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## Characterization, luminescent and magnetic analysis of five new lanthanide complexes based on carboxylate ligands

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#### ABSTRACT

Five new lanthanide complexes,  $[Pr(HL^1)(H_2O)_4]Cl_2 \cdot 2H_2O$  (1),  $[Ho(HL^1)(H_2O)_3]Cl_2 \cdot 2H_2O$  (2),  $[Dy(HL^1)(H_2O)_3]Cl_2 \cdot 2H_2O$  (3),  $[Dy(H_2L^2)_2(H_2O)_6]Cl_3$  (4) and  $[Ce(H_2L^3)(CH_3CO_2)_2(H_2O)_2] \cdot H_2O$  (5), based on carboxylate ligands have been prepared. All complexes have been characterized via elemental analysis, single-crystal X-ray diffraction, powder X-ray diffraction and thermogravimetric analysis. According to single-crystal X-ray analysis, 1–3 and 5 are coordination polymers (CPs) with 1D zigzag chains, while 4 is a 0D structure. The 3D supramolecular structures of 1–4 are formed by the interaction of  $C/N - H \cdots Cl$  hydrogen bonds and  $\pi \cdots \pi$  stacking interactions. In addition, the luminescent and magnetic properties of 1–5 have been discussed.

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Lanthanide complexes; hydrogen bonding;  $\pi \cdots \pi$ stacking; luminescent; magnetic



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#### 1. Introduction

In recent years, the versatile structures and functions of coordination polymers, such as catalysis, gas adsorption, magnetism, luminescence, have attracted great attention [1–3]. The combination of metal and organic linkers can provide greater flexibility for CPs, and its performance can be adjusted in various aspects [4, 5]. Compared with transition metal CPs, lanthanide metal CPs were far from being developed despite their inherent properties offered by the lanthanide metal ions. This may be due to the complex formation of some lanthanide metal ions being more difficult to control than with transition metals [6]. At present, lanthanide metal CPs were favored for their intrinsic optics and magnetic properties because of their 4f configurations [7–9]. It is well known that self-assembly is a method for constructing a lanthanide coordination polymer via organizing the coordination of lanthanide ions with a polydentate ligand. However, most of them are polynuclear complexes and 3D coordination polymers, while lanthanide coordination polymers of 1D molecules are rarely reported [10].

Recently, the design of organic connectors has attracted extensive attention, especially the assembly strategy of coordination networks via hydrogen bonds. Hydrogen bonding plays an important role in the expansion of CPs' supramolecular networks. Many polydentate ligands have been widely used in the construction of coordination polymers [11–14]. The structure of the complex depends to a large extent on the different metals and structures of ligands [15].

According to the above information, we have chosen 6-carboxyl-1*H*-benzimidazole-2-propionic acid  $(H_3L^1)$ , 2-(4-hydroxyphenyl)-1*H*-benzimidazole-6-carboxylic acid  $(H_3L^2)$ and 2-(hydroxymethyl)-1*H*-benzo[*d*]imidazole-6-carboxylic acid  $(H_3L^3)$  as the ligands and five new lanthanide complexes have been prepared (Scheme 1). Compared with the previous study, the purpose of this study was to compare the structure and properties of the complexes based on three ligands,  $H_3L^1$ ,  $H_3L^2$  and  $H_3L^3$  [16]. Complexes 1–5 were characterized via single-crystal X-ray diffraction, elemental analysis, powder X-ray diffraction (PXRD) and thermogravimetric analysis (TGA). Subsequently, the fluorescence emissions and magnetic properties of 1–5 were explored.

#### 2. Experimental

#### 2.1. Materials and methods

All reagents used for the synthesis were commercially available and employed without purification. 3,4-Diaminobenzoic acid, 1,2-ethanedicarboxylic acid and 4-hydroxybenzoic acid were purchased from J&K Scientific LTD, whose purities are 98%, 96% and 98%, respectively. 2-(Hydroxymethyl)-1*H*-benzo[*d*]imidazole-6-carboxylic acid ( $H_3L^3$ ) used in this work was synthesized according to the literature procedure [17]. Elemental analyses (C, N, H) were performed on a Thermo Flash EA 1112-NCHS-O analyzer. Nuclear magnetic resonance (<sup>1</sup>H NMR) data were collected on an INOVA-400 NMR spectrometer, and chemical shifts are reported in  $\delta$  relative to TMS. The X-ray powder diffraction (XRPD) data were recorded on a Rigaku D/Max-2500 diffractometer, 40 kev, 2 h, range 5–60°. The thermogravimetric analysis (TGA) data were obtained via



