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Supramolecular architectures from the self-assembly of lanthanide coordination compounds containing glycine and phen via hydrogen bonding and π–π stacking interactions

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Abstract

Single crystal X-ray diffraction shows that $[La(gly)_2(H_2O)_2(phen)_2(CH_3CH_2OH)](ClO_4)_3(phen)_3 \cdot 3H_2O$ (**1**), $[Ln(gly)_2(H_2O)_2(phen)_2](ClO_4)_3\ (phen)_4 \cdot nH_2O$ [$n = 0$, Ln = Nd (**2**); $n = 1$, Ln = Ho (**3**)], and $[Yb(gly)_4(H_2O)(phen)](ClO_4)_4(phen)_2(gly+H) \cdot 2H_2O$ (**4**) (gly = glycine, phen = 1,10-phenanthroline) with the coordination number 9 for La^{3+}, 8 for Nd^{3+} and Ho^{3+}, and 7 for Yb^{3+}, exhibit the effect of lanthanide contraction. Complexes **1**–**4** are all mononuclear structures, with the ligand glycine coordinated to the Ln^{3+} ion in the monodentate mode and in zwitterionic form. There exist free phen molecules and solvent molecules in the lattice. Therefore, there are different types of hydrogen bonding and π–π stacking interactions in the crystals that give rise to different supramolecular architectures. The structure of **1** is composed of 1D chains which extend in the [1 0 0] direction, while those of **2** and **3** are 2D structures extending in the (0 0 1) plane. However, complex **4** shows a complicated 3D network.

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1. Introduction

'Supramolecular chemistry' is the chemistry of the intermolecular bond, covering the structures and functions of the entities formed by association of two or more chemical species [1] through weaker non-covalent bond interactions such as hydrogen bonding, electrostatic interactions, electron-donor/electron-acceptor interactions and π–π stacking interactions [2,3]. Recently, a variety of supramolecular coordination compounds based on metal coordination have been synthesized [4–11]. In fact, the unique organized structures of some supramolecular compounds are based on the weak non-covalent interactions between their components [1]. From the point of view of coordination chemistry, the interactions between the ligands of a mixed-ligand complex can lead to a supramolecular formation [1,12]. We have found that the lanthanide complexes of amino acid with phen are photochromic in aqueous solution [13–15]. To extend our study, we here report the structures of four lanthanide supramolecular coordination compounds containing glycine and phen.

2. Experimental

2.1. Preparation of the complexes **1**, **2**, **3** and **4**

The stock solutions of $Ln(ClO_4)_3$ (Ln = La, Nd, Ho and Yb) were prepared by dissolving Ln_2O_3 in concentrated $HClO_4$, and then the pH was approximately adjusted to 4. The single crystals of lanthanide (La, Nd, Ho and Yb) compounds with the glycine and phen, hereafter denoted as **1**, **2**, **3** and **4**, were obtained by heating the mixture of the ethanolic solution of phen (0.226 g, 1.14 mmol) and glycine (0.128 g, 0.171 mmol) and the aqueous solution of $Ln(ClO_4)_3$ (1.0 ml, 0.57 mmol) with the molar ratio of $Ln(ClO_4)_3$:glycine:phen = 1:3:2 at 70 °C for 6 h, and then evaporating the mother liquor at room temperature. The

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percentage yields are 59.5, 55.4, 60.2% according to the mass of phen for **1**–**3**, and 60.7% according to the mass of glycine for **4**. *Anal*. Calc. for $C_{66}H_{66}Cl_3LaN_{12}O_{22}$: C, 48.79; H, 4.09; N, 10.34; Found: C, 48.41; H, 4.02; N, 9.66. *Anal*. Calc. for $C_{76}H_{62}Cl_3NdN_{14}O_{18}$: C, 53.38; H, 3.65; N, 11.47; Found: C, 53.15; H, 3.59; N, 11.85. *Anal*. Calc. for $C_{76}H_{64}Cl_3HoN_{14}O_{19}$: C, 52.20; H, 3.69; N, 11.21; Found: C, 52.15; H, 3.25; N, 11.17. *Anal*. Calc. for $C_{46}H_{56}Cl_4YbN_{11}O_{29}$: C, 35.83; H, 3.66; N, 9.99%. It seems that $[Yb(gly)_4(H_2O)(phen)](ClO_4)_4\ (phen)_2(gly+H)\cdot 2H_2O$ is air sensitive, and satisfactory data were not obtained.

2.2. X-ray crystallographic analyses

Intensity data of the complexes were measured at 293 K on a Bruker SMART CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods using SHELXS-97 [16]. The non-hydrogen atoms of one uncoordinating phen (N7, N8, C29–C40), the oxygen atoms of all the ClO_4^- anions in **1**, the oxygen atoms of all the ClO_4^- anions in **2**, and the oxygen atoms of one ClO_4^- anion (O21–O24) and the lattice water (O25) in **3** were fixed as isotropic atoms. The other non-hydrogen atoms were anisotropically refined by full-matrix least-squares based on F^2 using SHELXL-97 [16]. The hydrogen atoms attached to the coordinating water molecules of **2** and **3** are located from the difference Fourier map. Only one hydrogen atom of the coordinating water molecule in **4** is located from the difference Fourier map. The hydrogen atoms attached to the lattice water molecules in **1**–**4** and those to the coordinating water molecules in **1** are missing. The other hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The crystal data for **1**–**4** are summarized in Table 1. The rather high wR_2 values for the structures of the four title complexes are due to the high thermal motion of perchlorate anions and free phen molecules. Selected bond distances and bond angles in **1**–**4** are listed in Tables 2–5, respectively.

