See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/241072378

Three novel lanthanide MOFs constructed from 1,3-benzenedicarboxylic acid and 1,10phenanthroline: Hydrothermal synthesis, crystal structure and thermal properties

ARTICLE in JOURNAL OF MOLECULAR STRUCTURE · OCTOBER 2011

Impact Factor: 1.6 · DOI: 10.1016/j.molstruc.2011.07.014

CITATIONS READS 13 42

4 AUTHORS, INCLUDING:



Chong-Chen Wang

SEE PROFILE

44 PUBLICATIONS 387 CITATIONS



Zhihua Wang

Huazhong University of Science and Techn...

28 PUBLICATIONS 392 CITATIONS

SEE PROFILE

Provided for non-commercial research and education use. Not for reproduction, distribution or commercial use.



This article appeared in a journal published by Elsevier. The attached copy is furnished to the author for internal non-commercial research and education use, including for instruction at the authors institution and sharing with colleagues.

Other uses, including reproduction and distribution, or selling or licensing copies, or posting to personal, institutional or third party websites are prohibited.

In most cases authors are permitted to post their version of the article (e.g. in Word or Tex form) to their personal website or institutional repository. Authors requiring further information regarding Elsevier's archiving and manuscript policies are encouraged to visit:

http://www.elsevier.com/copyright

Journal of Molecular Structure 1004 (2011) 39-44

Contents lists available at SciVerse ScienceDirect



Journal of Molecular Structure



journal homepage: www.elsevier.com/locate/molstruc

Three novel lanthanide MOFs constructed from 1,3-benzenedicarboxylic acid and 1,10-phenanthroline: Hydrothermal synthesis, crystal structure and thermal properties

Chongchen Wang^{a,b}, Zhihua Wang^a, Fubo Gu^a, Guangsheng Guo^{a,*}

^a State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China ^b Key Laboratory of Urban Stormwater System and Water Environment (Beijing University of Civil Engineering and Architecture), Ministry of Education, Beijing 100044, China

ARTICLE INFO

Article history: Received 26 May 2011 Received in revised form 4 July 2011 Accepted 7 July 2011 Available online 28 July 2011

Keywords: Lanthanide 1,3-Benzenedicarboxylic acid Metal-organic framework Hydrothermal synthesis Thermal stable

ABSTRACT

Three lanthanide based metal–organic frameworks, $[Ln_2(bdc)_3(phen)H_2O]$ ·H₂O (Ln = La(1), Pr(2) and Yb(3)) were obtained from 1,3-benzenedicarboxylic acid (H₂bdc), 1,10-phenanthroline (phen) and corresponding lanthanide(III) salts by hydrothermal synthesis. Single-crystal X-ray diffraction reveals that **1–3** are isomorphous and isostructural, composed of 2-D sheets constructed from dbc and lanthanide ions, and further extended to 3-D supramolecular framework through π – π interactions between phen rings of the neighboring chains. In all of the three MOFs, bdc act as both tetra-monodentate ligand to link two Ln1 and two Ln2 ions (Ln = La(1), Pr(2) and Yb(3)) respectively, and counter-ions to balance the charge of the title complexes. Thermogravimetric analyses of **1–3** display a considerable thermal stability.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

Metal-organic frameworks (MOFs) based on the lanthanide family are attracting ever increasing attention due to not only their versatile architecture [1-4], but also their potential application in hydrogen storage [5], catalysis [6], magnetism [7], fluorescence [8], and so on. Many thermally stable and highly porous MOFs result from the versatile binding of polycarboxylate ligands to rare earth metal ions, in which no additional counter-ions are needed [2-4]. 1,3-Benzenedicarboxylates (bdc) are often adopted as components for building MOFs with or without the auxiliary ligands [9-16], because of bdc is a kind of polydentate ligand which may act as a linker with different geometric effects to connect metal ions into multidimensional structures via various coordination modes. Its two carboxylic groups may be completely or only partly deprotonated, resulting in versatile coordination modes, as listed in Scheme 1(a-f) [16]. While 1,10-phenanthroline is a good ligand for lanthanide ions and can construct supramolecular structure via C–H···O hydrogen bonding interactions and π - π aromatic interactions [3,18]. And the large size of phen can effectively prevent the formation of interpenetration. In addition, the strong

