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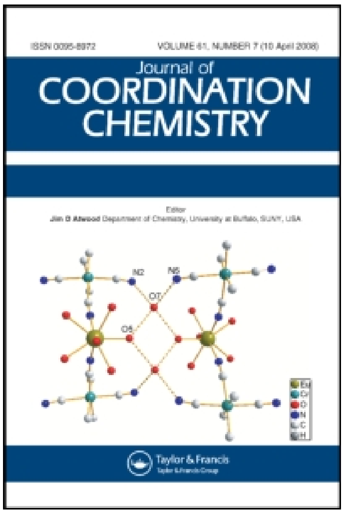

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Syntheses of rare earth metal complexes with aminopolycarboxylic acids and study on structural changes: Nine-coordinated mononuclear $K_2[Dy^{III}(dtpa)(H_2O)]\cdot 6H_2O$ and binuclear $K_4[Ho^{III}_2(dtpa)_2]\cdot 4H_2O$

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Syntheses of rare earth metal complexes with aminopolycarboxylic acids and study on structural changes: Nine-coordinated mononuclear $K_2[Dy^{III}(dtpa)(H_2O)]\cdot 6H_2O$ and binuclear $K_4[Ho^{III}_2(dtpa)_2]\cdot 4H_2O$

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The crystal and molecular structures of mononuclear $K_2[Dy^{III}(dtpa)(H_2O)]\cdot 6H_2O$ (H_5dtpa = diethylenetriaminepentaacetic acid) and binuclear $K_4[Ho^{III}_2(dtpa)_2]\cdot 4H_2O$ complexes have been determined by single-crystal X-ray structure analyses. The crystal of $K_2[Dy^{III}(dtpa)(H_2O)]\cdot 6H_2O$ complex belongs to the triclinic crystal system, $P\bar{1}$ space group. The $[Dy^{III}(dtpa)(H_2O)]^{2-}$ complex anion has a nine-coordinate pseudo-monocapped square antiprismatic structure, in which the nine coordinated atoms (three N and six O) are from one dtpa ligand and one water molecule. The crystal of $K_4[Ho^{III}_2(dtpa)_2]\cdot 4H_2O$ complex belongs to triclinic crystal system, $P\bar{1}$ space group. The $[Ho^{III}_2(dtpa)_2]^{4-}$ complex anion is composed of two identical parts and every $Ho^{III}O_6N_3$ has a nine-coordinate, distorted monocapped square antiprismatic structure, in which the dtpa ligand coordinates to one central Ho^{III} ion with three N atoms and five O atoms and to the other Ho^{III} ion with one O atom in the same coordinated carboxylic group. Although the Dy^{III} and Ho^{III} ions have close ionic radii (1.052 and 1.041 Å) and electronic configuration (f^9 and f^{10}) they form mononuclear and binuclear nine-coordinate complexes, respectively. Perhaps there is a critical ionic radius for mononuclear and binuclear structures, namely the dtpa complexes of rare earth metals with larger ionic radii than 1.052 Å of Dy^{III} ion adopt a mononuclear nine-coordinate structure, while those with smaller ionic radii than 1.041 Å of Ho^{III} ion adopt a binuclear nine-coordinate structure.

Keywords: Dy^{III}; Ho^{III}; Diethylenetriaminepentaacetic acid (H_5dtpa); Mononuclear; Binuclear; Complexes; Molecular structure

1. Introduction

Coordination chemistry of rare earth (RE) metals and aminopolycarboxylic acids is widely investigated because of importance in medicinal and biochemical

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applications [1,2], such as some Nd^{III} complexes having good anti-inflammation activity, Gd^{III} complexes as contrast agents in magnetic resonance imaging (MRI) [3–6] and Tb^{III} and Eu^{III} complexes used to diagnose some diseases as the ionic probes for their characteristic fluorescence [7]. In addition, many radioactive RE metal ions can emit special radial rays with suitable half-life and moderate energy [8]; their complexes are usually applied in the diagnosis and therapies of diseases, for example: the $^{165}Dy^{III}$ and $^{166}Ho^{III}$ complexes were used in synovectomy of rheumatoid knee [9,10]. Though many RE metal or radioactive RE metal complexes have quite good effects on the diagnoses and therapies to diseases, flushing these ions after they finish the tasks as medicine or diagnose agent is important; these ions enter the body as stable complexes and have the selectivity and affinity on the focus position and then depart from the body quickly after the diagnoses and therapies [11]. Understanding the character of the RE metal or radioactive RE metal complexes in details may lead to improvement. For these reasons interest in the molecular structures of the RE metal complexes with aminopolycarboxylic acids exists [12–19].