3. Results and discussion

The molecular structure of **1** is shown in Fig. 1(a). For **1**, unexpectedly, the solvent molecule C_2H_5OH is also involved in the coordination. The central La^{3+} ion is nine-coordinated with two oxygen atoms from two water molecules, two oxygen atoms from two glycine molecules which are in zwitterionic form, one oxygen atom from one ethanol molecule, and four nitrogen atoms from two phen molecules which are almost perpendicular to each other (the dihedral angle is 86.5°). The bond lengths of La–O range from 2.499 to 2.646 Å, while those of La–N range from 2.748 to 2.805 Å. The coordination polyhedron for **1** is a tricapped trigonal prism. Outside the coordination sphere, there are three ClO_4^- ions as counteranions, three lattice water molecules and three uncoordinating phen molecules. In **2** and **3**, the central metal ions Nd^{3+} and Ho^{3+} have the same inner coordination sphere and similar outer coordination sphere except for the lack of a lattice water molecule in **2**. For **2** and **3**, the central lanthanide(III) ions are eight-coordinated with two oxygen atoms from two H_2O molecules, two oxygen atoms from two glycine molecules which are in zwitterionic form, and four nitrogen atoms from two phen molecules. The Ln–O and Ln–N distances are in the range of 2.434–2.452, 2.622–2.653 Å, respectively, for Ln = Nd, and 2.338–2.342 Å, 2.519–2.535 Å, respectively, for Ln = Ho. Outside the coordination sphere there are three ClO_4^- ions as the counteranions, and four uncoordinating phen molecules. For **3**, there is one more lattice H_2O molecule. Ho^{3+} in **3** has a similar coordination environment to Nd^{3+} in **2**. Therefore, **3** has the same coordination polyhedron, a triangular dodecahedron as **2** does. Unlike the above three complexes, complex **4** has two independent coordination cations (see Fig. 1(c and d)) because its ligands orientate differently. The coordination environment around Yb^{3+} changes obviously compared with **1**, **2** and **3**. The central Yb^{3+} ions in Fig. 1c and d are both seven-coordinated with four oxygen atoms from the carboxyl group of four glycine, one oxygen atom from a water molecule and two nitrogen atoms from one phen. The bond distances of Yb–O and Yb–N range from 2.206 to 2.334 Å and 2.464 to 2.478 Å, respectively. They have the same coordination environment. Their coordination polyhedra are both monocapped trigonal prisms with the oxygen atom from H_2O occupying the capped position. Outside the coordination sphere, there are four ClO_4^- anions, two phen molecules, two lattice water molecules, and one protonated glycine cation.

Due to lanthanide contraction, from La^{3+} to Yb^{3+}, the ionic radii become smaller gradually. Therefore, the coordinated atoms around different lanthanide ions are selective in number and type. Nd^{3+} and Ho^{3+} are located in the middle of the lanthanide series. They are all eight-coordinated. Lanthanum has the largest ionic radius. Compared with the coordination sphere of Nd^{3+} and Ho^{3+}, one more coordination site of La^{3+} is filled by one oxygen atom from the solvent ethanol to complete a coordination number of nine. Yb^{3+} has the smallest radius among the four lanthanide ions, which requires smaller ligands and relatively fewer coordinated atoms around it because of the steric effect. It is only seven-coordinated with one phen molecule, four glycine and one H_2O. In addition, it can be seen from Tables 2–5 that from complexes **1**–**4**, the bond distances between the lanthanide ion and the coordinated atom from the

Table 1
Summary of crystallographic data for **1**, **2**, **3** and **4**

Compound	**1**	**2**	**3**	**4**
Empirical formula	$C_{66}H_{66}Cl_3LaN_{12}O_{22}$	$C_{76}H_{62}Cl_3NdN_{14}O_{18}$	$C_{76}H_{64}Cl_3HoN_{14}O_{19}$	$C_{46}H_{56}Cl_4YbN_{11}O_{29}$
M	1624.57	1709.99	1748.69	1541.86
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	C_2/c	C_2/c	C_2/c
a (Å)	14.022(8)	17.826(10)	17.665(3)	21.246(6)
b (Å)	15.254(10)	12.063(6)	12.057(2)	28.818(8)
c (Å)	19.441(12)	34.486(18)	34.074(6)	19.312(5)
α (°)	69.669(12)	90	90	90
β (°)	79.485(13)	92.114(9)	91.750(4)	90.579(5)
γ (°)	65.371(11)	90	90	90
V (Å^3)	3541(4)	7410(7)	7254(2)	11823(5)
Z	2	4	4	8
D_{calc} (g cm^{-3})	1.524	1.533	1.601	1.732
μ (mm^{-1})	0.801	0.891	1.287	1.863
Reflections collected	14402, 12130	14446, 6449	14318, 6216	24439, 10409
Total, independent, R_{int}	0.1306	0.0461	0.0542	0.0937
Final R_1, wR_2 [a]	0.1018, 0.2059	0.0620, 0.1574	0.0454, 0.0910	0.0503, 0.0953

[a] The values were calculated for data with $[I > 2\sigma(I)]$.

