

New ternary lanthanide coordination polymers of 1,4-naphthalenedicarboxylate with 1,10-phenanthroline

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Abstract

Three isostructural 2-D square grid coordination polymers $[\text{Ln}_2(\text{NDC})_3(\text{phen})_2(\text{H}_2\text{O})_2]$ ($\text{Ln} = \text{La}$ (**1**), Eu (**2**), Ho (**3**), $\text{NDC} = 1,4$ -naphthalenedicarboxylate, $\text{phen} = 1,10$ -phenanthroline) were synthesized by hydrothermal reactions of lanthanide chloride with 1,4-naphthalenedicarboxylic acid and phen . The 2-D coordination polymers were assembled into 3-D networks via $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond. The photophysical property, magnetic property and thermal stability of complex **2** were investigated.

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The field of coordination polymers has undergone an explosive growth since numerous one, two, and three-dimensional structures have been obtained [1–15] for detailed studies of their structural characteristics, such as diverse coordination modes, intriguing architecture, and their potential applications as catalysts, luminescent materials, magnetic materials. Our research mainly focuses on the construction of lanthanide-organic frameworks with varieties of topologies and porosity [16–23] because lanthanide ion has high coordination number and can afford enough coordination sites for different ligands, which can lead to the syntheses of lanthanide coordination polymers with unprecedented structures. The organic ligands employed come from the family of dicarboxylic acids which are frequently selected as good

linkers to generate layers, chains, or clusters of transition metal or lanthanide ions. 1,4-naphthalenedicarboxylate is a rigid linear bifunctional ligand, and its coordination polymers with transition metal ions have been reported [24–27]. We have obtained two heptanuclear lanthanide hydroxo clusters of the dicubane-like type which are used as a secondary building unit to form a 3-D framework through the linkage of NDC [22]. Besides this, no other lanthanide coordination polymers of NDC are reported. In the present case, the hydrothermal syntheses [28] and crystal structures [29] and properties of coordination polymers of lanthanide 1,4-naphthalenedicarboxylate with the ancillary ligand, 1,10-phenanthroline (phen) are reported.

Since the three title complexes are isostructural, only the structure of **2** will be discussed. The asymmetric unit of **2** consists of $[\text{Eu}_2(\text{NDC})_3(\text{phen})_2(\text{H}_2\text{O})_2]$ as the building unit (Fig. 1). There are two independent $\text{Eu}(\text{III})$ ions where Eu1 and Eu2 are both eight-coordinate with N_2O_6 donor set in a dodecahedral environment. In **2**,

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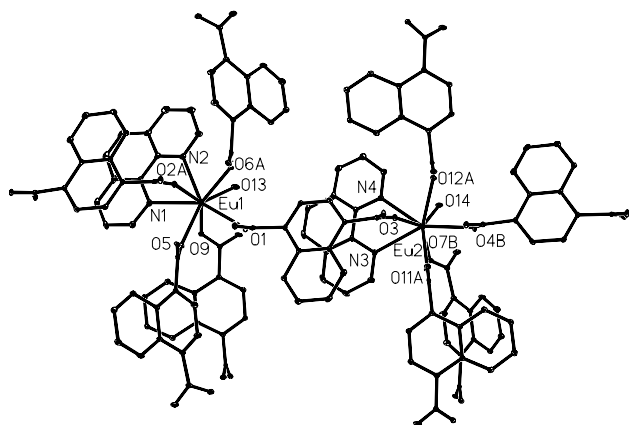


Fig. 1. Coordination environment of complex **2**. The related coordination atoms are labeled out. All hydrogen atoms are omitted for clarity. Thermal ellipsoids are shown at 10% probability.