Scheme 1. The ligands  $(H_3L^1, H_3L^2 \text{ and } H_3L^3)$  studied in this work.

a Perkin-Elmer TG-7 thermal analyzer range 25 to 1000 °C in an argon environment at a heating rate of 10 °C min<sup>-1</sup>. The solid-state luminescence spectra were measured on a Hitachi F-4500 fluorescence spectrophotometer, with a Xe arc lamp as the light source and a 2.5-nm bandwidth at room temperature. Magnetic measurements were carried out with a SQUID MPMS-XL-7 magnetometer.

#### 2.2. Synthesis

**6-Carboxyl-1H-benzimidazole-2-propionic acid** (H<sub>3</sub>L<sup>1</sup>): 3,4-Diaminobenzoic acid (10.00 mmol) 1.520 g and 1,2-ethanedicarboxylic acid (15.00 mmol) 1.770 g were added to 30 mL of hydrochloric acid (5 M) in a 50-mL round bottomed bottle equipped with a magnetic agitator. The reaction mixture was heated continuously for 7 h. The solid crude product was washed with a large amount of water and then dried in the air. Then, the residue was filtered off and the filtrate was concentrated. After that, the resulting yellow solid was collected (yield: 51.2%, 1.200 g). <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>). δ: 13.00 (s, 3H, carboxylic and imidazole), 7.83–8.26 (m, 3H, benzene), 2.42-3.35 (d, 4H, methylene). Anal. Calcd (%) for C<sub>11</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 56.41; H, 4.30; N, 11.96; O, 27.33. Found: C, 56.63; H, 4.62; N, 11.75; O, 27.10. IR (KBr pellets, cm<sup>-1</sup>): 3100(NH, s), 2927(CH<sub>2</sub>, s), 2831(s), 2746(s), 2634(s), 1698(C=O, vs), 1634(C=C, w), 1615(m), 1568(m), 1508(aromatic ring framework, s), 1453(w), 1422(s), 1353(w), 1313(s), 1258(C-N, m), 1201(s), 1127(w), 1087(w), 1044(w), 1019(w), 968(w), 925(OH wagging vibration, m), 909(m), 840(m), 803(w), 791(w), 769(w), 743(w), 676(w), 639(w).

2-(4-Hydroxyphenyl)-1H-benzimidazole-6-carboxylic acid (H<sub>3</sub>L<sup>2</sup>): A mixture of 3,4diaminobenzoic acid (1.520 g, 10.00 mmol), 4-hydroxybenzoic acid (1.380 g, 10.00 mmol) and glacial acetic acid (30 mL) was stirred for about 10 min, and then, the reaction mixture was refluxed for 7.5 h. The mixed solution was cooled to room temperature and the solid products precipitated. The solid crude product was washed with a large amount of water and then dried in the air. Then residue was filtered off and the filtrate was concentrated. Light green solid powder  $H_3L^2$  was obtained (yield: 29.2%, mass: 0.790 g). <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ ).  $\delta$ : 13.00 (s, 2H, carboxylic and NH), 10.29 (s, 1H, hydroxyl), 8.2–7.1 (m, 7H, benzene). Anal. Calcd (%) for C<sub>14</sub>H<sub>10</sub>N<sub>2</sub>O<sub>4</sub>: C, 56.41; H, 4.30; N, 11.96; O, 27.33. Found: C, 56.12; H,4.55; N, 11.73; O, 27.57. IR (KBr pellets, cm<sup>-1</sup>): 3152(OH, s), 3053(NH, m), 2630(w), 2511(w), 1689(C=O, s), 1625(m), 1609(aromatic ring framework, s), 1453(w), 1476(m), 1433(s), 1382(m), 1317(m), 1277(s), 1255(C-N, m), 1232(m), 1179(m), 1124(w), 1084(w), 1012(w), 974(w), 947(OH wagging vibration, w), 885(w), 844(m), 768(w), 748(w), 727(w), 689(w), 647(w), 632(w).

