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Lanthanide contraction and pH value controlled structural change in a series of rare earth complexes with *p*-aminobenzoic acid

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Abstract

A series of rare earth complexes with *p*-aminobenzoic acid (HL) have been synthesized: $[RE_2L_6(H_2O)_2]_n$ [RE = La (1), Ce(2), Pr(3), Sm(4), Eu(5), Tb(6), Dy(7), Er(9)] and $[RE_2L_6(H_2O)_4] \cdot 2H_2O$ [RE = Tb(6'), Ho(8), Yb(10), Lu(11), Y(12)]. The crystal structures of 1, 2, 6, 6', 7, 9 and 12 have been determined and the isomorphous relationships of the others have been identified. Their structures change from twodimensional (2D) array (the coordinated) for 6', 8 and 10–12, as controlled by lanthanide contraction. The structural type has been found influenced by the pH value of the reaction mixtures.

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Keywords: Rare earth; Structure; p-aminobenzoic acid; Lanthanide contraction; pH value

1. Introduction

p-Aminobenzoic acid (HL), a biologically important ligand, can form complexes with various metal ions. In order to gain some understanding on the interaction between biological ligands and metal ions, various complexes using HL as ligand have been synthesized, and their crystal structures studied. In complexes containing Na^+ or K^+ , the ligand L⁻ is not directly coordinated to the metal ion, which is surrounded by coordination H_2O molecules [1]. In complexes of $Ba^{2+},\ Ag^+,\ Zn^{2+},\ Cd^{2+}$ and Ni^{2+} [1–5], both the carboxylic group and the amino group of L⁻ are coordinated to the metal. However, in complexes of Sr^{2+} , Mg^{2+} and Co^{2+} with L⁻ [1,6,7], only the oxygen atoms of the carboxylic groups are coordinated to the metal ion and the amino groups of the L⁻ ligands are not coordinated. Therefore, the effect of metal ions on the structural type of their HL complexes is apparent. Structural investigations of HL rare earth (RE) complexes are sparse. Based on their

X-ray powder diffraction patterns, Brzyska and Rzaczyńska suggested that the HL complexes of RE elements La-Tm, Y and Yb-Lu are isostructural [8]. Nevertheless, a systematic structural investigation on complexes of the lanthanide series with this ligand has not existed to date. The p-aminobenzoic acid complexes of some RE metals Nd, Dy and Yb have been synthesized and their crystal structures determined [9–11]. The results show that the crystal structures of the Dy^{3+} and Yb^{3+} complexes are alike, whereas the crystal structure of the Nd^{3+} complex is clearly different from the two complexes mentioned above. The effect of lanthanide contraction on the structure of RE complexes has been reported earlier [12-18] that, using 3,5pyrazoldicarboxylic acid (H₃pdc) as the ligand, lanthanide complexes (Ln = La, Ce, Eu, Er and Lu) of three different structural types (two-dimensional single layer, two-dimensional double layer and three dimensional array) can be obtained [18]. Nitrilotriacetic acid (H₃NTA) is an important derivative of glycine. A series of Ln-Cu-NTA complexes have been synthesized in our laboratory. Crystal structures of these complexes indicate that their dimensional diversity is controlled by lanthanide contraction [17]. As an extension of this work, we herein report the synthesis and structural diversity of a series of RE-L⁻ complexes.

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Table 1

Pan et al. [18] have suggested that the pH of the reactions plays a crucial role in the formation of either single- or double-layered structures, because the tri-acid ligand (H₃pdc) could coordinate either in the form of H₂pdc⁻ or Hpdc²⁻, which is controlled by the amount of H⁺ in a reaction mixture. By adjusting the pH value, they successfully isolated a single-phase, double-layered erbium structure at pH 5, and a single-layered structure at pH 1, respectively. Nonetheless, the effect of reaction pH on the structure of the RE complex formed using a monoacid with an amino group as the ligand, such as HL, has not been reported before.

In order to further investigate the structure characteristics of RE complexes with *p*-aminobenzoic acid, to gain better knowledge on the different factors that may influence the structure of these complexes, we have synthesized a series of HL complexes of RE^{3+} ions (RE = La, Ce, Pr, Sm, Eu, Tb, Dy, Ho, Er, Yb, Lu and Y). The structures of these complexes have been determined. The effects of lanthanide contraction and pH value on compound structure have been studied.

