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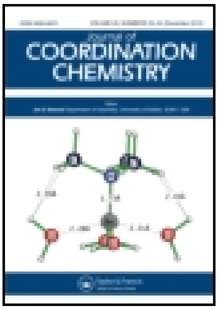

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Urothermal synthesis of an unprecedented pillar-layered metal-organic framework

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Urothermal synthesis of an unprecedented pillar-layered metal–organic framework

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$Ce_2(bdc)_6 \cdot (H_2O)_4$ (bdc = 1,4-benzenedicarboxylic acid) (**1**) was urothermally synthesized through a mixture of $Ce(NO_3)_3 \cdot 6H_2O$ and 1,4-bdc in e-urea/H_2O (e-urea = 2-imidazolidinone hemihydrate) mixed solvent. A prominent feature of **1** is the unprecedented pillar-layered framework in which 1,4-bdc is both linker and pillar. Compound **1** displays strong blue-light emission.

Keywords: Urothermal method; MOF; Topology; Pillar-layer

1. Introduction

Metal–organic frameworks (MOFs) receive attention for potential applications and fascinating architectures and topologies [1, 2]. MOFs are porous, crystalline materials that comprise metal or metal oxide "nodes" connected by organic "linker" compounds [3]. The use of lanthanide salts and organic linkers in the synthesis of MOFs has gained attention owing to photophysical and magnetic properties, as well as gas adsorption, although it is difficult to predict the structure of the lanthanide coordination polymers because of the various coordination numbers and geometries of lanthanide ions. Choice of organic linkers is essential for preparing lanthanide organic polymers. The hard Lewis base nature of multicarboxylate-containing ligands makes such molecules suitable for connecting lanthanide ions [4, 5]. As a simple bicarboxylate, terephthalic acid (H_2bdc, 1,4-benzenedicarboxylic acid) has drawn much attention in preparing lanthanide coordination polymers because the two carboxylates after double deprotonation have affinity for lanthanides and the rod-like topology induces low steric hindrance, allowing formation of porous frameworks [6, 7].

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Besides metal center and organic linkers, solvents also play a role in determining structures of MOFs. Synthetic methods such as hydrothermal, solvothermal, and ionothermal syntheses have been established and widely used to construct MOFs [8–10]. Urothermal synthesis [11] as an emerging synthetic method is garnering more and more attention [12] as a variety of crystalline solids can be prepared by the urothermal method. Compared to other methods, urothermal syntheses of MOFs remain largely unexplored.

Herein, we report urothermal synthesis, characterization, and structural features of $Ce_2(bdc)_6 \cdot (H_2O)_4$ (**1**-Ce). The isotypic structures of the terbium and europium analogs firstly reported by Yaghi were synthesized by hydrothermal method [6a]. Structure analysis shows that **1** has a unique pillar-layered framework wherein bdc is linker and pillar. Photoluminescence reveals that **1** displays strong blue-light emission.

2. Experimental

2.1. *Materials and general methods*

Chemicals were obtained from commercial sources and used without purification. Elemental analyses of C, H, and N were measured on a Vario MICRO E III elemental analyzer. IR spectra (KBr pellets) were recorded on a Magna 750 FT-IR spectrophotometer. Powder X-ray diffraction (XRD) data were recorded on a Rigaku MultiFlex diffractometer with a scan speed of $5^\circ C\,min^{-1}$. Thermal stability studies were carried out on a NETSCHZ STA-449C thermoanalyzer under N_2 (30–800°C range) at a heating rate of $10^\circ C\,min^{-1}$. Fluorescence spectra were measured with a HORIBA Jobin-Yvon FluoroMax-4 spectrometer.

