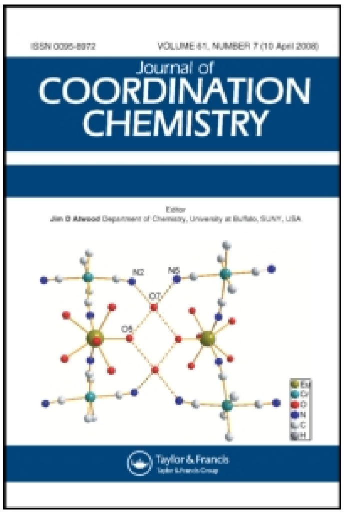

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Rare earth metal complexes with triethylenetetraminehexaacetic acid

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Rare earth metal complexes with triethylenetetraminehexaacetic acid

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The crystal and molecular structures of $K_4[Eu_2^{III}(Httha)_2]\cdot 13.5H_2O$ (ttha = triethylenetetraminehexaacetic acid), $K_4[Tb_2^{III}(Httha)_2]\cdot 14H_2O$, $K_3[Dy^{III}(ttha)]\cdot 5H_2O$, $K_3[Ho^{III}(ttha)]\cdot 5H_2O$ and $K_3[Er^{III}(ttha)]\cdot 5H_2O$ have been determined by single-crystal X-ray structure analyses. The crystal data of these five complexes are as follows: (1) $K_4[Eu_2^{III}(Httha)_2]\cdot 13.5H_2O$, monoclinic crystal system, $P2(1)/n$ space group, $Z = 4$, $\mu = 2.339\,\mathrm{mm}^{-1}$ and $F(000) = 3404$. The final R and wR are 0.0514 and 0.0906 for 11,144 $[I > 2.0\sigma(I)]$ unique reflections, and 0.0976 and 0.1068 for all 26,048 reflections, respectively. (2) $K_4[Tb_2^{III}(Httha)_2]\cdot 14H_2O$, monoclinic crystal system, $P2(1)/n$ space group, $Z = 4$, $\mu = 2.611\,\mathrm{mm}^{-1}$ and $F(000) = 3424$. The final R and wR are 0.0339 and 0.0667 for 10,699 $[I > 2.0\sigma(I)]$ unique reflections, and 0.0543 and 0.0741 for all 22,190 reflections, respectively. (3) $K_3[Dy^{III}(ttha)]\cdot 5H_2O$, monoclinic crystal system, $P2(1)/c$ space group, $Z = 4$, $\mu = 3.096\,\mathrm{mm}^{-1}$ and $F(000) = 1716$. The final R and wR are 0.0252 and 0.0600 for 5905 $[I > 2.0\sigma(I)]$ unique reflections, and 0.0336 and 0.0629 for all 16,415 reflections, respectively. (4) $K_3[Ho^{III}(ttha)]\cdot 5H_2O$, monoclinic crystal system, $P2(1)/c$ space group, $Z = 4$, $\mu = 3.217\,\mathrm{mm}^{-1}$ and $F(000) = 1720$. The final R and wR are 0.0395 and 0.0796 for 5145 $[I > 2.0\sigma(I)]$ unique reflections, and 0.0546 and 0.0833 for all 11,567 reflections, respectively. 5. $K_3[Er^{III}(ttha)]\cdot 5H_2O$, monoclinic crystal system, $P2(1)/c$ space group, $Z = 4$, $\mu = 3.398\,\mathrm{mm}^{-1}$ and $F(000) = 1724$. The final R and wR are 0.0212 and 0.0463 for 5130 $[I > 2.0\sigma(I)]$ unique reflections, and 0.0258 and 0.0477 for all 11,796 reflections, respectively. The structure of $K_4[Eu_2^{III}(Httha)_2]\cdot 13.5H_2O$ is composed of two parts, each has a binuclear nine-coordinate structure with distorted monocapped square antiprismatic prisms, in which the ttha ligand coordinates to one central Eu^{III} ion with three N atoms and four O atoms and to the other Eu^{III} ion with two O atoms. The $K_4[Tb_2^{III}(Httha)_2]\cdot 14H_2O$ complex molecule is also composed of two parts in structure, each part has a binuclear nine-coordinate structure with distorted tri-capped trigonal prism. The $[Dy^{III}(ttha)]^{3-}$ complex anion has a mononuclear nine-coordinate structure with distorted monocapped square antiprismatic geometry, in which the ttha ligand coordinates to the central Dy^{III} ion with four N atoms and five O atoms. The $[Ho^{III}(ttha)]^{3-}$ and $[Er^{III}(ttha)]^{3-}$ complex anions also have nine-coordinate structures, but the geometric conformation is close to a distorted tricapped trigonal prism. In addition, there is a free non-coordinated carboxyl group ($-CH_2COO^-$) in the $[Ho^{III}(ttha)]^{3-}$ and $[Er^{III}(ttha)]^{3-}$ complex anions. The free carboxyl group could be embellished by biological molecules which have selectivity and affinity to focus positions.

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Keywords: Rare earth; Triethylenetetraminehexaacetic acid (ttha); Complexes; Molecular structure

1. Introduction

Rare earth metal complexes attract attention because they have biological activity [1–4]. For example, Gd^{III} complexes were often used as contrast agents in magnetic resonance imaging (MRI) [5]; Tb^{III} and Eu^{III} complexes, as ionic probes, have been used to diagnose some diseases with their characteristic fluorescence [6, 7]. Radioactive rare earth metal ions emit radial rays with suitable half-life and moderate energy, so their complexes are applied in diagnoses and therapies. For example: $^{153}Sm^{III}$ complexes are widely used for tumour therapy of brain, liver, lung, heart and bone tissues [8, 9]; many ^{90}Y complexes have been used for the treatment of every kind of cancer [10] and the $^{166}Ho^{III}$ and $^{169}Er^{III}$ complexes have been used for synovitherapy [11].

Although rare earth metal and radioactive rare earth metal complexes are effective for diagnoses and therapies, the ions need to be removed from the body. These ions should enter into the body as stable complexes having selectivity and affinity on the focus position and quickly be evacuated from the body after the diagnosis or therapy [12, 13]. Structures of the rare earth metal complexes decide the luminescence properties, fluorescent spectra and distribution in an organism, so improvements should arise from the understanding of the structures of rare earth and radioactive rare earth metal complexes. Structures of rare earth metal complexes with aminopolycarboxylic acids have been examined [14–17]. In general, structures or coordination numbers of most metal complexes depend on the ionic radii, electronic configuration and oxidation state of central metal ions as well as the ligands [18–23]; this is also true for rare earth metal complexes. Trivalent rare earth metal ions form eight-, nine- and ten-coordinate complexes with aminopolycarboxylic acid ligands of different ionic radii (0.1172 nm of La^{III}; 0.1001 nm of Lu^{III}) and electronic configuration (f^0 of La^{III}; f^{14} of Lu^{III}) though the differences of ionic radii and ligand field stabilization energies (LFSE) are extremely small. For the nitrilotriacetic acid (nta) series, the Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III} and Er^{III} ions form nine-coordinate complexes [24–26], and Tm^{III}, Yb^{III} and Lu^{III} ions form eight-coordinate complexes [27]. For the ethylenediaminetetraacetic acid (edta) series, the La^{III} ion, owing to its large ionic radius and lack of f-orbital electrons, forms ten-coordinate complexes [28], the Er^{III}, Tm^{III}, Yb^{III} and Lu^{III} ions having small ionic radii and many f-orbital electrons form eight-coordinate complexes [29], and the Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III} and Ho^{III} ions between Ce^{III} and Er^{III} ions form nine-coordinate complexes [30–32]. Analogously, for the triethylenetetraaminehexaacetic acid (ttha) series, the La^{III}, Ce^{III}, Pr^{III} and Nd^{III} ions form ten-coordinate complexes [33–35], the Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III} and Er^{III} ions form nine-coordinate complexes [36–41], and the Tm^{III}, Yb^{III} and Lu^{III} ions form eight-coordinate complexes [42–43]. Fundamental rules about coordination numbers of rare earth metal complexes with aminopolycarboxylic acid ligand indicate La^{III}, Ce^{III}, Pr^{III} and Nd^{III} ions generally adopt ten-coordinate structure, the Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III} and Er^{III} ions are nine-coordinate and Tm^{III}, Yb^{III} and Lu^{III}, only select eight-coordinate structure.

Coordination polyhedra of trivalent rare earth metal complexes with aminopolycarboxylic acid ligands also depend on the ionic radii and electronic configuration. For example, the potassium salt of Yb^{III} complex with ttha ligand adopts the mononuclear nine-coordinate structure, while the same salt of Gd^{III} with ttha ligand has a binuclear nine-coordinate structure. Hence, it was forecasted that there should be a critical ionic radius between two neighboring rare earth metal ions, which determines whether the complex has a binuclear or mononuclear nine-coordinate structure. In order to determine this critical ionic radius, the Eu^{III}, Tb^{III}, Dy^{III}, Ho^{III} and Er^{III} complexes with ttha ligand were synthesized and their crystal and molecular structures were determined. The binuclear nine-coordinate $K_4[Eu_2^{III}(Httha)_2]\cdot 13.5H_2O$ and $K_4[Tb_2^{III}(Httha)_2]\cdot 14H_2O$ complexes like $K_4[Gd_2^{III}(Httha)_2]\cdot 14H_2O$ [44] and $K_4[Y_2^{III}(Httha)_2]\cdot 13.5H_2O$ [40], and mononuclear nine-coordinate $K_3[Dy^{III}(ttha)]\cdot 5H_2O$, $K_3[Ho^{III}(ttha)]\cdot 5H_2O$ and $K_3[Er^{III}(ttha)]\cdot 5H_2O$ complexes like $K_3[Yb^{III}(ttha)]\cdot 5H_2O$ were obtained, so it is considered that the critical ionic radius exists between Tb^{III} and Dy^{III}. Therefore, it can be inferred that rare earth metal ions having ionic radii larger than 1.063 Å of Tb^{III} ion will form binuclear nine-coordinate complexes with ttha, while rare earth metal ions having ionic radius smaller than 1.052 Å will form mononuclear nine-coordinate complexes with ttha. Furthermore, it was found that the coordination polyhedra of these complexes also depend on the ionic radii of the central rare earth ion. The two Eu^{III} ions in binuclear nine-coordinate $K_4[Eu_2^{III}(Httha)_2]\cdot 13.5H_2O$ adopt monocapped, square-antiprismatic conformations; in binuclear nine-coordinate $K_4[Gd_2^{III}(Httha)_2]\cdot 14H_2O$ complex one Gd^{III} ion adopts the monocapped square antiprismatic conformation and the other Gd^{III} ion has the tricapped trigonal prismatic conformation; and the two Tb^{III} ions in binuclear nine-coordinate $K_4[Tb_2^{III}(Httha)_2]\cdot 14H_2O$ adopt tricapped trigonal prismatic conformations. For mononuclear nine-coordinate complexes, the $[Dy^{III}(ttha)]^{3-}$ in $K_3[Dy^{III}(ttha)]\cdot 5H_2O$ is a monocapped square antiprism; the $[Ho^{III}(ttha)]^{3-}$ and $[Er^{III}(ttha)]^{3-}$ complex ions in $K_3[Ho^{III}(ttha)]\cdot 5H_2O$ and $K_3[Er^{III}(ttha)]\cdot 5H_2O$ adopt tricapped trigonal prismatic conformations. A metal complex customarily adopts a consistent coordination polyhedron with electronic orbit distribution of central metal ion, while the coordination polyhedron also is restricted by the repulsion among coordinate atoms. Because Eu^{III} has a large ionic radius which can reduce repulsion among coordinated atoms, both parts in $[Eu_2^{III}(Httha)_2]^{4-}$ adopt the monocapped, square-antiprismatic conformation. In $[Tb_2^{III}(Httha)_2]^{4-}$ both Tb molecules adopt the tricapped trigonal prismatic conformation to minimize the repulsion. Molecular structures and coordination polyhedra of trivalent rare earth metal complexes with aminopolycarboxylic acid ligands all depend on the ionic radii and electronic configuration of central metal ions, although the differences between ionic radii and LFSE are very small.

