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Syntheses, Structural Determination, and Binding Studies of Mononuclear Nine-Coordinate $(EnH_2)_{1.5}[Ho^{III}(Ttha)] \cdot 4.5H_2O$ and Two Dimensional Unlimited Network $(EnH_2)[Ho^{III}(Egta)(H_2O)]_2 \cdot 6H_2O$[1]

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Abstract—Two novel complexes, $(EnH_2)_{1.5}[Ho^{III}(Ttha)] \cdot 4.5H_2O$ (**I**) (En = ethylenediamine and H_6Ttha = triethylenetetramine-N,N,N',N'',N''',N'''-hexaacetic acid) and $(EnH_2)[Ho^{III}(Egta)(H_2O)]_2 \cdot 6H_2O$ (**II**) (H_4Egta = ethyleneglycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetic acid), were synthesized and their crystal structures were determined by single crystal X-ray diffraction techniques. Complex **I** has a nine-coordinate mononuclear structure with distorted tricapped trigonal prismatic conformation and crystallizes in the monoclinic crystal system with $P2/n$ space group. The crystal data are as follows: $a = 17.7541(18)$, $b = 9.6810(10)$, $c = 22.166(2)$ Å, $\beta = 118.913(2)°$, and $V = 3335.0(6)$ Å^3. Complex **II** has a mononuclear nine-coordinate structure with pseudo-monocapped square antiprismatic conformation and crystallizes in the monoclinic crystal system with $P2_1/n$ space group. The crystal data are as follows: $a = 12.978(8)$, $b = 12.685(8)$, $c = 14.905(9)$ Å, $\beta = 105.333(7)°$, and $V = 2366(2)$ Å^3. In **I**, there are two types of EnH_2^{2+} anions. They connect to $[Ho^{III}(Ttha)]^{3-}$ by hydrogen bonds leading to the formation of 3D pore structure along z axis. In **II**, EnH_2^{2+} cation connects three adjacent $[Ho^{III}(Egta)(H_2O)]^-$ complex anions through hydrogen bonds, these hydrogen bonds lead to the formation of 2D network structure in [101] plane. The results showed that ligand structures play a crucial role in crystal and molecular structure of their complexes. In addition, the protonated (EnH_2^{2+}) cations conjugating to $[Ho^{III}(Ttha)]^{3-}$ and $[Ho^{III}(Egta)(H_2O)]^-$ complex anions are reviewed, which act as an important beginning for study of Ho(III) complexes conjugating with other various amino and heterocyclic biomolecule.

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INTRODUCTION

Rare earth metals always attract chemist interest due to their diverse biological activities and many potential applications [1–3]. For example, Tb(III) and Eu(III) complexes can be used to diagnose some diseases as the ionic probes for their characteristic fluorescence [4–6]. Nd(III) complexes have good anti-inflammation activity [7, 8]. Many Gd(III) complexes have been used as contrast agents for magnetic resonance imaging (MRI) diagnoses since there are seven high-spin single electrons in the *f*-orbits of Gd^{3+} ion, the most in all the rare earth metal ions [9, 10]. As a radioactive rare earth metal ion, the Ho^{3+} ion can emit appropriate rays, thus, the complexes have been adopted to diagnose and treat various tumors effectively [11, 12].

The structures or coordination numbers of rare earth metal complexes with aminopolycarboxylic acids generally depend on the ionic radius, ligand structure and environment of the complex ions, namely, counter ion. It is well known that the differences in ionic radii (from 0.1172 nm of La(III) to 0.1001 nm of Lu(III)) among rare earth metal ions and the crystal field stabilization energy of their complexes are very small. Even so, the rare earth metal ions can form ten-, nine- and eight-coordinate complexes with some aminopolycarboxylic acids. For the triethylenetetramine-N,N,N',N'',N''',N'''-hexaacetic acid (H_6Ttha) ligand, the La^{3+}, Ce^{3+}, Pr^{3+}, and Nd^{3+} ions with large ionic radii and less *f*-orbital electrons form ten-coordinate complexes [13–15]. The Tm^{3+}, Yb^{3+}, and Lu^{3+} ions with small ionic radii and many *f*-orbital electrons form only eight-coordinate complexes [16, 17]. And that, the intermediate states of Sm^{3+}, Eu^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Ho^{3+}, and Er^{3+} ions take nine-coordinate structure [18–21]. The same regularity is also showed in the rare earth metal complexes with ethyleneglycol-bis(2-aminoethylether)-N,N,N',N'-tetraacetic acid

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ligand. However, due to the different ligands, for same rare earth metal ion their coordinate structures must show markedly different characters. The coordinate structures of the rare earth metal complexes decide the luminescence properties, fluorescent spectra as well as distribution in an organism. Apparently, in order to obtain the needful rare earth metal complexes with aminopolycarboxylic acids, in any way the hypothesis and improvements should arise from the understanding of the structures of rare earth and radioactive rare earth metal complexes. Therefore, the structures of many rare earth metal complexes with aminopolycarboxylic acids have been research specially [22–25].