2. Experimental section

2.1. Materials and apparatus

RE oxides of over 99.9% purity were obtained from the Rare Earth Company in Beijing. Solutions of RECl₃ were prepared by dissolving RE oxides in hydrochloric acid. Analytical grade hydrochloric acid and aqueous ammonia were purchased from the Chemical Reagent Company in Beijing.

Analyses of C, H, and N were performed on a German Elementar Vario EL instrument. IR spectra were measured using KBr pellets with a Nicolet Magna-IR 750 spectrometer at 295 K. Thermal analyses were performed on a Du Pont 1090B thermal analyzer.

2.2. Preparations of complexes

RE complexes were prepared with the following procedure: Aqueous solution of HL (0.9 mmol), the pH value of which was adjusted to ca. 4 with aqueous ammonia, was mixed with RECl₃ (0.3 mmol) under stirring. The pH value of the solution was adjusted carefully to ca. 4.0 or 5.0. After filtration, the solution was left to stand at room temperature. Single crystals of the complexes were obtained in ca. 40% yield after one week. The results of elemental analysis are listed in Table 1.

2.3. X-ray crystallographic study

All data collections were carried out on a Nonius Kappa CCD diffractometer or a Siemens P4 four-circle diffractometer with graphite-monochromated Mo K α

Results of C, H and N analyses for complexes (outside brackets, calculated data; inside brackets, found data)

Complexes	Formula	N (%)	C (%)	H (%)
1	LaC21N2O7H20	7.43 (6.67)	44.62 (44.57)	3.57 (3.19)
2	$CeC_{21}N_{3}O_{7}H_{20}$	7.42 (7.28)	44.52 (44.55)	3.56 (3.46)
3	$PrC_{21}N_{3}O_{7}H_{20}$	7.41 (7.02)	44.46 (44.50)	3.55 (3.14)
4	SmC ₂₁ N ₃ O ₇ H ₂₀	7.29 (7.19)	43.73 (43.98)	3.50 (3.45)
5	EuC21N3O7H20	7.27 (7.15)	43.61 (43.62)	3.49 (3.57)
6	TbC21N3O7H20	7.18 (6.93)	43.08 (42.56)	3.42 (3.37)
6′	TbC21N3O9H24	6.76 (7.11)	40.59 (40.86)	3.89 (3.51)
7	DyC21N3O7H20	7.14 (7.40)	42.83 (43.31)	3.42 (3.41)
8	HoC21N3O9H24	6.70 (6.66)	40.19 (40.43)	3.83 (3.82)
9	ErC21N3O7H20	7.08 (6.52)	42.50 (42.35)	3.37 (2.96)
10	YbC21N3O9H24	6.61 (6.59)	39.69 (39.84)	3.81 (3.71)
11	$LuC_{21}N_3O_9H_{24}$	6.59 (6.53)	39.57 (39.69)	3.80 (3.65)
12	$YC_{21}N_{3}O_{9}H_{24}$	7.62 (7.61)	45.75 (46.58)	4.39 (4.26)

radiation (0.71073 Å). For example, with $\text{TbC}_{21}\text{H}_{20}\text{N}_{3}\text{O}_{7}$ (6), intensity data was collected on a Nonius Kappa CCD diffractometer in the ω -scan mode. The structures were solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms of water molecules were located from difference electronic Fourier maps. Other hydrogen atoms were placed by calculated positions and refined isotropically. Crystal data, details of data collection and refinement are listed in Table 2. Crystal cell parameters of all the complexes are listed in Table 3. Important bond lengths and angles are given in Tables 4a-4d.

