-Nd(1)-O(7)#4	126.5(4)
O(10)#1-Nd(1)-O(9)#5	122.1(6)	O(6)-Nd(1)-O(9)#5	34.3(5)	O(5)#2-Nd(1)-O(9)#5	81.1(4)
O(4)#3-Nd(1)-O(9)#5	86.8(4)	O(2)-Nd(1)-O(9)#5	141.0(3)	O(1)-Nd(1)-O(9)#5	132.8(4)
N(2)-Nd(1)-O(9)#5	60.8(4)	N(1)-Nd(1)-O(9)#5	69.1(3)	O(7)#4-Nd(1)-O(9)#5	152.7(4)
O(10)#1-Nd(1)-O(6)#4	13.6(6)	O(6)-Nd(1)-O(6)#4	75.0(5)	O(5)#2-Nd(1)-O(6)#4	68.2(3)
O(4)#3-Nd(1)-O(6)#4	73.8(3)	O(2)-Nd(1)-O(6)#4	105.9(3)	O(1)-Nd(1)-O(6)#4	103.4(3)
N(2)-Nd(1)-O(6)#4	144.3(3)	N(1)-Nd(1)-O(6)#4	150.3(3)	O(7)#4-Nd(1)-O(6)#4	45.9(3)
O(9)#5-Nd(1)-O(6)#4	108.6(4)	Nd(1)-O(6)-Nd(1)#4	105.0(5)		

Symmetry transformations used to generate equivalent atoms: #1: $x, y+1, z$; #2: $x, -y+3/2, z-1/2$; #3: $-x+2, y-1/2, -z+3/2$;

#4: $-x+2, -y+1, -z+1$; #5: $-x+2, -y, -z+1$; #6: $-x+2, y+1/2, -z+3/2$.

K on a Bruker Smart Apex 1000 CCD diffractometer with Mo $K\alpha$ radiation ($\lambda=0.071\ 073\ \text{nm}$). A summary of the crystallography data and structure refinement is given in Table 1, and selected bond lengths and angles of the complex **1** are listed in Table 2. The structure was solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL-97 system^[19].

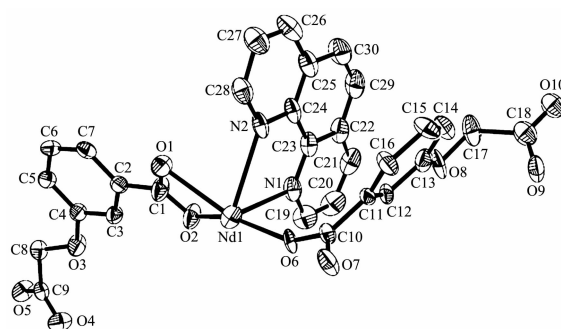
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2 Results and discussion

2.1 Description of the structure

As shown in Fig.1, the asymmetrical unit of the

cell of compound **1** contains one crystallographically unique Nd(III) atom, one and a half 3-CPOA²⁻ ligands, one phen ligand. The 3-CPOA²⁻ ligand takes two centrosymmetric orientations, which results in disordered positions.



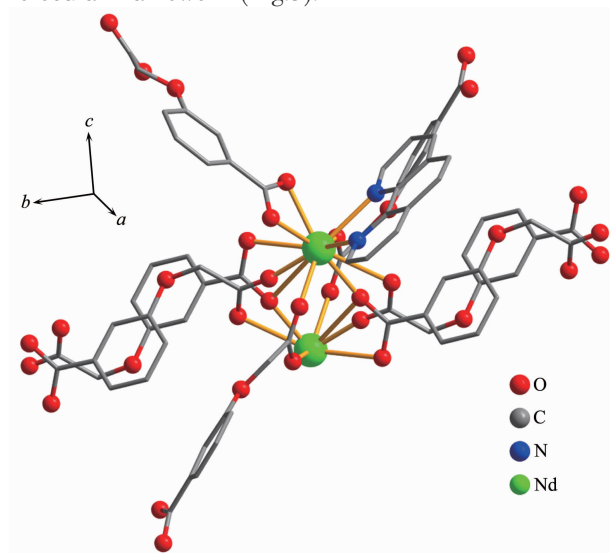
H atoms were omitted for clarity

Fig.1 Drawing of the asymmetric unit of complex **1**

The Nd(III) center is eleven-coordinated by two N atoms of one phen ligand, nine carboxylate O atoms

from seven different 3-CPOA²⁻ ligands. The distances of Nd-O and Nd-N bonds span the range of 0.223 6(16)~0.288 0(16) and 0.263 4(8)~0.265 4(7) nm, which are in good with the bond lengths observed in other eleven-coordinated Nd(III) complexes^[20-21].

The two carboxylate groups of the 3-CPOA²⁻ ligand adopt two different coordination modes: $\mu_1\text{-}\eta^1\text{:}\eta^1$ didentate mode and $\mu_2\text{-}\eta^1\text{:}\eta^1$ didentate mode. Two crystallographically equal Nd(III) centers are bridged by two O atoms of carboxylate groups from two different 3-CPOA²⁻ ligands and two carboxyl groups from two individual 3-CPOA²⁻ ligands in bidentate mode into a binuclear unit (Fig.2) with a Nd-Nd distance of 0.409 7(3) nm, which is further joined by 3-CPOA²⁻ ligands to form a 3D metal-organic supra-molecular framework (Fig.3).