2.2. *Synthesis*

2.2.1. Synthesis of 1. A mixture of $Ce(NO_3)_3 \cdot 6H_2O$ (0.111 g), bdc (0.0653 g), 2-imidazalidinone hemihydrate (e-urea, 2.2459 g) and 2 mL water in a 23 mL Teflon-lined airtight reactor was heated to 120°C in an oven and kept at the temperature for 5 days. Colorless crystals were isolated, washed with water and ethanol, and dried at room temperature. Compound **1** is air stable and insoluble in common solvents. Isotypic structures of the terbium and europium analogs can also be synthesized by the same method using the corresponding metal salt to replace $Ce(NO_3)_3 \cdot 6H_2O$. The powder XRD results (figure S1) of the $Ln_2(bdc)_6 \cdot (H_2O)_4$ (Ln=Ce, Tb, Eu) show that the solids are isostructural. Anal. Calcd (%) for $Ce_2(bdc)_6 \cdot (H_2O)_4(Ce_2C_{24}O_{16}H_{20})$: C, 34.13; H, 2.39; N, 0. Found: C, 34.10; H, 2.25; N, 0. IR (KBr pellet, cm^{-1}): 3460 (b), 3059 (s), 1618 (m), 1591 (m), 1552 (s), 1512 (s), 1427 (s), 1407 (s), 1315 (s), 1163 (w), 1104 (w), 894 (w), 750 (m), 590 (m), 560 (m), 540 (m), 426 (m).

2.3. *Crystal structure determination*

Suitable single crystal of **1** was carefully selected under an optical microscope and glued to a thin glass fiber. Crystallographic data for **1** were collected with a

Table 1. Crystal data for **1**.

Chemical formula	$C_{12}H_{10}CeO_8$
Formula weight	422.32
Crystal system	Triclinic
Unit cell dimensions (Å, °)	
a	6.2473(4)
b	10.2116(7)
c	10.2756(6)
α	102.396(6)
β	91.629(5)
γ	101.783(6)
Volume (Å^3), Z	624.96(7), 2
Temperature (K)	293(2)
Space group	$P\bar{1}$
Reflections measured	3936
Independent reflections	2199
R_{int}	0.0314
Final R_1 values $[I > 2\sigma(I)]$	0.0793
Final $wR(F^2)$ values $[I > 2\sigma(I)]$	0.2183
Final R_1 values (all data)	0.0827
Final $wR(F^2)$ values (all data)	0.2201
Goodness of fit on F^2	1.121
CCDC number	875876

Table 2. Selected bond lengths (Å) and angles (°) for **1**.

Ce(1)–O(6)#1	2.38(3)	Ce(1)–O(1)	2.54(4)
Ce(1)–O(4)#2	2.40(3)	Ce(1)–O(2)#4	2.58(3)
Ce(1)–O(5)	2.42(3)	Ce(1)–O(1W)	2.61(3)
Ce(1)–O(3)#3	2.42(3)	Ce(1)–O(2W)	2.63(3)
O(6)#1–Ce(1)–O(4)#2	143.3(13)	O(1)–Ce(1)–O(2)#4	137.9(10)
O(6)#1–Ce(1)–O(5)	96.1(13)	O(6)#1–Ce(1)–O(1W)	71.9(12)
O(4)#2–Ce(1)–O(5)	89.3(12)	O(4)#2–Ce(1)–O(1W)	144.5(12)
O(6)#1–Ce(1)–O(3)#3	95.6(12)	O(5)–Ce(1)–O(1W)	79.0(12)
O(4)#2–Ce(1)–O(3)#3	101.4(13)	O(3)#3–Ce(1)–O(1W)	72.1(12)
O(5)–Ce(1)–O(3)#3	143.5(13)	O(1)–Ce(1)–O(1W)	128.6(11)
O(6)#1–Ce(1)–O(1)	68.8(12)	O(2)#4–Ce(1)–O(1W)	71.0(11)
O(4)#2–Ce(1)–O(1)	78.1(12)	O(6)#1–Ce(1)–O(2W)	78.4(12)
O(5)–Ce(1)–O(1)	73.7(12)	O(4)#2–Ce(1)–O(2W)	75.6(11)
O(3)#3–Ce(1)–O(1)	142.5(12)	O(5)–Ce(1)–O(2W)	142.8(11)
O(6)#1–Ce(1)–O(2)#4	142.8(12)	O(3)#3–Ce(1)–O(2W)	73.5(11)
O(4)#2–Ce(1)–O(2)#4	73.6(12)	O(1)–Ce(1)–O(2W)	70.0(11)
O(5)–Ce(1)–O(2)#4	75.4(12)	O(2)#4–Ce(1)–O(2W)	129.5(10)
O(3)#3–Ce(1)–O(2)#4	74.4(12)	O(1W)–Ce(1)–O(2W)	131.4(11)