2. Experimental

2.1. *Preparation of $K_4[Eu_2^{III}(Httha)_2]\cdot 13.5H_2O$ (1)*

10.0 mmol (4.94 g) H_6ttha was added to 100 mL warm water, and then 5.0 mmol (1.76 g) Eu_2O_3 powder was added. After stirring and refluxing for 10.0 h, the pH was adjusted to 5.5 by aqueous $KHCO_3$ and the solution concentrated to 15.0 mL. Pale yellow crystals appeared after three weeks at room temperature. The Eu and K were analyzed using oxalic acid and sodium tetraphenylborate, respectively. The elemental analysis results of $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$ are as follows (%): Eu 18.14, K 9.22, C 25.59, H 4.62, N 6.58, which are based on the chemical formula (%) (Eu 18.07, K 9.30, C 25.70, H 4.61, N 6.66).

2.2. *Preparation of $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$ (2)*

10.0 mmol (4.94 g) H_6ttha was added to 100 mL warm water, and then 2.50 mmol (1.87 g) Tb_4O_7 powder was added. After stirring and refluxing for 10.0 h, the pH was adjusted to 5.5 by aqueous $KHCO_3$ and the solution concentrated to 15.0 mL. Pale yellow crystals appeared after three weeks at room temperature. The Tb and K were analyzed using oxalic acid and sodium tetraphenylborate, respectively. The elemental analysis results of $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$ follow (%): Tb 18.67, K 9.20, C 25.43, H 4.60, N 6.52, based on the chemical formula (%) (Tb 18.64, K 9.17, C 25.36, H 4.61, N 6.57).

2.3. *Preparation of $K_3[Dy^{III}(ttha)] \cdot 5H_2O$ (3)*

10.0 mmol (4.94 g) H_6ttha was added to 100 mL warm water, and then 5.0 mmol (1.86 g) Dy_2O_3 powder was added. After stirring and refluxing for 10.0 h, pH was adjusted to 5.0 by aqueous $KHCO_3$ and the solution concentrated to 15.0 mL. The colourless crystal appeared after three weeks at room temperature. The Dy and K were analyzed using oxalic acid and sodium tetraphenylboron, respectively. The elemental analysis results of $K_3[Dy^{III}(ttha)] \cdot 5H_2O$ are as follows (%): Dy 18.88, K 13.73, C 25.24, H 4.02, N 6.58, based on the chemical formula (%) (Dy 18.93, K 13.67, C 25.19, H 3.99, N 6.53).

2.4. *Preparation of $K_3[Ho^{III}(ttha)] \cdot 5H_2O$ (4)*

10.0 mmol (4.94 g) H_6ttha was added to 100 mL warm water, and then 5.0 mmol (1.89 g) Ho_2O_3 powder was added. After stirring and refluxing for 4.0 h, pH was adjusted to 5.0 by aqueous $KHCO_3$ and the solution concentrated to 15.0 mL. The baby pink crystal appeared after two weeks at room temperature. The Ho and K were analyzed using oxalic acid and sodium tetraphenylboron, respectively. The elemental analysis of $K_3[Ho^{III}(ttha)] \cdot 5H_2O$ are as follows (%): Ho 19.10, K 13.69, C 25.11, H 3.99, N 6.50, based on the chemical formula (Ho 19.16, K 13.63, C 25.12, H 3.98, N 6.51).

2.5. *Preparation of $K_3[Er^{III}(ttha)] \cdot 5H_2O$ (5)*

10.0 mmol (4.94 g) H_6ttha was added to 100 mL warm water, and then 5.0 mmol (1.91 g) Er_2O_3 powder was added. After stirring and refluxing for 5.0 h, pH was adjusted to 5.5 by aqueous $KHCO_3$ and the solution concentrated to 25.0 mL. The pink crystal appeared after three weeks at room temperature. The Er and K were analyzed using oxalic acid and sodium tetraphenylboron, respectively. The elemental analysis of $K_3[Er^{III}(ttha)] \cdot 5H_2O$ are as follows (%): Er 19.45, K 13.51, C 25.09, H 3.94, N 6.46, based on the chemical formula (Er 19.38, K 13.59, C 25.05, H 3.97, N 6.49).

2.6. *Physical measurements*

2.6.1. IR determination. IR spectra of H_6ttha, $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$, $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$, $K_3[Dy^{III}(ttha)] \cdot 5H_2O$, $K_3[Ho^{III}(ttha)] \cdot 5H_2O$ and $K_3[Er^{III}(ttha)] \cdot 5H_2O$ were determined on a Shimadzu-IR 408 spectrograph by mull and KBr.

2.6.2. Crystal structure determination. The details of crystal data collection and refinement parameters for $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$, $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$, $K_3[Dy^{III}(ttha)] \cdot 5H_2O$, $K_3[Ho^{III}(ttha)] \cdot 5H_2O$ and $K_3[Er^{III}(ttha)] \cdot 5H_2O$ are listed in table 1. Data were collected with a Bruker SMART CCD type X-ray diffractometer system using graphite-monochromated Mo Kα radiation ($\lambda = 0.071073$ nm). The structures were solved by directed methods. The non-hydrogen atoms were refined with anisostropic thermal parameters by full-matrix. All calculations were carried out using the SHELXTL-97 program on PDP11/44 and Pentium MMX/166 computers [45]. The structures of the complex anions are shown in figures 1 and 2 for $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$, figures 3 and 4 for $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$, figures 5 and 6 for $K_3[Dy^{III}(ttha)] \cdot 5H_2O$, figures 7 and 8 for $K_3[Ho^{III}(ttha)] \cdot 5H_2O$, and figures 9 and 10 for $K_3[Er^{III}(ttha)] \cdot 5H_2O$, respectively. All non-hydrogen fractional atomic coordinates and equivalent isotropic temperature factors of these complexes are listed in tables 2–6. Selected bond distances and bond angles are listed from tables 7–11.

3. Results and discussion

3.1. *Molecular and crystal structures of binuclear nine-coordinate $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$*

The $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$ complex has a binuclear molecular structure (figure 1). Every Eu^{III} ion is coordinated with three N and six O atoms, in which four O atoms are from one ttha ligand and two O atoms from the other ttha ligand, both $Eu^{III}N_3O_6$ parts in the $[Eu_2^{III}(Httha)_2]^{4-}$ complex anion have a nine-coordinate pseudo-monocapped square antiprismatic conformation. As shown in figure 2, the atoms around Eu(1) form a square antiprism, the set of O(1), O(3), O(15) and N(7) and the set of O(13), O(17), N(5) and N(6) make two approximate parallel square planes. O(19), as the additional coordinate atom, is above the plane formed by O(1), O(3), O(15) and N(7). Because of the repulsion of these four coordinate (O(1), O(3), O(15) and N(7)) atoms, the Eu(1)–O(19) bond distance (2.477(3) Å) should ordinarily be the longest Eu^{III}–O bond distances around Eu(1). However, the hydrogen bonds between the crystal water and coordinate carboxyl O atom and the crystal water and uncoordinate carboxyl O atom result in Eu(1)–O(13) being the longest Eu^{III}–O bond distances around Eu(1). From the bond angles, it can be found that these two planes are close to each other because of the repulsion of the O(19). The average angle of ∠O(19)Eu(1)O(1), ∠O(19)Eu(1)O(3), ∠O(19)Eu(1)O(15) and ∠O(19)Eu(1)N(7) is 69.49(11)° near 70° that most complexes with the nine-coordinate pseudo-monocapped square antiprismatic conformation adopt, in which the biggest and smallest angles are 74.85(14)° and 61.61(11)°, respectively. The average angle of ∠O(19)Eu(1)O(13), ∠O(19)Eu(1)O(17), ∠O(19)Eu(1)N(5) and ∠O(19)Eu(1)N(6) is 128.02(11)° slightly larger than 125.28° that is the theoretical angle of standard monocapped square

Table 1. Crystal data and structure refinement parameters for all complexes.

Parameters	K–Eu^{III}-ttha	K–Tb^{III}-ttha	K–Dy^{III}-ttha	K–Ho^{III}-ttha	K–Er^{III}-ttha
Empirical formula	$C_{36}H_{77}Eu_2K_4N_8O_{37.5}$	$C_{36}H_{78}Tb_2K_4N_8O_{38}$	$C_{18}H_{34}DyK_3N_4O_{17}$	$C_{18}H_{34}HoK_3N_4O_{17}$	$C_{18}H_{34}ErK_3N_4O_{17}$
Formula weight	1682.36	1705.29	858.28	860.71	863.04
Temperature (K)	293(2)	293(2)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P2_1/c$	$P2_1/c$	$P2_1/c$
Unit cell dimensions					
a (Å)	11.337(3)	11.326(3)	10.262(4)	10.290(9)	10.250(3)
b (Å)	25.753(6)	25.675(7)	12.418(5)	12.466(11)	12.455(4)
c (Å)	22.138(6)	22.076(6)	22.723(10)	22.790(2)	22.786(7)
β, deg	102.871(5)	102.943(5)	91.111(7)	91.322(16)	91.209(5)
V (Å^3), Z	6301(3), 4	6256(3), 4	2895(2), 4	2923(5), 4	29083(15), 4
D (Calcd) (Mg m^{-3})	1.773	1.802	1.969	1.956	1.971
Absolute co-efficient (mm^{-1})	2.339	2.611	3.096	3.217	3.398
F(000)	3404	3424	1716	1720	1724
Crystal size (mm^3)	$0.18 \times 0.14 \times 0.12$	$0.32 \times 0.30 \times 0.24$	$0.18 \times 0.14 \times 0.12$	$0.30 \times 0.25 \times 0.20$	$0.30 \times 0.25 \times 0.20$
θ range for data collection (deg)	1.23–25.03	2.25–25.03	1.87–26.42	1.86–25.03	1.86–25.03
Limiting indices	$-13 \le h \le 11$	$-6 \le h \le 13$	$-10 \le h \le 12$	$-12 \le h \le 9$	$-11 \le h \le 12$
	$-30 \le k \le 21$	$-30 \le k \le 30$	$-15 \le h \le 13$	$-14 \le k \le 14$	$-14 \le k \le 14$
	$-26 \le l \le 26$	$-25 \le l \le 23$	$-24 \le h \le 28$	$-27 \le l \le 23$	$-18 \le l \le 27$
Reflections collected	26,048	22,190	16,415	11,567	11,796
Independent reflections	11,144 ($R_{int} = 0.0741$)	10,699 ($R_{int} = 0.0379$)	5905 ($R_{int} = 0.0275$)	5145 ($R_{int} = 0.0346$)	5130 ($R_{int} = 0.0183$)
Max, min transmissions	1.000000, 0.832998	1.000000, 0.723246	1.000000, 0.798443	0.5655, 0.4453	0.5497, 0.4288
Data/restraints/params	11,144/0/793	10,699/0/793	5905/0/388	5145/0/388	5130/31/428
Goodness-of-fit on F^2	1.025	1.007	1.074	1.081	1.022
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0514$	$\mathrm{R}1 = 0.0339$	$R1 = 0.0252$	$R1 = 0.0395$	$R1 = 0.0212$
	$wR2 = 0.0906$	$wR2 = 0.0667$	$wR2 = 0.0600$	$wR2 = 0.0796$	$wR2 = 0.0463$
R indices (all data)	$R1 = 0.0976$	$R1 = 0.0543$	$R1 = 0.0336$	$R1 = 0.0546$	$R1 = 0.0258$
	$wR2 = 0.1068$	$wR2 = 0.0741$	$wR2 = 0.0629$	$wR2 = 0.0833$	$wR2 = 0.0477$
Largest diff. peak and hole (e Å^{-3})	1.197 and −0.774	0.958 and −0.726	0.665 and −0.971	0.900 and −2.669	0.449 and −0.567

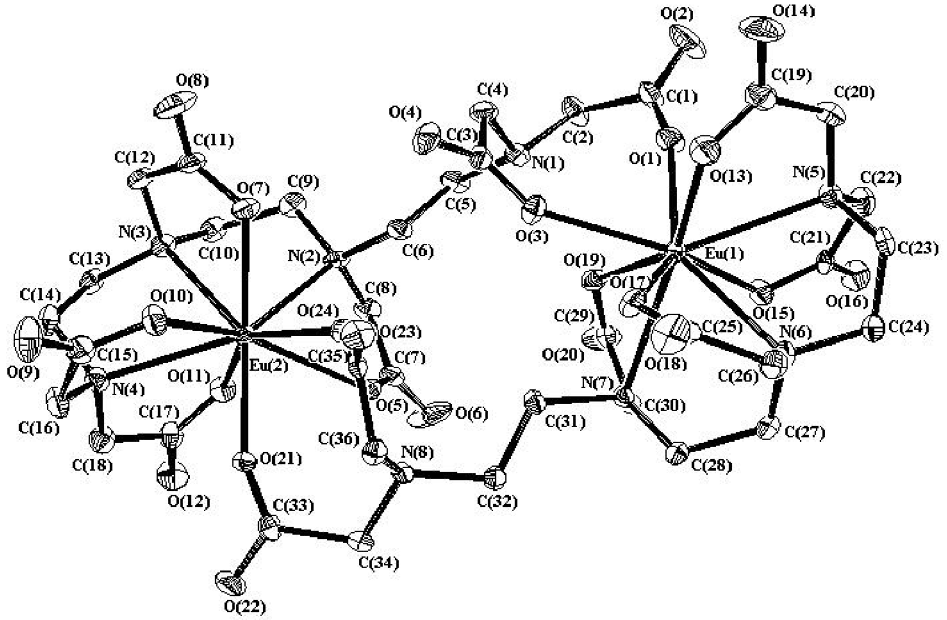

Figure 1. Molecular structure of $[\mathrm{Eu}_2^{\mathrm{III}}(\mathrm{Httha})_2]^{4-}$.