3. Results and discussion

3.1. IR spectra

Since the IR spectra of isomorphous complexes are generally alike, complex 7 and 6' are chosen as representatives in the following discussion. The IR resonances of the carboxylate moiety, $\nu_{as}(OCO)$ and $\nu_{s}(OCO)$, in free L⁻ ion and coordinated L⁻ ligands, are compared. After coordination to the metal ion center, the v_{as} (OCO) absorption is found red-shifted from 1601 to 1589 and 1592 cm^{-1} ; the $v_{\rm s}({\rm OCO})$ absorption has also red-shifted from 1423 cm⁻¹ down to 1398 and 1417 cm⁻¹, in complexes 7 and 6', respectively. These results indicate that the carboxyl groups of the ligand are bound to the metal ions [19]. The value of $v_{\rm s}(\rm C-N)$ at 1326 cm⁻¹ in NH₄L shifted 30 cm⁻¹ down to 1296 cm^{-1} in complex 7, whereas this shifting is not found in complex 6'. These results suggest that the N atoms of the ligands are coordinated to the metal ions in complex $[Dy_2L_6(H_2O)_2]_n$, and they are not coordinated in complex $[Tb_2L_6(H_2O)_4] \cdot 2H_2O$ [19].

Table 2	
Crystallographic data for complexes 1, 6, 6' and 12	

Empirical formula	LaC ₂₁ H ₂₀ N ₃ O ₇ (1)	TbC ₂₁ H ₂₀ N ₃ O ₇ (6)	$TbC_{21}H_{24}N_3O_9(6')$	YC ₂₁ H ₂₄ N ₃ O ₉ (12)
Crystal size (mm)	$0.35 \times 0.15 \times 0.1$	$0.20 \times 0.18 \times 0.05$	$0.3 \times 0.2 \times 0.1$	$0.50\times0.46\times0.46$
<i>T</i> (K)	293 (2)	293 (2)	293 (2)	289 (2)
Crystal system	Monoclinic,	Monoclinic,	Triclinic	Triclinic
Space group	$P2_1/n$	$P2_1/n$	$P\overline{1}$	$P\overline{1}$
a (Å)	9.8404 (2)	9.7278 (2)	9.09640 (10)	9.0680 (10)
<i>b</i> (Å)	22.7519 (5)	22.7462 (4)	11.01170 (10)	10.9943 (8)
<i>c</i> (Å)	9.8811 (2)	9.8147 (2)	12.7430 (2)	12.716 (2)
α (°)	90	90.00	89.3725 (5)	88.740 (8)
β (°)	100.043 (3)	99.9410 (10)	72.0360 (6)	71.990 (10)
γ (°)	90	90.00	75.0730 (7)	74.447 (9)
$V(\text{\AA}^3)$	2178.36 (8)	2139.10 (7)	1169.97 (2)	1158.9 (2)
Ζ	4	4	2	2
Μ	565.31	585.32	621.35	551.34
$D_c ({\rm g}{\rm cm}^{-3})$	1.724	1.817	1.764	1.580
$\mu (\mathrm{mm}^{-1})$	2.009	3.355	3.078	2.573
F (000)	1120	1152	616	564
λ (Å) (Mo K_{α})	0.71073	0.71073	0.71073	0.71073
Monochromator	Graphite	Graphite	Graphite	Graphite
θ range for data collection (°)	3.41-27.47	3.41-27.50	3.45-27.47	1.69-25.01
Index range <i>h</i> ; <i>k</i> ; <i>l</i>	-12-12; -29-29;	-12-12; -29-29;	-11-11; -14-14;	0-10; -12-13;
	-12-12	-12-12	-16-16	-14 - 15
Reflections collected	32158	32765	24082	4318
Independent reflections	4963 ($R_{int} = 7.01\%$)	4909 ($R_{int} = 7.12\%$)	5250 ($R_{\rm int} = 4.4\%$)	$4038 \ (R_{\rm int} = 1.92\%)$
Observed reflections $[I > 2\sigma(I)]$	2952	2954	4813	3215
Number of parameters refined	351	292	350	392
$R[I > 2\sigma(I)]$	0.0286	0.0311	0.0311	0.0288
$wR [I > 2\sigma(I)]$	0.0516	0.0682	0.0763	0.0553
Goodness-of-fit on F^2	1.004	0.993	1.066	0.926