NDC ligand adopts two coordination modes of bridging bidentate–monodentate (namely tridentate) and bis (bridging bidentate) (namely tetradentate). For convenience, the NDC ligand containing O1, O5, and O9 are named as NDC1, NDC2, and NDC3, respectively, which represent the three orientations of NDC ligand in complex **2**. In NDC1, NDC2, and NDC3, the two carboxylates and the naphthalene ring are not coplanar. The dihedral angles between the naphthalene ring and two carboxylates 109.5° and 109.2° in NDC1, 150.1° and 103.6° in NDC2, 136.2° and 5.3° in NDC3. NDC1 adopts a tetradentate coordination mode, while NDC2 and NDC3 both adopt a tridentate coordination mode. In Fig. 1, Eu1 is coordinated by two nitrogen atoms (N1, N2) from a phen molecule, one oxygen atom (O13) from a water molecule, two oxygen atoms (O1, O2A) from two NDC1 ligands, two oxygen atoms (O5, O6A) from two NDC2 ligands, and one oxygen atom (O9) from a NDC3 ligand. Eu2 is coordinated with two nitrogen atoms (N3, N4) from a phen, one oxygen atom (O14) from a water molecule, two oxygen atoms (O3, O4B) from two NDC1 ligands, one oxygen atom (O7B) from one NDC2 ligand, and two oxygen atoms (O11A, O12A) from two NDC3 ligands. Thus the framework of complex **2** is built from a binuclear unit $[\text{Eu}_2(\text{NDC})_3(\text{phen})_2(\text{H}_2\text{O})_2]$. First, every NDC1 ligand bridges two binuclear units, forming a tetranuclear unit. The tetranuclear unit extends in the $[0\bar{1}1]$ direction through the linkage of NDC1 ligand, forming 1-D chains. The carboxylate group of NDC2 and NDC3 ligands both orientate in the $[011]$ direction. Then NDC2 and NDC3 link the Eu(III) ions in $[011]$ direction, forming a 2-D square grid structure with a dimension of $10.5 \times 11.1 \text{ \AA}$ (Fig. 2). The vertex of every grid is composed of two Eu(III) ions. The edge in $[0\bar{1}1]$ direction is made of one NDC1 ligand, while the edge in $[011]$ direction is composed of one NDC2 and one NDC3 ligand. Between coordinating water molecules

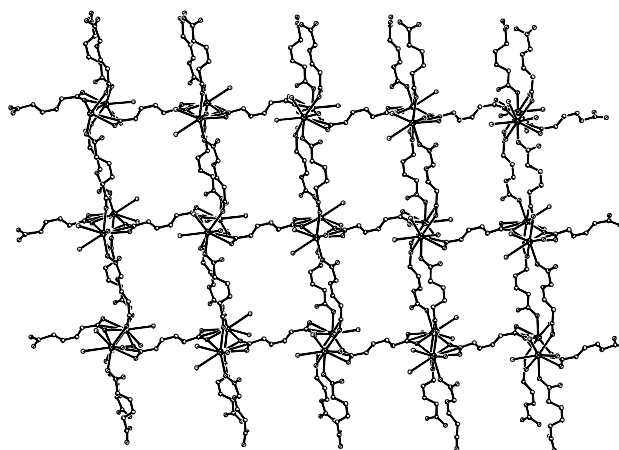


Fig. 2. The 2-D square grid structure of complex **2** viewed along the *a*-axis. For the interest of clarity, the benzo group of NDC ligand and all the carbon atoms of phen molecule were omitted.

and uncoordinating carboxylate oxygen atoms of NDC2 and NDC3 in the adjacent layer, there is $\text{O} \cdots \text{H} \cdots \text{O}$ hydrogen bonding, which extends the 2-D structure to a 3-D supramolecular structure. And the grids are packed without dislocation.

In **1**, **2** and **3**, the average bond distance of Ln–O is 2.553, 2.397, and 2.340 Å, respectively and that of Ln–N is 2.737, 2.626, and 2.565 Å, respectively, which exhibits the characteristic of lanthanide contraction. And the average Ln–O and Ln–N bond distances of complex **2** (2.397, 2.626 Å) are similar to those of the europium complex of 1,4-benzenedicarboxylate with phen (2.395, 2.621 Å) [20]. This may be attributed to the structural similarity of NDC ligand with 1,4-benzenedicarboxylate. We have successfully investigated the lanthanide-organic framework based on lanthanide 2,6-naphthalenedicarboxylate in the presence of 1,10-phenanthroline [23]. For the same lanthanide ion and with the presence of the same ancillary ligand, 2,6-naphthalenedicarboxylate links the Ho^{3+} ions to a 3-D porous metal-organic framework. While 1,4-naphthalenedicarboxylate links the Ho^{3+} ions to a 2-D square grid structure. Isomeric 2,6-naphthalenedicarboxylate and 1,4-naphthalenedicarboxylate are both linear bifunctional ligand. As linkers, the length of 2,6-naphthalenedicarboxylate is about 9.0 Å, while that of 1,4-naphthalenedicarboxylate is only 7.0 Å. Therefore, the position of dicarboxylate group and the bridge length can affect the self-assembly of ternary lanthanide coordination polymers.

TGA results show that complex **2** underwent the first loss of 2.2% from 156 to 193 °C, corresponding to the loss of two coordination water molecules (calculated: 2.7%), leaving a framework of $[\text{Eu}_2(\text{NDC})_3(\text{phen})_2]$. It continued to decompose at 387 °C and ended at 669 °C with residue Eu_2O_3 in 27.3% obtained (calculated: 26.2%).

