

Synthesis of Lanthanide Coordination Polymers with Benzophenone-4,4'-dicarboxylate: Effect of Lanthanide Contraction on Structures

WANG, Yi-Bo(王轶博) JIN, Lin-Pei*(金林培)

Department of Chemistry, Beijing Normal University, Beijing 100875, China

Four lanthanide coordination polymers with benzophenone-4,4'-dicarboxylic acid (H_2bpndc) and 1,10-phenanthroline (phen), $[Ln_2(bpndc)_3(phen)]$ ($Ln=La$ (**1**), Pr (**2**) and Tb (**3**)), $[Yb(bpndc)_{1.5}(phen)]\cdot 0.5H_2O$ (**4**) were obtained through solvothermal synthesis. The crystallographic data show that **1**, **2**, and **3** are isostructural, the Ln(III) ions in **1**, **2** and **3** are all eight- and ten-coordinated, respectively, and thus the Ln(III) ions are connected by $bpndc$ ligands, resulting in an interpenetrating 3D structure. While in **4**, the Yb(III) ions are eight-coordinated and connected by $bpndc$ ligands into a 3D structure with 1D rhombic channels, which result from the effect of lanthanide contraction from La(III) to Yb(III) ions, and the $bpndc$ ligands in **1**, **2**, **3**, and **4** display three types of coordination modes.

Keywords coordination polymer, solvothermal synthesis, lanthanide, X-ray diffraction

Introduction

Recently, the coordination polymers based on dicarboxylic acid have been studied extensively for their importance as promising materials.¹⁻⁷ So the rational design and synthesis of novel coordination polymers with useful functions attract considerable attention. As well known, the design of extended structure with potential applications can be realized by starting with connecting ligands capable of binding metal centers strongly and predictably to afford the structures with expected functions.⁸ Moreover, the covalent metal-ligand bonds are stronger than hydrogen bonds and have more intense directionality than π - π stacking *etc.* Thus metal-ligand interactions can direct the formation of the target metal-organic polymers. In view of this, dicarboxylic acid ligands are very suitable for acting as connectors to construct coordination polymers due to their multifunctional carboxyl groups and multiple coordination sites. In the dicarboxylic acid ligands, the linear ligands are liable to form the porous coordination polymers^{1,2,9-11} and layered polymers with intriguing structure.^{5,12} But there are not many researches on lanthanide based coordination polymers with linear dicarboxylic acid ligands^{1,2,8} and even less attention has been paid to the effect of lanthanide contraction on structures of coordination polymers. Based on these conceptions, the title complexes, $[Ln_2(bpndc)_3(phen)]$ ($Ln=La$ (**1**), Pr (**2**), Tb (**3**)) and $[Yb(bpndc)_{1.5}(phen)]\cdot 0.5H_2O$ (**4**) were synthesized and characterized.

Experimental

Materials and instruments

$LaCl_3\cdot 7H_2O$, $PrCl_3\cdot 7H_2O$, $TbCl_3\cdot 6H_2O$, and $YbCl_3\cdot 6H_2O$ were prepared by dissolving their oxides in hydrochloric acid, respectively, and then dried. Benzophenone-4,4'-dicarboxylic acid was purchased from Aldrich and used without further purification. All other reagents were commercially available and used as received.

The X-ray single crystal data collections for complexes **1**, **2**, **3** and **4** were performed on a Bruker Smart 1000 CCD diffractometer, using graphite-monochromated Mo $K\alpha$ radiation ($\lambda=0.071073$ nm). Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least square on F^2 using the SHELXTL-97 program. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement.

Elemental analyses were performed on an Elementar Vario EL analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellets technique.

Preparation of complexes 1—4

Synthesis of $[La_2(bpndc)_3(phen)]$ (1**):** The solvothermal reaction of $LaCl_3\cdot 7H_2O$ (0.056 g, 0.15 mmol), benzophenone-4,4'-dicarboxylic acid (0.061 g, 0.225 mmol), 1,10-phenanthroline (0.04 g, 0.2 mmol), NaOH

* E-mail: lpjin@bnu.edu.cn; Fax: 010-58802075; Tel.: 010-58805522

Received March 15, 2004; revised and accepted July 6, 2004.

