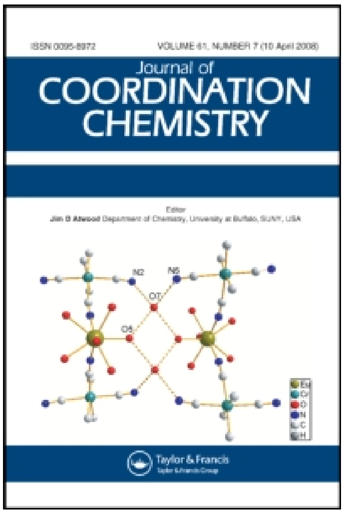

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Syntheses and structural determination of eight-coordinate $Na[Yb^{III}(Cydta)(H_2O)_2]\cdot 5H_2O$ and $[Yb^{III}(Hegta)]\cdot 2H_2O$ complexes

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$Na[Yb^{III}(Cydta)(H_2O)_2]\cdot 5H_2O$ (**1**) (H_4Cydta = *trans*-1,2-cyclohexanediamine-N,N,N′,N′-tetraacetic acid) and $[Yb^{III}(Hegta)]\cdot 2H_2O$ (**2**) (H_4egta = ethyleneglycol-*bis*-(2-aminoethylether)-N,N,N′,N′-tetraacetic acid) were prepared and their composition and structures were determined by elemental analyses and single-crystal X-ray diffraction techniques. Complex **1** crystallized in the triclinic crystal system with space group $P\bar{1}$; the Yb^{III} is eight-coordinate by a hexadentate Cydta and two water molecules. Complex **2** is a protonated egta complex, crystallized in the monoclinic crystal system with space group $P2_1/c$; Yb^{III} is coordinated only by the octadentate Hegta ligand. Both these complexes adopt a pseudo-square antiprismatic conformation.

Keywords: Yb^{III} ion; *Trans*-1,2-cyclohexanediamine-N,N,N′,N′-tetraacetic acid (H_4Cydta); Ethyleneglycol-*bis* (2-aminoethylether)-N,N,N′,N′-tetraacetic acid (H_4egta); Eight-coordination

1. Introduction

Rare earth metals have diverse biological activities and many applications [1–7]. Their compounds promote the growth of animals and plants, and function as anti-inflammation, antibacterium, anticoagulation, and anticancer materials [8]. Radioactive ytterbium ($^{169}Yb^{III}$) complexes have been used in the diagnoses and treatments of cancers in brain, liver, lung, and bone tissues [9]. Soluble and stable Yb^{III} complexes formed by combining aminopolycarboxylic acids such as H_4dtpa (=diethylenetriamine-N,N,N′,N″,N″-pentaacetic acid) could be injected into the focus position of human bodies because these complexes have high affinities to tumor tissues [8]. In general, biological activity and chemical properties of complexes depend on their molecular structure and conformation. It is necessary to determine structures and composition for further application.

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Rare earth metal ions can form eight-, nine-, and ten-coordinate complexes with various aminopolycarboxylic acid ligands depending on ionic radii and electronic configurations. We have found that these complexes have some intrinsic laws in coordination number and coordinate structure [10–16]. For Yb^{III} ion, with the critical ionic radius of 1.008 Å, the chances of forming eight- and nine-coordinate complexes are equivalent. For instance, both $[Yb^{III}(nta)_2]^{3-}$ (H_3nta = nitrilotriacetic acid) in $K_3[Yb^{III}(nta)_2]\cdot 5H_2O$ and $Na_3[Yb^{III}(nta)_2]\cdot 6H_2O$ adopt an eight-coordinate structure with pseudo-square antiprismatic conformations [17, 18]. Contrarily, in $K_3[Yb^{III}(nta)_2(H_2O)]\cdot 5H_2O$, $[Yb^{III}(nta)_2(H_2O)]^{3-}$ adopts a nine-coordinate monocapped square antiprismatic structure [18]; in $(NH_4)_4[Yb_2^{III}(dtpta)_2]\cdot 9H_2O$, the two YbN_2O_7 parts form nine-coordinate monocapped square antiprismatic structures [9]. Thus, the coordination number that Yb^{III} selects is mainly associated with the shape of ligand and the coordinate environment. For most aminopolycarboxylic acid ligands, a rigid ring or a protonated carboxyl group fixes the conformation for coordination. Comparing with normal ligands, such complexes should adopt low-coordinate structures. In our opinions, Yb^{III} would have a great chance in forming eight-coordinate complexes.