* Corresponding author. Address: State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China. Tel.: +86 10 6443 4808 (G. Guo). absorptions within a large wavelength range for its $\pi - \pi^*$ transition of phen was considered as an important "antennas", from which the energy can be effectively transferred to Ln(III) ions for intense emissions [19]. For example, photoluminescence measurements show that [HNMe₂][Ln₂(*m*-bdc)₃(phen)₂](Ln = Eu and Tb, *m*-H₂bdc = 1,3-benzenedicarboxylic acid, phen = 1,10-phenanthroline) are highly emissive at room temperature with quantum yields of 86.87% (at 330 nm) and 85.62% (at 345 nm), respectively, and may be good candidates for light-emitting diodes (LEDs) and light application [19].

With this paper, we present the hydrothermal synthesis and structural characterization of three novel lanthanide MOFs, $[La_2(bdc)_3(phen)H_2O]\cdot H_2O$ (1), $[Pr_2(bdc)_3(phen)H_2O]\cdot H_2O$ (2) and $[Yb_2(bdc)_3(phen)H_2O]\cdot H_2O$ (3), constructed from bdc, 1,10-phenanthroline (phen) and corresponding lanthanide(III) ions.

2. Experimental

2.1. Materials and general methods

All commercially available chemicals are reagent grade, and used as received without further purification. Elemental analysis of C, H and N for the title compound was performed by Elementar Vario EL-III. Infrared (IR) spectra, in the region (400–4000 cm⁻¹), were recorded on Nicolet 6700 Fourier Transform infrared spectrophotometer. TGA was performed from room temperature

E-mail address: guogs@mail.buct.edu.cn (G. Guo).

^{0022-2860/\$ -} see front matter @ 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.molstruc.2011.07.014

C. Wang et al./Journal of Molecular Structure 1004 (2011) 39-44



Scheme 1. Some typical coordination modes of 1,3-dbc anions.

to 900 °C in an air stream at a rate of 10 °C min⁻¹ on a ZRY-1P TGA system using α -Al₂O₃ as reference material.

2.2. Synthesis

2.2.1. $[La_2(bdc)_3(phen)H_2O] \cdot H_2O$ (1)

A mixture of LaBr₃·7H₂O (0.5 mmol, 0.2524 g), 1,10-phenanthroline (0.5 mmol, 0.0991 g) and H₂bdc (0.5 mmol, 0.1220 g) in 1:1:1 molar ratio was sealed in a 25 mL Teflon-lined stainless steel Parr bomb containing deionized H₂O (14 mL), heated at 140 °C for 96 h, and then cooled down to room temperature. Colorless blocklike crystals were isolated and washed with deionized water and ethanol (yield 79% based on LaBr₃·7H₂O). Anal. Calcd. for **2**, $C_{36}H_{23.64}Br_{0.12}La_2N_2O_{13.88}$: C, 43.47; N, 2.82; H, 2.42. Found: C, 44.10; N, 2.92; H, 2.55. IR (KBr)/cm⁻¹: 3429.50, 1645.75, 1617.92, 1581.99, 1545.59, 1519.18, 1479.96, 1453.43, 1400.20, 1274.49, 1220.91, 1160.61, 1102.96, 1081.22, 1000.12, 969.65, 916.46, 842.42, 816.25, 782.98, 744.39, 727.80, 709.99, 670.24, 654.88, 636.98.

2.2.2. $[Pr_2(bdc)_3(phen)H_2O] \cdot H_2O$ (2)

Green block-like crystals of **2** (yield 74% based on $PrCl_3 \cdot 7H_2O$) were synthesized from a mixture of $PrCl_3 \cdot 7H_2O$ (0.5 mmol, 0.1863 g), 1,10-phenanthroline (0.5 mmol, 0.0991 g) and H_2bdc (0.5 mmol, 0.1220 g) in 1:1:1 molar ratio under the same conditions as above. Anal. Calcd. for **2**, $C_{36}H_{24}N_2O_{14}Pr_2$: C, 43.61;

Table 1

Details of X-ray data collection and refinement for compounds 1, 2 and 3

N, 2.83; H, 2.42. Found: C, 43.91; N, 3.01; H, 2.98. IR (KBr)/cm⁻¹: 3435.16, 1616.19, 1545.60, 1513.45, 1477.49, 1448.34, 1385.55, 1160.82, 1104.36, 1082.61, 843.69, 821.06, 784.22, 748.37, 729.95, 711.93, 699.35, 655.0, 630.95, 542.25.