In general, the structures or coordination numbers of RE metal complexes with aminopolycarboxylic acids depend on the ionic radius, electronic configuration and oxidation state of the central metal ion. It is well known that differences in ionic radii among RE metal ions and the crystal field stabilization energy (CFSE) of their complexes are very small, but the RE metal ions can form ten-, nine- and eight-coordinate complexes with aminopolycarboxylic acids. For example, some RE metal ions with radii from 1.098 Å to 1.030 Å, i.e., Sm^{III} (1.098 Å and f^5), Eu^{III} (1.087 Å and f^6), Gd^{III} (1.078 Å and f^7), Tb^{III} (1.063 Å and f^8), Dy^{III} (1.052 Å and f^9), Ho^{III} (1.041 Å and f^{10}) and Er^{III} (1.030 Å and f^{11}) form nine-coordinate complexes. Recently, an interesting phenomenon of Gd^{III} ion (ionic radius of 1.078 Å) forms a mononuclear nine-coordinate complex with diethylenetriaminepentaacetic acid (H_5dtpa) ligand [20], while the Yb^{III} ion having the relatively small ionic radius of 1.008 Å forms a binuclear nine-coordinate complex with the same ligand [21]. A critical ionic radius of mononuclear and binuclear nine-coordinate structure between two neighboring RE metal ions may exist. In order to look for this interesting critical ionic radius, Dy^{III} and Ho^{III} complexes with dtpa were synthesized and their crystal and molecular structures determined, respectively. The mononuclear nine-coordinate $K_2[Dy^{III}(dtpa)(H_2O)] \cdot 6H_2O$ and binuclear nine-coordinate $K_4[Ho^{III}{}_2(dtpa)_2] \cdot 4H_2O$ complexes were obtained indicating the critical ionic radius exists between Dy^{III} and Ho^{III} ions. Therefore, RE metal ions having ionic radius larger than 1.052 Å of Dy^{III} will form mononuclear nine-coordinate complexes with dtpa ligand, while RE metal ions having the ionic radius smaller than 1.041 Å of Ho^{III} will form binuclear nine-coordinate complexes with dtpa ligand.

2. Experimental

2.1. *Preparation of $K_2[Dy^{III}(dtpa)(H_2O)] \cdot 6H_2O$ (1)*

1.96 g (5.0 mmol) H_5dtpa was added to 100 mL water, and then 0.93 g (2.5 mmol) Dy_2O_3 powder was added in batches. The mixture was stirred and refluxed for 6.0 h, the pH was adjusted to 6.5 by aqueous $KHCO_3$. After the solution became transparent it was concentrated to 20 mL. Colorless crystals appeared after two weeks at room temperature. The Dy and K were analyzed using oxalic acid and sodium tetraphenylboron [22], respectively. Anal. found (%): Dy 22.18, K 10.52, C 22.80, H 4.11, N 5.72. Calcd (%): Dy 22.05, K 10.61, C 22.81, H 4.10, N 5.70. This formula is consistent with the result of diffraction analysis.

2.2. *Preparation of $K_4[Ho^{III}_2(dtpa)_2]\cdot4H_2O$ (2)*

1.96 g (5.0 mmol) H_5dtpa was added to 100 mL water, and then 0.94 g (2.5 mmol) Ho_2O_3 powder was added slowly. The mixture was stirred and refluxed for 15.0 h; the pH was adjusted to 6.0 by aqueous $KHCO_3$ and after the solution became transparent it was concentrated to 25 mL. Pink crystals appeared after three weeks at room temperature. The Ho and K were also analyzed using oxalic acid and sodium tetraphenylboron, respectively. Anal. found (%): Ho 22.65, K 10.96, C 23.33, H 3.90, N 5.81. Calcd (%): Ho 22.86, K 10.84, C 23.31, H 3.91, N 5.82. This formula is consistent with the diffraction analysis.