Due to the relatively small radius (1.041 Å) and many electronic configuration (f^{10}) among rare-earth metal ions, the Ho^{3+} should have some specific physicochemical properties and structural characteristics. In order to get deeper insight into the Ho(III) complexes with H_6Ttha and H_4Egta ligands and the effects caused by their differences, $(EnH_2)_{1.5}[Ho^{III}(Ttha)] \cdot 4.5H_2O$ (**I**) and $(EnH_2)[Ho^{III}(Egta)(H_2O)]_2 \cdot 6H_2O$ (**II**) were synthesized to compare their crystal and molecular structures. As expected, **I** and **II** are both nine-coordinate, but the coordinate structure is different. That is, they take distorted tricapped trigonal prismatic conformation and pseudo-monocapped square antiprismatic conformation, respectively. This study supports the idea that the structures of the rare earth metal complexes with aminopolycarboxylic acid are mainly determined by radii of the central metal ions, ligand structure and counter ion as mentioned above. In addition, the binding between EnH_2^{2+} and $[Ho^{III}(Ttha)]^{3-}$ in **I** or $(EnH_2)^{2+}$ and $[Ho^{III}(Egta)]^-$ in **II** was also reviewed, providing the basis for the investigation on the interaction of Ho(III) complexes with amino and heterocyclic biomolecules.

EXPERIMENTAL

Synthesis of I. H_6Ttha (A.R., Beijing SHLHT Science & Trade Co., Ltd., China) (2.4722 g, 5.0 mmol) was added to 100 mL warm water and Ho_2O_3 powder (99.999%, Yuelong Rare Earth Co., Ltd., China) (0.9447 g, 2.5 mmol) was added to above solution slowly. The solution became transparent after the mixture had been stirred and refluxed for 15 h, and then the pH value was adjusted to 6.0 by dilute En aqueous solution. Finally, the solution was concentrated to 25 mL. A white crystal appeared after eleven weeks at room temperature.

Synthesis of II. H_4Egta (A.R., Beijing SHLHT Science & Trade Co., Ltd., China) (1.9017 g, 5.0 mmol) was added to 100 mL warm water and Ho_2O_3 powder (99.999%, Yuelong Rare Earth Co., Ltd., China) (0.9447 g, 2.5 mmol) was added to above warm solution slowly. The solution became transparent after the mixture had been stirred and refluxed for 18 h, and then the pH value was adjusted to 6.0 by dilute En aqueous solution. Finally, the solution was concentrated to 25 mL and put for static cultivation. A white yellow crystal appeared after ten weeks at room temperature.

X-ray structure determination. X-ray intensity data were collected on a Bruker SMART CCD type X-ray diffractometer system with graphite-monochromatized MoK_α radiation (λ = 0.71073 Å). The structure was solved by direct methods on F^2. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All the calculations were performed by the SHELXTL-97 program on PDP11/44 and Pentium MMX/166 computers. The crystal data and structure refinement for two complexes were listed in Table 1. The selected bond distances and bond angles of two complexes were listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 831523 (**I**) and 831524 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

As seen from Fig. 1a, each Ho^{3+} ion in **I** is surrounded by four amine N atoms and five carboxylic O atoms, all come from one H_6Ttha ligand. It should be noticed that $[Ho^{III}(Ttha)]^{3-}$ complex anions have a non-coordinate carboxyl group anion, namely (O(11)–C(17)–O(12)). It is similar to the findings that previously some have been reported, for instance, $(EnH_2)_3[Tb^{III}(Ttha)]_2 \cdot 11H_2O$ [26] and $(EnH_2)_3[Gd^{III}(Ttha)]_2 \cdot 11H_2O$ [27]. This is because that, generally speaking, Ho^{3+} ions form nine-coordinate complexes with aminopolycarboxylic acids, but H_6Ttha is a polydentate ligand. Apparently, that place is very special because this may be modified by some functional groups or biological molecules to become some specific target probes with great diagnostic effect.

Obviously, the $Ho(1)N_4O_5$ part (Fig. 2a) is mononuclear nine-coordinate geometry with distorted tricapped trigonal prismatic conformation. The coordinate atoms (O(1), O(7), and N(4) and O(3), O(5), and N(2)) around Ho(1) form two approximately parallel trigonal planes, the dihedral angle between the two planes are 13.54°, forming a trigonal prism. The O(9), N(1), and N(3) atoms are above the three approximately quadrangular planes formed by O(1), O(3), O(5), and N(4) and O(1), O(3), O(7), and N(2) and O(5), O(7), N(2), and N(4) shape three capped positions, respectively. The total angles of O(9)Ho(1)N(1), O(9)Ho(1)N(3), and N(1)Ho(1)N(3) are 359.886°, indicating that the Ho(1), O(9), N(1), and N(3) lie in the same plane.