The Eu(III) ion is frequently used as a structural probe to investigate the local symmetry. The lowest emission level 5D_0 and the ground state 7F_0 are both nondegenerate. Therefore, the number of excitation peaks corresponding to the $^7F_0 \rightarrow ^5D_0$ transition will reveal the number of Eu(III) ions with different coordination environments in the compound [30]. Fig. 3(a) and (b) show the high-resolution emission spectra of **2** corresponding to $^5D_0 \rightarrow ^7F_J$ ($J=0-4$) transitions excited by 355 nm at 77 and 293 K, respectively. The intensity ratios of $^5D_0 \rightarrow ^7F_2/^5D_0 \rightarrow ^7F_1$ are 3.29 (a) and 5.35 (b) show that the Eu(III) ions are not located in inversion centers [30], and that **2** emits red light when exposed to ultraviolet radiation. The emission peaks in Fig. 3(a) show line-narrowing at 77 K and thus become more developed. The obvious four peaks in the emission region of $^5D_0 \rightarrow ^7F_1$ reveals that there is more than one Eu^{3+} ion site in the crystal of **2**. The excitation spectrum (Fig. 4) of **2** was recorded at 77 K setting $16,303 \text{ cm}^{-1}$ as the analyzing wavenumber. Fig. 4 is composed of two

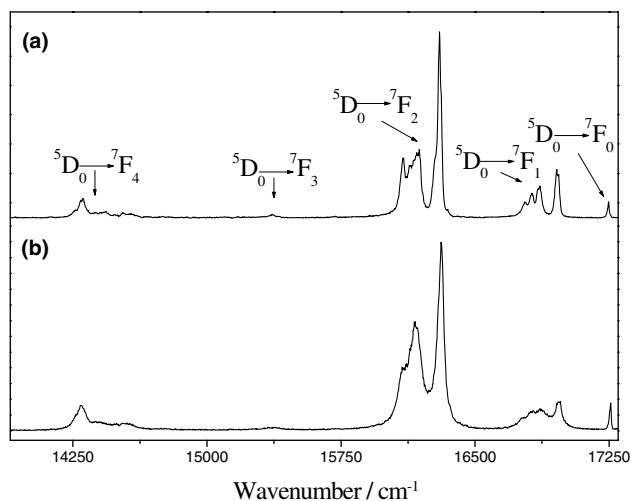


Fig. 3. Emission spectra of **2** corresponding to $^5D_0 \rightarrow ^7F_J$ ($J=0-4$) transitions at 77 K (a) and 293 K (b), $\lambda_{\text{exc}} = 355 \text{ nm}$.

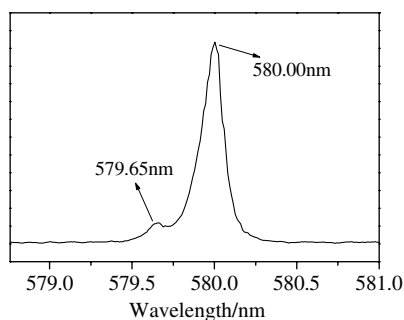


Fig. 4. Excitation spectrum of **2** at 77 K, analyzing wavenumber: $16,303 \text{ cm}^{-1}$.

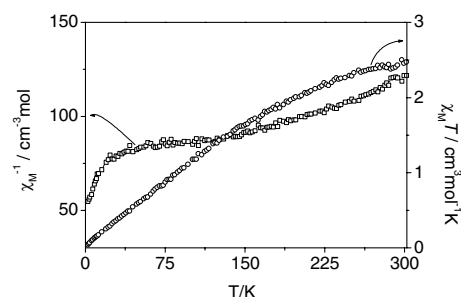


Fig. 5. Plot of the temperature dependence of $\chi_M T$ (○) and χ_M^{-1} (□) for **2** (per $[\text{Eu}]_2$ unit).

components with peak positions at 579.65 and 580.00 nm, respectively. This means that there exist two Eu(III) ion sites in **2**, which is in agreement with the result of single-crystal X-ray diffraction.

The variable temperature magnetic susceptibility of **2** was measured in the range of 2–302 K. The plot of $\chi_M T$ vs. T is shown in Fig. 5, where χ_M is the corrected molar magnetic susceptibility per $[\text{Eu}]_2$ unit. The observed $\chi_M T$ at room temperature is $2.50 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$, less than the value 3.0 for two Eu(III) ions calculated by van Vleck allowing for population of the lower excited state of 7F_J (Eu^{3+}) in **2** at 293 K [31]. As the temperature is lowered, $\chi_M T$ decreases continuously, which should be attributed to the depopulation of the stark levels for a single Eu(III) ion. At the lowest temperature, $\chi_M T$ is close to zero, indicating a $J=0$ ground state of the Eu(III) ion (7F_0). The magnetic susceptibility above 150 K follows the Curie–Weiss law due to the presence of thermally populated excited states.