2.3. *Physical measurements*

2.3.1. IR determination. H_5dtpa, $K_2[Dy^{III}(dtpa)(H_2O)]\cdot6H_2O$ and $K_4[Ho^{III}_2(dtpa)_2]\cdot4H_2O$ were prepared as mulls or press slice with KBr and their spectra were determined on a Shimadzu-IR 408 spectrograph.

2.3.2. TG-DTA determination. TG-DTA of $K_2[Dy^{III}(dtpa)(H_2O)]\cdot6H_2O$ and $K_4[Ho^{III}_2(dtpa)_2]\cdot4H_2O$ were determined by a Rigaku-Denki-TA 100-II thermal analyzer. Sample amounts of 4.26 mg and 4.34 mg were placed in Al pans, with a heating rate of 10°C/min under air.

2.3.3. Crystal structure determination. The details of crystal data collection and refinement parameters for $K_2[Dy^{III}(dtpa)(H_2O)]\cdot6H_2O$ and $K_4[Ho^{III}_2(dtpa)_2]\cdot4H_2O$ are all listed in table 1. Data were collected with a Bruker SMART CCD type X-ray diffractometer system using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by directed methods. All non-hydrogen atoms were refined with anisostropic thermal parameters by full-matrix. Calculations were carried out by using the SHELXTL-97 program [23] on PDP11/44 and Pentium MMX/166 computers. The structures of the complex anions and the molecular packing of the complexes in the unit cell are shown in figures 1 and 3 for $K_2[Dy^{III}(dtpa)(H_2O)]\cdot6H_2O$, and figures 2 and 4 for $K_4[Ho^{III}_2(dtpa)_2]\cdot4H_2O$. All non-hydrogen fractional atomic coordinates and equivalent isotropic temperature factors of these two complexes are omitted. Selected bond distances and bond angles of these two complexes are listed in tables 2 and 3, respectively.

3. Results and discussion

3.1. *Molecular and crystal structures of $K_2[Dy^{III}(dtpa)(H_2O)]\cdot6H_2O$ (1)*

As seen in figure 1, Dy^{III} ion is nine-coordinate with three nitrogen atoms (average Dy–N bond distance 2.686 Å) and five carboxylic oxygen atoms (average Dy–O bond distance 2.405 Å), all from the same dtpa ligand and a coordinate water molecule,

Table 1. Crystal data and structure refinement parameters for $K_2[Dy^{III}(dtpa)(H_2O)] \cdot 6H_2O$ and $K_4[Ho^{III}{}_2(dtpa)_2] \cdot 4H_2O$.

	$K_2[Dy^{III}(dtpa)(H_2O)] \cdot 6H_2O$	$K_4[Ho^{III}{}_2(dtpa)_2] \cdot 4H_2O$
Empirical formula	K2C14H30N3O16Dy	K4C28H56N6O30 Ho2
Formula weight/g mol^{-1}	737.10	1443.02
Temperature/K	293(2)	293(2)
Wavelength/Å	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimensions		
a/Å	9.174(5)	9.507(3)
b/Å	12.294(7)	10.502(4)
c/Å	12.324(7)	13.518(5)
α/°	98.286(9)	78.308(5)
β/°	91.680(9)	71.541(5)
γ/°	109.143(8)	70.583(5)
Volume/Å^3	1295.1(13)	1200.3(7)
Z	2	1
Calculated density/mg m^{-3}	1.890	2.003
Absorption coefficient/mm^{-1}	3.283	3.920
F(000)	734	1436
Crystal size/mm^3	0.30 × 0.25 × 0.20	0.40 × 0.34 × 0.32
θ range for data collection/°	1.68–25.02	2.07–26.43
Index ranges	$-9 \le h \le 10$, $-14 \le k \le 14$, $-14 \le l \le 10$	$-11 \le h \le 7$, $-13 \le k \le 13$, $-16 \le l \le 12$
Reflections collected	5168	5615
Independent reflections	4489 [R(int) = 0.0169]	4460[R(int) = 0.0203]
Completeness to θ_{max}/%	98.3	90.4
Maximum and minimum transmission	0.5597 and 0.4392	1.000000 and 0.640080
Data/restraints/parameters	4489/0/326	4460/0/317
Goodness-of-fit on F^2	1.085	1.056
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0268$, $wR_2 = 0.0743$	$R_1 = 0.0263$, $wR_2 = 0.0678$
R indices (all data)	$R_1 = 0.0314$, $wR_2 = 0.0766$	$R_1 = 0.0289$, $wR_2 = 0.0695$
Largest difference peak and hole/e Å^{-3}	0.904 and −0.780	1.356 and −1.572
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	