Because of the repulsion between the capped atoms (O(9), N(1), and N(3)) and the planes (formed by O(1), O(3), O(5), and N(4); O(1), O(3), O(7), and

Table 1. Crystal data and structure refinement for **I** and **II**

Parameter	Value	
	I	**II**
Formula weight	827.59	1288.75
Temperature, K	298(2)	293(2)
Crystal system	Monoclinic	Monoclinic
Space group	$P2/n$	$P2_1/n$
Unit cell dimensions		
a , Å	17.7541(18)	12.978(8)
b , Å	9.6810(10)	12.685(8)
c , Å	22.166(2)	14.905(9)
β, deg	118.913(2)	105.333(7)
Volume, Å^3	3335.0(6)	2366(2)
Z	4	2
ρ_{calcd}, mg/cm^3	1.648	1.809
Absorption coefficient, mm^{-1}	2.452	3.416
$F(000)$	1688	1292
Crystal size, mm	0.50 × 0.48 × 0.44	0.41 × 0.30 × 0.16
θ Range for data collection, deg	2.35–25.02	2.29–25.02
Limiting indices	$-21 \le h \le 10$, $-11 \le k \le 11$, $-26 \le l \le 26$	$-15 \le h \le 13$, $-15 \le k \le 15$, $-17 \le l \le 15$
Reflections collected	16285	11530
Independent reflections	5866 ($R_{int} = 0.0487$)	4175 ($R_{int} = 0.0402$)
Completeness to θ_{max}, %	99.5	99.9
Max and min transmission	0.4117 and 0.3736	0.6110 and 0.3349
Goodness-of-fit on F^2	1.084	1.069
Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.0517$, $wR_2 = 0.1323$	$R_1 = 0.0310$, $wR_2 = 0.0688$
R indices (all data)	$R_1 = 0.0783$, $wR_2 = 0.1518$	$R_1 = 0.0458$, $wR_2 = 0.0782$
Largest diff. peak and hole, e Å^{-3}	1.709 and –1.176	1.143 and –1.086
Absorption correction	Empirical from equivalents	

N(2); O(5), O(7), N(2), and N(4)), the Ho(1)N_4O_5 part is not standard tricapped trigonal prismatic conformation. To the O(1), O(3), O(5), and N(4) square plane, the value of the trigonal dihedral angle between Δ(O(1)O(3)O(5)) and Δ(O(1)N(4)O(5)) is about 13.34°, the value of the trigonal dihedral angle between Δ(O(3)O(5)N(4)) and Δ(O(3)O(1)N(4)) is about 13.45°. To O(1), O(3), O(7), and N(2) square plane, the value of the trigonal dihedral angle between Δ(O(1)O(3)N(2)) and Δ(O(1)O(7)N(2)) is 13.86°, the value of the trigonal dihedral angle between (O(1)O(3)O(7)) and Δ(O(3)O(7)N(2)) is 13.45°. Similarly, to O(5), O(7), N(2), and N(4) square plane, the value of the trigonal dihedral angle between Δ(O(5)O(7)N(2)) and Δ(O(5)O(7)N(4)) is 9.32°, the value of the trigonal dihedral angle between Δ(O(5)N(2)N(4)) and Δ(O(7)N(2)N(4)) is 8.24°. Of course, if the values of the trigonal dihedral angle trend to 0°, it is the greater chance of four atoms of dihedral angle in the same plane. Obviously, these data predict

Table 2. Selected bond distances (Å) of **I** and **II**

Bond	*d*, Å	Bond	*d*, Å	Bond	*d*, Å
			I		
Ho(1)–O(1)	2.385(7)	Ho(1)–O(7)	2.319(6)	Ho(1)–N(2)	2.624(8)
Ho(1)–O(3)	2.326(6)	Ho(1)–O(9)	2.337(6)	Ho(1)–N(3)	2.713(7)
Ho(1)–O(5)	2.338(6)	Ho(1)–N(1)	2.608(8)	Ho(1)–N(4)	2.643(6)
			II		
Ho(1)–O(1)	2.488(4)	Ho(1)–O(5)	2.341(4)	Ho(1)–O(11)	2.445(4)
Ho(1)–O(2)	2.474(4)	Ho(1)–O(7)	2.342(3)	Ho(1)–N(1)	2.623(4)
Ho(1)–O(3)	2.348(4)	Ho(1)–O(9)	2.324(4)	Ho(1)–N(2)	2.623(4)

that four atoms of every side of triangular prism are almost located in the same plane, even though the $Ho(1)N_4O_5$ part is not standard tricapped trigonal prismatic conformation. The torsion angle between two trigonal planes (ΔO(1)O(7)N(4) and ΔO(3)O(5)N(2)) is 23.41°. It shows that the structure is distorted tricapped trigonal prismatic conformation.

Furthermore, as seen from Table 2, the Ho(1)–O bond distances range from 2.385(7) Å Ho(1)–O(1) to 2.319(6) Å Ho(1)–O(7), and the average value is 2.341(6) Å. While the Ho(1)–N bond distances range from 2.713(7) Å Ho(1)–N(3) to 2.608(8) Å Ho(1)–N(1), and the average value is 2.652(7) Å. From the above we can come to the conclusion that Ho(1)–O bonds are much stable than Ho(1)–N bonds.