Project supported by the National Natural Science Foundation of China (No. 20331010).

(0.438 mL, 0.284 mmol), H₂O (5 mL) and ethanol (5 mL) was performed in 23 mL Teflon-lined stainless steel autoclave at 180 °C for 3 d, then the mixture was cooled to room temperature. The colorless needle-like crystals were separated from the reaction mixture and washed with ethanol to give a *ca.* 63.2% yield (0.060 g) of **1** based on LaCl₃•7H₂O. Anal. calcd (found) for **1**: C 53.45 (53.46), H 2.52 (2.47), N 2.19 (2.11).

Syntheses of complexes **2**, **3** and **4** are similar to that of **1**. The light green needle-like crystals of **2** gave a *ca.* 71.8% yield (0.068 g) based on PrCl₃•7H₂O. Anal. calcd (found) for **2**: C 53.28 (53.34), H 2.51 (2.37), N 2.18 (1.85). The colorless needle-like crystals of **3** gave a *ca.* 67.1% yield (0.066 g) based on TbCl₃•6H₂O. Anal.

calcd (found) for **3**: C 52.55 (52.24), H 2.12 (1.80), N 2.48 (2.30). The colorless needle-like crystals of **4** gave a *ca.* 61.5% yield (0.071 g) based on YbCl₃•6H₂O. Anal. calcd (found) for **4**: C 52.20 (52.22), H 2.77 (2.61), N 3.66 (3.18).

Results and discussion

The crystallographic data of **1**–**4** are given in Table 1, which show that complexes **1**–**3** are isostructural, and herein only complexes **2** and **4** will be described in detail. The selected bond lengths and angles of **2** and **4** are listed in Tables 2 and 3.

Table 1 Crystal data for **1**–**4**

Complex	1	2	3	4
Empirical formula	C ₅₇ H ₃₂ N ₂ O ₁₅ La ₂	C ₅₇ H ₃₂ N ₂ O ₁₅ Pr ₂	C ₅₇ H ₃₂ N ₂ O ₁₅ Tb ₂	C _{34.5} H ₂₁ N ₂ O ₈ Yb
Formula weight	1262.67	1266.67	1302.69	764.57
Crystal system	Hexagonal	Hexagonal	Hexagonal	Monoclinic
Space group	<i>P</i> 6(5)22	<i>P</i> 6(5)22	<i>P</i> 6(5)22	<i>C</i> 2/ <i>c</i>
<i>a</i> /nm	1.5482(3)	1.5469(2)	1.54007(19)	3.0832(11)
<i>b</i> /nm	1.5482(3)	1.5469(2)	1.54007(19)	0.9948(4)
<i>c</i> /nm	4.0320(15)	4.0115(11)	3.9484(10)	2.3147(8)
β (°)	90	90	90	121.185(5)
<i>Z</i>	6	6	6	8
<i>V</i> /nm ³	8.369(4)	8.312(3)	8.110(2)	6.074(4)
ρ_{calcd} /(g•cm ⁻³)	1.503	1.518	1.600	1.672
Temp./K	293(2)	293(2)	293(2)	293(2)
μ /mm ⁻¹	1.577	1.805	2.663	3.136
Reflections collected	27861, 4782	42879, 4872	34031, 4808	17112, 6242
Total, independent				
<i>R</i> _{int}	0.2806	0.1466	0.1475	0.0503
λ (Mo K α), nm	0.071073	0.071073	0.071073	0.071073
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2 σ (<i>I</i>)]	0.0864, 0.1418	0.0569, 0.1266	0.0586, 0.1222	0.0392, 0.0789

