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研究简报

基于 3,4-吡啶二羧酸配体的钆(Ⅲ)配合物的合成、晶体结构及热性质

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Synthesis, Crystal Structure and Thermal Properties of A Gadolinium(Ⅲ) Coordination Polymer Constructed by Pyridine-3,4-dicarboxylate Ligand

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Abstract: The hydrothermal reaction of pyridine-3,4-dicarboxylic acid ($pydcH_2$), 4,4′-bipyridine and $GdCl_3\cdot 6H_2O$ yield a novel gadolinium coordination polymer $\{[Gd_2(pydc)_2(\mu_3\text{-}OH)_2(H_2O)_2]\cdot H_2O\}_n$ (**1**). The compound was characterized by elemental analysis, thermal analysis, IR spectra and single-crystal X-ray structure analysis. The crystal of the Gd(Ⅲ) complex belongs to triclinic system, space group $P\bar{1}$ with: a=0.796 25(16) nm, b=0.944 46(19) nm, c=1.262 1(3) nm, α=76.50(3)°, β=84.95(3)°, γ=83.04(3)°, Z=2, V=0.914 4(3) nm^3, D_c=2.669 g·cm^{-1}, μ=7.269 mm^{-1}, F(000)=692, and R_1=0.033 3, wR_2=0.062 3. The crystal structure revealed that compound **1** has a 2D layer structure incorporating 1D Gd-O-Gd double chain, and hydrogen bonding interactions result in the former of 3D supramolecular network structure. CCDC: 669079.

Key words: gadolinium(Ⅲ) complex; pyridine-3,4-dicarboxylate; hydrothermal synthesis; crystal structure; thermal stability

In recent years, the rational design and synthesis of metal-organic coordination polymers (MOCPs) has become an exciting field for their novel structural architectures and potential applications in ion exchange, adsorption, nonlinear optics and magnetism[1~7]. Among the most extensively studied metal-organic frameworks are those based on carboxylate ligands for exhibiting various coordination modes to finish various structures with honeycomb, brickwall, rectangular grid, bilayer, ladder, diamonds and open frameworks[8,9]. As a member of multicarboxylate ligands containing N-donor, Pyridine-3,4-dicarboxylic acid has unique feathers compared to *p*-pyridinecarboxylic acid and *m*-pyridinecarboxylic acid, showing an excellent building block with

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charge and multi-connecting ability[10,11]. On the other hand, Lanthanide complexes have attracted extensive interest in recent years, in that they possess interesting magnetic and fluorescence properties, so they are likely to provide new materials that possess specific properties and desired features[12~14]. However, to the best of knowledge, there has been only a few reported polymers constructed by lanthanide metal and pydc ligand hitherto[15~18]. On the basis of the aforementioned points, our aim is to synthesize novel high-dimensional polymers through combining respective merits of pyridine-3,4-dicarboxylic acid and lanthanide metal. In this paper, we report a novel lanthanide metal complex $\{[Gd_2(pydc)_2(\mu_3\text{-}OH)_2(H_2O)_2]\cdot H_2O\}_n$, its thermal behavior was also investigated.

1 Experimental

1.1 General

The starting compound $GdCl_3\cdot 6H_2O$ was prepared by reacting its oxide Gd_2O_3 with a stoichiometric amount of hydrochloric acid followed by drying. All the other reagents are of commercially available and were used as received without further purification. IR spectra were recorded on a FTIR-8900 spectrophotometer as KBr pellets in the range 4 000~400 cm^{-1}. Elemental analyses (C, H and N) were determined with a Vario EL Elemental analyzer. Thermogravimetric analysis (TGA) were performed on a TGA-7 instrument in a static atmosphere of air with a heating rate of 7 ℃·min^{-1}.

