Russian Journal of Coordination Chemistry, Vol. 30, No. 2, 2004, pp. 130–136. From Koordinatsionnaya Khimiya, Vol. 30, No. 2, 2004, pp. 141–147.
Original English Text Copyright © 2004 by Wang, Zhang, Jia, Zhang, Liu.

Syntheses and Structural Researches of Nine-Coordinated $(NH_4)[Eu^{III}(Edta)(H_2O)_3] \cdot H_2O$ and $(NH_4)_3[Eu^{III}(Ttha)] \cdot 5H_2O$[1]

J. Wang, X. D. Zhang, W. G. Jia, Y. Zhang, and Z. R. Liu
Department of Chemistry, Liaoning University, Shenyang, 110036 P. R. China

Received January 10, 2003

Abstract—The crystal and molecular structures of the $(NH_4)[Eu^{III}(Edta)(H_2O)_3] \cdot H_2O$ (**I**); $Edta^{4-}$ is an ethylenediaminetetraacetate anion) and $(NH_4)_3[Eu^{III}(Ttha)] \cdot 5H_2O$ (**II**); $Ttha^{6-}$ is a triethylenetetraminehexaacetate anion) complexes have been determined by single-crystal X-ray structure analysis. The crystal of complex **I** is orthorhombic with *Fdd*2 space group. The crystal data are as follows: $a = 1.9505(8)$ nm, $b = 3.5445(14)$ nm, $c = 1.2442(5)$ nm, $V = 8.602(6)$ nm^3, $Z = 16$, $M = 531.29$, $p = 1.579$ g cm^{-3}, $\mu = 2.970$ mm^{-1}, and $F(OOO) = 3924$. The final R and wR values are 0.0378 and 0.1030 for 2799 ($I > 2.0\sigma(I)$) unique reflections, and 0.0495 and 0.1072 for all 6237 reflections, respectively. The nine-coordinated $[Eu^{III}(Edta)(H_2O)_3]^-$ complex anion has a pseudo-monocapped square antiprismatic structure in which the nine coordinated atoms, two N and four O are from one Edta ligand and three O atoms from water molecules. The crystal of complex **II** is monoclinic with $P2_1/c$ space group. The crystal data are as follows: $a = 1.0387(3)$ nm, $b = 1.2737(4)$ nm, $c = 2.3031(7)$ nm, $\beta = 90.870(5)°$, $V = 3.047(2)$ nm^3, $Z = 4$, $M = 784.58$, C 51.83, H 4.32, N 115.12. $\rho = 1.710$ g cm^{-3}, $\mu = 2.143$ mm^{-1} and $F(000) = 1608$. The final R and wR are 0.0400 and 0.0720 for 5909 ($I > 2.0\sigma(I)$) unique reflections, and 0.0747 and 0.0799 for all 13825 reflections, respectively. The nine-coordinated $[Eu^{III}(Ttha)]^{3-}$ complex anion has a pseudo-monocapped square antiprismatic structure in which the Ttha acts as an ninedentate ligand with four N atoms of amino groups and five O atoms of carboxylic groups actually, in addition, there is a non-coordinated free carboxylic group in the structure.

The great attention has been paid to the rare earth metal complexes all along because these metal ions show biological activities [1–3]. For example, some Nd(III) complexes exhibit good antiinflammation activity; the most high-spin (seven unpair-single electrons) Gd(III) complexes were often used as contrast agent in magnetic resonance imaging diagnoses [4]; the Tb(III) and Eu(III) complexes have been used to diagnose some diseases qua the ionic probes for their character fluorescence [5]. Recently, we are cooperating with Dr. J. Kang and studying the luminescence properties and fluorescence spectra of the Eu(III) complexes with aminopolycarboxylic acids at low temperature [6].

