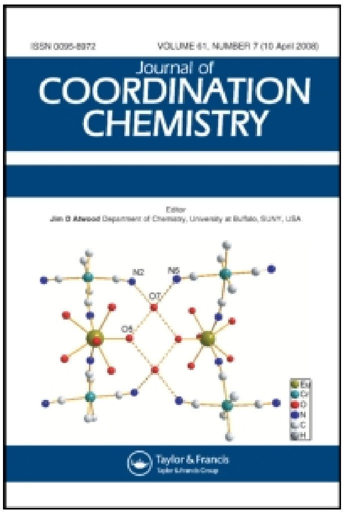

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The syntheses and structures of ten-coordinate $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ and nine-coordinate $K_4[(Httha)_2] \cdot 14H_2O$ complexes

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The title complexes, $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ and $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$ ($H_6ttha =$ triethylenetetraaminehexaacetic acid), have been prepared and characterized using IR, elemental analyses and single-crystal X-ray diffraction techniques. The crystal of $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ has a ten-coordinate mononuclear structure with a distorted bicapped square antiprismatic prism, belonging to the triclinic crystal system and $P\bar{1}$ space group. The crystal data are as follows: $a = 9.697(4)$ Å, $b = 16.183(6)$ Å, $c = 20.957(8)$ Å, $V = 2963.0(19)$ Å^3, $Z = 2$. The crystal of $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$ belongs to the monoclinic crystal system and $P21/n$ space group, with $a = 11.2787(10)$ Å, $b = 25.706(2)$ Å, $c = 22.058(2)$ Å, $V = 6231.5(10)$ Å^3, $Z = 4$, and is a binuclear nine-coordinate pseudo-monocapped square antiprism. The results provide the dividing point of nine-coordinate and ten-coordinate rare earth complexes with ttha ligand.

Keywords: Synthesis; Structure; Samarium; Praseodymium; Complex; ttha

1. Introduction

Rare earth metals attract interest due to their diverse biological activities and many potential applications [1–7]. For example, some Nd^{III} complexes have good anti-inflamation activity; many Gd^{III} complexes are often used as contrast agents in magnetic resonance imaging because of its seven high-spin electrons, [8]; Tb^{III} and Eu^{III} complexes have been used as ionic probes to diagnose some diseases with their characteristic fluorescence [9]. Moreover, Pr^{III} in solids exhibits prominent optical features [10–18]. The $^{153}Sm^{III}$ complexes as radioactive drugs expand treatment options for osteosarcoma, offering patients with bone cancer a treatment that specifically targets and kills tumor cells in the bone [19–22]. In general, rare earth metal ions form eight-, nine- and ten-coordinate complexes with aminopolycarboxylic acid ligands since they have different ionic radii and electronic configurations. After years of research, we have found that these complexes have some intrinsic laws in coordination number and coordinate structure [23–29]. Taking rare earth metal complexes with triethylene-tetraaminehexaacetic acid ($=H_6ttha$) ligand for example, the La^{III}, with a particularly large ionic radius forms ten-coordinate complex [30] with Tm^{III}, Yb^{III} and Lu^{III}, which

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have much smaller ionic radii and many f-electrons, form eight-coordinate complexes [31]. The rest, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III} and Er^{III}, only form nine-coordinate complexes [32–37]. As a part of our ongoing research in this field, to determine which rare earth metal ion, between La^{III} and Eu^{III}, forms ten-coordinate complex like La^{III} ion, and which one adopts nine-coordinate structure like Eu^{III}, Pr^{III} and Sm^{III} complexes with ttha ligand were synthesized and their crystal and molecular structures were determined.

