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Synthesis, structures and luminescent properties of novel coordination polymers constructed by lanthanide salts and benzimidazole-5,6-dicarboxylic acid

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ABSTRACT

Two three-dimensional (3D) novel lanthanide complexes with the H_2L═benzimidazole-5,6-dicarboxylate $[Ln_2L_3(H_2O)]$ [Ln = Eu (**1**), Tb (**2**)] and one two-dimensional (2D) novel lanthanide complex $[Pr(L)(HL)$-$H_2O]\cdot H_2O$ (**3**) were synthesized by hydrothermal reaction at 180 °C and characterized by elemental analysis, infrared spectra and single-crystal X-ray diffraction. The result showed that complexes **1** and **2** are isostructural and build porous 3D networks by L^{2-} groups linking Ln(III) atoms via tetradentate (bridging and bridging) and pentadentate (bridging/chelating and bridging) coordination modes. Complex **3** is a eight-coordinated Pr(III) chain complex, exhibiting a 2D polymeric network with parallel Pr-carboxylate chains along the crystallographic *c*-axis. In addition, it is found that in these structures, coordination modes of L^{2-} and HL^- are versatile and can adopt different conformations according to distinct dimensions of polymeric structures. The photoluminescent properties of **1**, **2** and thermogravimetric analyses of the three complexes were discussed in detail.

1. Introduction

Research on coordination polymers, in the context of superamolecular chemistry and crystal engineering, has undergone rapid enormous expansion, based on their potential applications as materials for catalysis, sensing, molecular electronics, and magnetic devices [1–24]. Coordination polymers are composed of metal centers that are essentially polymerized into extended structures through organic linker molecules. From this point of view, we choose benzimidazole-5,6-dicarboxylic acid (H_2L) as a good organic ligand to construct 3D coordination frameworks, and the considerations of it are as follows [25,26]: (i) as a multidentate and rigid ligand with multiproton acceptor–donor sites, H_2L, possessing two nitrogen atoms of imidazole ring and four oxygen atoms of carboxylate groups, might be utilized as a versatile linker in generating multidimensional structures; (ii) with both nitrogen and oxygen donor atoms, H_2L can display a variety of interesting bonding geometries, for example, monodentate, chelating, bidentate bridging, monodentate bridging and chelating bridging; and (iii) to the best of our knowledge, few examples of the lanthanide complexes with benzimidazole-5,6-dicarboxylate acid have been reported in coordination chemistry [27].

Recently, some interesting results have been published in which transition–metal atoms were linked via the dianion of H_2L so forming coordination polymers exhibiting hydrogen-bonding, π–π stacking, and metallophilic interactions [25–27]. On the other hand, in contrast to the production of coordination polymers with d-block transition metal ions, the design and control over high-dimensional lanthanide-based frameworks is currently a formidable task owing to their high and variable coordination numbers and flexible coordination environments [28–31]. And in our group, some of us have been working in the field of the lanthanide-based coordination polymers [32–34]. Therefore, we choose H_2L as an organic building block in an attempt to construct rare earth-organic polymers with new structural features. In this contribution, we explore the potential for the formation of coordination polymers by examining several frameworks within the Ln–H_2L system, such as $[Ln_2L_3(H_2O)]$ [Ln = Eu (**1**), Tb (**2**)] and $[Pr(L)(HL)H_2O]\cdot H_2O$ (**3**). As we known, the reported coordination modes of L^{2-} and L^- had been listed in Scheme 1(A–F) [27], while the coordination modes of L^{2-} (Scheme 1 G and H) in complexes **1** and **2** display novel coordination fashions. Furthermore, complexes of Eu^{3+} and Tb^{3+} showing strong luminescence in the visible region have been discussed in detail.