### Tetraaqua-(6-carboxyl-1*H*-benzimidazole-2-propionic acid)praseodymium(III) dichloride dihydrate solvate

 $[Pr(HL^{1})(H_{2}O)_{4}]Cl_{2}\cdot 2H_{2}O$  (1):  $PrCl_{3}\cdot 6H_{2}O$  (35.54 mg, 0.100 mmol) and  $H_{3}L^{1}$  (23.40 mg, 0.100 mmol) in 4 mL of solvent ( $v_{H2O}$ :  $v_{CH3CN} = 1$ :5) were placed in a 25-mL Teflonlined stainless steel vessel and heated at 140 °C for 12 h, and then cooled to room temperature at a rate of 5 °C h<sup>-1</sup> to form yellow block-shaped crystals; the yield is *ca*. 13% based on  $H_{3}L^{1}$ , mass: 7.020 mg. Anal. Calcd (%) for  $C_{11}H_{21}Cl_{2}N_{2}O_{10}Pr$ : C, 23.89; H, 3.83; N, 5.06. Found: C, 23.68; H, 3.98; N, 5.34. IR (cm<sup>-1</sup>, KBr pellets): 3293(OH, from the coordinated water molecular, s), 3053(m), 2391(w), 1909(w), 1820(w), 1624(C = O, s), 1525(C = O, s), 1448(aromatic ring framework, s), 1407(s), 1335(s), 1312(s), 1244(C-N, m), 1190(s), 1132(m), 1055(w), 1020(w), 980(w), 948(m), 914(w), 881(w), 854(w), 826(m), 790(m), 767(m), 735(m), 687(s), 659(s), 554(m), 555(m), 516(m), 437(w).

## Synthesis of triaqua-(6-carboxyl-1*H*-benzimidazole-2-propionic acid)-holmium(III) dichloride dihydrate solvate

 $[Ho(HL^1)(H_2O)_3]Cl_2 \cdot 2H_2O$  (**2**):  $HoCl_3 \cdot 6H_2O$  (38.00 mg, 0.100 mmol) and  $H_3L^1$  (23.40 mg, 0.100 mmol) in 4 mL solvent ( $v_{H2O}$ :  $v_{CH3CN} = 1:5$ ) were sealed in a 25-mL Teflon-lined stainless steel vessel and heated at 130 °C for 12 h, and then cooled to room temperature at a rate of 5 °C h<sup>-1</sup> to form yellow block-shaped crystals. For **3**, the yield is *ca*. 26% based on  $H_3L$ , mass: 14.740 mg. Anal. Calcd (%) for  $C_{11}H_{19}Cl_2N_2O_9Ho$ : C, 23.63; H, 3.42; N, 5.01. Found: C, 23.30; H, 3.63; N, 5.25. IR (cm<sup>-1</sup>, KBr pellets): 3220(OH, from the coordinated water molecular, s), 2253(w), 1661(w), 1624(C = O, s), 1543(C = O, s), 1457(aromatic ring framework, s), 1402(s), 1304(s), 1227(C-N, m)m), 1162(m), 1025(m), 944(w), 891(w), 852(w), 831(w), 779(m), 730(m), 679(m).

# Triaqua-(6-carboxyl-1*H*-benzimidazole-2-propionic acid)-dysprosium(III) dichloride dihydrate solvate

 $[Dy(HL^1)(H_2O)_3]Cl_2 \cdot 2H_2O$  (**3**):  $DyCl_3 \cdot 6H_2O$  (35.54 mg, 0.100 mmol) and  $H_3L^1$  (23.40 mg, 0.100 mmol) in 4 mL solvent ( $v_{H2O}$ :  $v_{CH3CN} = 1$ :5) were placed in a 25-mL Teflon-lined stainless steel vessel and heated at 140 °C for 12 h, and then cooled to room temperature at a rate of 5 °C h<sup>-1</sup> to form yellow block-shaped crystals; yield is *ca.* 14% based on  $H_3L$ , mass: 8.190 mg. Anal. Calcd (%) for  $C_{11}H_{21}Cl_2N_2O_{10}Dy$ : C, 23.00; H, 3.68; N, 4.87. Found: C, 23.31; H, 3.44; N, 4.69. IR (cm<sup>-1</sup>, KBr pellets): 3306(OH, from the coordinated water molecular, s), 2929(w), 1586(C = O, s), 1530(C = O, s), 1434(aromatic ring framework, s), 1407(s), 1305(s), 1221(C-N, m), 1176(m), 1052(w), 1028(w), 1007(w), 977(w), 948(w), 910(w), 883(w), 826(w), 782(w), 745(w), 684(m), 649(m).