3.2. Thermal analysis

Complex **6** lost its coordinated water molecule in the temperature range 182.7–207.9 °C (loss of weight found: 2.92%; loss of weight calculated based on the loss of one water molecule for TbL₃·H₂O: 3.08%); the complex loses weight rapidly from thermal decomposition in the temperature range 372.6–456.6 °C. Complex **6**' rapidly lost its crystal water molecule when exposed to air at room temperature; therefore, the thermal analysis of **6**' was performed when no more weight change was observed in

molecules in the temperature range 189.6–205.5 °C (loss of weight found: 2.91%; loss of weight calculated based on the loss of one water molecule for TbL₃·2H₂O: 2.99%). The complex quickly decomposed in the temperature range 430.4–439.4 °C, that is, complex **6**' lost the second coordination water molecule during thermal decomposition. These results are consistent with the bond length comparisons from the structural analysis discussed below. The Tb–O(7) (water) bond length (2.499 Å) is the longest among all Tb-O bonds in complex **6** [see Table 4b].

air. Complex 6' lost only one of its two coordination water

Table 3			
Crystal cell	parameters	of com	olexes

Sample no.	Space group	a(Å)	b(A)	$c(\mathring{A})$	$\alpha(^{\circ})$	β(°)	γ(°)	pН
1	$P2_1/n$	9.8404 (2)	22.7519 (5)	9.8811 (2)	90	100.043 (3)	90	4.0
2	$P2_1/n$	9.8257 (2)	22.7462 (4)	9.8498 (2)	90	100.0091 (8)	90	5.0
3	$P2_1/n$	9.823 (1)	22.732 (3)	9.826 (1)	90	100.05 (1)	90	4.0
4	$P2_1/n$	9.7761 (5)	22.7388 (5)	9.8366 (4)	90	99.9697 (5)	90	5.0
5	$P2_1/n$	9.7609 (4)	22.7802 (5)	9.8376 (3)	90	99.905 (2)	90	5.0
6	$P2_1/n$	9.7278 (2)	22.7462 (4)	9.8147 (2)	90	99.9410 (10)	90	5.0
6'	$P\bar{1}$	9.09640 (10)	11.01170 (10)	12.7430 (2)	89.3725 (5)	72.0360 (6)	75.0730 (7)	4.0
7	$P2_1/n$	9.72190 (10)	22.7544 (5)	9.8065 (2)	90	99.9360 (10)	90	5.0
8	Pī	9.0637 (11)	10.9934 (11)	12.7192 (17)	88.8481 (99)	72.0048 (104)	74.5697 (93)	4.0
9	$P2_1/n$	9.7214 (2)	22.7475 (5)	9.7812 (2)	90	99.9280 (10)	90	5.0
10	Pī	8.8173 (4)	10.5753 (5)	12.2574 (4)	89.840 (3)	71.627 (3)	73.913 (2)	5.0
11	$P\overline{1}$	9.0317 (5)	10.9519 (4)	12.7067 (5)	88.3277 (4)	71.9684 (6)	74.2445 (4)	5.0
12	$P\overline{1}$	9.068 (1)	10.994 (1)	12.716 (2)	88.740 (8)	71.99 (1)	74.447 (9)	4.0

Table 4c

Table 4a Selected bond lengths (Å) and angles (°) for complex 1

Bond lengths (Å)			
La(1)-O(4)#1	2.451 (2)	La(1)-O(3)	2.467 (2)
La(1)-O(5)	2.486 (2)	La(1)-O(6)#2	2.488 (2)
La(1) - O(1)	2.550 (2)	La(1) - O(2)	2.580 (2)
La(1)-O(7)	2.638 (2)	La(1)-N(2)#3	2.777 (3)
La(1)-O(6)	2.982 (2)		
Bond angles (°)			
O(4)#1-La(1)-O(3)	91.04 (7)	O(4)#1-La(1)-O(5)	85.46 (8)
O(3)-La(1)-O(5)	136.32 (8)	O(4)#1-La(1)-O(6)#2	146.12 (7)
O(3)-La(1)-O(6)#2	95.62 (7)	O(5)-La(1)-O(6)#2	111.06 (7)
O(4)#1-La(1)-O(1)	72.55 (7)	O(3)-La(1)-O(1)	123.98 (7)
O(5)-La(1)-O(1)	96.36 (8)	O(6)#2-La(1)-O(1)	76.24 (7)
O(4)#1-La(1)-O(2)	71.72 (7)	O(3)-La(1)-O(2)	72.91 (7)
O(5)-La(1)-O(2)	144.19 (8)	O(6)#2-La(1)-O(2)	78.60 (7)
O(1)-La(1)-O(2)	51.08 (6)	O(4)#1-La(1)-O(7)	72.95 (7)
O(3)-La(1)-O(7)	72.41 (7)	O(5)-La(1)-O(7)	64.94 (8)
O(6)#2-La(1)-O(7)	140.56 (7)	O(1)-La(1)-O(7)	141.79 (7)
O(2)-La(1)-O(7)	129.16 (6)	O(4)#1-La(1)-N(2)#3	140.93 (8)
O(3)-La(1)-N(2)#3	79.61 (8)	O(5)-La(1)-N(2)#3	76.32 (9)
O(6)#2-La(1)-N(2)#3	72.90 (8)	O(1)-La(1)-N(2)#3	142.86 (7)
O(2)-La(1)-N(2)#3	137.85 (8)	O(7)-La(1)-N(2)#3	68.05 (8)

