First Examples of Ternary Lanthanide 2,2′-Diphenyldicarboxylate Complexes: Hydrothermal Syntheses and Structures of Lanthanide Coordination Polymers of 2,2′-Diphenyldicarboxylic Acid and 1,10-Phenanthroline

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In the four new lanthanide coordination polymers $\{[La_2(2,2'\text{-}dpdc)_3(phen)(H_2O)]\cdot 2H_2O\}_n$ (**1**), $[Eu_2(2,2'\text{-}dpdc)_3(phen)(H_2O)_2]_n$ (**2**), $\{[Ln_2(2,2'\text{-}dpdc)_3(phen)_2(H_2O)_2]\cdot 4H_2O\}_n$ [Ln = Tb (**3**), Yb (**4**)] (2,2′-dpdc = 2,2′-diphenyldicarboxylate, phen = 1,10-phenanthroline), prepared by hydrothermal synthesis, the 2,2′-dpdc dianion affords tetradentate, pentadentate, and hexadentate coordination modes. Complex **1** is a two-dimensional network of infinite 1-D chains assembled through π–π interactions, with nine- and ten-coordinate La^{3+}, and arranged in wave-like layers. In **2**, Eu^{3+} possesses nine- and ten-coordinate geometries bridged by 2,2′-dpdc ligands to give a 3-D structure. The isomorphous complexes **3** and **4**, in which Tb^{3+} and Yb^{3+} ions are both nine-coordinate, have two-dimensional structures of 1-D zigzag chains stacked via hydrogen bonds and π–π interactions of phen molecules. The high-resolution emission spectrum of **2** shows two Eu^{3+} ion sites, which is consistent with the results of the X-ray crystal structure analysis.

Introduction

The design and syntheses of one-, two-, three-dimensional coordination polymers is an attractive area of research due to their structural characteristics, such as diverse coordination modes, intriguing architecture, and porosity, and also to their tremendous potential as catalysts,[1,2] luminescent materials,[3−6] in reversible guest exchange,[7−10] and magnetism.[11−14] Coordination polymers are built by the rational selection of metal ions and the use of structurally interesting ligands with specific functionality to construct metal-organic frameworks. The synthesis of coordination polymers with fascinating structures requires careful selection of the organic ligands.

Hydrogen bonds are well suited for the design of polymeric arrangement and crystal engineering because of their important directional interactions, and because they can interlink 1-D, or 2-D structures into higher-dimensionality systems.[15,16] Ligands with aromatic rings may be assembled into a supramolecular structure via π−π interactions. As a building block to construct coordination polymers, 2,2′-diphenyldicarboxylic acid (2,2′-H_2dpdc) is considered because (1) it affords various coordination modes due to its multifunctional carboxylate groups, and it can bridge metal atoms; (2) as a flexible ligand it allows the formation of multi-dimensional structures constructed from different directions; (3) it displays high reactivity to d and f elements, especially lanthanides since the carboxyl group has a strong affinity for Ln^{3+}. A few transition metal coordination polymers using 2,2′-dpdc as bridging ligand have been reported.[17,18] The coordination modes of 2,2′-dpdc ligands in these polymeric complexes are shown in Scheme 1 (a). Lanthanide ions have larger radii and higher coordination numbers than transition metals, as well as luminescent properties for fluorescent probes, and so their introduction into metal-organic frameworks may generate polymers with a distinctive molecular structure and unusual properties. In addition, phen groups can enhance the luminescent properties of lanthanide complexes. However, to the best of our knowledge, there have been no systematic studies on lanthanide supramolecular coordination polymers with the 2,2′-dpdc ligand.

The hydrothermal method is effective for the crystal growth of many coordination polymers.[19,20] Under hydrothermal conditions, the properties of the reactants and the interactions between organic and inorganic partners are quite different from those under conventional conditions in water. Therefore, various simple precursors and metastable compounds may be produced by hydrothermal reactions, and it facilitates crystal growth from solution.[21,22] Thus, we chose the 2,2′-dpdc ligand as a reactant to build multi-dimensional architectures by a hydrothermal reaction. Our current focus on rational synthetic strategies for lanthanide coordination polymers, using the hydrothermal method, has yielded some fascinating crystal structures with luminescent properties.[23−25] Herein, we report the syntheses and struc-

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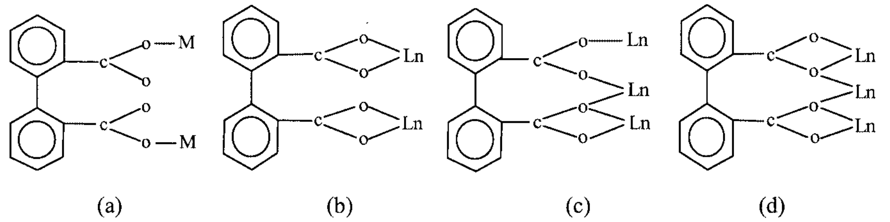

Scheme 1. Coordination modes of 2,2′-dpdc in transition metal 2,2′-dpdc complexes and complexes **1−4**

tures of four lanthanide complexes with 2,2′-dpdc ligand and phen ligand.

Results and Discussion

Crystal data of the title complexes (Table 1) and selected bond lengths and angles of **1−4** (Tables 2−4) are given here. The 2,2′-dpdc ligands are all completely deprotonated and afford three types of coordination modes (Scheme 1, b, c and d). The crystallographic analyses reveal a two-dimensional network (**1**, **3** and **4**) or a three-dimensional structure (**2**) made up of infinite 1-D chains, and that complexes **3** and **4** are isomorphous.

Crystal Structure of $\{[La_2(2,2'\text{-dpdc})_3(phen)(H_2O)]\cdot 2H_2O\}_n$ (1)

In the crystal structure of **1**, $[La_2(2,2'\text{-dpdc})_3(phen)(H_2O)]\cdot 2H_2O$, the 2,2′-dpdc ligands exhibit penta- and hexadentate coordination modes (Scheme 1, c and d). In an asymmetric unit, there are two types of environment for La^{3+} centers (Figure 1). La(1) is coordinated to ten atoms: eight carboxylate oxygen atoms (O1, O2, O1A, O4A, O5A, O6A, O11A, O12A) of three pentadentate 2,2′-dpdc ligands and one hexadentate 2,2′-dpdc ligand, and two nitrogen atoms (N1, N2) of one phen ligand. The mean La(1)−O(carboxylate) distance is 2.670 Å. La(2) is coordinated by eight carboxylate oxygen atoms (O3, O5, O7, O9, O10, O8B, O10B, O11B) of three pentadentate 2,2′-dpdc ligands and two hexadentate 2,2′-dpdc ligands, and one oxygen atom (O13) provided by a water molecule. The mean La(2)−O(carboxylate) distance is 2.568 Å. La(1) and La(2) are linked by a pentadentate 2,2′-dpdc ligand with an interatomic distance of 7.990 Å. Clearly, the steric hindrance around La(1) is greater than that around La(2) − La(1)−O(carboxylate) bonds are longer than La(2)−O(carboxylate) bonds. Influenced by the steric hindrance and coordination modes of the 2,2′-dpdc ligand and phen, the carboxylate planes of the pentadentate 2,2′-dpdc ligand connecting La(1) and La(2) deflect their aromatic rings with similar dihedral angles, 38.1° and 39.0°.