#### Hexaaqua-bis[2-(4-hydroxyphenyl)-1*H*-benzimidazole-6-carboxylic acid]-trichloride-dysprosium(III)

 $[Dy(H_2L^2)_2(H_2O)_6]CI_3$  (4):  $DyCI_3\cdot 6H_2O$  (33.60 mg, 0.100 mmol) and  $H_3L^2$  (25.40 mg, 0.100 mmol) in 4 mL solvent ( $v_{H2O}$ :  $v_{CH3CN} = 1$ :7) were sealed in a 25-mL Teflon-lined stainless steel vessel heated at 130 °C for 12 h, and then cooled to room temperature at a rate of 5 °C h<sup>-1</sup> to form yellow block-shaped crystals. Yield is *ca.* 13% based on  $H_3L^2$ , mass: 11.180 mg. Anal. Calcd (%) for  $C_{28}H_{28}CI_3N_4O_{12}Dy$ : C, 38.15; H, 3.20; N, 6.36. Found: C, 38.40; H, 3.39; N, 6.12. IR (cm<sup>-1</sup>, KBr pellets): 3369(OH, from the coordinated

Complexes	1	2	3	4	5
Formula	$C_{11}H_{21}CI_2PrN_2O_{10}$	C11H19CI2H0N2O9	C <sub>11</sub> H <sub>19</sub> Cl <sub>2</sub> DyN <sub>2</sub> O <sub>9</sub>	C <sub>28</sub> H <sub>28</sub> Cl <sub>3</sub> DyN <sub>4</sub> O <sub>12</sub>	C <sub>13</sub> H <sub>19</sub> CeN <sub>2</sub> O <sub>10</sub>
Formula wt.	553.11	559.11	556.68	881.39	503.42
Crystal systems	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
Т (К)	100.00(10)	100.00(10)	100.00(10)	293.02(10)	100.01(10)
a (Å)	8.9330(9)	8.1486(3)	8.1647(3)	8.8507(3)	8.419(5)
b (Å)	10.3129(9)	11.2568(5)	11.2846(4)	10.2373(3)	10.6521(7)
c (Å)	11.2529(11)	11.2746(5)	11.3294(4)	20.4863(8)	10.8090(7)
a (°)	77.343(8)	113.333(4)	113.443(4)	100.288(3)	88.749(6)
b (°)	87.393(8)	109.815(4)	109.882(4)	97.385(3)	68.881(6)
g (°)	71.208(9)	92.189(3)	92.135(3)	90.207(3)	83.135(5)
V (Å <sup>3</sup> )	957.21(17)	875.40(7)	882.40(6)	1810.54(11)	896.66(10)
Z	2	2	2	2	2
D (Mg/m <sup>3</sup> )	1.919	2.121	2.095	1.167	1.865
$\mu$ (mm <sup>-1</sup> )	2.875	4.872	4.584	2.346	2.593
F(000)	548	544	542	874	498
Measured reflns.	10862	14258	10003	13390	11087
Obsd. reflns.	3379	3085	3106	6367	4243
R <sub>int</sub>	0.041	0.0344	0.0354	0.036	0.0312
R <sup>a</sup> /wR <sup>b</sup>	0.026/0.0562	0.0195/0.0458	0.0211/0.0480	0.0316/0.0723	0.0244/0.0534

Table 1. Crystal data and structure refinement summary for 1–5.

 $\label{eq:rescaled_$ 

water molecular, s), 1899(w), 1610(s), 1553(C = O, s), 1487(aromatic ring framework, s), 1286(s), 1259(C-N, m), 1182(s), 1128(w), 1021(w), 952(w), 899(w), 840(w), 812(w), 771(m), 734(w), 684(w), 641(m), 572(m), 516(w).