yielding a slightly distorted monocapped square-antiprismatic structure, in which the top and bottom planes are defined by the set O(1), O(3), O(5) and O(9) and the set of O(7), N(1), N(2) and N(3), respectively. The ninth atom O(11) is above the plane formed by O(1), O(3), O(5) and O(9). Because of the repulsion of these four O atoms, the bond distance (2.477(4) Å) of Dy^{III}–O(11) is the longest. The average distance of Dy^{III}–O bonds other than Dy^{III}–O(11) is 2.390 Å in which the longest and shortest ones are 2.438(3) Å and 2.363(4) Å, respectively. In addition, the repulsion forces the top plane near the bottom plane resulting in geometric distortion, so the average of angles ∠O(1)Dy(1)O(11), ∠O(3)Dy(1)O(11), ∠O(5)Dy(1)O(11) and ∠O(9)Dy(1)O(11) is 72.59(11)° close to the 72° that most nine-coordinate pseudo-monocapped square-antiprismatic complexes adopt and is bigger than the theoretical angle of a monocapped, square-antiprism, in which the biggest and smallest angles are 80.16(11)° and 68.40(11)°, respectively. Moreover, the ∠O(5)Dy(1)O(11) is obviously bigger than the other three corresponding angles, attributable to O(5) in the five-member Dy(1)O(5)C(8)C(7)N(2) ring, in which the C(8) retains sp^2 hybridization, and the other three carbon atoms deviate from sp^2 hybridization.

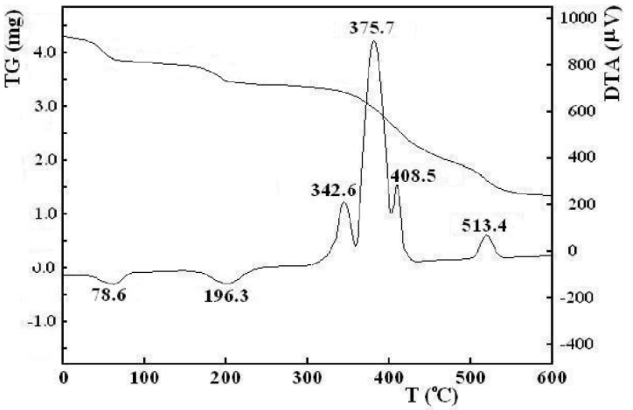

Figure 1. TG-DTA of $[Dy^{III}(dtpa)(H_2O)]^{2-}$.

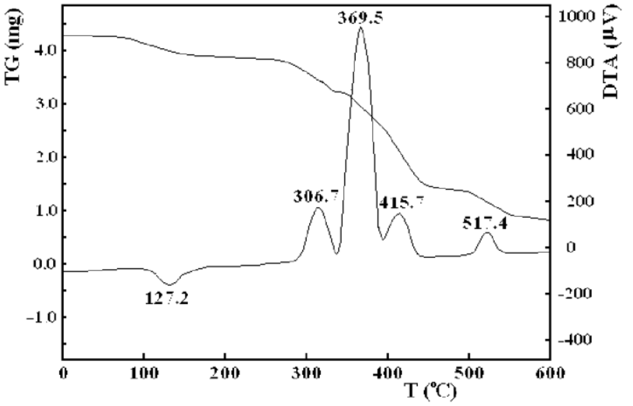

Figure 2. TG-DTA of $[Ho^{III}_2(dtpa)_2]^{4-}$.