We know that the electronic configuration of the rare earth metal ions determines the luminescence properties and fluorescence spectra of the complexes, but the electronic configuration rests with the coordinate structures of the complexes. In order to explain the luminescence properties and fluorescence spectra of the Eu(III) complexes with aminopolycarboxylic acids particularly and explore the relationships among coordinate structure, electronic configuration and fluorescence spectrum, it is very important to determine their molecular and crystal structures. The Edta (H_4Edta = ethylenediaminetetraacetic acid) is a simple and useful ligand in all aminopolycarboxylic acids [7, 8]. The 1 : 1 complexes are thought to be typical for all trivalent rare earth metal ions with Edta ligand, but these complexes have different coordination structures or coordination numbers [9]. For example, the La(III) (having ionic radius of 0.1172 nm and electronic configuration of f^0) with Edta ligand forms the ten-coordinated complex having a slightly distorted bicapped square antiprismatic structure [10], the Y(III) (0.1040 nm and f^0), and Gd(III) (0.1078 nm and high-spin f^7) form with Edta ligand the nine-coordinated complexes having a slightly distorted monocapped square antiprismatic structure [11, 12]. However, the Dy(III) (0.1052 nm and high-spin f^9), Ho(III) (0.1041 nm and high-spin f^{10}), and Er(III) (0.1030 nm and high-spin f^{11}) form with Edta ligand the eight-coordinated complexes having a slightly distorted square antiprismatic structure. In these complexes, the Edta ligand is coordinated to various rare earth metal ions and acts as a hexadentate ligand. Because the Eu^{3+} ion has the ionic radius of 0.1087 nm and electronic configuration of high-spin f^6 which are similar to ones of Y^{3+} (0.1040 nm and f^0) and Gd^{3+} (0.1078 nm and high-spin f^7) ions, it should also form the nine-coordinated complexes with Edta ligand like the Y^{3+} and Gd^{3+} ions in principle. The nine-coordinated $(NH_4)[Eu^{III}(Edta)(H_2O)_3] \cdot H_2O$ (**I**) complex has been produced inefficiently. In order to verify this forecast, the $((NH_4)_3[Eu^{III}(Ttha)] \cdot 5H_2O$ (**II**); $Ttha^{6-}$ is a triethylenetetraminehexaacetate anion) complex was

---

[1] This article was submitted by the authors in English.

also prepared and the determined result indicated that the Eu^{3+} ion still takes the nine-coordinated structure with Ttha ligand. Besides, the $[Eu^{III}(Ttha)]^{3-}$ part has an interesting molecular structure in which there is a non-coordinated free carboxylic group and the Ttha ligand gives only nine donor atoms (four amino N and five carboxylic O atoms) although it is a decadentate ligand. The $[Eu^{III}(Ttha)]^{3-}$ complex anion is likely to be used as the targeting fluorescent diagnostic reagent with directional function through embellishing this non-coordinated free carboxylic group.

EXPERIMENTAL

Synthesis of $(NH_4)[Eu^{III}(Edta)(H_2O)_3] \cdot H_2O$ (I). 1.46 g (5.0 mmol) H_4Edta was added to 100 ml water, and then 0.87 g (2.5 mmol) Eu_2O_3 powder was added in batches. The mixture was stirred and refluxed for 15.5 h, the pH was adjusted to 6.5 with aqueous NH_3 after the solution became transparent and then the solution was concentrated to 25 ml. The colorless crystals appeared after two weeks at room temperature.

For $C_{10}H_{20}EuN_3O_{12}$				
anal. cacld (%):	Eu, 28.60;	C, 22.61;	H, 4.74;	N, 7.91.
Found (%):	Eu, 28.68;	C, 22.60;	H, 4.76;	N, 7.90.

This formula is approximately consistent with the result of X-ray diffraction analysis.

Synthesis of $(NH_4)_3[Eu^{III}(Ttha)] \cdot 5H_2O$ (II). 2.47g (5.0 mmol) H_6Ttha was added to 100 ml water, and then 0.87 g (2.5 mmol) Eu_2O_3 powder was added to above solution slowly. The mixture was stirred and refluxed for 10 h at the same time, the pH was adjusted to 5 by aqueous NH_3 after the solution became transparent and then the solution was concentrated to 25 ml. The colorless crystals appeared after three weeks at room temperature.