Table 2 Selected bond lengths (nm) and bond angles (°) for **2**

Pr(1)—O(1)	0.2499(8)	Pr(2)—O(2)#4	0.2566(7)
Pr(1)—O(1)#1	0.2499(8)	Pr(2)—O(4)#3	0.2729(16)
Pr(1)—O(2)	0.2602(7)	Pr(2)—O(4)#5	0.2729(16)
Pr(1)—O(2)#1	0.2602(7)	Pr(2)—O(5)#3	0.274(2)
Pr(1)—O(5)#2	0.249(2)	Pr(2)—O(5)#5	0.274(2)
Pr(1)—O(5)#3	0.249(2)	Pr(2)—O(7)	0.2345(10)
Pr(1)—O(6)	0.2400(8)	Pr(2)—O(7)#4	0.2345(10)
Pr(1)—O(6)#1	0.2400(8)	Pr(2)—N(1)	0.2693(8)
Pr(2)—O(2)	0.2566(7)	Pr(2)—N(1)#4	0.2693(8)
O(1)-Pr(1)-O(1)#1	73.4(5)	O(2)#4-Pr(2)-O(5)#3	138.3(5)
O(1)-Pr(1)-O(2)	50.2(2)	O(2)#4-Pr(2)-O(5)#5	68.8(5)
O(1)-Pr(1)-O(2)#1	77.4(3)	O(2)#4-Pr(2)-O(7)#4	76.6(3)
O(1)-Pr(1)-O(5)#2	14.94(5)	O(4)#3-Pr(2)-O(4)#5	123.7(7)

Continued

O(1)-Pr(1)-O(5)#3	90.8(5)	O(4)#3-Pr(2)-O(5)#3	47.6(3)
O(1)-Pr(1)-O(6)	125.5(3)	O(4)#3-Pr(2)-O(5)#5	116.6(6)
O(1)-Pr(1)-O(6)#1	74.6(3)	O(4)#3-Pr(2)-O(7)#4	71.0(4)
O(1)#1-Pr(1)-O(2)	77.4(3)	O(4)#5-Pr(2)-O(5)#3	116.6(6)
O(1)#1-Pr(1)-O(2)#1	50.2(2)	O(4)#5-Pr(2)-O(5)#5	47.6(3)
O(1)#1-Pr(1)-O(5)#2	90.8(5)	O(4)#5-Pr(2)-O(7)#4	127.1(4)
O(1)#1-Pr(1)-O(5)#3	149.4(5)	O(5)#3-Pr(2)-O(5)#5	152.3(10)
O(1)#1-Pr(1)-O(6)#1	125.5(3)	O(5)#3-Pr(2)-O(7)#4	108.7(5)
O(2)-Pr(1)-O(2)#1	115.3(3)	O(5)#5-Pr(2)-O(7)#4	79.7(5)
O(2)-Pr(1)-O(5)#2	152.4(5)	O(7)-Pr(2)-O(2)#4	76.0(3)
O(2)-Pr(1)-O(5)#3	72.4(5)	O(7)-Pr(2)-O(4)#3	127.1(4)
O(2)-Pr(1)-O(6)	80.5(3)	O(7)-Pr(2)-O(4)#5	71.0(4)
O(2)-Pr(1)-O(6)#1	112.1(3)	O(7)-Pr(2)-O(5)#3	79.7(5)
O(2)#1-Pr(1)-O(5)#2	72.4(5)	O(7)-Pr(2)-O(5)#5	108.7(5)
O(2)#1-Pr(1)-O(5)#3	152.4(5)	O(7)-Pr(2)-O(7)#4	145.8(5)
O(2)#1-Pr(1)-O(6)#1	80.5(3)	N(1)-Pr(2)-O(2)	138.7(3)
O(5)#2-Pr(1)-O(5)#3	114.0(10)	N(1)-Pr(2)-O(2)#4	131.0(3)
O(5)#2-Pr(1)-O(6)#1	95.1(6)	N(1)-Pr(2)-O(4)#3	54.3(4)
O(6)-Pr(1)-O(1)#1	74.6(3)	N(1)-Pr(2)-O(4)#5	76.0(5)
O(6)-Pr(1)-O(2)#1	112.1(3)	N(1)-Pr(2)-O(5)#3	89.6(5)
O(6)-Pr(1)-O(5)#2	72.3(5)	N(1)-Pr(2)-O(5)#5	65.7(6)
O(6)-Pr(1)-O(5)#3	95.1(6)	N(1)-Pr(2)-O(7)	135.6(4)
O(6)-Pr(1)-O(6)#1	157.3(5)	N(1)-Pr(2)-O(7)#4	78.5(4)
O(6)#1-Pr(1)-O(5)#3	72.3(5)	N(1)#4-Pr(2)-O(2)	131.0(3)
O(2)-Pr(2)-O(2)#4	72.9(3)	N(1)#4-Pr(2)-O(2)#4	138.7(3)
O(2)-Pr(2)-O(4)#3	86.6(4)	N(1)#4-Pr(2)-O(4)#3	76.0(5)
O(2)-Pr(2)-O(4)#5	145.0(4)	N(1)#4-Pr(2)-O(4)#5	54.3(4)
O(2)-Pr(2)-O(5)#3	68.8(5)	N(1)#4-Pr(2)-O(5)#3	65.7(6)
O(2)-Pr(2)-O(5)#5	138.3(5)	N(1)#4-Pr(2)-O(5)#5	89.6(5)
O(2)-Pr(2)-O(7)	76.6(3)	N(1)#4-Pr(2)-O(7)	78.5(4)
O(2)-Pr(2)-O(7)#4	76.0(3)	N(1)#4-Pr(2)-O(7)#4	135.6(4)
O(2)#4-Pr(2)-O(4)#3	145.0(4)	N(1)-Pr(2)-N(1)#4	58.0(5)
O(2)#4-Pr(2)-O(4)#5	86.6(4)		