### Synthesis of diaqua-diacetate-2-(hydroxymethyl)-1H-benzo[d]imidazole-6-carboxylic acid-cerium(III) hydrate solvate

 $[Ce(H_2L^3)(CH_3CO_2)_2(H_2O)_2]$ ·H<sub>2</sub>O (5):  $Ce(CH_3COO)_3$ ·xH<sub>2</sub>O (31.72 mg, 0.100 mmol) and  $H_3L^3$  (19.22 mg, 0.1 mmol) in 14 mL solvent ( $v_{H2O}$ :  $v_{CH3CH2OH}$  = 1:2) were refluxed for 4 h. The system was left for several days at ambient temperature. Colorless block-like single crystals of 5 formed. Yield is ca. 26% based on  $H_3L^3$ , mass: 12.877 mg. Anal. Calcd (%) for C13H19N2O10Ce: C, 31.01; H, 3.80; N, 5.56. Found: C, 31.38; H, 3.53; N, 5.83. IR (cm<sup>-1</sup>, KBr pellets): 3567 (OH, from the free water molecule, m), 3452 (m), 3262 (OH, from the coordinated water molecule, s), 2994(m), 2361(w), 1643(C = 0, from the coordinated acetate molecule, w), 1536(C = O, s), 1487(C = O, s), 1452(aromatic ring framework, s), 1411(s), 1371(m), 1287(m), 1244(C-N, m), 1203(w), 1123(w), 1096(w), 1044(m), 1014(m), 945(w), 892(w), 829(w), 793(w), 756(w), 694(m), 671(m), 614(w).

#### 2.3. X-Ray crystallography

X-ray crystallography data of all complexes were gathered at room temperature on a Bruker APEX II Smart CCD diffractometer with Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). In this study, we used the SADABS program to calibrate the semi-empirical absorption of data [18]. The program SAINT was used to integrate the diffraction profile [19]. All five structures were solved using SHELXS-2014 using the Patterson method and followed by successive Fourier and difference Fourier synthesis [20]. Full-matrix least-squares refinements were performed on  $F^2$  using SHELXL-2014 with anisotropic displacement parameters for all non-hydrogen atoms [20]. We have placed the crystal data of **1–5** in Table 1, and the bond length, bond angle and hydrogen bond data are located in tables S1 and S2 of ESI.

#### 3. Results and discussion

#### 3.1. Crystal structures of 1–3

Complexes 1–3 are isostructural. Complex 1 has only one coordinated water molecule more than 2 and 3; this is the only difference (Figures S2 and S3 of Supplementary Information). Complex 1 crystallizes in the same cubic P-1 space group and binuclear structure. Take 1 as an example; the metal ion is connected to two H<sub>3</sub>L<sup>1</sup> ligand molecules and four coordination water molecules (Figure 1(a)). It also contains two unbonded lattice water molecules. As shown in Figure 1(b), nine coordinated atoms form a square-face monocapped antiprismatic coordination geometry, *SAPRS*-[PrO<sub>9</sub>]. In 1–3, the bond lengths of Pr – O and the angles of O – Pr – O are in the range of 2.410(2)–2.684(2) Å and 50.00(7)–148.20(8)°, the bond lengths of Ho – O and the angles of O – Dy – O are in the range of 2.410(2)–2.684(2) Å and 50.00(7)–148.20(8)°, respectively.

The Ln(III) ions are linked into a 1D polymeric chain structure by these bridging  $H_3L^2$  ligands (Figure 1(c)). The neighboring 1D chains are further joined together by  $\pi\cdots\pi$  stacking interactions to generate a 2D supramolecular layer structure (Figure 1(d)). The centroid-to-centroid distances are in the range of 3.574(2)-3.848(2) Å, which are all in their normal ranges [21]. Therefore, we can confirm that **1**–**3** have  $\pi\cdots\pi$  stacking interactions. Between the adjacent 2D layers, there are unbound chloride anions and coordinated water molecules; the non-classic O – H…Cl weak hydrogen bonding interactions are formed by unbound chloride anions and display a 3D supramolecular structure. The hydrogen bond spacing of **1**–**3** is also similar (Figure 1(e)). In **1**–**3**, O – H…Cl distances range from 3.11-3.14 Å, 3.12-3.13 Å and 3.15-3.18 Å, respectively (table S2).