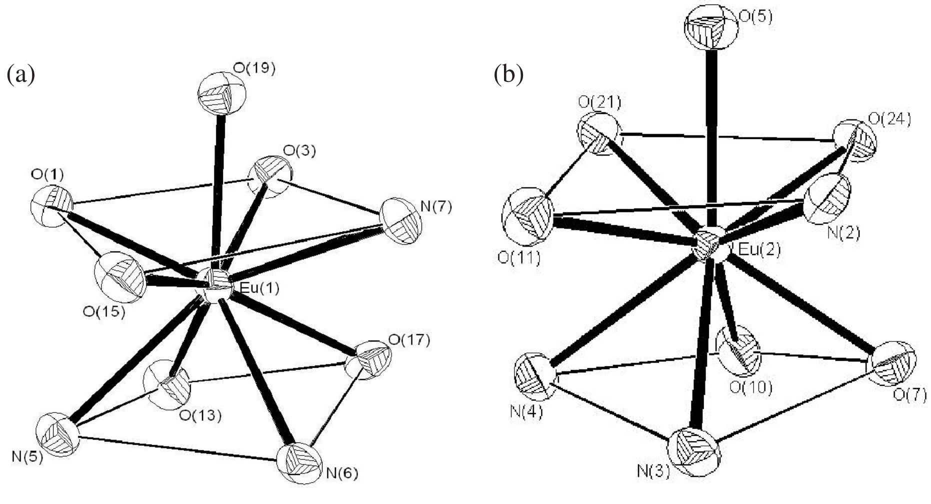

Figure 2. Coordination polyhedron of $[\mathrm{Eu}_2^{\mathrm{III}}(\mathrm{Httha})_2]^{4-}$. (a) Around Eu(1). (b) Around Eu(2).

antiprismatic conformation; the biggest and smallest angles are 143.08(14)° and 118.61(11)°, respectively. Around Eu(2), the set of O(11), O(21), O(24) and N(2) and the set of O(7), O(10), N(3) and N(4) make two approximate parallel square planes, forming a square antiprism. O(5) is above the plane formed by O(11), O(21), O(24) and N(2). Because of the repulsion of O(11), O(21), O(24) and N(2), the Eu(2)–O(5) bond distance (2.477(3) Å) is the longest $\mathrm{Eu^{III}}$–O bond distance around Eu(2).

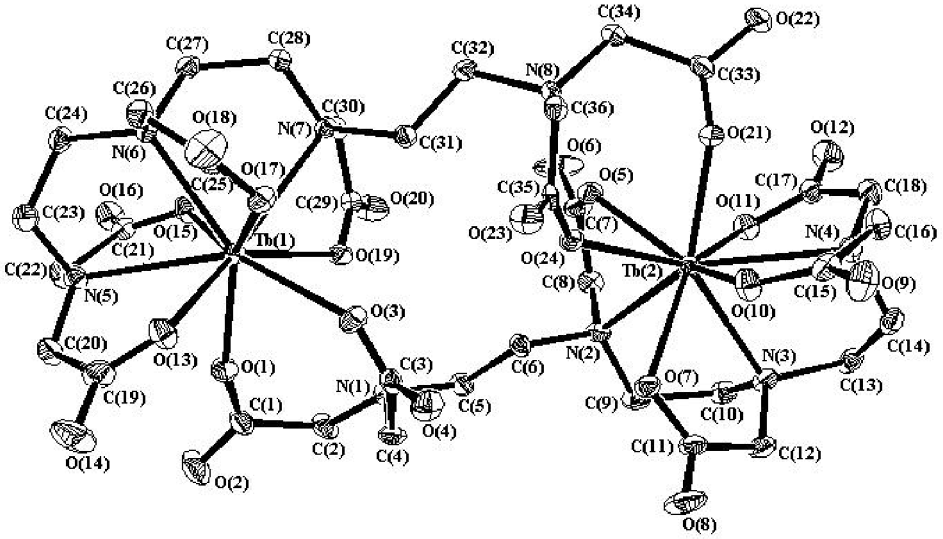

Figure 3. Molecular structure of $[Tb_2^{III}(Httha)_2]^{4-}$.

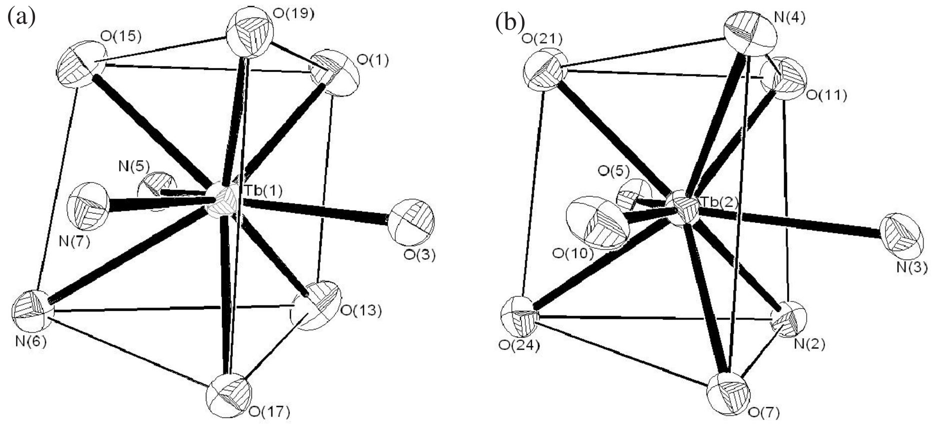

Figure 4. Coordination polyhedron of $[Tb_2^{III}(Httha)_2]^{4-}$. (a) Around Tb(1). (b) Around Tb(2).

The O(5) also repulses these four atoms and from the changes in bond angles the repulsion brings the two planes closer to each other. The average angle of ∠O(5)Eu(2)O(11), ∠O(5)Eu(2)O(21), ∠O(5)Eu(2)O(24), ∠O(5)Eu(2)N(2) is 69.60(11)°, close to 70°; the biggest and smallest angles are 72.35(14)° and 62.28(11)°, respectively. The average angle of ∠O(5)Eu(2)O(7), ∠O(5)Eu(2)O(10), ∠O(5)Eu(2)N(3) and ∠O(5)Eu(2)N(4) is 128.46(11)° slightly larger than 125.28°; the biggest and smallest angles are 142.64(14)° and 119.14(11)°, respectively (figure 2).

Two protons did not dissociate from the amino N atoms of ttha ligand and form $\equiv NH^+$ with two N atoms in $[Eu_2^{III}(Httha)_2]^{4-}$. The $\equiv NH^+$ has a positive charge and produces electrostatic repulsion to the Eu^{III} ion so that the N(1) and N(8) in the ttha ligand do not coordinate with Eu^{III}.

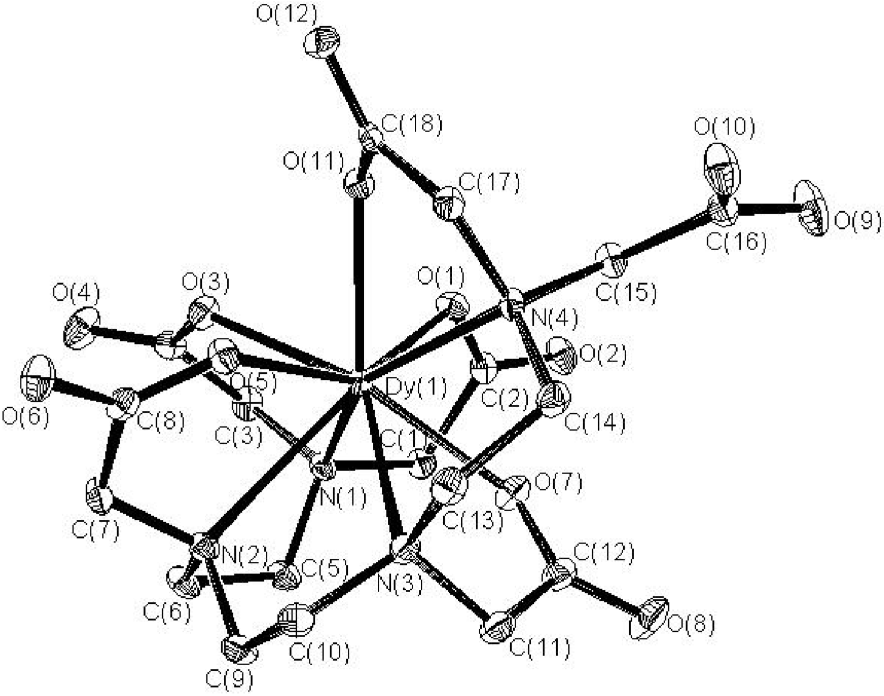

Figure 5. Molecular structure of $[Dy^{III}(ttha)]^{3-}$.

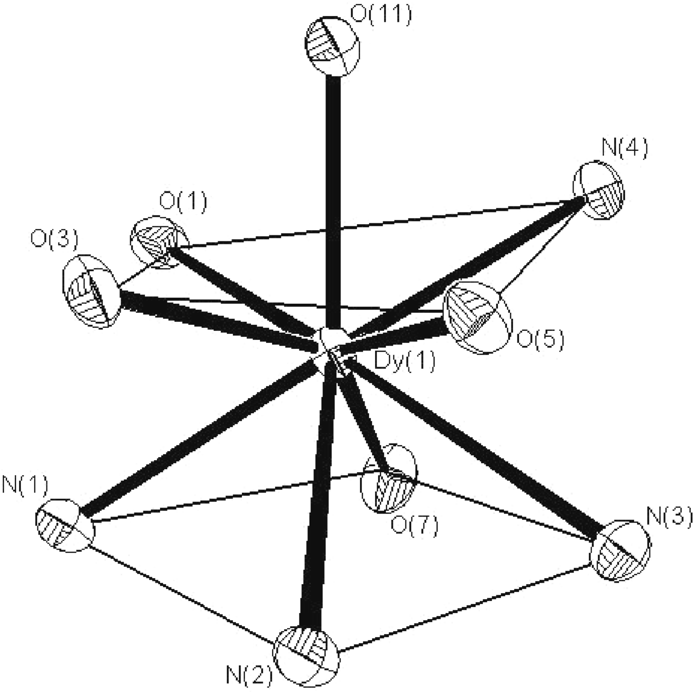

Figure 6. Coordination polyhedron of $[Dy^{III}(ttha)]^{3-}$.

