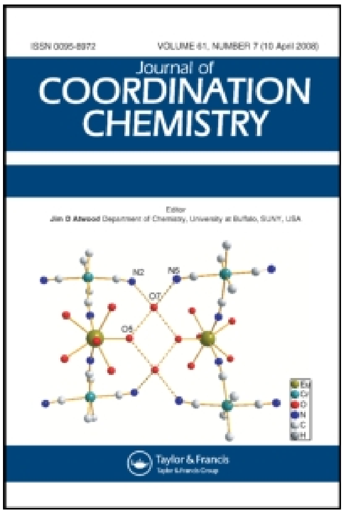

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Synthesis and structural determination of the first eight-coordinate rare earth metal complex with a six-member ring, $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$

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Synthesis and structural determination of the first eight-coordinate rare earth metal complex with a six-member ring, $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$

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$(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ has been synthesized and characterized by infrared spectrum, fluorescence spectrum, elemental analyses and single-crystal X-ray diffraction techniques. It crystallizes in the monoclinic system with space group $P2_1/n$, $a = 12.7700(15)$ Å, $b = 9.3885(11)$ Å, $c = 14.4070(18)$ Å, $\alpha = 90°$, $\beta = 95.950(2)°$, $\gamma = 90°$, $V = 1718.0(4)$ Å^3, $Z = 4$, $M = 508.28$, $D_c = 1.965\,g\,cm^{-3}$, $\mu = 3.708\,mm^{-1}$, $F(000) = 1108$. The structure was refined to $R_1 = 0.0238$ for 3469 observed reflections ($I > 2\sigma(I)$). The $Eu^{III}N_2O_6$ part in the $[Eu^{III}(pdta)(H_2O)]^-$ complex anion has an eight-coordinate structure with a distorted square anti-prismatic conformation, in which six coordination positions, two nitrogen atoms and four oxygen atoms are from one pdta (=propylenediaminetetraacetic acid) ligand, the seventh position is an oxygen (O(8A)) from another pdta and the eighth coordination site is occupied by a water molecule. $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ is the first eight-coordinate complex with a six-member ring in the rare earth metal complexes with aminopolycarboxylic acid ligands.

Keywords: Eu^{III}; pdta (propylenediaminetetraacetic acid); Structure

1. Introduction

Rare earth complexes have potential applications and exhibit various biological activities [1–3]. For example, some Nd^{III} complexes have good anti-inflammation activity; Gd^{III} complexes are often used as contrast agents in magnetic resonance imaging: there are seven high-spin single electrons in the f-orbits of Gd^{III} [4]; Tb^{III} complexes have been used as ionic probes to diagnose some diseases because of their characteristic fluorescence [5]. Moreover, Pr^{III} in solids has exhibited prominent optical features [6, 7]. The $^{153}Sm^{III}$ complexes, as a radioactive drug, may be used to treat osteosarcoma [8, 9]. Eu^{III} complexes are often taken as the rare earth fluorescent ionic probes to investigate the structures of biologic molecules [10, 11]. It is well known that the luminescence properties and fluorescent spectra of complexes depend on the electronic configuration of the central rare earth metal ions [12, 13], and the electronic

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configuration depends on the molecular structures of complexes, and therefore it is very valuable to research the relationship between molecular structures and luminescence properties. However, there are few reports about their relationship. Recently, some research on the luminescence properties and fluorescent spectra of Eu^{III} complexes with various aminopolycarboxylic acid ligands have been put in practice at low temperatures [14]. It is important for explaining the luminescence properties and fluorescent spectra of the Eu^{III} complexes with aminopolycarboxylic acids to determine their molecular and crystal structures. A part of our research on coordination numbers and structures of rare earth metal complexes with aminocarboxylic acid ligands, the $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ complex was synthesized and the structure determined. Previously, it was reported that most aminocarboxylic acid rare earth metal complexes are nine-coordinate monocapped square anti-prismatic or tricapped trigonal prismatic conformations; all the chelates in these complexes are five-member rings, composed of central metal ion and ethylenediamine or glycin. $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ is the first example with a six-member ring and validates our premise that coordination numbers and coordinate structures of rare earth metal complexes with aminocarboxylic acid ligands not only depend on the ionic radius and electronic configuration of central metal ion, but also the shape of aminocarboxylic acid ligands.