The OHoO bond angles are placed in the range from 148.9(2)° O(1)Ho(1)O(5) to 71.3(2)° O(1)Ho(1)O(7). The OHoN bond angles vary from 137.3(2)° O(3)Ho(1)N(3) to 63.1(3)° O(1)Ho(1)N(1). And the NHoN bond angles change from 147.8(2)° N(1)HoN(4) to 67.7(2)° N(3)HoN(4). Among them, the largest and smallest bond angles are 148.9(2)° O(1)Ho(1)O(5) and 63.1(3)° O(1)Ho(1)N(1), respectively. The reason might be that the O(1) atom forms hydrogen bond with the adjacent crystal water molecule. According to these data, and on the basis of the definitions of nine-coordinate complex given by Muetterties and Guggenberger [28], we can firmly conclude that the conformation around Ho(1) indeed keeps a distorted tricapped trigonal prismatic conformation.

The results given in this paper and the ones reported previously indicate that the Ho^{3+} ion could form nine-coordinate complexes with some aminopolycarboxylic acids due to the ionic radius of 1.041 Å and electronic configuration of f^{10}, and all chelating rings are five-membered rings in the complex structure. In the previous study, we reported the syntheses and structures of $(NH_4)_3[Ho^{III}(Ttha)] \cdot 5H_2O$ [29] in depth. It was found that Ho^{3+} adopts a nine-coordinate mononuclear structure. In the present work, we use En interaction with the $[Ho^{III}(Ttha)]^{3-}$ complex anion, yielding **I**, while it also adopts a nine-coordinate mononuclear structure. Therefore, we can make forecast that if the biomolecule like amino acids were used to interact with $[Ho^{III}(Ttha)]^{3-}$ complex anion, we could also get a series of nine-coordinate mononuclear complexes.

As shown in Fig. 3a, there are four molecules of **I** in a unit cell. The complex molecules connect with one another through hydrogen bonds and electrostatic forces with crystal water and protonated cations $\left(EnH_2^{2+}\right)$. As seen from Fig. 4a, there are two types of EnH_2^{2+} cations. The first type of EnH_2^{2+} cation forms hydrogen bonds with three adjacent $[Ho^{III}(Ttha)]^{3-}$ complex anions, i.e., N(5) of the first type of EnH_2^{2+} links two O atoms (O(9) and O(10)), that is, one uncoordinated carboxyl O atom (O(10)) and one coordinated carboxyl O atom (O(9)) from the same $[Ho^{III}(Ttha)]^{3-}$ complex anion. The second EnH_2^{2+} cation which is highly symmetric, forms hydrogen bonds with two adjacent $[Ho^{III}(Ttha)]^{3-}$ complex. The N(6) atom of the first type of EnH_2^{2+} connects with three O atoms (O(4), O(6), and O(11)) from three $[Ho^{III}(Ttha)]^{3-}$ complex anions, respectively. Among them, O(11) is a non-coordinated carboxyl O atom. Meanwhile, the second EnH_2^{2+} cation which is highly symmetric, forms hydrogen bonds with two adjacent $[Ho^{III}(Ttha)]^{3-}$ complex anions. The N(7) atom of the second type of EnH_2^{2+} connects two uncoordinated carboxyl O atoms (O(2) and O(8)), which come from a same $[Ho^{III}(Ttha)]^{3-}$ complex anions, respectively. He N(8) atom of the second types of EnH_2^{2+} links two non-coordinated carboxyl O atoms (O(12)) from two $[Ho^{III}(Ttha)]^{3-}$ com-

