

2-丙基-1*H*-4,5-咪唑二酸构筑的混核锌-钕配位聚合物的合成、晶体结构及磁性质

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摘要: 通过水热方法, 合成了一个杂金属的配位聚合物 $\{[\text{NdZn}(\text{H}_2\text{pimda})_3(\text{Hpimda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**1**), (H_3pimda =2-丙基-1*H*-4,5-咪唑二酸), 并对其结构和磁性质进行了研究。结构分析结果表明配合物 **1** 的晶体属于单斜晶系, $P2_1/c$ 空间群。配合物 **1** 是由配体 2-丙基-1*H*-4,5-咪唑二酸连接而成的二维层状结构, 该二维层通过氢键延伸为三维超分子结构。磁性研究表明, 配合物 **1** 中相邻钕离子间存在着反铁磁相互作用。

关键词: 3d-4f 配位聚合物; 2-丙基-1*H*-4,5-咪唑二酸; 氢键; 磁性质

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Synthesis, Crystal Structure and Magnetic Properties of a Zn-Nd Heterometallic Coordination Polymer Constructed by 2-Propyl-1*H*-imidazole-4,5-dicarboxylic Acid

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Abstract: A novel 3d-4f heterometallic coordination polymer, namely, $\{[\text{NdZn}(\text{H}_2\text{pimda})_3(\text{Hpimda})(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}\}_n$ (**1**), (H_3pimda =2-propyl-1*H*-imidazole-4,5-dicarboxylic acid) has been hydrothermally synthesized by using Nd_2O_3 , $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and H_3pimda as raw materials, and characterized by elemental analysis, IR, TG analysis and single crystal X-ray diffraction. The complex **1** crystallizes in the monoclinic system, space group $P2_1/c$ with $a=1.190\ 78(2)$ nm, $b=1.307\ 84(3)$ nm, $c=2.740\ 70(5)$ nm, $\beta=97.930\ 0(10)^\circ$, $V=4.227\ 41(14)$ nm³, $D_c=1.652$ g·cm⁻³, $Z=4$, $R=0.049\ 2$ and $wR=0.111\ 5$ ($I>2\sigma(I)$). Polymer **1** possesses two-dimensional (2D) network, which further build three-dimensional (3D) supramolecular architecture via N—H···O hydrogen-bonding interactions. Variable temperature magnetic susceptibility studies reveal that complex **1** displays weak antiferromagnetic coupling between the neighboring Nd(III) ions. CCDC: 906826.

Key words: 3d-4f coordination polymer; 2-propyl-1*H*-imidazole-4,5-dicarboxylic acid; hydrogen bond; magnetic property

The rational design and syntheses of lanthanide-transition metal (*d-f*) heterometallic complexes are one of the most attractive areas of materials research due to their many superior functional properties and actual or potential applications^[1-5]. However, there are great

challenges in the synthesis of 3d-4f heterometallic coordination polymers, due to the fact that competition reactions of lanthanide and transition metal ions coordinated to the same ligand often leads to the formation of alternative homometallic coordination

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polymers. A feasible strategy for synthesizing 3*d*-4*f* heterometallic coordination polymers is using N/O mixed ligands based on the guidance of the hard-soft acid base theory^[1-8].

Based on this principle, 2-propyl-1*H*-imidazole-4,5-dicarboxylic acid (H₃pimda) with two types of coordination sites was finally selected as the ligand, which may overcome the competition reaction between d and f block ions. Herein we report the synthesis, crystal structure and magnetic properties of a novel 3*d*-4*f* heterometallic coordination polymer, namely, {[NdZn(H₂pimda)₃(Hpimda)(H₂O)₂]·H₂O}_n (**1**).

1 Experimental

1.1 Reagents and physical measurements

All 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. 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 {[NdZn(H₂pimda)₃(Hpimda)(H₂O)₂]·H₂O}_n (**1**)

A mixture of Zn(NO₃)₂·6H₂O (0.150 g, 0.5 mmol), Nd₂O₃ (0.168 g, 0.5 mmol), H₃pimda (0.400 g, 2.0 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. Colorless block-shaped crystals of **1** were isolated manually, and washed with distilled water. Yield: 60% (based on Zn). Anal. Calcd for C₃₂H₄₁ZnNdN₈O₁₉ (**1**)(%): C 36.56, H 3.93, N 10.66; found (%): C 36.21, H 4.12, N 10.96. IR (KBr, cm⁻¹): 3 417 s, 2 970 m, 2 876 w, 1 725 m, 1 589 m, 1 532 s, 1 472 s, 1 415 m, 1 387 m, 1 265 m, 1 121 w, 1 054 w,

1 032 w, 975 w, 813 m, 775 w, 661 w, 515 w.

