新型金属—有机超分子配合物的研究

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Syntheses and characterization of novel lanthanide adamantine–dicarboxylate coordination complexes

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ABSTRACT

Hydrothermal reactions of 1,10-phenanthroline (phen), 1,3-adamantanedicarboxylic acid (H_2L) and lanthanide chlorides yielded six compounds: [*Ln*(L)(HL)(phen)] (*Ln* = Pr, **1**; Nd, **2**), [*Ln*(L)(HL)(phen)(H_2O)] (Sm, **3**; Eu, **4**), [Tb(L)(HL)(phen)(H_2O)]$_2 \cdot 2H_2O$ (**5**), [Er_3(L)$_4$(OH)(phen)]$_2$ (**6**). Compounds **1–4** are structurally featured by one-dimensional polymeric chains; 5 hold binuclear structure constructed from eight-coordinated lanthanide center LnN_2O_6 of distorted bicapped trigonal prism bridged by dicarboxylate ligands; 6 shows that erbium ions are in mono and bicapped trigonal prismatic geometries, respectively, which are further connected by μ_3-OH to give rise to trinuclear structure. Thermogravimetric analyses of **1**, **3** and **5** were performed. Fluorescent measurements of **4** and **5** were carried out, respectively.

1. Introduction

Design and syntheses of lanthanide complexes are of great interest due to their various topological networks and crystal packing motifs as well as potential applications in fluorescent probes, magnetic materials, catalysts, molecular sensors [1–13]. In virtue of the large radii and high coordination number of lanthanide metals, the assembly of lanthanide complexes may encounter many difficulties and great challenges in terms of controlling their shapes and dimensions. However, the fascinating structures and special properties of lanthanide complexes have attracted increasing attention of scientists, and extensive investigation has been reported in the recent years [14–26].

It has been documented that the geometries and properties of organic ligands exert great effect on structural frameworks of lanthanide complexes, thus much effort has been devoted to modify the building blocks and to control the assembled motifs for desired products through the selection of different organic ligands. Previous studies have shown that rigid bridging ligands containing multicarboxylate groups are versatile ones for constructions of the robust networks or other porous coordination polymers [27–35]. As known, lanthanide ions have high affinity for hard donor atoms, and ligands with oxygen or hybrid oxygen–nitrogen atoms, especially multicarboxylate ligands are usually employed in construction for lanthanide complexes. 1,3-adamantanedicarboxylic acid possesses intriguing coordination behaviors and potential hydrogen-bond interactions, such as asymmetric geometry and multiple coordination sites. However, former studies on the coordination chemistry of 1,3-adamantanedicarboxylic acid are mainly focused on transition metals [36–38], and those on lanthanide matals were very limited [39]. Recently we began to use adamantanedicarboxylic acid as organic ligand to synthesize lanthanide complexes, aiming at studying the coordination chemistry of lanthanide adamantanedicarboxylic acid as well as at obtaining some novel structures. By means of hydrothermal technique, six new lanthanide complexes have successfully prepared with 1,3-adamantanedicarboxylic acid. This paper will report about the syntheses and characterizations of a series of lanthanide adamantine–dicarboxylate complexes, [*Ln*(L)(HL)(phen)] (*Ln* = Pr, **1**; Nd, **2**), [*Ln*(L)(HL)(phen)(H_2O)] (Sm, **3**; Eu, **4**), [Tb(L)(HL)(phen)(H_2O)]$_2 \cdot 2H_2O$ (**5**), [Er_3(L)$_4$(OH)(phen)]$_2$ (**6**).

2. Experimental section

2.1. Materials and methods

Except $LnCl_3 \cdot nH_2O$, which was prepared in our laboratory, all chemicals of reagent grade were commercially available and used without further purification. Elemental analyses(C, H and N) were performed using a Perkin-Elmer 2400 CHNS/O analyzer. The infrared spectrum of KBr pellets in the range 4000–400 cm^{-1} was recorded on a Shimadzu FTIR-8900 spectrometer.