The one-dimensional chain of **1** (Figure 2) can be viewed as composed of an $\{[La_2(2,2'\text{-dpdc})_3(phen)(H_2O)]\cdot 2H_2O\}_2$ building block. In Figure 2, La1A and La1C (or La1B and La1D) are associated by two chelating-bridging carboxylate groups of two pentadentate 2,2′-dpdc ligands and are 4.487Å apart; La2C and La1A (La2D and La1B, La1C and La2A, or La1D and La2B) are linked by three carboxylate groups of two pentadentate 2,2′-dpdc ligands and one hexa-

Table 1. Crystal data for **1−4**

	1	**2**	**3**	**4**
Empirical formula	$C_{54}H_{38}La_2N_2O_{15}$	$C_{54}Eu_2H_{36}N_2O_{14}$	$C_{33}H_{26}N_2O_9Tb$	$C_{33}H_{26}N_2O_9Yb$
FW	1232.68	1240.77	753.54	767.58
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/n$	$C2/c$	$C2/c$
a [Å]	12.390(3)	14.378(6)	24.480(8)	24.412(10)
b [Å]	15.419(3)	20.933(9)	12.104(4)	12.129(4)
c [Å]	15.951(3)	15.457(6)	22.940(7)	22.580(8)
α [°]	117.53(3)	90(3)	90	90
β [°]	95.18(3)	95.757(7)	115.571(5)	115.167(10)
γ [°]	107.28(3)	90	90	90
Z	2	4	8	8
V [Å^3]	2485.4(9)	4629(3)	6131(3)	6051(4)
$\rho_{calcd.}$ [g·cm^{-3}]	1.647	1.781	1.613	1.696
T [K]	293(2)	293(2)	293(2)	293(2)
μ [mm^{-1}]	1.768	2.760	2.363	3.150
Reflections collected: total, independent	14108, 9956	18917, 8168	12234, 5311	12678, 5542
R_{int}	0.0442	0.0376	0.0407	0.0374
λ (Mo-K_α) [Å]	0.71073	0.71073	0.71073	0.71073
R_1, wR_2 [$I > 2\sigma(I)$]	0.0517, 0.1033	0.0290, 0.0548	0.0320, 0.0729	0.0378, 0.0833

Table 2. Selected bond lengths [Å] and bond angles [°] for **1**; symmetry operations: #1: $-x+1, -y+1, -z$; #2: $x, y, z-1$; #3: $-x+1, -y+1, -z+1$

La(1)−O(1)	2.667(5)	La(2)−O(3)	2.481(5)
La(1)−O(1)#1	2.676(5)	La(2)−O(5)	2.609(5)
La(1)−O(2)	2.683(6)	La(2)−O(7)	2.470(6)
La(1)−O(4)#1	2.500(5)	La(2)−O(8)#3	2.610(6)
La(1)−O(5)#1	2.684(5)	La(2)−O(9)	2.648(5)
La(1)−O(6)#1	2.732(5)	La(2)−O(10)	2.633(5)
La(1)−O(11)#2	2.912(5)	La(2)−O(10)#3	2.511(5)
La(1)−O(12)#2	2.508(5)	La(2)−O(11)#3	2.581(5)
La(1)−N(1)	2.782(6)	La(2)−O(13)	2.726(8)
La(1)−N(2)	2.754(7)	O(11)#2−La(1)−N(1)	110.84(17)
O(1)−La(1)−O(2)	49.42(16)	O(11)#2−La(1)−N(2)	71.33(17)
O(1)−La(1)−O(1)#1	65.78(19)	O(12)#2−La(1)−N(1)	71.97(17)
O(1)−La(1)−O(4)#1	99.24(17)	O(12)#2−La(1)−N(2)	73.16(19)
O(1)−La(1)−O(5)#1	81.43(15)	N(1)−La(1)−N(2)	60.2(2)
O(1)−La(1)−O(6)#1	71.20(16)	O(3)−La(2)−O(5)	73.88(17)
O(1)−La(1)−O(11)#2	139.77(15)	O(3)−La(2)−O(7)	140.96(18)
O(1)−La(1)−O(12)#2	130.34(18)	O(3)−La(2)−O(9)	82.37(19)
O(1)−La(1)−N(1)	102.42(18)	O(3)−La(2)−O(10)	119.31(17)
O(1)−La(1)−N(2)	147.85(17)	O(3)−La(2)−O(13)	68.4(2)
O(1)#1−La(1)−O(4)#1	69.26(16)	O(3)−La(2)−O(8)#3	78.75(18)
O(1)#1−La(1)−O(5)#1	117.92(15)	O(3)−La(2)−O(10)#3	148.51(19)
O(1)#1−La(1)−O(6)#1	136.71(16)	O(3)−La(2)−O(11)#3	94.65(17)
O(1)#1−La(1)−O(11)#2	146.87(16)	O(5)−La(2)−O(7)	69.16(16)
O(1)#1−La(1)−O(12)#2	141.74(16)	O(5)−La(2)−O(9)	76.06(16)
O(1)#1−La(1)−N(1)	70.41(17)	O(5)−La(2)−O(10)	116.58(16)
O(1)#1−La(1)−N(2)	82.40(17)	O(5)−La(2)−O(13)	117.8(2)
O(2)−La(1)−O(1)#1	91.18(16)	O(5)−La(2)−O(8)#3	150.75(17)
O(2)−La(1)−O(4)#1	148.52(17)	O(5)−La(2)−O(10)#3	130.72(17)
O(2)−La(1)−O(5)#1	105.86(16)	O(5)−La(2)−O(11)#3	68.63(16)
O(2)−La(1)−O(6)#1	63.24(16)	O(7)−La(2)−O(9)	77.06(19)
O(2)−La(1)−O(11)#2	121.26(16)	O(7)−La(2)−O(10)	69.20(18)
O(2)−La(1)−O(12)#2	83.79(17)	O(7)−La(2)−O(13)	141.8(2)
O(2)−La(1)−N(1)	72.10(19)	O(7)−La(2)−O(8)#3	133.52(17)
O(2)−La(1)−N(2)	131.32(17)	O(7)−La(2)−O(10)#3	69.86(18)
O(4)#1−La(1)−O(5)#1	65.95(16)	O(7)−La(2)−O(11)#3	83.48(19)
O(4)#1−La(1)−O(6)#1	114.49(16)	O(8)#3−La(2)−O(10)#3	78.52(18)
O(4)#1−La(1)−O(11)#2	83.39(16)	O(8)#3−La(2)−O(11)#3	124.5(2)
O(4)#1−La(1)−O(12)#2	126.89(18)	O(9)−La(2)−O(10)	49.47(15)
O(4)#1−La(1)−N(1)	120.11(18)	O(9)−La(2)−O(13)	140.5(2)
O(4)#1−La(1)−N(2)	72.12(18)	O(9)−La(2)−O(8)#3	90.4(2)
O(5)#1−La(1)−O(6)#1	48.62(16)	O(9)−La(2)−O(10)#3	119.24(16)
O(5)#1−La(1)−O(11)#2	62.89(15)	O(9)−La(2)−O(11)#3	143.89(18)
O(5)#1−La(1)−O(12)#2	99.84(16)	O(10)−La(2)−O(13)	124.7(2)
O(5)#1−La(1)−N(1)	171.63(16)	O(10)−La(2)−O(8)#3	68.86(19)
O(5)#1−La(1)−N(2)	119.78(18)	O(10)−La(2)−O(10)#3	71.29(18)
O(6)#1−La(1)−O(11)#2	71.32(16)	O(10)−La(2)−O(11)#3	145.99(16)
O(6)#1−La(1)−O(12)#2	73.30(17)	O(10)#3−La(2)−O(11)#3	80.69(16)
O(6)#1−La(1)−N(1)	125.29(18)	O(13)−La(2)−O(8)#3	59.0(2)
O(6)#1−La(1)−N(2)	140.84(18)	O(13)−La(2)−O(10)#3	81.2(2)
O(11)#2−La(1)−O(12)#2	47.73(15)	O(13)−La(2)−O(11)#3	67.3(2)

dentate 2,2′-dpdc ligand through bridging or chelating-bridging coordination modes, and are 4.398 Å apart. La2A and La2D of two neighboring building blocks are connected by two bridging carboxylate groups of two pentadentate 2,2′-dpdc ligands and by two chelating-bridging carboxylate groups of two hexadentate 2,2′-dpdc ligands. Thus, the number of 2,2′-dpdc ligands linking two La^{3+} ions (4 for La2A and La2D, 3 for La2C and La1A, 2 for La1A and La1C, and 1 for La1A and La2A) increases with the decreasing distances between the two La^{3+} ions in the 1-D chain structure; the difference in La···La distances in **1** may be due to the different coordination modes and spatial arrangement of the 2,2′-dpdc ligands. In the chain of **1**, the lattice water molecules form strong hydrogen bonds with the carboxylate oxygen atoms of 2,2′-dpdc ligands and the coordinated water molecules simultaneously (Figure 2). The oxygen atoms of the carboxylate groups and coordinated water behave as H-bond acceptors. Thus, three types of hydrogen-bond interactions are observed (Figure 2): (1) between coordinated water (O13A) and lattice water (O15A), $O_w \cdots O_w$ (3.066 Å); (2) between lattice water (O15A) and carboxylate oxygen (O3A and O8BA), $O_w \cdots$O(carboxylate)