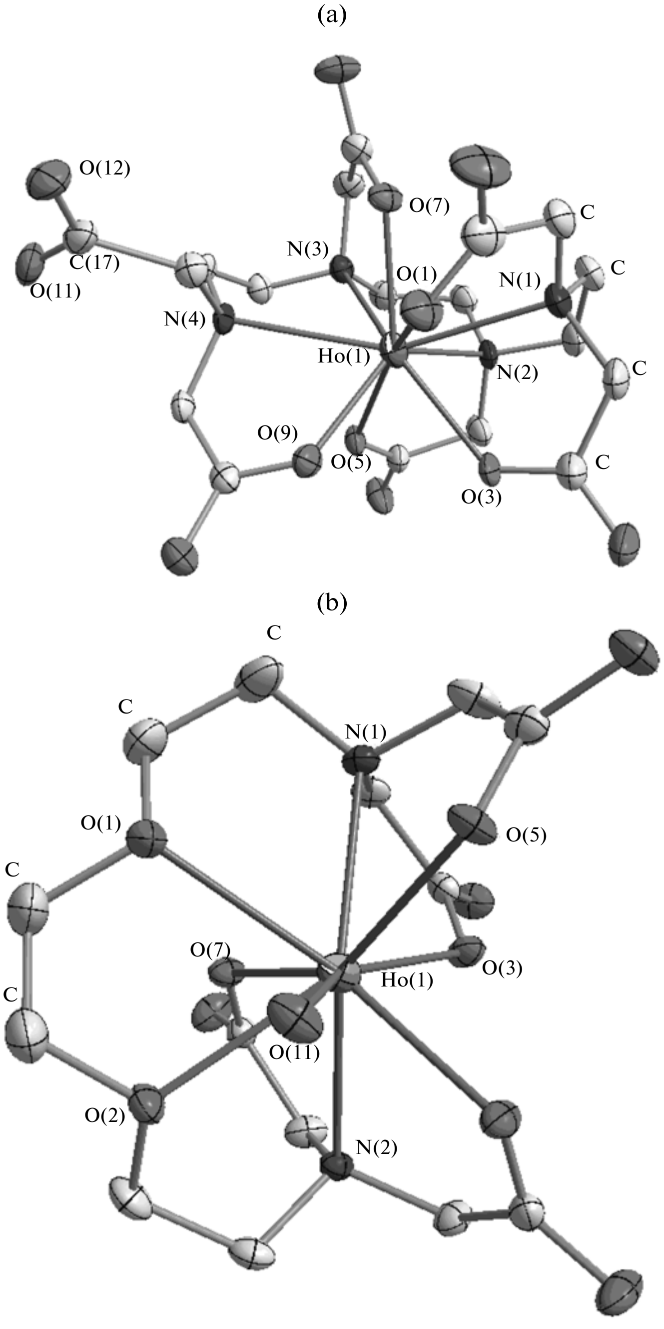

Fig. 1. Molecular structure of **I** (a) and **II** (b).

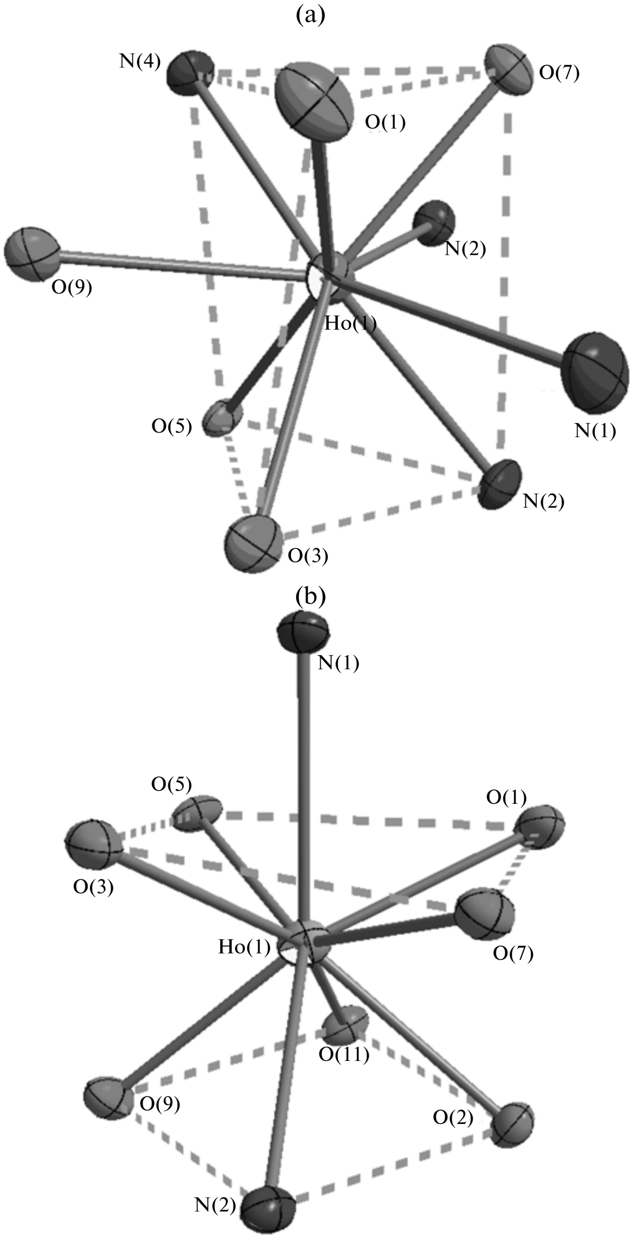

Fig. 2. Coordination polyhedron of **I** (a) and **II** (b).

plex anions, respectively. Because of different coordinate environments, the dihedral angle of two types of ethylenediamine cations $\left(\mathrm{EnH}_2^{2+}\right)$ are 175.13°, 143.10°, and 32.98°, respectively. The dihedral angle of first and second ethylenediamine cations $\left(\mathrm{EnH}_2^{2+}\right)$ are close to *trans*-configuration, while third ethylenediamine cation $\left(\mathrm{EnH}_2^{2+}\right)$ is a tortuous unstable Newman structure. It prefigures the amino acids as a part of protein can interact with $[\mathrm{Ho^{III}(Ttha)}]^{3-}$ complex anions through different binding manner, this may be due to the structure of counter ion.