2. Experimental

2.1. *Syntheses of complexes*

H_6ttha (2.47 g, 5.0 mmol) was added to 100 mL water, and Pr_6O_{11} (0.85 g, 0.83 mmol) powder was slowly added the solution. The solution became transparent when the mixture had been stirred and refluxed for 15.0 h, and then the pH was adjusted to 6.5 by aqueous $KHCO_3$. Finally the solution was concentrated to 25 mL. Green crystals of Pr^{III} complex were obtained after three weeks at room temperature. Anal. Found (%): Pr 16.78, C 25.80, H 4.05, N 6.66, K 14.08; Calcd (%): Pr 16.84, C 25.84, H 4.09, N 6.70, K 14.02. This formula is consistent with the result of diffraction analysis. A colorless crystal of Sm^{III} complex was also obtained by using Sm_2O_3 powder following the same procedure. Anal. Found (%): Sm 17.79, C 25.66, H 4.53, N 6.68, K 9.29; Calcd (%): Sm 17.83, C 25.64, H 4.54, N 6.65, K 9.28, consistent with the result of diffraction analysis.

2.2. *Crystal structure determination*

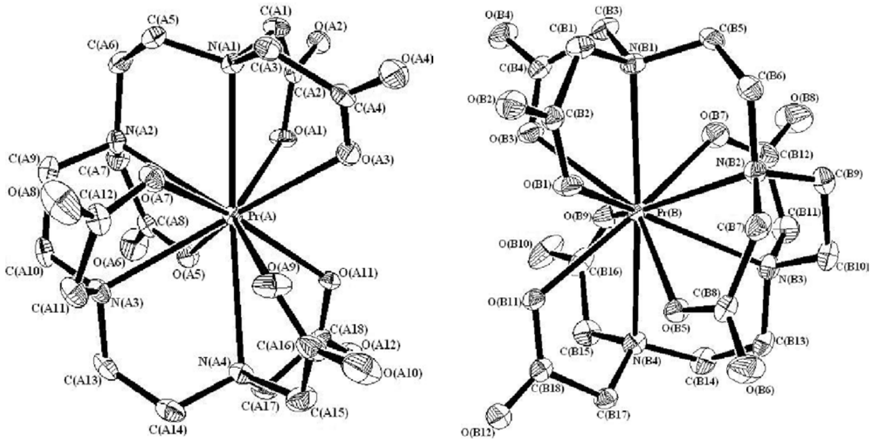
Data were collected with a Bruker SMART CCD X-ray diffractometer system using graphite-monochromated Mo-Kα radiation ($\lambda = 0.071073$ nm). The structure was solved by direct methods. Non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix. All calculations were carried out by using the SHELXTL-97 program on PDP11/44 and Pentium MMX/166 computers. The details of crystal data collection and refinement parameters for $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ and $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$ are listed in table 1. The structures of the complexes are shown in figures 1 and 4, respectively. The molecular packing of the complexes in unit cell are shown in figures 3 and 6. Coordination polyhedra of the complexes are shown in figures 2 and 5. The selected bond distances and angles for $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ are listed in table 2 and for complex $K_4[Sm_2{}^{III}(Httha)_2] \cdot 14H_2O$ in table 3.

2.3. *IR determination*

H_6ttha, $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ and $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$ were mulled and pressed with KBr. Their IR spectra were determined on a Shimadzu-IR 408 spectrograph.

Table 1. Crystal data and structure refinement for complexes $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ and $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$.

