



Solvent-induced copper–lanthanide heterometallic coordination polymers based on pyridine-2,3-dicarboxylic acid: Syntheses, structures, and electrochemical properties



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ABSTRACT

Six copper–lanthanide heterometallic coordination polymers (CPs) $[\text{LnCu}(2,3\text{-pydc})_2(\text{HCOO})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ [$\text{Ln} = \text{La}$ (**1**), Pr (**2**), Nd (**3**), Sm (**4**), Eu (**5**), and Gd (**6**), 2,3- H_2pydc = pyridine-2,3-dicarboxylic acid] were synthesized successfully by the reactions of 2,3- H_2pydc with $\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ under solvothermal conditions of H_2O –DMF or H_2O –DMF–MeOH. They were structurally characterized by single-crystal X-ray diffraction and powder X-ray diffraction (PXRD). CPs **1**–**6** possess isostructural 2D (4,4) layer architectures built from the dinuclear $\text{Ln}_2(\text{HCOO})_2$ and $\text{Cu}_2(2,3\text{-pydc})_4$ units. The reaction solvents have an important effect on the formation of **1**–**6**. The electrochemical properties of **1**–**6** were investigated.

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1. Introduction

The rational design and synthesis of 3d–4f heterometallic complexes have attracted increasing attention because of not only their fascinating structures but also their potential applications as important functional materials in magnetism, luminescence, adsorption, and catalysis [1–8]. Compared with individual transition metal or lanthanide complexes, the construction of 3d–4f heterometallic complexes is still a challenging task due to the complicated competing reactions between the 3d and 4f ions. In general, the organic compounds containing both N- and O-donors are considered as effective ligands for constructing 3d–4f heterometallic complexes because the 4f ions behave as hard acids with strong affinity to O-donors, whereas the 3d ions are soft or borderline acids having a strong tendency to bind to N-donors as well as O-donors [9]. Schiff-base-like compounds and N-containing carboxylic acids are two main classes of multidentate ligands containing both N- and O-donors. The former ligands are mainly employed to construct discrete or low-dimensional 3d–4f heterometallic complexes [10–16], whereas the latter ligands are mainly used to prepare 3d–4f heterometallic coordination polymers (CPs) [17–23].

As an important multidentate N-containing carboxylic acid, pyridine-2,3-dicarboxylic acid (2,3- H_2pydc) has been utilized to prepare 3d–4f heterometallic CPs. However, most of them were synthesized under hydrothermal reactions [24–27], and the 2,3-pydc-based 3d–4f heterometallic CPs obtained under solvothermal conditions have rarely been observed [28]. Therefore, in this work, we selected H_2O –DMF and H_2O –DMF–MeOH as solvothermal systems, and synthesized successfully six new 2,3-pydc-based copper–lanthanide heterometallic CPs $[\text{LnCu}(2,3\text{-pydc})_2(\text{HCOO})(\text{H}_2\text{O})_3] \cdot \text{H}_2\text{O}$ [$\text{Ln} = \text{La}$ (**1**), Pr (**2**), Nd (**3**), Sm (**4**), Eu (**5**), and Gd (**6**)]. In addition, the electrochemical properties of **1**–**6** were also investigated.

2. Experimental

2.1. Materials and measurements

$\text{LnCl}_3 \cdot n\text{H}_2\text{O}$ were prepared by the reactions of Ln_2O_3 and hydrochloric acid in aqueous solution. Other reagents were commercially available and used without further purification. Elemental analyses for C, H, and N were carried out on a Perkin–Elmer 2400 CHN elemental analyzer. FT-IR data were recorded on a Magna FT-IR 560 spectrometer using KBr plates. Powder XRD data were collected on a Bruker AXS D8-Advanced diffractometer with $\text{Cu K}\alpha$ ($\lambda = 1.5406 \text{ \AA}$) radiation. Thermogravimetric data were monitored by a Pyris–Diamond thermal analyzer in the temperature

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range of 30–800 °C at a heating rate of 10 °C min⁻¹ under a flowing N₂ atmosphere. Electrochemical measurements were performed on a CHI 440 electrochemical workstation. A conventional three-electrode system was used at room temperature. The carbon paste electrodes (CPEs) bulk-modified with **1–6** were used as the working electrodes. A saturated calomel electrode (SCE) and a platinum wire were used as the reference and auxiliary electrodes, respectively.