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

Bond distances			
La(1)–O(1)	2.499(8)	La(1)–O(3)	2.518(7)
La(1)–O(5)	2.528(9)	La(1)–O(6)	2.65(1)
La(1)–O(7)	2.636(8)	La(1)–N(3)	2.75(1)
La(1)–N(4)	2.75(1)	La(1)–N(2)	2.781(9)
La(1)–N(1)	2.805(9)		
Bond angles			
O(1)–La(1)–O(3)	145.3(3)	O(1)–La(1)–O(5)	74.3(3)
O(3)–La(1)–O(5)	100.7(3)	O(1)–La(1)–O(6)	136.5(3)
O(3)–La(1)–O(6)	68.0(4)	O(5)–La(1)–O(6)	140.0(3)
O(1)–La(1)–O(7)	65.4(3)	O(3)–La(1)–O(7)	131.8(3)
O(5)–La(1)–O(7)	127.2(3)	O(6)–La(1)–O(7)	71.3(3)
O(1)–La(1)–N(3)	88.2(3)	O(3)–La(1)–N(3)	74.8(3)
O(5)–La(1)–N(3)	141.8(3)	O(6)–La(1)–N(3)	74.4(3)
O(7)–La(1)–N(3)	70.4(3)	O(1)–La(1)–N(4)	71.8(3)
O(3)–La(1)–N(4)	73.5(3)	O(5)–La(1)–N(4)	82.2(3)
O(6)–La(1)–N(4)	126.2(3)	O(7)–La(1)–N(4)	113.8(3)
N(3)–La(1)–N(4)	60.0(3)	O(1)–La(1)–N(2)	75.5(3)
O(3)–La(1)–N(2)	135.4(3)	O(5)–La(1)–N(2)	67.7(3)
O(6)–La(1)–N(2)	93.1(3)	O(7)–La(1)–N(2)	70.3(3)
N(3)–La(1)–N(2)	140.7(3)	N(4)–La(1)–N(2)	140.4(3)
O(1)–La(1)–N(1)	130.2(3)	O(3)–La(1)–N(1)	76.8(3)
O(5)–La(1)–N(1)	71.4(3)	O(6)–La(1)–N(1)	68.7(3)
O(7)–La(1)–N(1)	110.9(3)	N(3)–La(1)–N(1)	139.7(3)
N(4)–La(1)–N(1)	135.3(3)	N(2)–La(1)–N(1)	58.6(3)

Table 3
Selected bond distances (Å) and bond angles (°) for **2**

Bond distances			
Nd(1)–O(2)$^{\#1}$	2.434(5)	Nd(1)–O(2)	2.434(5)
Nd(1)–O(1)$^{\#1}$	2.452(4)	Nd(1)–O(1)	2.452(4)
Nd(1)–N(2)$^{\#1}$	2.622(5)	Nd(1)–N(2)	2.622(5)
Nd(1)–N(1)	2.653(5)	Nd(1)–N(1)$^{\#1}$	2.653(5)
Bond angles			
O(2)$^{\#1}$–Nd(1)–O(2)	114.8(3)	O(2)$^{\#1}$–Nd(1)–O(1)$^{\#1}$	75.4(2)
O(2)–Nd(1)–O(1)$^{\#1}$	148.9(2)	O(2)$^{\#1}$–Nd(1)–O(1)	148.9(2)
O(2)–Nd(1)–O(1)	75.4(2)	O(1)$^{\#1}$–Nd(1)–O(1)	111.9(3)
O(2)$^{\#1}$–Nd(1)–N(2)$^{\#1}$	75.3(2)	O(2)–Nd(1)–N(2)$^{\#1}$	80.2(2)
O(1)$^{\#1}$–Nd(1)–N(2)$^{\#1}$	130.6(2)	O(1)–Nd(1)–N(2)$^{\#1}$	77.9(2)
O(2)$^{\#1}$–Nd(1)–N(2)	80.2(2)	O(2)–Nd(1)–N(2)	75.3(2)
O(1)$^{\#1}$–Nd(1)–N(2)	77.9(2)	O(1)–Nd(1)–N(2)	130.6(2)
N(2)$^{\#1}$–Nd(1)–N(2)	133.6(2)	O(2)$^{\#1}$–Nd(1)–N(1)	133.5(2)
O(2)–Nd(1)–N(1)	83.3(2)	O(1)$^{\#1}$–Nd(1)–N(1)	70.5(2)
O(1)–Nd(1)–N(1)	75.0(2)	N(2)$^{\#1}$–Nd(1)–N(1)	151.0(2)
N(2)–Nd(1)–N(1)	62.8(2)	O(2)$^{\#1}$–Nd(1)–N(1)$^{\#1}$	83.3(2)
O(2)–Nd(1)–N(1)$^{\#1}$	133.5(2)	O(1)$^{\#1}$–Nd(1)–N(1)$^{\#1}$	75.0(2)
O(1)–Nd(1)–N(1)$^{\#1}$	70.5(2)	N(2)$^{\#1}$–Nd(1)–N(1)$^{\#1}$	62.8(2)
N(2)–Nd(1)–N(1)$^{\#1}$	151.0(2)	N(1)–Nd(1)–N(1)$^{\#1}$	116.0(2)

$^{\#1}-x+1, y, -z+1/2$; $^{\#2}-x, y, -z+1/2$.

same ligand tend to become shorter. The average Ln–O distances in **1**, **2**, **3** and **4** are 2.565, 2.443, 2.340 and 2.247 Å, respectively, indicating the effect of lanthanide contraction on molecular structure.