Complex	$K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$	$K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$
Empirical formula	$C_{36}H_{68}K_6N_8O_{34}Pr_2$	$C_{36}H_{76}K_4N_8O_{38}Sm_2$
Formula weight ($g\,mol^{-1}$)	1673.40	1686.15
Temperature (K)	293(2)	294(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
Unit cell dimensions (Å)		
a	9.697(4)	11.2787(10)
b	16.183(6)	25.706(2)
c	20.957(8)	22.058(2)
Volume ($Å^3$)	2963.0(19)	6231.5(10)
Z	2	4
Calculated density ($mg\,m^{-3}$)	1.876	1.797
Absorption coefficient (mm^{-1})	2.148	2.237
$F(000)$	1688	3408
Crystal size (mm^3)	$0.24 \times 0.20 \times 0.12$	$0.24 \times 0.10 \times 0.08$
θ range for data collection (°)	1.03–25.01	1.23–25.01
Index ranges	$-11 \le h \le 11$, $-16 \le k \le 19$, $-21 \le l \le 24$	$-13 \le h \le 13$, $-30 \le k \le 16$, $-23 \le l \le 26$
Reflections collected/unique	15,489/10,412 [$R(\text{int}) = 0.0227$]	31,782/11,004 [$R(\text{int}) = 0.0522$]
Completeness to $\theta_{\max}$ (%)	99.6	100.0
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	10,412/8/775	11,004/5/817
Goodness of fit on F^2	1.073	1.040
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0320$, $wR_2 = 0.0690$	$R_1 = 0.0376$, $wR_2 = 0.0781$
R indices (all data)	$R_1 = 0.0508$, $wR_2 = 0.0837$	$R_1 = 0.0657$, $wR_2 = 0.0884$



(a) **(b)**

Figure 1. Molecular structure of $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$.

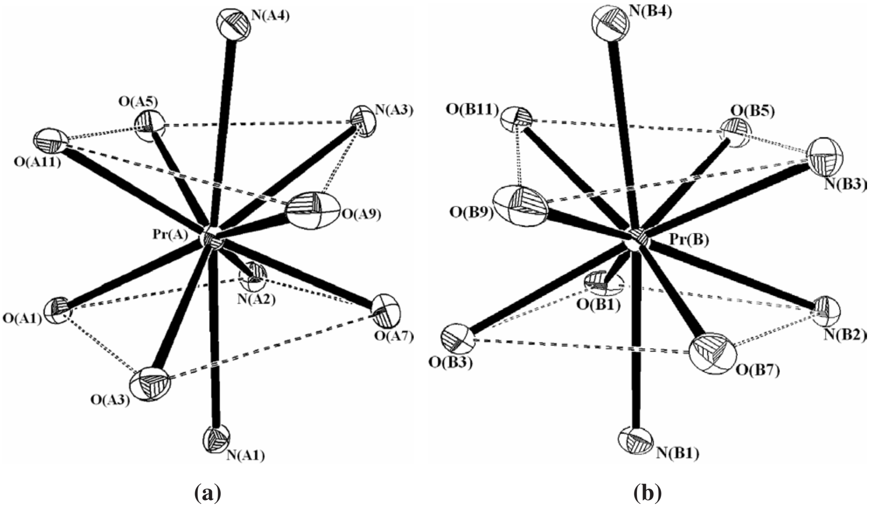


Figure 2. Coordination polyhedron of Pr in $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$.

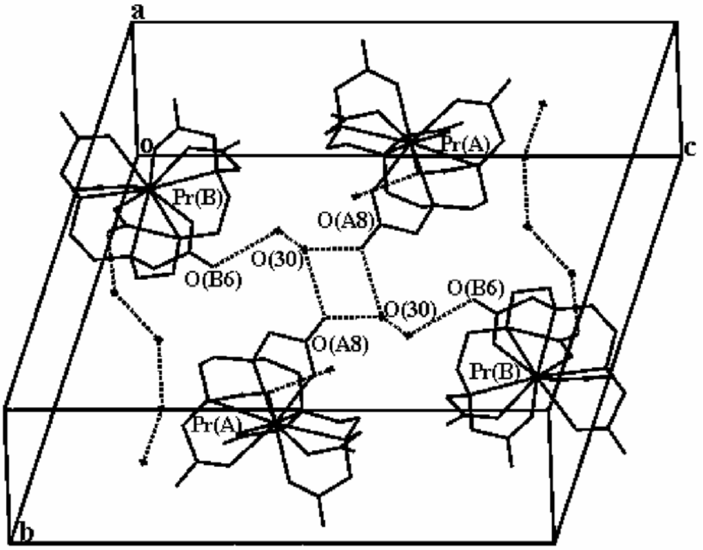


Figure 3. Arrangement of $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ in unit cell.