To validate our prediction, H_4Cydta (=*trans*-1,2-cyclohexanediamine-N,N,N′,N′-tetraacetic acid) and H_4egta (=ethyleneglycol-*bis*-(2-aminoethylether)-N,N,N′,N′-tetra-acetic acid) were chosen as ligands for Yb^{III} with $Na[Yb^{III}(Cydta)(H_2O)_2]\cdot 5H_2O$ and $[Yb^{III}(Hegta)]\cdot 2H_2O$ synthesized, and crystal structures determined. Based on the given steric factors (crystal system and crystal cell volume) and special crystal environment (Na^+ ion charge and crystal water number), the former is eight-coordinate with square antiprismatic conformation because of the rigid hexamethylene ring; the latter is a pseudo-square antiprismatic conformation due to the existence of a protonated carboxylic group, and also is eight-coordinate.

2. Experimental

2.1. *Syntheses of complexes*

2.1.1. $Na[Yb^{III}(Cydta)(H_2O)_2]\cdot 5H_2O$ (1). $H_4Cydta\cdot H_2O$ (A.R., Beijing SHLHT Science & Trade Co., Ltd., China) (1.7317 g, 5.0 mmol) was added to 100 mL warm water and Yb_2O_3 (99.999%, Beijing Hengye Zhongyuan Chemical Co., Ltd., China) (0.9852 g, 2.5 mmol) powder was added to the above solution slowly. The solution became transparent after the mixture was stirred and refluxed for 15 h, and then the pH was adjusted to 6.0 by $NaHCO_3$ aqueous solution. Finally, the solution was concentrated to 25 mL. Pale yellow crystals appeared after 3 weeks at room temperature. For $YbC_{14}H_{32}N_2O_{15}$: Anal. Found (%): Yb 26.02, C 25.33, H 4.84, N 4.22; Calcd (%): Yb 26.04, C 25.31, H 4.85, N 4.22. This formula is consistent with the results of diffraction analysis.

2.1.2. $[Yb^{III}(Hegta)]\cdot 2H_2O$ (2). 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 Yb_2O_3 (0.9852 g, 2.5 mmol) powder was added slowly. The solution became transparent after the mixture had been stirred and refluxed for 15 h, and then the pH was adjusted to 6.0 by $KHCO_3$ aqueous solution and the solution was concentrated to 25 mL. Colorless crystals appeared after 3 weeks at room temperature. For $C_{14}H_{25}N_2O_{10}Yb$: Anal. Found (%): Yb 31.22, C 30.32, H 4.56, N 5.04; Calcd (%): Yb 31.21, C 30.33, H 4.55, N 5.05. This formula is consistent with the result of diffraction analysis.

2.2. *IR spectrum determination*

The IR spectra of $H_4Cydta \cdot H_2O$ (a-1), $Na[Yb^{III}(Cydta)(H_2O)_2] \cdot 5H_2O$ (a-2), H_4egta (b-1) and $[Yb^{III}(Hegta)] \cdot 2H_2O$ (b-2) were determined, respectively, by a Shimadzu-IR 408 spectrograph. Spectra are provided in the Supplementary material.

2.3. *UV-Vis spectrum determination*

The UV-Vis spectra of $Na[Yb^{III}(Cydta)(H_2O)_2] \cdot 5H_2O$ (**1**) and $[Yb^{III}(Hegta)] \cdot 2H_2O$ (**2**) as well as the Yb^{III} ion in aqueous solutions were determined, respectively, by a Carry-50 UV-Vis spectrophotometer (Supplementary material).

2.4. *TG-DTA graph determination*

The TG-DTA graphs of **1** and **2** were determined, respectively, by a Rigaku-Denki-TA 100-II thermal analyzer (Supplementary material).