1.2 Preparation of $\{[Gd_2(pydc)_2(\mu_3\text{-}OH)_2(H_2O)_2]\cdot H_2O\}_n$

Compound **1** was synthesized from the reaction mixture of $GdCl_3\cdot 6H_2O$ (0.074 3 g, 0.2 mmol), pyridine-3,4-dicarboxylic acid (0.033 4 g, 0.2 mmol), 4,4′-bipyridine (0.031 2 g, 0.4 mmol) and water (8 mL) in a 15 mL Teflon reactor, under autogenous pressure at 180 ℃ for 5 days and then cooled to room temperature slowly. Colorless crystals of compound **1** were obtained, yield 53%. Anal. Calcd. for $C_{14}H_{14}Gd_2N_2O_{13}$ (%): C, 22.95; H, 1.93; N, 3.82. Found(%): C, 22.83; H, 2.05; N, 3.52. IR (KBr, cm^{-1}): 3 522 m (ν_{OH}), 1 577s (ν^{as}_{COO}), 1 430m(ν^{s}_{coo}), 1 396s (ν^{s}_{COO}), 420w ($\nu_{Gd\text{-}O}$).

1.3 Crystal structure determination

Diffraction data of **1** were collected on a Bruker P4 SMART-CCD area detector diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at 293(2) K and using the φ-ω-scan mode. Data reductions and absorption corrections were performed with SAINT and SADABS software, respectively. The structure was solved by direct methods and refined on F^2 by full-matrix least squares using SHELXTL program. All non-hydrogen atoms were treated anisotropically. The positions of hydrogen atoms were generated geometrically. Crystallographic data and experimental details for structural analyses are summarized in Table 1.

CCDC: 669079.

Table 1 Crystallographic data and structural refinement for 1

Empirical formula	$C_{14}H_{14}Gd_2N_2O_{13}$	D_c /(Mg·m^{-3})	2.661
Formula weight	732.77	μ / mm^{-1}	7.269
Temperature / K	293(2)	F(000)	688
Wavelength / nm	0.071 073	Crystal size / mm	0.12×0.10×0.06
Crystal system	Triclinic	θ range / (°)	3.07~27.48
Space group	$P\bar{1}$	Limiting indices	$-10 \leqslant h \leqslant 10, -12 \leqslant k \leqslant 12, -16 \leqslant l \leqslant 16$
a / nm	0.796 25(16)	Reflections collected / unique (R_{int})	9 775 / 4 181 (0.0395)
b / nm	0.944 46(19)	Reflections observed [$I>2\sigma(I)$]	3485
c / nm	1.262 1(3)	Completeness to θ=27.48° / %	99.8
α / (°)	76.50(3)	Data / restraints / parameters	4 181 / 0 / 280
β / (°)	84.95(3)	Goodness-of-fit on F^2	1.093
γ / (°)	83.04(3)	Final R indices [$I>2\sigma(I)$]	R_1=0.033 1, wR_2=0.061 3
V	914.4(3)	R indices (all data)	R_1=0.046 3, wR_2=0.064 4
Z	2	Largest diff. peak and hole / (e·nm^{-3})	1 081 and −989

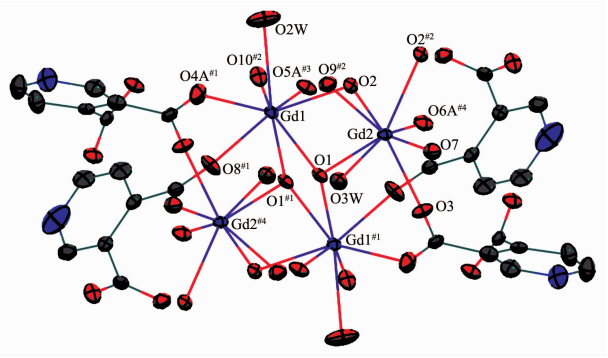
2 Results and discussion

2.1 Synthesis of complex 1

In the synthesis of title compounds, we chosen pyrisine-3,4-dicarboxylic acid and 4,4′-bipyridine as organic build in order to synthesize Gd complex with these two ligands, but the structure of result product don′t include 4,4′-bpy. Interestingly, Complex **1** has not been successfully obtained when we removed the 4,4′-bipyridine from the reaction system, which illustrates that 4,4′-bpy play a key role in the formation and crystallization of the title compound. The reason that the title compound don′t conclude 4,4′-bipyridine ligand may be that N atom is difficult to coordinate with lanthanide ion compared with O atom.

2.2 Crystal structure of 1

An ORTEP drawing of the asymmetric unit of $\{[Gd_2(pydc)_2(\mu_3\text{-}OH)_2(H_2O)_2]\cdot H_2O\}_n$ is shown in Fig.1. Selected bond distances and angles are listed in Table 2.