3. Results and discussion

3.1. *IR spectra*

3.1.1. $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$. The ν(C–N) at $1095\,cm^{-1}$ is red-shifted $30\,cm^{-1}$ compared to H_6ttha ($1125\,cm^{-1}$), which indicates that the amine nitrogen from ttha

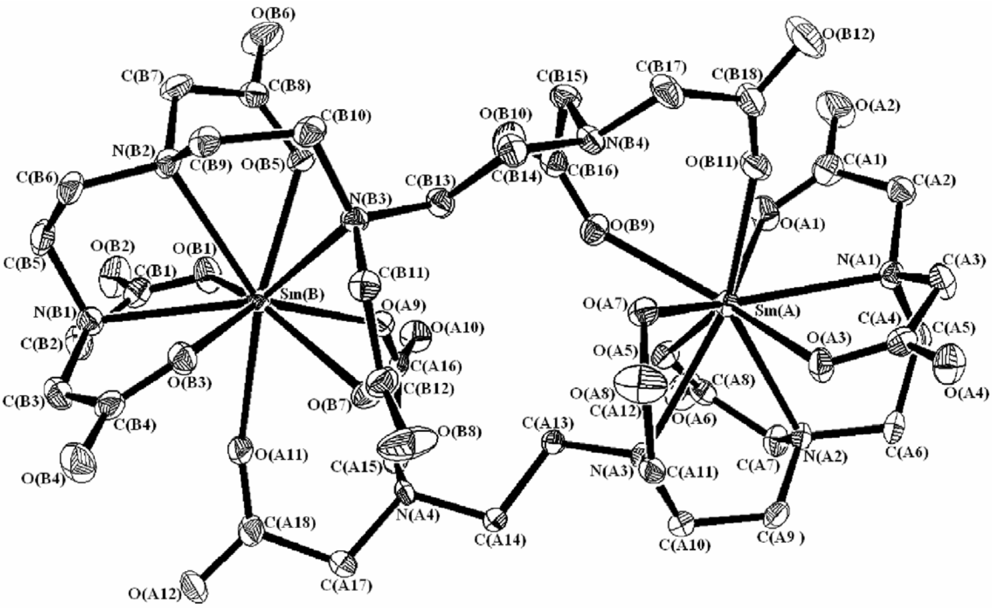
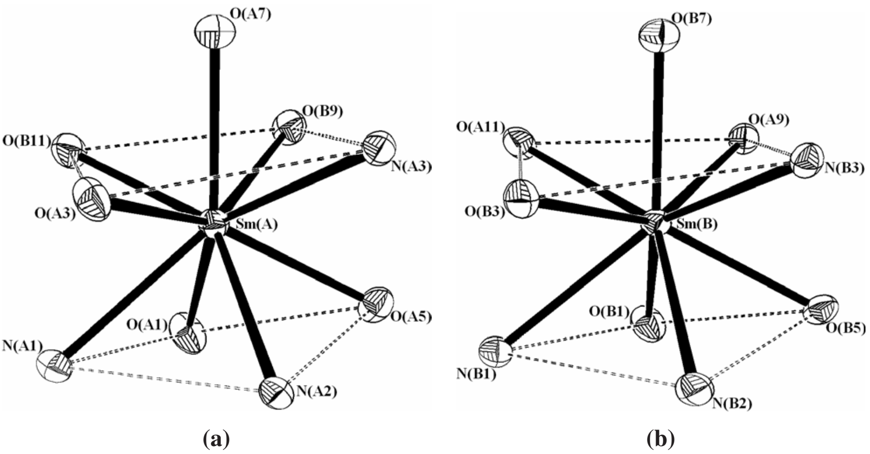


Figure 4. Molecular structure of $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$.