2. Experimental

2.1. *Synthesis of complexes*

H_4pdta (1.53 g, 5.0 mmol) was added to 100 mL water, and Eu_2O_3 (0.88 g, 5.0 mmol) powder was added slowly to 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 dilute aqueous NH_3. Finally the solution was concentrated to 25 mL, and light pink crystals were obtained after three weeks at room temperature. Anal. Found (%): Eu 29.87, C 25.96, H 4.38, N 8.29; Calcd (%): Eu 29.90, C 25.99, H 4.36, N 8.27. The formula ($C_{11}H_{22}EuN_3O_{10}$) is approximately consistent with the result of diffraction analysis.

2.2. *Infrared spectrum determination*

The infrared spectra of H_4pdta and $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ were determined by Shimadzu-IR 408 spectrograph, and the results are shown in figure 1.

2.3. *Fluorescence spectrum determination*

The fluorescence properties of $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ and $(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$ complexes were detected by spectrofluorimeter under excitation at 255 nm wavelength ultraviolet light; the emission spectra are shown in figure 2.

2.4. *X-ray diffraction determination*

The details of crystal data collection and refinement parameters for $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ are listed in table 1. The data were collected on a

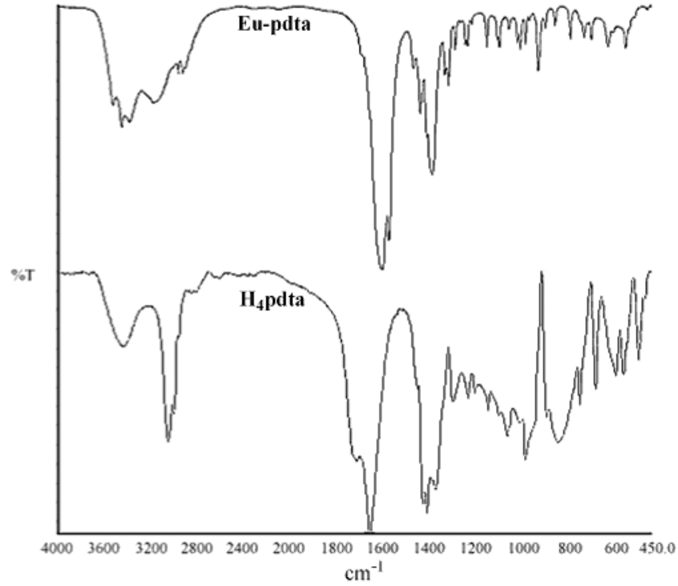


Figure 1. IR spectra of $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ and H_4 pdta ligand at room temperature.

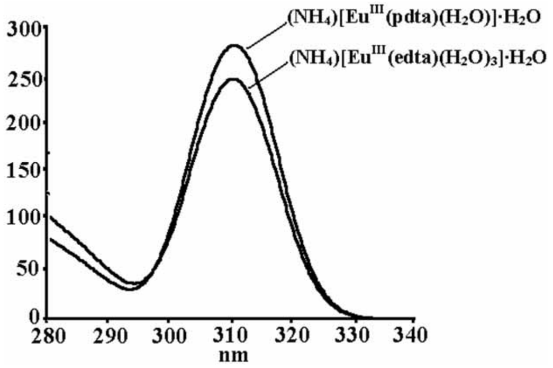


Figure 2. Emission luminescence spectra of $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ and $(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$.

Bruker SMART CCD type X-ray diffractometer system with graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods. All calculations were performed using the SHELXL-97 program on PDP11/44 and Pentium MMX/166 computers. The molecular structure of $(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$ is shown in figure 3. The coordination polyhedron around Eu^{III} in $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ is shown in figure 4. The molecular packing of the complexes in the unit cell is shown in figure 5, and the infinite zigzag chain is shown in figure 6. Final atomic coordinates and equivalent isotropic displacement parameters for all non-hydrogen atoms were presented in table 2.

Table 1. Crystal data and structure refinement for $(NH_4)[Eu^{III}(pdta)(H_2O)]\cdot H_2O$.