Every two $[\mathrm{Ho^{III}(Ttha)}]^{3-}$ complex anions are interconnected together by sharing the highly symmetric ethylenediamine (N(7)–C(21)–C(22)–N(8)), forming a basic secondary building unit (SBU) (Fig. 5a). The bond lengths of N(7)–O(8) are 2.716 and 2.778 Å, respectively. The two neighboring SBU are further connected by sharing two ethylenediamines (N(5)–C(19)–C(20)–N(6)) along *x* axis, with O(9)–N(5),

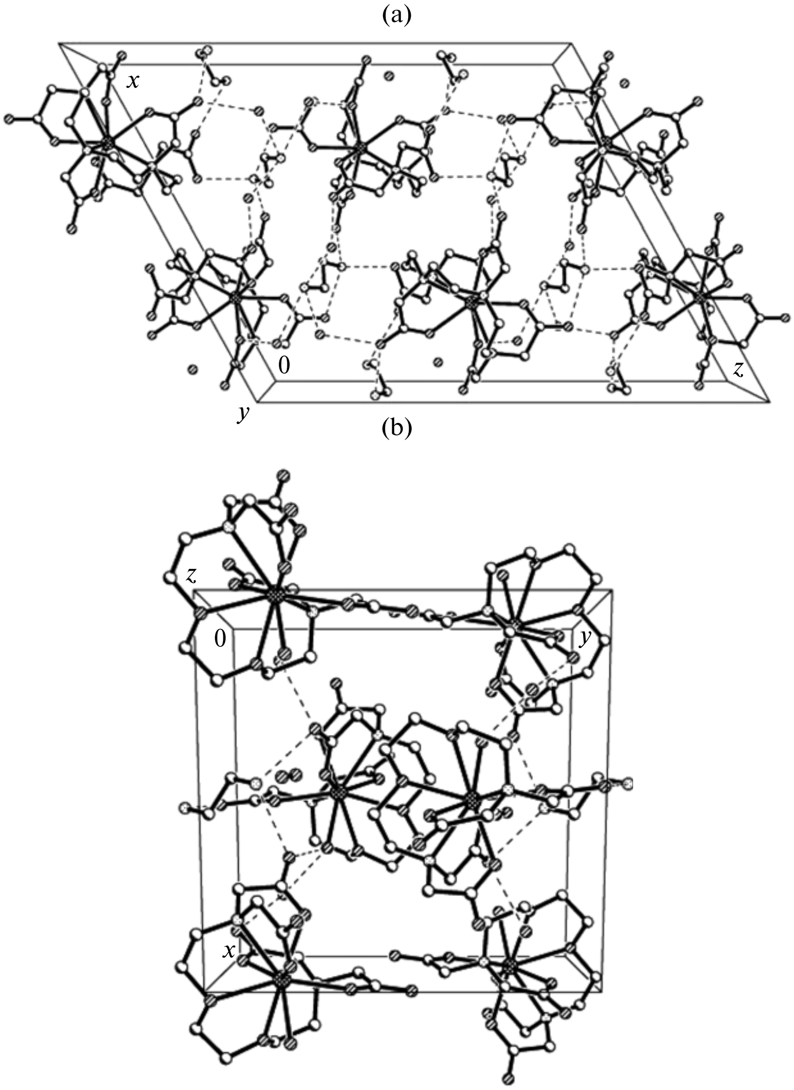

Fig. 3. Arrangement of **I** (a) and **II** (b) in unit cell (dashed lines represent intermolecular hydrogen bonds).

O(10)–N(5), O(4)–N(6), O(6)–N(6), and O(11)–N(6) bond distances of 3.030, 2.975, 2.804, 2.762, and 2.750 Å, respectively, resulting in the formation of infinite 1D chain by *x* axis. The two 1D chains are linked by sharing the ethylenediamine (N(5)–C(19)–C(20)–N(6)) along *y* axis, leading to the formation of 2D ladder-like network. The 2D ladder-like network are further consolidated via soft hydrogen bonds between the water molecules and carboxyl oxygen atoms as well as nitrogen atoms from ethylenediamine to extend into 3D pore structure by *z* axis, which contributes to strengthen the whole structure. In this pore structure, there are one types of pores. The sharp of pore is ellipse. The long axis distance of the ellipsoidal pore is 11.691 Å, minor axis distance is 7.201 Å. This new finding has opened a new way in studying function complexes, especially, the value in the purification and separation of mixture.

As shown in Fig. 1b, it shows that the nine-coordinated structure of **II** is a 1 : 1 proportion of rare earth metal ions to ligand stoichiometry. The central Ho^{3+} ion stays in a nine-coordinate environment, and is coordinated with two amine N atoms and seven O atoms, of which one O atom (O(11)) belongs to a coordinate water molecule. The remaining two amine N atoms, four carboxyl O atoms and two ethyleneglycol O atoms all belong to one octadentate H_4Egta ligand. Unlike complex **I**, excepting water molecule, the eight atoms from one octadentate H_4Egta ligand shape seven structurally stable five-member rings with Ho^{3+} ion as well as the atoms in each five-member ring are almost coplanar.