(a) **(b)**

Figure 5. Coordination polyhedron of Sm in $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$.

coordinates to Pr^{III}. ν_{as}(COOH) in H_6ttha at $1738\,cm^{-1}$ disappeared in the complex showing that there are no free carboxylic groups in $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$. The ν_{as}(COO) at $1642\,cm^{-1}$ of H_6ttha red-shifts to $1590\,cm^{-1}$ and ν_s(COO) at $1389\,cm^{-1}$ of H_6ttha blue-shifts to $1409\,cm^{-1}$ in the complex, confirming that all $–COO^-$ groups coordinate to Pr^{III} too. There is a broad ν(OH) band of H_2O near $3423\,cm^{-1}$ showing H_2O in $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$.

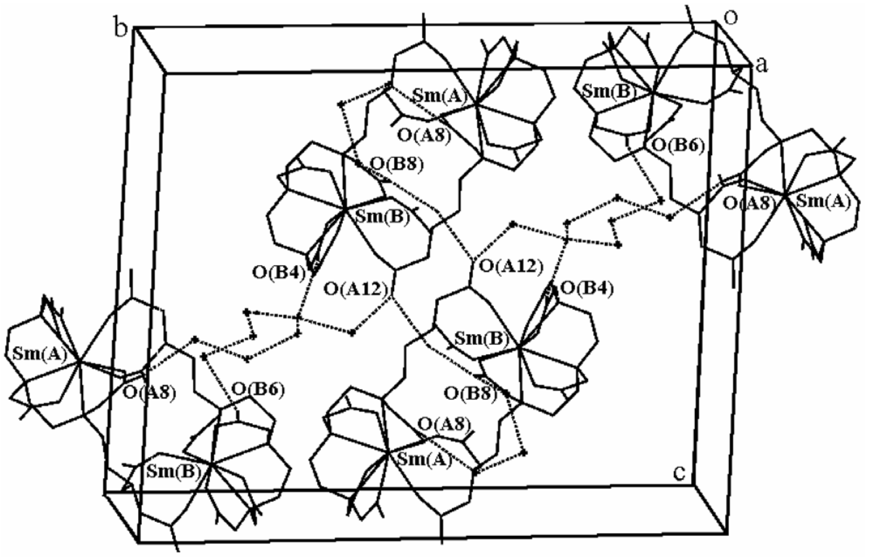


Figure 6. Arrangement of $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$ in unit cell.

Table 2. Selected bond distances (Å) and angles (°) for $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$.

Pr(A)–O(A1)	2.510(3)	Pr(B)–O(B1)	2.534(3)
Pr(A)–O(A3)	2.577(3)	Pr(B)–O(B3)	2.551(3)
Pr(A)–O(A5)	2.476(3)	Pr(B)–O(B5)	2.442(3)
Pr(A)–O(A7)	2.453(3)	Pr(B)–O(B7)	2.482(3)
Pr(A)–O(A9)	2.532(3)	Pr(B)–O(B9)	2.537(4)
Pr(A)–O(A11)	2.517(3)	Pr(B)–O(B11)	2.481(3)
Pr(A)–N(A1)	2.771(4)	Pr(B)–N(B1)	2.777(4)
Pr(A)–N(A2)	2.783(4)	Pr(B)–N(B2)	2.780(4)
Pr(A)–N(A3)	2.774(4)	Pr(B)–N(B3)	2.774(4)
Pr(A)–N(A4)	2.875(4)	Pr(B)–N(B4)	2.909(4)
O(A1)–Pr(A)–O(A3)	75.54(11)	O(B1)–Pr(B)–O(B3)	74.56(11)
O(A1)–Pr(A)–O(A5)	72.06(11)	O(B1)–Pr(B)–O(B5)	71.76(11)
O(A1)–Pr(A)–O(A7)	128.34(10)	O(B1)–Pr(B)–O(B7)	130.09(11)
O(A1)–Pr(A)–O(A9)	140.40(12)	O(B1)–Pr(B)–O(B9)	139.27(12)
O(A1)–Pr(A)–O(A11)	70.34(10)	O(B1)–Pr(B)–O(B11)	70.25(10)
O(A1)–Pr(A)–N(A1)	63.00(10)	O(B1)–Pr(B)–N(B1)	62.65(11)
O(A1)–Pr(A)–N(A2)	74.59(11)	O(B1)–Pr(B)–N(B2)	75.29(11)
O(A1)–Pr(A)–N(A3)	135.52(11)	O(B1)–Pr(B)–N(B3)	135.33(11)
O(A1)–Pr(A)–N(A4)	126.13(10)	O(B1)–Pr(B)–N(B4)	125.08(11)