2.2.3. [Yb₂(bdc)₃(phen)H₂O]·H₂O (**3**)

Colorless block-like crystals of **1** (yield 68% based on YbBr₃·6H₂O) were synthesized from a mixture of YbBr₃·6H₂O (0.5 mmol, 0.2063 g), 1,10-phenanathroline (0.5 mmol, 0.0991 g) and H₂bpdc (0.5 mmol, 0.1220 g) in 1:1:1 molar ratio under the same conditions as above. Anal. Calcd. for **3**, $C_{36}H_{23.55}Br_{0.15}$ N₂O_{13.85}Yb₂: C, 40.61; N, 2.63; H, 2.26. Found: C, 41.21; N, 2.85; H, 3.90. IR (KBr)/cm⁻¹: 3419.51, 1637.50, 1615.58, 1583.00, 1546.60, 1537.77, 1519.41, 1478.01, 1443.95, 1386.49, 1279.45, 1221.08, 1103.27, 1083.86, 1000.40, 977.36, 930.51, 864.68, 841.58, 822.09, 792.87, 780.90, 746.92, 727.14, 711.01, 700.18, 654.31, 637.16, 543.95.

2.3. X-ray crystallography

X-ray single-crystal data collection for compounds 1, 2 and 3 was performed with Bruker CCD area detector diffractometer with a graphite-monochromatized Mo K α radiation (λ = 0.71073 Å) using φ - ω mode at 298(2) K. The SMART software [20] was used for data collection and the SAINT software [21] for data extraction. Empirical absorption corrections were performed with the SADABS program [22]. The structure has been solved by direct methods (SHELXS-97) [23] and refined by full-matrix-least squares techniques on F2 with anisotropic thermal parameters for all of the non-hydrogen atoms (SHELXL-97) [23]. All hydrogen atoms were located by Fourier difference synthesis and geometrical analysis. These hydrogen atoms were allowed to ride on their respective parent atoms. All structural calculations were carried out using the SHELX-97 program package [23]. Crystallographic data and structural refinements for compound 1, 2 and 3 are summarized in Table 1. Selected bond lengths and angles for all compounds are listed in Table 3.

3. Results and discussion

3.1. Synthesis

Under hydrothermal conditions (140 °C), compounds 1-3 were successfully synthesized as colorless, green and colorless crystals respectively by the reactions of 1,3-benzenedicarboxylates (bdc),

Formula	$C_{36}H_{23.64}Br_{0.12}La_2N_2O_{13.88}$	$C_{36}H_{24}N_2O_{14}Pr_2$	$C_{36H_{23,55}Br_{0.15}N_2O_{13.85}Yb_2}$
М	993.7	990.39	1063.78
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	Pbca	Pbca	Pbca
a (Å)	14.5587(14)	14.4930(15)	14.5587(14)
b (Å)	20.683(2)	20.638(2)	20.683(2)
<i>c</i> (Å)	23.360(2)	23.459(3)	23.360(2)
α (°)	90	90	90
β (°)	90	90	90
γ (°)	90	90	90
V (Å ³)	7034.0(13)	7016.7(13)	7034.0(13)
Ζ	8	8	8
μ (Mo K $lpha$) (mm $^{-1}$)	2.607	2.819	5.53
Total reflections	33,129	33,527	33,134
Unique	6188	6188	6200
R _{int}	0.1111	0.0703	0.1295
R_1	0.0533	0.0661	0.0682
ωR_2	0.1248	0.1423	0.169
R_1 (all data)	0.0964	0.0883	0.1172
ωR_2 (all data)	0.1608	0.1582	0.1983

 Table 2

 Selected IR data and their assignment of complexes 1, 2 and 3 (cm⁻¹).