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Thermogravimetric measurements were carried out from room temperature to 1000 °C for **1**, to 800 °C for **3** and **5** on preweighed samples in nitrogen stream using a Seiko Exstar6000 TG/DTA6300 apparatus with a heating rate of 10 °C/min. All the excitation and emission spectra were measured with an Aminco Bowman Series 2 instrument with a xenon arc lamp as the excitation light source for the solid-state samples at room temperature.

2.2. Preparation of complexes

2.2.1. Synthesis of [Pr(L)(HL)(phen)] (1)

Pale green powder of $PrCl_3 \cdot nH_2O$ was obtained by slow evaporation of a solution of Pr_2O_3 dissolved in HCl (10 mL) under water boiling condition. A mixture of 1,3-adamantanedicarboxylic acid (H_2L, 0.30 mmol, 0.0673 g), the above-prepared $PrCl_3 \cdot nH_2O$ (0.106 g) and 1,10-phenanthroline (phen, 0.30 mmol, 0.0595 g) in water (10 mL) was stirred for 1.0 h, and then sealed in a 23 mL Teflon-lined stainless autoclave, which was heated at 170 °C for six days and thereafter cooled slowly at 10 °C/h to room temperature, and pale green crystals were seperated by filtering and washing with absolute ethanol (Yield 40%, based on Pr_2O_3). Anal. Cacd (%) for $C_{36}H_{37}N_2O_8Pr$ (766.61): C 56.40, H 4.86, N 3.65. Found (%): C 56.85, H 4.97, N 3.59. IR(ν cm^{-1}): 3396ms, 3055vw, 2903s, 2849s, 1684vs, 1608vs, 1518vs, 1408vs, 847s, 731s.

2.2.2. Synthesis of [Nd(L)(HL)(phen)] (2)

Pale red crystal were prepared analogously to **1** except using Nd_2O_3 instead of Pr_2O_3 (Yield 35%). Anal. Cacd (%) for $C_{36}H_{37}N_2O_8Nd$ (769.94): C 56.16, H 4.84, N 3.64. Found (%): C56.19, H 4.71, N 3.58. IR (ν cm^{-1}): 3422ms, 3080vw, 2883s, 2847s, 1697vs, 1589vs, 1518vs, 1408vs, 851s, 731s.

2.2.3. Synthesis of [Sm(L)(HL)(phen)(H_2O)] (3)

Yellow powder of $SmCl_3 \cdot nH_2O$ was obtained by slow evaporation of a solution of Sm_2O_3 (0.150 mmol, 0.0525 g) dissolved in HCl (10 mL) under water boiling condition. A mixture of 1,3-adamantanedicarboxylic acid (0.30 mmol, 0.0673 g), the above-prepared $SmCl_3 \cdot nH_2O$ and 1,10-phenanthroline (0.30 mmol, 0.0595 g) in water (10 mL) was stirred for 30 min, and then sealed in a 23 mL Teflon-lined stainless autoclave, which was heated at 160 °C for three days and thereafter cooled slowly to room temperature, and pale yellow crystals were seperated by filtering and washing (Yield 30%, based on Sm_2O_3). Anal. Cacd (%) for $C_{36}H_{39}N_2O_9Sm$ (794.07): C 54.45, H 4.95, N 3.53. Found (%): C 55.01, H 4.81, N 3.64. IR(ν cm^{-1}): 3402ms, 3080w, 2902s, 1685vs, 1610vs, 1514vs, 1408vs, 848s, 729s.

2.2.4. Synthesis of [Eu(L)(HL)(phen)(H_2O)] (4)

Colorless crystals were prepared analogously to **3** except using Eu_2O_3 instead of Sm_2O_3 (Yield 45%). Anal. Cacd (%) for $C_{36}H_{39}N_2O_9Eu$ (796.67): C 54.34, H 4.94, N 3.52. Found (%): C54.57, H 4.82, N 3.48. IR (ν cm^{-1}): 3410ms, 3059vw, 2902s, 2849s, 1684vs, 1612vs, 1522vs, 1418vs, 847s, 730s.

