两个基于 2-氨基-5-巯基-1,3,4-噻二唑乙酸的稀土配合物的合成、晶体结构和性质研究

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摘要：用 2-氨基-5-巯基-1,3,4-噻二唑乙酸(Hatma)为配体合成出 2 种新型同构的稀土配合物[Ln(atma)$_3$(H$_2$O)$_2$]$_n$ (Ln=La (**1**),Nd (**2**))。配体和 2 个配合物的结构均由 X-射线单晶衍射法确定,同时对配合物进行了 IR,TGA 及元素分析。单晶结构表明,配体属单斜晶系,*C2/c* 空间群,晶胞参数为 *a*=2.141 9(9) nm,*b*=0.400 76(17) nm,*c*=1.750 0(8) nm,*V*=1.495 0(11) nm³,*Z*=4；配合物 **1** 和 **2** 的晶体都属于三斜晶系,空间群为 *P*1̄,配合物 **1** 的晶胞参数为 *a*=0.882 0(3) nm,*b*=1.230 6(4) nm,*c*=1.258 6(4) nm,*V*=1.291 3(7) nm³,*Z*=2；配合物 **2** 的晶胞参数为 *a*=0.883 4(4) nm,*b*=1.228 3(5) nm,*c*=1.251 0(5) nm,*V*=1.282 1(9) nm³,*Z*=2。2 个配合物均形成一维链状空间结构,通过丰富的氢键连接形成三维超分子结构。抗菌试验表明,配合物比配体表现出更好的生物活性。初步的植物生长实验表明,配合物对油菜和小麦的生长具有一定的促进作用。

关键词：稀土；配位聚合物；晶体结构；生物活性

Synthesis, Crystal Structure and Properties of Two Coordination Polymers Constructed by Lanthanide and [5-Amino-1,3,4-thiadiazol-2-yl]thioglycolic Acid

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Abstract: Two lanthanide(Ⅲ) complexes, [Ln(atma)$_3$(H$_2$O)$_2$]$_n$ have been synthesized (Ln=La (**1**) and Nd (**2**); Hatma= [5-amino-1,3,4-thiadiazol-2-yl]thioglycolic acid). The structure of Hatma ligand and complexes **1**, **2** have been determined by X-ray structural analysis and the structure parameters were analyzed as follows: Hatma, monoclinic, *C2/c*, *a*=2.141 9(9) nm, *b*=0.400 76(17) nm, *c*=1.750 0(8) nm, *V*=1.495 0(11) nm³, *Z*=4; **1**, triclinic, *P*1̄, *a*=0.882 0(3) nm, *b*=1.230 6(4) nm, *c*=1.258 6(4) nm, *V*=1.291 3(7) nm³, *Z*=2; **2**, triclinic, *P*1̄, *a*=0.883 4(4) nm, *b*=1.228 3(5) nm, *c*=1.251 0(5) nm, *V*=1.282 1(9) nm³, *Z*=2. These two complexes are isomorphic and have one-dimensional chain and rich hydrogen bonds which result in three-dimensional supramolecular structures. The complexes were determined by IR, TGA, elemental analysis and single crystal X-ray diffraction. The antimicrobial assays indicate that the two complexes show better activities than free ligand Hatma. The promoting

effects of the title complexes on rape and wheat growth were also tested preliminarily. CCDC: 902095, Hatma; 830535, **1**; 830536, **2**.

Key words: rare earth; coordination polymer; crystal structure; biological activity

0　Introduction

Lanthanide ion is a subject of increasing interest in coordination chemistry and bioinorganic[1-2]. Lanthanide-containing coordination polymers (CPs) have received special attention because of their diverse structural networks and unique optical properties, which may create novel functional materials[3-4]. At the same time, rare earth complexes also have inspired many efforts on the design and synthesis of potential versatile agents for biomedical applications owing to their special electronic configuration[5].

During recent years, the study of coordination compounds with biologically active ligands have received much attention[6-7].

Thiadiazoles, their derivatives and related compounds have been studied for their plant growth regulating effects as well as antimicrobial activity[8-11].

In order to investigate the interaction between lanthanide(Ⅲ) metals and heterocyclic amino acid and to continue our research in thiadiazoles for biological and coordination polymer interests [12-14]. Two novel CPs, [Ln(atma)$_3$(H$_2$O)$_2$]$_n$ (Ln=La(1) and Nd(2)) with flexible ligand-[5-amino-1,3,4-thiadiazol-2-yl]thioglycolic acid (Hatma) containing carboxyl groups as building blocks were synthesized. The two complexes have hydrogen bonded three-dimensional porous structures, which were characterized by IR, elemental analysis, single crystal X-ray diffraction measurements and thermo-gravimetric analyses (TGA). Moreover, the antimicrobial (bacterium and fungus) activities of the free ligand and its complexes have also been studied. The complexes have broad-spectrum antimicrobial activity. The title complexes have better regulating activities than rare earth salts and heteroauxin on the growth of the rape and wheat.

1　Experimental

1.1　General considerations

Materials and Instruments: All of the chemicals are commercially available and used without further purification. Elemental analyses were performed with a Perkin-Elmer 240 elemental analyzer. The IR (KBr pellet) spectra were recorded on a Perkin-Elmer FT-IR spectrometer in the 4 000~400 cm^{-1} range. ^{1}H NMR spectra were recorded on a Varian Mercury Plus-400 MHz spectrometer. Thermogravimetric analyses (TGA) were carried out in an N$_2$ atmosphere with a heating rate of 10 ℃·min^{-1} on a CA Instruments DTA-TGA 2960 type simultaneous analyzer.