The nine-coordinate structure of Dy^{III} complex with a dtpa ligand verified our previous inference on the coordinate structure and coordination number of the RE metal complexes with aminopolycarboxylic acids [24–26].

In one unit cell, there are two complex molecules shown in figure 3. The two molecules are mainly associated with two intermolecular hydrogen bonds ($Ow \cdots O = 2.731$ Å), in which both molecules are connected with one molecule's O atom from its coordinated water and the other molecule's carbonyl O atom. Moreover, the two molecules are also linked by hydrogen bonding from crystal water, which plays a weak role for the combination. A net structure is formed in a unit cell through the hydrogen bonds and static interaction.

3.2. *Molecular and crystal structures of $K_4[Ho^{III}_2(dtpa)_2] \cdot 4H_2O$ (2)*

It is shown in figure 2 that the $[Ho^{III}_2(dtpa)_2]^{4-}$ anion has a binuclear molecular structure, in which every Ho^{III} ion is coordinated with nine atoms, with three nitrogen

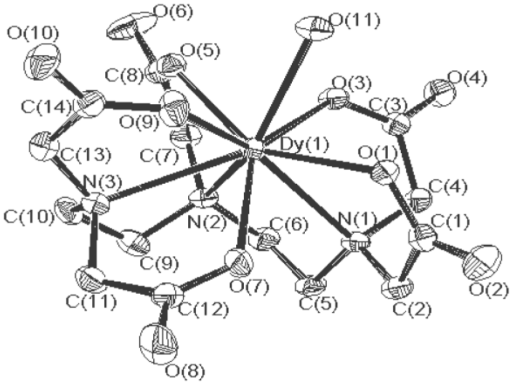

Figure 3. Molecular structure of $[Dy^{III}(dtpa)(H_2O)]^{2-}$.

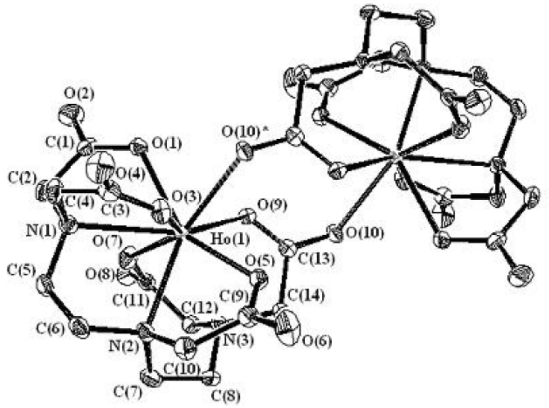

Figure 4. Molecular structure of $[Ho^{III}_2(dtpa)_2]^{4-}$.

atoms and five oxygen atoms supplied by a dtpa ligand and the ninth oxygen atom from a coordinated carboxylic group of an adjacent dtpa ligand. Every $Ho^{III}N_3O_6$ in the $[Ho^{III}_2(dtpa)_2]^{4-}$ complex anion forms a nine-coordinate pseudo-monocapped square antiprismatic structure. In the atoms around Ho(1), the set of O(1), O(3), O(5) and O(9) and the set of N(1), N(2), N(3) and O(7) form two approximate square planes. The O(10)* from another dtpa ligand is above the plane formed by O(1), O(3), O(5) and O(9). Because of repulsion, the Ho^{III}–O(10)* bond distance (2.403(3) Å) is the longest one among all the Ho^{III}–O bond distances in the $[Ho^{III}_2(dtpa)_2]^{4-}$ complex anion. The average bond distance of coordinated carboxylate is 2.342(3) Å except Ho^{III}–O(10)* in which the longest and the shortest ones are 2.376(3) Å and 2.324(3) Å, respectively. Because of the center of symmetry, the structures of two $Ho^{III}N_3O_6$ parts are identical. The Ho^{III} ion having ionic radius of 1.041 Å is slightly bigger than Yb^{III} (1.008 Å) with electronic configuration of f^{10} forms a nine-coordinate monocapped square-antiprismatic complex with the dtpa ligand and the whole molecule selects a binuclear nine-coordinate structure. Although it is not known why the Ho^{III} complex with dtpa takes a binuclear nine-coordinate structure, it can be

Table 2. Selected bond distances (Å) and angles (°) of $K_2[Dy^{III}(dtpa)(H_2O)] \cdot 6H_2O$.