Table 3. Selected bond lengths [Å] and bond angles [°] for **2**;symmetry operations: #1: $-x, -y + 2, -z + 2$; #2: $-x + 1, -y + 2, -z + 2$

Eu(1)−O(2)	2.464(3)	Eu(2)−O(1)	2.820(3)
Eu(1)−O(3)	2.350(3)	Eu(2)−O(2)	2.567(3)
Eu(1)−O(3)#2	2.534(3)	Eu(2)−O(7)	2.496(3)
Eu(1)−O(4)#2	2.505(3)	Eu(2)−O(8)	2.671(3)
Eu(1)−O(5)	2.573(3)	Eu(2)−O(9)	2.431(3)
Eu(1)−O(6)	2.414(3)	Eu(2)−O(10)	2.465(3)
Eu(1)−O(7)	2.459(3)	Eu(2)−O(13)	2.497(3)
Eu(1)−O(11)#1	2.490(3)	Eu(2)−O(14)	2.435(3)
Eu(1)−O(12)#1	2.397(3)	Eu(2)−N(1)	2.657(4)
O(2)−Eu(1)−O(3)	90.54(10)	Eu(2)−N(2)	2.582(4)
O(2)−Eu(1)−O(3)#2	157.12(9)	O(1)−Eu(2)−O(13)	101.51(10)
O(2)−Eu(1)−O(4)#2	145.17(10)	O(1)−Eu(2)−O(14)	64.08(10)
O(2)−Eu(1)−O(5)	73.53(10)	O(1)−Eu(2)−N(1)	127.96(11)
O(2)−Eu(1)−O(6)	121.06(10)	O(1)−Eu(2)−N(2)	135.66(11)
O(2)−Eu(1)−O(7)	67.07(10)	O(2)−Eu(2)−O(7)	64.97(9)
O(2)−Eu(1)−O(11)#1	74.25(10)	O(2)−Eu(2)−O(8)	105.42(10)
O(2)−Eu(1)−O(12)#1	96.64(11)	O(2)−Eu(2)−O(9)	84.43(10)
O(3)−Eu(1)−O(5)	81.43(10)	O(2)−Eu(2)−O(10)	113.07(10)
O(3)−Eu(1)−O(6)	100.51(10)	O(2)−Eu(2)−O(13)	69.97(10)
O(3)−Eu(1)−O(7)	150.85(10)	O(2)−Eu(2)−O(14)	80.21(10)
O(3)−Eu(1)−O(3)#2	67.58(12)	O(2)−Eu(2)−N(1)	146.41(11)
O(3)−Eu(1)−O(4)#2	117.11(10)	O(2)−Eu(2)−N(2)	147.99(12)
O(3)−Eu(1)−O(11)#1	121.01(11)	O(7)−Eu(2)−O(8)	49.79(9)
O(3)−Eu(1)−O(12)#1	73.44(11)	O(7)−Eu(2)−O(9)	144.53(10)
O(3)#2−Eu(1)−O(5)	108.05(10)	O(7)−Eu(2)−O(10)	154.76(10)
O(3)#2−Eu(1)−O(11)#1	110.54(10)	O(7)−Eu(2)−O(13)	85.35(10)
O(3)#2−Eu(1)−O(12)#1	71.46(10)	O(7)−Eu(2)−O(14)	71.40(10)
O(4)#2−Eu(1)−O(5)	128.26(10)	O(7)−Eu(2)−N(1)	88.11(11)
O(4)#2−Eu(1)−O(3)#2	51.64(9)	O(7)−Eu(2)−N(2)	121.70(11)
O(4)#2−Eu(1)−O(11)#1	73.34(10)	O(8)−Eu(2)−O(9)	131.65(11)
O(4)#2−Eu(1)−O(12)#1	73.68(11)	O(8)−Eu(2)−O(10)	141.45(10)
O(5)−Eu(1)−O(6)	51.92(10)	O(8)−Eu(2)−O(13)	72.63(11)
O(5)−Eu(1)−O(7)	74.59(10)	O(8)−Eu(2)−O(14)	105.70(11)
O(5)−Eu(1)−O(11)#1	140.54(10)	O(8)−Eu(2)−N(1)	65.93(11)
O(5)−Eu(1)−O(12)#1	153.00(11)	O(8)−Eu(2)−N(2)	71.98(11)
O(6)−Eu(1)−O(7)	77.56(10)	O(9)−Eu(2)−O(10)	53.33(10)
O(6)−Eu(1)−O(3)#2	71.77(10)	O(9)−Eu(2)−O(13)	66.73(11)
O(6)−Eu(1)−O(4)#2	76.63(11)	O(9)−Eu(2)−O(14)	122.64(11)
O(6)−Eu(1)−O(11)#1	136.46(11)	O(9)−Eu(2)−N(1)	126.43(12)
O(6)−Eu(1)−O(12)#1	142.11(11)	O(9)−Eu(2)−N(2)	75.62(12)
O(7)−Eu(1)−O(3)#2	135.78(10)	O(10)−Eu(2)−O(13)	118.44(11)
O(7)−Eu(1)−O(4)#2	91.03(10)	O(10)−Eu(2)−O(14)	83.40(10)
O(7)−Eu(1)−O(11)#1	72.26(10)	O(10)−Eu(2)−N(1)	82.50(11)
O(7)−Eu(1)−O(12)#1	125.49(10)	O(10)−Eu(2)−N(2)	74.31(11)
O(11)#1−Eu(1)−O(12)#1	53.25(10)	O(13)−Eu(2)−O(14)	148.01(10)
O(1)−Eu(2)−O(2)	47.94(9)	O(13)−Eu(2)−N(1)	130.30(12)
O(1)−Eu(2)−O(7)	102.38(9)	O(13)−Eu(2)−N(2)	79.15(12)
O(1)−Eu(2)−O(8)	151.27(9)	O(14)−Eu(2)−N(1)	71.98(11)
O(1)−Eu(2)−O(9)	64.78(10)	O(14)−Eu(2)−N(2)	131.69(12)
O(1)−Eu(2)−O(10)	66.53(10)	N(1)−Eu(2)−N(2)	63.12(13)

(3.003 Å), (3) another between lattice water (O14A) and carboxylate oxygen (O2B), $O_w \cdots O$(carboxylate) (3.033 Å). The phen molecules in a chain of **1** are parallel, but no π−π stacking interactions are found. However, the phen molecules of neighboring chains, which are stacked along the *a* axis, are parallel and 3.48 Å apart. Therefore, the chains packing in the *a* direction interdigitate to assemble into an extended network through π−π stacking interactions of phen molecules. The La^{3+} ions are arranged in a ruffled sheet parallel to the *ac* plane in waving pattern and the 2,2′-dpdc ligands and phen molecules run through the whole sheet.