3.1.2. $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$. The ν(C–N) at 1090 cm^{-1} is red-shifted 35 cm^{-1} compared to H_6ttha (1125 cm^{-1}), indicating that the amine nitrogen atoms from ttha coordinate to Sm^{III}. ν_{as}(COOH) in H_6ttha at 1738 cm^{-1} disappear in the complex, showing no free carboxylic groups in $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$. The ν_{as}(COO) at 1642 cm^{-1} of H_6ttha red-shifts to 1589 cm^{-1} and the ν_s(COO) at 1389 cm^{-1} of H_6ttha blue-shifts to 1396 cm^{-1} in the complex, confirming all $–COO^-$ groups coordinate to Sm^{III}. A broad band at 3380 cm^{-1} shows water of crystallization in $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$.

Table 3. Selected bond distances (Å) and angles (°) for $K_4[Sm_2^{III}(Httha)_2]\cdot 14H_2O$.

Sm(A)–O(A1)	2.430(4)	Sm(B)–O(B1)	2.421(4)
Sm(A)–O(A3)	2.422(4)	Sm(B)–O(B3)	2.385(3)
Sm(A)–O(A5)	2.391(3)	Sm(B)–O(B5)	2.402(3)
Sm(A)–O(A7)	2.415(3)	Sm(B)–O(B7)	2.485(4)
Sm(A)–O(B9)	2.416(4)	Sm(B)–O(A9)	2.423(3)
Sm(A)–O(B11)	2.429(4)	Sm(B)–O(A11)	2.419(4)
Sm(A)–N(A1)	2.660(4)	Sm(B)–N(B1)	2.633(4)
Sm(A)–N(A2)	2.666(4)	Sm(B)–N(B2)	2.695(4)
Sm(A)–N(A3)	2.759(4)	Sm(B)–N(B3)	2.681(4)
O(A1)–Sm(A)–O(A3)	127.96(12)	O(A9)–Sm(B)–O(A11)	78.26(11)
O(A1)–Sm(A)–O(A5)	72.22(13)	O(A9)–Sm(B)–O(B1)	76.58(12)
O(A1)–Sm(A)–O(A7)	143.91(13)	O(A9)–Sm(B)–O(B3)	142.60(12)
O(A1)–Sm(A)–O(B9)	81.51(13)	O(A9)–Sm(B)–O(B5)	75.21(11)
O(A1)–Sm(A)–O(B11)	77.08(13)	O(A9)–Sm(B)–O(B7)	72.38(12)
O(A1)–Sm(A)–N(A1)	63.50(13)	O(A9)–Sm(B)–N(B1)	135.21(12)
O(A1)–Sm(A)–N(A2)	94.00(13)	O(A9)–Sm(B)–N(B2)	138.86(12)
O(A1)–Sm(A)–N(A3)	143.73(13)	O(A9)–Sm(B)–N(B3)	93.65(12)

3.2. *Molecular and crystal structures*

3.2.1. $K_6[Pr^{III}(ttha)]_2\cdot 10H_2O$. Figure 1 shows that Pr^{III} forms a 1 : 1 ratio, ten-coordinate complex with a ttha ligand, the same as $K[KLa^{III}(Httha)(H_2O)]\cdot 8H_2O$ [30]. Two relatively independent Pr^{III} ions are basically in similar coordination environments.