Apparently, the coordination geometry around the central Ho^{3+} ion in $[Ho^{III}(Egta)(H_2O)]^-$ complex anion (Fig. 2b) is a nine-coordinate pseudo-mono-capped square antiprism, with the capping position occupied by one amine N atom (N(1)). The above quadrilateral plane of antiprism is formed by one ethyleneglycol O atom (O(1)), and three carboxyl O atoms (O(3), O(5), and O(7)). The bottom quadrilateral plane is done by one amine N atom (N(2)), one coordinate water O atom (O(11)), one ethyleneglycol O atom (O(2)) and one carboxyl O atom (O(9)). The twist angle of the two (above and bottom) quadrilateral planes is about 67.71°, which accords with the prismatic geometry.

The series of bond distances for **II** are given in Table 2. The Ho(1)–O bond lengths are considerably different in the wide range from 2.488(4) Å Ho(1)–O(1) to 2.324(4) Å Ho(1)–O(9), and the average value is 2.395(4) Å, while two same Ho(1)–N bonds are 2.623(4) Å Ho(1)–N(1) and Ho(1)–N(1). In any case, the Ho(1)–O bond distances are significantly shorter than the Ho(1)–N bond distances, the same conclusion researched that the Ho(1)–O bonds are stronger than the Ho(1)–N bonds.

Otherwise, as seen from Fig. 2b, it can be found that, to the top square plane, the value of the trigonal dihedral angle between Δ(O(1)O(3)O(5)) and Δ(O(1)O(3)O(7)) is about 12.92°, and between Δ(O(1)O(5)O(7)) and Δ(O(3)O(5)O(7)) is about 12.84°. To the bottom square plane, the value of the trigonal dihedral angle between Δ(O(2)O(11)N(2)) and Δ(O(9)O(11)N(2)) is 6.84° and between Δ(O(2)O(9)N(2)) and Δ(O(2)O(9)O(11)) is 6.02°. In view of these calculated data and according to Guggenberger and Muetterties' method [28], we may safely come to conclusion that the conformation of HoN_2O_7 in $[Ho^{III}(Egta)(H_2O)]^-$ complex anion indeed keeps a pseudo-monocapped square antiprismatic polyhedron but distorted slightly. The conclusion is consistent with other Ho(III) complexes with aminopolycarboxylic acid ligands, e.g., $K_3[Gd^{III}(Nta)_2(H_2O)] \cdot 6H_2O$ [30]. Thus, it can be speculated that the Ho^{3+} forms the nine-coordinate complexes with aminopolycarboxylic acid ligands if the coordinate rings are all five-membered. In addition, the same as complex **I**, if some biomolecule such as small peptide or amino acid are used to conjugate to these Ho(III) complexes, we could also obtain a nine-coordinate pseudo monocapped square antiprismatic geometry.

As shown in Fig. 3b, there are two molecules of **II** in a unit cell. The complex molecules connect with one another through hydrogen bonds and electrostatic forces with crystallization water and protonated ethylenediamine cations $\left(EnH_2^{2+}\right)$, and then crystallize in a monoclinic system with $P2_1/n$ space group. As seen from Fig. 4b, the EnH_2^{2+} cation is located in a center symmetric structure, and the symmetric center is in the middle position of the ethylene. Each ethylenediamine cation $\left(EnH_2^{2+}\right)$ forms hydrogen bonds with three adjacent $[Ho^{III}(Egta)(H_2O)]^-$ complex anions. That is, every N(3) connects four O atoms (O(4), O(5), O(6), and O(10)), in which O(5) and O(6) come from a same carboxyl group of one $[Ho^{III}(Egta)(H_2O)]^-$ complex anion, and the O(4) and O(10) come from two carboxyl groups of two $[Ho^{III}(Egta)(H_2O)]^-$ complex anions, respectively. The distances of N(3)–O(4), N(3)–O(5), N(3)–O(6), and N(3)–O(10) are 2.768, 3.052, 2.786, and 2.767 Å, respectively. Shown in Fig. 5b, every four $[Ho^{III}(Egta)(H_2O)]^-$ complex anions are interconnected together by sharing ethylenediamine (N(3)–C(15)–C(15)–N(3)), forming a basic SBU. The two neighboring SBU are further connected resulting in the formation of 2D network in [101] plane. Owing to this special coordination environment, the Newman' pattern dihedral angle of ethyl-

