Research paper

Three-dimensional lanthanide frameworks constructed of two-dimensional squares strung on one-dimensional double chains: Syntheses, structures, and luminescent properties

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ABSTRACT

Two coordination polymers, $\{[Ln_2(BPDSDC)(BDC)(H_2O)_6]\cdot 4H_2O\}_n$ (Ln = Tb(**1**) and Eu(**2**)), constructed from biphenyl-3,3′-disulfonyl-4,4′-dicarboxylate ($BPDSDC^{4-}$) and 1,4-benzenedicarboxylate (BDC^{2-}) ligands were synthesized and structurally characterized. The solid state structure of $\{[Ln_2(BPDSDC)(BDC)(H_2O)_6]\cdot 4H_2O\}_n$ consists of one-dimensional (1D) Ln-BPDSDC double chains and two-dimensional (2D) Ln-BDC squares featuring the $Ln_2(COO)_4$ paddle-wheel units and the nanosized grids. Each grid of the 2D squares is threaded by a 1D Ln-BPDSDC double chain, wherein the two parts are interacted through coordination bonds between lanthanide centers of the 2D squares and sulfonate oxygen atoms from 1D chains. Thus the 1D Ln-BPDSDC double chains are threaded through the 2D squares stacked in an eclipsed fashion to give a three-dimensional (3D) distinct architecture. The two compounds emit the characteristic Tb(III) and Eu(III) emissions in the solid state, respectively. Temperature-dependent luminescent studies show the emission intensities for both compounds decrease as temperature increases, which indicates these compounds have the potential for sensing temperature.

1. Introduction

Coordination polymers formed from metal ions and bridging organic ligands are an important class of functional materials displaying diverse physical properties and intriguing structural topologies [1–4]. The interesting physical properties such as magnetism, electricity, and luminescence endowed by inorganic metal ions and organic ligands can be incorporated into a single coordination polymer, providing access to a new kind of functionalized materials. As an important series of metal ions, lanthanide ions attracted much attention because they can display distinctive intrinsic optical and magnetic properties arising from 4f configuration [5–7]. Since the lanthanide ions have the binding preference for oxygen atom, the carboxylate ligands are extensively utilized to construct the lanthanide-based coordination polymers [8–10]. In fact, the carboxylate ligand with a rich diversity of coordination modes and appropriate connectivities proved to be an effective component in the design of the coordination polymers [11–13]. Additionally, the structural complexity can be further enhanced through the design of carboxylate derivatives such as the sulfonate–carboxylate ligand, leading to a new type of materials [14,15]. The sulfonate ligand is known as a poor ligand with the weaker ligation nature of the sulfonate group [16,17]. However,

the sulfonate-carboxylate ligand with the strong coordination ability of carboxylate group is expected to be an interesting class of organic ligand, although they are much less well-investigated [18–20]. For examples, a Cu(II) compound based on 5-sulfoisophthalate ligand undergo a thermally induced single-crystal to single-crystal structural transformation, involving the coordination bonds related to the sulfonate oxygen atoms [21]. A series of lanthanide compounds with 4,8-disulfonyl-2,6-naphthalenedicarboxylate ligand showing various structures and interesting luminescent and magnetic properties have been reported [22]. Recently, we demonstrated a series of lanthanide compounds based on a novel sulfonate–carboxylate ligand of biphenyl-3,3′-disulfonyl-4,4′-dicarboxylate ($BPDSDC^{4-}$) exhibiting high proton conductivity associated with the hydrophilic channels decorated by sulfonate groups [23]. The $BPDSDC^{4-}$ ligand is based on the π-system of biphenyl backbone, which is expected to enhance the luminescent properties of the resulting lanthanide compounds. In this contribution, the 1,4-benzenedicarboxylate (BDC^{2-}) is introduced into the lanthanide-BPDSDC system, providing novel compounds, $\{[Ln_2(BPDSDC)(BDC)(H_2O)_6]\cdot 4H_2O\}_n$ (Ln = Tb(**1**) and Eu(**2**)), which contain the 2D squares of lanthanide-BDC and 1D double chains of lanthanide-BPDSDC and exhibit interesting characteristic lanthanide luminescence.