#### 3.2. Crystal structure of $[Dy(H_2L^2)_2(H_2O)_6]Cl_3$ (4)

The crystal structure indicates that **4** is a 0D structure, which crystallized in the triclinic P - 1 space group. The Dy ion is surrounded by two oxygen atoms (O3, O4) from two different H<sub>3</sub>L<sup>2</sup> ligands and six oxygen atoms (O7, O8, O9, O10, O11, and O12) from six distinct coordinated water molecules (Figure 2(a)). Finally, Dy1 reveals distorted [DyO<sub>8</sub>] dodecahedron geometry (Figure 2(b)). The bond lengths of Dy – O and the angles of O - Dy - O are in the range of 2.273(3)–2.429(2) Å and 70.92(10)–147.33(9)°, respectively. Compared with **1–3**, the dimensions of **4** are lower than that of **3**.

According to Figure 2c, the asymmetric units are linked to form a 1D polymeric chain structure with  $O - H \cdots Cl1$  weak hydrogen bonding interactions. The adjacent 1D chains are bridged via  $O - H \cdots Cl2$  and  $N - H \cdots Cl2$  to form a 2D layer structure (Figure 2(d)). In **4**, the 3D supramolecular form is developed by  $\pi \cdots \pi$  interactions between imidazole rings of parallel ligands and the average centroid-centroid separation is

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(a)



(b)



**Figure 1.** (a) Coordination environment of **1** with ellipsoids drawn at 80% probability. (b) The *SAPRS*-[LnO<sub>9</sub>] unit. (c) The 1D chain structure of **1**. Symmetry code: -x + 2, -y, -z-1. (d) The 2D layer structure of **1** along the *c*-axis (the black dashed lines represent the  $\pi \cdots \pi$  stacking interactions). (e) The 3D supramolecular structure of **1** viewed along the *c*-axis (the sky blue dashed lines represent the  $0 - H \cdots Cl$  weak hydrogen bonding interactions, Cl: pink).

3.499(1) Å (Figure 2(e)). In previous reports, a complex (Ho-complex) synthesized by  $H_3L^2$  ligands was 0D structure as well [16]. According to Figure 2f, the Ho-complex is also a 3D supramolecular structure formed by hydrogen bonding and  $\pi \cdots \pi$  interactions. The difference between **4** and the Ho-complex is the manner of hydrogen



Figure 1. Continued.

bonding. We found that different ligands have some effect on the structure of the complexes. In **4**,  $O - H \cdots CI$  distances are from 3.08 to 3.28 Å, and  $N - H \cdots CI$  distances are 3.13 Å (table S2). Compared with other similar studies, the hydrogen bond distance of **1–4** is shorter [22].

### 3.3. Crystal structure of $[Ce(H_2L^3)(CH_3CO_2)_2(H_2O)_2] \cdot H_2O$ (5)

The crystal structure indicates that **5** is a 1D structure and composed of a single core  $[CeO_{10}]$  cluster, which crystallizes in the triclinic system with space group P - 1. The asymmetric unit of **5** consists of one and a half Ce(III) ions, one H<sub>3</sub>L<sup>3</sup> ligand, four acetic acid molecules and two distinct coordinated water molecules. As shown in Figure 3a, the 10-coordinate Ce1 ion is ligated by two oxygen atoms (O2, O3) from one ligand, six oxygen atoms (O4, O4<sup>#</sup>, O5, O8, O8<sup>#</sup>, O9) from four distinct coordinated acetic acid molecules and two oxygen atoms (O6, O7) from two distinct coordinated water molecules. Ce1 shows a tetrakaidecahedron geometry around the Ce(III) ion in **5** 

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(a)



(b)



(c)

**Figure 2.** (a) Coordination environment of **4** with ellipsoids drawn at 80% probability. (b) Polyhedral view showing dodecahedron geometry around the Dy(III) ion in **4** (c) The 1D chain structure of **4**. Symmetry code: -x + 2, -y, -z-1. (d) The 2D layer structure of **4** along the *c*-axis (the sky blue dashed lines represent the  $O - H \cdots CI$  weak hydrogen bonding interactions, CI: pink). (e) The 3D supramolecular structure of **4** viewed along the *c*-axis (the black dashed lines represent the  $\pi \cdots \pi$  stacking interactions). (f) The 3D supramolecular structure of Ho-complex in reference 16.







(e)



(f)

Figure 2. Continued.



(a)



(b)



(c)

**Figure 3.** (a) Coordination environment of **5** with ellipsoids drawn at 80% probability. (b) Polyhedral view showing tetrakaidecahedron geometry around the Ce(III) ion in **5**. (c) The 1D chain structure of **4**. Symmetry code: x-1, y, z.