Complex	$(NH_4)[Eu^{III}(pdta)(H_2O)]\cdot H_2O$
Empirical formula	$C_{11}H_{22}EuN_3O_{10}$
Formula weight	508.28
Temperature (K)	294(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions (Å, °)	
a	12.7700(15)
b	9.3885(11)
c	14.4070(18)
β	95.950(2)
Volume (Å^3)	1718.0(4)
Z	4
Calculated density (mg m^{-3})	1.965
Absorption coefficient (mm^{-1})	3.708
$F(000)$	1008
Crystal size (mm^3)	$0.20 \times 0.16 \times 0.12$
θ range for data collection (°)	2.03–26.25
Index ranges	$-14 \le h \le 15$, $-11 \le k \le 11$ $-16 \le l \le 17$
Reflections collected	9326
Independent reflections	3469 [$R(\text{int}) = 0.0294$]
Completeness to $\theta_{\max}$ (%)	99.7
Max. and min. transmission	1.0000 and 0.5490
Data/restraints/parameters	3469/6/226
Goodness-of-fit on F^2	1.025
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0238$, $wR_2 = 0.0565$
R indices (all data)	$R_1 = 0.0337$, $wR_2 = 0.0612$
Largest difference peak and hole (e Å^{-3})	1.016 and −0.745
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2

The selected bond distances and bond angles of $(NH_4)[Eu^{III}(pdta)(H_2O)]\cdot H_2O$ are listed in table 3. The corresponding bond distances and bond angles of $(NH_4)[Eu^{III}(edta)(H_2O)_3]\cdot H_2O$ and $K_3[Eu(nta)_2(H_2O)]\cdot 5.5H_2O$ are also given in table 3 to compare with those of $(NH_4)[Eu^{III}(pdta)(H_2O)]\cdot H_2O$.

3. Results and discussion

3.1. *Infrared spectrum of $(NH_4)[Eu^{III}(pdta)(H_2O)]\cdot H_2O$*

As shown in figure 1, the ν(C–N) is at 937 cm^{-1} and blue-shifts 86 cm^{-1} compared with that of H_4pdta (851 cm^{-1}), which indicates that two amine atoms from pdta coordinate to Eu^{III}. The original ν_{as}(COOH) (1715 cm^{-1}) of H_4pdta disappears. The ν_{as}(COO) (1661 cm^{-1}) of H_4pdta red-shifts to 1611 cm^{-1} in the complex, and the ν_s(COO) (1415 cm^{-1}) of H_4pdta red-shifts to 1392 cm^{-1}, confirming that oxygen of all four –COO$^-$ groups coordinate to the central Eu^{III} ion, too. There is a broad ν(OH) band of H_2O near 3455 cm^{-1} showing the existence of H_2O in the complex.

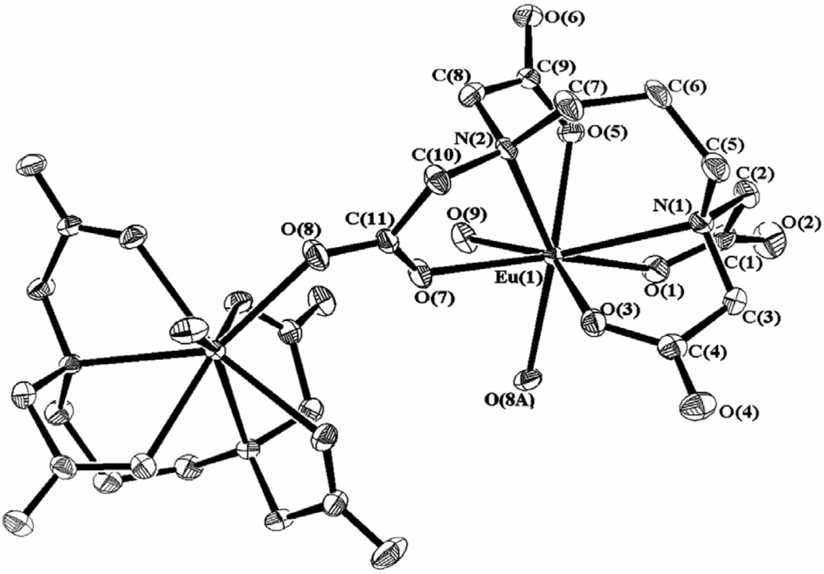


Figure 3. Molecular structure of $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$.