2. Experiment

2.1. Materials and methods

All chemicals purchased were of reagent grade or better and were used without further purification. Lanthanide chloride salts

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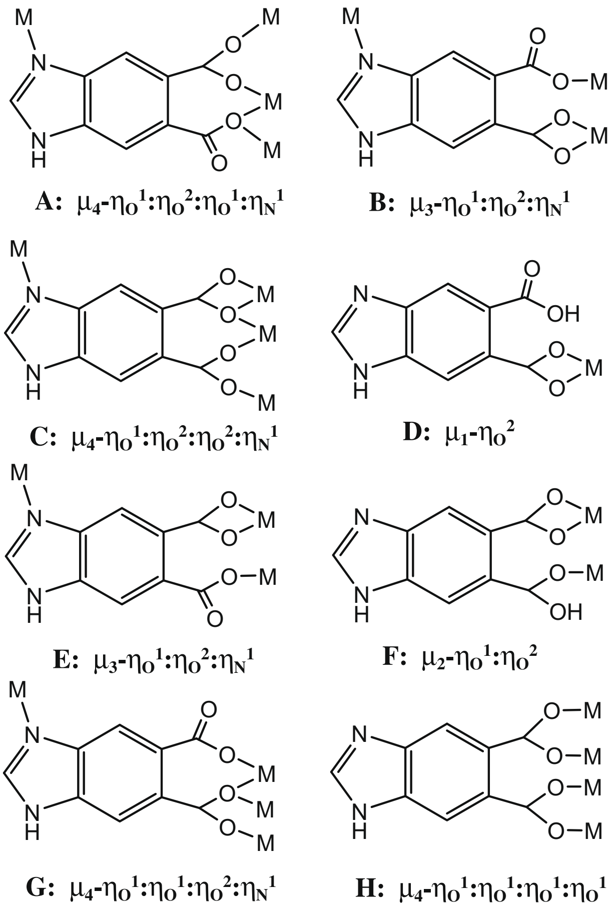

Scheme 1. Coordination modes of the L^{2-} and HL^- ligands.

were prepared via dissolving lanthanide oxides with 6 M HNO_3 and then evaporating at 100 °C until the crystal film formed. C and H analyses were made on a Perkin–Elmer 240C automatic analyzer at the analysis center of Liaoning Normal University. Infrared (IR) spectra were recorded on JASCO FT/IR-480 PLUS Fourier transform spectrophotometer with pressed KBr pellets in the range 200–4000 cm^{-1}. The luminescence spectra were reported on a JASCO FP-6500 spectrofluorimeter (solid) in the range of 200–850 nm. Thermogravimetric analyses (TGA) were performed under N_2 atmosphere at 1 atm with a heating rate of 10 °C/min on a Perkin Elmer Diamond TG/DTA. Content of lanthanide was analyzed on a Plasma-Spec(I)-AES model ICP spectrometer. X-ray powder diffraction (XRD) data were collected on a Bruker Advance-D8 with CuKα radiation, in the range $5° < 2\theta < 60°$, with a step size of 0.02° (2θ) and an acquisition time of 2 s per step.

2.2. Synthesis of complexes

2.2.1. Synthesis of complexes [$Eu_2L_3(H_2O)$] (**1**) and [$Tb_2L_3(H_2O)$] (**2**)

The complex was prepared by hydrothermal reaction. Eu(NO_3)$_3$·6H_2O (0.28 g, 0.63 mmol), benzimidazole-5,6-dicarboxylic acid (H_2L, 0.10 g, 0.60 mmol), KOH (1 M, 0.05 ml) and H_2O (15 mL) were mixed in 25 mL beaker. The molar ratio of Eu(NO_3)$_3$·6H_2O:H_2L was 1:0.95. The mixture was sealed in the bomb and heated at 180 °C for 3 days, then cooled at 10 °C/3 h to 100 °C, followed by slow cooling to room temperature. After filtration, the product was washed with distilled water and then dried at room temperature. White block crystals suitable for X-ray diffraction analysis were obtained. Yield: over 50% based on Eu(III). *Anal.* Calc. for $C_{27}H_{14}N_6O_{13}Eu_2$ (Mr = 934.36): C, 34.67; H, 1.50; N, 8.99%; Eu, 32.53. Found: C, 34.47; H:1.77; N, 8.80; Eu, 32.40%. IR data (KBr pellet, ν [cm^{-1}]): 3397(w), 3154(w), 1578(s), 1538(s), 1479(s), 1467(s), 1426(s), 1378(s), 1284(m), 1267(m), 1201(w), 1112(w), 968(w), 906(w), 884(m), 861(m), 697(w), 632(m), 573(w), 554(m), 434(w), 406(s), 386(w), 359(w).