In the reported binary complexes of lanthanide perchlorate with glycine, the ligand glycine coordinates with the lanthanide ion in the bidentate bridging or tridentate bridging mode. Therefore, the binary complexes of lanthanide perchlorate with glycine are liable to form polymers. So far, no mononuclear structure has been found. In the 1:1(Ln:Gly) complex, $[Er_2(Gly)_2(H_2O)_{12}](ClO_4)_6\cdot 4H_2O$ [17], two Er^{3+} ions are bridged by two carboxylate groups in a *syn–syn* mode to form a binuclear structure. The 1:2 complex, $[Er_2(Gly)_4(H_2O)_8](ClO_4)_6\cdot 4C_4H_8O_2$ [18], is also a binuclear structure. The carboxylate groups of four glycine bridge two Er^{3+} ions in a bidentate *syn–syn* mode. The 1:3 complexes of lanthanide perchlorate with glycine, $[Ln_2(Gly)_6(H_2O)_4](ClO_4)_6\cdot n H_2O$ [Ln = La [19],

Table 4
Selected bond distances (Å) and bond angles (°) for **3**

Bond distances			
Ho(1)–O(1)$^{\#1}$	2.338(4)	Ho(1)–O(1)	2.338(4)
Ho(1)–O(3)$^{\#1}$	2.342(4)	Ho(1)–O(3)	2.342(4)
Ho(1)–N(2)$^{\#1}$	2.519(4)	Ho(1)–N(2)	2.519(4)
Ho(1)–N(1)	2.535(4)	Ho(1)–N(1)$^{\#1}$	2.535(4)
Bond angles			
O(1)$^{\#1}$–Ho(1)–O(1)	111.1(2)	O(1)$^{\#1}$–Ho(1)–O(3)$^{\#1}$	148.8(1)
O(1)–Ho(1)–O(3)$^{\#1}$	77.9(2)	O(1)$^{\#1}$–Ho(1)–O(3)	77.9(2)
O(1)–Ho(1)–O(3)	148.8(1)	O(3)$^{\#1}$–Ho(1)–O(3)	110.4(2)
O(1)$^{\#1}$–Ho(1)–N(2)$^{\#1}$	133.2(1)	O(1)–Ho(1)–N(2)$^{\#1}$	80.3(1)
O(3)$^{\#1}$–Ho(1)–N(2)$^{\#1}$	76.9(1)	O(3)–Ho(1)–N(2)$^{\#1}$	73.0(1)
O(1)$^{\#1}$–Ho(1)–N(2)	80.3(1)	O(1)–Ho(1)–N(2)	133.2(1)
O(3)$^{\#1}$–Ho(1)–N(2)	73.0(1)	O(3)–Ho(1)–N(2)	76.9(1)
N(2)$^{\#1}$–Ho(1)–N(2)	125.7(2)	O(1)$^{\#1}$–Ho(1)–N(1)	71.4 (1)
O(1)–Ho(1)–N(1)	75.6(1)	O(3)$^{\#1}$–Ho(1)–N(1)	82.9(1)
O(3)–Ho(1)–N(1)	134.2(1)	N(2)$^{\#1}$–Ho(1)–N(1)	151.2(1)
N(2)–Ho(1)–N(1)	65.3(1)	O(1)$^{\#1}$–Ho(1)–N(1)$^{\#1}$	75.6(1)
O(1)–Ho(1)–N(1)$^{\#1}$	71.4(1)	O(3)$^{\#1}$–Ho(1)–N(1)$^{\#1}$	134.2(1)
O(3)–Ho(1)–N(1)$^{\#1}$	82.9(1)	N(2)$^{\#1}$–Ho(1)–N(1)$^{\#1}$	65.3(1)
N(2)–Ho(1)–N(1)$^{\#1}$	151.3(1)	N(1)–Ho(1)–N(1)$^{\#1}$	119.6(2)

$^{\#1}-x, y, -z+1/2$.