Symmetry codes: #1 −x, −y, −z+1; #2 −x+1, −y, −z+1; #3 x, y−1, z; #4 −x+1, −y+1, −z+1

Fig.1　ORTEP drawing for complex **1** with the atom labelling scheme

Single crystal structure reveals that the complex crystallizes in triclinic $P\bar{1}$ space group and is a two-dimensional neutral metallopolymer. Each asymmetric unit in **1** contains two gadolinium ions, two pydc anions, two OH^- groups, two aqua ligands, and one isolated water molecular. There are two crystallographically different gadolinium ions in **1**, they all exhibit distorted

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

Gd(1)-O(2)	0.232 5(3)	Gd(1)-O(4)#1	0.237 0(4)	Gd(1)-O(9)#2	0.238 0(4)
Gd(1)-O(6)#3	0.239 1(4)	Gd(1)-O(1)#1	0.240 6(3)	Gd(1)-O(8)#1	0.242 2(4)
Gd(1)-O(1)	0.245 2(4)	Gd(1)-O(2W)	0.256 1(3)	Gd(1)-Gd(2)	0.388 59(10)
Gd(2)-O(10)#2	0.231 3(4)	Gd(2)-O(3)	0.233 6(4)	Gd(2)-O(1)	0.237 9(3)
Gd(2)-O(7)	0.237 9(4)	Gd(2)-O(2)#2	0.240 1(3)	Gd(2)-O(5)#4	0.241 3(4)
Gd(2)-O(2)	0.247 5(3)	Gd(2)-O(3W)	0.248 9(4)	Gd(2)-Gd(2)#2	0.407 42(14)
O(2)-Gd(1)-O(4)#1	144.05(13)	O(2)-Gd(1)-O(9)#2	81.58(12)	O(4)#1-Gd(1)-O(9)#2	102.98(14)
O(2)-Gd(1)-O(6)#3	71.80(12)	O(2)-Gd(1)-O(1)	68.76(12)	O(4)#1-Gd(1)-O(6)#3	81.67(15)
O(2)-Gd(1)-O(1)#1	101.62(12)	O(2)-Gd(1)-O(8)#1	138.78(13)	O(9)#2-Gd(1)-O(1)#1	152.50(13)
O(9)#2-Gd(1)-O(8)#1	76.35(13)	O(1)#1-Gd(1)-O(1)	69.36(14)	O(9)#2-Gd(1)-O(6)#3	136.41(13)
O(1)#1-Gd(1)-O(8)#1	84.11(13)	O(9)#2-Gd(1)-O(1)	86.99(13)	O(4)#1-Gd(1)-O(1)#1	90.42(13)
O(4A)#1-Gd(1)-O(1)	146.23(12)	O(2)-Gd(1)-O(2W)	77.31(194)	O(6)#3-Gd(1)-O(1)#1	68.67(12)
O(5A)#3-Gd(1)-O(1)	113.19(13)	O(8)#1-Gd(1)-O(1)	75.66(13)	O(4A)#1-Gd(1)-O(8)#1	75.58(15)
O(9)#2-Gd(1)-O(2W)	66.98(14)	O(1)#1-Gd(1)-O(2W)	140.51(12)	O(6)#3-Gd(1)-O(8)#1	144.23(13)
O(10)#2-Gd(2)-O(3)	141.02(14)	O(3)-Gd(2)-O(1)	87.74(13)	O(10)#2-Gd(2)-O(2)#2	76.18(13)
O(9)#2-Gd(2)-O(1)	89.06(13)	O(3)-Gd(2)-O(7)	71.10(13)	O(10)#2-Gd(2)-O(5)#4	80.05(14)
O(10)#2-Gd(2)-O(7)	147.28(13)	O(1)-Gd(2)-O(7)	85.88(13)	O(2)#2-Gd(2)-O(5)#4	76.79(12)
O(3)-Gd(2)-O(2)#2	130.15(13)	O(1)-Gd(2)-O(2)#2	134.02(12)	O(3)-Gd(2)-O(5)#4	79.90(13)
O(7)-Gd(2)-O(2)#2	84.32(13)	O(3)-Gd(2)-O(2)	136.64(12)	O(7)-Gd(2)-O(5)#4	120.94(14)
O(7)-Gd(2)-O(2)	72.04(13)	O(1)-Gd(2)-O(2)	67.54(12)	O(1)-Gd(2)-O(6A)#4	143.75(13)
O(10)#2-Gd(2)-O(2)	76.15(13)	O(3)-Gd(2)-O(3W)	72.02(14)	O(10)#2-Gd(2)-O(3W)	69.92(13)
O(2)#2-Gd(2)-O(2)	66.68(13)	O(7)-Gd(2)-O(3W)	137.85(13)	O(2)#2-Gd(2)-O(3W)	136.21(13)