Bond distances					
Dy(1)–O(1)	2.438(3)	Dy(1)–O(7)	2.382(3)	Dy(1)–N(1)	2.659(4)
Dy(1)–O(3)	2.378(3)	Dy(1)–O(9)	2.390(4)	Dy(1)–N(2)	2.658(4)
Dy(1)–O(5)	2.363(4)	Dy(1)–O(11)	2.477(4)	Dy(1)–N(3)	2.740(4)

Bond angles			
O(1)–Dy(1)–O(3)	86.12(11)	O(5)–Dy(1)–N(1)	128.04(12)
O(1)–Dy(1)–O(5)	147.26(11)	O(5)–Dy(1)–N(2)	68.10(11)
O(1)–Dy(1)–O(7)	70.25(12)	O(5)–Dy(1)–N(3)	73.67(11)
O(1)–Dy(1)–O(9)	93.77(11)	O(7)–Dy(1)–O(9)	74.41(13)
O(1)–Dy(1)–O(11)	68.40(11)	O(7)–Dy(1)–O(11)	123.02(13)
O(1)–Dy(1)–N(1)	63.04(12)	O(7)–Dy(1)–N(1)	75.81(12)
O(1)–Dy(1)–N(2)	131.44(11)	O(7)–Dy(1)–N(2)	99.98(13)
O(1)–Dy(1)–N(3)	134.60(11)	O(7)–Dy(1)–N(3)	65.55(12)
O(3)–Dy(1)–O(5)	74.72(11)	O(9)–Dy(1)–O(11)	71.08(12)
O(3)–Dy(1)–O(7)	141.68(12)	O(9)–Dy(1)–N(1)	147.15(13)
O(3)–Dy(1)–O(9)	138.84(12)	O(9)–Dy(1)–N(2)	130.50(12)
O(3)–Dy(1)–O(11)	70.73(12)	O(9)–Dy(1)–N(3)	65.20(12)
O(3)–Dy(1)–N(1)	66.54(11)	O(11)–Dy(1)–N(1)	115.68(12)
O(3)–Dy(1)–N(2)	73.14(12)	O(11)–Dy(1)–N(2)	136.85(12)
O(3)–Dy(1)–N(3)	136.61(12)	O(11)–Dy(1)–N(3)	130.53(12)
O(5)–Dy(1)–O(7)	138.87(11)	N(1)–Dy(1)–N(2)	68.43(13)
O(5)–Dy(1)–O(9)	84.23(12)	N(1)–Dy(1)–N(3)	113.56(12)
O(5)–Dy(1)–O(11)	80.18(11)	N(2)–Dy(1)–N(3)	67.91(13)

Table 3. Selected bond distances (Å) and angles (°) of $K_4[Ho^{III}_2(dtpa)_2] \cdot 4H_2O$.

Bond distances					
Ho(1)–O(1)	2.338(3)	Ho(1)–O(7)	2.332(3)	Ho(1)–N(1)	2.600(3)
Ho(1)–O(3)	2.338(3)	Ho(1)–O(9)	2.376(3)	Ho(1)–N(2)	2.574(3)
Ho(1)–O(5)	2.324(3)	Ho(1)–O(10)*	2.403(3)	Ho(1)–N(3)	2.704(3)