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

In complex **6'** [see Table 4c], the Tb–O(7) (water) bond length (2.419 Å) is longer than the average value (2.391 Å) of Tb–O (COO) bond lengths, and Tb-O(8) (water) bond length (2.351 Å) is shorter than the average value (2.391 Å). Consequently, the temperature required for the loss of one [H₂O(8)] of the two coordinated water molecules is much higher than that for the loss of the other [H₂O(7)]; and the loss of the second water molecule [H₂O(8)] is accompanied by the loss of the L⁻ ligand from the compound.

Table 4b Selected bond lengths (Å) and angles (°) for complex 6

Bond lengths (Å)			
Tb(1)-O(6)#1	2.287 (3)	Tb(1)-O(4)	2.446 (3)
Tb(1)-O(5)	2.319 (3)	Tb(1)-O(3)	2.452 (3)
Tb(1)-O(1)	2.327 (2)	Tb(1)-O(7)	2.499 (3)
Tb(1)-O(2)#2	2.335 (3)	Tb(1)-N(1)#3	2.688 (3)
Bond angles (°)			
O(6)#1-Tb(1)-O(5)	103.29 (10)	O(6)#1-Tb(1)-O(1)	92.77 (10)
O(5)-Tb(1)-O(1)	143.97 (10)	O(6)#1-Tb(1)-O(2)#2	148.42 (10)
O(5)-Tb(1)-O(2)#2	89.09 (10)	O(1)-Tb(1)-O(2)#2	93.78 (10)
O(6)#1-Tb(1)-O(4)	77.07 (10)	O(5) - Tb(1) - O(4)	87.57 (10)
O(1)-Tb(1)-O(4)	127.78 (9)	O(2)#2-Tb(1)-O(4)	74.53 (9)
O(6)#1-Tb(1)-O(3)	79.65 (10)	O(5) - Tb(1) - O(3)	139.71 (9)
O(1)-Tb(1)-O(3)	74.41 (9)	O(2)#2-Tb(1)-O(3)	72.49 (10)
O(4)-Tb(1)-O(3)	53.42 (8)	O(6)#1-Tb(1)-O(7)	138.09 (10)
O(5)-Tb(1)-O(7)	71.10 (10)	O(1) - Tb(1) - O(7)	75.39 (9)
O(2)#2-Tb(1)-O(7)	73.33 (10)	O(4) - Tb(1) - O(7)	141.35 (10)
O(3)-Tb(1)-O(7)	132.06 (9)	O(6)#1-Tb(1)-N(1)#3	69.29 (10)
O(5)-Tb(1)-N(1)#3	74.71 (10)	O(1)-Tb(1)-N(1)#3	81.44 (9)
O(2)#2-Tb(1)-N(1)#3	142.28 (10)	O(4)-Tb(1)-N(1)#3	136.57 (9)
O(3)-Tb(1)-N(1)#3	139.38 (10)	O(7)-Tb(1)-N(1)#3	69.24 (10)