Crystal Structure of $[Eu_2(2,2'\text{-dpdc})_3(\text{phen})\cdot(H_2O)_2]_n$ (2)

Complex **2** is a 3-D structure of $[Eu_2(2,2'\text{-dpdc})_3(\text{phen})\cdot(H_2O)_2]_n$. Unlike **1**, the 2,2′-dpdc ligands in **2** present not only pentadentate and hexadentate coordination modes, but also a tetradentate one (Scheme 1, b, c, and d). The asymmetric unit of **2** also contains two crystallographically independent Eu^{3+} ions (Figure 3). Eu(1) is coordinated by three oxygen atoms (O5, O6 and O7) of two carboxylate groups of a pentadentate 2,2′-dpdc ligand, two oxygen atoms (O2, O3) of two carboxylate groups of one

Table 4. Selected bond lengths [Å] and bond angles [°] for **3** and **4**; symmetry operation: #1 $-x$, $-y + 1$, $-z$

3		4	
Tb(1)−O(1)	2.423(3)	Yb(1)−O(1)	2.358(4)
Tb(1)−O(2)	2.379(3)	Yb(1)−O(2)	2.320(4)
Tb(1)−O(3)#1	2.400(3)	Yb(1)−O(3)#1	2.299(5)
Tb(1)−O(4)#1	2.509(3)	Yb(1)−O(4)#1	2.607(6)
Tb(1)−O(5)	2.405(3)	Yb(1)−O(5)	2.316(4)
Tb(1)−O(6)	2.564(3)	Yb(1)−O(6)	2.558(4)
Tb(1)−O(7)	2.443(3)	Yb(1)−O(7)	2.362(4)
Tb(1)−N(1)	2.532(3)	Yb(1)−N(1)	2.466(5)
Tb(1)−N(2)	2.548(3)	Yb(1)−N(2)	2.489(5)
O(1)−Tb(1)−O(2)	54.04(10)	O(1)−Yb(1)−O(2)	55.56(14)
O(1)−Tb(1)−O(5)	84.48(10)	O(1)−Yb(1)−O(5)	82.86(15)
O(1)−Tb(1)−O(6)	76.80(10)	O(1)−Yb(1)−O(6)	76.53(15)
O(1)−Tb(1)−O(7)	128.15(10)	O(1)−Yb(1)−O(7)	128.79(15)
O(1)−Tb(1)−O(3)#1	87.55(11)	O(1)−Yb(1)−O(3)#1	85.12(16)
O(1)−Tb(1)−O(4)#1	77.29(10)	O(1)−Yb(1)−O(4)#1	75.57(15)
O(1)−Tb(1)−N(1)	156.48(11)	O(1)−Yb(1)−N(1)	153.79(16)
O(1)−Tb(1)−N(2)	128.32(10)	O(1)−Yb(1)−N(2)	129.27(15)
O(2)−Tb(1)−O(5)	133.66(10)	O(2)−Yb(1)−O(5)	133.18(15)
O(2)−Tb(1)−O(6)	74.20(10)	O(2)−Yb(1)−O(6)	74.18(15)
O(2)−Tb(1)−O(7)	106.12(10)	O(2)−Yb(1)−O(7)	105.47(15)
O(2)−Tb(1)−O(3)#1	81.46(10)	O(2)−Yb(1)−O(3)#1	82.58(17)
O(2)−Tb(1)−O(4)#1	114.68(10)	O(2)−Yb(1)−O(4)#1	116.14(15)
O(2)−Tb(1)−N(1)	141.17(10)	O(2)−Yb(1)−N(1)	142.61(16)
O(2)−Tb(1)−N(2)	76.40(10)	O(2)−Yb(1)−N(2)	76.31(15)
O(3)#1−Tb(1)−O(4)#1	53.04(10)	O(3)#1−Yb(1)−O(4)#1	52.40(17)
O(3)#1−Tb(1)−N(1)	79.72(11)	O(3)#1−Yb(1)−N(1)	80.86(17)
O(3)#1−Tb(1)−N(2)	69.93(11)	O(3)#1−Yb(1)−N(2)	72.78(17)
O(4)#1−Tb(1)−N(1)	79.26(11)	O(4)#1−Yb(1)−N(1)	78.33(16)
O(4)#1−Tb(1)−N(2)	116.97(10)	O(4)#1−Yb(1)−N(2)	118.64(16)
O(5)−Tb(1)−O(6)	77.14(11)	O(5)−Yb(1)−O(6)	76.10(16)
O(5)−Tb(1)−O(7)	82.25(10)	O(5)−Yb(1)−O(7)	83.04(15)
O(5)−Tb(1)−O(3)#1	120.36(10)	O(5)−Yb(1)−O(3)#1	117.37(18)
O(5)−Tb(1)−O(4)#1	67.57(10)	O(5)−Yb(1)−O(4)#1	65.07(16)
O(5)−Tb(1)−N(1)	85.03(11)	O(5)−Yb(1)−N(1)	84.11(16)
O(5)−Tb(1)−N(2)	147.11(11)	O(5)−Yb(1)−N(2)	147.85(15)
O(6)−Tb(1)−O(7)	51.41(9)	O(6)−Yb(1)−O(7)	52.30(14)
O(6)−Tb(1)−O(3)#1	155.59(11)	O(6)−Yb(1)−O(3)#1	155.87(16)
O(6)−Tb(1)−O(4)#1	137.69(10)	O(6)−Yb(1)−O(4)#1	134.26(16)
O(6)−Tb(1)−N(1)	121.02(10)	O(6)−Yb(1)−N(1)	121.91(15)
O(6)−Tb(1)−N(2)	105.34(11)	O(6)−Yb(1)−N(2)	107.09(16)
O(7)−Tb(1)−O(3)#1	141.25(10)	O(7)−Yb(1)−O(3)#1	143.96(16)
O(7)−Tb(1)−O(4)#1	139.05(10)	O(7)−Yb(1)−O(4)#1	138.04(15)
O(7)−Tb(1)−N(1)	70.87(10)	O(7)−Yb(1)−N(1)	71.62(15)
O(7)−Tb(1)−N(2)	75.04(10)	O(7)−Yb(1)−N(2)	75.18(15)
N(1)−Tb(1)−N(2)	65.31(11)	N(1)−Yb(1)−N(2)	66.83(16)

hexadentate 2,2′-dpdc ligand in bridging mode, two oxygen atoms (O3A, O4A) of one carboxylate group of another hexadentate 2,2′-dpdc ligand in chelating mode, and two oxygen atoms (O11A, O12A) of a carboxylate group of a tetradentate 2,2′-dpdc ligand. The coordination sphere of Eu(2) differs from that of Eu(1) and is ten-coordinate. Around Eu(2), one tetradentate 2,2′-dpdc ligand chelates to Eu(2) through O9 and O10, one hexadentate 2,2′-dpdc ligand is simultaneously coordinated to Eu(1) and Eu(2) through O1 and O2 in chelating-bridging mode, and the pentadentate 2,2′-dpdc ligand is coordinated to Eu(1) and Eu(2) through O7 and O8 in the same mode. Of these oxygen atoms, O2 and O7 act as μ$_2$-oxygen atoms, connecting Eu(1) and Eu(2) with an Eu(1)···Eu(2) distance of 4.185 Å. Besides these six oxygen atoms, there are two nitrogen atoms (N1, N2) of one phen molecule and two oxygen atoms (O13, O14) of two coordinated water molecules to complete the ten-coordinate geometry of Eu(2). The mean Eu(2)−O(carboxylate) distance (2.575Å) is longer than Eu(1)−O(carboxylate) (2.465 Å), possibly because Eu(2) has a larger coordination number than Eu(1) [Eu(1) is nine-coordinate], resulting in a larger steric effect in the Eu(2) environment.