Symmetry operations: #1 $-y, -x, -z+1/6$; #2 $x-1, y, z$; #3 $-y, -x+1, -z+1/6$; #4 $-x, -x+y, -z+1/3$; #5 $y, -x+y+1, z+1/6$.

Table 3 Selected bond lengths (nm) and bond angles ($^{\circ}$) for 4

Yb(1)—O(1)	0.2292(4)	Yb(1)—O(6)	0.2220(4)
Yb(1)—O(2)#1	0.2277(5)	Yb(1)—O(7)#1	0.2287(4)
Yb(1)—O(4)#2	0.2449(4)	Yb(1)—N(1)	0.2519(6)
Yb(1)—O(5)#2	0.2319(4)	Yb(1)—N(2)	0.2513(6)
O(1)-Yb(1)-O(2)#1	126.06(15)	O(6)-Yb(1)-O(7)#1	123.46(16)
O(1)-Yb(1)-O(4)#2	149.07(17)	O(1)-Yb(1)-N(1)	69.83(16)
O(1)-Yb(1)-O(5)#2	142.07(16)	O(2)#1-Yb(1)-N(1)	147.52(17)

Continued

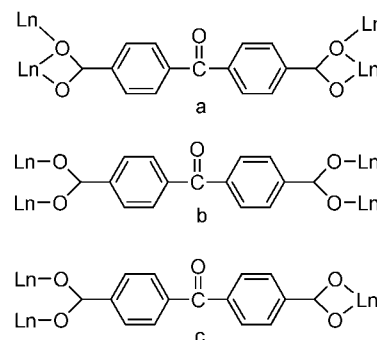
O(1)-Yb(1)-O(6)	79.87(16)	O(4)#2-Yb(1)-N(1)	103.75(16)
O(1)-Yb(1)-O(7)#1	78.19(16)	O(5)#2-Yb(1)-N(1)	75.43(17)
O(2)#1-Yb(1)-O(4)#2	76.02(16)	O(6)-Yb(1)-N(1)	137.86(17)
O(2)#1-Yb(1)-O(5)#2	78.73(16)	O(7)#1-Yb(1)-N(1)	78.75(17)
O(2)#1-Yb(1)-O(6)	74.46(16)	O(1)-Yb(1)-N(2)	77.38(17)
O(2)#1-Yb(1)-O(7)#1	77.93(16)	O(2)#1-Yb(1)-N(2)	140.37(17)
O(4)#2-Yb(1)-O(5)#2	54.58(15)	O(4)#2-Yb(1)-N(2)	72.73(17)
O(4)#2-Yb(1)-O(6)	87.40(16)	O(5)#2-Yb(1)-N(2)	101.65(18)
O(4)#2-Yb(1)-O(7)#1	131.46(16)	O(6)-Yb(1)-N(2)	80.32(18)
O(5)#2-Yb(1)-O(6)	137.87(15)	O(7)#1-Yb(1)-N(2)	141.65(17)
O(5)#2-Yb(1)-O(7)#1	80.62(16)		