2.5. *X-ray structure determination*

X-ray intensity data were collected on a Bruker SMART CCD X-ray diffractometer system with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares. All calculations were performed by the SHELXTL-97 program on PDP11/44 and Pentium MMX/166 computers. Figures 1 and 2 illustrate the perspective views of **1** and **2**; figures 3 and 4 show their coordinating polyhedrons; and the Supplementary material shows their molecular packing in a unit cell. The crystal data and structure refinements are listed in table 1. Final atomic coordinates and equivalent isotropic displacement parameters for all the non-hydrogen fractions are presented in the Supplementary material and selected bond distances and angles are listed in table 2.

3. Results and discussion

3.1. *Infrared spectra of the complexes*

A comparison of infrared (IR) spectra between $H_4Cydta \cdot H_2O$ and $Na[Yb^{III}Cydta)(H_2O)_2] \cdot 5H_2O$ reveals considerable change due to coordination. The ν(C–N) of **1** appears at 1114 cm^{-1} and red-shifts 57 cm^{-1} compared to 1171 cm^{-1} of

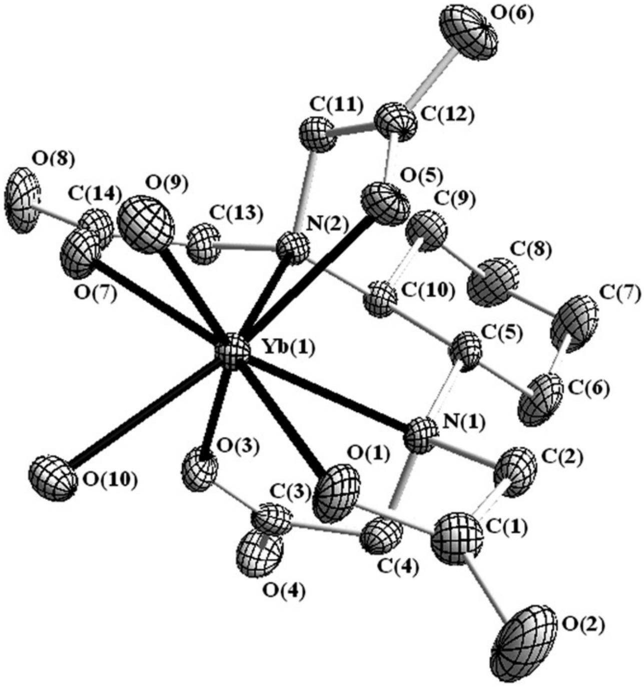

Figure 1. Molecular structure of **1**.

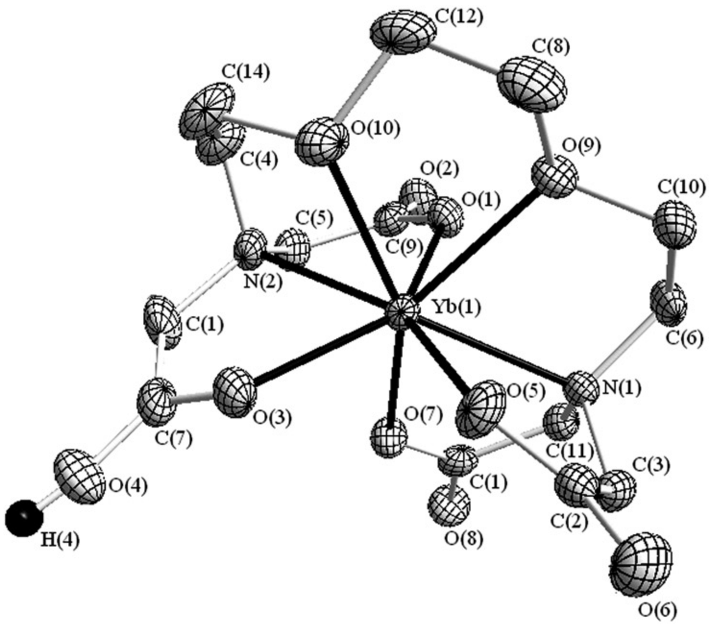

Figure 2. Molecular structure of **2**.