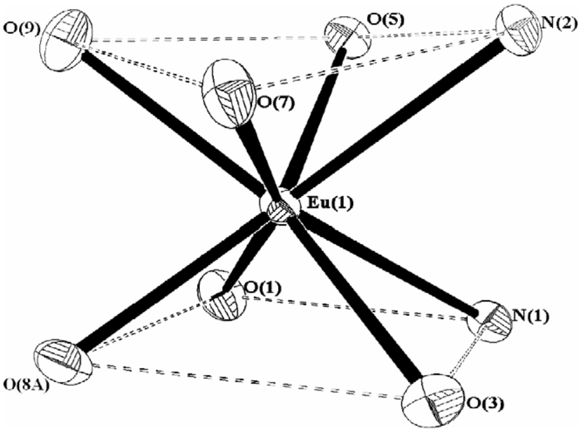


Figure 4. Coordination polyhedron of Eu^{III} in $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$.

3.2. *Fluorescence spectrum of $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ and $(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$*

The result of X-ray diffraction determination reveals that $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ is an eight-coordinate complex; however, as shown in figure 2, its fluorescence spectrum is the same as that of $(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$ [15], which is nine coordinate. This indicates that the structure of the complex anion has changed in water, and is nine coordinate. The following two reasons may explain this phenomenon. First, the ionic radius of Eu^{III} is relatively large, so it tends to be nine coordinate. Second, in water solution, solvent water molecules continually attack the Eu^{III} ion,

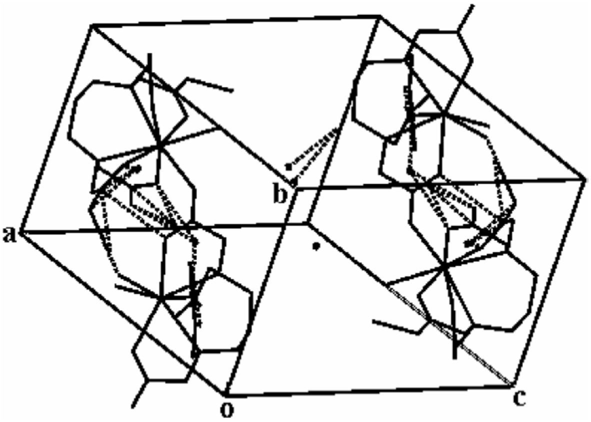


Figure 5. Arrangement of $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ in unit cell.

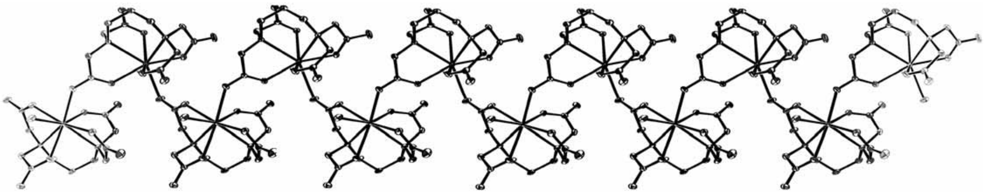


Figure 6. Infinite long zigzag type chain.

and therefore water is able to coordinate to the Eu^{III} ion occupying the ninth coordination site.

3.3. *Molecular and crystal structure of $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$*

As shown in figure 3, a carboxyl group bridges two complexes yielding a dinuclear molecule. As shown in figure 4, in each part of the dinuclear molecule, the Eu^{III} ion is coordinated by two nitrogen atoms (both Eu^{III}–N distances are 2.632(3) Å), five carboxyl oxygen atoms and one oxygen atom from water (average Eu^{III}–O bond distance is 2.381(2) Å). Four carboxyl oxygen atoms are from the same pdta ligand and the fifth is from the other. In the $[Eu^{III}(pdta)(H_2O)]^-$ complex anion, the $Eu^{III}N_2O_6$ part adopts an eight-coordinate structure with almost standard square anti-prismatic conformation, in which the set of O(5), O(7), O(9) (from water molecule) and N(2) and the set of O(1), O(3), O(8A) (from the other pdta ligand) and N(1) form two approximate parallel square planes, with torsion angle about 45°. The Eu^{III}–O bond distances range from 2.344(2) to 2.438(2) Å, while two Eu^{III}–N bond distances are 2.632(3) Å. Because O(9) comes from water not pdta ligand, the Eu^{III}–O(9) bond distance is the longest Eu^{III}–O bond distance. Differing from the $[Eu^{III}(edta)(H_2O)_3]^-$ and $[Eu^{III}(nta)_2(H_2O)]^{3-}$ complex anions [16–18], $[Eu^{III}(pdta)(H_2O)]^-$ is eight-coordinate, so that the repulsive force among coordinate atoms is smaller than those nine- and ten-coordinate structures.