The compound is insoluble in water and common organic solvents, such as methanol, ethanol, acetone, and DMF.

1.3 Structure determinations

Single-crystal diffraction data of **1** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo *K*α radiation (λ=0.071 073 nm) at room temperature. The structure was solved using direct methods and successive Fourier difference synthesis (SHELXS-97^[9]), and refined using the full-matrix leastsquares method on *F*² with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97). An empirical absorption correction was applied using the SADABS program. In the structure, the disordered propyl carbon atoms of the ligands were restrained in order to obtain reasonable thermal parameters. The hydrogen atoms of the H₂pimda⁻ and Hpimda²⁻ ligands were placed in calculated positions and refined using a riding on attached atoms with isotropic thermal parameters 1.2 times those of their carrier atoms. The hydrogen atoms of the water molecules were located by difference maps and constrained to ride on their parent O atoms. 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 hydrogen bonds in crystal packing of the complex **1** are listed in Table 3.

CCDC: 906826.

2 Results and discussion

2.1 Description of the structure

Single-crystal X-ray diffraction analysis reveals that complex **1** crystallizes in monoclinic space group *P*2₁/*c*. As shown in Fig.1, the asymmetrical unit of the cell of compound **1** contains one crystallographically unique Nd (III) ion, one Zn (II) ion, three H₂pimda⁻ ligands, one Hpimda²⁻ ligand, two coordinated water molecules and one lattice water molecule. The nine-coordinated Nd (III) ion has a distorted tricapped trigonal geometry with one N atom of one H₂pimda⁻ ligand, six carboxylate O atoms from two Hpimda²⁻

Table 1 Crystal data for complex 1

Complex	1	Crystal size / mm	0.28×0.26×0.24
Chemical formula	C ₃₂ H ₄₁ NdZnN ₈ O ₁₉	θ range for data collection	1.73~25.50
Formula weight	1 051.34	Limiting indices	$-14 \leq h \leq 13, -15 \leq k \leq 15, -33 \leq l \leq 30$
Crystal system	Monoclinic	Reflections collected / unique (R_{in})	22 452 / 7 861 (0.022 7)
Space group	$P2_1/c$	D_c / (g·cm ⁻³)	1.652
a / nm	1.190 78(2)	μ / mm ⁻¹	1.867
b / nm	1.307 84(3)	Data / restraints / parameters	7 861 / 54 / 557
c / nm	2.740 70(5)	Goodness-of-fit on F^2	1.077
β / (°)	97.930 0(10)	Final R indices ($I \geq 2\sigma(I)$) R_1, wR_2	0.049 2, 0.111 5
V / nm ³	4.227 41(14)	R indices (all data) R_1, wR_2	0.058 1, 0.116 9
Z	4	Largest diff. peak and hole / (e·nm ⁻³)	1 352 and -1 988
$F(000)$	2 124		