Unlike **1**, in the 1-D chain of **2**, every four Eu^{3+} (Eu2B, Eu1B, Eu1D, Eu2D), two tetradentate 2,2′-dpdc ligands, two pentadentate 2,2′-dpdc ligands and two hexadentate 2,2′-dpdc ligands fabricate one {[Eu$_2$(2,2′-dpdc)$_3$(phen)]·(H$_2$O)$_2$}$_2$ building block along the *a* axis (Figure 4). In each building block, two carboxylate groups of the hexadentate 2,2′-dpdc ligand are coordinated to

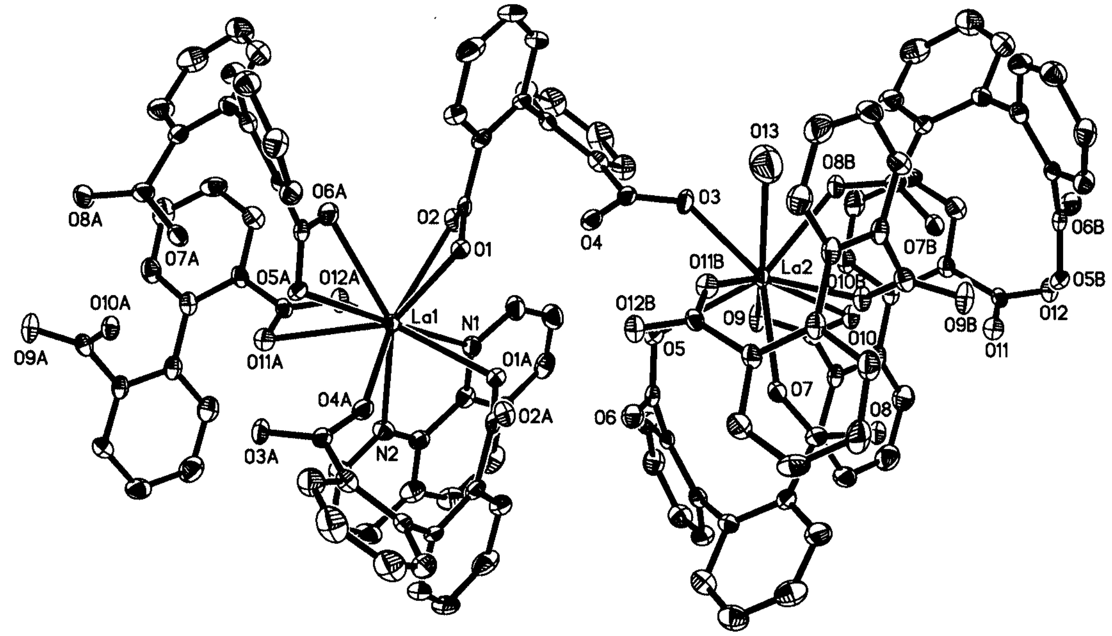

Figure 1. Coordination environment of the two La^{III} ions in **1** with thermal ellipsoids at 30% probability; all hydrogen atoms are omitted for clarity

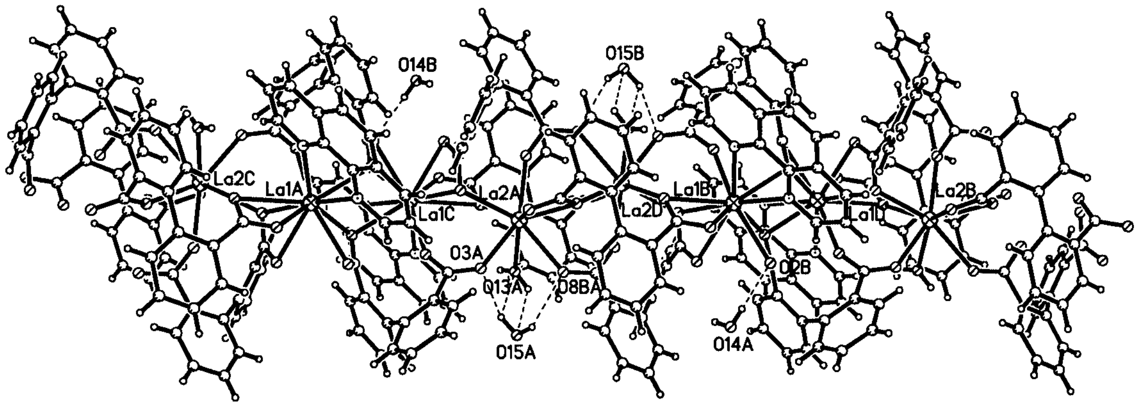

Figure 2. 1-D chain of **1** viewed along the *a* axis; hydrogen bonds containing lattice water are shown as dotted lines

three Eu^{3+} ions in chelating-bridging coordination mode. Each pentadentate 2,2′-dpdc ligand only links two Eu^{3+} ions belonging to the same asymmetric unit. Two pentadentate and two hexadentate 2,2′-dpdc ligands construct one building block through bridging four Eu^{3+} ions, while two carboxylate groups of each tetradentate 2,2′-dpdc ligand coordinate with two Eu^{3+} ions of two adjacent building blocks in chelating-bridging mode. Thus, it is tetradentate 2,2′-dpdc ligands that connect two adjacent building blocks, forming a 1-D infinite chain along the *a* axis. The phen molecules of adjacent chains are parallel and stacked next to each other (3.47 Å apart). The carbon atoms of these parallel phen molecules are also involved in weak C−H···O hydrogen bonds with the carboxylate oxygen atoms of 2,2′-dpdc ligands, and the C···O(carboxylate) distances are all 3.198 Å (Figure 5). Consequently, a three-dimensional supramolecular polymer is generated not only by coordination bonds but also by intermolecular hydrogen bonds and interchain π−π interactions.

Crystal Structure of $\{[Ln_2(2,2'\text{-dpdc})_3(phen)_2(H_2O)_2]\cdot 4H_2O\}_n$ [Ln=Tb (3), Yb (4)]

Since complexes **3** and **4** are isomorphous we will only describe the crystal structure of **3**. In **3**, each 2,2′-dpdc ligand shows the tetradentate coordination mode only (Scheme 1, b). Each Tb^{3+} is nine-coordinate and the coordination geometry is roughly a tricapped trigonal prism. Around each Tb center are two nitrogen atoms (N1, N2) of one phen, six carboxylate oxygen atoms (O1, O2, O3A, O4A, O6, O7) of three chelating carboxylate groups of three tetradentate bridging 2,2′-dpdc ligands, and one oxygen atom (O5) of coordinated water (Figure 6). The mean Tb−O(carboxylate) distance (2.453 Å) is longer than those in $[Tb_2(BDC)_3(H_2O)_4]_n$ [3] and $[Tb_2(oba)_3(2,2'\text{-bpy})_2]_n$,[27]