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

Selected bond lengths (Å) and angles (°) for complex 6'Bond lengths (Å) Tb(1) - O(3)2.277 (2) Tb(1)-O(4)#1 2.264 (3) Tb(1)-O(8) 2.351 (2) Tb(1)-O(6) 2.367 (2) Tb(1)-O(7) 2.419 (2) Tb(1)-O(2) 2.422 (3) Tb(1)-O(5) 2.504 (2) Tb(1)-O(1) 2.514 (2) *Bond angles* (°) 109.25 (12) O(4)#1-Tb(1)-O(8)O(4)#1-Tb(1)-O(3)86.80 (12) O(3) - Tb(1) - O(8)156.27 (11) O(4)#1-Tb(1)-O(6) 83.84 (11) O(3)-Tb(1)-O(6) 123.23 (10) O(8)-Tb(1)-O(6) 74.55 (9) O(4)#1-Tb(1)-O(7)73.32 (10) O(3)-Tb(1)-O(7) 80.86 (10) O(8)-Tb(1)-O(7) 87.53 (9) 151.74 (10) O(6) - Tb(1) - O(7)O(4)#1-Tb(1)-O(2) 163.26 (11) O(3)-Tb(1)-O(2) 77.24 (11) O(8) - Tb(1) - O(2)92.34 (11) O(6) - Tb(1) - O(2)79.83 (9) O(7)-Tb(1)-O(2) O(4)#1-Tb(1)-O(5) 123.37 (8) 74.95 (10) O(3)-Tb(1)-O(5) O(8) - Tb(1) - O(5)76.35 (9) 125.90 (8) 53.45 (8) O(6)-Tb(1)-O(5) O(7) - Tb(1) - O(5)131.69 (8) 92.22 (9) O(2) - Tb(1) - O(5)O(4)#1-Tb(1)-O(1) 142.92 (10) O(3) - Tb(1) - O(1)78.22 (9) O(8) - Tb(1) - O(1)78.54 (9) O(6) - Tb(1) - O(1)123.45 (8) O(7) - Tb(1) - O(1)72.20(8) O(2)-Tb(1)-O(1) 52.53 (8) O(5)-Tb(1)-O(1) 140.38 (8)

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

3.3. Description of structures of complexes

Complex 1 is monoclinic and has space group $P2_1/n$. As shown in Fig. 1, in this complex, each La^{3+} ion is chelated by two carboxyl groups, coordinated by three carboxylic oxygen atoms from three ligands, one nitrogen atom from another ligand and one water molecule. Therefore, each La^{3+} ion is nine-coordinated by six L^- ligands and one H₂O molecule. In complex 1, the ligand is coordinated to the La^{3+} ion in three different coordination

Table 4d Selected bond lengths (Å) and angles (°) for complex 12

Bond lengths (Å)			
Y-O(1)	2.2347 (18)	Y-O(2)#1	2.236 (2)
Y-O(7)	2.310 (2)	Y-O(6)	2.3383 (18)
Y-O(8)	2.387 (2)	Y-O(4)	2.3928 (18)
Y-O(3)	2.4822 (17)	Y-O(5)	2.4861 (18)
Bond angles (°)			
O(1)-Y-O(2)#1	108.23 (8)	O(1) - Y - O(7)	157.00 (9)
O(2)-Y-O(7)#1	85.42 (8)	O(1) - Y - O(6)	124.05 (7)
O(2)-Y-O(6)#1	83.00 (7)	O(7) - Y - O(6)	74.91 (8)
O(1)-Y-O(8)	78.95 (7)	O(2)-Y-O(8)#1	73.86 (7)
O(7)-Y-O(8)	87.62 (9)	O(6) - Y - O(8)	152.06 (7)
O(1) - Y - O(4)	79.22 (7)	O(2)-Y-O(4)#1	162.27 (7)
O(7) - Y - O(4)	93.26 (8)	O(6) - Y - O(4)	79.60 (7)
O(8) - Y - O(4)	123.79 (7)	O(1) - Y - O(3)	79.84 (7)
O(2)-Y-O(3)#1	142.74 (7)	O(7) - Y - O(3)	78.29 (8)
O(6)-Y-O(3)	123.46 (6)	O(8) - Y - O(3)	72.19 (7)
O(4) - Y - O(3)	53.26 (6)	O(1) - Y - O(5)	75.67 (6)
O(2)-Y-O(5)#1	75.58 (7)	O(7) - Y - O(5)	126.60 (8)
O(6)-Y-O(5)	53.78 (6)	O(8)-Y-O(5)	131.21 (7)
O(4) - Y - O(5)	91.30 (6)	O(3)-Y-O(5)	140.22 (6)