Table 2. Non-hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($Å^2 \times 10^3$) (U_{eq}) for $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$.

Atom	x/a	y/b	z/c	U_{eq}	Atom	x/a	y/b	z/c	U_{eq}
Eu(1)	3993(1)	104(1)	7937(1)	19(1)	C(3)	4428(3)	2676(3)	6500(3)	31(1)
O(1)	4400(2)	2307(2)	8650(2)	35(1)	C(4)	3557(3)	1796(3)	5995(2)	28(1)
O(2)	5443(2)	4161(3)	8965(2)	55(1)	C(5)	5918(3)	1143(4)	6381(3)	33(1)
O(3)	3425(2)	550(2)	6340(2)	31(1)	C(6)	6496(3)	−198(3)	6720(3)	33(1)
O(4)	3017(2)	2299(3)	5319(2)	37(1)	C(7)	5876(3)	−1566(4)	6542(3)	36(1)
O(5)	5684(2)	−327(2)	8763(2)	28(1)	C(8)	5563(3)	−2590(4)	8029(3)	34(1)
O(6)	6943(2)	−1914(3)	9182(2)	42(1)	C(9)	6125(3)	−1542(3)	8706(3)	28(1)
O(7)	3040(2)	−2046(2)	7635(2)	33(1)	C(10)	4309(3)	−2929(4)	6690(3)	31(1)
O(8A)	2746(2)	−4128(3)	6925(2)	39(1)	C(11)	3292(3)	−3049(3)	7126(2)	26(1)
O(9)	3694(2)	−885(3)	9452(2)	36(1)	N(1)	5215(2)	1762(3)	7044(2)	25(1)
O(10)	8593(3)	70(3)	9272(3)	92(2)	N(2)	5059(2)	−1909(3)	7178(2)	23(1)
C(1)	5188(3)	3079(3)	8520(3)	33(1)	N(3)	6700(2)	5692(3)	302(2)	36(1)
C(2)	5844(3)	2635(4)	7748(3)	34(1)					

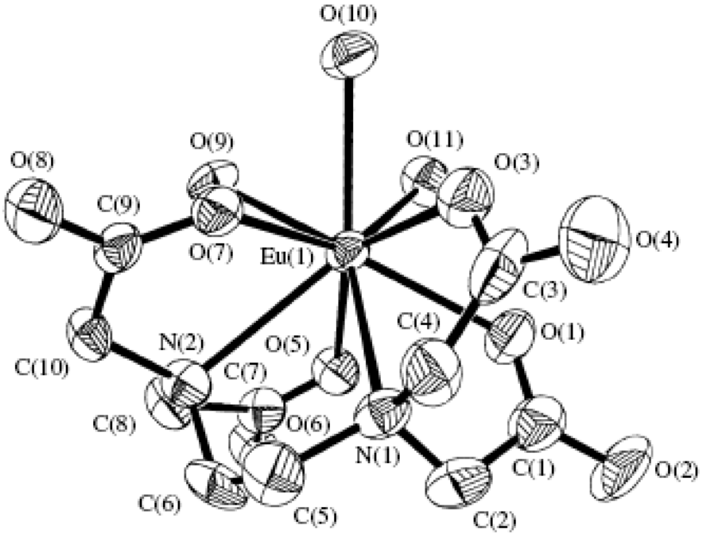
Therefore, in the $[Eu^{III}(pdta)(H_2O)]^-$ complex anion, the Eu^{III}–O(9) bond distance is obviously shorter than corresponding ones in the $[Eu^{III}(edta)(H_2O)_3]^-$ and $[Eu^{III}(nta)_2(H_2O)]^{3-}$ complex anions.