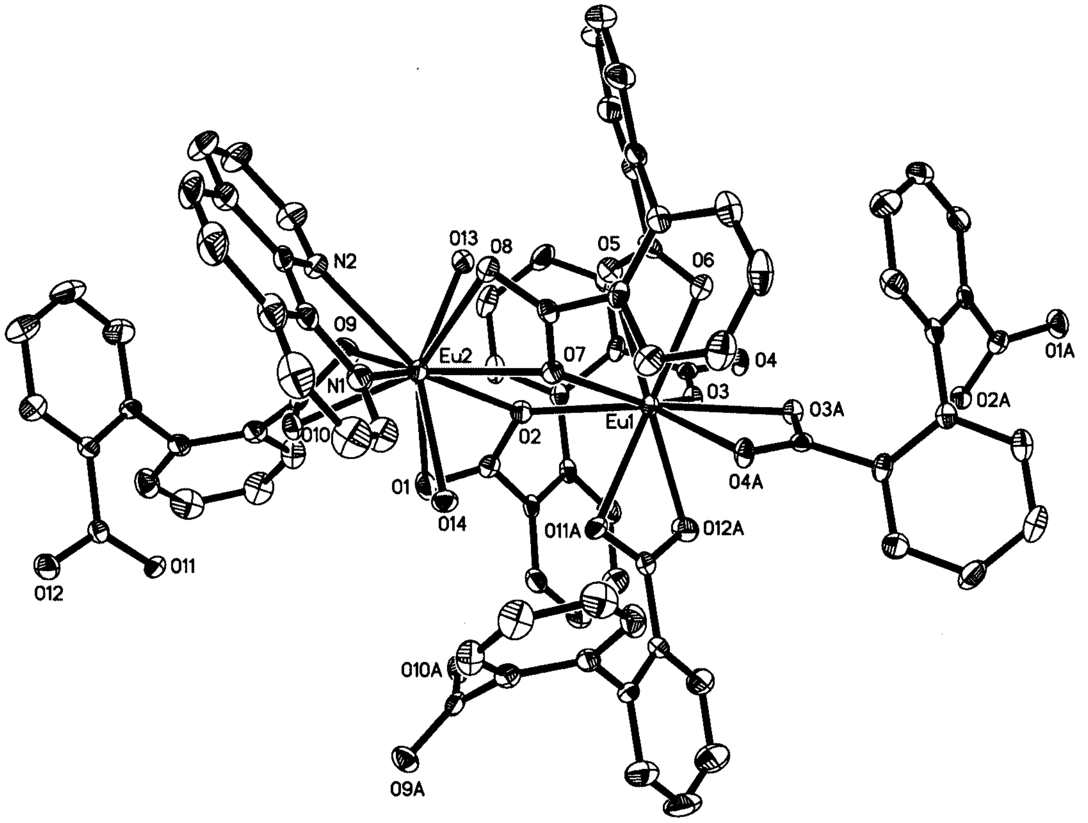

Figure 3. Coordination environment of the two Eu^{III} ions in **2** with thermal ellipsoids at 30% probability; all hydrogen atoms are omitted for clarity

which may be due to the larger steric hindrance of 2,2′-dpdc ligands and phen molecules. The coordination environment shows that there are three tetradentate 2,2′-dpdc ligands to chelate each Tb^{3+}, which is fewer than the 2,2′-dpdc ligands coordinated with La^{3+}. In addition, the 2,2′-dpdc ligand presents a tetradentate coordination mode to furnish the nine-coordinate coordination geometry in **3** and **4** because of the smaller radii of Tb^{3+} and Yb^{3+} ions.

In **3**, the dinuclear species $[Tb_2(2,2'\text{-dpdc})_3(phen)_2(H_2O)_2]\cdot4H_2O$ is centrosymmetric, and these units are linked through 2,2′-dpdc ligands; a 1-D infinite zigzag chain is then constructed through coordination bonds. In each dinuclear motif, there are three chelating-bridging tetradentate 2,2′-dpdc ligands and two phen molecules coordinated to two Tb^{3+} ions. Two Tb^{3+} ions are linked by two chelating-bridging tetradentate 2,2′-dpdc ligands with a $Tb^{3+}\cdots Tb^{3+}$ distance of 6.992 Å. Two neighboring $[Tb_2(2,2'\text{-dpdc})_3(phen)_2(H_2O)_2]\cdot4H_2O$ dinuclear motifs are connected by the third 2,2′-dpdc ligand by four $Tb^{3+}-O$(carboxylate) bonds. Two adjacent Tb^{3+} ions of two different dinuclear motifs are 6.317 Å apart.

In the 2-D network of **3**, there are hydrogen bonds between a coordination carboxylate atom (O7AD) and the C−H of a phen molecule (C8FC) of a neighboring chain, C···O(carboxylate) (3.313 Å). At the same time, the adjacent chains are stacked in a staggered fashion along the *b* axis through π−π interactions between phen molecules of two neighboring chains (3.434 Å apart). Hence, phen is crucial to the formation and stabilization of the structure of **3** because of its simultaneous participation in formation of the hydrogen bonds and π−π interactions. Thus, a two-dimensional layered supramolecular array parallel to the *bc* plane is constructed with the chains pulled together by a series of interchain hydrogen bonds and π−π interactions along the *b* axis (Figure 7). The Tb^{3+} ions are distributed on the layer in an undulating way and the Tb···Tb distance of neighboring chains is 12.104 Å. The 2,2′-dpdc ligands and phen interdigitate the whole undulating plane.

In terms of the structural characteristics and the formation of the supramolecular architecture of the title complexes, several parallels can be obtained: (1) Each complex has one or two coordinated water molecules to meet the high coordination number of Ln^{III} ions. (2) Much lattice water is held within the 1-D chains of **1**, **3** and **4**, therefore extensive intramolecular hydrogen bonds are formed among lattice water molecules, coordinated water molecules and carboxylate groups, which further stabilize the 1-D chain structure. Therefore, water molecules not only act as a reaction medium in the formation of these supramolecular structures, but also contribute positively to the interaction with 2,2′-dpdc ligands by hydrogen bonds. (3) The 2-D network (for **1**, **3** and **4**) and the 3-D structure (for **2**) are all constructed by 1-D chains linked through hydrogen bonds and packed by π−π interactions between phen molecules of adjacent chains (for **1**, **2**, **3**, and **4**). However, the title complexes also exhibit considerable differences with regard to

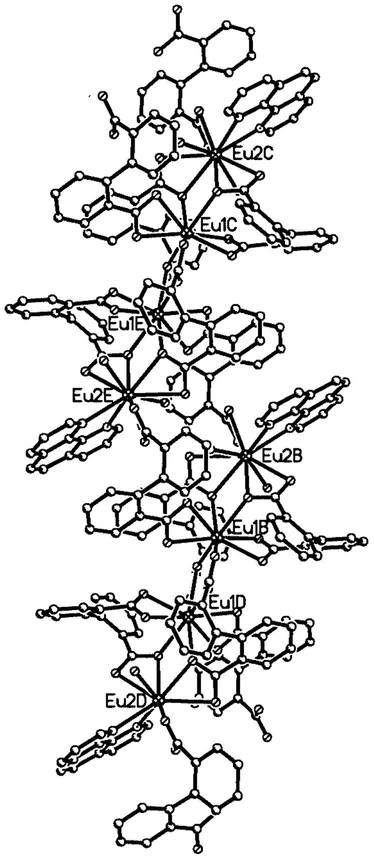

Figure 4. 1-D chain of **2** viewed along the *b* axis; all hydrogen atoms are omitted for clarity

the lattice water, hydrogen bonds, and π−π interactions. One difference is the absence of lattice water within the structure of **2** and, correspondingly, no O···H−O hydrogen bonds are observed. In addition, a 3-D network of **2** is formed by O···C−H (phen) hydrogen bonds and π−π interactions of phen from different orientations.

Lanthanide contraction clearly effects the formation and crystal structure of the title compounds. First, the Ln−O bond lengths decrease with increasing lanthanide atomic number: the mean Ln−O(carboxylate) distance follows the order La−O(carboxylate) > Eu−O(carboxylate) > Tb−O(carboxylate) > Yb−O(carboxylate); the mean Ln−O_w distances are 2.736, 2.466, 2.403, and 2.316 Å for La, Eu, Tb, and Yb, respectively. Similarly, the mean Ln−N distances are 2.768, 2.620, 2.540, and 2.478 Å for La, Eu, Tb, and Yb, respectively. Secondly, the coordination number and the number of 2,2′-dpdc ligands around Ln^{3+} all decrease with decreasing ionic radii of the lanthanides. Thirdly, the variations in coordination modes of 2,2′-dpdc ligands in these complexes are connected with the decreasing ionic radii of the La^{3+}, Eu^{3+}, Tb^{3+} and Yb^{3+} ions. As La^{3+} has the largest ionic radius in **1**−**4** the 2,2′-dpdc ligands adopt pentadentate and hexadentate coordination modes in **1** (Scheme 1, c and d). The tetradentate and pentadentate coordination modes of 2,2′-dpdc ligands in **2** (Scheme 1, b and c) and the tetradentate coordination modes of 2,2′-dpdc ligands in **3** and **4** reflect the decreasing