1.2　Synthesis of the metal-organic coordination polymer [Ln(atma)$_3$(H$_2$O)$_2$]$_n$

[5-amino-1, 3, 4-thiadiazol-2-yl]thioglycolic acid (Hatma) was synthesized by the 2-amino-5-mercapto-1,3,4-thiadiazole with choroacetic acid following a literature method[13].

A mixture of La$_2$O$_3$ (0.163 g, 0.5 mmol), Hatma (0.096 g, 0.5 mmol), C$_2$H$_5$OH (10 mL) and H$_2$O (5 mL) was sealed in a 23 mL Teflon-lined stainless steel vessel and heated to 180 ℃ for 3 days and then cooled to room temperature at a rate of 5 ℃·h^{-1}. Color-less rectangular block crystals suitable for single crystal X-ray diffraction were obtained. The products were washed with H$_2$O and dried in air. Yield: 0.060 g (47%). Elem anal. Calcd. for C$_{12}$H$_{18}$LaN$_9$O$_9$S$_6$ (%): C, 18.87; H, 2.38; N, 16.51; S, 25.19. Found(%): C,18.83; H, 2.29; N, 16.63; S, 25.21.

Compound **2** was prepared using a similar method to that employed for the synthesis of compound **1**, with Nd$_2$O$_3$ (0.168 g, 0.5 mmol) in place of La$_2$O$_3$. Purple rectangular block crystals suitable for single-crystal X-ray diffraction were obtained. The products were washed with H$_2$O and dried in air. Yield: 0.065 g (51%). Elem anal. Calcd for C$_{12}$H$_{18}$N$_9$NdO$_9$S$_6$ (%): C, 18.74; H, 2.36; N, 16.39; S, 25.02. Found (%): C,18.71; H, 2.33; N, 16.44; S, 25.00.

1.3　Single crystal X-ray diffraction

Crystal data for complex were collected on a Bruker SMART Apex Ⅱ CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ=0.071 073

nm) at 296 K. The structures were solved using a direct method and refined by full-matrix leastsquares on F^2 using the SHELXTL crystallographic software package. For ligand, all hydrogen atoms were placed in calculated positions. For complexes **1**, **2**, lattice water hydrogen atoms were located from difference Fourier maps while the rest were placed on calculated positions.

CCDC: 902095, Hatma; 830535, **1**; 830536, **2**.

1.4 Test of antibacterial activity

Minimum inhibitory concentrations (MICs) were determined by broth dilution technique[15]. To determine the MIC, stock solutions of Ln(Ⅲ) complexes and their ligand were serially diluted using standard two-fold tube dilution procedures and 2 mL of overnight culture (adjusted to an optical density of McFarland 0.5 standard) of bacteria were added to each tube. After 24 h of incubation at 37 ℃ the MIC was determined as the lowest concentration of the compound for the tube (s) showing similar turbidity to that of the negative control (no nutrient broth added).

1.5 Test of antifungal activity

Antifungal activities of the lanthanide(Ⅲ) complexes and their ligand against selected phytopathogenic fungi was assessed by the poisoned food technique[16]. Potato dextrose agar (PDA) was used as growth medium. DMF

was used to prepare solutions of the compounds. The solutions were then mixed with sterilized PDA to maintain the concentration of the complexes at 0.01% (conc. 50 mg·L^{-1}); 20 cm³ of these were each poured into a petri dish. After the medium had solidified, a 5mm mycelial disc for each fungus was placed in the centre of each assay plate against the control. Linear growth of the fungus was measured in mm after five days incubation at (25±2) ℃.

1.6 Test of plant growth regulation activity

Method of plate culture[17] was adopted and compounds solutions were prepared in the concentration of 100, 10, 1, 0.1, 0.01 and 0.001 mg·L^{-1}, where after, rape and wheat seed were cultured in a 10 cm petri dish with 10 ml of different solution and a circular filter paper. Then, the plants were allowed to grow at room temperature, the roots and shoots length was gained after 4 d.

2 Results and discussion

2.1 Description of crystal structures

A summary of the crystallographic data and refinement parameters are given in table 1. Selected bond lengths and angles for Hatma, **1** and **2** are listed in table 2. Hydrogen bonding parameters for Hatma, **1** and **2** are shown in table 3.

Table 1 Crystallographic data, data collection and refinement for Hatma, 1 and 2

Compound	Hatma	**1**	**2**
Empirical formula	$C_4H_6N_3O_{2.50}S_2$	$C_{12}H_{18}LaN_9O_9S_6$	$C_{12}H_{18}NdN_9O_9S_6$
Formula weigh	200.24	763.62	768.95
Temperature / K	296(2)	296(2)	296(2)
Crystal system	Monoclinic	Triclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$	$P\bar{1}$
a / nm	2.141 9(9)	0.882 0(3)	0.883 4(4)
b / nm	0.400 76(17)	1.230 6(4)	1.228 3(5)
c / nm	1.750 0(8)	1.258 6(4)	1.251 0(5)
α / (°)		108.488(3)	108.543(3)
β / (°)	95.606(4)	90.368(3)	90.076(3)
γ / (°)		94.269(3)	94.688(3)
Volume / nm³	1.495 0(11)	1.291 3(7)	1.282 1(9)
Z	4	2	2
D_c / (g·cm^{-3})	1.779	1.964	1.992
$F(000)$	824	756	762
Crystal size / mm	0.33×0.31×0.28	0.35×0.32×0.25	0.32×0.30×0.26
Absorption coefficient / mm^{-1}	0.671	2.201	2.576