Years of research indicate that, for most rare earth metal complexes, there are some intrinsic laws on their coordination numbers and coordinate structures. Generally, the rare earth metal ions can form eight-, nine- and ten-coordinate complexes with various aminopolycarboxylic acid ligands since their ionic radii and electronic configurations are different [19–23]. In addition, the shape of aminopolycarboxylic acid ligands can also influence the coordination numbers and coordinate structures of rare earth metal complexes. Because the ionic radius of Eu^{III} ion is relatively big, and there are just six f-electrons, it can form nine-coordinate complexes with edta (ethylenediaminetetraacetic acid), dtpa (diethylenetriaminepentaacetate acid), ttha (triethylenetetraminehexaacetic acid) and nta (nitrilotriacetic acid) ligands, whose structures adopt the distorted monocapped square anti-prismatic conformation or tricapped trigonal prismatic conformation. However, as mentioned above, the $[Eu^{III}(pdta)(H_2O)]^-$ complex anion adopts the eight-coordinate structure with almost standard square anti-prismatic conformation. The structures and compositions of three kinds of aminopolycarboxylic acid ligands, show that if the ethylenediamine part of edta, which can form a five-member ring with central metal ion, is replaced by a propylenediamine, which can form a six-member ring with central metal ion, edta becomes pdta, and that if the ethylenediamine is cut off in the middle, the half part of edta is equal to a nta ligand. The following reasons may explain why the $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ adopts the different coordination number and coordinate structure compared with $(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$ and $K_3[Eu^{III}(nta)_2(H_2O)] \cdot 5.5H_2O$. First, the bond distances of Eu^{III}–O(8A) and Eu^{III}–O(9) in $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$ are shorter than corresponding ones in the $(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$ and $K_3[Eu^{III}(nta)_2(H_2O)] \cdot 5.5H_2O$, so the tetragonal plane formed by O(1), O(7), O(8A) and O(9) is very small and the ninth coordinate atom, which comes from the water molecule or carboxylic group, can hardly pierce this surface and coordinate to the Eu^{III} ion. Secondly, in three kinds of complex anions, $[Eu^{III}(edta)(H_2O)_3]^-$, $[Eu^{III}(pdta)(H_2O)]^-$ and $[Eu^{III}(nta)_2(H_2O)]^{3-}$, the bond angles composed of N(1),

Table 3. Selected bond distances (Å) and angles (°) for $(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$, $(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$ and $K_3[Eu^{III}(nta)_2(H_2O)] \cdot 5.5H_2O$ (only in the coordination polyhedron).

Bond	$(NH_4)[Eu^{III}(pdta)(H_2O)] \cdot H_2O$	$(NH_4)[Eu^{III}(edta)(H_2O)_3] \cdot H_2O$	$K_3[Eu^{III}(nta)_2(H_2O)] \cdot 5.5H_2O$
Bond distances			
Eu(1)–O(1)	2.344(2)	2.413(10)	2.465(3)
Eu(1)–O(3)	2.378(2)	2.446(8)	2.409(3)
Eu(1)–O(5)	2.389(3)	2.394(9)	2.410(4)
Eu(1)–O(7)	2.374(2)	2.458(8)	2.403(3)
Eu(1)–O(9)	2.438(2)	2.427(9)	2.422(4)
Eu(1)–O(8A)	2.363(2)	2.474(8)	2.397(3)
Eu(1)–O(11)	–	2.539(8)	2.536(3)
Eu(1)–N(1)	2.632(3)	2.679(9)	2.685(4)
Eu(1)–N(2)	2.632(3)	2.710(11)	2.671(4)
Bond angles			
O(1)–Eu(1)–O(3)	107.49(9)	138.4(3)	135.39(12)
O(1)–Eu(1)–O(5)	77.49(8)	77.5(3)	78.03(11)
O(1)–Eu(1)–O(7)	156.45(8)	141.0(3)	145.53(11)
O(1)–Eu(1)–O(9)	89.54(8)	103.9(3)	87.35(12)
O(1)–Eu(1)–O(8A)	82.01(9)	69.1(3)	66.65(12)
O(1)–Eu(1)–O(11)	–	77.5(3)	68.58(11)
O(1)–Eu(1)–N(1)	64.98(8)	66.5(3)	63.18(12)
O(1)–Eu(1)–N(2)	135.68(8)	126.2(3)	127.83(11)
O(3)–Eu(1)–O(5)	132.97(8)	128.3(3)	128.79(12)
O(3)–Eu(1)–O(7)	82.72(8)	79.8(3)	80.52(12)
O(3)–Eu(1)–O(9)	150.82(8)	139.5(3)	139.30(11)
O(3)–Eu(1)–O(8A)	80.34(9)	73.4(3)	74.43(12)
O(3)–Eu(1)–O(11)	–	71.1(3)	77.09(12)
O(3)–Eu(1)–N(1)	63.87(9)	63.2(3)	65.70(11)
O(3)–Eu(1)–N(2)	81.01(9)	79.5(3)	74.75(12)
O(5)–Eu(1)–O(7)	111.53(8)	89.4(3)	82.44(12)
O(5)–Eu(1)–O(9)	72.96(8)	74.1(3)	72.34(12)
O(5)–Eu(1)–O(8A)	144.92(9)	143.0(3)	143.17(12)
O(5)–Eu(1)–O(11)	–	138.0(3)	137.73(12)
O(5)–Eu(1)–N(1)	78.05(9)	76.8(3)	65.47(12)
O(5)–Eu(1)–N(2)	66.80(8)	65.4(3)	72.01(13)