Assignments	1	2	3				
Carboxylate gro	Carboxylate group						
$v_{\sigma\sigma}$	1617.92, 1545.59	1616.19, 1545.60	1615.58, 1546.60				
v_{σ}	1453.43, 1400.20	1448.34, 1400.20	1443.95, 1386.49				
phen							
$v_{X=N\sigma}$	1519.18	1513.45	1519.41				
δ_{H-X}	842.42, 727.80	843.69, 729.95	841.58, 727.14				

1,10-phenanthroline (phen) and the corresponding lanthanide(III) salts with yields of more than 68% (based on corresponding input LnX_3 (X = Cl or Br) compounds). We failed to synthesize the title compounds under different reaction temperatures, like 120 °C, 130 °C, 150 °C, 160 °C and 170 °C, which indicates the temperature is a key factor to hydrothermally synthesize the title compounds.

3.2. Infrared spectroscopy

In the IR spectrum of complex **1**, a strong absorption at 3429.50 cm⁻¹ is assigned to stretching vibration of hydroxyl, implying the presence of water molecules. The characteristic bands of dicarboxylate unit occur at 1617.92 cm⁻¹ and 1545.59 cm⁻¹ for asymmetric stretching, and at 1453.43 cm⁻¹ and 1400.20 cm⁻¹ for symmetric stretching. Those at 816.25, 744.39, 709.99 and 654.88 cm⁻¹ are assigned to phenyl group. And the characteristic bands of phen occur at 1519.18 cm⁻¹ ($\nu_{N=C}$), 842.42 cm⁻¹ and 727.80 cm⁻¹($\delta_{C=H}$). The selected IR data and their assignments of complexes **1**, 2 and **3** are listed in Table 2. IR spectra support the results of the single crystal X-ray analysis.

3.3. Structural description for 1, 2 and 3

Compounds **1**, 2 and **3** are isomorphous and isostructural, hence, only the crystal structure of **2** is described in detail. The compound **2** consists of a network of distorted dodecahedral $Pr10_6N_2$ units and distorted pentagonal bipyramidal $Pr2O_7$ units, being connected by bdc ligands and coordination water.

The coordination environments around Pr(III) ions and numbering scheme of ${\bf 2}$ are illustrated in Fig. 1. There are two distinct ${\rm Pr}^{3+}$ ions with different coordination spheres in the structure. The local geometry around Pr1 is an eight-coordinated dodecahedron made up of two nitrogen atoms (N1 and N2) from a phen ligand, with Pr-N bond being 2.789(10) Å, and six oxygen atoms from six different bdc ligands, with Pr-O bonds ranging from 2.340(9) to 2.746(10) Å, as listed in Table 3. While Pr2 ions are seven-coordinated and the coordination geometry is a distorted pentagonal bipyramidal, and the coordination environment around each Pr2 ions are completed by six oxygen atoms, Pr–O bond length being 2.388(9)-2.459(9) Å, from six carboxylate groups attached on six different bdc ligands respectively, and one oxygen atom (Pr-O 2.567(9)Å) from water molecule. All the Pr-O and Pr-N bond lengthens are similar to those found in [Pr₂(mBDC)₃(phen)(- H_2O]_{*n*}·0.5*n* H_2O [17] (mBDC = isophthalate, phen = 1,10-phenanthroline). The selected bond lengths of complexes 1-3 are listed in Table 3.

In compound **2**, the Pr1 and Pr2 center ions are linked into infinite 2-D layer viewed along *a*-axis by dbc ligands via Pr–O bonds, in which bdc act as both tetra-monodentate ligand to link two Pr1 and Pr2 ions respectively, and counter-ions to balance the charge of the title complex, as illustrated in Fig. 2. The adjacent layers are stacked in a staggered fashion through π - π interactions between phen rings of the neighboring sheets. Thus,



Fig. 1. (a) Numbering scheme and coordination environment around the two crystallographically independent Pr(III) centers in **2**. Hydrogen atoms are omitted for clarity. (b) and (c) Highlight of the coordination polyhedra for the two crystallographically independent Pr(III) ions.