2.2. Syntheses of **1–3**

A mixture of LnCl₃·*n*H₂O (Ln = La, Pr, or Nd) (0.10 mmol), Cu(NO₃)₂·3H₂O (0.10 mmol), 2,3-H₂pydc (0.15 mmol), distilled water (4 mL), and DMF (4 mL) was sealed in a 10 mL glass vial and heated to 85 °C, and then maintained at this temperature for 96 h. Thereafter, the glass vial was slowly cooled to room temperature, whereupon blue block-shaped crystals were obtained. For **1**, yield 41% (based on La). Elem. Anal. Calc. (found) for C₁₅H₁₅CuLaN₂O₁₄ (649.74): C, 27.73 (27.81); H, 2.33 (2.26); N, 4.31 (4.42)%. For **2**, yield 48% (based on Pr). Elem. Anal. Calc. (found) for C₁₅H₁₅CuPrN₂O₁₄ (651.74): C, 27.64 (27.77); H, 2.32 (2.28); N, 4.30 (4.37)%. For **3**, yield 47% (based on Nd). Elem. Anal. Calc. (found) for C₁₅H₁₅CuNdN₂O₁₄ (655.07): C, 27.50 (27.68); H, 2.31 (2.24); N, 4.28 (4.36)%. IR (KBr, cm⁻¹) for **1**: 3446 (m), 3074 (w), 2361 (m), 1629 (s), 1585 (s), 1404 (s), 1367 (s), 1273 (m), 1168 (w), 1119 (m), 883 (w), 837 (w), 800 (m), 702 (m), 553 (w), 480 (m). For **2**: 3447 (m), 3072 (w), 2363 (w), 1627 (s), 1585 (s), 1404 (s), 1366 (s), 1273 (w), 1169 (w), 1119 (m), 883 (w), 837 (m), 802 (w), 702 (m), 554 (w), 480 (m). For **3**: 3447 (m), 3074 (w), 2363 (m), 1629 (s), 1585 (s), 1404 (s), 1364 (s), 1273 (w), 1170 (w), 1116 (m), 881 (w), 837 (m), 804 (w), 700 (m), 554 (w), 480 (w).

2.3. Syntheses of **4–6**

A mixture of LnCl₃·*n*H₂O (Ln = Sm, Eu, or Gd) (0.10 mmol), Cu(NO₃)₂·3H₂O (0.10 mmol), 2,3-H₂pydc (0.15 mmol), distilled water (2.5 mL), DMF (4.5 mL), and methanol (1 mL) was sealed in a 10 mL glass vial and heated to 85 °C, and then maintained at this temperature for 96 h. Thereafter, the glass vial was slowly cooled to room temperature, whereupon blue block-shaped crystals were obtained. For **4**, yield 45% (based on Sm). Elem. Anal. Calc. (found) for C₁₅H₁₅CuSmN₂O₁₄ (661.18): C, 27.25 (27.39); H, 2.29 (2.25); N, 4.24 (4.29)%. For **5**, yield 46% (based on Eu). Elem. Anal. Calc. (found) for C₁₅H₁₅CuEuN₂O₁₄ (662.79): C, 27.18 (27.33); H, 2.28 (2.31); N, 4.23 (4.28)%. For **6**, yield 47% (based on Gd). Elem. Anal. Calc. (found) for C₁₅H₁₅CuGdN₂O₁₄ (668.08): C, 26.97 (27.12); H, 2.26 (2.21); N, 4.19 (4.08)%. IR (KBr, cm⁻¹) for **4**: 3458 (m), 3084 (w), 2372 (w), 1639 (s), 1598 (s), 1404 (s), 1366 (s), 1273 (w), 1182 (w), 1130 (m), 894 (w), 848 (w), 813 (w), 713 (m), 584 (w), 491 (m). For **5**: 3458 (m), 3084 (w), 2374 (w), 1635 (s), 1598 (s), 1417 (s), 1377 (s), 1284 (m), 1182 (w), 1130 (m), 894 (m), 848 (w), 815 (w), 714 (m), 565 (w), 491 (w). For **6**: 3458 (m), 3084 (w), 2372 (w), 1639 (s), 1598 (s), 1417 (s), 1375 (s), 1284 (w), 1182 (w), 1130 (m), 895 (w), 848 (m), 815 (w), 713 (m), 565 (w), 489 (m).