Figure 4. (a) Solid-state photoluminescence spectrum of 1–3 and  $H_3L^1$ . (b) Solid-state photoluminescence spectrum of 4, 5,  $H_3L^2$  and  $H_3L^3$ .

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**Figure 5.** Variation of  $\chi_m T$  and  ${\chi_m}^{-1}$  of 1–5 (solid line is a curve fitted by the Curie formula).



Figure 5. Continued.

(Figure 3(b)). The bond lengths of Ce – O and the angles of O – Ce – O are in the range of 2.4720(17)–2.7846(18) Å and 48.51(5)–144.78(6)°, respectively. The trinuclear subunits are interconnected to each other using oxygen atoms of the  $H_2L^3$  ligand to Ce1, and an infinite 1D chain is generated (Figure 3(c)). Compared with 1–4, 5 is not a supramolecular structure, indicating that chloride ions play a key role in the formation of hydrogen bonds.

According to IR, after the three ligands coordinated to the lanthanide metal to form a complex, the IR characteristic peak of the coordinated functional group was blue-shifted. In this study, we can determine whether the ligand is coordinated with the lanthanide metal through the change of the infrared characteristic peak.

#### 3.4. Thermogravimetric analyses and PXRD

In order to study the thermal stability of 1-5, thermal gravimetric (TG) analyses were carried out in an argon atmosphere from room temperature to 1000 °C (Figure S4 of

Supplementary Information). For 1-5, the first weight loss readily occurred under the flow of argon gas attributing to the liberation of the water molecules. For 1, a weight loss of 18.01% from 25–210 °C corresponds to six  $H_2O$  molecules losses (calcd 19.50%). It then begins to disintegrate at about 260 °C, which may include decomposition of the ligand and organic backbone. After 940 °C, the final residue of 54.80% may be  $Pr_2O_3$  (calcd 59.62%). For 2, the weight loss of 14.50% in the range 25–215 °C corresponds to five H<sub>2</sub>O molecules lost (calcd 16.10%), and then, it starts to decompose at 220 °C. After 935 °C, the final residue of 65.84% may be  $Ho_2O_3$  (calcd 67.58%). The TGA curve of **3** shows a weight loss of 14.60% from 25–190 °C, corresponding to five H<sub>2</sub>O molecules lost (calcd 16.15%), then ligands decompose and the networks collapse beyond the decomposition at about 260 °C, after which the residue may be  $Dy_2O_3$ , carbon and unburned organic fragments. Complex 4 reveals a 12.70% (calcd 12.24%) weight loss from 25–70 °C, corresponding to the removal of six water molecules. This is followed by severe weight loss from unidentified products, possibly due to the disintegration of the frame at about 330 °C. At 935 °C, the final residue of 56.59% may be  $Dy_2(CO_3)_3$  (calcd 57.23%). For 5, the weight loss of 10.74% from 25–120 °C is equivalent to three water molecules (10.45%). After that, the structures begin to collapse with increasing temperature at about 360°C.

To explore the purity of the sample, the powder X-ray diffraction (PXRD) analyses of **1–5** were carried out. As shown in Figure S5 of Supplementary Information, the experimental results show that the analytical complexes were single phase, which were consistent with the peaks in the diffraction spectrum simulated from the single-crystal data.

#### 3.5. Fluorescent properties of 1-5

Lanthanide complexes have attracted widespread interest due to their luminous properties [23]. Reasonable selections of complexes and conjugated organic components as well as metal centers can effectively obtain new luminescent materials [24]. Therefore, the solid-state photoluminescence properties of 1-5 and ligands  $H_3L^1$ ,  $H_3L^2$ and  $H_3L^3$  were studied at room temperature. The maximum excitation wavelengths of  $H_3L^1$  and 1-3 were 350, 345, 300 and 345 nm, respectively. The maximum emission wavelengths were 375, 390, 435 and 390 nm, respectively. Compared with the ligands, red shifts occur due to the ligand to metal charge transfer (LMCT) (Figure 4(a)). Complex 2 exhibits a broad feature with multiple maxima covering almost the entire visible region, which can be ascribed to the coordination mode of the ligand and coordination environment of the metal centers. The maximum excitation wavelengths of H<sub>3</sub>L<sup>2</sup>, H<sub>3</sub>L<sup>3</sup>, 4 and 5 were 300, 280, 350 and 280 nm, respectively, with maximum emission wavelengths of 580, 540, 485 and 375 nm (Figure 4(b)). We found that  $H_3L^3$ also has an absorption wavelength at 378 nm, which can be attributed to the  $n \rightarrow \pi^*$ or  $\pi \rightarrow \pi^*$  transition in ligand-centered electronic transitions. Compared with the ligand, the emission band of 4 is blue-shifted due to the metal to ligand charge transfer (MLCT). The emission band of 5 is also blue-shifted compared with ligand. In comparison with **3**, the maximum emission wavelength of **4** is higher. The two differences in