Complex **2** was synthesized by a method similar to that of complex **1** except that Eu(NO_3)$_3$·6H_2O was replaced by Tb(NO_3)$_3$·6H_2O (the molar ratio of Eu(NO_3)$_3$·6H_2O:H_2L was 1:1.15) light yellow crystals were obtained. Yield: over 58% based on Tb(III). *Anal.* Calc. for $C_{27}H_{14}N_6O_{13}Tb_2$ (Mr = 948.28): C, 34.17; H, 2.95; N, 8.86; Tb, 33.52%. Found: C, 34.00; H:3.16 N, 8.69; Tb, 33.32%. IR data (KBr pellet, ν [cm^{-1}]): 3397(w), 3154(w), 1580(s), 1542(s), 1468(s), 1428(s), 1380(s), 1285(m), 1193(w), 1112(w), 969(w), 905(w), 882(m), 858(m), 692(w), 634(m), 556(w), 437(w), 404(s), 386(w), 361(w), 325(w).

2.2.2. Synthesis of complex [$Pr(L)(HL)H_2O$]·H_2O (**3**)

The complex **3** was prepared by hydrothermal reaction. Pr(NO_3)$_3$·6H_2O (0.21 g, 0.48 mmol), benzimidazole-5,6-dicarboxylic acid (H_2L, 0.10 g, 0.60 mmol), and H_2O (15 mL) were mixed in 25 mL beaker. The molar ratio of Pr(NO_3)$_3$·6H_2O:H_2L is 1:1.25. The mixture was sealed in the bomb and heated at 180 °C for 3 days, then cooled at 10 °C/3 h to 100 °C, followed by slow cooling to room temperature. After filtration, the product was washed with distilled water and then dried at room temperature. Light green block crystals were obtained. Yield: over 69% based on Pr(III). *Anal.* Calc. for $C_{18}H_{13}N_4O_{10}Pr$ (Mr = 586.23): C, 36.85; H, 2.22; N, 9.55; Pr, 24.04%. Found: C, 36.78; H: 2.39; N, 9.33; Pr, 23.95%. IR data (KBr pellet, ν [cm^{-1}]): 3436(w), 3224(w), 1860(w), 1710(s),1626(w), 1592(s), 1570(s), 1533(s), 1511(s), 1462(s), 1403(s), 1366(s), 1286(m), 1247(m), 1187(m), 1138(m), 1046(w), 1023(w), 957(m), 935(w), 905(w), 895(m), 867(s), 823(s), 801(s), 792(s), 765(s), 717(w), 685(m), 659(w), 634(s), 561(s), 505(w), 409(s), 397(s).

2.3. X-ray data collection and refinement of crystal structure

Suitable single crystals of three complexes were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer for complexes **1**–**2** and Rigaku R-AXIS RAPID IP diffractometer for complex **3** with graphite monochromatized MoKα radiation (λ = 0.71073 Å). All absorption corrections were performed using the SADABS program [35]. Crystal structures were solved by the direct method. All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were fixed at calculated positions with isotropic thermal parameters. All calculations were performed using the SHELXS-97 program [36]. Crystal data and details of the data collection and the structure refinement were given in Table 1. Selected bond lengths and bond angles of complexes **1**–**3** were listed in Table 2.

2.3. Thermal analysis

Thermogravimetric analyses (TGA) experiments were carried out on a Perkin Elmer Diamond TG/DTA instrument. The samples are initially heated for 1 h at 50 °C to remove the rudimental air. During the simple ramping experiment, weight changes were recorded as a function of temperature for a 10 °C min^{-1} temperature gradient between 50 and 800 °C in nitrogen environments.