In summary, we have successfully synthesized three isostructural 2-D square grid lanthanide coordination polymers under hydrothermal condition. In each of the title complexes, the Ln^{3+} ions are identical in the coordination atoms, the coordination number and the ligands. But the conformational variation of the ligand, 1,4-naphthalenedicarboxylate, gives rise to two chemically independent Ln^{3+} ions, which is also confirmed by Eu^{3+} fluorescent probe. The effect of position of dicarboxylate group and the bridge length on the self-assembly of ternary lanthanide coordination polymers with 1,10-phenanthroline is also discussed through comparing the corresponding ternary complexes of 2,6-naphthalenedicarboxylate and 1,4-naphthalenedicarboxylate. The former forms a porous 3-D structure with coordination bonds, while the later forms a 2-D structure.

Acknowledgement

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Appendix A. Supplementary data

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication: CCDC Nos. 247708–247710 for **1**, **2** and **3**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>). Supplementary data associated with this article can be found, in the online version at doi:10.1016/j.inoche.2004.11.005.

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- [28] Preparation for **1**: A mixture of 1,4-naphthalenedicarboxylic acid (0.033 g, 0.15 mmol), NaAc·3H₂O (0.04 g, 0.3 mmol), LaCl₃·7H₂O (0.038 g, 0.1 mmol), phen·H₂O (0.02 g, 0.1 mmol), H₂O (15 ml), and aqueous NaOH (0.5 ml, 0.32 mmol) was sealed in a 25 ml stainless steel reactor with Teflon liner and heated at 160 °C for 75 h. Yellow crystals of **1** were obtained in 52% yield (0.034 g). Anal. Calc. for C₆₀H₃₈La₂N₄O₁₄ (**1**): C, 54.73; H, 2.91; N, 4.25. Found: C, 54.91; H, 3.03; N, 4.32%. IR data (KBr pellet, ν/cm⁻¹): 3444 s, 1609 s, 1583 s, 1541 s, 1516 s, 1461 m, 1428 s, 1415 s, 1368 s, 1267 m, 1214 m, 840 m, 789 m, 729 m, 566 m. Similar preparation process was applied to the complexes **2** and **3**. Anal. Calc. for C₆₀H₃₈Eu₂N₄O₁₄ (**2**): C, 53.67; H, 2.85; N, 4.17. Found: C, 53.28; H, 2.99; N, 3.77%. IR data (KBr pellet, ν/cm⁻¹): 3447 s, 1626 s, 1586 s, 1540 s, 1516 s, 1460 m, 1430 s, 1361 s, 1346 s, 1267 m, 1214 m, 841 m, 728 m, 569 m. Anal. Calc. for C₆₀H₃₈Ho₂N₄O₁₄ (**3**): C, 52.65; H, 2.80; N, 4.09. Found: C, 52.52; H, 2.46; N, 4.15%. IR data (KBr pellet, ν/cm⁻¹): 3424 m, 1619 s, 1591 s, 1517 s, 1464 s, 1420 s, 1364 s, 1263 m, 844 s, 728 m, 563 m.
- [29] Collection of X-ray single-crystal data for complexes **1**, **2** and **3** was performed on a Bruker Smart 1000 CCD diffractometer, using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least square on F² using the SHELXTL-97 program. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. Crystal data for C₆₀H₃₈La₂N₄O₁₄ (**1**): M_r = 1316.76, triclinic, P $\bar{1}$, a = 11.842(4), b = 14.525(5), c = 16.168(5) Å, α = 84.198(6)°, β = 69.245(5)°, γ = 89.964(5)°, V = 2585(1) Å³, Z = 2, D_c = 1.691 g cm⁻³, μ = 1.706 mm⁻¹, R = 0.0419, wR = 0.0682. Crystal data for C₆₀H₃₈Eu₂N₄O₁₄ (**2**): M_r = 1342.86, triclinic, P $\bar{1}$, a = 11.675(4), b = 14.311(5), c = 16.114(6) Å, α = 84.024(6)°, β = 68.908(5)°, γ = 88.579(6)°, V = 2498(2) Å³, Z = 2, D_c = 1.785 g cm⁻³, μ = 2.566 mm⁻¹, R = 0.0407, wR = 0.0771. Crystal data for C₆₀H₃₈Ho₂N₄O₁₄ (**3**): M_r = 1368.80, triclinic, P $\bar{1}$, a = 11.656(5), b = 14.191(6), c = 16.015(6) Å, α = 84.138(9)°, β = 69.404(8)°, γ = 88.091(9)°, V = 2467(2) Å³, Z = 2, D_c = 1.843 g cm⁻³, μ = 3.263 mm⁻¹, R = 0.0764, wR = 0.0928.
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