Bond angles			
O(1)–Ho(1)–O(3)	92.20(11)	O(5)–Ho(1)–N(1)	129.35(10)
O(1)–Ho(1)–O(5)	147.97(11)	O(5)–Ho(1)–N(2)	68.18(10)
O(1)–Ho(1)–O(7)	74.74(11)	O(5)–Ho(1)–N(3)	71.52(10)
O(1)–Ho(1)–O(9)	84.64(10)	O(7)–Ho(1)–O(9)	78.60(10)
O(1)–Ho(1)–O(10)*	71.43(10)	O(7)–Ho(1)–O(10)*	137.05(11)
O(1)–Ho(1)–N(1)	65.08(11)	O(7)–Ho(1)–N(1)	69.38(11)
O(1)–Ho(1)–N(2)	135.99(10)	O(7)–Ho(1)–N(2)	87.02(11)
O(1)–Ho(1)–N(3)	131.15(10)	O(7)–Ho(1)–N(3)	64.49(10)
O(3)–Ho(1)–O(5)	73.86(10)	O(9)–Ho(1)–O(10)*	72.68(10)
O(3)–Ho(1)–O(7)	135.39(10)	O(9)–Ho(1)–N(1)	140.31(10)
O(3)–Ho(1)–O(9)	143.61(10)	O(9)–Ho(1)–N(2)	131.09(10)
O(3)–Ho(1)–O(10)*	71.98(10)	O(9)–Ho(1)–N(3)	62.57(10)
O(3)–Ho(1)–N(1)	66.48(10)	O(10)*–Ho(1)–N(1)	116.79(10)
O(3)–Ho(1)–N(2)	73.15(11)	O(10)*–Ho(1)–N(2)	135.91(10)
O(3)–Ho(1)–N(3)	135.79(10)	O(10)*–Ho(1)–N(3)	124.03(9)
O(5)–Ho(1)–O(7)	134.96(10)	N(1)–Ho(1)–N(2)	71.06(11)
O(5)–Ho(1)–O(9)	89.93(9)	N(1)–Ho(1)–N(3)	119.05(11)
O(5)–Ho(1)–O(10)*	76.81(10)	N(2)–Ho(1)–N(3)	69.00(11)

Symmetry code. *1 $-x+1$, $-y+1$, $-z$.

predicted that there should be a critical ionic radius of mononuclear and binuclear molecular structure between the Dy^{III} and Ho^{III} ions. RE metal ions like Eu^{III}, Gd^{III} and Dy^{III} having ionic radius larger than 1.052 Å will form mononuclear nine-coordinate complexes, while those RE metal ions like Ho^{III}, Er^{III}, Tm^{III} and Yb^{III}

with ionic radius smaller than 1.041 Å will form binuclear nine-coordinate complexes. These results verify that the structure and coordination number of the RE metal complexes with aminopolycarboxylic acids depend on the ionic radius, electronic configuration of central metal ions and ligand shape. The molecular structure also depends on these factors.

In one unit cell, there is one complex molecule shown in figure 4. The two $[Ho^{III}(dtpa)]^{2-}$ parts are connected by two carboxylate groups (as the bridges) which gives a oxygen atom to coordinate one of Ho^{III} central ions in the $[Ho^{III}_2(dtpa)_2]^{4-}$ complex anion. Some crystal waters also join these two parts with hydrogen bonds. A net structure forms in a unit cell through the hydrogen bonds and static interactions.

3.3. *IR spectrum*

3.3.1. $K_2[Dy^{III}(dtpa)(H_2O)]\cdot 6H_2O$. The ν(C–N) at 1102 cm^{-1} is red-shifted 25 cm^{-1} compared to H_5dtpa (1128 cm^{-1}) indicating that the N atoms from dtpa coordinate to Dy^{III}. The ν_{as}(COOH) of dtpa at 1728 cm^{-1} disappeared in the complex, ν_{as}(COO) at 1642 cm^{-1} of H_5dtpa red-shifts to 1580 cm^{-1} and ν_s(COO) at 1389 cm^{-1} of H_5dtpa blue-shifts to 1392 cm^{-1} in the complex, confirming that the O atoms of all $-COO^-$ groups coordinate to Dy^{III} ions. A broad ν(OH) band of H_2O near 3460 cm^{-1} shows the existence of H_2O in the $K_2[Dy^{III}(dtpa)(H_2O)]\cdot 6H_2O$ complex.