Symmetry transformations used to generate equivalent atoms: #1: $-x+1, -y+1, -z+1$, #2: $-x, -y, -z$, #3: $x+1, y+1, z$, #4: $x+1, y, z$.

Siemens Smart CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at $T = 293(2)$ K. Absorption corrections were made using SADABS [13]. The structures were solved using direct methods and refined by full-matrix least squares on F^2 by using the SHELX-97 program package [14]. All non-hydrogen atoms were refined anisotropically. Crystal parameters and details of the data collection and refinement are given in table 1 and selected bond lengths and angles for **1** are given in table 2.

3. Results and discussion

3.1. *Description of the structure*

The crystal structure of **1** includes one Ce^{3+}, one and a half bdc ligands, and two coordinated water molecules (figure 1). Ce is eight-coordinate by six oxygen atoms from six different bdc ligands and two water molecules. Both bdc ligands are μ_4-bridges, bonding to four adjacent Ce^{3+} centers by four oxygen atoms. Ce and bdc crosslink to form the 3-D framework including a 1-D channel running along the *b*-axis (figure 2), filled by coordinated water.

The prominent feature of **1** is the pillar-layered framework. Generally, two different ligands play the roles of pillar and layer, such as the classic combination of polycarboxylic acid and bipyridine ligands [15], but for **1**, bdc plays both roles. Not considering the aromatic ring of the ligands, Ce centers as a node are linked by μ_2-carboxylates (figure 2a) into a 2-D $[Ce(CO_2^-)_3]_n$ layer (figure 2b). Although each Ce bonds to six carboxyl groups and each carboxylate bonds to two Ce ions, the 2-D layer can be simplified as a (4,4) layer (figure 2c). The (4,4) layer is further pillared by the aromatic ring of bdc to form a 3-D framework (figure 2d). Thus, the complicated framework can be simplified as a 6-connected **pcu** network (figure 2e).

The e-urea exhibits distinct roles in construction of **1**. The first role of e-urea is as solvent, and it has good solubility for metal salts and organic ligands. The second role of e-urea is as organic amine through decomposition, first reported by Wang *et al.* [12b]. Yaghi and co-workers [6a] reported terbium and europium analogs synthesized using water as solvent and triethylamine as the base. Herein, we used e-urea which acted as solvent and organic base, indicating the urothermal method has unique advantages compared to other common methods.

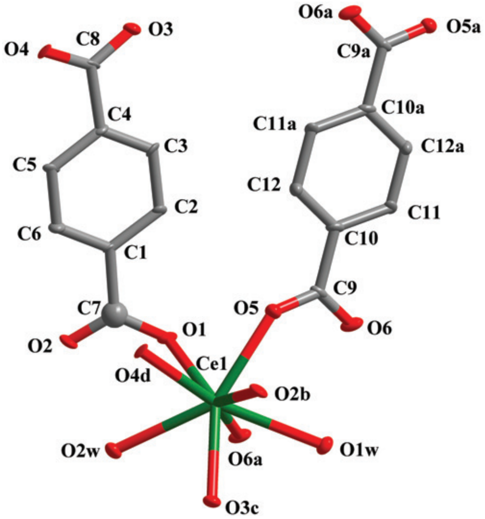

Figure 1. The coordination environment of Ce in **1**. Symmetry transformations used to generate equivalent atoms: a: $1-x, 1-y, 1-z$; b: $1+x, y, z$; c: $1+x, 1+y, z$; d: $-x, -y, -z$.