2.4. X-ray crystallographic study

X-ray diffraction data for **1–6** were collected on a Bruker Smart APEX II diffractometer with Mo Kα (λ = 0.71073 Å) radiation at 296 (2) K. The structures were solved by direct methods and refined by full-matrix least-squares methods on *F*² with the SHELXTL package [29]. All non-hydrogen atoms were refined with anisotropic temperature parameters. Pertinent crystal parameters and refinement results for **1–6** are summarized in Table 1. Selected bond lengths for **1–6** are listed in Table S1.

2.5. Preparation of **1–6**-CPEs

A carbon paste electrode bulk-modified with **1** (**1**-CPE) was fabricated as follows: CP **1** (0.03 g) and graphite powder (0.50 g) were mixed and ground together with an agate mortar and pestle for approximately 30 min to achieve uniformity. Paraffin oil (0.15 mL) was added to the above-mentioned mixture with stirring. The resulting mixture was packed into a glass tube (3 mm inner diameter) to a length of 8 mm. The tube surface was wiped with the weighing paper. The electrical contact was established with a copper stick [30]. A similar procedure was used to prepare **2–6**-CPEs.

3. Results and discussion

3.1. Syntheses

In this work, we prepared six 2D 2,3-pydc-based copper-lanthanide heterometallic CPs [LnCu(HCOO)(2,3-pydc)₂(H₂O)₃]·H₂O [Ln = La (**1**), Pr (**2**), Nd (**3**), Sm (**4**), Eu (**5**), and Gd (**6**)] by the reactions of LnCl₃·*n*H₂O, Cu(NO₃)₂·3H₂O, and 2,3-H₂pydc under solvothermal conditions of H₂O–DMF or H₂O–DMF–MeOH. The HCOO anion is derived from the decomposition of DMF under solvothermal conditions [31–33]. Cai and co-workers also synthesized previously a series of 2,3-pydc-based copper-lanthanide heterometallic CPs by the reactions of Ln₂O₃, CuI, and 2,3-H₂pydc under solvothermal conditions of H₂O–CH₃CN, namely, 1D [Ln₂Cu₃(2,3-pydc)₆(H₂O)₁₂]·12H₂O (Ln = La and Nd), 2D [Ln₂Cu₃(2,3-pydc)₆(H₂O)₈]·6H₂O (Ln = Sm and Gd), and 3D [Ln₂Cu₃(2,3-pydc)₆(H₂O)₁₀]·10H₂O (Ln = Tb, Ho, Er, Yb, and Lu) [28]. The different starting materials and reaction solvents result in distinct two series of 2,3-pydc-based copper-lanthanide heterometallic CPs.

Furthermore, in this work, the volume ratio of reaction solvents is also crucial to the formation of **1–6**. When the volume ratio of H₂O and DMF was 1:1, the good single-crystal product and high yield for **1–3** were obtained, whereas the good single-crystal product and high yield for **4–6** resulted from the volume ratio of 2.5:4.5:1 for H₂O, DMF, and MeOH. Therefore, the decomposition of DMF under solvothermal conditions and the volume ratio of reaction solvents dominate the formation of **1–6**. Unfortunately, in such reaction system, we did not obtain corresponding heavy-lanthanide-containing CPs, although we made some efforts by tuning reaction solvents and their volume ratios.

3.2. Crystal structures of **1–6**

X-ray single-crystal diffraction analyses reveal that CPs **1–6** are isostructural and crystallize in the triclinic space group *P* $\bar{1}$. Thus, only the crystal structure of **1** is described here as a representative example. CP **1** is composed of one La^{III} ion, one Cu^{II} ion, two 2,3-pydc anions, one HCOO anion, three coordinated water molecules, and one interstitial water molecule (Fig. 1). The La1 ion is nine-coordinated with nine oxygen atoms from two 2,3-pydc anions, two HCOO anions, and three coordinated water molecules. These nine oxygen atoms surround La1 to form a distorted monocapped square antiprismatic coordination geometry (Fig. S1). The La–O bond distances are in the range of 2.479(3)–2.641(4) Å (Table S1). The Cu1 ion is five-coordinated with three oxygen atoms and two nitrogen atoms from three 2,3-pydc anions, featuring a square-pyramidal coordination geometry (Fig. S1). The Cu–O bond distances fall in the range of 1.944(3)–2.279(3) Å, and the Cu–N bond lengths are 1.963(4) and 1.988(4) Å (Table S1).

In **1**, two HCOO anions bridge two La^{III} ions into a dinuclear La₂(HCOO)₂ unit. Two Cu^{II} ions are linked by four 2,3-pydc anions into a dinuclear Cu₂(2,3-pydc)₄ unit. The dinuclear La₂(HCOO)₂ and

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