Table 5
Selected bond distances (Å) and bond angles (°) for **4**

Bond distances			
Yb(1)–O(3)	2.213(5)	Yb(1)–O(3)$^{\#1}$	2.213(5)
Yb(1)–O(1)	2.246(5)	Yb(1)–O(1)$^{\#1}$	2.246(5)
Yb(1)–O(5)	2.312(7)	Yb(1)–N(1)	2.464(6)
Yb(1)–N(1)$^{\#1}$	2.464(6)	Yb(2)–O(8)$^{\#2}$	2.206(5)
Yb(2)–O(8)	2.206(5)	Yb(2)–O(6)	2.246(5)
Yb(2)–O(6)$^{\#2}$	2.246(5)	Yb(2)–O(10)	2.334(7)
Yb(2)–N(4)$^{\#2}$	2.478(6)	Yb(2)–N(4)	2.478(6)
Bond angles			
O(3)–Yb(1)–O(3)$^{\#1}$	162.0(3)	O(3)–Yb(1)–O(1)	83.4(2)
O(3)$^{\#1}$–Yb(1)–O(1)	93.1(2)	O(3)–Yb(1)–O(1)$^{\#1}$	93.1(2)
O(3)$^{\#1}$–Yb(1)–O(1)$^{\#1}$	83.4(2)	O(1)–Yb(1)–O(1)$^{\#1}$	157.0(3)
O(3)–Yb(1)–O(5)	81.0(1)	O(3)$^{\#1}$–Yb(1)–O(5)	81.0(1)
O(1)–Yb(1)–O(5)	78.5(1)	O(1)$^{\#1}$–Yb(1)–O(5)	78.5(1)
O(3)–Yb(1)–N(1)	115.8(2)	O(3)$^{\#1}$–Yb(1)–N(1)	80.0(2)
O(1)–Yb(1)–N(1)	75.8(2)	O(1)$^{\#1}$–Yb(1)–N(1)	125.5(2)
O(5)–Yb(1)–N(1)	146.9(2)	O(3)–Yb(1)–N(1)$^{\#1}$	80.0(2)
O(3)$^{\#1}$–Yb(1)–N(1)$^{\#1}$	115.8(2)	O(1)–Yb(1)–N(1)$^{\#1}$	125.5(2)
O(1)$^{\#1}$–Yb(1)–N(1)$^{\#1}$	75.8(2)	O(5)–Yb(1)–N(1)$^{\#1}$	146.9(2)
N(1)–Yb(1)–N(1)$^{\#1}$	66.1(3)	O(8)$^{\#2}$–Yb(2)–O(8)	166.9(3)
O(8)$^{\#2}$–Yb(2)–O(6)	95.8(2)	O(8)–Yb(2)–O(6)	81.4(2)
O(8)$^{\#2}$–Yb(2)–O(6)$^{\#2}$	81.4(2)	O(8)–Yb(2)–O(6)$^{\#2}$	95.8(2)
O(6)–Yb(2)–O(6)$^{\#2}$	155.2(3)	O(8)$^{\#2}$–Yb(2)–O(10)	83.4(1)
O(8)–Yb(2)–O(10)	83.4(1)	O(6)–Yb(2)–O(10)	77.6(1)
O(6)$^{\#2}$–Yb(2)–O(10)	77.6(1)	O(8)$^{\#2}$–Yb(2)–N(4)$^{\#2}$	112.3(2)
O(8)–Yb(2)–N(4)$^{\#2}$	79.2(2)	O(6)–Yb(2)–N(4)$^{\#2}$	126.5(2)
O(6)$^{\#2}$–Yb(2)–N(4)$^{\#2}$	76.5(2)	O(10)–Yb(2)–N(4)$^{\#2}$	146.9(2)
O(8)$^{\#2}$–Yb(2)–N(4)	79.2(2)	O(8)–Yb(2)–N(4)	112.3(2)
O(6)–Yb(2)–N(4)	76.5(2)	O(6)$^{\#2}$–Yb(2)–N(4)	126.5(2)
O(10)–Yb(2)–N(4)	146.9(2)	N(4)$^{\#2}$–Yb(2)–N(4)	66.1(3)

$^{\#1}-x$, y, $-z+3/2$; $^{\#2}-x$, y, $-z+1/2$.

$n = 0$; Ln = Pr [20], Nd [21], $n = 5$; Ln = Ho [22], $n = 2$; Ln = Sm [23], $n = 1$] are all 1D chains. In this paper, the four title complexes are all mononuclear, and the ligand glycine molecules coordinate with the metal ions in the monodentate mode. This may be due to the presence of a second large ligand, phen, which coordinates with the central ion in a bidentate chelating mode, making it difficult to form a polymer or dimer.

In the title complexes, there are uncoordinating phen and solvent molecules in the lattice. Between the aromatic rings of phen, there exist π–π stacking interactions. There are three types of π–π stacking interactions in the crystals of complexes **1**–**4** as shown in Scheme 1. The distances between the adjacent aromatic rings range from 3.35 to 3.64 Å. Many amino and carboxyl groups, H_2O, ClO_4^- and free phen are involved in various kinds of hydrogen bonding such as N–H···N, O–H···N, O–H···O and N–H···O. The probable hydrogen bonds in the complexes **1**–**4** are listed in Table 6. Hydrogen bonding and π–π stacking interactions both belong to non-covalent bond interactions which make the crystal a supramolecular architecture. Because of the different inner coordination spheres and outer spheres, the four complexes have different crystal structures. Their supramolecular architectures are built in different ways.

For **1**, the free phen molecules are connected to the amine-nitrogen of coordinating glycine through N–H···N hydrogen bonds as shown in Fig. 2(a). Every glycine is connected with two free phen, while one of these two phen is simultaneously connected with two amino groups from the adjacent two coordination compounds in the [1 0 0] direction. Therefore, there are altogether three free phen molecules outside the coordination sphere. The free phen molecules are all almost parallel to the coordinating phen with nitrogen atoms labelled with N3 and N4 in Fig. 1(a). Among them there exist π–π stacking interactions of type I shown in Scheme 1. The distance between the adjacent phen is 3.49 Å. In addition, there are weak π–π stacking interactions of type II between the other coordinating phen molecules from the adjacent complexes in the [0 0 1] direction. The distance between two parallel aromatic rings is 3.64 Å. Besides uncoordinating phen molecules, there are also uncoordinating water molecules and counter anions ClO_4^- in the lattice. Therefore, there is N–H···O hydrogen bonding between the amino group of the coordinating amino acid and the lattice water or ClO_4^-, and O–H···O hydrogen bonding between the lattice water and the coordinating water or between the lattice water molecules as shown in Fig. 2(a). Thus free phen molecules are hydrogen bonded to the mononuclear complex cations which are connected together through the hydrogen bonding of one free phen to two complex cations and the π–π stacking interactions between phen molecules, resulting in a 1D ladder-like supramolecular architecture.