O(7)–Eu(1)–O(9)	73.43(8)	71.4(3)	77.46(12)
O(7)–Eu(1)–O(8A)	78.83(8)	75.7(3)	73.51(11)
O(7)–Eu(1)–O(11)	–	142.0(3)	144.42(12)
O(7)–Eu(1)–N(1)	137.05(8)	139.2(3)	137.24(12)
O(7)–Eu(1)–N(2)	65.83(8)	72.1(3)	63.13(12)
O(9)–Eu(1)–O(8A)	78.77(9)	72.2(3)	135.85(11)
O(9)–Eu(1)–O(11)	–	117.5(3)	79.45(12)
O(9)–Eu(1)–N(1)	144.96(9)	130.9(3)	122.48(12)
O(9)–Eu(1)–N(2)	103.51(8)	129.1(3)	129.28(13)
O(8A)–Eu(1)–O(11)	–	73.1(3)	71.80(11)
O(8A)–Eu(1)–N(1)	118.06(8)	129.3(3)	112.08(11)
O(8A)–Eu(1)–N(2)	141.71(9)	138.5(3)	135.41(12)
O(11)–Eu(1)–N(1)	–	65.6(3)	66.82(13)
O(11)–Eu(1)–N(2)	–	113.2(3)	95.12(12)
N(1)–Eu(1)–N(2)	82.16(9)	67.9(3)	125.41(13)



Eu^{III} and N(2) are 67.9(3)°, 82.16(9)° and 125.41(13)° respectively, and N(1)–Eu^{III}–N(2) of $[Eu^{III}(pdta)(H_2O)]^-$ is in the middle of three. The N(1)–Eu^{III}–N(2) of $[Eu^{III}(edta)(H_2O)_3]^-$ is narrow, so there is more space for other coordinate atoms, and the corresponding tetragonal plane is broader than that of $[Eu^{III}(pdta)(H_2O)]^-$. Therefore, there is space for a water molecule as the ninth coordinate atom, allowing $[Eu^{III}(edta)(H_2O)_3]^-$ to adopt a monocapped square anti-prismatic conformation. As for the $[Eu^{III}(nta)_2(H_2O)]^{3-}$, its N(1)–$Eu^{III}$–N(2) is also broad, which makes O(1)–Eu^{III}–O(7) and O(8)–Eu^{III}–O(9) comparatively broad. The set of O(1), O(7), O(8) and O(9) also forms a broad tetragonal plane, and an oxygen atom (from the water molecule), as the ninth coordinate atom, pierces into this broad surface and coordinates to the Eu^{III} ion allowing $[Eu^{III}(nta)_2(H_2O)]^{3-}$ to adopt a tricapped trigonal prismatic conformation.

In one unit cell, as shown in figure 5, there are four molecules, which are connected by electrostatic interactions and intermolecular hydrogen bonds between carboxyl oxygen atoms of pdta ligand and crystal water molecules.

As shown in figure 6, the complex anions are bridged by O(7)–C(11)–O(8A) groups, so an infinite zigzag type chain appears.

4. Conclusion

The Eu^{III} complex with pdta ligand was synthesized and its composition and structure have been determined as $(NH_4)[Eu^{III}(pdta)(H_2O)]\cdot H_2O$ by single-crystal X-ray diffraction analyses, infrared spectrum, and elemental analyses. In the $[Eu^{III}(pdta)(H_2O)]^-$ complex anion, the $Eu^{III}N_2O_6$ part has an eight-coordinate structure with square anti-prismatic conformation.

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