Symmetry modes: #1: −x, −y, −z+1; #2: −x+1, −y, −z+1; #3: x, y−1, z; #4: −x+1, −y+1, −z+1; #5: x, y+1, z.

bicapped trigonal prism geometries. Each gadolinium center is coordinated by four carboxylate oxygen atoms from four different pydc ligands [Gd-O(pydc)= 0.234 3(4)~0.244 6(4) nm], three birding oxygen atoms from three OH^- ligands [Gd-O(OH^-)=0.234 2(4)~0.248 8(4) nm] and one oxygen atom from the terminal water molecular [Gd(1)-O(H_2O)=0.250 8(5)~0.258 4(5) nm], The Gd-O bond distances range from 0.229 9(5) to 0.272 7(6) nm and the O-Gd-O bond angles range from 66.87(18)° to 152.35(14)°, which are all within the range of those observed for other Gd(Ⅲ) complexes with oxygen donor ligands[19,20]. Gd(1) and Gd(2) centers are connected together via μ_3-oxygen atoms of OH^- groups in an edge-sharing mode to form a one-dimensional double chain along *a* axis with adjacent Gd⋯Gd distance of 0.399 51(14) and 0.407 44(14) nm. The one-dimensional double chains are linked to each other via bridging carboxylate oxygen atoms of the pydc groups to form a two-dimensional layer structure (Fig.2). The interlayer free water molecules are hydrogen bonded to the pydc nitrogen atoms and coordinated water molecules in the adjacent layers.

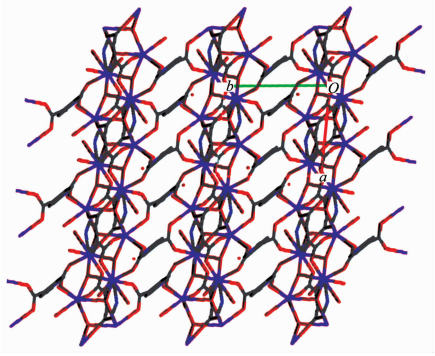


Fig.2 2D layered structures of complex **1**

These 2D layers are stacked along the c axis into a 3D supramolecular architecture through hydrogen bonding (Fig.3). The typical hydrogen bonds are O(3W)–H(3WB)⋯O(1W) and O(1W)–H(1WA)⋯N(1)#7. Details of the hydrogen bonds are given in Table 3. It should be noteworthy that, all the pydc ligands adopt bidentate-bidentate mode to connect four Gd atoms (Scheme 1), which not only plays a key role in joining adjacent double chains, but also participates in the construction of double chains.

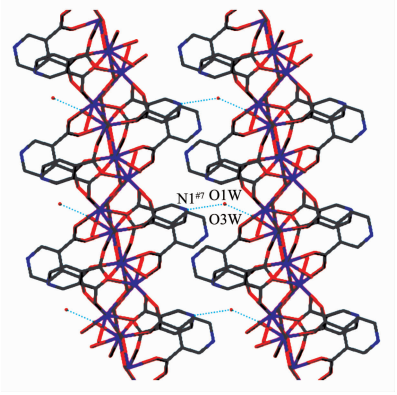
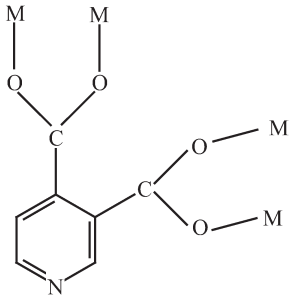