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

Nd(1)-O(1)	0.239 7(4)	Nd(1)-O(3)	0.249 0(4)	Nd(1)-O(3) ⁱⁱ	0.258 4(4)
Nd(1)-O(4) ⁱⁱ	0.264 3(5)	Nd(1)-O(5)	0.247 7(4)	Nd(1)-O(16) ⁱ	0.246 6(4)
Nd(1)-O(17)	0.246 9(5)	Nd(1)-O(18)	0.246 6(4)	Nd(1)-N(3)	0.259 3(5)
Zn(1)-O(2)	0.213 9(4)	Zn(1)-O(9)	0.213 4(5)	Zn(1)-O(13)	0.219 9(5)
Zn(1)-N(1)	0.212 2(5)	Zn(1)-N(5)	0.210 8(5)	Zn(1)-N(7)	0.214 8(5)
O(1)-Nd(1)-O(18)	107.55(17)	O(1)-Nd(1)-O(16) ⁱ	138.78(16)	O(18)-Nd(1)-O(16) ⁱ	75.23(16)
O(1)-Nd(1)-O(17)	70.16(15)	O(18)-Nd(1)-O(17)	72.63(16)	O(16) ⁱ -Nd(1)-O(17)	71.87(16)
O(1)-Nd(1)-O(5)	72.46(15)	O(18)-Nd(1)-O(5)	140.87(13)	O(16) ⁱ -Nd(1)-O(5)	131.36(15)
O(17)-Nd(1)-O(5)	136.67(14)	O(1)-Nd(1)-O(3)	71.97(13)	O(18)-Nd(1)-O(3)	70.75(14)
O(16) ⁱ -Nd(1)-O(3)	140.66(15)	O(17)-Nd(1)-O(3)	114.59(16)	O(5)-Nd(1)-O(3)	72.42(13)
O(1)-Nd(1)-O(3) ⁱⁱ	131.57(13)	O(18)-Nd(1)-O(3) ⁱⁱ	77.24(15)	O(16) ⁱ -Nd(1)-O(3) ⁱⁱ	89.57(15)
O(17)-Nd(1)-O(3) ⁱⁱ	147.70(14)	O(5)-Nd(1)-O(3) ⁱⁱ	75.33(13)	O(3)-Nd(1)-O(3) ⁱⁱ	64.33(15)
O(1)-Nd(1)-N(3)	75.36(15)	O(18)-Nd(1)-N(3)	153.48(15)	O(16) ⁱ -Nd(1)-N(3)	85.51(16)
O(17)-Nd(1)-N(3)	84.24(17)	O(5)-Nd(1)-N(3)	65.61(14)	O(3)-Nd(1)-N(3)	132.68(14)
O(3) ⁱⁱ -Nd(1)-N(3)	121.34(15)	O(1)-Nd(1)-O(4) ⁱⁱ	138.22(14)	O(18)-Nd(1)-O(4) ⁱⁱ	111.86(16)
O(16) ⁱ -Nd(1)-O(4) ⁱⁱ	66.88(15)	O(17)-Nd(1)-O(4) ⁱⁱ	135.05(15)	O(5)-Nd(1)-O(4) ⁱⁱ	68.43(15)
O(3)-Nd(1)-O(4) ⁱⁱ	108.51(13)	O(3) ^{#2} -Nd(1)-O(4) ⁱⁱ	49.37(12)	N(3)-Nd(1)-O(4) ⁱⁱ	75.66(15)
Nd(1)-O(3)-Nd(1) ⁱⁱ	115.67(15)	N(5)-Zn(1)-N(1)	100.90(19)	N(5)-Zn(1)-O(9)	78.73(13)
N(1)-Zn(1)-O(9)	168.26(19)	N(5)-Zn(1)-O(2)	94.17(17)	N(1)-Zn(1)-O(2)	77.56(17)
O(9)-Zn(1)-O(2)	90.74(16)	N(5)-Zn(1)-N(7)	161.42(17)	N(1)-Zn(1)-N(7)	95.21(17)
O(9)-Zn(1)-N(7)	87.37(18)	O(2)-Zn(1)-N(7)	98.32(18)	N(5)-Zn(1)-O(13)	90.72(18)
N(1)-Zn(1)-O(13)	102.30(17)	O(9)-Zn(1)-O(13)	89.40(16)	O(2)-Zn(1)-O(13)	175.05(15)
N(7)-Zn(1)-O(13)	76.74(18)				

Symmetry transformations used to generate equivalent atoms: ⁱ $x, -y+1/2, z+1/2$; ⁱⁱ $-x+2, -y, -z+2$.

ligands and two H₂pimda⁻ ligands, and two O atoms of two coordinated water molecules. The distances of Nd-O and Nd-N bonds are 0.239 7(4)~0.264 3(5) nm and 0.259 3(5) nm, which are in good with the bond lengths observed in other Nd(III) complexes^[1-2,4-5]. The Cd(II) ion is six-coordinated by three N and three O

atoms from two H₂pimda⁻ ligands and one Hpimda²⁻ ligand, resulting in a distorted octahedral coordination geometry. The distances of Cd-O and Cd-N bonds span the range of 0.213 4(5)~0.219 9(5) nm and 0.210 8(5)~0.214 8(5) nm, which is compared to those of other Zn(II) complexes^[5,10]. In complex **1**, the H₃pimda ligands