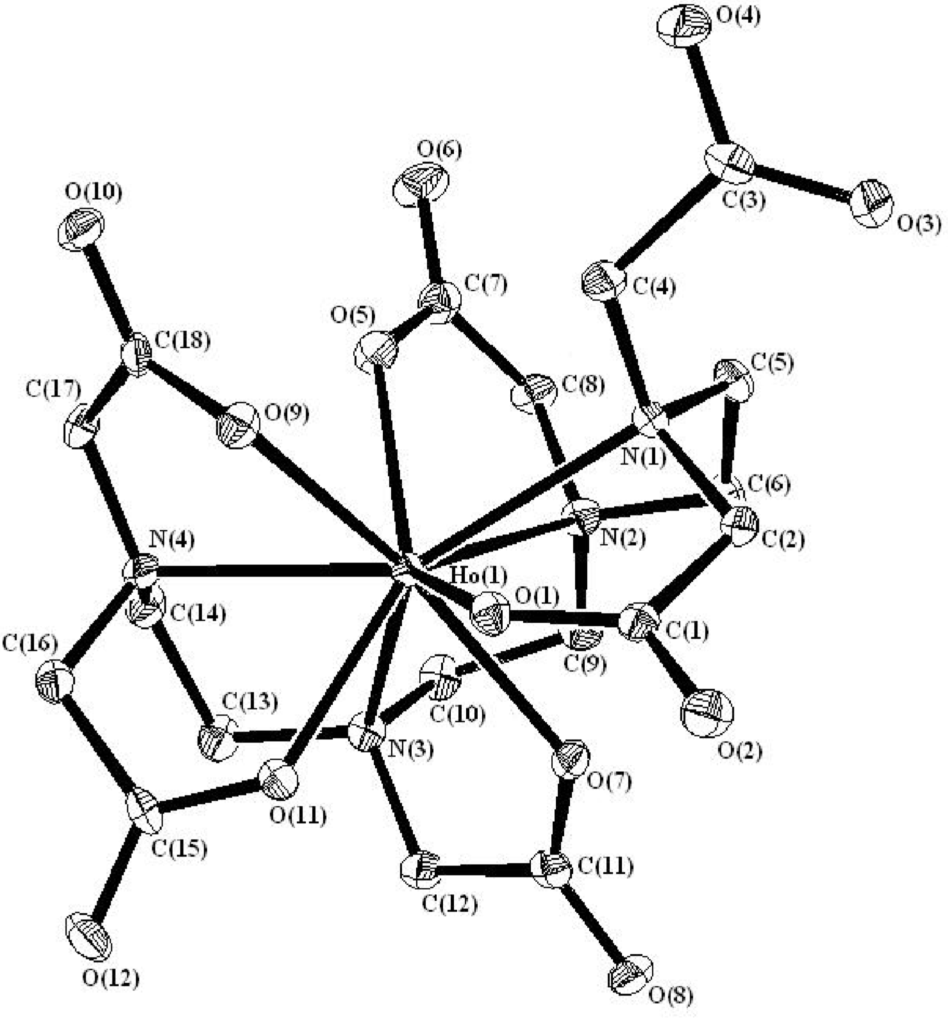

Figure 7. Molecular structure of $[Ho^{III}(ttha)]^{3-}$.

3.2. *Molecular and crystal structures of binuclear nine-coordinate $K_4[Tb^{III}_2(Httha)_2]\cdot 14H_2O$*

The $K_4[Tb^{III}_2(Httha)_2]\cdot 14H_2O$ complex also has a binuclear molecular structure like $K_4[Eu^{III}_2(Httha)_2]\cdot 13.5H_2O$ (figure 3). However, differing from $[Eu^{III}_2(Httha)_2]^{4-}$ the two $Tb^{III}N_3O_6$ parts in the $[Tb^{III}_2(Httha)_2]^{4-}$ complex anion form a the nine-coordinate pseudo-tricapped trigonal prismatic geometry. As shown in figure 4, the atoms around Tb(1) form two approximate parallel trigonal planes; O(1), O(15) and O(19) and O(13), O(17) and N(6). The O(3), N(5) and N(7) atoms as the seventh, eighth and ninth coordinate atoms lie above the planes formed by O(1), O(13), O(17) and O(19), O(1), O(13), O(15) and N(6), O(15), O(17), O(19) and N(6), respectively. The total of ∠O(3)Tb(1)N(5), ∠N(5)Tb(1)N(7) and ∠O(3)Tb(1)N(7) is 359.80(11)° close to 360°,

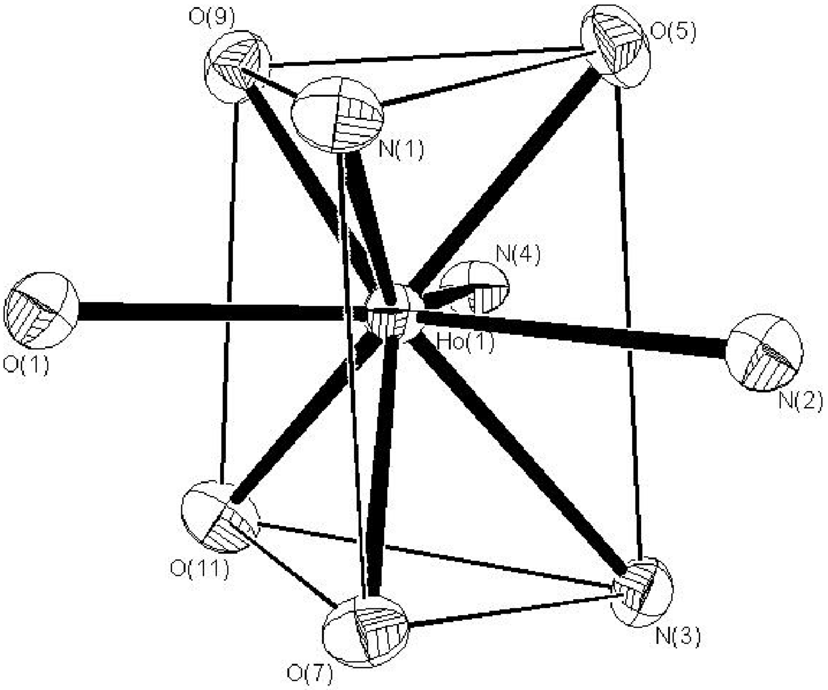

Figure 8. Coordination polyhedron of $[Ho^{III}(ttha)]^{3-}$.

indicating that Tb(1), O(3), N(5) and N(7) are in the same plane. Around Tb(2), the set of O(11), O(21) and N(4) and the set of O(7), O(24) and N(2) form two approximately parallel trigonal planes, forming a trigonal prism. The O(5), O(10) and N(3) as the seventh, eighth and ninth coordinated atoms are above the planes formed by O(11), O(21), O(24) and N(2), O(7), O(21), O(24) and N(4), O(7), O(11), N(2) and N(4), respectively. The total angle of ∠O(5)Tb(2)O(10), ∠O(10)Tb(2)N(3) and ∠O(5)Tb(2)N(3) is 359.69(11)° close to 360°, indicating that Tb(2), O(5), O(10) and N(3) are in the same plane. Like $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$, two protons did not dissociate from the ttha ligands and formed $\equiv NH^+$ with two of N atoms which result in two non-coordinated N atoms.

Perhaps Gd^{III} has a critical ionic radius changing coordination polyhedron which lead its complex with ttha ligand, $K_4[Gd_2^{III}(Httha)_2] \cdot 14H_2O$, to form two different parts unlike $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$ and $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$. In $[Gd_2^{III}(Httha)_2]^{4-}$, one $Gd^{III}N_3O_6$ part adopts a pseudo-monocapped square antiprismatic conformation; the other $Gd^{III}N_3O_6$ has pseudo-tricapped trigonal prismatic conformation. In addition, the high-spin f^7 electronic configuration does not determine which polyhedron is formed for Gd^{III}, because the LFSE of this electronic configuration is zero. Rare earth metal ions having bigger ionic radii and fewer f-orbit electrons may have monocapped square antiprismatic geometry, while rare earth metal ions having smaller ionic radii and many f-orbit electrons may be tricapped trigonal prismatic.

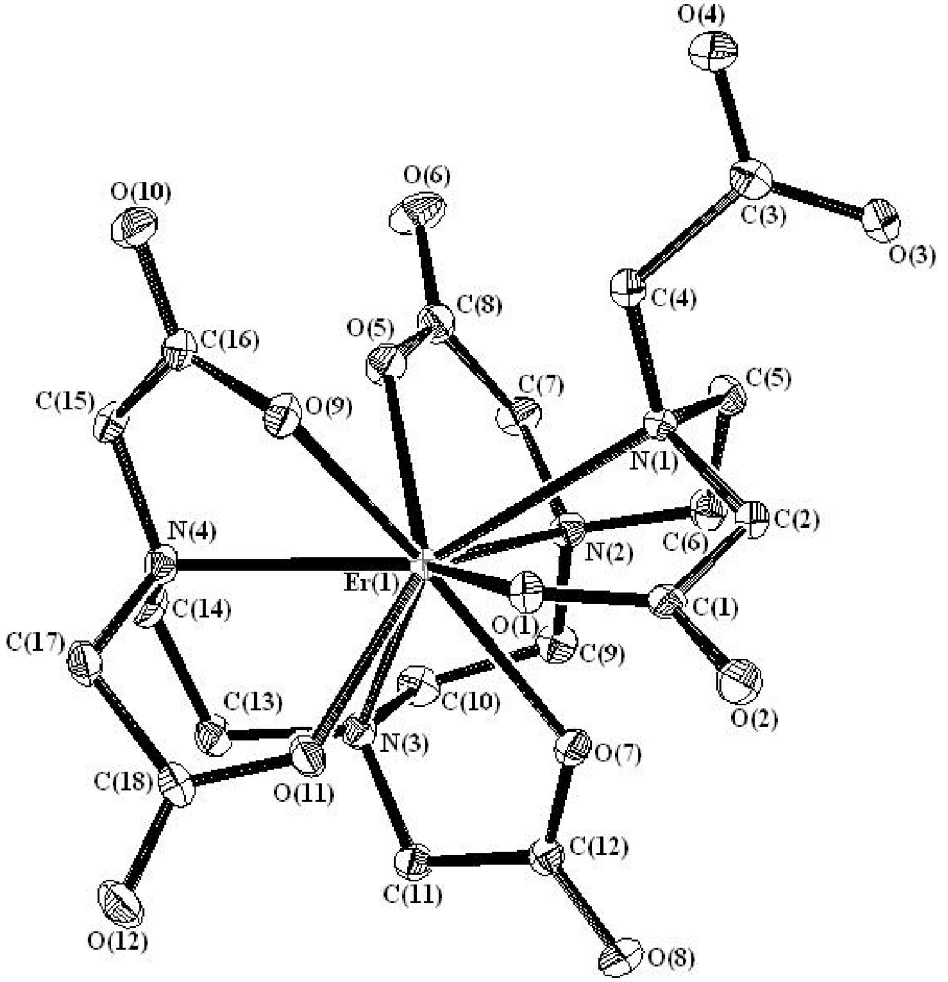

Figure 9. Molecular structure of $[Er^{III}(ttha)]^{3-}$.