2.2.5. Synthesis of [Tb(L)(HL)(phen)(H_2O)]$_2 \cdots 2H_2O$ (5)

Pale green powder of $TbCl_3 \cdot nH_2O$ was obtained by slow evaporation of a solution of Tb_4O_7 (0.07 mmol, 0.0549 g) dissolved in HCl (5 mL) under water boiling condition. A mixture of 1,3-adamantanedicarboxylate (0.30 mmol, 0.0672 g), $TbCl_3 \cdot nH_2O$ nd 1,10-phenanthroline (0.30 mmol, 0.0595 g) in water (10 mL) was stirred for 30 min, and sealed in a 23 mL Teflon-lined stainless autoclave, which was heated at 170 °C for three days and thereafter cooled slowly to room temperature, and Pale green crystals were seperated by filtering and washing (Yield 30%). Anal. Cacd (%) for $C_{36}H_{41}N_2O_{10}Tb$ (820.65): C 52.69, H 5.04, N 3.41. Found (%): C 52.78, H 5.13, N 3.36. IR (ν cm^{-1}): 3410ms, 3059vw, 2902s, 2849s, 1684vs, 1612vs, 1522vs, 1418vs, 847s, 729s.

2.2.6. Synthesis of [$Er_3(L)_4(OH)(phen)$]2 (6)

Pale red crystals were prepared similarly to **5** except using Er_2O_3 instead of Y_2O_3 (Yield 15%). Anal. Cacd (%) for $C_{120}H_{130}N_4O_{34}Er_6$ (3175.92): C 45.38, H 4.13, N 1.76; Found: C 45.51, H 4.06, N 1.79; IR (ν cm^{-1}): 3410ms, 3059vw, 2902s, 2849s, 1684vs, 1612vs, 1522vs, 1418vs, 847s, 731s.

2.3. X-ray crystallography

Suitable crystals of **1–6** were selected under a polarizing microscope and fixed with epoxy cement on respective fine glass fibers which were then mounted on a RIGAKU RAXIS-RAPID diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å) for cell determination and subsequent data collection for in the range of $3.22 \leqslant \theta \leqslant 27.48°$. Empirical absorption corrections were applied using the SADABS program. SHELXS-97 and SHELXL-97 programs were used for structure solution and refinement [40,41]. The structures were solved by using direct methods and followed by successive Fourier and difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic displacement parameters by full-matrix least-squares technique and all hydrogen atoms with isotropic displacement parameters. Detailed information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Tables 2–7 (See in Supporting Materials). Crystallographic data (excluding structure factors) for complexes **1–6** in this paper have been deposited with Cambridge Crystallographic Data Centre as supplementary publications.