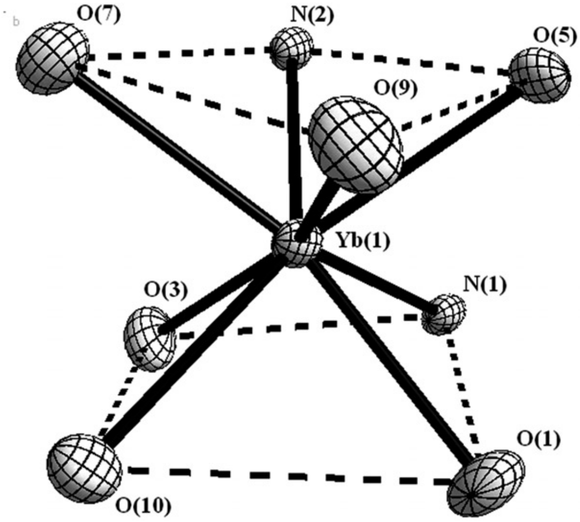

Figure 3. Coordination polyhedron of **1**.

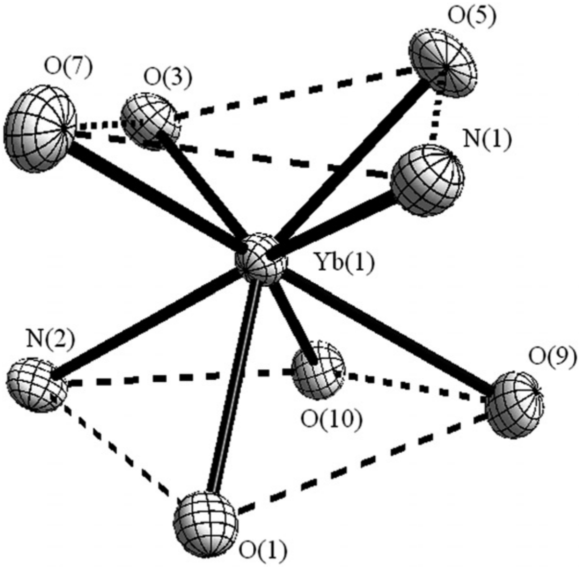

Figure 4. Coordination polyhedron of **2**.

$H_4Cydta \cdot H_2O$, indicating that two nitrogens of Cydta coordinate to Yb^{III}. The $\nu_{as}(COOH)$ of $H_4Cydta \cdot H_2O$ at 1751 cm^{-1} disappears after coordination, showing that there is no free carboxylic group in **1**. The $\nu_{as}(COO)$ at 1587 cm^{-1} and the $\nu_s(COO)$ at 1432 cm^{-1} of $H_4Cydta \cdot H_2O$ blue-shift and red-shift to 1618 cm^{-1} and 1400 cm^{-1}, respectively, confirms that oxygens of carboxylate coordinate to Yb^{III} too. There are broad $\nu(OH)$ bonds near 3435 cm^{-1} revealing the existence of H_2O molecules in the complex.

Table 1. Crystal data and structure refinement for **1** and **2**.

Complex	**1**	**2**
Formula weight	664.45	586.40
Temperature (K)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
Unit cell dimensions (Å, °)		
a	8.370(3)	14.100(3)
b	9.961(3)	9.770(2)
c	14.734(5)	14.730(3)
α	88.591(5)	90
β	76.286(5)	110.40(3)
γ	88.285(5)	90
Volume (Å^3), Z	1192.7(7), 2	1901.9(7), 4
ρ_{Calcd} (mg cm^{-3})	1.850	2.048
Absorption coefficient (mm^{-1})	4.012	4.986
$F(000)$	662	1156
Crystal size (mm^3)	$0.25 \times 0.15 \times 0.10$	$0.12 \times 0.10 \times 0.08$
θ range for data collection (°)	3.27–26.32	1.54–25.50
Limiting indices	$-9 \leq h \leq 9$; $-11 \leq k \leq 8$; $17 \leq l \leq 12$	$-13 \leq h \leq 17$; $-11 \leq k \leq 10$; $-17 \leq l \leq 14$
Reflections collected	4187	9798
Independent reflections	3690 [R(int) = 0.0274]	3535 [R(int) = 0.0356]
Completeness to $\theta_{\max}$ (%)	99.55	99.8
Max. and min. transmission	0.6898 and 0.4337	0.6912 and 0.5861
Goodness-of-fit on F^2	1.076	0.996
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0301$, $wR_2 = 0.0749$	$R_1 = 0.0276$, $wR_2 = 0.0702$
R indices (all data)	$R_1 = 0.0394$, $wR_2 = 0.0884$	$R_1 = 0.0341$, $wR_2 = 0.0747$
Largest difference peak and hole (eÅ^{-3})	0.826 and –0.939	1.155 and –1.351
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	