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2. Experimental

2.1. General remarks

All chemicals are commercially available and used as received without further purification. IR (KBr pellets) spectra were recorded in the 400–4000 cm^{-1} range using a Perkin-Elmer Spectrum One FT-IR spectrometer. Elemental analyses were carried out on Elementar Perkin-Elmer 2400CHN microanalyzer. Thermogravimetric analyses were carried out on a PE Diamond TG/DTA unit at a heating rate of 10 °C/min under an air atmosphere. Powder X-ray diffraction patterns were performed on a Rigaku Miniflex II powder diffractometer using Cu-Kα radiation ($\lambda = 1.5418$ Å). The excitation/emission spectra and decays were recorded on an Edinburgh FLS980 fluorescence spectrophotometer equipped with both continuous (450 W) Xenon and pulsed flash lamps. Temperature-dependent emission spectra were recorded using an Oxford Instruments liquid nitrogen flow cryostat.

2.2. Syntheses of compounds

2.2.1. Synthesis of {[Tb₂(BPDSDC)(BDC)(H₂O)₆]·4H₂O}ₙ (1)

A mixture of $Tb(NO_3)_3 \cdot 6H_2O$ (0.0272 g, 0.06 mmol), H_4BPDSDC(0.0161 g, 0.04 mmol), and 1,4-benzenedicarboxylic acid (0.0132 g, 0.08 mmol) in H_2O (10 mL) was introduced into a 25 mL Parr Teflon-lined stainless steel vessel. The vessel was sealed and heated to 100 °C for 3 days. Then the resulting mixture was cooled naturally to form colorless block crystals. (yield: 29% on the basis of Tb $(NO_3)_3 \cdot 6H_2O$). Anal. calcd. for $C_{22}H_{30}O_{24}S_2Tb_2$ (1060.42): C, 24.92; H, 2.85%. Found: C, 24.90; H, 2.81%. Main IR features (cm^{-1}, KBr pellet): 3414 (m), 1605 (s), 1576 (s), 1396 (s), 1229 (m), 1165 (s), 1090 (m), 1024 (m), 861 (m), 848 (m), 788 (m), 753 (s), 671 (w), 626 (m), 587 (w), 524 (m), 431 (m).

2.2.2. Synthesis of {[Eu₂(BPDSDC)(BDC)(H₂O)₆]·4H₂O}ₙ (2)

A mixture of $Eu(NO_3)_3 \cdot 6H_2O$ (0.0272 g, 0.06 mmol), H_4BPDSDC(0.0161 g, 0.04 mmol), and 1,4-benzenedicarboxylic acid (0.0132 g, 0.08 mmol) in H_2O (10 mL) was introduced into a 25 mL Parr Teflon-lined stainless steel vessel. The vessel was sealed and heated to 100 °C for 3 days. Then the resulting mixture was cooled naturally to form colorless block crystals. (yield: 26% on the basis of Eu $(NO_3)_3 \cdot 6H_2O$). Anal. calcd. for $C_{22}H_{30}O_{24}S_2Eu_2$ (1046.50): C, 25.25; H, 2.89%. Found: C, 25.28; H, 2.79%. Main IR features (cm^{-1}, KBr pellet): 3423 (m), 1614 (s), 1577 (s), 1475 (w), 1396 (s), 1223 (m), 1165 (s), 1091 (m), 1025 (m), 861 (m), 848 (m), 788 (m), 754 (s), 671 (w), 628 (m), 585 (w), 523 (m), 431 (m).

2.3. X-ray crystallographic study

Single-crystal X-ray diffraction experiments were performed at 293(2) K using a Rigaku Oxford SuperNova diffractometer equipped with an Eos detector and a Mo-Ka radiation ($\lambda = 0.71073$ Å). CrysAlisPro software package was used for collecting data, absorption correction and data reduction [24]. The structure was solved by the direct methods using SHELXT [25] and refined by the full-matrix least-squares method on F^2 using SHELXTL [26]. All non-hydrogen atoms are refined with anisotropic thermal parameters. Hydrogen atoms bonded to carbon atoms were assigned to calculated positions. Water hydrogen atoms couldn't be located. The R_1 values are defined as $R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$ and $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$. Details of the crystal parameters, data collection, and refinement are summarized in Table 1. Important bond lengths are listed in Table 2.