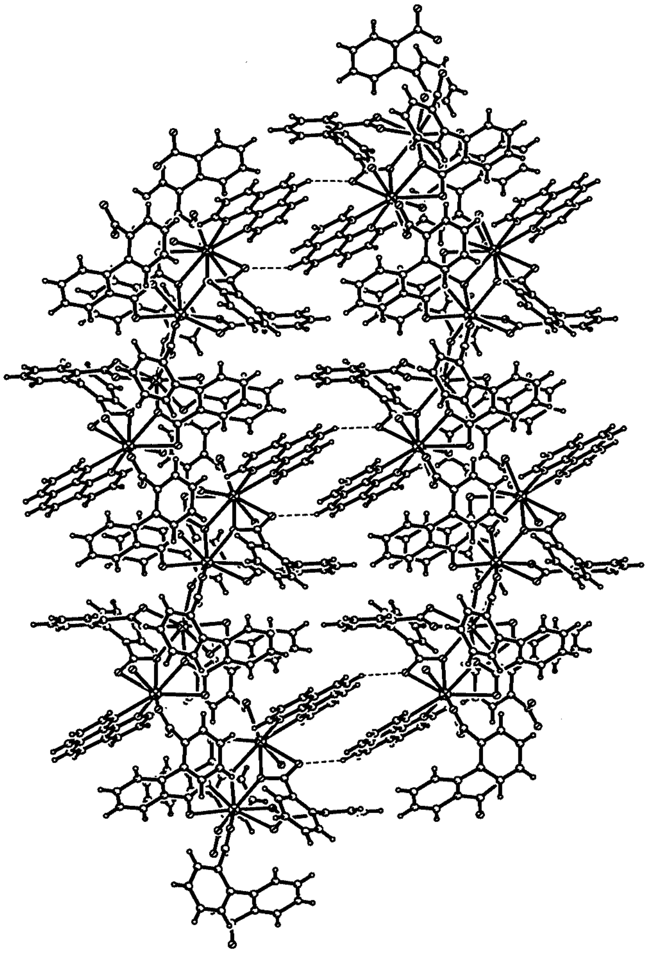

Figure 5. 2-D structure of **2** viewed along the *a* axis; hydrogen bonds are shown as dotted lines

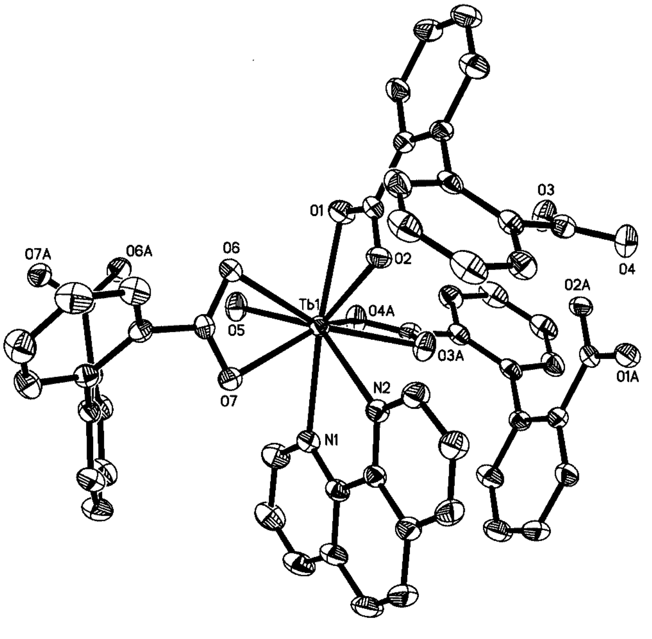

Figure 6. Coordination environment of the Tb^{III} ion in **3** with thermal ellipsoids at 30% probability; all hydrogen atoms are omitted for clarity

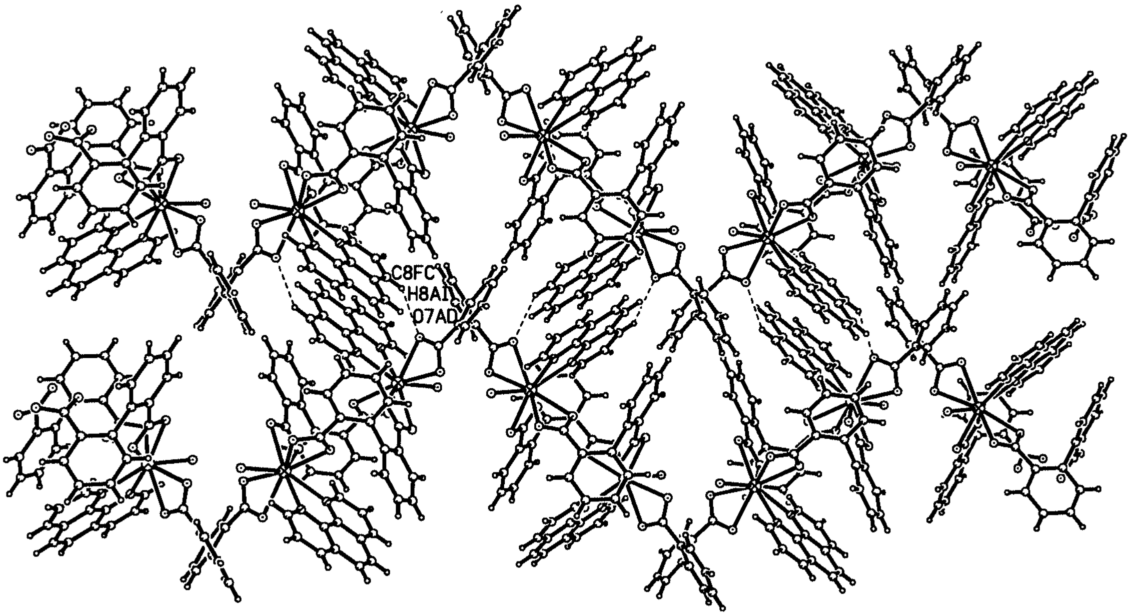

Figure 7. 2-D network of **3** viewed along the *a* axis

ionic radii of the respective lanthanides with increasing atomic number. These results are all in line with lanthanide contraction.

Contrasting the title complexes with binary lanthanide 2,2′-diphenyldicarboxylate complexes,[25] the mean Ln−O(carboxylate) distances for La, Eu and Tb in the title complexes are all longer than those in the binary complexes. Obviously, this is due to the steric hindrance of phen molecules. Similarly, because of the participation of phen molecules, the title complexes exhibit 2-D (**1**, **3** and **4**) or 3-D (**2**) supramolecular architectures constructed by 1-D chains through hydrogen bonds of neighbouring chains, while the binary complexes show 1-D chain structures. As regards 2,2′-dpdc ligands, there is a hexadentate coordination mode in the title complexes that is not present in the binary lanthanide complexes (Scheme 1, d). In addition, the tetradentate coordination mode of 2,2′-dpdc ligands in the binary complexes is quite different from that in the title complexes.

Photophysical Properties of 2

Eu^{3+} complexes can undergo characteristic Eu^{3+} ion emission when excited, and Eu^{3+} is usually regarded as a structural probe to determine the local ion sites based on its unique nondegenerate lowest emission level of $^5D_0$. In the asymmetric unit of the coordination polymer **2**, the two Eu^{3+} ions have obviously different coordination environments: one is coordinated by phen, while the other is not, which led us to probe its local structure in detail.

Figure 8 illustrates the emission spectrum of **2** corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) transitions in the range of 13900−17300 cm^{-1} at 77 K, in which the $^5D_0 \rightarrow {}^7F_3$ transition is too weak to be observed. The apparent four peaks corresponding to the $^5D_0 \rightarrow {}^7F_1$ transition and the shoulder at the peak (Figure 8, insert) corresponding to the $^5D_0 \rightarrow {}^7F_0$ transition both imply that there is more than one Eu^{3+} ion site in **2**. To further investigate the Eu^{3+} ion sites in the coordination polymer, selective excitation technology was applied. The excitation spectra (Figure 9, a and b) at 77 K were obtained by setting 16235 and 16204 cm^{-1} as the analyzing wavenumbers. Scanning in the range of 578.0−581.0 nm revealed two sharp excitation peaks, which show that there are two Eu^{3+} ion sites,[28] located at 579.58 nm and 579.84 nm, respectively, which is in good agreement with the results of X-ray diffraction.