The IR spectra of H_4egta and **2** show that ν(C–N) of **2** at 1045 cm^{-1} red-shifts 55 cm^{-1} compared to 1100 cm^{-1} of H_4egta, indicating that nitrogen of H_4egta coordinates to Yb$^{\text{III}}$. The ν_{as}(O–C–O) at 1138 cm^{-1} of H_4egta red-shifts to 1091 cm^{-1} in the complex, indicating that oxygens of ethers coordinate to Yb$^{\text{III}}$. The ν_{as}(COOH) of H_4egta at 1742 cm^{-1} disappears, showing that there is no free carboxylic group in **2** and ν_{as}(COO) at 1466 cm^{-1}, and ν_{s}(COO) at 1431 cm^{-1} of H_4egta blue-shift and red-shift to 1629 cm^{-1} and 1384 cm^{-1}, respectively, in **2**, confirming that the oxygen of carboxylic groups coordinate with Yb$^{\text{III}}$. In addition, there are broad ν(OH) bonds near 3432 cm^{-1} from H_2O in the complex.

3.2. *UV-Vis spectra of the complexes*

UV-Vis spectra of **1**, **2** and Yb$^{\text{III}}$ ion in aqueous solutions shift only slightly. Because of 6s and 6p orbits, the inner 4f orbit is affected by external ligand field only to a small extent. As hexadentate and octadentate ligands, Cydta and egta form much stronger ligand fields than water. The maximum absorption peaks blue-shift 1.50 nm and 3.00 nm, respectively, for **1** and **2** relative to 310.00 nm of Yb$^{\text{III}}$.

Table 2. Selected bond distances (Å) and angles (°) of **1** and **2**.