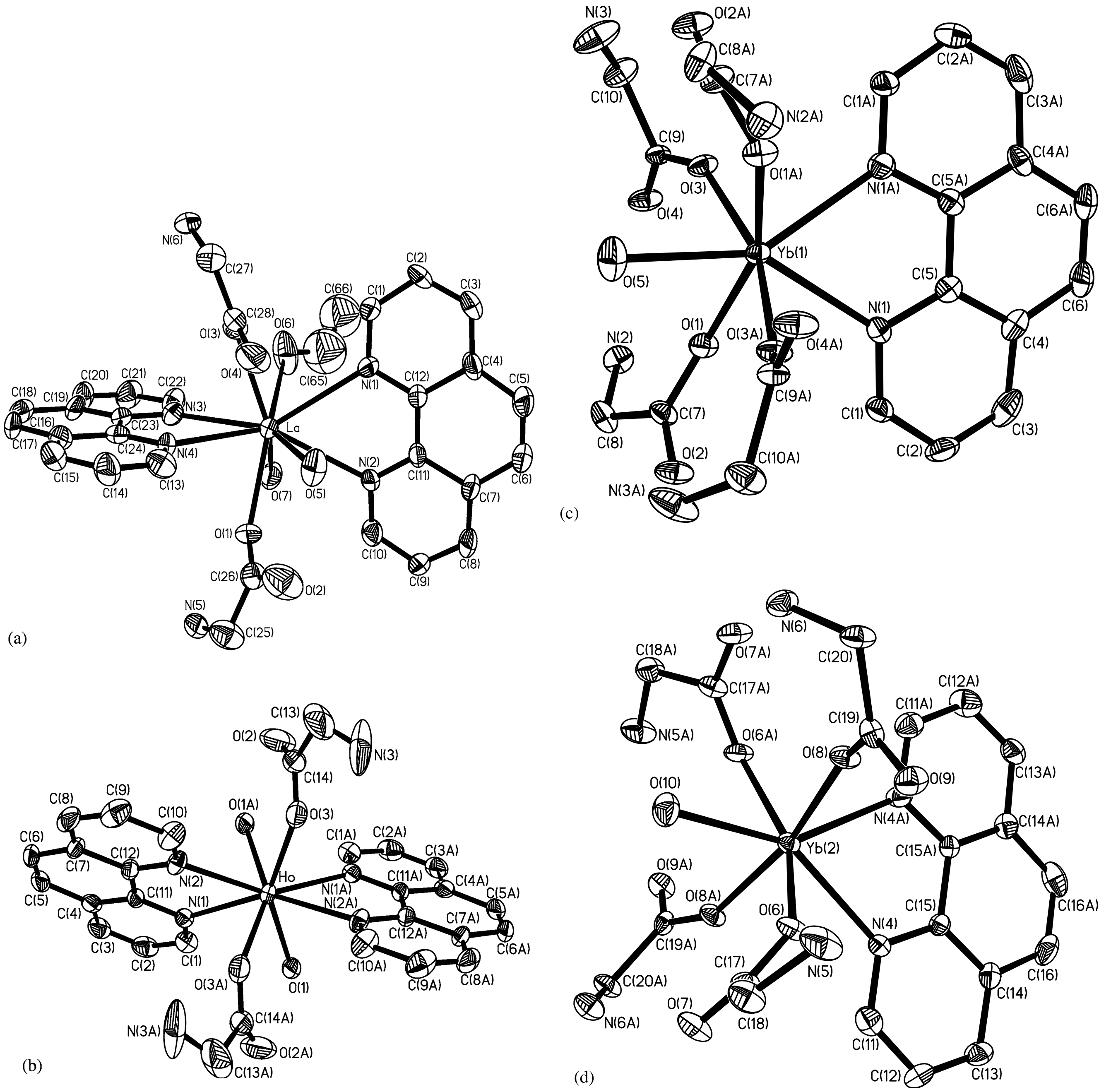
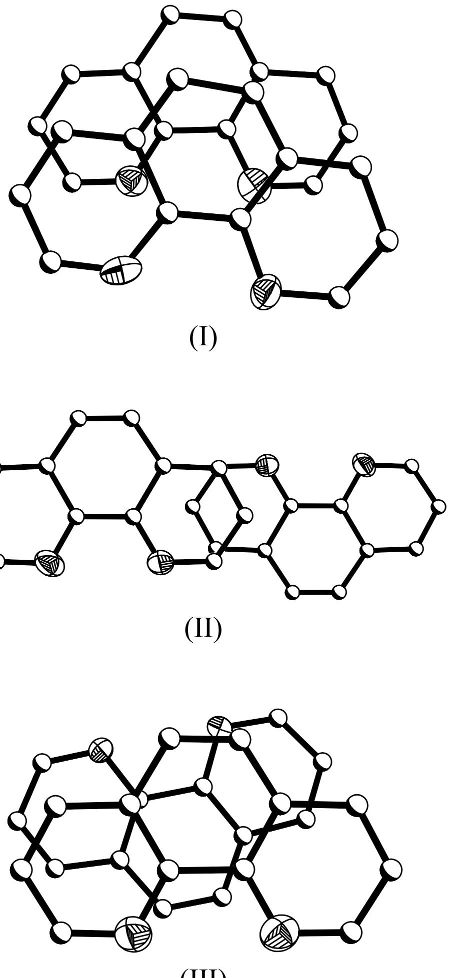


Fig. 1. ORTEP-diagram of the complex cations $[La(gly)_2(H_2O)_2(phen)_2(CH_3CH_2OH)]^{3+}$ (a), $[Ho(gly)_2(H_2O)_2(phen)_2]^{3+}$ (b) and $[Yb(gly)_4(H_2O)(phen)]^{3+}$ (c and d) with thermal ellipsoids at 30% probability. For the interest of clarity, all hydrogen atoms were omitted.