Continued Table 1

Reflections collected / unique	3 456, 1 298	7 607, 4 545	9 025, 4 625
θ range for data collection / (°)	2.34~25.00	2.79~25.20	2.78~25.40
Limiting indices	$-22 \leqslant h \leqslant 24$;	$-10 \leqslant h \leqslant 10$;	$-10 \leqslant h \leqslant 10$;
	$-4 \leqslant k \leqslant 3$;	$-14 \leqslant k \leqslant 14$;	$-14 \leqslant k \leqslant 14$;
	$-20 \leqslant l \leqslant 20$	$-15 \leqslant l \leqslant 13$	$-14 \leqslant l \leqslant 15$
Data / restraints / parameters	1 298 / 0 / 105	4 545 / 9 / 359	4 625 / 9 / 358
Goodness-of-fit on F^2	1.043	1.081	1.068
R indices ($I>2\sigma(I)$) R_1, wR_2	0.035 8, 0.088 7	0.029 8, 0.071 1	0.026 6, 0.051 6
R indices (all data) R_1, wR_2	0.042 4, 0.092 4	0.034 1, 0.073 6	0.032 6, 0.053 6

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

			Hatma		
C(1)-N(2)	0.131 9(3)	C(1)-N(1)	0.131 8(3)	C(1)-S(1)	0.173 3(3)
C(2)-N(3)	0.128 8(3)	C(2)-S(2)	0.174 5(2)	C(2)-S(1)	0.174 7(2)
C(3)-C(4)	0.151 6(3)	C(3)-S(2)	0.180 8(2)	C(4)-O(2)	0.127 1(3)
N(2)-N(3)	0.138 6(3)	C(4)-O(1)	0.123 4(3)		
N(2)-C(1)-N(1)	125.6(2)	N(2)-C(1)-S(1)	111.10(18)	N(1)-C(1)-S(1)	123.3(2)
N(3)-C(2)-S(2)	125.35(19)	N(3)-C(2)-S(1)	115.53(18)	S(2)-C(2)-S(1)	119.10(14)
C(4)-C(3)-S(2)	108.91(17)	O(1)-C(4)-O(2)	125.0(2)	O(1)-C(4)-C(3)	118.5(2)
C(2)-S(2)-C(3)	98.68(12)	C(1)-S(1)-C(2)	87.39(12)	O(2)-C(4)-C(3)	116.6(2)
C(1)-N(2)-N(3)	116.1(2)	C(2)-N(3)-N(2)	109.9(2)		
			1		
O(8)-La(1)	0.252 6(3)	La(1)-O(3)	0.258 1(3)	La(1)-O(4)	0.267 8(3)
O(7)-La(1)	0.260 2(3)	La(1)-O(2)	0.262 8(3)	La(1)-O(1)	0.269 3(3)
La(1)-O(5)i	0.257 7(3)	La(1)-O(2)ii	0.251 2(2)	La(1)-O(6)	0.244 7(3)
O(6)-La(1)-O(2)ii	148.71(9)	O(5)i-La(1)-O(4)	67.64(9)	O(2)-La(1)-O(4)	65.02(8)
O(6)-La(1)-O(8)	74.45(9)	O(6)-La(1)-O(2)	129.04(9)	O(6)-La(1)-O(1)	81.50(9)
O(2)ii-La(1)-O(8)	75.74(9)	O(3)-La(1)-O(7)	139.37(10)	O(2)ii-La(1)-O(1)	114.75(8)
O(6)-La(1)-O(5)i	109.55(9)	O(2)ii-La(1)-O(2)	67.52(9)	O(8)-La(1)-O(1)	136.01(9)
O(2)ii-La(1)-O(5)i	71.80(8)	O(8)-La(1)-O(2)	131.19(9)	O(8)-La(1)-O(7)	70.84(10)
O(8)-La(1)-O(5)i	76.18(10)	O(5)i-La(1)-O(2)	118.59(8)	O(5)i-La(1)-O(1)	147.49(9)
O(6)-La(1)-O(3)	75.67(9)	O(3)-La(1)-O(2)	95.57(8)	O(3)-La(1)-O(1)	72.08(9)
O(2)ii-La(1)-O(3)	133.59(8)	O(7)-La(1)-O(2)	70.77(9)	O(7)-La(1)-O(1)	70.42(9)
O(8)-La(1)-O(3)	133.24(10)	O(6)-La(1)-O(4)	124.98(8)	O(2)-La(1)-O(1)	48.83(8)
O(5)i-La(1)-O(3)	81.03(10)	O(2)ii-La(1)-O(4)	85.21(8)	O(4)-La(1)-O(1)	80.89(9)
O(6)-La(1)-O(7)	83.88(9)	O(8)-La(1)-O(4)	142.89(10)	O(7)-La(1)-O(4)	135.79(9)
O(2)ii-La(1)-O(7)	77.58(9)	O(3)-La(1)-O(4)	49.32(8)	La(1)ii-O(2)-La(1)	112.48(9)
O(5)i-La(1)-O(7)	139.39(10)				
			2		
Nd(1)-O(3)i	0.236 8(2)	Nd(1)-O(7)	0.254 4(3)	Nd(1)-O(1)	0.251 5(3)
Nd(1)-O(6)ii	0.244 8(2)	Nd(1)-O(6)	0.258 4(2)	Nd(1)-O(5)	0.262 3(2)
Nd(1)-O(8)	0.247 3(3)	Nd(1)-O(2)	0.262 3(2)	Nd(1)-O(4)	0.251 2(3)
O(3)i-Nd(1)-O(6)ii	149.23(8)	O(7)-Nd(1)-O(6)	71.16(8)	O(3)i-Nd(1)-O(5)	80.76(8)