3. Results and discussion

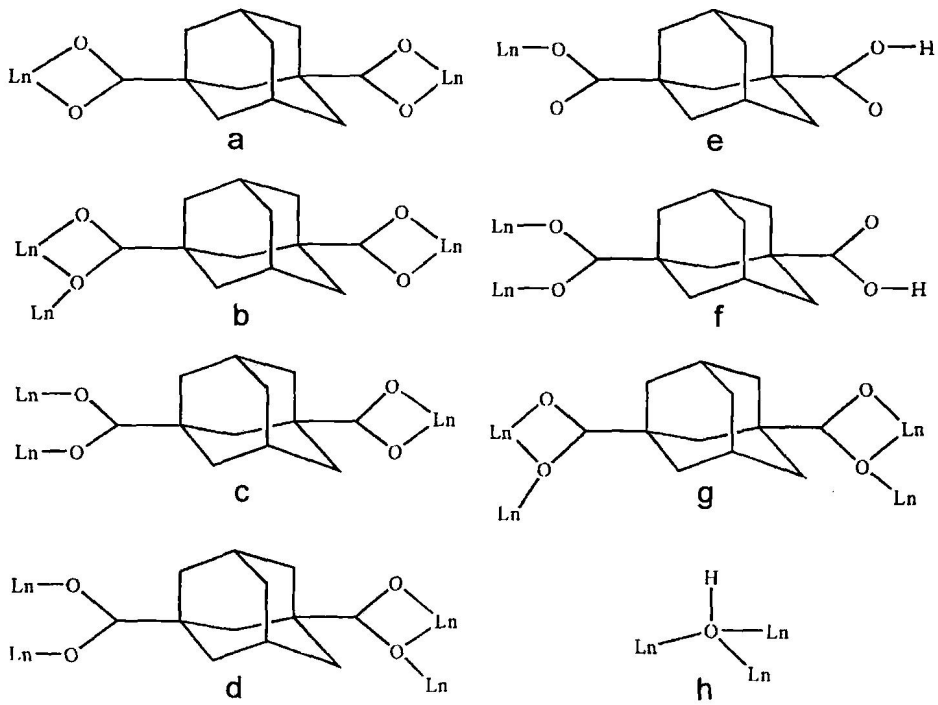
3.1. Syntheses of the complexes

Owing the hydrophobility of the adamantane framework, 1,3-adamantanedicarboxylic acid was found to be uneasily dissolved in common solvents such as H_2O, MeOH, EtOH, THF, etc. under ambient condition, therefore, the reactions of the dicarboxylatic acid with lanthanide chlorides were carried out under the similar hydrothermal conditions in order to obtain new complexes with novel networks. Six lanthanide metal-organic complexes suitable for single crystal X-ray diffraction were obtained. 1,3-adamantanedicarboxylates function as linkers in various fashions (monodentate, bidente bridging, bidentate chelate, bidente chelating–bridging etc.) through its carboxylate groups in these complexes (Scheme 1), demonstrating its versatility in construction of the robust network or porous functional materials [36–39]. The structural analyses show that *Ln*(III) ions are the nine-coordinated modes in **1** and **2**, the eight-coordinated modes in **3**, **4** and **5**, the 8/7-coordinated fashions in **6**, respectively. On the other hand, complexes **1**, **2**, **3** and **4** possess one-dimensional chain frameworks, however, complex **5** is binuclear structure, and complex **6** has double chains extended by two inequivalved structural units. The different geometries and structures may result from the effects of the lanthanide contraction on crystal structural formation, which would offer a helpful route to design and synthesize lanthanide compounds with the special structural networks.

Table 1
Crystallographic data for **1–6**

	1	2	3	4	5	6
Empirical formula	$C_{36}H_{37}N_2O_8Pr$	$C_{36}H_{37}NdN_2O_8$	$C_{36}H_{39}N_2O_9Sm$	$C_{36}H_{39}EuN_2O_9$	$C_{36}H_{41}N_2O_{10}Tb$	$C_{120}H_{130}Er_6N_4O_{34}$
Formula mass	766.59	769.92	794.04	795.65	820.63	3175.84
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a	11.167(2)	11.141(2)	11.153(2)	11.133(2)	8.636(2)	12.805(3)
b	12.407(3)	12.403(3)	12.329(3)	12.312(3)	13.573(3)	18.094(4)
c	13.292(3)	13.302(3)	12.651(3)	12.681(3)	14.579(3)	26.128(5)
α (deg)	109.38(3)	109.36(3)	109.04(3)	109.13(3)	94.59(3)	80.69(3)
β (deg)	98.54(3)	98.57(3)	97.19(3)	97.31(3)	96.33(3)	86.39(3)
γ (deg)	110.16(3)	110.20(3)	99.83(3)	99.72(3)	92.30(3)	84.09(3)
V (Å^3)	1557.4(5)	1553.7(5)	1589.5(5)	1587.2(5)	1691.0(6)	5936.2(2)
Z	2	2	2	2	2	2
ρ (Mg/m^3)	1.635	1.646	1.659	1.665	1.612	1.777
μ (mm^{-1})	1.623	1.730	1.909	2.038	2.513	4.274
F(000)	780	782	806	808	832	3116
θ range (deg)	3.02–27.48	3.02–27.48	3.04–27.48	3.04–27.48	3.02–27.48	3.04–27.48
Reflns collected	15337	15251	15768	15453	16764	54559
Reflns independent	7068	7009	7237	7168	7671	25969
Reflns observed	6789	6423	6872	6663	6824	18087
R1 [$I \geq 2\sigma(I)$]	0.0188	0.0427	0.0300	0.0320	0.0276	0.0611
R1 (all data)	0.0202	0.0468	0.0318	0.0357	0.0344	0.0940
GOF	1.190	1.095	1.192	1.161	1.074	1.002

(a) $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.