3.3. *Molecular and crystal structures of mononuclear nine-coordinate $K_3[Dy^{III}(ttha)]\cdot 5H_2O$ complex*

The Dy^{III} ion forms a mononuclear complex with ttha in which the central Dy^{III} ion is coordinated with four N and five O atoms from one ttha ligand (figure 5). The $Dy^{III}N_4O_5$ makes a nine-coordinate distorted monocapped square antiprismatic conformation (figure 6), in which the set of O(1), O(3), O(5) and N(4) and the set of O(7), N(1), N(2) and N(3) form two approximately parallel square planes, which compose a square antiprism. The O(11) atom is above the plane formed by O(1), O(3), O(5) and N(4). Because of the repulsion from these four coordinate (O(1), O(3), O(5) and N(4)) atoms, the Dy(1)–O(11) bond distance (2.358(3) Å) is the longest Dy^{III}–O bond distance in $[Dy^{III}(ttha)]^{3-}$. O(11) also repulses these four atoms bringing these two planes closer to each other. The average angle of ∠O(11)Dy(1)O(1), ∠O(11)Dy(1)O(3), ∠O(11)Dy(1)O(5) and ∠O(11)Dy(1)N(4) is 71.89(11)°, close to 70° that most complexes

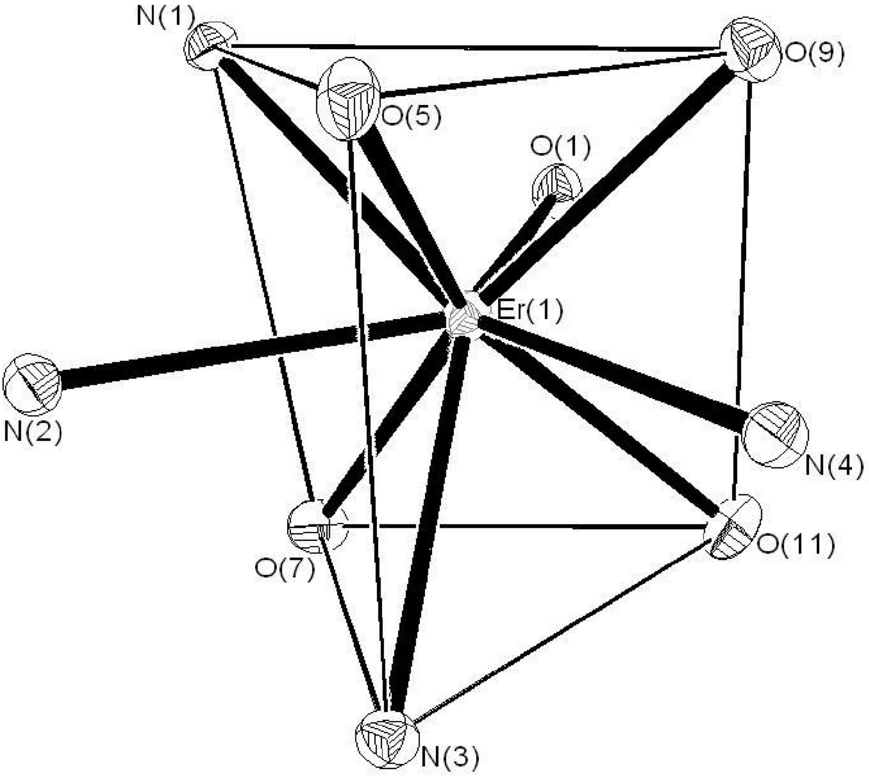

Figure 10. Coordination polyhedron of [Er^{III}(ttha)]$^{3-}$.

with a nine-coordinate pseudo-monocapped square antiprismatic conformation adopt; the biggest and smallest angles are 75.64(14)° and 64.29(11)°, respectively. The average angle of ∠O(11)Dy(1)O(5), ∠O(11)Dy(1)N(1), ∠O(11)Dy(1)O(2) and ∠O(11)Dy(1)N(3) is 127.33(11)°, slightly larger than the theoretical bond angle (125.28°) of standard monocapped square antiprismatic geometry. The biggest and smallest angles are 134.74(14)° and 123.69(11)°, respectively.

A smaller ionic radius causes the Dy^{III} complex with ttha to be mononuclear in order to release the inner tensile forces. In addition, although the radius of Dy^{III} ion is smaller than Tb^{III} ion, the [Dy^{III}(ttha)]$^{3-}$ complex anion does not adopt the nine-coordinate pseudo-tricapped trigonal prismatic conformation, which indicates that this ionic radius can endure the repulsion among coordinate atoms.

3.4. *Molecular and crystal structures of mononuclear nine-coordinate $K_3[Ho^{III}(ttha)]\cdot 5H_2O$ and $K_3[Er^{III}(ttha)]\cdot 5H_2O$ complex complex*

Figures 7 and 9 show that the [Ho^{III}(ttha)]$^{3-}$ and [Er^{III}(ttha)]$^{3-}$ complex anions also have the mononuclear nine-coordinate structure with similar distorted tricapped trigonal prismatic conformation (figures 8 and 10). In the [Ho^{III}(ttha)]$^{3-}$ complex anion, O(5), O(9) and N(1) and O(7), O(11) and N(3) form two approximately parallel trigonal planes, forming a trigonal prism. The O(1), N(2) and N(4) atoms are above

Table 2. Non-hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å) (U_{eq}) of $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Eu(1)	4464(1)	5962(1)	1781(1)	24(1)	C(11)	3512(7)	3107(3)	3193(4)	33(2)
Eu(2)	6027(1)	3705(1)	3872(1)	23(1)	C(12)	4267(7)	2622(3)	3317(4)	34(2)
N(1)	4349(6)	4492(2)	1413(3)	28(2)	C(13)	6211(7)	2356(3)	3978(4)	34(2)
N(2)	6147(5)	3601(2)	2679(3)	26(2)	C(14)	6006(8)	2520(3)	4594(4)	42(2)
N(3)	5593(6)	2726(2)	3479(3)	31(2)	C(15)	4716(8)	3459(3)	5043(4)	38(2)
N(4)	6534(6)	3041(2)	4794(3)	32(2)	C(16)	5958(8)	3228(3)	5296(4)	42(2)
N(5)	3764(6)	6623(2)	850(3)	29(2)	C(17)	8550(8)	3112(3)	4497(4)	36(2)
N(6)	5115(6)	6927(2)	2147(3)	28(2)	C(18)	7862(8)	3010(3)	5001(4)	41(2)
N(7)	6479(5)	5985(2)	2737(3)	25(1)	C(19)	1743(8)	6287(3)	962(4)	39(2)
N(8)	7062(5)	5130(2)	4194(3)	24(1)	C(20)	2499(7)	6502(3)	523(4)	34(2)
O(1)	3751(5)	5436(2)	867(3)	38(1)	C(21)	5854(7)	6417(3)	709(4)	27(2)
O(2)	3062(7)	5075(3)	−58(3)	76(2)	C(22)	4588(8)	6596(3)	418(4)	39(2)
O(3)	3706(5)	5203(2)	2209(2)	35(1)	C(23)	3779(7)	7154(3)	1133(4)	31(2)
O(4)	2320(5)	4675(2)	2442(3)	43(2)	C(24)	4956(7)	7266(3)	1591(4)	30(2)
O(5)	7404(5)	4293(2)	3471(2)	31(1)	C(25)	3676(7)	6706(3)	2830(4)	28(2)
O(6)	8956(7)	4306(3)	3005(3)	81(3)	C(26)	4343(7)	7121(3)	2567(4)	32(2)
O(7)	4049(5)	3539(2)	3250(2)	32(1)	C(27)	6399(7)	6920(3)	2471(4)	33(2)
O(8)	2397(6)	3057(2)	3068(4)	64(2)	C(28)	6700(7)	6523(3)	2987(3)	28(2)
O(9)	3943(6)	3438(2)	5358(3)	57(2)	C(29)	7036(7)	5352(3)	2001(4)	28(2)
O(10)	4577(5)	3684(2)	4521(3)	40(1)	C(30)	7463(7)	5794(3)	2455(3)	26(2)
O(11)	7927(5)	3284(2)	3978(3)	35(1)	C(31)	6262(7)	5618(3)	3222(3)	27(2)
O(12)	9648(5)	3034(2)	4619(3)	52(2)	C(32)	7294(7)	5575(3)	3795(3)	28(2)
O(13)	2315(5)	6159(2)	1498(3)	41(2)	C(33)	8027(8)	4482(3)	4998(4)	30(2)
O(14)	647(6)	6240(3)	757(3)	68(2)	C(34)	8130(7)	5017(3)	4709(4)	33(2)
O(15)	6011(5)	6213(2)	1254(2)	34(1)	C(35)	4842(7)	4933(3)	4029(3)	26(2)
O(16)	6639(5)	6461(2)	411(3)	42(2)	C(36)	5927(7)	5212(3)	4425(4)	28(2)
O(17)	3853(5)	6238(2)	2696(2)	31(1)	K(1)	8378(2)	5706(1)	816(1)	55(1)
O(18)	2984(6)	6842(2)	3161(3)	53(2)	K(2)	9932(2)	4671(1)	2047(1)	56(1)
O(19)	5911(5)	5262(2)	1862(2)	30(1)	K(3)	2319(2)	5617(1)	3142(1)	47(1)
O(20)	7799(5)	5116(2)	1782(3)	52(2)	K(4)	2503(2)	4186(1)	3628(1)	42(1)
O(21)	7179(5)	4189(2)	4734(2)	35(1)	O(25)	9263(7)	6012(3)	−370(4)	94(3)
O(22)	8799(6)	4392(2)	5480(3)	54(2)	O(26)	10,312(7)	5771(3)	1992(3)	86(3)
O(23)	3827(5)	5093(2)	4058(3)	39(1)	O(27)	10,292(8)	4989(3)	826(4)	94(3)
O(24)	5067(5)	4548(2)	3710(2)	28(1)	O(28)	7688(10)	4235(3)	997(4)	119(4)
C(1)	3610(8)	5067(3)	490(4)	39(2)	O(29)	525(8)	6537(3)	2869(4)	100(3)
C(2)	4210(9)	4546(3)	726(4)	44(2)	O(30)	656(6)	4973(2)	3510(3)	55(2)
C(3)	3047(7)	4806(3)	2135(4)	28(2)	O(31)	1645(7)	3760(3)	4587(4)	84(3)
C(4)	3135(7)	4457(3)	1586(4)	33(2)	O(32)	10,501(9)	3613(3)	2433(6)	150(5)
C(5)	5169(7)	4045(3)	1657(3)	34(2)	O(33)	5954(7)	6895(2)	−766(3)	64(2)
C(6)	5357(7)	4025(3)	2359(3)	28(2)	O(34)	−350(7)	6359(3)	3877(4)	78(2)
C(7)	7967(8)	4138(3)	3071(4)	33(2)	O(35)	10,792(7)	2652(3)	5720(4)	95(3)
C(8)	7410(7)	3693(3)	2655(4)	32(2)	O(36)	2592(8)	7845(3)	3529(4)	108(3)
C(9)	5724(8)	3079(3)	2433(4)	34(2)	O(37)	3311(9)	2509(3)	5844(5)	119(4)
C(10)	6109(8)	2665(3)	2926(4)	36(2)	O(38)	9910(20)	3337(5)	1246(6)	115(8)

the three approximate quadrangular planes formed by O(7), O(9), O(11) and N(1), O(5), O(7), N(1) and N(3) and O(5), O(9), O(11) and N(3) and form three capped positions, respectively. The total angles of ∠O(1)Ho(1)N(2), ∠O(1)Ho(1)N(4) and ∠N(2)Ho(1)N(4) are 360.00(15)° indicating that the Ho(1), O(1), N(2) and N(4) lie in the same plane.

Analogously, in $[Er^{III}(ttha)]^{3-}$, O(5), O(9) and N(1) and O(7), O(11) and N(3) form two approximately parallel trigonal planes, also forming a trigonal prism. O(1), N(2) and N(4) are above the three approximate quadrangular planes formed by O(7), O(9), O(11) and N(1), O(5), O(7), N(1) and N(3) and O(5), O(9), O(11) and N(3), respectively.