Continued Table 2

O(6)^{ii}-Nd(1)-O(8)	76.58(8)	O(3)^{i}-Nd(1)-O(2)	125.30(8)	O(1)-Nd(1)-O(7)	140.51(9)
O(3)i-Nd(1)-O(4)	107.33(9)	O(6)^{ii}-Nd(1)-O(2)	84.48(8)	O(3)^{i}-Nd(1)-O(6)	128.95(8)
O(6)^{ii}-Nd(1)-O(4)	74.18(8)	O(8)-Nd(1)-O(2)	142.12(9)	O(6)^{ii}-Nd(1)-O(6)	66.61(9)
O(8)-Nd(1)-O(4)	74.93(9)	O(4)-Nd(1)-O(2)	68.41(8)	O(6)^{ii}-Nd(1)-O(5)	115.49(7)
O(3)^{i}-Nd(1)-O(1)	75.01(8)	O(1)-Nd(1)-O(2)	50.39(8)	O(8)-Nd(1)-O(5)	137.45(9)
O(6)^{ii}-Nd(1)-O(1)	133.40(8)	O(7)-Nd(1)-O(2)	136.70(8)	O(4)-Nd(1)-O(5)	146.54(8)
O(3)^{i}-Nd(1)-O(8)	74.37(9)	O(8)-Nd(1)-O(1)	130.32(9)	O(1)-Nd(1)-O(5)	72.72(9)
O(3)^{i}-Nd(1)-O(7)	82.62(9)	O(4)-Nd(1)-O(1)	78.12(8)	O(7)-Nd(1)-O(5)	71.85(9)
O(6)^{ii}-Nd(1)-O(7)	78.62(9)	O(8)-Nd(1)-O(7)	71.15(9)	O(6)-Nd(1)-O(5)	49.99(7)
O(8)-Nd(1)-O(6)	131.25(8)	O(4)-Nd(1)-O(7)	140.43(9)	O(2)-Nd(1)-O(5)	80.35(8)
O(4)-Nd(1)-O(6)	120.94(7)	O(6)-Nd(1)-O(2)	65.55(8)	Nd(1)^{ii}-O(6)-Nd(1)	113.39(8)
O(1)-Nd(1)-O(6)	98.40(8)				

Symmetry transformations used to generate equivalent atoms: **1**: ^{i} −x+1, −y+2, −z+1; ^{ii} −x+2, −y+2, −z+1; **2**: ^{i} −x+1, −y, −z+2; ^{ii} −x, −y, −z+2.

Table 3　Hydrogen bonding distances (nm) and angles (°) for Hatma, 1 and 2

D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠DHA / (°)
Hatma				
N(1)−H(1A)⋯O(2)^{i}	0.086	0.219	0.293 0(3)	145
N(1)−H(1B)⋯O(1W)^{ii}	0.086	0.21	0.291 8(3)	158
O(1W)−H(1Y)⋯O(1)^{v}	0.085	0.197	0.280 1(3)	167
N(2)−H(2)⋯O(2)^{iii}	0.086	0.174	0.259 9(3)	172
O(1W)−H(1X)⋯O(1)^{iv}	0.085	0.2	0.280 1(3)	156
1				
N(1)−H(1A)⋯O(9)^{v}	0.086	0.255	0.311 3(5)	124
N(1)−H(1B)⋯N(9)^{iv}	0.086	0.214	0.289 1(5)	145
O(7)−H(1W)⋯N(8)^{iii}	0.087(2)	0.203(2)	0.286 0(4)	161(5)
O(7)−H(2W)⋯O(4)^{ii}	0.086(4)	0.196(4)	0.279 9(4)	165(5)
O(8)−H(3W)⋯O(3)^{i}	0.086(2)	0.182(19)	0.268 2(4)	176(5)
O(8)−H(4W)⋯O(9)^{i}	0.087(4)	0.182(4)	0.268 1(5)	173(3)
O(9)−H(5W)⋯N(3)^{vi}	0.085(4)	0.203(4)	0.286 2(5)	169(5)
N(4)−H(6A)⋯N(5)^{vii}	0.086	0.226	0.303 6(6)	151
N(4)−H(6B)⋯O(1)^{v}	0.086	0.249	0.328 1(5)	154
O(9)−H(6W)⋯N(2)^{v}	0.085(4)	0.207(4)	0.287 0(5)	158(4)
N(7)−H(11A)⋯S(2)^{iii}	0.086	0.28	0.339 6(5)	128
N(7)−H(11B)⋯N(6)^{i}	0.086	0.226	0.298 0(6)	142
C(4)−H(4B)⋯O(5)^{viii}	0.097	0.242	0.314 2(5)	131
C(14)−H(14B)⋯N(8)^{iii}	0.097	0.26	0.326 4(6)	126
2				
O(9)−H(1W)⋯N(8)	0.086(4)	0.203(4)	0.286 1(5)	161(4)
O(9)−H(2W)⋯N(7)^{vi}	0.084(4)	0.203(4)	0.286 2(5)	169(5)
N(3)−H(3A)⋯N(2)^{v}	0.086	0.225	0.303 9(5)	152
N(3)−H(3B)⋯O(5)^{iii}	0.086	0.246	0.326 3(5)	155
O(7)−H(3W)⋯N(5)^{iv}	0.085(2)	0.203(2)	0.286 1(4)	166(3)
O(7)−H(4W)⋯O(2)^{ii}	0.084(3)	0.197(3)	0.278 9(4)	166(4)
O(8)−H(5W)⋯O(1)^{i}	0.0845(19)	0.187(2)	0.271 2(4)	177(5)

Continued Table 3

N(6)–H(6C)⋯S(5)[vii]	0.086	0.278	0.339 2(4)	129
N(6)–H(6D)⋯N(1)	0.086	0.224	0.296 8(5)	142
O(8)–H(6W)⋯O(9)[viii]	0.083(4)	0.186(4)	0.268 8(5)	174(4)
N(9)–H(9A)⋯O(9)	0.086	0.256	0.311 2(5)	123
N(9)–H(9B)⋯N(4)[ix]	0.086	0.215	0.289 4(5)	145
C(10)–H(10A)⋯O(4)[ii]	0.097	0.248	0.319 4(5)	131