C. Wang et al./Journal of Molecular Structure 1004 (2011) 39-44

Table 3			
Selected bo	nds for compo	unds 1, 2	and 3 (

elected bonds for compounds 1 , 2 and 3 (Å).					
La1		Pr2		Yb3	
La(1)-O(8)#1	2.374(8)	Pr(1)—O(8)	2.340(9)	Yb(1)—O(8)#1	2.372(10)
La(1)-O(1)	2.425(7)	Pr(1) - O(1)	2.370(8)	Yb(1)—O(1)	2.406(9)
La(1)-O(9)	2.410(7)	Pr(1)-O(9)	2.380(8)	Yb(1)-O(9)	2.419(9)
La(1)-O(5)	2.444(8)	Pr(1)-O(5)	2.390(9)	Yb(1)-O(5)	2.434(10)
La(1)-O(3)	2.607(7)	Pr(1)-O(3)#1	2.582(9)	Yb(1)-O(3)	2.614(9)
La(1)-O(12)#1	2.718(8)	Pr(1)-O(12)	2.746(10)	Yb(1)-O(12)#1	2.721(10)
La(1)-N(2)	2.789(10)	Pr(1)-N(2)	2.739(12)	Yb(1)—N(2)	2.793(13)
La(1) - N(1)	2.789(10)	Pr(1) - N(1)	2.740(12)	Yb(1)-N(1)	2.787(13)
La(2)-O(10)#2	2.392(8)	Pr(2)-O(10)#2	2.359(9)	Yb(2)-O(10)#2	2.400(10)
La(2)-O(2)	2.426(8)	Pr(2)-O(2)	2.388(9)	Yb(2)-O(2)	2.438(10)
La(2)-O(11)	2.436(8)	Pr(2)-O(11)#2	2.440(10)	Yb(2)-O(11)	2.435(10)
La(2)-O(7)	2.483(8)	Pr(2)-O(7)#2	2.439(9)	Yb(2)-O(7)	2.478(10)
La(2) - O(4)	2.476(7)	Pr(2)-O(4)#1	2.457(8)	Yb(2)-O(4)	2.498(9)
La(2)-O(6)	2.484(7)	Pr(2) - O(6)	2.459(9)	Yb(2)-O(6)	2.485(9)
La(2)—O(13)	2.598(7)	Pr(2)—O(13)	2.567(9)	Yb(2)-0(13)	2.599(10)

Symmetry codes: #1 x - 1/2, -y + 1/2, -z + 2; #2 x + 1/2, -y + 1/2, -z + 2.



Fig. 2. Two dimensional metal-organic layer structure constructed by Pr(III) and dbc viewed from *a*-axis in 2.

a three-dimensional supramolecular framework is constructed with layers pulled together by π - π interactions (Fig. 3). Intramolecular hydrogen-bonding interactions between coordination water molecules and oxygen atoms from COO⁻ groups attached on the bdc ligands contribute to strengthen the layer constructed from Pr(III), bdc ligands and water molecules, and the lattice water molecules are situated among the 3D framework and stabilized by hydrogen bonding interactions. The distances and angles of the hydrogen bonds of compounds 1, 2 and 3 are listed in Table 4.

It was worthy to noting that in compound **1**, the H15 atom attached on the bdc ligand are disordered with Br1 atom, which were split during the refinement resulting in a site occupancy ratio of 0.88/0.12, and in compound **3**, the similar disorder happens with site occupancy ratio of 0.85/0.15.

Up to now, only a few lanthanide-based MOFs constructed from both H₂bdc and phen were reported, e.g. [Pr₂(m-BDC)₃(phen)- $(H_2O)]_n \cdot 0.5nH_2O$, $[Tb_4(mBDC)_6(phen)]_n$ and $[Er_4(mBDC)_6(phen)]_n$ [17], $[Eu_2(1,3-BDC)_3(phen)_2(H_2O)_2]_n \cdot 4nH_2O$ and $[Yb_2(1,3-BDC)_3 (phen)_{1/2}]_n$ [18], $[HNMe_2][Ln_2(m-bdc)_3(phen)_2]$ (Ln = Eu, Gd and Tb)[19]. In [Pr₂(m-BDC)₃(phen)(H₂O)]_n 0.5nH₂O [17], Pr ions show seven-coordinated and eight-coordinated geometry, comparable to the Pr ions in compound 2. And three metal environments exist in $[Yb_2(1,3-BDC)_3(phen)_{1/2}]_n$ [18], naming six-, seven- and eightcoordinated, which are different from the Yb ions in compound 3.