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

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Fig. 1. An ORTEP view of complex 1 showing the connection between La^{3+} ions and ligands. Hydrogen atoms are omitted for clarity.

modes (mode 1, 2 and 3). In mode 1, the carboxyl group with the bridging oxygen $(\mu_2 - O)$ connects two neighboring La³⁺ ions in a tridentate-bridging mode. In mode 2, the carboxyl group acts as a bidentate-bridge connecting two La^{3+} ions that are coordinated by μ_2 -O, forming a onedimensional chain. In other words, the carboxyl groups have two types of bridging mode in the one-dimensional chain, that is, either two tridentate-bridging carboxyl groups or two bidentate-bridging carboxyl groups exist between the two neighboring La^{3+} ions. The amino group of the L^{-} ligand that has a bidentate-bridging carboxyl group (mode 2) is coordinated to a La³⁺ ion from the adjacent chain, forming a two-dimensional plane (Fig. 2). In mode 3, the carboxyl group chelates the La³⁺ ion. The amino groups are not coordinated to any La^{3+} ion in both mode 1 and 3. In complex 1, the coordination water or carboxyl groups and the uncoordinated amino groups from different layers are



Fig. 2. A two-dimensional structure of complex 1 showing the connection between the chains. Hydrogen atoms are omitted for clarity.



Fig. 3. An ORTEP view of complex 6 showing the connection between Tb^{3+} ions and ligands. Hydrogen atoms are omitted for clarity.

linked together through hydrogen bonds forming a threedimensional structure.

As shown in Figs. 3 and 4, the structure of complex **6** is similar to that of complex **1**. There is also a two-dimensional structure of complex **6** where the ligand L^- has three different coordination modes (mode 1, 2 and 3), and the links formed between the metal ions are similar except for mode 1 between complexes **1** and **6**. The two tridentate-bridging carboxyl groups from the L^- ligands (mode 1) between two neighboring La³⁺ ions are replaced by two bidentate-bridging carboxyl groups (mode 1) between two neighboring Tb³⁺ ions, that is, there is no bridging oxygen (μ_2 -O) in complex **6**. As a result, each Tb³⁺ ion is eight-coordinated by six ligands (L⁻) and one H₂O molecule.

Complex **6**' is triclinic and has space group $P_{\overline{1}}$. It is a binuclear complex that has two bidentate carboxyl groups bridging the two Tb³⁺ ions (see Fig. 5). Each Tb³⁺ ion is also chelated by two carboxyl groups, and coordinated by two H₂O molecules. The amino groups in the ligands are not connected to the Tb³⁺ ions. Therefore, each Tb³⁺ ion is eight-coordinated by four ligands (L⁻) and two H₂O molecules. Moreover, in the crystal structure of complex **6**', the coordination H₂O molecules in each binuclear compound are linked to the amino groups or carboxyl groups of adjacent binuclear molecules through hydrogen bonds. Uncoordinated H₂O molecules in the crystal lattice are linked to the amino groups or carboxyl groups of the ligands through hydrogen bonds as well.

Based on the results of elemental analyses (see Table 1) and crystal cell parameters (shown in Table 3) for complex 2-5, and 7-12, we have found that complexes 2-5, 7 and 9 are isomorphous with 6, and complexes 8 and 10-12 are isomorphous with 6'. Details of data collection and refinements are listed in Table 2. Selected bond lengths and angles for complexes 1, 6, 6' and 12 are listed in Table 4a-d.

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Fig. 4. A two-dimensional structure of complex $\mathbf{6}$ showing the connection between the chains. Hydrogen atoms and the L⁻ ligands in mode 3 are omitted for clarity.