3.2. *Thermogravimetric analysis*

The thermogravimetric analysis curve indicates that weight loss of 8.60% occurred from 30°C to 260°C, corresponding to loss of two coordinated water molecules (expected 8.52%) and the desolved form is thermally stable to 550°C (figure S2).

3.3. *Photoluminescent property*

Photoluminescence in solid state at room temperature shows that **1** emits intense blue light centered at 430 nm upon photo-excitation at 330 nm (figure 3). In comparison,

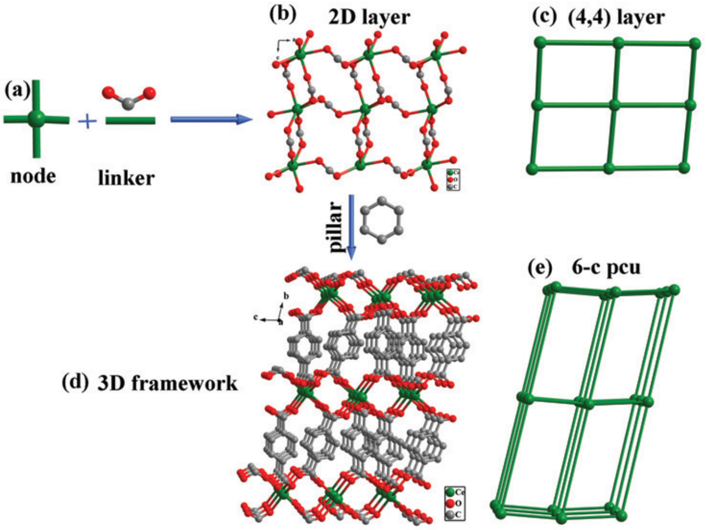

Figure 2. (a) The defined node and linker in **1**: node, Ce; linker, carboxyl group; (b) the 2-D [Ce(CO$_2^-$)$_3$]$_n$ layer; (c) the (4,4) topology of the 2-D layer; (d) the 3-D framework of **1**; (e) the 6-connected **pcu** topology of **1** simplified by the method mentioned above.

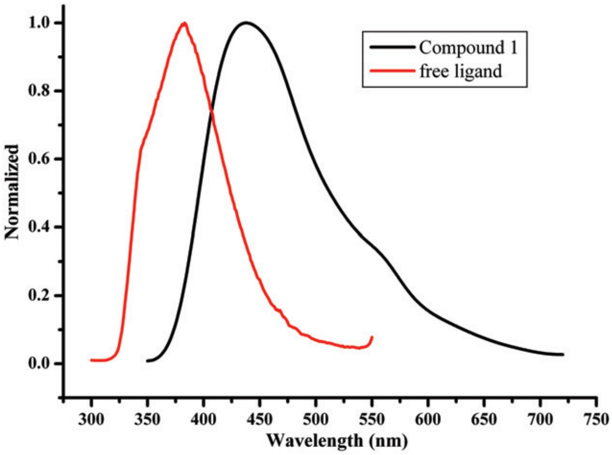

Figure 3. Emission spectra of **1** and the free ligand measured in the solid state at room temperature.

free H_2bdc shows emission at 380 nm upon excitation at 280 nm. The emission of **1** is attributed to ligand centered $\pi^* \rightarrow n$ transitions. The red-shift of bdc within this MOF is attributed to the formation of the framework structure [5].

4. Conclusion

$Ce_2(bdc)_6 \cdot (H_2O)_4$ synthesized by the urothermal method exhibits a pillar-layered framework in which bdc is the linker and pillar simultaneously. The urothermal synthesis is useful for construction of MOFs as porous materials.

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