For $C_{18}H_{46}EuN_7O_{17}$				
anal. cacld (%):	Eu, 19.37;	C, 27.55;	H, 5.91;	N, 12.50.
Found (%):	Eu, 19.30;	C, 27.56;	H, 5.90;	N, 12.52.

This formula is approximately consistent with the result of X-ray diffraction analysis.

IR analysis. H_4Edta, H_6Ttha, complexes **I** and **II** mull and press slice with KBr, respectively. Their IR spectra were recorded on a Shimadzu-IR 408 spectrograph.

X-ray diffraction analysis. The details of crystal data collection and refinement parameters for complexes **I** and **II** are listed in Table 1. Data were collected with a Bruker SMART CCD type X-ray diffractometer using graphite-monochromated MoK_α radiation (λ = 0.071073 nm). The structures were solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix method. All calculations were carried with SHELXTL97 program on PDP11/44 and Pentium MMX/166 computers. The structures of the complex anions and the molecular packing of the complexes in unit cell are shown in Figs. 1 and 2 for **I**, Figs. 3 and 4 for **II**, respectively. The coordination polyhedrons around Eu^{3+} ions in $[Eu^{III}(Edta)(H_2O)_3]^-$ and $[Eu^{III}(Ttha)]^{3-}$ complex anions are shown in Figs. 5 and 6, respectively. All the non-hydrogen fractional atomic coordinates and equivalent isotropic temperature factors of these two complexes are listed in Table 2 and Table 3, respectively. The selected bond distances and bond angles of these two complexes are listed in Tables 4 and 5, respectively.

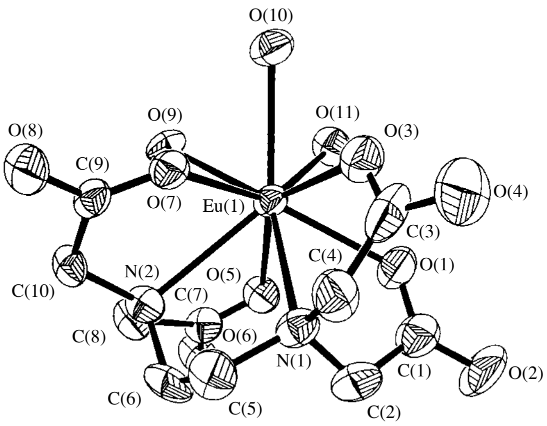

Fig. 1. Molecular structure of $[Eu^{III}(Edta)(H_2O)_3]^-$.

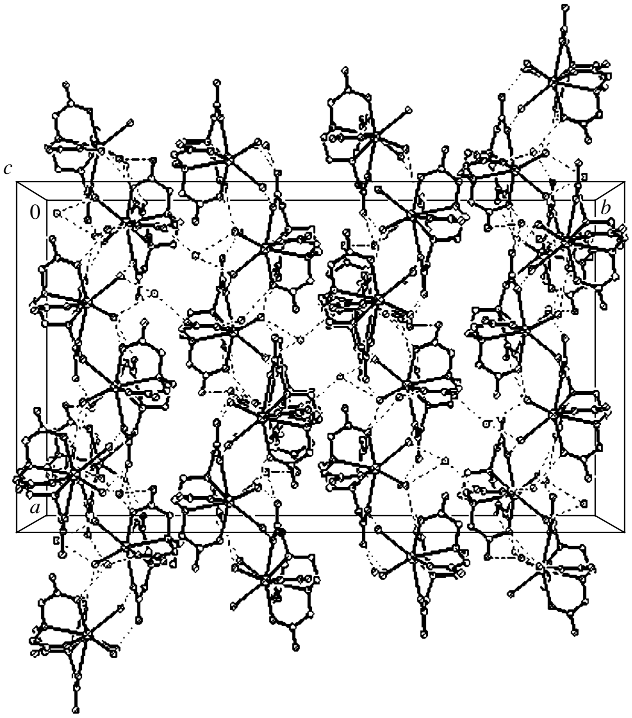

Fig. 2. Packing of $(NH_4)[Eu^{III}(Edta)(H_2O)_3] \cdot H_2O$ molecules in unit cell.