Symmetry transformations used to generate equivalent atoms: Hatam: [i] $-1/2+x$, $1/2+y$, z; [ii] $1/2+x$, $-1/2+y$, z; [iii] $3/2-x$, $1/2-y$, $-z$; [iv] $3/2-x$, $-1/2+y$, $1/2-z$; [v] $-1/2+x$, $-1/2+y$, z; **1**: [i] $1-x$, $2-y$, $1-z$; [ii] $2-x$, $2-y$, $1-z$; [iii] $1-x$, $2-y$, $-z$; [iv] $1-x$, $1-y$, $-z$; [v] $1-x$, $1-y$, $1-z$; [vi] $-1+x$, y, z; [vii] $1-x$, $1-y$, $2-z$; [viii] $1+x$, y, z; **2**: [i] $1-x$, $-y$, $2-z$; [ii] $-x$, $-y$, $2-z$; [iii] $1-x$, $1-y$, $2-z$; [iv] x, y, $1+z$; [v] $1-x$, $1-y$, $1-z$; [vi] $-x$, $1-y$, $2-z$; [vii] x, y, $-1+z$; [viii] x, $-1+y$, z; [ix] x, $1+y$, $1+z$.
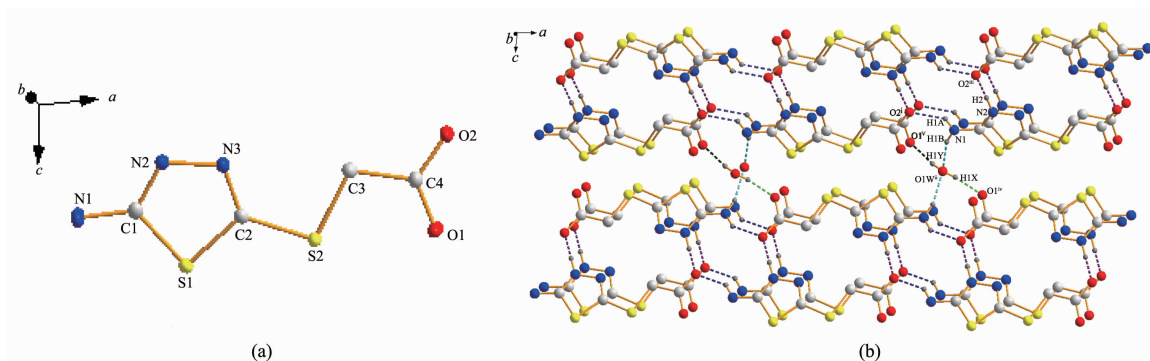

(a) Displacement ellipsoids are drawn at the 30% probability level; H-atoms are depicted as spheres of arbitrary radii;　(b) Only hydrogen atoms involved in the hydrogen bonds are shown. Hydrogen bonds are indicated by dash lines. Symmetry codes: [i] $-1/2+x$, $1/2+y$, z; [ii] $1/2+x$, $-1/2+y$, z; [iii] $3/2-x$, $1/2-y$, $-z$; [iv] $3/2-x$, $-1/2+y$, $1/2-z$; [v] $-1/2+x$, $-1/2+y$, z

Fig.1 (a) Molecular structure of Hatma ligand, (b) Hydrogen bonding interactions in Hatma

The structure of the versatile bridged heterocyclic amino acid ligand-Hatma is shown in Fig.1a. This ligand crystallizes in the monoclinic system, space group $C2/c$. The ligand-Hatma is a zwitterion, having transferred a proton from the carboxylic acid group to 1,3,4-thiadiazol ring because the electron-rich N(2) atom of thiadiazol ring presents stronger alkaline. Since the heterocyclic amino acid moiety has both hydrogen bond donors and hydrogen bond acceptors, the species provide the possibility of forming hydrogen bonds in the crystal. As shown in Fig. 1b, a series of hydrogen bonds are formed between the carboxylate oxygen atom and the thiadiazole N atom, the carboxylate oxygen atom and NH$_2$, the lattice water and the carboxylate oxygen atoms, the lattice water and the NH$_2$, respectively, which stabilize the crystal structure of Hatma.