Fig.3 3D supramolecular structure of complex **1**



Scheme 1 Coordination modes of PDC ligand in complex **1**

Table 3 Hydrogen bonds and bond angles for 1

D–H⋯A	*d*(D-H) / nm	*d*(H⋯A) / nm	*d*(D⋯A) / nm	∠(DHA) / (°)
O(3W)–H(3WB)⋯O(1W)	0.085	0.191	0.27 36(6)	164.9
O(3W)–H(3WA)⋯O(4)#6	0.085	0.227	0.309 8(6)	166.3
O(2W)–H(2WB)⋯O(5)#2	0.085	0.220	0.303 3(6)	167.2
O(2W)–H(2WA)⋯O(7)#2	0.085	0.234	0.319 4(6)	179.5
O(1W)–H(1WB)⋯O(9)#2	0.085	0.253	0.313 9(6)	129
O(1W)–H(1WB)⋯O(8)#1	0.085	0.234	0.310 5(7)	150.3
O(1W)–H(1WA)⋯N(1)#7	0.085	0.205	0.289 4(7)	169.7
O(2)–H(2)⋯O(7)	0.098	0.233	0.285 6(5)	113.1
O(1)–H(1)⋯O(3W)	0.098	0.240	0.289 5(5)	110.4

Symmetry modes: #1: $-x, -y, -z+1$; #2: $-x+1, -y, -z+1$; #3: $x, y-1, z$; #4: $-x+1, -y+1, -z+1$; #5: $x, y+1, z$; #6: $-x, -y+1, -z+1$; #7: $x, y, z-1$.

2.3 IR spectra

The IR spectrum of the title complex shows characteristic bands of carboxylate groups of the pydc ligand at 1 577 cm^{-1} for asymmetric vibration and 1 430 and 1 396 cm^{-1} for symmetric vibration. The separations between $\nu_{asym(CO_2)}$ and $\nu_{sym(CO_2)}$ bands show that the carboxylate groups coordinate to the metal atoms in a bridging fashion[21]. The absence of the characteristic bands at around 1 700 cm^{-1} in compounds **1** attributed to the protonated carboxylic group indicates that the complete deprotonation of pydcH_2 ligand upon reaction with Gd ion. A new strong characteristic absorption peak at 3 522 cm^{-1} confirm the presences of of the water. The ν(Gd-O) vibration is also observed at 420 cm^{-1}. These assignments are consistent with the structural analysis results.

2.4 Thermal analysis

The thermal behaviour of $\{[Gd_2(pydc)_2(\mu_3\text{-}OH)_2(H_2O)_2]\cdot H_2O\}_n$ was followed up to 900 ℃ in a static atmosphere of air with a heating rate of 7 ℃·min^{-1} (Fig.4).

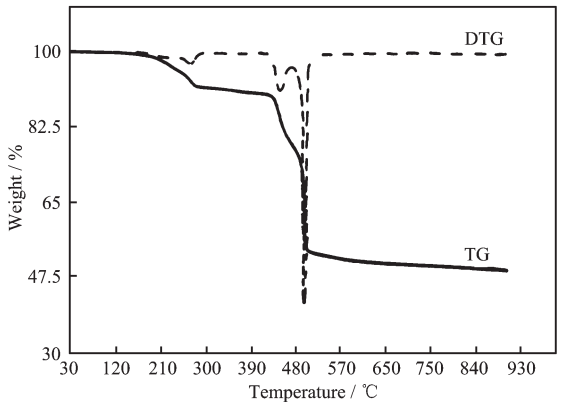


Fig.4　TGA-DTG curve of the title compound

Complex **1** is stable up to 189 ℃, above which its structure begins to collapse. The TG curve of the complex **1** is divided into three stages. The first weight loss 8.1% occurs in the temperature range 189~291 ℃, which can be attributed to the loss of both lattice and coordinated water molecules (calcd. 7.4%). The second stage between 291 and 403 ℃ corresponds to decomposition of two OH^- groups. The observed mass loss is 4.2% which is consistent with the theoretical value of 4.6%. The third stage, which occurs in the temperature range 403 ~518 ℃ with a DTG peak at 489 ℃, corresponds to the decomposition of the organic ligands. The observed mass loss of 38.1% agrees well with the calculated mass loss of 38.5%. The total mass loss of all decomposition process of 50.4% (calcd. 50.5%) for **1** and the remaining weight of 49.6% may correspond to the final product of Gd_2O_3 (calcd. 49.5%).

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