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

There are two types of coordination modes of bpndc ligands (Scheme 1, a and b) in **2**. Each carboxyl group links Pr(III) ions through tridentate chelating-bridging and bidentate bridging coordination modes in hexadentate and tetradentate bpndc ligands, respectively. Obviously, the carboxyl oxygen atom between two phenyl rings in bpndc ligand does not participate in the coordination to Pr(III) ion. The asymmetric unit of **2** contains two crystallographically independent Pr(III) ions, as shown in Figure 1. Pr(1) is eight-coordinated by two oxygen atoms [O(6), O(6A)] of two carboxyl groups from two tetradentate bpndc ligands (Scheme 1b) and six oxygen atoms [O(5B), O(5C), O(1), O(2), O(1A), O(2A)] of four chelating-bridging carboxyl groups from four hexadentate bpndc ligands (Scheme 1a), as shown in Figure 1a. The distances of Pr(1)—O (carboxyl) vary from 0.2400(8) to 0.2602(7) nm with mean distance being 0.2498 nm. While Pr(2) is ten-coordinated to eight carboxyl oxygen atoms which comprise two oxygen atoms [O(7), O(7D)] from two carboxyl groups of two tetradentate bpndc ligands (Scheme 1b) and six oxygen atoms [O(2), O(2C), O(4C), O(5C), O(4E), O(5E)] from four chelating-bridging carboxyl groups of four hexadentate bpndc ligands, and two nitrogen atoms [N(1), N(1A)] of one phen molecule (Figure 1b). The Pr(2)—O (carboxyl) bond lengths are in the range of 0.2345(2) to 0.274(2) nm with the mean distance of Pr(2)—O (carboxyl) and the Pr(2)—N bonds being 0.2595 nm and 0.2693(11) nm, respectively. Thus, the mean distance of Pr—O (carboxyl) is 0.2547 nm. Pr(1) and Pr(2) ions are linked together by two hexadentate bpndc ligands with chelating-bridging fashion of the carboxyl groups and one tetradentate bpndc ligand with bridging fashion of the carboxyl group to form an asymmetric unit of **2**. From the difference of coordination numbers between two crystallographically independent Pr(III) ions, it can be known that the steric hindrance around Pr(2) is greater than that around Pr(1) due to the coordinated phen molecule.

In **2**, Pr(1) ions are ligated by bpndc ligands into a 3D structure with 1D channels along *a*-axis. Similarly,

Scheme 1 The coordination modes of bpndc ligands in **1**, **2**, **3** and **4**



Pr(2) atoms are bridged by bpndc ligands into a 3D structure. But the phen molecules coordinated to Pr(2) atoms occupy the 1D channels and are all parallel to each other along the *b*-axis. Thus the condensed 3D structure of **2** is formed by these two interpenetrated 3D structures built up of bpndc ligands and Pr(1) and Pr(2) atoms, respectively. The nearest separation of Pr \cdots Pr is 0.4084 nm.