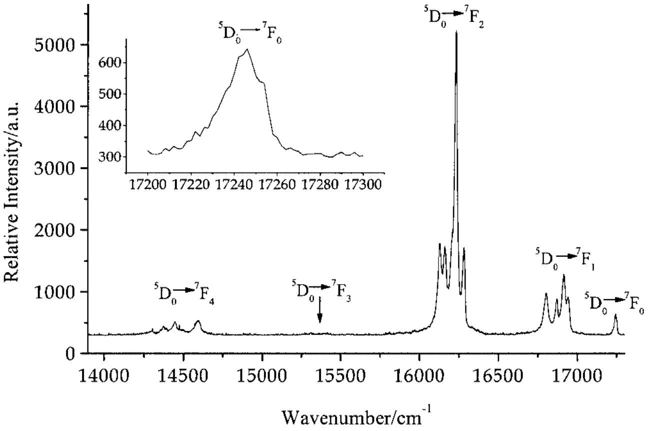

Figure 8. Emission spectrum of **2** corresponding to $^5D_0 \rightarrow {}^7F_J$ ($J = 0-4$) transitions at 77 K, λ_{exc} = 355 nm

Conclusion

Complexes **1**−**4** exhibit 2-D (**1**, **3**, and **4**) and 3-D (**2**) structures, and **3** and **4** are isomorphous. The 2,2′-dpdc li-

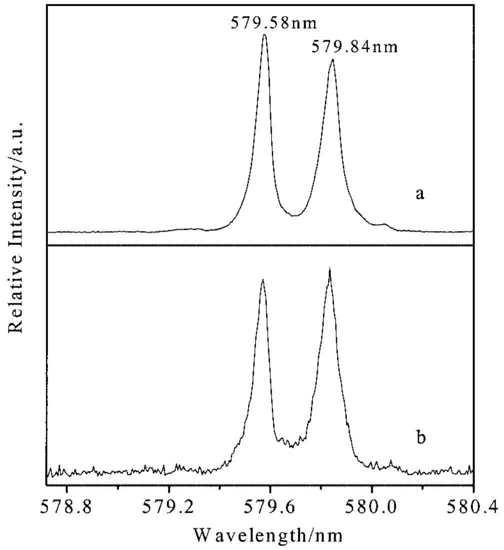

Figure 9. Excitation spectra of **2** at 77 K, analyzing wavenumber: (a) 16235 and (b) 16204 cm^{-1}

gands in these complexes adopt tetradentate, pentadentate and hexadentate coordination modes. The components of the building blocks for the title complexes, the coordination mode of the carboxylate groups, Ln−O and Ln−N distances, and the coordination number all clearly indicate the effect of lanthanide contraction on the formation and structure of the ternary lanthanide 2,2′-diphenyldicarboxylate complexes with 1,10-phenanthroline. Utilizing the characteristic emission of Eu^{3+} ions as a conformation probe, we confirm that there are two Eu^{3+} ion sites in **2**. Finally, the phen molecule clearly contributes to the formation of 2-D and 3-D structures in the title complexes.

Experimental Section

General: Materials: $LaCl_3 \cdot 7H_2O$, $EuCl_3 \cdot 6H_2O$, $TbCl_3 \cdot 6H_2O$, and $YbCl_3 \cdot 6H_2O$ were prepared by dissolving their respective oxides in hydrochloric acid followed by drying. 2,2′-Diphenyldicarboxylic acid was purchased from Aldrich and used without further purification. All the other reagents were commercially available and used as received. Instrumentation: Elemental analyses were performed with an Elementar Vario EL analyzer. The IR spectra were recorded with a Nicolet Avatar 360 FT-IR spectrometer as KBr pellets. For the emission studies, the excitation light source was a YAG-Nd laser that emits at 1.064 μm, and the excitation wavelength was 355 nm. The sample was placed in a Dewar, cooled with liquid nitrogen, and the fluorescence was collected at right angles through a Spex 1403 monochromator with a photomultiplier tube, then averaged by Boxcar integrator and, finally, the data were transferred to a computer.

X-ray Crystallographic Study: X-ray single-crystal data collection for complexes **1**, **2**, **3** and **4** was performed with a Bruker Smart 1000 CCD diffractometer, using graphite-monochromated Mo-K_α radiation (λ = 0.71073Å). Semiempirical absorption corrections were applied using the SADABS program. The structures were solved by direct methods and refined by full-matrix least-squares on $|F|^2$ using the SHELXTL-97 program.[26] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. CCDC-201295 to -201298 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].

Syntheses

$\{[La_2(2,2'\text{-dpdc})_3(phen)(H_2O)] \cdot 2H_2O\}_n$ (1): A mixture of $LaCl_3 \cdot 7H_2O$(0.111 g, 0.3 mmol), 2,2′-diphenyldicarboxylic acid (0.109 g, 0.45 mmol), phen·H_2O (0.059 g, 0.3 mmol), H_2O (10 mL), and an aqueous solution of NaOH (0.625 mL, 0.4 mmol) was heated in a stainless-steel reactor (23-mL capacity) with a Teflon liner at 170 °C for 3 d and then slowly cooled to room temperature by air cooling. The yellowish crystals so obtained were collected by filtration, washed with ethanol, and then air-dried to give a 57.9% yield (0.107 g). $C_{54}H_{38}La_2N_2O_{15}$ (1232.68): calcd. C 52.62, H 3.11, N 2.27; found C 52.85, H 2.68, N 2.09. IR (KBr pellet): ṽ = 3436 (m), 1600 (s), 1577 (s), 1544 (s), 1442 (s), 1406 (s), 756 (m), 730 (m) cm^{-1}.

$[Eu_2(2,2'\text{-dpdc})_3(phen) \cdot (H_2O)_2]_n$ (2): A mixture of $EuCl_3 \cdot 6H_2O$-(0.11 g, 0.3 mmol), 2,2′-diphenyldicarboxylic acid (0.109 g, 0.45 mmol), phen·H_2O (0.059 g, 0.3 mmol), H_2O (10 mL), and aqueous solution of NaOH (0.56 mL, 0.366 mmol) was heated in a stainless-steel reactor (23-mL capacity) with Teflon liner at 190 °C for 3 d and then slowly cooled to room temperature by air-cooling. The resultant flesh-colored crystals were collected by filtration, washed with ethanol, and then air-dried; 62.3% yield (0.116 g). $C_{54}H_{36}Eu_2N_2O_{14}$ (1240.77): calcd. C 52.27, H 2.93, N 2.26; found C 52.78, H 2.58, N 2.04. IR (KBr pellet): ṽ = 3551 (m), 1621 (s), 1552 (s), 1525 (s), 1442 (s), 1407 (s), 772 (m), 762 (m) cm^{-1}.

$\{[Ln(2,2'\text{-dpdc})_{1.5}(phen)(H_2O)] \cdot 2H_2O\}_n$ [Ln =Tb (3), Yb (4)]: The syntheses of complexes **3** and **4** followed the same procedure as for **2.** Colorless and pale yellow crystals of **3** and **4**, respectively, were obtained by filtration and washed with ethanol, then air-dried to give yields of 53.1% (0.061 g) and 58.3% (0.067 g), respectively. $C_{33}H_{26}N_2O_9Tb$ (**3**) (753.54): calcd. C 52.57, H 3.48, N 3.723; found C 52.54, H 3.01, N 3.43. IR (KBr pellet): ṽ = 3423 (m), 1600 (s), 1576 (s), 1544 (s), 1477 (s), 1408 (s), 766 (m), 728 (m) cm^{-1}. $C_{33}H_{26}N_2O_9Yb$ (**4**) (767.58): calcd. C 51.61, H 3.42, N 3.65; found C 51.46, H 3.24, N 3.60. IR (KBr pellet): ṽ = 3422 (m), 1600 (s), 1577 (s), 1546 (s), 1479 (s), 1412 (s), 766 (m), 726 (m) cm^{-1}.

Acknowledgments

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