Scheme 1. Linking fashions of the adamantanedicarboxylate groups.

3.2. Description of the crystal structures

X-ray diffraction studies reveal that the asymmetric unit of complex **1** contains one Pr(III) ion, one phen ligand and two kinds of coordiantion styles of 1,3-adamantanedicarboxylate ligand (HL^{1-}, L^{2-}). As shown in Fig. 1a, the nine-coordinated Pr(III) ion is in a tricapped trigonal antiprism LnN_2O_7 defined by seven oxygen atoms of the different 1,3-adamantanedicarboxylate and two N atoms of one phen ligand with Pr–O distances ranging from 2.408 to 2.742 Å (average 2.512 Å), Pr–N distances of 2.674 and 2.700 Å (average 2.687 Å). For adamantane-dicarboxylate ligand of each structural unit, L^{2-} acts as a μ_3-bridge to link three Pr(III) ion with one carboxylate group adopting a bidentate chelate mode coordinating to one praseodymium ion and the other adopting a bidente chelating-bridging mode connecting two praseodymium ion (Scheme 1b) [42,43]; HL^{1-}, the monoprotonated adamantanedicarboxylate, links two praseodymium ions through the carboxylate group acting as a bidentate bridge mode and the protonated end remains uncoordinated (Scheme 1f). Two adjacent praseodymium ions are held together to form a dimeric subunit

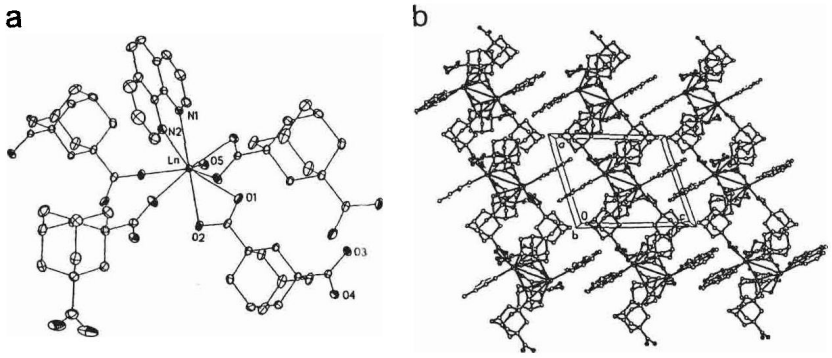


Fig. 1. (a) ORTEP view of coordination environments of *Ln*(III) ion with 30% displacement ellipsoids and (b) two dimensional layer structure projected along *b* axis in **1** and **2**.

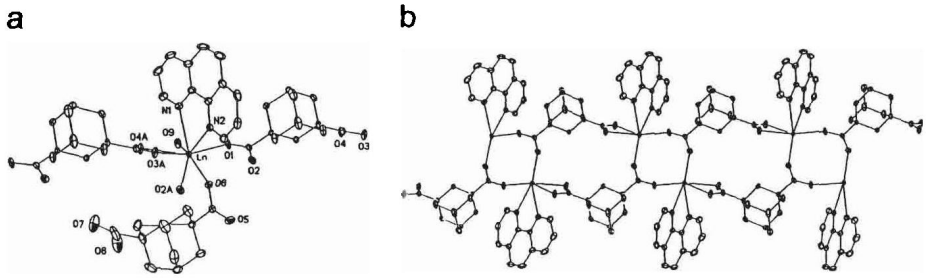


Fig. 2. (a) ORTEP view of coordination environments of *Ln*(III) ion with 30% displacement ellipsoids and (b) a fragment of a double chain along *c* axis in **3** and **4**.

$[Pr_2(L)_2(HL)_2(phen)_2]$ by the carboxylates with Pr–Pr distance of 3.96 Å, implying no significant direct interaction between metal ions.