In **4**, bpndc ligands exhibit two types of coordination modes: (a) two deprotonated carboxyl groups of a bpndc ligand link four Yb(III) ions in bridging bidentate mode (Scheme 1b); (b) two carboxyl groups of a bpndc ligand are both deprotonated and one connects two Yb(III) ions in bridging bidentate fashion, while the other bonds to one Yb(III) ion in chelating bidentate mode (Scheme 1c). Different from **1**, **2** and **3**, there is one coordination environment of Yb(III) ions in **4** for the smaller radius of Yb(III) ion, as shown in Figure 2. Yb(1) is eight-coordinated to two oxygen atoms [O(4B), O(5B)] of one carboxyl group from one tetradentate bpndc ligand (Scheme 1c) in chelating coordination mode and four oxygen atoms [O(1), O(2A), O(6), O(7A)] of two carboxyl groups from two tetradentate bpndc ligands (Scheme 1c) and two carboxyl groups from two tetradentate bpndc ligands (Scheme 1b) in bridging

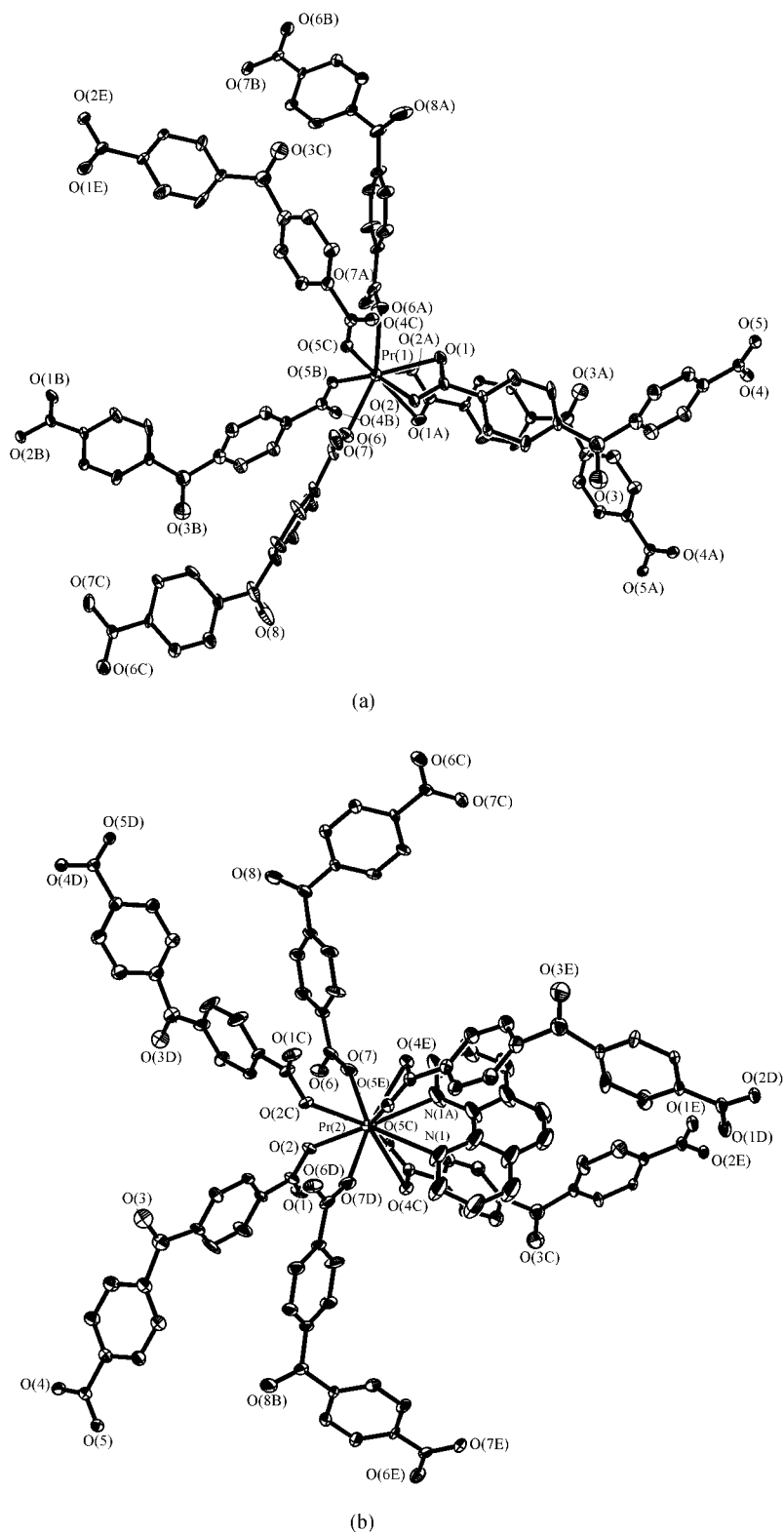


Figure 1 The coordination environments of Pr(1) (a) and Pr(2) (b) of **2** with thermal ellipsoids at 15% probability. All hydrogen atoms are omitted for clarity.