Bond	*d* (Å)	Bond	*d* (Å)	Bond	*d* (Å)
1					
Yb–O(1)	2.262(4)	Yb–O(7)	2.275(4)	Yb–N(1)	2.546(5)
Yb–O(3)	2.273(4)	Yb–O(9)	2.355(4)	Yb–N(2)	2.510(5)
Yb–O(5)	2.285(4)	Yb–O(10)	2.293(4)		
2					
Yb(1)–O(1)	2.287(3)	Yb(1)–O(7)	2.235(3)	Yb(1)–N(1)	2.473(3)
Yb(1)–O(3)	2.249(3)	Yb(1)–O(9)	2.423(3)	Yb(1)–N(2)	2.507(4)
Yb(1)–O(5)	2.253(3)	Yb(1)–O(10)	2.360(3)		
Angle	*ω* (°)	Angle	*ω* (°)	Angle	*ω* (°)
1					
O(1)–Yb(1)–O(3)	102.21(17)	O(5)–Yb(1)–O(9)	71.78(14)	O(10)–Yb–N(1)	124.39(15)
O(1)–Yb(1)–O(5)	85.84(15)	O(5)–Yb–O(10)	142.82(15)	O(1)–Yb–N(2)	136.05(15)
O(1)–Yb(1)–O(7)	156.03(15)	O(7)–Yb(1)–O(9)	81.74(15)	O(3)–Yb–N(2)	76.72(16)
O(1)–Yb(1)–O(9)	83.82(15)	O(7)–Yb–O(10)	81.38(15)	O(5)–Yb–N(2)	69.64(14)
O(1)–Yb–O(10)	76.30(15)	O(9)–Yb–O(10)	74.05(15)	O(7)–Yb–N(2)	67.92(15)
O(3)–Yb(1)–O(5)	137.84(14)	O(1)–Yb–N(1)	67.89(15)	O(9)–Yb–N(2)	119.39(15)
O(3)–Yb(1)–O(7)	81.50(16)	O(3)–Yb–N(1)	69.68(15)	O(10)–Yb–N(2)	142.79(15)
O(3)–Yb(1)–O(9)	149.57(15)	O(5)–Yb–N(1)	75.72(15)	N(1)–Yb–N(2)	70.91(15)
O(3)–Yb–O(10)	78.46(16)	O(7)–Yb–N(1)	133.95(15)		
O(5)–Yb(1)–O(7)	107.47(15)	O(9)–Yb–N(1)	138.04(15)		
2					
O(1)–Yb(1)–O(3)	137.01(11)	O(5)–Yb(1)–O(9)	77.28(11)	O(10)–Yb(1)–N(1)	137.68(11)
O(1)–Yb(1)–O(5)	143.21(11)	O(5)–Yb(1)–O(10)	95.18(12)	O(1)–Yb(1)–N(2)	67.76(11)
O(1)–Yb(1)–O(7)	85.60(12)	O(7)–Yb(1)–O(9)	136.96(11)	O(3)–Yb(1)–N(2)	69.59(11)
O(1)–Yb(1)–O(9)	72.33(11)	O(7)–Yb(1)–O(10)	151.84(11)	O(5)–Yb(1)–N(2)	148.26(12)
O(1)–Yb(1)–O(10)	91.91(12)	O(9)–Yb(1)–O(10)	67.42(11)	O(7)–Yb(1)–N(2)	81.15(12)
O(3)–Yb(1)–O(5)	79.77(12)	O(1)–Yb(1)–N(1)	80.07(12)	O(9)–Yb(1)–N(2)	120.75(12)
O(3)–Yb(1)–O(7)	82.84(12)	O(3)–Yb(1)–N(1)	132.29(12)	O(10)–Yb(1)–N(2)	72.02(12)
O(3)–Yb(1)–O(9)	137.73(11)	O(5)–Yb(1)–N(1)	70.51(11)	N(1)–Yb(1)–N(2)	137.81(12)
O(3)–Yb(1)–O(10)	79.98(12)	O(7)–Yb(1)–N(1)	69.49(12)		
O(5)–Yb(1)–O(7)	103.55(12)	O(9)–Yb(1)–N(1)	70.58(11)		

3.3. *TG-DTA analyses of the complexes*

For **1** the first weight loss occurs from 61.2°C to 123.1°C, producing a DTA peak located at 86.7°C from dehydration, corresponding to an expulsion of five crystal waters and two coordination waters per formula weight. The weight loss is about 19.32%. Three consecutive exothermic peaks appear at 305.2°C, 345.7°C, and 382.6°C, corresponding to the oxidation and combustion of Na[Yb^{III}(Cydta)]. At 537.8°C, the decomposition and combustion of aminocarboxylate, carboxylate and carbonate take place. Finally, the Na_2O and Yb_2O_3 mixture identified by chemical methods and X-ray diffraction is formed with about 65.68% total mass loss.

Thermal decomposition of **2** is similar to that of **1**. The first stage of weight loss is from 56.4°C to 130.7°C, producing a DTA peak at 85.6°C. This endothermic step is dehydration, corresponding to an expulsion of two crystal waters per formula weight. The weight loss is about 7.12%. Three consecutive exothermic peaks at 287.2°C, 332.7°C, and 418.6°C correspond to the oxidation and combustion of [Yb^{III}(Hegta)]. The peak corresponding to the decomposition and combustion of its aminocarboxylate, carboxylate, and carbonate appears at 527.8°C. Finally, Yb_2O_3 powder is identified by chemical methods and X-ray diffraction. The total mass loss is 64.45%.