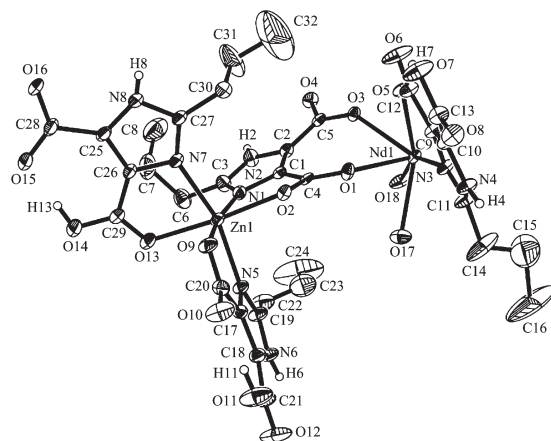
Table 3 Hydrogen bond lengths and angles of complex **1**

D-H...A	<i>d</i> (D-H) / nm	<i>d</i> (H...A) / nm	<i>d</i> (D...A) / nm	∠DHA / (°)
N(8)-H(8)···O(19) ^{iv}	0.076	0.200	0.272 1	158.9
N(6)-H(6)···O(7) ^v	0.086	0.201	0.283 7	160.6
N(4)-H(4)···O(2) ^{vi}	0.086	0.197	0.281 0	164.3
O(19)-H(6W)···O(10) ^{viii}	0.085	0.185	0.269 8	179.6
O(19)-H(5W)···O(4) ^{viii}	0.085	0.194	0.277 6	167.7
O(18)-H(4W)···O(15) ⁱ	0.085	0.207	0.283 8	151.3
O(18)-H(3W)···O(5) ⁱⁱ	0.085	0.194	0.271 3	152.4
O(17)-H(2W)···O(12) ^{ix}	0.084	0.225	0.290 9	135.6
O(17)-H(1W)···O(8) ^{vi}	0.084	0.189	0.272 4	170.1
O(14)-H(13)···O(15)	0.082	0.171	0.251 9	166.3
O(11)-H(11)···O(10)	0.082	0.173	0.254 7	178.3
O(7)-H(7)···O(6)	0.082	0.163	0.244 6	177.3

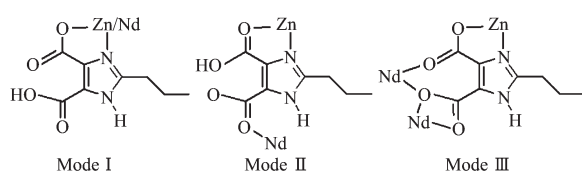
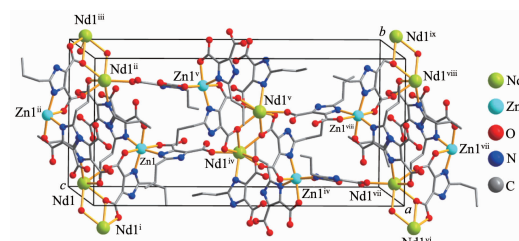
Symmetry code: ⁱ *x*, -*y*+1/2, *z*+1/2; ⁱⁱ -*x*+2, -*y*, -*z*+2; ^{iv} *x*+1, -*y*+1/2, *z*+1/2; ^v *x*-1, *y*, *z*; ^{vi} -*x*+2, -*y*+1, -*z*+2; ^{viii} -*x*+1, -*y*+1, -*z*+1; ^{viii} -*x*+1, -*y*, -*z*+1; ^{ix} -*x*+1, -*y*+1, -*z*+2.

adopt three different coordination modes: μ_1 -didentate mode, μ_2 -tridentate mode and μ_3 -pentadentate mode, respectively (Scheme 1).

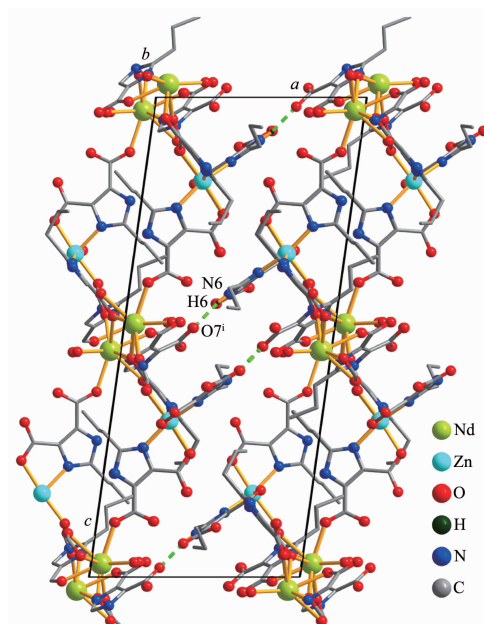
The Hpimda²⁻ ligand connects two Nd(III) and one Zn(II) ions to form a [Nd₂Zn] trinuclear unit (Scheme 1, mode III). The trinuclear units are further linked by the coordination interaction of H₂pimda⁻ ligands to generate a 2D sheet (Scheme 1, mode II; Fig.2). The