Table 1
Crystal data and structural refinements for Tb(1) and Eu(2).

	Tb(**1**)	Eu(**2**)
Empirical Formula	$C_{22}H_{30}O_{24}S_2Tb_2$	$C_{22}H_{30}O_{24}S_2Eu_2$
Molecular mass	1060.42	1046.50
Temperature[K]	296(2)	296(2)
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Z	2	2
a [Å]	10.4693(2)	10.4060(5)
b [Å]	11.0590(2)	11.0721(5)
c [Å]	14.9262(3)	14.9186(5)
α, deg	72.580(2)	72.552(4)
β, deg	80.777(2)	80.225(3)
γ, deg	80.196(2)	79.695(4)
V [Å³]	1613.80(6)	1600.93(13)
D_c [g·cm⁻³]	2.182	2.171
μ[mm⁻¹]	4.575	4.112
Measured reflections	33,249	32,655
Independent reflections	6596	6529
Observed reflections.[$I > 2\sigma(I)$]	6134	6157
R[int]	0.0354	0.0414
R_1[obsd. refl.]	0.0252	0.0248
wR_2 [obsd. refl.]	0.0635	0.0617

Table 2
Selected bond distances (Å) for Tb(**1**) and Eu(**2**).

Tb(**1**)		Eu(**2**)	
Tb1–O6	2.447(3)	Eu1–O6	2.460(2)
Tb1–O9	2.402(3)	Eu1–O9	2.420(3)
Tb1–O1B	2.323(3)	Eu1–O1B	2.335(3)
Tb1–O3B	2.462(3)	Eu1–O3B	2.453(3)
Tb1–O6A	2.567(3)	Eu1–O6A	2.577(2)
Tb1–O7A	2.504(3)	Eu1–O7A	2.513(2)
Tb1–O1W	2.474(3)	Eu1–O1W	2.503(3)
Tb1–O2W	2.402(3)	Eu1–O2W	2.429(3)
Tb1–O3W	2.366(3)	Eu1–O3W	2.389(3)
Tb2–O8	2.521(3)	Eu2–O8	2.510(3)
Tb2–O11	2.293(3)	Eu2–O11	2.349(3)
Tb2–O13	2.321(3)	Eu2–O13	2.338(2)
Tb2–O12C	2.346(3)	Eu2–O12C	2.381(3)
Tb2–O14C	2.321(3)	Eu2–O14C	2.344(3)
Tb2–O4W	2.448(3)	Eu2–O4W	2.480(3)
Tb2–O5W	2.422(3)	Eu2–O5W	2.451(3)
Tb2–O6W	2.507(4)	Eu2–O6W	2.509(3)

Symmetry transformation for equivalent atoms: A − x + 1, − y, − z + 2; B − x + 1, − y, − z + 1; C − x, − y + 1, − z + 1.

3. Results and discussion

3.1. Crystal structure of {[Ln₂(BPDSDC)(BDC)(H₂O)₆]·4H₂O}ₙ

Single-crystal X-ray diffraction analyses revealed that the two compounds are isomorphous and crystallize in a triclinic P-1 space group (Table 1). The Tb(1) was selected for describing their structures. There two Tb(III) ions, one BPDSDC⁴⁻ ligand, two half-occupied BDC²⁻ ligands, six coordinated water molecules, and four lattice water molecules compose the asymmetric unit of Tb(**1**). The Tb(III) ions have the coordination number of 8 and 9. Tb1 ion is nine-coordinated by two sulfonate oxygen atoms and four carboxylate oxygen atoms from three BPDSDC⁴⁻ ligand, and three aqua ligands (Fig. 1). The coordination polyhedron of Tb2 ion consists of four carboxylate oxygen atoms of four BDC²⁻ ligands, one sulfonate oxygen atom of a BPDSDC⁴⁻ ligand, and three water oxygen atoms. The Tb–O bond lengths are in the range of 2.293(3)–2.567(3) Å (Table 2), which are comparable to those in other lanthanide-carboxylate compounds [23,27]. The BPDSDC⁴⁻ and BDC²⁻ ligands all are coordinated to four lanthanide ions (Scheme S1 in Supplementary material). The BPDSDC⁴⁻ ligand binds to four metal ions through its two unidentate carboxylate oxygen atoms, three unidentate