Single crystal X-ray diffraction analysis reveals that **1** and **2** are isostructural, both crystallizing in triclinic space group $P\bar{1}$. Therefore, only the structure of [La(atma)$_3$(H$_2$O)$_2$]$_n$ (**1**) is described in detail. The asymmetric unit consists of one La(Ⅲ), three atma-anions, two aqua ligands and one lattice water molecule. As shown in Fig. 2, the La (1) center is nine-coordinated, completed by nine oxygen atoms from five atma anions and two-coordinated water molecules, and the coordination geometry of the La(1) center can be described as a distorted monocapped square antiprism geometry. Among the above-mentioned nine oxygen atoms, five (O (1), O(2), O(6), O(5)[i], O(2)[ii]) are from four bridging atma ligands, another two (O(3), O(4)) is from a chelating atma ligand and the remaining two (O(7), O(8)) are from two-coordinated water molecules. The La-O bond lengths vary from 0.248 5(4) to 0.269 3(3) nm, while the O-La-O bond angles range from 48.83(8)° to 148.71(9)°, which may be compared with those observed in the La(Ⅲ) compounds based on the carboxylate ligands[18-20]. All the Hatma molecules are take part in the coordination to the lanthanum centers and there are three coordination modes of atma in the structure: (a) the atma anion acts as a bidentate chelating ligand towards the La1 center
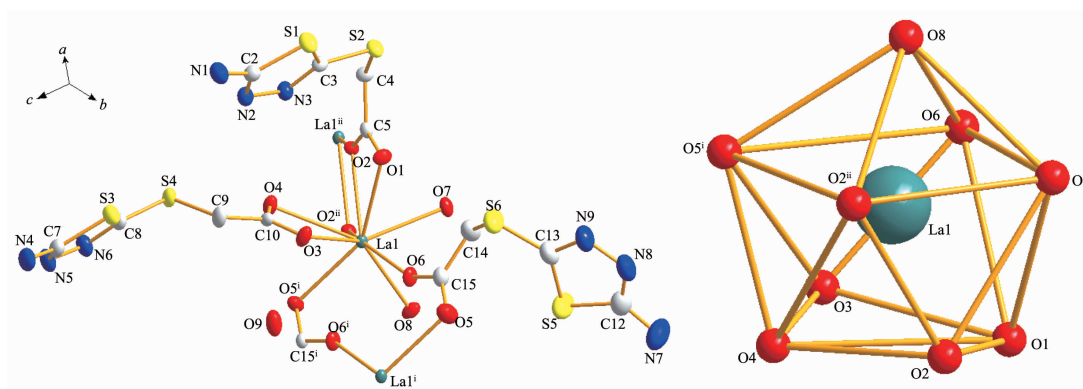
H atoms are omitted for clarity; Symmetry codes: ^{i} −x+1, −y+2, −z+1; ^{ii} −x+2, −y+2, −z+1

Fig.2 Coordination environment with thermal ellipsoids shown at 30% probability and polyhedron of **1**
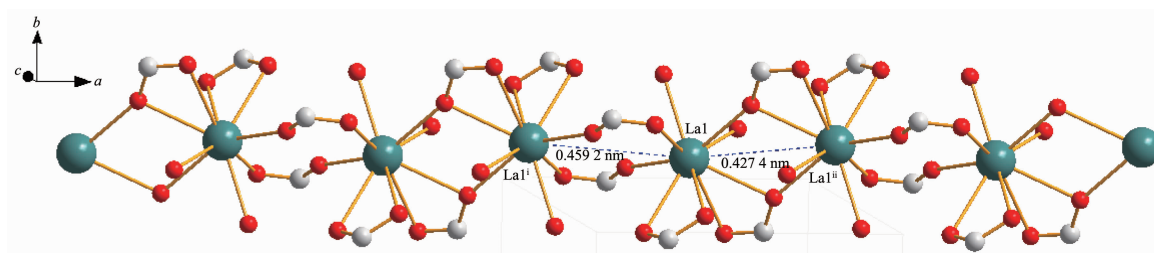
Symmetry codes: ^{i} −x+1, −y+2, −z+1; ^{ii} −x+2, −y+2, −z+1

Fig.3 One-dimensional chain structure in **1**

(O(3), O(4)); (b) tridentate chelating-bridging atma group through the carboxyl (O(1), O(2), O(2)^{ii}); (c) the atma anion acts as a bidentate bridging ligand towards the La(1) center (O(5)^{i}, O(6)). In the case of the bidentate atma ligand, the La(1)⋯O(6)^{iv} distance of 0.294 4(3) nm is too long to be considered bonding, hence the C(15)^{i}-O(5)^{i}-O(6)^{i} ligand cannot be bridging tridentate. The coor-dination modes of carboxylate groups are very similar to [Ln(cpia)(H$_2$O)$_2$]$_n$·nH$_2$O (Ln=Ce(1), Pr(2), Nd(3), Sm(4), Eu(5), Gd(6), Dy(7), Er(8), Tm(9) and Y(10))[21]. Two adjacent La(Ⅲ) atoms, separated by an La-La distance of 0.427 37(15) nm, are bridged by two carbox-ylate groups to give a bimetallic unit [La$_2$(COO)$_2$(COO)$_2$(H$_2$O)$_4$] which was further linked by another four bidentate bridging ligands to give rise to a one-dimensional Lanthanum chain, as illustrated in Fig.3. Obviously, the different bridge modes link the La(Ⅲ) ions with different distances in complex alternatively[18,21]. The dihedral angle between the different La$_2$O$_2$ subunits is *ca.* 45.741°. A deeper view of the compound [La(atma)$_3$(H$_2$O)$_2$]$_n$ (**1**) indicates that there are rich intermolecular hydrogen bonds between the coordinated ligands, coordinated water molecules and lattice water molecules,

which play an important role in the crystal packing of the complex. In the complex, the parallel chains are further engaged in intermolecular hydrogen bonding implying N(7)−H(11A)⋯S(2)^{iii}, O(7)−H(1W)⋯N(8)^{iii} and C(14)−H(14B)⋯N(8)^{iii} to form two-dimensional (2D) layer supramolecular structure as shown in Fig.4. In addition, the layers further extended into an infinite three-dimensional (3D) supramolecular framework by seven types of intermolecular hydrogen bonds (O(9)−H(6W)⋯N(2)^{v}, O(8)−H(4W)⋯O(9)^{i}, O(9)−H(5W)⋯N(3)^{vi}, N(1)−H(1B)⋯N(9)^{iv}, N(4)−H(6B)⋯O(1)^{v}, N(4)−H(6A)⋯N(5)^{vii} and N(1)−H(1A)⋯O(9)^{v}) from two adjacent layers[22]. All above hydrogen-bonding interactions may enhance the stability of the solid-state structure of **1**.
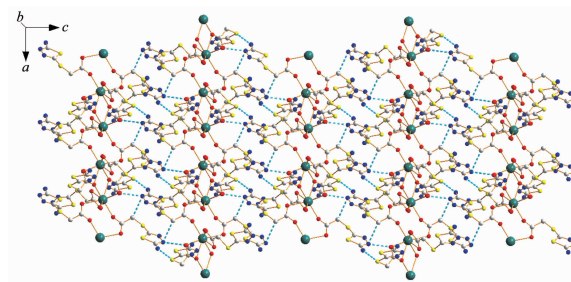
H atoms are omitted for clarity