fluorescence intensity of **3** and **4** can be attributed to the different coordination mode of the ligand.

#### 3.6. Magnetic properties

Thermally dependent magnetic properties of 1-5 were measured in the range 2-300 K at 1000 Oe (Figure 5). The  $\gamma_m T$  value of **1** at 300 K is 1.35 emu mol<sup>-1</sup> K, which is lower than two separated Pr(III) ions, which has a value of 3.20 emu mol<sup>-1</sup> K (q = 0.8). As the temperature drops, the  $\chi_m T$  value of **1** continued to decrease at 2 K, reaching 0.175 emu  $mol^{-1}$  K, indicating the possible presence of weak antiferromagnetic exchange between the Pr(III) ions. For **2** and **3**, the  $\chi_m T$  values at 300 K are 13.2 and 13.5 emu mol<sup>-1</sup> K, respectively, which are lower than two isolated metal ions wth spin-only values of 28.14 and 28.34 emu mol<sup>-1</sup> K (g = 5/4, 4/3). As the temperature drops, the  $\chi_m T$  values of these two Ln complexes gradually decrease to 7.1 and 4.5 emu  $mol^{-1}$  K at 2 K, respectively, indicating the possible presence of weak antiferromagnetic exchange. The  $\chi_m T$  value of **4** at room temperature is  $10.75 \text{ emu mol}^{-1}$  K. This is less than the theoretical value of 14.18 emu mol<sup>-1</sup> K for the one Dy(III) ion (q = 4/3), and then, the  $\gamma_m T$  value drops to  $8.53 \text{ emu mol}^{-1}$  K at 2 K, indicating the possible presence of weak antiferromagnetic exchange between the Dy(III) ions. The experimental value of  $\chi_m T$  is 1.21 emu mol<sup>-1</sup> K at 300 K for **5**, which is higher than the theoretical value of  $0.80 \text{ emu mol}^{-1}$  K for the one Ce(III) ion (q = 6/7). Then, the  $\gamma_m T$  value drops to 0.10 emu mol<sup>-1</sup> K at 2 K, indicating the possible presence of weak antiferromagnetic exchange between the Ce(III) ions. In complexes 1–5, the error between the fitted value of  $\gamma_m T$  and the theoretical value of  $\gamma_m T$ can be explained in terms of three factors: (1) the antiferromagnetic interactions between the lanthanide ions; (2) spin-orbital coupling of lanthanide complexes, which leads to the 4f configuration splitting into  ${}^{2S+1}L_J$  states, and finally into Stark components under the ligand field perturbation [25]; (3) magnetic anisotropy [26]. To sum up, complexes 1-5 may exhibit antiferromagnetic properties.

#### 4. Conclusion

Five new lanthanide coordination polymers (1–5) were obtained from  $H_3L^1$ ,  $H_3L^2$  and  $H_3L^3$  ligands under hydrothermal conditions. According to single-crystal X-ray analysis, 1–3 and 5 are CPs as 1 D zigzag chains, and 4 is a 0D structure, which the complexes 1–4 further assembled solely by the non-classic O – H…Cl weak hydrogen bonding and  $\pi$ … $\pi$  stacking interactions to form 3D supramolecular structure. Complexes 1–5 showed moderate thermal stabilities. The fluorescence properties of 1–5 were studied. Complexes 1–5 may display antiferromagnetic couplings. Hence, the research in this field is of significance, and further research will be focused on the synthesis of novel Ln-CPs with interesting properties.

#### **Disclosure statement**

No potential conflict of interest was reported by the authors.

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