3.4. *Molecular and crystal structures*

3.4.1. Na[Yb^{III}(Cydta)(H$_2$O)$_2$]·5H$_2$O. As shown in figure 1, in **1** the Yb^{III} is eight-coordinate by two N atoms and four O atoms from one hexadentate Cydta, as well as two water molecules. The coordination polyhedron of Yb^{III}N$_2$O$_6$ (figure 3) adopts a pseudo-square antiprismatic structure, in which there are two approximately parallel square planes (O(5), O(7), O(9), and N(2); O(1), O(3), O(10), and N(1), respectively). The torsion angle of the two square planes is about 45°. The Yb^{III}–O bond distances range from 2.262(4) Å (Yb^{III}–O(1)) to 2.355(4) Å (Yb^{III}–O(9)). The Yb^{III}–N bond distances are 2.546(5) Å (Yb^{III}–N(1)) and 2.510(5) Å (Yb^{III}–N(2)), both longer than the Yb^{III}–O bond distances. The bond distances between Yb^{III} and coordinated water, Yb^{III}–O(9) and Yb^{III}–O(10), are 2.355(4) Å and 2.293(4) Å, respectively. These values are comparable with many bond distances observed in rare earth metal complexes with aminopolycarboxylic acid ligands containing coordinated water [19].

As we predicted, **1** adopts an eight-coordinate structure with pseudo-square antiprismatic conformation. Besides some steric factors (crystal system and crystal cell volume) and special crystal environment (Na$^+$ ion charge and crystal water number), the undeniable reasons are the relatively small radius of Yb^{III} and the rigid ring in Cydta. Aminopolycarboxylic acid ligands, in general, form several five-member coordinate rings. If a rigid ring such as cyclohexyl exists in aminopolycarboxylic acid ligands, the space retractility of coordinated carboxylic group would be restricted, limiting the coordination number and coordinate conformation, even though the ionic radius of Yb^{III} is appropriate for eight- and nine-coordination. For example, in Na$_2$[Sm^{III}(Cydta)][Sm^{III}(Cydta)(H$_2$O)$_3$]·11H$_2$O, because of the relatively big radius of Sm^{III} ion and a rigid Cydta, all Sm^{III} ions form nine-coordinate complexes [20]. However, Na[Er^{III}(edta)(H$_2$O)$_3$]·5H$_2$O, with relatively small ionic radius and no rigid ring, is also nine-coordinate [21].

The dihedral angle between the planes of O(7), O(9), and N(2) and O(5), O(9), and N(2) is 5.069° in top square plane, and the dihedral angle between planes of O(3), O(10), and N(1) and O(1), O(3), and N(1) is 11.734° in the bottom square plane. According to Guggenberger and Muetterties' views [22], if the dihedral angle for nine-coordinate rare earth metal complexes is between 0° and 26.4° then their structures are described as monocapped square antiprismatic. Of course, this law is similar for eight-coordinate complexes. So, **1** is considered to adopt a pseudo-square antiprismatic structure.

In one unit cell (Supplemental material) there are two Na[Yb^{III}(Cydta)(H$_2$O)$_2$]·5H$_2$O molecules connected through hydrogen bond and electrostatic bonding with Na$^+$. Each Na$^+$ bridges two [Yb^{III}(Cydta)(H$_2$O)$_2$]$^-$ anions and is five-coordinate by five oxygens from one carboxylic group, one coordinated water, and three crystal waters. The hydrogen bonds, in one unit cell, link the crystal water, coordinated water, and coordinated and non-coordinated carboxylates of Cydta. Because of the relatively strong hydrogen bonds between coordinated water and coordinated carboxylic O of the adjacent [Yb^{III}(Cydta)(H$_2$O)$_2$]$^-$, two [Yb^{III}(Cydta)(H$_2$O)$_2$]$^-$ complex anions form the bimolecular structure. A network structure is formed through hydrogen bonds and electrostatic bonding.

3.4.2. [Yb^{III}(Hegta)]·2H$_2$O. In **2** Yb^{III} is coordinated by only one Hegta without coordinated water in a pseudo-square antiprismatic structure, six oxygens and two nitrogens from one egta ligand coordinate. There is a protonated carboxylic group in egta, O(4).

As shown in figure 4, two approximately parallel square planes, composed of O(1), O(9), O(10), and N(2) and O(3), O(5), O(7), and N(1), respectively, form the pseudo-square antiprismatic structure of **2**. The dihedral angle between O(3), O(5), and O(7) and O(3), O(5), and N(1) is 16.41(8)° in the top square plane and the dihedral angle between O(1), O(10), and N(2) and O(9), O(10), and N(2) is 17.21(9)° in the bottom square plane, close to that of standard monocapped square antiprismatic structure. So, the structure of **2** is also an eight-coordinate pseudo-square antiprismatic conformation.