3.4. Effect of lanthanide contraction and pH on the crystal structure

In order to learn the effect of pH on structure, the solution pH of the reaction mixture was carefully adjusted to ca. 4.0 or ca. 5.0, respectively, during the synthesis of the complexes. However, single crystals suitable for X-ray structure analysis were obtained only for complexes 1-12 and 6'. Corresponding solution pH values of the reaction mixtures are listed in Table 3. These results indicate that light-RE ions, which have relatively large ion radii, tend to form two-dimensional (2D) array structures (monoclinic, $P2_1/n$ with a high metal ion coordination number (nine coordination) (e.g. complex 1) or with a eight-coordinated metal ion, such as complexes 2-5 and the NdL₃·3H₂O [10] complex, which is isostructural with complexs 2-5, each of which has six L⁻ ligands surrounding a metal ion; in these complexes, the N atoms of the amino groups are also able to coordinate to the RE ions in existence of the carboxyl groups and water molecules due to there is the adequate space around the metal ions. The heavy-RE ions, which have smaller ion radii, tend to form binuclear complexes (triclinic, $P\bar{1}$) with a lower metal coordination number (eight coordination), such as complexes 10 and 11, each of which has four L⁻ ligands surrounding a metal ion. A compound identical to complex 10 has been reported in the literature [9]. The structures of the middle-RE ion complexes (e.g. Tb^{3+} , and Dy^{3+} , Ho^{3+} ; Er^{3+} may be included. The crystal structure of complex DyL₃·3H₂O obtained by Khiyalov et al. [11] is different from complex 7 but is identical to complex 6'.), they (6, 6', 7, 8, 9) may be affected by the reaction pH. A possible explanation for this is that, coordination of the amino group to the metal ion is more favorable at high pH

than at low pH. This is because the concentration of H^+ ions, which can protonate amino groups and subsequently affect their coordination ability with a metal ion, is lower in a high pH solution than in a low pH solution. Furthermore, sizes of the middle RE ions are suitable for formation of complexes coordinated by either six L⁻ ligands or four L⁻ ligands. Therefore, for the middle-RE ions, the complexes



Fig. 5. An ORTEP view of complex 6' showing the connection between Tb³⁺ ions and ligands. Hydrogen atoms and crystal water molecule are omitted for clarity.

obtained in the higher pH solutions (ca. 5.0) belong to twodimensional (2D) array structures in which the N atoms of the amino groups can be coordinated to the metal ions, and the complexes formed in the lower pH solutions (ca. 4.0) possess binuclear structures in which the N atoms of the amino groups are uncoordinated; however, for light-RE or heavy-RE ions, the effect of solution pH on the crystal structure of the complexes can be neglected in the range of pH 4–5. The above observations indicate that various coordination modes of ligand L⁻ and the structural change of the RE complexes are controlled by lanthanide contraction. As for the complexes of the middle-RE ions, the effect of solution pH on the crystal structure should also be taken into consideration.

According to the regularity, it may be suitable to divide the RE elements into three groups according to the structure of their corresponding RE-L complexes. La, the complex of which has a 2D layered structure (monoclinic, $P2_1/n$) where the La^{3+} ion is nine-coordinated, belongs to group 1. Ce and Pr, the complexes of which have 2D structures (monoclinic, $P2_1/n$ where the RE³⁺ (RE = Ce, Pr) ion is eightcoordinated, are in group 2. Nd-Eu may also belong to group 2. Yb and Lu, the complexes of which have different structural types (triclinic, $P\bar{1}$) where the coordination number of the RE^{3+} ion (RE = Yb, Lu) is eight, form group 3. Tb-Er can be assigned to either group 2 or group 3, because they have medium ion radii and consequently, their complexes could have different structural types depending on the reaction pH (4.0 or 5.0). Based on the results shown in Table 3, the Y-L complex (complex 12) may have similar properties since the radius of the Y^{3+} ion (1.019 Å) is close to that of the Ho^{3+} ion (1.015 Å).

4. Conclusion

A series of RE complexes with *p*-aminobenzoic acid have been synthesized. The structural variation of these RE complexes is controlled by lanthanide contraction. It may be suitable to divide the RE elements into three groups according to the structure of their corresponding RE-L complexes. For complexes of middle-RE ions, effect of solution pH on their structure should also be taken into consideration.

CCDC-228747, 228748, 230046, 230047, 230048, 230049, 230050 contains the supplementary crystallographic data for this paper. 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 336033).

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