3.3.2. $K_4[Ho^{III}_2(dtpa)_2]\cdot 4H_2O$. The ν(C–N) at 1100 cm^{-1} red-shifts 28 cm^{-1} compared to H_5dtpa (1128 cm^{-1}) indicating that the N atoms from dtpa coordinate to Ho^{III}. The ν_{as}(COOH) in H_5dtpa at 1728 cm^{-1} disappeared in the complex, and ν_{as}(COO) at 1642 cm^{-1} of H_5dtpa red-shifts to 1582 cm^{-1} (bridge carboxylate) and 1612 cm^{-1} (non-bridge carboxylate groups) in the complex and ν_s(COO) at 1360 cm^{-1} of H_5dtpa blue-shifts to 1395 cm^{-1} (bridge carboxylate groups) and 1405 cm^{-1} (non-bridge carboxylate groups) in the complex, confirming that the O atoms of $-COO^-$ groups coordinate to the central Ho^{III} ion and also to the other Ho^{III} ion. A broad ν(OH) band of H_2O near 3460 cm^{-1} shows the existence of H_2O in the $K_4[Ho^{III}_2(dtpa)_2]\cdot 4H_2O$ complex.

3.4. *Thermal analyses*

3.4.1. $K_2[Dy^{III}(dtpa)(H_2O)]\cdot 6H_2O$. Thermal decomposition of the complex was studied using TG-DTA as indicated in figure 5. The complex releases six crystal waters in the first endothermic step between 65.1 and 92.9°C (14.63%) and then loses one coordination water in a second endothermic step between 190.5 and 211.3°C (2.56%). Three exothermic peaks at 342.6°C, 375.7°C and 408.5°C correspond to decomposed aminocarboxylate, carboxylate and carbonate, respectively. Finally the carbonate becomes $K_2O\cdot Dy_2O_3$ identified by chemical methods and X-ray diffraction, with 62.35% mass loss.

3.4.2. $K_4[Ho^{III}_2(dtpa)_2]\cdot 4H_2O$. Differing from the $K_2[Dy^{III}(dtpa)(H_2O)]\cdot 6H_2O$ (DTA and TG curves in figure 6), the complex releases four crystal waters in an endothermic step between approximately 116.2 and 134.8°C (5.01%). Three exothermic peaks were also found at 306.4°C, 369.5°C and 415.7°C which correspond to

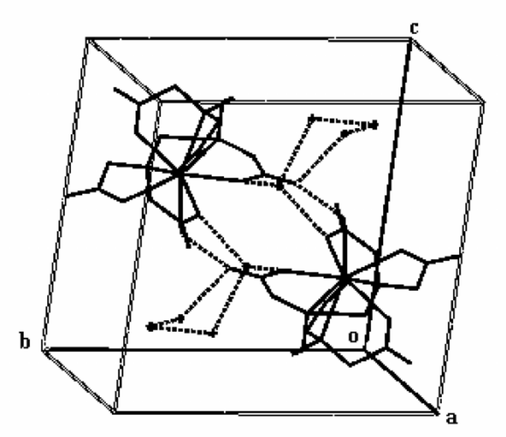

Figure 5. Arrangement of $K_2[Dy^{III}(dtpa)(H_2O)] \cdot 6H_2O$ in unit cell.

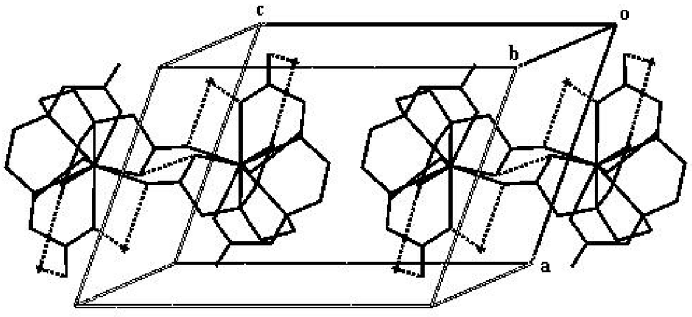

Figure 6. Arrangement of $K_4[Ho^{III}{}_2(dtpa)_2] \cdot 4H_2O$ in unit cell.

decomposed aminocarboxylate, carboxylate and carbonate, respectively. The carbonate finally becomes $K_2O \cdot Ho_2O_3$, identified by chemical methods and X-ray diffraction, total mass loss 61.15%.

Supplementary material

Crystallographic data for the structural analyses have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 235946 and 235947 for $K_2[Dy^{III}(dtpa)(H_2O)] \cdot 6H_2O$ and $K_4[Ho^{III}{}_2(dtpa)_2] \cdot 4H_2O$, respectively. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

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