$[Pr_2(L)_2(HL)_2(phen)_2]$ can be viewed as the basic building block for the whole structure of **1**. Each pair of such blocks are bridged by adamantanedicarboxylate bridging, giving rise to a double chain. The chains are further connected through strong offset face-to-face $\pi\cdots\pi$ stacking interaction with a mean interplanar distance of 3.25 Å between the adjacent aromatic rings to generate two-dimensional network (Fig. 1b). Complex **1** finally forms three-dimensional packing structure by hydrogen bond of the carboxylate oxygen atoms with $O\cdots O$ distance 2.658 Å and $\angle(O\text{–}H\cdots O) = 161°$, as well as weak C–H···O and C–H···N interactions with $C\cdots O = 3.385$ Å and $\angle(C\text{–}H\cdots O) = 149°$; $C\cdots N = 3.349$ Å, and $\angle(C\text{–}H\cdots N) = 155°$, respectively (Fig. S10).

Complex **2**, being isomorphous to **1**, possesses one-dimensional network by covalent bonding. The Nd–O distances fall in a range from 2.393–2.742 Å (average 2.509 Å), and Nd–N from 2.660 to 2.685 Å (average 2.673 Å), which slightly shorter than oens in **1**, resulting from the effect of lanthanide contraction.

Complexes **3** and **4** are allomers with one-dimensional chain structure by covalent bonding. Two kinds of coordination modes of adamantanedicarboxylate (HL^{1-}, L^{2-}) are present in the structre: L^{2-} acts as μ_3-bridge to link three *Ln*(III) ion, in which one carboxylate group adopts a bidentate chelate mode coordinating to one lanthanide ion while the other adopts a bidente bridging mode connecting two lanthanide ion (Scheme 1c) [42–45]; and HL^{1-}, the protonated adamantanedicarboxylate, links only one lanthanide ion through the carboxylate group acting as a monodentate mode while the protonated one remains uncoordinated to metal ion (Scheme 1e). As shown in Fig. 2a, the Sm(III) or Eu(III) ion is in a eight-coordinated geometry defined by four oxygen atoms from L^{2-}, one oxygen from the HL^{1-}, one aqua oxygen atom and two nitrogen atoms from phen ligand, forming a

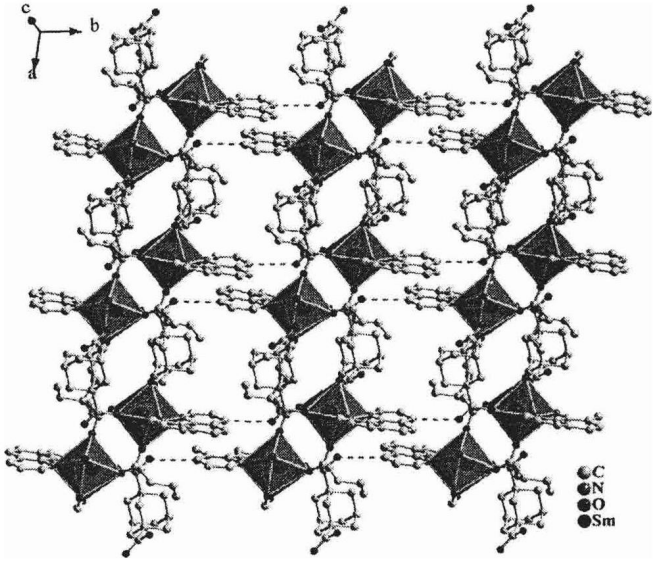


Fig. 3. Two-dimensional network through hydrogen bonds in **3** and **4**.

distorted bicapped trigonal prism LnN_2O_6 with the metal to ligating atom distances Sm–O = 2.297–2.512 Å, Sm–N = 2.633–2.659 Å in 3; Eu–O = 2.2291–2.499 Å, Eu–N = 2.620–2.643 Å in 4. $[Ln_2(L)_2(phen)_2]$, being as dimeric subunits, are formed by carboxylate linkers, which are reproduced through adamantanedicarboxylate bridging, giving rise to a double chain structure (Fig. 2b). The chains are further extended into two-dimensional network through hydrogen bonds between the carboxylate and aqua oxygen atoms with distance $O\text{–}H\cdots O = 2.647\text{–}2.878$ Å and $\angle(O\text{–}H\cdots O) = 150°$, as well as weak C–H···O interaction with $C\text{–}H\cdots O = 3.352$ Å and $\angle(C\text{–}H\cdots O) = 147°$ in 3;