Table 3. Non-hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å) (U_{eq}) of $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Tb(1)	4464(1)	5965(1)	1783(1)	23(1)	C(11)	3515(4)	3111(2)	3197(2)	33(1)
Tb(2)	6023(1)	3703(1)	3871(1)	22(1)	C(12)	4267(4)	2624(2)	3322(3)	35(1)
N(1)	4345(3)	4494(1)	1412(2)	28(1)	C(13)	6200(5)	2356(2)	3974(2)	37(1)
N(2)	6136(3)	3605(1)	2683(2)	27(1)	C(14)	6009(5)	2526(2)	4604(2)	36(1)
N(3)	5591(3)	2723(1)	3480(2)	30(1)	C(15)	4722(5)	3468(2)	5034(3)	34(1)
N(4)	6531(3)	3042(2)	4798(2)	30(1)	C(16)	5970(5)	3235(2)	5299(2)	38(1)
N(5)	3752(3)	6624(2)	851(2)	28(1)	C(17)	8537(4)	3117(2)	4495(3)	33(1)
N(6)	5096(3)	6927(1)	2143(2)	26(1)	C(18)	7867(4)	3020(2)	5007(2)	37(1)
N(7)	6472(3)	5985(1)	2739(2)	23(1)	C(19)	1780(5)	6281(2)	981(3)	41(1)
N(8)	7054(3)	5130(1)	4194(2)	23(1)	C(20)	2502(4)	6501(2)	533(2)	34(1)
O(1)	3757(3)	5447(1)	874(2)	37(1)	C(21)	5841(4)	6409(2)	720(2)	31(1)
O(2)	3095(5)	5083(2)	−51(2)	74(2)	C(22)	4567(4)	6594(2)	418(2)	36(1)
O(3)	3712(3)	5215(1)	2211(2)	33(1)	C(23)	3771(4)	7155(2)	1126(2)	34(1)
O(4)	2324(3)	4683(1)	2444(2)	43(1)	C(24)	4943(4)	7275(2)	1588(2)	31(1)
O(5)	7386(3)	4292(1)	3475(2)	31(1)	C(25)	3673(4)	6702(2)	2824(2)	31(1)
O(6)	8945(4)	4303(2)	3018(2)	76(2)	C(26)	4330(5)	7121(2)	2559(2)	34(1)
O(7)	4063(3)	3541(1)	3250(2)	30(1)	C(27)	6399(4)	6925(2)	2472(2)	29(1)
O(8)	2400(3)	3063(1)	3071(2)	63(1)	C(28)	6688(4)	6525(2)	2986(2)	28(1)
O(9)	4582(3)	3686(1)	4512(2)	38(1)	C(29)	7029(4)	5353(2)	2008(2)	29(1)
O(10)	3947(3)	3447(1)	5349(2)	49(1)	C(30)	7463(4)	5795(2)	2458(2)	27(1)
O(11)	7904(3)	3291(1)	3972(2)	34(1)	C(31)	6259(4)	5624(2)	3223(2)	26(1)
O(12)	9635(3)	3039(2)	4602(2)	52(1)	C(32)	7293(4)	5578(2)	3802(2)	28(1)
O(13)	2338(3)	6153(1)	1514(2)	40(1)	C(33)	8004(5)	4480(2)	4996(2)	32(1)
O(14)	661(3)	6226(2)	772(2)	69(1)	C(34)	8132(4)	5014(2)	4710(2)	31(1)
O(15)	6008(3)	6211(1)	1261(2)	33(1)	C(35)	4838(4)	4923(2)	4027(2)	25(1)
O(16)	6635(3)	6450(1)	417(2)	41(1)	C(36)	5916(4)	5210(2)	4425(2)	26(1)
O(17)	3865(3)	6236(1)	2692(2)	31(1)	K(1)	8361(1)	5696(1)	816(1)	55(1)
O(18)	2979(4)	6835(2)	3160(2)	52(1)	K(2)	9924(1)	4675(1)	2055(1)	53(1)
O(19)	5897(3)	5270(1)	1863(2)	30(1)	K(3)	2321(1)	5621(1)	3141(1)	45(1)
O(20)	7779(3)	5109(2)	1793(2)	53(1)	K(4)	2502(1)	4185(1)	3622(1)	40(1)
O(21)	7168(3)	4184(1)	4732(2)	33(1)	O(25)	9264(4)	6006(2)	−363(2)	88(2)
O(22)	8785(4)	4380(1)	5480(2)	55(1)	O(26)	10,285(4)	5772(2)	1995(2)	79(2)
O(23)	5065(3)	4540(1)	3710(1)	27(1)	O(27)	10,279(5)	4980(2)	839(2)	90(2)
O(24)	3821(3)	5086(1)	4053(2)	38(1)	O(28)	7730(6)	4221(2)	1013(3)	117(2)
C(1)	3623(5)	5075(2)	497(3)	39(1)	O(29)	519(4)	6537(2)	2875(3)	92(2)
C(2)	4234(5)	4557(2)	724(2)	41(1)	O(30)	657(3)	4982(2)	3513(2)	56(1)
C(3)	3060(4)	4813(2)	2133(2)	29(1)	O(31)	10,470(5)	3616(2)	2461(3)	122(2)
C(4)	3142(4)	4455(2)	1579(2)	32(1)	O(32)	1638(4)	3769(2)	4582(2)	79(2)
C(5)	5182(5)	4049(2)	1662(2)	33(1)	O(33)	5947(4)	6897(2)	−764(2)	59(1)
C(6)	5335(4)	4026(2)	2359(2)	28(1)	O(34)	−355(4)	6357(2)	3877(2)	74(1)
C(7)	7962(5)	4138(2)	3082(2)	34(1)	O(35)	10,789(4)	2651(2)	5707(2)	88(2)
C(8)	7412(4)	3693(2)	2656(2)	33(1)	O(36)	2579(5)	7837(2)	3544(3)	104(2)
C(9)	5714(4)	3082(2)	2437(2)	32(1)	O(37)	3333(5)	2513(2)	5836(3)	109(2)
C(10)	6111(4)	2664(2)	2924(2)	34(1)	O(38)	9905(11)	3331(3)	1225(3)	226(5)

The total angles of ∠O(1)Er(1)N(2), ∠O(1)Er(1)N(4) and ∠N(2)Er(1)N(4) are 360.00(7)° indicating that Er(1), O(1), N(2) and N(4) lie on the same plane.

These two nine-coordinate $[Ho^{III}(ttha)]^{3-}$ and $[Er^{III}(ttha)]^{3-}$ complexes contain a non-coordinate free carboxyl group ($-CH_2COO^-$).

Like Ho^{III}, the Er^{III} ion having ionic radius of 0.1030 nm and electronic configuration of f^{11} also forms a nine-coordinate complex with distorted tricapped trigonal prismatic structure with one ttha ligand. There is an inherent relationship among the molecular and crystal structures and ionic radius and electronic configuration of central metal ion.

Table 4. Non-hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å) (U_{eq}) of $K_3[Dy^{III}(ttha)] \cdot 5H_2O$.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Dy(1)	2523(1)	2663(1)	8696(1)	16(1)	C(6)	4772(3)	4033(3)	7829(2)	27(1)
N(1)	4999(3)	2495(2)	8508(1)	20(1)	C(7)	2933(3)	5146(3)	8114(2)	26(1)
N(2)	3335(3)	4090(2)	7891(1)	22(1)	C(8)	1659(3)	5109(3)	8446(2)	22(1)
N(3)	1083(3)	2660(2)	7684(1)	22(1)	C(9)	2718(4)	3896(3)	7307(2)	28(1)
N(4)	202(3)	1761(2)	8823(1)	19(1)	C(10)	1290(3)	3649(3)	7345(2)	26(1)
O(1)	3668(2)	1361(2)	9287(1)	23(1)	C(11)	1421(4)	1722(3)	7317(2)	28(1)
O(2)	4816(2)	−139(2)	9167(1)	33(1)	C(12)	2157(3)	862(3)	7650(2)	27(1)
O(3)	3769(2)	3939(2)	9215(1)	26(1)	C(13)	−299(3)	2587(3)	7853(2)	26(1)
O(4)	5573(3)	4885(2)	9347(1)	40(1)	C(14)	−528(3)	1652(3)	8259(2)	25(1)
O(5)	1320(2)	4225(2)	8664(1)	24(1)	C(15)	410(3)	701(3)	9100(2)	23(1)
O(6)	1046(2)	5956(2)	8492(1)	33(1)	C(16)	−775(3)	−13(3)	9208(2)	24(1)
O(7)	2697(2)	1121(2)	8132(1)	29(1)	C(17)	−478(3)	2503(3)	9220(2)	22(1)
O(8)	2218(3)	−44(2)	7425(1)	44(1)	C(18)	420(3)	2961(2)	9688(2)	20(1)
O(9)	−538(3)	−982(2)	9274(2)	45(1)	K(1)	1406(1)	7687(1)	9117(1)	31(1)
O(10)	−1882(2)	394(2)	9228(1)	37(1)	K(2)	3097(1)	1481(1)	10449(1)	30(1)
O(11)	1632(2)	2798(2)	9643(1)	21(1)	K(3)	2077(1)	4931(1)	10020(1)	29(1)
O(12)	−82(2)	3507(2)	10080(1)	27(1)	O(13)	3274(3)	8638(2)	9877(1)	41(1)
C(1)	5332(3)	1341(3)	8569(2)	24(1)	O(14)	3655(3)	6502(2)	9483(2)	50(1)
C(2)	4554(3)	813(3)	9048(2)	23(1)	O(15)	3088(3)	8585(2)	8352(2)	58(1)
C(3)	5745(3)	3121(3)	8950(2)	26(1)	O(16)	3794(6)	3040(4)	11247(2)	137(3)
C(4)	4985(3)	4065(3)	9187(2)	24(1)	O(17)	1546(3)	4896(3)	11201(1)	49(1)
C(5)	5265(3)	2895(3)	7909(2)	27(1)					

Table 5. Non-hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å) (U_{eq}) of $K_3[Ho^{III}(ttha)] \cdot 5H_2O$.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Ho(1)	2519(1)	2662(1)	3694(1)	18(1)	C(6)	−307(6)	2597(5)	2858(3)	29(1)
N(1)	197(4)	1761(4)	3821(2)	22(1)	C(7)	2152(6)	871(5)	2646(3)	30(2)
N(2)	1077(5)	2666(4)	2683(2)	25(1)	C(8)	1429(6)	1724(5)	2315(3)	28(2)
N(3)	3330(5)	4087(4)	2890(2)	23(1)	C(9)	1277(6)	3655(4)	2346(3)	28(2)
N(4)	4994(5)	2487(3)	3502(2)	23(1)	C(10)	2711(6)	3906(5)	2310(3)	28(1)
O(1)	−1897(4)	394(3)	4227(2)	40(1)	C(11)	1655(6)	5103(5)	3452(3)	24(1)
O(2)	−541(4)	−978(3)	4276(2)	46(1)	C(12)	2924(6)	5139(4)	3119(3)	29(2)
O(3)	1638(4)	2799(3)	4638(2)	23(1)	C(13)	4772(6)	4029(5)	2831(3)	31(2)
O(4)	−76(4)	3508(3)	5076(2)	30(1)	C(14)	5254(6)	2893(5)	2910(3)	30(2)
O(5)	2688(4)	1130(3)	3129(2)	29(1)	C(15)	4988(6)	4060(5)	4187(3)	26(1)
O(6)	2225(5)	−34(3)	2420(2)	44(1)	C(16)	5732(6)	3113(5)	3944(3)	26(1)
O(7)	1307(4)	4217(3)	3661(2)	24(1)	C(17)	5321(6)	1340(4)	3564(3)	25(1)
O(8)	1048(4)	5950(3)	3505(2)	33(1)	C(18)	4532(5)	806(5)	4044(3)	23(1)
O(9)	3649(4)	1363(3)	4280(2)	25(1)	K(1)	2079(1)	4932(1)	5017(1)	31(1)
O(10)	4806(4)	−138(3)	4166(2)	34(1)	K(2)	1404(1)	7687(1)	4118(1)	34(1)
O(11)	3765(4)	3930(3)	4210(2)	27(1)	K(3)	3102(1)	1479(1)	5445(1)	32(1)
O(12)	5575(4)	4870(4)	4350(2)	41(1)	O(13)	1554(5)	4886(4)	6204(2)	49(1)
C(1)	−777(6)	−8(5)	4202(3)	27(1)	O(14)	3689(5)	6500(4)	4479(2)	51(1)
C(2)	414(6)	701(4)	4099(3)	26(1)	O(15)	3083(6)	8591(4)	3343(2)	59(2)
C(3)	419(6)	2961(4)	4686(3)	21(1)	O(16)	3288(5)	8636(3)	4885(2)	43(1)
C(4)	−479(5)	2504(4)	4219(3)	23(1)	O(17)	3772(9)	3063(5)	6245(3)	126(4)
C(5)	−534(6)	1655(5)	3259(3)	26(1)					

3.5. *IR spectrum*

3.5.1. $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$ and $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$ complexes. The ν(C–N) of $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$ and $K_4[Tb_2^{III}(Httha)_2] \cdot 14H_2O$ complexes

Table 6. Non-hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors (Å) (U_{eq}) of $K_3[Er^{III}(ttha)] \cdot 5H_2O$.