For **2** and **3**, their inner coordination spheres are similar. Outside their coordination spheres, there are four uncoordinating phen molecules, and the uncoordinating phen molecules are connected to the complex cations in the same way. Taking **2** as an example, two free phen molecules are connected to two coordinating water molecules through O–H···N hydrogen bonding, and the other two are connected to two coordinating glycine molecules through N–H···N hydrogen bonding. There are two orientations for the free phen as seen in Fig. 2(b). They are almost parallel to the two coordinating phen molecules, with the maximum dihedral angle between adjacent phen of 5.5°. The average distance between the adjacent aromatic planes is 3.45 Å. So there are π–π stacking interactions between every group of phen molecules with the same orientation, and the π–π stacking interactions in **2** and **3** are all of type I shown in Scheme 1. For **2**, outside the coordination sphere, besides free phen molecules, there are counter anions ClO_4^- which are not involved in any hydrogen bonding. Therefore, there are only two types of hydrogen bondings O–H···N and N–H···N in the crystal of **2**. While



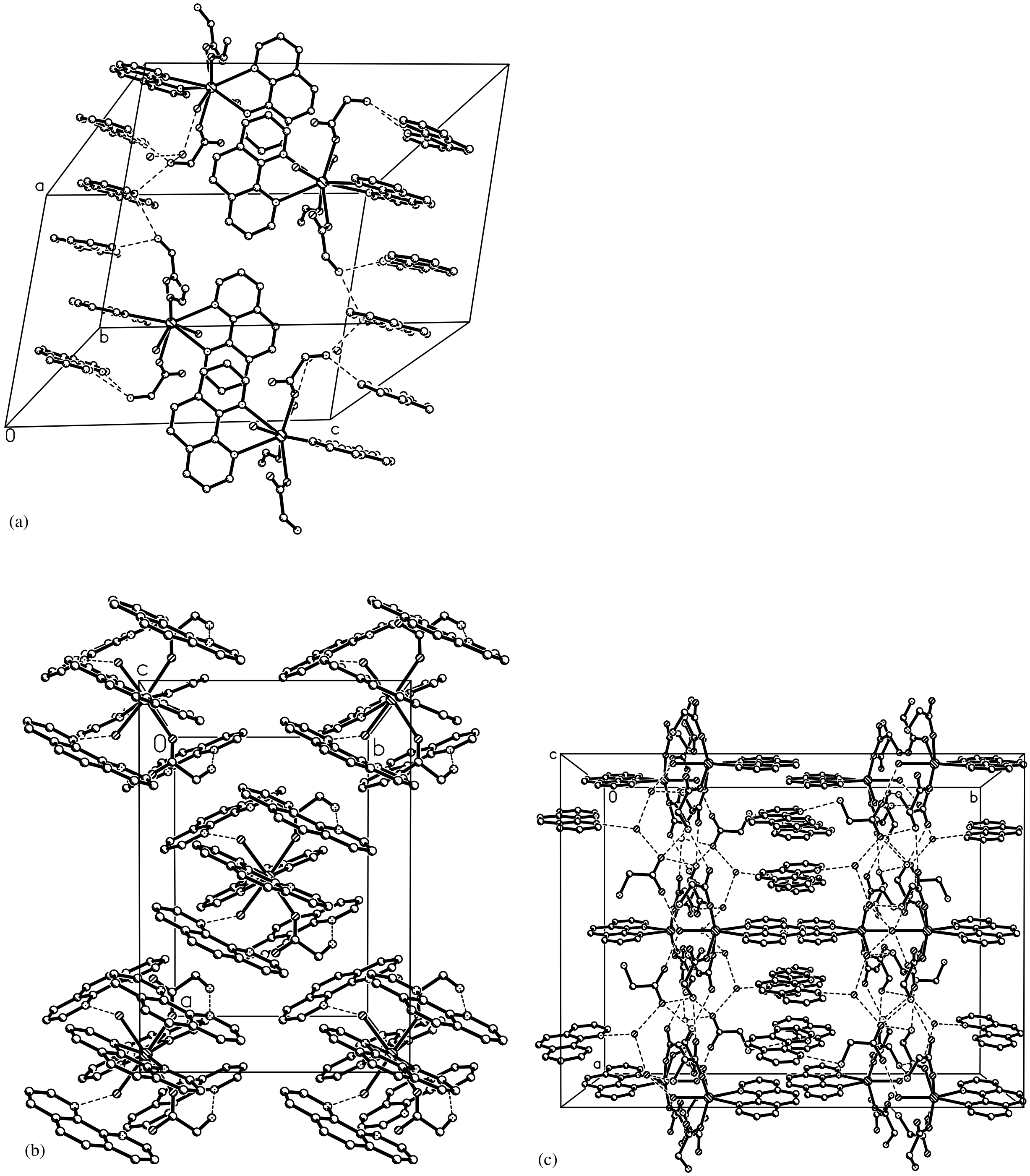
Scheme 1. Three types of π–π stacking interactions in the four title complexes. To make it clear, all nitrogen atoms are shown with ellipsoids at 50% probability.