Fig.4 View of the 2D polymer sheet of **1**

X-ray crystallographic analysis shows that the complex [Nd (atma)$_3$ (H$_2$O)$_2$]$_n$ (2) also exhibits a 1D chain-like structure in which the asymmetric unit consists of one Nd (III), three atma-anions, two aqua ligands and one lattice water molecule (Fig.5). The Nd-O bond lengths vary from 0.236 8(2) to 0.262 3(2) nm, being slightly shorter than the corresponding La-O bond lengths in complex 1. The O-Nd-O bond angles range from 49.99(7)° to 149.23(8)°, which are within the normal ranges[21-23]. The intrachain neighboring metallic distances of Nd(III)··· Nd(III) are 0.420 61(19)~0.486 20(21) nm, which is slightly longer than the La(III)···La(III) distance (0.427 37(15)~ 0.459 20(16) nm) in complex 1. There were also extensive hydrogen bonds, which participate in the stabilization of the complex architectures[22].
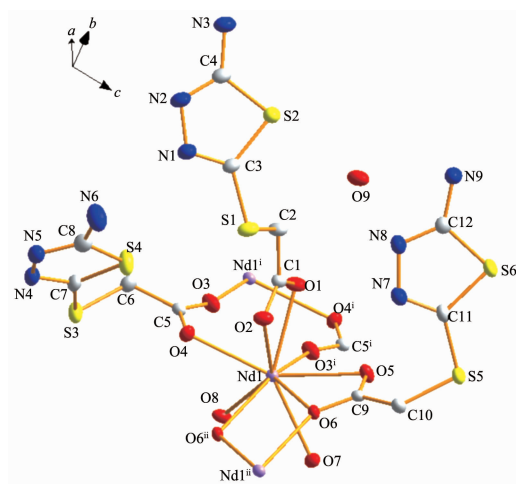
H atoms are omitted for clarity; Symmetry codes: ^{i} −x+1, −y, −z+2; ^{ii} −x, −y, −z+2

Fig.5 Coordination environment with thermal ellipsoids shown at 30% probability of 2

2.2 IR and thermogravimetric analysis

The infrared spectra (400~4 000 cm^{-1}) of the two coordination polymers have very similar absorption bands owing to their similar structural features. Compared with the ligand, the characteristic vibration peaks around 1 645 cm^{-1} for -COOH group in 1 and 2 were absent, indicating that the protons of carboxyl groups were deprotonated. The asymmetric and symmetric stretching bands of COO$^-$ groups appear at 1 605, 1 581, 1 508 and 1 418 cm^{-1} for 1, 1 609, 1 580, 1 511 and 1 422 cm^{-1} for 2, respectively, suggesting that the COO$^-$ groups functions in different coordination

modes[25], which is consistent with the X-ray diffraction structural analysis. The strong and broad absorptions at 3 300~3 500 cm^{-1} indicate the presence of ν(N-H) and ν(O-H) of thiadiazole and coordinated water.

In order to estimate the stability of the frameworks, thermal gravimetric analysis (TGA) of 1 and 2 were carried out in nitrogen atmosphere from 30 to 800 ℃. TG analysis shows that the thermal decomposition behavior of compounds 1 and 2 was similar and can be divided into two steps. Taking compound 1 as an example, the TGA measurement exhibits the first weight loss of 7.7% from 121.0 to 183.6 °C, which corresponds to the departure of both the lattice and coordinated water molecules (Calcd. 7.07%). The release of the water molecules at a high temperature is ascribed to the strong hydrogen-bonding interaction in complexes[26]. The second loss starts at a temperature above 220 ℃, which may be caused by the decomposition of the organic part, and does not end until 800 ℃.

2.3 Antibacterial studies

To study the antimicrobial activity of complexes, we have tested the antimicrobial ability of the free ligand and its complexes against seven kinds of bacteria, which include two Gram positive bacteria *Staphylococcus aureus* (ATCC-11632) and *Bacillus subtilis* (ATCC-6633) and five Gram negative bacteria *Escherichia coli* (ATCC-8739), *Pseudomonas aeruginosa* (ATCC-9027), *Proteus vulgaris* (ATCC-6380), *Shigella dysenteriae* (ATCC-51067) and *Salmonella choleraesuis* (ATCC-50020).

The results (Table 4) indicate that both heterocyclic amino acid and their complexes have antibacterial activity to the bacteria tested and the complexes have the higher activity than the ligand under identical experimental conditions. The complexes belong to broad spectrum antibacterial agents.

2.4 Antifungal studies

The antifungal activities of the compounds were also done by the poisoned food technique against the fungi viz., *Alternaria alternata*, *Fusarium oxysporum*, *Alternaria soluni*, *Botrytis Cinerea* and *Fusarium sulphureum* cultured on potato dextrose agar as medium. The percentage inhibition was calculated as 100$(C−T)/C$, where C is the average diameter of fungal growth on the

Table 4　MIC (mg·L⁻¹) results of Hatma and [Ln(atma)₃(H₂O)₂]ₙ

Compounds	Gram-positive bacteria		Gram-negative bacteria				
	S. aureus	*B.subtilis*	*E. coli*	*P. aeruginosa*	*S. choleraesuis*	*P. vulgaris*	*S. dysenteriae*
Hatma	160	160	80	80	160	80	320
Complex **1**	80	80	40	40	80	80	160
Complex **2**	160	80	40	160	80	160	160

MIC=minimum inhibitory concentration, that is, the lowest concentration of the compound to inhibit the growth of bacteria completely.