Atom	x	y	z	U_{eq}	Atom	x	y	z	U_{eq}
Er(1)	2486(1)	2661(1)	1308(1)	17(1)	C(6)	5319(3)	2593(3)	2145(1)	27(1)
N(1)	4799(2)	1764(2)	1181(1)	20(1)	C(7)	3594(3)	1729(3)	2685(1)	29(1)
N(2)	3940(2)	2666(2)	2316(1)	23(1)	C(8)	2856(3)	876(3)	2354(1)	28(1)
N(3)	1676(2)	4086(2)	2108(1)	22(1)	C(9)	3737(3)	3658(3)	2653(1)	27(1)
N(4)	12(2)	2481(2)	1498(1)	23(1)	C(10)	2296(3)	3899(3)	2691(1)	30(1)
O(1)	6890(2)	392(2)	774(1)	39(1)	C(11)	2077(3)	5136(2)	1879(1)	26(1)
O(2)	5536(2)	−978(2)	723(1)	45(1)	C(12)	3347(3)	5097(2)	1546(1)	22(1)
O(3)	3358(2)	2797(2)	366(1)	22(1)	C(13)	234(3)	4018(3)	2174(1)	28(1)
O(4)	5069(2)	3503(2)	−79(1)	29(1)	C(14)	−249(3)	2885(3)	2095(1)	29(1)
O(5)	2322(2)	1137(2)	1870(1)	29(1)	C(15)	−307(3)	1333(2)	1441(1)	25(1)
O(6)	2786(3)	−32(2)	2577(1)	44(1)	C(16)	473(3)	804(2)	958(1)	24(1)
O(7)	3692(2)	4205(2)	1337(1)	25(1)	C(17)	−730(3)	3108(3)	1055(2)	28(1)
O(8)	3956(2)	5941(2)	1485(1)	35(1)	C(18)	26(3)	4047(3)	813(1)	25(1)
O(9)	1360(2)	1361(2)	725(1)	25(1)	K(1)	3599(1)	7685(1)	881(1)	33(1)
O(10)	206(2)	−140(2)	833(1)	35(1)	K(2)	2922(1)	4933(1)	−13(1)	30(1)
O(11)	1245(2)	3928(2)	795(1)	26(1)	K(3)	1893(1)	1478(1)	−443(1)	32(1)
O(12)	−573(2)	4854(2)	643(1)	41(1)	O(13)	1713(3)	8619(2)	119(1)	44(1)
C(1)	4589(3)	697(2)	904(1)	24(1)	O(14)	1946(4)	8575(3)	1657(1)	62(1)
C(2)	5775(3)	−16(3)	794(1)	26(1)	O(15)	1314(3)	6501(2)	530(1)	54(1)
C(3)	5478(3)	2502(2)	782(1)	23(1)	O(16)	3433(3)	4879(3)	−1196(1)	51(1)
C(4)	4574(3)	2959(2)	316(1)	20(1)	O(17)	1303(7)	3097(4)	−1232(2)	119(2)
C(5)	5543(3)	1652(3)	1741(1)	25(1)					

Table 7. Selected bond distances (Å) and angles (°) of $K_4[Eu_2^{III}(Httha)_2] \cdot 13.5H_2O$.

Bond distances					
Eu(1)–O(1)	2.420(5)	Eu(1)–N(5)	2.654(6)	Eu(2)–O(11)	2.375(5)
Eu(1)–O(3)	2.413(5)	Eu(1)–N(6)	2.667(6)	Eu(2)–O(21)	2.405(5)
Eu(1)–O(13)	2.429(6)	Eu(1)–N(7)	2.748(6)	Eu(2)–O(24)	2.419(5)
Eu(1)–O(15)	2.402(5)	Eu(2)–O(5)	2.477(5)	Eu(2)–N(2)	2.688(6)
Eu(1)–O(17)	2.390(5)	Eu(2)–O(7)	2.395(5)	Eu(2)–N(3)	2.679(6)
Eu(1)–O(19)	2.418(5)	Eu(2)–O(10)	2.412(5)	Eu(2)–N(4)	2.626(6)
Bond angle					
O(1)–Eu(1)–O(3)	78.03(18)	O(15)–Eu(1)–N(6)	73.40(18)	O(7)–Eu(2)–N(2)	70.27(18)
O(1)–Eu(1)–O(13)	76.83(19)	O(15)–Eu(1)–N(7)	78.25(18)	O(7)–Eu(2)–N(3)	64.15(18)
O(1)–Eu(1)–O(15)	83.58(19)	O(17)–Eu(1)–O(19)	118.59(18)	O(7)–Eu(2)–N(4)	110.23(19)
O(1)–Eu(1)–O(17)	140.30(18)	O(17)–Eu(1)–N(5)	112.04(18)	O(10)–Eu(2)–O(11)	130.84(18)
O(1)–Eu(1)–O(19)	74.86(18)	O(17)–Eu(1)–N(6)	65.07(17)	O(10)–Eu(2)–O(21)	82.04(19)
O(1)–Eu(1)–N(5)	73.93(18)	O(17)–Eu(1)–N(7)	71.87(18)	O(10)–Eu(2)–O(24)	76.44(17)
O(1)–Eu(1)–N(6)	142.59(18)	O(19)–Eu(1)–N(5)	128.03(18)	O(10)–Eu(2)–N(2)	140.61(19)
O(1)–Eu(1)–N(7)	136.18(18)	O(19)–Eu(1)–N(6)	122.36(19)	O(10)–Eu(2)–N(3)	94.13(19)
O(3)–Eu(1)–O(13)	81.13(18)	O(19)–Eu(1)–N(7)	61.61(18)	O(10)–Eu(2)–N(4)	65.32(19)
O(3)–Eu(1)–O(15)	140.44(17)	N(5)–Eu(1)–N(6)	69.71(19)	O(11)–Eu(2)–O(21)	80.69(19)
O(3)–Eu(1)–O(17)	73.29(16)	N(5)–Eu(1)–N(7)	129.64(18)	O(11)–Eu(2)–O(24)	142.39(17)
O(3)–Eu(1)–O(19)	70.20(17)	N(6)–Eu(1)–N(7)	67.64(19)	O(11)–Eu(2)–N(2)	78.94(18)
O(3)–Eu(1)–N(5)	138.9(2)	O(5)–Eu(2)–O(7)	119.13(18)	O(11)–Eu(2)–N(3)	72.48(19)
O(3)–Eu(1)–N(6)	137.29(18)	O(5)–Eu(2)–O(10)	142.65(18)	O(11)–Eu(2)–N(4)	65.78(19)
O(3)–Eu(1)–N(7)	91.29(18)	O(5)–Eu(2)–O(11)	71.60(18)	O(21)–Eu(2)–O(24)	78.46(17)
O(13)–Eu(1)–O(15)	128.16(18)	O(5)–Eu(2)–O(21)	72.15(18)	O(21)–Eu(2)–N(2)	133.90(18)
O(13)–Eu(1)–O(17)	72.17(19)	O(5)–Eu(2)–O(24)	72.35(17)	O(21)–Eu(2)–N(3)	140.70(19)
O(13)–Eu(1)–O(19)	143.06(18)	O(5)–Eu(2)–N(2)	62.27(17)	O(21)–Eu(2)–N(4)	74.63(19)
O(13)–Eu(1)–N(5)	63.73(18)	O(5)–Eu(2)–N(3)	122.93(18)	O(24)–Eu(2)–N(2)	93.60(17)
O(13)–Eu(1)–N(6)	94.49(19)	O(5)–Eu(2)–N(4)	129.08(19)	O(24)–Eu(2)–N(3)	138.83(19)

(*Continued*)

Table 7. Continued.

Bond angle					
O(13)–Eu(1)–N(7)	143.92(18)	O(7)–Eu(2)–O(10)	70.34(19)	O(24)–Eu(2)–N(4)	135.49(18)
O(15)–Eu(1)–O(17)	135.46(18)	O(7)–Eu(2)–O(11)	133.42(18)	N(2)–Eu(2)–N(3)	68.42(18)
O(15)–Eu(1)–O(19)	71.30(17)	O(7)–Eu(2)–O(21)	145.32(18)	N(2)–Eu(2)–N(4)	130.43(19)
O(15)–Eu(1)–N(5)	64.82(18)	O(7)–Eu(2)–O(24)	75.04(17)	N(3)–Eu(2)–N(4)	68.4(2)

Table 8. Selected bond distances (Å) and angles (°) of $K_4[Tb_2^{III}(Httha)_2]\cdot 14H_2O$.

Bond distances					
Tb(1)–O(1)	2.392(3)	Tb(1)–N(5)	2.646(4)	Tb(2)–O(11)	2.344(3)
Tb(1)–O(3)	2.386(3)	Tb(1)–N(6)	2.643(4)	Tb(2)–O(21)	2.391(3)
Tb(1)–O(13)	2.396(3)	Tb(1)–N(7)	2.735(4)	Tb(2)–O(23)	2.398(3)
Tb(1)–O(15)	2.385(3)	Tb(2)–O(5)	2.458(3)	Tb(2)–N(2)	2.666(4)
Tb(1)–O(17)	2.362(3)	Tb(2)–O(7)	2.370(3)	Tb(2)–N(3)	2.669(4)
Tb(1)–O(19)	2.392(3)	Tb(2)–O(9)	2.389(3)	Tb(2)–N(4)	2.621(4)
Bond angle					
O(1)–Tb(1)–O(3)	78.48(11)	O(15)–Tb(1)–N(6)	73.73(11)	O(7)–Tb(2)–N(2)	70.09(11)
O(1)–Tb(1)–O(13)	76.97(12)	O(15)–Tb(1)–N(7)	78.18(11)	O(7)–Tb(2)–N(3)	64.35(11)
O(1)–Tb(1)–O(15)	83.42(12)	O(17)–Tb(1)–O(19)	118.39(11)	O(7)–Tb(2)–N(4)	110.57(11)
O(1)–Tb(1)–O(17)	140.41(11)	O(17)–Tb(1)–N(5)	112.16(11)	O(9)–Tb(2)–O(11)	131.48(12)
O(1)–Tb(1)–O(19)	74.97(14)	O(17)–Tb(1)–N(6)	65.16(11)	O(9)–Tb(2)–O(21)	81.88(12)
O(1)–Tb(1)–N(5)	73.58(12)	O(17)–Tb(1)–N(7)	71.71(11)	O(9)–Tb(2)–O(23)	75.96(11)
O(1)–Tb(1)–N(6)	142.15(11)	O(19)–Tb(1)–N(5)	128.19(11)	O(9)–Tb(2)–N(2)	140.43(12)
O(1)–Tb(1)–N(7)	136.21(11)	O(19)–Tb(1)–N(6)	122.76(11)	O(9)–Tb(2)–N(3)	94.27(12)
O(3)–Tb(1)–O(13)	80.32(12)	O(19)–Tb(1)–N(7)	61.54(11)	O(9)–Tb(2)–N(4)	65.49(12)
O(3)–Tb(1)–O(15)	140.40(11)	N(5)–Tb(1)–N(6)	69.60(12)	O(11)–Tb(2)–O(21)	80.67(11)
O(3)–Tb(1)–O(17)	72.85(11)	N(5)–Tb(1)–N(7)	130.11(11)	O(11)–Tb(2)–O(23)	142.21(11)
O(3)–Tb(1)–O(19)	70.40(11)	N(6)–Tb(1)–N(7)	68.18(11)	O(11)–Tb(2)–N(2)	78.97(11)
O(3)–Tb(1)–N(5)	138.63(12)	O(5)–Tb(2)–O(7)	118.95(11)	O(11)–Tb(2)–N(3)	72.68(11)
O(3)–Tb(1)–N(6)	137.08(11)	O(5)–Tb(2)–O(9)	142.07(11)	O(11)–Tb(2)–N(4)	66.26(11)
O(3)–Tb(1)–N(7)	91.05(11)	O(5)–Tb(2)–O(11)	71.48(11)	O(21)–Tb(2)–O(23)	78.57(11)
O(13)–Tb(1)–O(15)	129.20(12)	O(5)–Tb(2)–O(21)	72.12(11)	O(21)–Tb(2)–N(2)	133.98(11)
O(13)–Tb(1)–O(17)	71.83(12)	O(5)–Tb(2)–O(23)	72.23(10)	O(21)–Tb(2)–N(3)	140.49(11)
O(13)–Tb(1)–O(19)	142.69(12)	O(5)–Tb(2)–N(2)	62.37(11)	O(21)–Tb(2)–N(4)	74.21(12)
O(13)–Tb(1)–N(5)	64.19(11)	O(5)–Tb(2)–N(3)	123.34(11)	O(23)–Tb(2)–N(2)	93.36(11)
O(13)–Tb(1)–N(6)	94.41(12)	O(5)–Tb(2)–N(4)	129.10(11)	O(23)–Tb(2)–N(3)	138.82(11)
O(13)–Tb(1)–N(7)	143.47(12)	O(7)–Tb(2)–O(9)	70.34(12)	O(23)–Tb(2)–N(4)	135.13(11)
O(15)–Tb(1)–O(17)	135.57(11)	O(7)–Tb(2)–O(11)	133.59(11)	N(2)–Tb(2)–N(3)	68.80(12)
O(15)–Tb(1)–O(19)	70.99(11)	O(7)–Tb(2)–O(21)	145.23(11)	N(2)–Tb(2)–N(4)	131.04(12)
O(15)–Tb(1)–N(5)	65.41(11)	O(7)–Tb(2)–O(23)	74.78(10)	N(3)–Tb(2)–N(4)	68.59(12)