The Pr^{III}(A) ion is ten-coordinate with six carboxylic oxygen atoms and four amine nitrogen atoms from ttha, forming a distorted bicapped square antiprismatic coordination polyhedron shown in figure 2(a), in which the top and bottom planes are defined by the set O(A5), O(A11), O(A9) and N(A3) and O(A1), O(A3), O(A7) and N(A2), respectively, with torsion angle about 45°. The capping positions (top and bottom) are occupied by N(A4) and N(A1). The Pr^{III}(A)–O bond range is from 2.442(3) Å to 2.577(3) Å, and the Pr^{III}(A)–N bond range is from 2.771(4) Å to 2.909(4) Å, indicating that the Pr^{III}(A)–O bonds are stronger than the Pr^{III}(A)–N bonds because the Pr^{III}(A)–O bond distances are considerably shorter than the Pr^{III}(A)–N bond. It should be noted that the N(A4)–Pr(A)–N(A1) bond angle is 167.39(11)°, which indicates the two capped atoms and metal do not make a straight line.

In figure 2(b), the Pr^{III}(B) is also ten-coordinate with six carboxylic oxygen atoms and four amine nitrogen atoms from ttha, forming a distorted bicapped square antiprismatic coordination polyhedron, in which the top and bottom planes are defined by the set O(B5), O(B11), O(B9), and N(B3) and O(B1), O(B3), O(B7) and N(B2), respectively. The coordinated atoms N(B4) and N(B1) occupy two axial capping positions (top and bottom), respectively, with a N(B4)–Pr(B)–N(B1) bond angle of 168.64(11)°, which indicates that two capped atoms and the center metal ion are not linear.

In one unit cell for $K_6[Pr^{III}(ttha)]_2\cdot 10H_2O$ (shown in figure 3), there are two molecules, each including two complex molecules. The four molecules are associated with intermolecular hydrogen bonds via crystal waters, which play an important role in stabilizing the crystal structure. In the unit cell, there is a parallelogram constructed through two carboxylic oxygen atoms and two oxygen atoms from crystal waters (average Ow $\cdots$ O bond distance 2.746 Å); a structure forms in a unit cell through the hydrogen bonds and static interaction.

In the rare earth metal ions, the La^{III} has the largest ionic radius, and Pr^{III} also has a relatively large ionic radius compared with other rare earth metal ions. These two rare earth metal ions form ten-coordinate complexes.

3.2.2. $K_4[Sm_2^{III}(Httha)_2]\cdot 14H_2O$.

Although the ionic radius of Sm^{III} is only slightly smaller than that of Pr^{III}, the structure of $K_4[Sm_2^{III}(Httha)_2]\cdot 14H_2O$ is different from that of $K_6[Pr^{III}(ttha)]_2\cdot 10H_2O$. As shown in figure 4, the $K_4[Sm_2^{III}(Httha)_2]\cdot 14H_2O$ complex is a nine-coordinate binuclear molecular structure, similar to $K_4[Eu_2^{III}(ttha)_2]\cdot 13.5H_2O$ [33] and $K_4[Tb_2^{III}(ttha)_2]\cdot 13.5H_2O$ [33]. Each Sm^{III} is coordinated with six carboxylic oxygen atoms and three amine nitrogen atoms, with four oxygen atoms from one ttha and the rest from another ttha both $Sm^{III}N_3O_6$ parts in $[Sm_2^{III}(Httha)_2]^{4-}$ are nine-coordinate pseudo-monocapped square antiprisms.