coordination mode, respectively, as well as two nitrogen atoms [N(1), N(2)] of one phen molecule to complete a slightly distorted triangular dodecahedral geometry. The mean Yb—O (carboxyl) and Yb—N distances are 0.2307 and 0.2516 nm, respectively.

Yb(III) ions in **4** are linked by bpndc ligands into a 3D structure with 1D rhombic channels along *b*-axis. In **4**, the tetradentate bpndc ligands (Scheme 1c) along [001] and the tetradentate bpndc ligands (Scheme 1b)

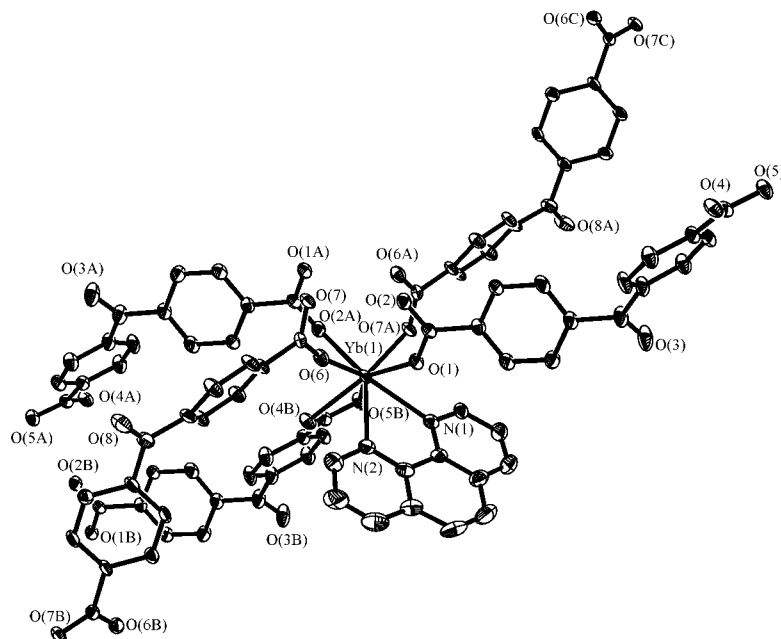


Figure 2 The coordination environment of Yb(1) of **4** with thermal ellipsoids at 25% probability. All hydrogen atoms are omitted for clarity.

along [101] acting as the edges of the rhombic channels connect Yb(III) ions through carboxyl groups, and the Yb(III) ions with distorted triangular dodecahedral geometry are located at the apexes of the rhombic channels (Figure 3). The nearest separation of Yb \cdots Yb is 0.4245 nm, and the lattice water molecules are held in the 3D structure of **4**.

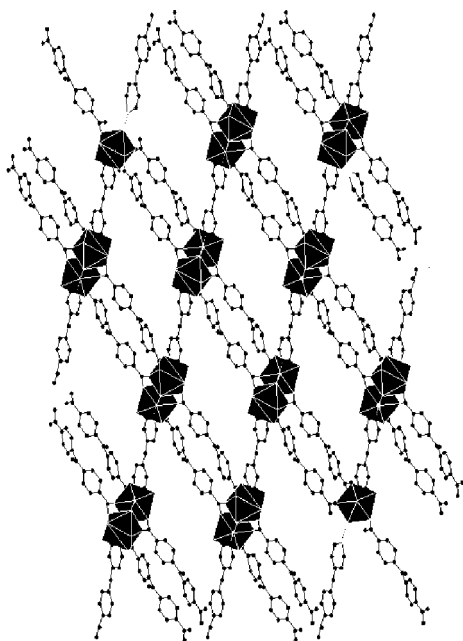


Figure 3 The 3D structure of **4** with 1D rhombic channel viewed along *b*-axis with all phen molecules and hydrogen atoms being omitted for clarity.