are at 1100 cm^{-1} and 1095 cm^{-1} with red-shifts of 28 and 33 cm^{-1} compared with H_6ttha at 1128 cm^{-1} indicating that some N atoms from ttha coordinate with the central Eu^{III} and Tb^{III} ions. The ν_{as}(COOH) of H_6ttha at 1736 cm^{-1} disappeared in the complexes, and ν_{as}(COO) at 1642 cm^{-1} for H_6ttha red-shifts to 1610 cm^{-1} and 1615 cm^{-1} in the complexes; ν_s(COO) at 1389 cm^{-1} of H_6ttha violet-shifts to 1400 cm^{-1} and 1395 cm^{-1} in the complexes, confirming that the O atoms of carboxylic groups coordinate with the central Eu^{III} and Tb^{III} ions also. A broad ν(OH) band of H_2O near 3430 cm^{-1} shows the existence of H_2O in the complexes.

3.5.2. $K_3[Dy^{III}(ttha)]\cdot 5H_2O$, $K_3[Ho^{III}(ttha)]\cdot 5H_2O$ and $K_3[Er^{III}(ttha)]\cdot 5H_2O$ complexes. The ν(C–N) at 1095 and 1090 cm^{-1} is red-shifted 33 and 38 cm^{-1} for $K_3[Dy^{III}(ttha)]\cdot 5H_2O$, $K_3[Ho^{III}(ttha)]\cdot 5H_2O$ and $K_3[Er^{III}(ttha)]\cdot 5H_2O$ complexes

Table 9. Selected bond distances (Å) and angles (°) of $K_3[Dy^{III}(ttha)] \cdot 5H_2O$.

Bond distances					
Dy(1)–O(1)	2.394(2)	Dy(1)–O(7)	2.314(2)	Dy(1)–N(2)	2.692(3)
Dy(1)–O(3)	2.340(2)	Dy(1)–O(11)	2.358(2)	Dy(1)–N(3)	2.711(3)
Dy(1)–O(5)	2.299(2)	Dy(1)–N(1)	2.594(3)	Dy(1)–N(4)	2.653(3)
Bond angle					
O(1)–Dy(1)–O(3)	85.28(9)	O(3)–Dy(1)–N(2)	73.97(9)	O(7)–Dy(1)–N(3)	64.83(9)
O(1)–Dy(1)–O(5)	147.67(9)	O(3)–Dy(1)–N(3)	135.40(9)	O(7)–Dy(1)–N(4)	77.88(9)
O(1)–Dy(1)–O(7)	73.11(9)	O(3)–Dy(1)–N(4)	135.56(8)	O(11)–Dy(1)–N(1)	123.69(8)
O(1)–Dy(1)–O(11)	74.47(8)	O(5)–Dy(1)–O(7)	136.66(9)	O(11)–Dy(1)–N(2)	134.75(8)
O(1)–Dy(1)–N(1)	64.30(8)	O(5)–Dy(1)–O(11)	75.64(8)	O(11)–Dy(1)–N(3)	124.02(9)
O(1)–Dy(1)–N(2)	132.10(8)	O(5)–Dy(1)–N(1)	126.13(8)	O(11)–Dy(1)–N(4)	64.29(8)
O(1)–Dy(1)–N(3)	136.73(8)	O(5)–Dy(1)–N(2)	66.18(9)	N(1)–Dy(1)–N(2)	67.88(8)
O(1)–Dy(1)–N(4)	94.93(8)	O(5)–Dy(1)–N(3)	71.96(9)	N(1)–Dy(1)–N(3)	112.30(9)
O(3)–Dy(1)–O(5)	74.50(9)	O(5)–Dy(1)–N(4)	82.93(9)	N(1)–Dy(1)–N(4)	150.30(8)
O(3)–Dy(1)–O(7)	142.41(9)	O(7)–Dy(1)–O(11)	126.86(9)	N(2)–Dy(1)–N(3)	66.05(9)
O(3)–Dy(1)–O(11)	73.16(8)	O(7)–Dy(1)–N(1)	75.84(9)	N(2)–Dy(1)–N(4)	129.95(9)
O(3)–Dy(1)–N(1)	67.06(8)	O(7)–Dy(1)–N(2)	97.99(10)	N(3)–Dy(1)–N(4)	67.41(9)

Table 10. Selected bond distances (Å) and angles (°) of $K_3[Ho^{III}(ttha)] \cdot 5H_2O$.

Bond distances					
Ho(1)–O(3)	2.359(4)	Ho(1)–O(9)	2.384(4)	Ho(1)–N(2)	2.713(5)
Ho(1)–O(5)	2.312(4)	Ho(1)–O(11)	2.334(4)	Ho(1)–N(3)	2.699(5)
Ho(1)–O(7)	2.304(4)	Ho(1)–N(1)	2.662(5)	Ho(1)–N(4)	2.604(5)
Bond angle					
O(3)–Ho(1)–O(5)	127.07(14)	O(5)–Ho(1)–N(2)	64.84(14)	O(9)–Ho(1)–N(3)	132.28(15)
O(3)–Ho(1)–O(7)	75.57(14)	O(5)–Ho(1)–N(3)	97.84(16)	O(9)–Ho(1)–N(4)	64.60(14)
O(3)–Ho(1)–O(9)	74.43(14)	O(5)–Ho(1)–N(4)	75.53(14)	O(11)–Ho(1)–N(1)	135.65(15)
O(3)–Ho(1)–O(11)	73.20(14)	O(7)–Ho(1)–O(9)	147.83(14)	O(11)–Ho(1)–N(2)	135.19(15)
O(3)–Ho(1)–N(1)	64.33(14)	O(7)–Ho(1)–O(11)	74.82(15)	O(11)–Ho(1)–N(3)	73.83(16)
O(3)–Ho(1)–N(2)	124.10(15)	O(7)–Ho(1)–N(1)	82.67(15)	O(11)–Ho(1)–N(4)	67.26(14)
O(3)–Ho(1)–N(3)	134.71(14)	O(7)–Ho(1)–N(2)	71.66(14)	N(1)–Ho(1)–N(2)	67.57(15)
O(3)–Ho(1)–N(4)	123.90(14)	O(7)–Ho(1)–N(3)	66.41(15)	N(1)–Ho(1)–N(3)	130.09(15)
O(5)–Ho(1)–O(7)	136.35(15)	O(7)–Ho(1)–N(4)	126.54(13)	N(1)–Ho(1)–N(4)	150.09(14)
O(5)–Ho(1)–O(9)	73.05(15)	O(9)–Ho(1)–O(11)	85.61(15)	N(2)–Ho(1)–N(3)	65.97(15)
O(5)–Ho(1)–O(11)	142.32(15)	O(9)–Ho(1)–N(1)	94.57(15)	N(2)–Ho(1)–N(4)	112.00(15)
O(5)–Ho(1)–N(1)	77.95(15)	O(9)–Ho(1)–N(2)	136.63(14)	N(3)–Ho(1)–N(4)	67.75(14)

Table 11. Selected bond distances (Å) and angles (°) of $K_3[Er^{III}(ttha)] \cdot 5H_2O$.

Bond distances					
Er(1)–O(3)	2.348(2)	Er(1)–O(9)	2.378(2)	Er(1)–N(2)	2.712(3)
Er(1)–O(5)	2.299(2)	Er(1)–O(11)	2.325(2)	Er(1)–N(3)	2.688(2)
Er(1)–O(7)	2.286(2)	Er(1)–N(1)	2.642(2)	Er(1)–N(4)	2.591(3)
Bond angle					
O(3)–Er(1)–O(5)	127.06(8)	O(5)–Er(1)–N(2)	64.85(8)	O(9)–Er(1)–N(3)	132.47(7)
O(3)–Er(1)–O(7)	75.54(7)	O(5)–Er(1)–N(3)	98.04(8)	O(9)–Er(1)–N(4)	64.50(7)
O(3)–Er(1)–O(9)	74.24(7)	O(5)–Er(1)–N(4)	75.62(8)	O(11)–Er(1)–N(1)	135.64(7)
O(3)–Er(1)–O(11)	72.98(7)	O(7)–Er(1)–O(9)	147.69(8)	O(11)–Er(1)–N(2)	135.14(8)
O(3)–Er(1)–N(1)	64.60(7)	O(7)–Er(1)–O(11)	74.57(8)	O(11)–Er(1)–N(3)	73.68(8)
O(3)–Er(1)–N(2)	124.14(7)	O(7)–Er(1)–N(1)	82.71(7)	O(11)–Er(1)–N(4)	67.41(8)
O(3)–Er(1)–N(3)	134.53(7)	O(7)–Er(1)–N(2)	71.71(7)	N(1)–Er(1)–N(2)	67.36(8)
O(3)–Er(1)–N(4)	123.52(7)	O(7)–Er(1)–N(3)	66.38(7)	N(1)–Er(1)–N(3)	130.07(8)
O(5)–Er(1)–O(7)	136.41(8)	O(7)–Er(1)–N(4)	126.75(7)	N(1)–Er(1)–N(4)	149.89(8)
O(5)–Er(1)–O(9)	73.03(8)	O(9)–Er(1)–O(11)	85.86(8)	N(2)–Er(1)–N(3)	66.17(8)
O(5)–Er(1)–O(11)	142.59(8)	O(9)–Er(1)–N(1)	94.42(7)	N(2)–Er(1)–N(4)	112.34(8)
O(5)–Er(1)–N(1)	77.75(8)	O(9)–Er(1)–N(2)	136.56(7)	N(3)–Er(1)–N(4)	68.05(8)

comparing with H_6ttha ($1128\,cm^{-1}$), indicating that the N atoms from ttha ligand coordinate to Dy^{III}, Ho^{III} and Er^{III} ions. The ν_{as}(COOH) in H_6ttha at $1736\,cm^{-1}$ still appeared in these three complexes indicating a free carboxylic group in the $K_3[Dy^{III}(ttha)] \cdot 5H_2O$, $K_3[Ho^{III}(ttha)] \cdot 5H_2O$ and $K_3[Er^{III}(ttha)] \cdot 5H_2O$. The ν_{as}(COO) at $1642\,cm^{-1}$ of H_6ttha red-shifts to 1600 and $1605\,cm^{-1}$ and ν_s(COO) at $1389\,cm^{-1}$ of H_6ttha blue-shifts to 1400 and $1405\,cm^{-1}$ in these three complexes confirming that the O atoms of $-COO^-$ groups also coordinate to Dy^{III}, Ho^{III} and Er^{III}. A broad ν(OH) band of H_2O near $3450\,cm^{-1}$ shows the existence of H_2O in $K_3[Dy^{III}(ttha)] \cdot 5H_2O$, $K_3[Ho^{III}(ttha)] \cdot 5H_2O$ and $K_3[Er^{III}(ttha)] \cdot 5H_2O$ complexes.

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