Fig. 3. Three dimensional framework viewed from *a*-axis direction of compound 2.

42

C. Wang et al./Journal of Molecular Structure 1004 (2011) 39-44

Hydrogen bonds for compound 1 , 2 and 3 (Å and °).					
D—H	<i>d</i> (D—H)	$d(H \cdot \cdot \cdot A)$	<dha< th=""><th>$d(D \cdot \cdot \cdot A)$</th><th>Α</th></dha<>	$d(D \cdot \cdot \cdot A)$	Α
La1					
013–H13C	0.850	1.915	171.12	2.757	O4[-x, -y + 1, -z + 2]
013–H13D	0.850	1.918	171.97	2.762	O14[-x + 1/2, -y + 1, z + 1/2]
014–H14C	0.850	2.268	133.62	2.920	O6[-x + 1/2, -y + 1, z - 1/2]
014–H14D	0.850	2.273	133.82	2.926	011[-x + 1/2, -y + 1, z - 1/2]
Pr2					
013–H13C	0.850	1.922	171.94	2.766	O4[-x + 1/2, y - 1/2, z]
013–H13D	0.850	1.962	172.93	2.807	014[-x+1, y-1/2, -z+3/2]
014–H14C	0.850	2.174	150.45	2.944	O6[-x + 1, y + 1/2, -z + 3/2]
014–H14D	0.850	2.182	150.54	2.952	011[-x + 3/2, -y + 1, z + 1/2]
Yb3					
013–H13C	0.850	1.885	171.63	2.728	O4[-x, -y + 1, -z + 2]
013–H13D	0.850	1.877	169.82	2.717	014[-x + 1/2, -y + 1, z + 1/2]
014—H14C	0.850	2.198	132.20	2.840	O6[-x + 1/2, -y + 1, z - 1/2]
014-H14D	0.850	2.312	137.28	2.992	O11[-x + 1/2, -y + 1, z - 1/2]

Table	5
-------	---

Table 4

Thermogravimetric analysis data of 1-3.

	1	2	3
Dehydration temperature (°C)	105–185	110–200	110–200
Loss of water found (calcd.) (%)	4.20 (3.62)	4.10 (3.63)	3.44 (3.38)
Decomposition temperature (°C)	400	420	435



Fig. 4. The TGA curve of the compound 2.

3.4. Thermal properties

Thermogravimetric analyses of **1–3** were performed in the air stream from room temperature to 900 °C. The loss of one lattice water and one coordinated water molecule of compounds **1–3** was observed with their dehydration temperatures in range of 105–185 °C, 110–200 °C and 110–200 °C, respectively. No apparent temperature differences were observed when dehydration of the lattice water and coordinated water molecules occurred. Further decomposition processes of the compounds **1–3** begin at above 400, 420 and 435 °C, giving the final residual products of La₂O₃, Pr₂O₃ and Yb₂O₃ respectively, as listed in Table 5.

Taking **2** for example, the TGA curve presents two main stages of decomposition. The first step, from 110 to 200 °C, is assigned to loss of one non-coordinated water molecule and one coordinated water molecules, with a weight decrease of 4.10% (calcd 3.63%). The second, from 420 to 575 °C is due to the ligands decomposition, which shows a weight decrease of 64.8% (calcd 63.8%). The final residue, Pr_2O_3 , is 31.1% (calcd 32.6%), in which Pr is 26.5%, is well agreement with $[Pr_2(bdc)_3(phen)H_2O]\cdot H_2O$ (requires 28.3%), as shown in Fig. 4.

Compounds **1–3** represent considerable thermal stability, which indicate that high coordination number as well as the coordination environment of lanthanide ions with bdc ligand has profound effects on the overall framework rigidity and thermal stability.

4. Conclusions

Three lanthanide coordination polymers with bdc and phen were self-assembled by hydrothermal method. The bdc ligands in polymers **1–3** adopt tetra-monodentate coordination mode to coordinate the center ions into infinite 2-D sheets, and further built up into 3-D supramolecular framework through π – π interactions between phen rings of the neighboring sheets. In all the three MOFs, bdc also act as counter-ions to balance the charge of the title complexes. The considerable thermal stability of these polymers can be attributed to the high coordination number of the lanthanide ions and the strong metal–O bonds.