H atoms were omitted for clarity

Fig.2 Dinuclear unit in compound 1

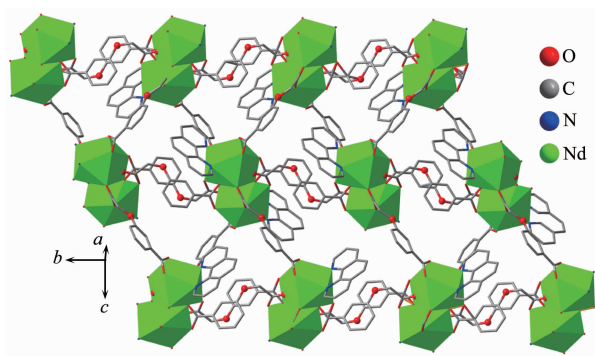


Fig.3 View of 3D network for compound 1 along a axis

2.2 TG analysis and PXRD results

Powder X-ray diffraction experiment was carried

out for compound 1. The pattern for the as-synthesized bulk material closely matches the simulated one from the single-crystal structure analysis, which is indicative of the pure solid-state phase (Fig.4). In order to examine the thermal stability of the network, thermal gravimetric analyses (TG) were carried out for crystalline samples of compound 1 in the temperature range 20~800 °C. As shown in Fig.5, complex 1 was stable up to 370 °C, and then began to decompose.

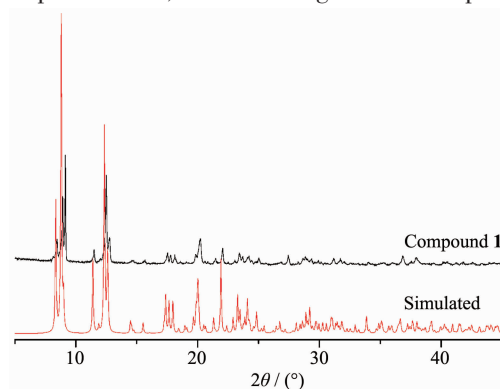


Fig.4 PXRD pattern of compound 1 at room temperature

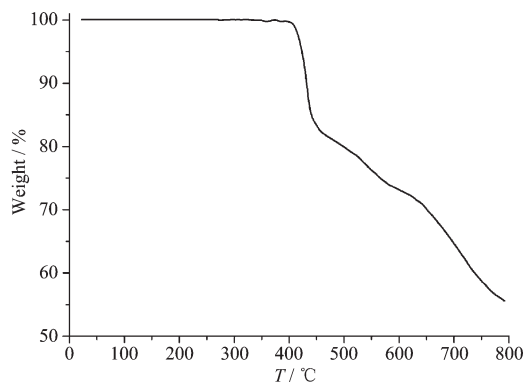


Fig.5 TG curve of compound 1

2.3 Magnetic properties

The magnetic behaviors of compound 1 are shown in Fig.6. The $\chi_M T$ value at room temperature is $1.72 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, which is close to the value expected ($1.64 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$) for one insulated Nd(III) ion ($S=3/2$, $L=6$, $^4I_{9/2}$, $g=8/11$). $\chi_M T$ value decreases continuously to a value of $0.72 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. Between 100 and 300 K, the magnetic susceptibilities can be fitted to the Curie-Weiss law, $\chi_M = C_M / (T - \theta)$, with $C_M = 1.94 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, $\theta = -31.6 \text{ K}$. These results demonstrate a strong antiferromagnetic interactions between the adjacent Nd(III) centers.

According to the chain topology of compound 1,

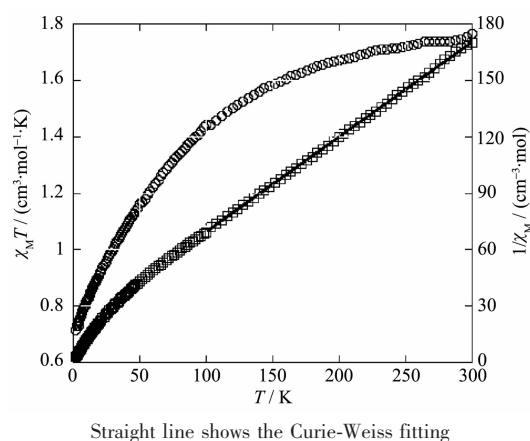


Fig.6 Temperature dependence of $\chi_M T$ (open circle) and $1/\chi_M$ (open square) vs T for compound **1**

because of the long metal-metal distance between the metal centers of dinuclear units, only the coupling interactions between the metal centers within them are considered. There are two set of magnetic exchange pathways within the dinuclear units, which consist of two carboxylate groups in syn-syn fashion and two η^2 -O bridges from the μ_2 -carboxylate groups, cooperatively contributed by the antiferromagnetic coupling transported by mixed bridges, with large Nd-O-Nd ($105.0(5)^\circ$) angle. The larger antiferromagnetic coupling observed in compound **1** can be attributed to the small Nd...Nd separation ($0.409\ 7(5)$ nm) in the diametric Nd(III) ions.

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