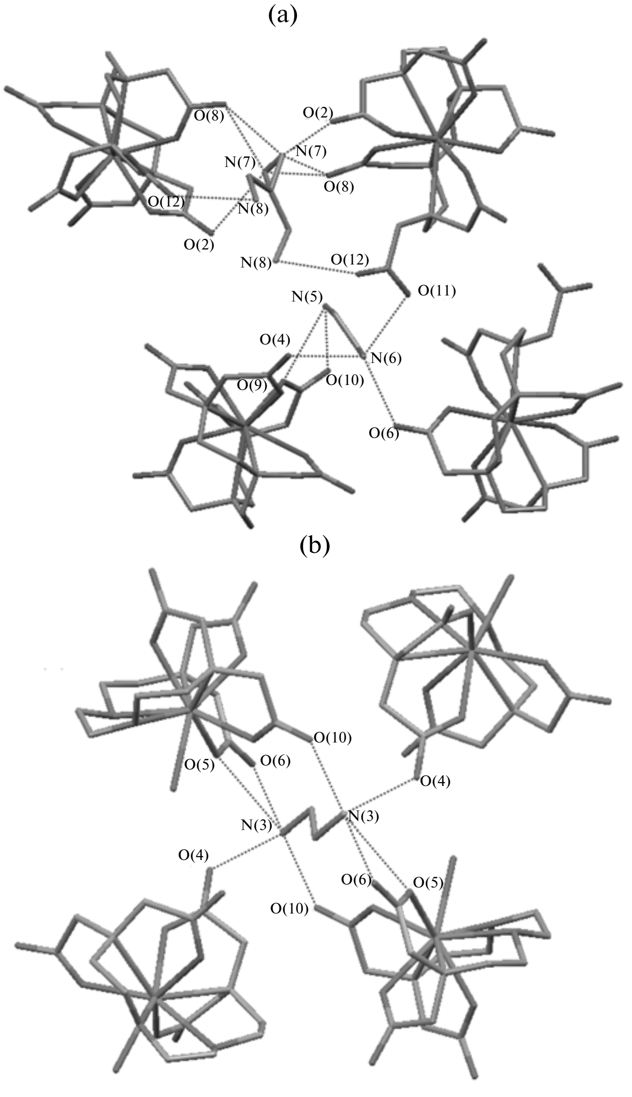

Fig. 4. Bindings between EnH_2^{2+} and $[Ho^{III}(Ttha)]^{3-}$ in **I** (a) and EnH_2^{2+} and $[Ho^{III}(Egta)(H_2O)]^-$ in **II** (b) (dashed lines represent intermolecular hydrogen bonds).

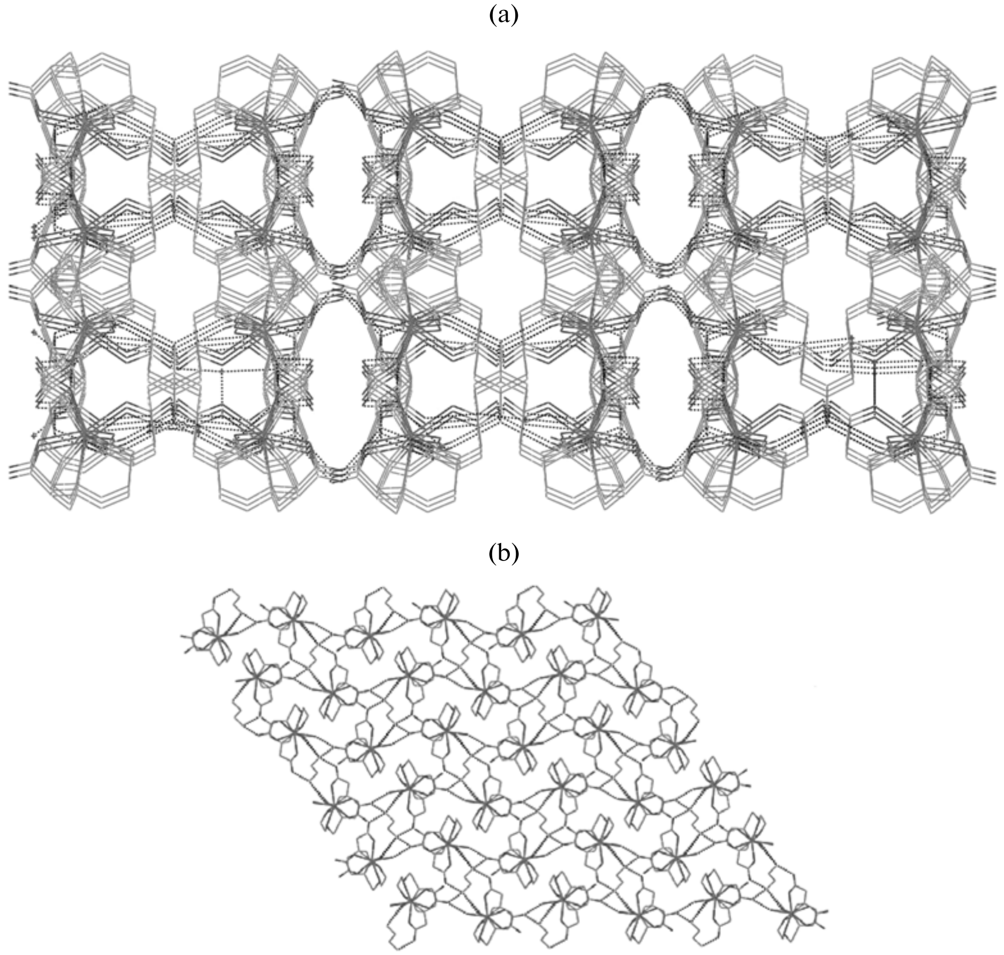

Fig. 5. Gives the extended 3D pore structure of **I** (a) and **II** (b).

enediamine is exactly 180°. Thus, four atoms of ethylenediamine all locate in the same plane. Therefore, it can be observed that amino acids as a part of protein can interact with $[Ho^{III}(Egta)(H_2O)]^-$ complex anion through different binding manner.

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