It is shown in table 2 that the Yb^{III}–O bond distances in **2** range from 2.235(3) Å (Yb^{III}–O(7)) to 2.423(3) Å (Yb^{III}–O(9)). The Yb^{III}–N bond distances are 2.473(3) Å (Yb^{III}–N(1)) and 2.507(4) Å (Yb^{III}–N(2)), respectively. Yb^{III}–O(9) (2.423(3) Å) and Yb^{III}–O(10) (2.360(3) Å are much longer than the other Yb^{III}–O bond distances (the average bond distance is 2.256(3) Å). O(1), O(3), O(5), and O(7) belong to carboxylic groups while O(9) and O(10) do not, distorting the geometric configuration of **2**.

Similar to $Na[Yb^{III}(Cydta)(H_2O)_2] \cdot 5H_2O$, some steric factors and special crystal environment also play a critical role for $[Yb^{III}(Hegta)] \cdot 2H_2O$ in adopting an eight-coordinate pseudo-square antiprismatic conformation. The protonated carboxylic group forms hydrogen bonds with adjacent crystallization water, also contributing to the distorted geometric configuration. Because of protonation, O(4) loses coordination ability; O(3) belonging to the protonated carboxylic group coordinates to Yb^{III} making the ∠O(3)–C(7)–C(1) bond angle change to 117.2(4)°, close to 120°, causing the Yb^{III}–O(3)–C(7)–C(1)–N(2) tetragon to become rigid, further distorting the geometric configuration of **2**.

In general, protonated carboxylic group decreased coordination capability in aminopolycarboxylic acid ligands. Thus, $[Ge^{IV}(Hedta)(OH)]$ (H_4edta = ethylenediamine-N, N, N′, N′-tetraacetic acid) [23], $[Ru^{III}(Hedta)Cl] \cdot 2H_2O$ [24], and $[Ir^{III}(Hedta)Cl] \cdot 2H_2O$ [25] contain a non-coordinated, protonated carboxylic group. For metal ions with large ionic radii the protonated carboxylic groups still coordinate, such as in $[Fe^{II}(H_2O)_4][Fe^{II}(Hedta)(H_2O)]_2 \cdot 4H_2O$ [11], $[Fe^{II}(H_2edta)(H_2O)] \cdot 2H_2O$ [11], $[Ti^{III}(Hedta)(H_2O)] \cdot H_2O$, $[V^{III}(Hedta)(H_2O)] \cdot H_2O$ [10], $[Mn^{II}(H_2O)_4][Mn^{II}(Hedta)(H_2O)]_2 \cdot 4H_2O$ [26], ψ-seven-coordinate $[Sb^{III}(Hedta)] \cdot 2H_2O$ [27], and 10-coordinate $[La^{III}(Hedta)(H_2O)_4]$ [28]. Here, **2** is the first example of a rare earth metal complex with protonated egta (Hegta).

In one unit cell, there are four $[Yb^{III}(Hegta)] \cdot 2H_2O$ molecules. Two adjacent molecules connect through hydrogen bonds and are associated with one crystallization water. H(4) atom connects the O(4) of carboxylic group and the O(12) of crystallization water. A layer structure is formed through hydrogen bonds and electrostatic bondings.

4. Conclusions

Two Yb^{III} complexes with aminopolycarboxylic acid ligands, H_4Cydta (*trans*-1,2-cyclohexanediamine-N,N,N′,N′-tetraacetic acid) and H_4egta (ethyleneglycol-*bis*-(2-aminoethylether)-N,N,N′,N′-tetraacetic acid), have been synthesized. Based on some given special steric factor, mainly due to the existence of a rigid ring or a protonated carboxyl group, both **1** and **2** adopt an eight-coordinate pseudo-square antiprismatic conformation. The ligand shape and coordinate environment play an important role in the coordination number and structure.

Supplementary material

CCDC 714060 $Na[Yb^{III}Cydta)(H_2O)_2]\cdot 5H_2O$ and CCDC 714061 $[Yb^{III}(Hegta)]\ 2H_2O$ 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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