Table 5　Antifungal activities of Hatma and [Ln(atma)₃(H₂O)₂]ₙ

Compounds	Inhibition of mycelial growth / %				
	Alternaria soluni	*Fusarium oxysporum*	*Botrytis Cinerea*	*Alternaria alternate*	*Fusarium sulphureum*
Hatma	30.9	27.9	28.6	54.6	47.1
La(NO₃)₃	29.5	23.2	32.7	38.2	38.0
Nd(NO₃)₃	7.2	1.5	8.2	5.5	11.3
Complex **1**	39.7	28.4	34.7	60.0	52.1
Complex **2**	45.5	31.3	32.7	61.8	48.6
Griseofulvinas	57.3	64.2	40.8	76.4	51.4

conc. 50 mg·L⁻¹.

control plate and T is the average diameter of fungal growth on the test plate. The results are shown in table 5. The fungal activities of each compounds were compared with Griseofulvin as standard drug.

The investigation of antifungal activity of the ligand and its metal complexes reveals that all metal complexes are more fungitoxic than their parent ligand and metal salts, especially for [Nd(atma)₃(H₂O)₂]ₙ (**2**) (Table 5). The two complexes studied here exhibit a little bit lower activities than the standard drugs at 50 mg·L⁻¹.

2.5　Plant growth regulation studies

The free ligand and its complexes were investigated for plant growth regulation activity. The percentage plant growth activity was calculated according to the following equation:

Percentage plant growth activity=$(L-L_1)/L_1\times100\%$

Where L is the root or shoot length cultured in compound solution, and L_1 is the root or shoot length cultured in the distilled water under the same condition (Table 6, Table 7).

From the results summarized in table 6 and 7, it is apparent that most of the compounds exhibit inhibition activity at high concentration, while display enhancing roots and shoots elongation activity at a low concentration.

When compared with heteroauxin and rare earth salts it is seen that the complexes have weak inhibition of roots and shoots elongation at high concentration, while showing remarkable enhancement in roots and shoots elongation at the low concentration of 0.001 mg·L⁻¹ for rape and 0.01 mg·L⁻¹ for wheat. The free ligand also show notable growth-promoting activity for the rape

Table 6　Data of rape growth regulating activity

c / (mg·L⁻¹)	Plant growth activity[a] / %					
	Hatma	La(NO₃)₃	Nd(NO₃)₃	Complex **1**	Complex **2**	Heteroauxin
0.001	61.6	−8.2	−7.2	40.8	40.8	16.4
0.01	37	−18.8	−13.7	27.4	20.5	4.2
0.1	12.6	−14.3	−27.3	4.8	8.7	−1.4
1	30.7	−21.8	−35.5	8.6	−1.4	−9.7
10	2.5	−25.1	−38.1	5.6	−16.8	−76.5
100	−0.3	−31.9	−40.0	−19.6	−40.2	−84.0

[a] Solution was prepared in the proportion of $V_{H_2O}:V_{DMF}$=99.5:0.5, and 0.1 g Tween-80 was added to promote the compound to dissolve.

Table 7　Data of wheat growth regulating activity

| | c / (mg·L^{-1}) | Plant growth activity^a / % | | | | | |
		Hatma	La(NO$_3$)$_3$	Nd(NO$_3$)$_3$	Complex **1**	Complex **2**	Heteroauxin
bs^b	0.001	30.5	1.1	−4.0	8.9	17.6	23.9
	0.01	53.1	36.9	15.0	34.3	33.6	31.3
	0.1	13.5	−5.1	0.5	−26.0	10.6	−16.2
	1	6	−25.5	−16.2	−15.0	7.3	−55.6
	10	−16.3	−20.2	−17.4	−40.5	−13.3	−100.0
	100	−24.3	−34.1	−50.7	−40.0	−37.6	−100.0
br^c	0.001	24.1	−33.5	−26.4	−17.9	−33.7	−19.2
	0.01	41.9	−18.8	−9.8	−2.5	9.5	32.2
	0.1	37.4	−22.8	−25.6	−9.8	4	13.9
	1	25.1	−35.8	−26.6	−7.4	−0.4	−32.0
	10	0.3	−46.3	−41	−48.0	−29.6	−41.7
	100	−21.3	−65.0	−49.2	−66.7	−20.9	−42.5

^{a}Solution was prepared in the proportion of $V_{H_2O}:V_{DMF}$=99.5:0.5, and 0.1 g Tween-80 was added to promote the compound to dissolved;
^{b}Growth regulating activity for wheat shoots; ^{c}Growth regulating activity for wheat roots.

and wheat.

The preliminary biological activity tests show that the title complexes have better regulating activities than rare earth salts and heteroauxin for the growth of the rape and wheat.

3　Conclusions

In conclusion, two lanthanide metal coordination polymers have been synthesized by hydrothermal reactions. The 3D supramolecular structure were formed by self-assembly of lanthanide(Ⅲ) metals and a versatile bridged heterocyclic amino acid ligand-Hatma. The structures have been determined by single crystal X-ray analysis.

The antimicrobial experiment results indicate that the complexes of heterocyclic amino acid and rare earth have higher antimicrobial activity than ligand and rare earth salts at the same concentrations, which is advantageous for their application in medicine. This significant increase in antimicrobial activity may come from the formation of chelate, a less polar form of the compound, there by increases its lipophilic character. The increased lipophilic character of chelate favours the interaction of these complexes with cell constituents, resulting in interference with normal cell processes [27]. The preliminary growth regulation activity tests show that the title complexes have better regulating activities

than rare earth salt and heteroauxin for the growth of the rape and wheat. The complexes may have broad application in medicine and agriculture.

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