H atoms were omitted for clarity except those bond to N and carboxylate O atoms

Fig.1 Drawing of the asymmetric unit of complex **1****Scheme 1** Coordination modes for H₂pimda/Hpimda²⁻ in compound **1**

Symmetry code: ⁱ -*x*+2, -*y*, -*z*+2; ⁱⁱ -*x*+2, -*y*+1, -*z*+2; ⁱⁱⁱ *x*, *y*+1, *z*; ^{iv} *x*, -*y*+1/2, *z*-1/2; ^v -*x*+2, *y*+1/2, -*z*+3/2; ^{vi} -*x*+2, -*y*, -*z*+1; ^{vii} *x*, *y*, *z*-1; ^{viii} -*x*+2, -*y*+1, -*z*+1; ^{ix} *x*, *y*+1, *z*-1

Fig.2 View of the 2D layer along the *bc* plane

Green dashed lines present N-H...O hydrogen bonds; Symmetry code: ⁱ *x*-1, *y*, *z*

Fig.3 3D structure formed by N-H...O hydrogen bonds in the adjacent sheets in compound **1**

2D layers are further extended into a 3D metal-organic supramolecular framework by N-H...O hydrogen bond interactions (N6-H6...O7ⁱ, N6...O7ⁱ=0.283 7(6) nm, ⁱ $x-1, y, z$; Fig.3; Table 3).

2.2 TG analysis

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 38~800 °C. As shown in Fig.4, the one lattice water and two coordinated water molecules were gradually lost in the temperature range 38~194 °C (observed: 5.01%; expected: 5.15%). Upon further heating, the framework began to decompose.

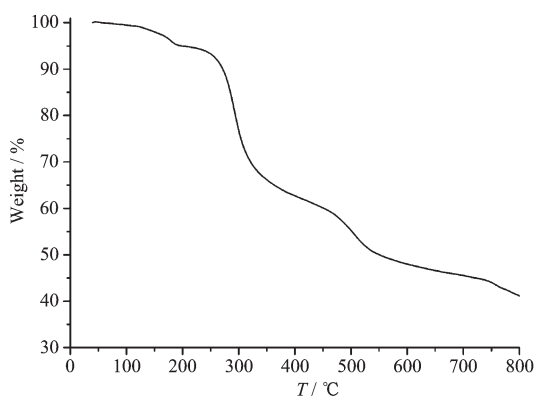
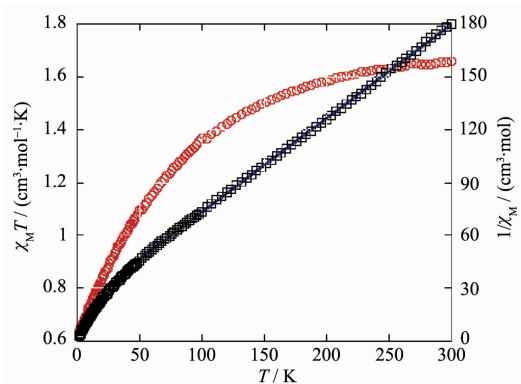


Fig.4 TG curve for compound **1**

2.3 Magnetic properties

The magnetic behaviors of compound **1** are shown in Fig.5. The $\chi_M T$ value at room temperature is $1.66 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, 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



Solid line shows the Curie-Weiss fitting

Fig.5 Temperature dependence of $\chi_M T$ (○) and $1/\chi_M$ (□) vs T for complex **1**

continuously to a value of $0.65 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$ at 2 K. Between 50 and 300 K, the magnetic susceptibilities can be fitted to the Curie-Weiss law, $\chi_M = C_M / (T - \theta)$, with $C_M = 1.95 \text{ cm}^3 \cdot \text{mol}^{-1} \cdot \text{K}$, $\theta = -31.8 \text{ K}$. These results demonstrate a strong antiferromagnetic interactions between the adjacent Nd(III) centers.

According to the sheet topology of compound **1**, because of the long metal-metal distance between the metal centers of Nd₂ dinuclear units (Fig.2), 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 ($115.7(4)^\circ$) angle (Fig.2). The larger antiferromagnetic coupling observed in compound **1** can be attributed to the small Nd...Nd separation ($0.429 6(4) \text{ nm}$) in the diametric Nd(III) ions.

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