Supplementary material

CCDC 823768, 823769 and 823770 contain the supplementary crystallographic data for **1**, 2 and **3**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or email: deposit@ccdc.cam.ac.uk.

Acknowledgements

The study was financially supported by National Natural Science Foundation of China (No. 20875007), Funding Project for Academic Human Resources Development in Institutions of Higher Learning under the Jurisdiction of Beijing Municipality (Grant No. PHR201008372 and PHR201106124).

References

- N.W. Ockwig, O. Delgado-Friedrichs, M. O'Keeffe, O. Yaghi, Acc. Chem. Res. 38 (2005) 176.
- [2] C.C. Wang, Z.H. Wang, F.B. Gu, G.S. Guang, J. Mol. Struct. 979 (2010) 92.
- [3] G.S. Guang, C.C. Wang, Y.C. Liu, Y. Liu, H.Y. Guo, Chin. J. Inorg. Chem. 26 (2010) 1583.
- [4] G.S. Guo, Y.C. Liu, J. Zhang, H.Y. Guo, J. Rare Earths 26 (2008) 633.
- [5] L.J. Murray, M. Dincă, J.R. Long, Chem. Soc. Rev. 38 (2009) 1294.
- [6] J.Y. Lee, O.K. Farha, J. Roberts, K.A. Scheidt, S.T. Nguyen, J.T. Hupp, Chem. Soc. Rev. 38 (2009) 1450.
- [7] M. Kurmoo, Soc. Rev. 38 (2009) 1353.

44

C. Wang et al./Journal of Molecular Structure 1004 (2011) 39-44

- [8] M.D. Allendorf, C.A. Bauer, R.K. Bhakta, R.J.T. Houk, Chem. Soc. Rev. 38 (2009) 1330.
- [9] D. Zhao, D. Yuan, A. Yakovenko, H.C. Zhou, Chem. Commun. 46 (2010) 4196.
- [10] D. Burrows, C.G. Frost, M.F. Mahon, M. Winsper, C. Richardson, J.P. Attfield, J.A. Rodgers, Dalton Trans. (2008) 6788.
- [11] M. Eddaoudi, J. Kim, J.B. Wachter, H.K. Chae, M. OKeeffe, O.M. Yaghi, J. Am.
- Chem. Soc. 123 (2001) 4368.
 [12] D.T. Vodak, M.E. Braun, J. Kim, M. Eddaoudi, O.M. Yaghi, Chem. Commun. (2001) 2534.
- [13] M.L. Hu, D.J. Xu, D.P. Cheng, J. Coord. Chem. 55 (2002) 11.
 [14] D. Sun, N. Zhang, Q.J. Xu, G.G. Luo, R.B. Huang, L.S. Zheng, J. Mol. Struct. 969 (2010) 176.
- [15] Z. Zhang, M. Pi, T. Wang, C.M. Jin, J. Mol. Struct. 992 (2011) 111.
 [16] Y.L. Qu, Y.X. Ke, S.M. Lu, R. Fan, G.Q. Pan, J.M. Li, J. Mol. Struct. 734 (2005) 7.

- (2005) 7.
 [17] Y.H. Wan, L.P. Zhang, L.P. Jin, J. Mol. Struct. 658 (2003) 253.
 [18] Y.H. Wan, L.P. Zhang, L.P. Ji, S. Gao, S.Z. Lu, Inorg. Chem. 42 (2003) 4985.
 [19] H.B. Zhang, Y. Peng, X.C. Shan, C.B. Tia, P. Lin, S.W. Du, Inorg. Chem. Commun., in press, doi: 10.1016/j.inoche.2011.04.014.
 [20] Bruker AXS, SMART, Version 5.611, Bruker AXS, Madison, WI, USA, 2000.
 [21] Bruker AXS, SAINT, Version 6.28, Bruker AXS, Madison, WI, USA, 2003.
 [23] GADABS, V2.03, Bruker AXS, Madison, WI, 2000.
 [24] G. M. Sheldrick, SHELX-97, Cöttingen University, Cernapy 1997.

- [23] G.M. Sheldrick, SHELX-97, Göttingen University, Germany, 1997.