As shown in figure 5, in the Sm(A) anion, the set O(B9), O(B11), O(A3) and N(A3) and N(A1), N(A2), O(A5) and O(A1) make two approximate parallel square planes in a square antiprism. The O(A7), as the ninth coordinated atom is above the plane formed by O(B9), O(B11), O(A3) and N(A3). Because of the repulsion of these four coordinated atoms, the Sm(A)–O(A7) bond distance (2.415(3) Å) should be the longest $Sm(A)^{III}$–O bonds distances. However, hydrogen bonds between the crystal waters and carboxylic oxygen atoms and between the crystal water and uncoordinated carboxylic oxygen atoms result in Sm(A)–O(A1) being the longest one. The changes of bond angles shows that the two planes are close because of the repulsion of O(A7). The average angle of O(A7)–Sm(A)–O(A3), O(A7)–Sm(A)–O(B11), O(A7)–Sm(A)–O(B9) and O(A7)–Sm(A)–N(A3) is 69.50(12)° near the 70° adopted by most complexes with the nine-coordinate pseudo-monocapped square antiprismatic structure, in which the largest and smallest angles are 77.72(12)° and 61.26(12)°, respectively. The average angle of O(A7)–Sm(A)–N(A1), O(A7)–Sm(A)–O(A1), O(A7)–Sm(A)–O(A5) and O(A7)–Sm(A)–N(A2) is 128.10(38)°, a little bigger than 125.28°, which is the theoretical angle of standard monocapped square antiprismatic conformation. The theoretical values of largest and smallest angles should be 143.91(13)° and 118.30(12)°, respectively.

Around Sm(B), the set O(A9), O(A11), O(B3) and N(B3) and O(B1), N(B1), N(B2) and O(B5) also make two approximate parallel square planes, which form a square antiprism. The coordinated atom O(B7) is above the plane, composed of O(B3), O(A11), O(A9) and N(B3). Because of the repulsion of these four coordinated atoms, the Sm(B)–O(B7) bond distance (2.485(4) Å) is the longest one among all $Sm(B)^{III}$–O bond distances. The O(B7) also repulses these four coordinated atoms causing the two planes close. The average angle of O(B7)–Sm(B)–O(B3), O(B7)–Sm(B)–O(A11), O(B7)–Sm(B)–O(A9), O(B7)–Sm(B)–N(B3) is 69.60(12)° close to 70°. The largest and smallest angles are 72.38(12)° and 61.92(12)°, respectively. The average angle of O(B7)–Sm(B)–N(B1), O(B7)–Sm(B)–O(B1), O(B7)–Sm(B)–O(B5) and O(B7)–Sm(B)–N(B2) is 128.58(12)° a little bigger than 125.28°. The theoretical values of the largest and smallest angles are 143.13(12)° and 118.86(12)° (figure 5), respectively.

Two protons do not dissociate from the amine nitrogen atoms of ttha ligand and formed $\equiv NH^+$ with two amine nitrogen atoms, in the $[Sm_2^{III}(Httha)_2]^{4-}$ complex anion. The two nitrogen atoms are protonated and do not coordinate with Sm^{III}.

In contrast to the structures reported previously, these two indicate a critical radius of rare earth metal complexes of ttha. The La^{III} [30] and Pr^{III} having relatively large ionic radii can form ten-coordinate complexes, and smaller rare earth metal ions (from Sm^{III} to Er^{III}) coordinate to ttha in nine-coordinate complexes [34–36].

4. Conclusion

In summary, two new complexes of Pr and Sm with ttha have been synthesized, with different coordination numbers as well as different crystal and molecular structures. The $K_6[Pr^{III}(ttha)]_2 \cdot 10H_2O$ is ten-coordinate with a distorted bicapped square antiprismatic prism, while $K_4[Sm_2^{III}(Httha)_2] \cdot 14H_2O$ is nine-coordinate, pseudo-monocapped square antiprism. These results indicate that the coordination number and molecular structure depend on the ionic radius and electronic configuration of the center metal as well as the shape of ligand. The syntheses of these two complexes also show that there is a critical radius between ten- and nine-coordinate complexes for rare earth metal ions with ttha.

Supplementary material

CCDC 250337 and CCDC 275963 contain the supplementary crystallographic data for this article. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033.

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