In **1** and **3**, the La—O (carboxyl) and Tb—O (carboxyl) bond lengths fall in the range of 0.240(2) to

0.288(2) nm and 0.2235(18) to 0.268(2) nm, respectively. The mean distances of La—O (carboxyl), Pr—O (carboxyl), and Tb—O (carboxyl) are 0.2581, 0.2547, and 0.2450 nm, respectively, the nearest separations of La \cdots La, Pr \cdots Pr, and Tb \cdots Tb are 0.4104, 0.4084, and 0.4006 nm, respectively, and the interlayer distances of La(III), Pr(III) and Tb(III) ions are 1.5482, 1.5468 and 1.5401 nm, respectively. It could be thus concluded that the Ln(III)—O, Ln \cdots Ln and interlayer distances decrease with the contraction of the ionic radii from La(III) to Tb(III).

Due to that the radius of Yb(III) ion is much smaller than that of La(III), Pr(III), and Tb(III) ions, the bpndc ligands in **4** adopt different coordination modes to Yb(III) ions from those in **1**, **2**, and **3**, which directly leads to the completely different 3D structure of **4** from that of **1**, **2**, and **3**. Obviously, the carboxyl groups of bpndc ligands exhibit tridentate chelating-bridging coordination mode for the larger radii of La(III) to Tb(III) ions, and the central metal ions in the asymmetric unit of **1**, **2** and **3** display two crystallographically independent coordination environments with coordination numbers being 8 and 10, respectively, while there is only one coordination environment around Yb(III) ion in **4**. Moreover, the number of bpndc ligands around each Yb(III) ion (5) is less than that around each Ln(III) ion (Ln=La, Pr, and Tb; 6). So it can be clearly seen that the lanthanide contraction has quite an effect on the formation and the structures of the title complexes.

Supplementary materials

The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. CCDC No. 231477-231480 contain the

supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk]

References

- 1 Dimos, A.; Tsaousis, D.; Michaelides, A.; Skoulika, S.; Golhen, S.; Ouahab, L.; Didierjean, C.; Aubry, A. *Chem. Mater.* **2002**, *14*, 2616.
- 2 Kiritsis, V.; Michaelides, A.; Shouluka, S.; Golhen, S.; Ouahab, L. *Inorg. Chem.* **1998**, *37*, 3407.
- 3 Kim, Y.; Jung, D.-Y. *Inorg. Chem.* **2000**, *39*, 1470.
- 4 Kurmoo, M. *J. Mater. Chem.* **1999**, *9*, 2595.
- 5 Vaidhyanathan, R.; Natarajan, S.; Rao, C. N. R. *J. Chem. Soc., Dalton Trans.* **2003**, 1459.
- 6 Wang, Y. B.; Zheng, X. J.; Zhuang, W. J.; Jin, L. P. *Eur. J. Inorg. Chem.* **2003**, *7*, 1355.
- 7 Wang, Y. B.; Zheng, X. J.; Zhuang, W. J.; Jin, L. P. *Eur. J. Inorg. Chem.* **2003**, *19*, 3572.
- 8 Robson, R. *J. Chem. Soc., Dalton Trans.* **2000**, 3735.
- 9 Rosi, N. L.; Eddaoudi, M.; Kim, J.; O'keeffe, M.; Yaghi, O. M. *Angew. Chem., Int. Ed.* **2002**, *41*, 284.
- 10 Pan, L.; Ching, N.; Huang, X. Y.; Li, J. *Inorg. Chem.* **2000**, *39*, 5333.
- 11 Seki, K.; Mori, W. *J. Phys. Chem. B* **2002**, *106*, 1380.
- 12 Pan, L.; Finkel, B. S.; Huang, X. Y.; Li, J. *Chem. Commun.* **2001**, 105.

(E0403152 ZHAO, X. J.)