Table 6
Hydrogen bonds in complexes **1**, **2**, **3** and **4**

	D	A	d(D···A) (Å)	Symmetry code for acceptor
1	N5	N9	3.046	$x+1, y, z$
	N5	N10	2.985	$x+1, y, z$
	N5	O41	2.874	$x+1, y, z$
	N5	N8	2.975	$-x+1, -y+1, -z+1$
	N5	N7	2.941	$-x+1, -y+1, -z+1$
	N6	N10	2.996	x, y, z
	N6	N11	2.847	x, y, z
	O41	O7	2.777	$x-1, y, z$
	O41	N5	2.874	$x-1, y, z$
	O41	O3	2.754	x, y, z
	O41	O42	2.743	x, y, z
	O42	O13	2.832	$x-1, y, z$
	O42	O21	2.922	x, y, z
	O43	O22	2.812	x, y, z
	O43	O33	2.632	x, y, z
2	O1	N6	2.832	$-x+1/2, y+1/2, -z+1/2$
	N3	N7	2.863	$-x+1/2, y-1/2, -z+1/2$
3	O1	N6	2.801	$-x, y, 1/2-z$
	N3	N5	2.799	$x, y-1, z$
	O25	O2	2.647	$-x+1/2, y+1/2, -z+1/2$
4	O5	O61	2.727	x, y, z
	O10	O51	2.855	$x, -y+1, z-1/2$
	N2	O52	2.814	$-x+1/2, y-1/2, -z+3/2$
	N2	O9	2.937	$-x+1/2, -y+1/2, -z+1$
	N3	O61	2.945	x, y, z
	N3	O7	2.74	x, y, z
	N5	O52	2.837	$x, -y+1, z-1/2$
	N5	O4	2.802	$-x+1/2, -y+1/2, -z+1$
	N6	O24	3.001	x, y, z
	N6	O2	2.804	$x, y, z-1$
	O61	O19	2.856	$-x, y, -z+3/2$
	O61	O62	2.754	$-x+1/2, y-1/2, -z+3/2$
	O62	N8	2.905	$-x+1/2, y-1/2, -z+3/2$
	O62	O52	2.741	x, y, z
	O62	O61	2.754	$-x+1/2, y+1/2, -z+3/2$
	N51	N10	2.855	x, y, z
	O51	O10	2.855	$-x, -y+1, -z+1$
	O52	N2	2.814	$-x+1/2, y+1/2, -z+3/2$
	O52	N5	2.837	$x, -y+1, z+1/2$

for **3**, outside the coordination sphere, besides free phen molecules and ClO_4^-, there is a water molecule, and it is hydrogen bonded to the uncoordinating oxygen atom from the carboxyl group of one coordinating glycine. That is to say, there is one more type of hydrogen bonding O–H···O in **3** than in **2**. But the O–H···O hydrogen bonding does not make any significant difference to the supramolecular architecture of **3**. It is the same as **2** as shown in Fig. 2(b). Around every mononuclear structure, there are four free phen molecules oriented in two directions. The mononuclear compounds are assembled through the π–π stacking interactions in [1 1 0] and $[1\ \bar{1}\ 0]$ directions, forming a 2D supramolecular architecture in the (0 0 1) plane.

For **4**, the free phen is not connected with the coordinating ligand via hydrogen bonding, but with the uncoordinating H_2O and protonated glycine in the lattice as shown in Fig. 2(c). Outside the coordination sphere of **4**, one H_2O molecule and the protonated glycine connect with a free phen through O–H···N and N–H···N hydrogen bonds, respectively. All phen including coordinating and uncoordinating ones are almost parallel to one another with the maximum dihedral angle between adjacent phen of 4.0°. Along the a axis, between every two adjacent coordinating phen molecules which are of the same orientation, lie two free phen molecules which are in the opposite orientation and hydrogen bonded with the uncoordinating water and glycine molecules, respectively. The average distance between the adjacent aromatic planes is 3.45 Å showing π–π stacking interactions between them. Between the coordinating phen and the uncoordinating phen, the π–π stacking interaction is of type III in Scheme 1, while between the two uncoordinating phen, it is of type I. In the inner coordination sphere of **4**, there are coordinating glycine and water molecules. Outside the coordina-



(a)

(b)

(c)

Fig. 2. Perspective view of the supramolecular architectures built by **1**, **2** and **4** via the hydrogen bonding and π–π stacking interactions. All hydrogen atoms and ClO_4^- were omitted for clarity. (a) 1D supramolecular structure of **1**; (b) 2D supramolecular architecture of **2**; (c) 3D network of **4**.

tion sphere of **4**, there are two free phen, four counter anions ClO_4^-, two H_2O and one protonated glycine. So the crystal of **4** contains many sites to form hydrogen bonds. Free phen and ClO_4^- can be hydrogen acceptors, while H_2O and glycine can be both hydrogen donors and acceptors. Therefore, the hydrogen bonding in **4** is the most abundant. It consists of four main types of hydrogen bonding: N–H···N, O–H···N, O–H···O and N–H···O as listed in Table 6. In the [1 0 0] and [0 1 0] directions, the mononuclear complex cations are assembled via π–π stacking interactions and hydrogen bonds, while in the [0 0 1] directions, it is hydrogen bonding that links 2D networks, forming a 3D supramolecular architecture.

As ternary lanthanide complexes of glycine with phen, complexes **1**–**4** have different molecular structures and crystal structures. Lanthanide contraction may account for this. The contraction of the radii of the metal ions requires a change of coordination environment. Different coordination environment and species in the lattice result in different non-covalent interactions which finally generate different supramolecular architectures.

4. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication: CCDC Nos. are 181751, 181752, 181754 and 181755 for **1**–**4**, respectively. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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