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

	I	**II**
Formula weight	531.29	784.58
Temperature, K	293(2)	293(2)
Crystal system	Orthorhombic	Monoclinic
Space group	$Fdd2$	$P2_1/c$
Unit cell dimensions		
a, nm	1.9505(8)	1.0387(3)
b, nm	3.5445(14)	1.2737(4)
c, nm	1.2442(5)	2.3031(7)
β, deg		90.870(5)
Volume, nm^3	8.602(6)	3.0468(17)
Z	16	4
Calculated density, mg m^{-3}	1.579	1.710
Absorption coefficient, mm^{-1}	2.970	2.143
$F(000)$	3924	1608
Crystal size, mm	0.25 × 0.20 × 0.15	0.30 × 0.20 × 0.16
θ range, deg	2.02–23.30	1.77–26.40
Index ranges	$-21 \le h \le 17$ $-22 \le k \le 39$ $-13 \le l \le 13$	$-12 \le h \le 12$ $-15 \le k \le 5$ $-28 \le l \le 26$
Reflections collected	6237	13825
Independent reflections	2799 ($R_{\text{int}} = 0.0376$)	5909 ($R_{\text{int}} = 0.0538$)
Final R indices ($I > 2\sigma(I)$)	$R = 0.0378$, $wR = 0.1030$	$R = 0.0400$, $wR = 0.0720$
R indices (all data)	$R = 0.0495$, $wR = 0.1072$	$R = 0.0747$, $wR = 0.0799$
Absorption correction	Semi-empirical from equivalents	
Refinement method	Full-matrix least-squares on F^2	

RESULTS AND DISCUSSION

It can be seen that ν(C–N) of **I** is at 1085 cm^{-1} and red-shifts 43 cm^{-1} comparing with that of H_4Edta (1128 cm^{-1}) which indicates that the two N atoms from an Edta ligand are coordinated to the central Eu^{3+} ion. For the vibration related -COOH group, it was found that the ν_{as}(COOH) in Edta at 1690 cm^{-1} disappeared in the IR spectrum of **I**, and ν_{as}(COO) at 1610 cm^{-1} of Edta red-shifts to 1578 cm^{-1} and ν_s(COO) at 1390 cm^{-1} of Edta violet-shifts to 1404 cm^{-1} for **I**, which confirms that the O atoms of all four –COO$^-$ groups are also coordinated with Eu^{3+} ion. There is a wide ν(OH) band of H_2O near 3440 cm^{-1} showing the existence of H_2O in the complex.

It can be observed that the ν(C–N) of **II** is at 1075 cm^{-1} and red-shifts 50 cm^{-1} comparing with that of H_6Ttha (1125 cm^{-1}) which indicates that the N atom from Ttha ligand coordinates with central Eu^{3+} ion. The ν_{as}(COOH) in Ttha at 1736 cm^{-1} disappeared in the IR spectrum of **II**. The ν_{as}(COO) at 1642 cm^{-1} of H_6Ttha red-shifts to 1603 cm^{-1} partly and ν_s(COO) at 1389 cm^{-1} of H_6Ttha blue-shifts to 1415 cm^{-1} partly for **II**, which not only confirms that the O atoms of some –COO$^-$ groups coordinate with central Eu^{3+} ion, but also shows that there is a non-coordinated free carboxylic group in the complex **II**. There is a wide ν(OH) band of H_2O near 3455 cm^{-1} showing the existence of H_2O in the complex.

It can be seen in Fig. 1 that the central Eu^{3+} ion of the structure **I** is coordinated with two N atoms and four O atoms from an Edta ligand, and the other three O atoms from three coordinated H_2O molecules in the $[Eu^{III}(Edta)(H_2O)_3]^-$ complex anion. The set of O(3), O(7), O(9) and O(11) atoms and the set of O(1), O(5), N(1) and N(2) atoms form two approximate squares, respectively, which make a square antiprism, so the $Eu^{III}N_2O_7$ part in the nine-coordinated $[Eu^{III}(Edta)(H_2O)_3]^-$ complex anion has a pseudo-mono-capped square antiprismatic structure (Fig. 5). The

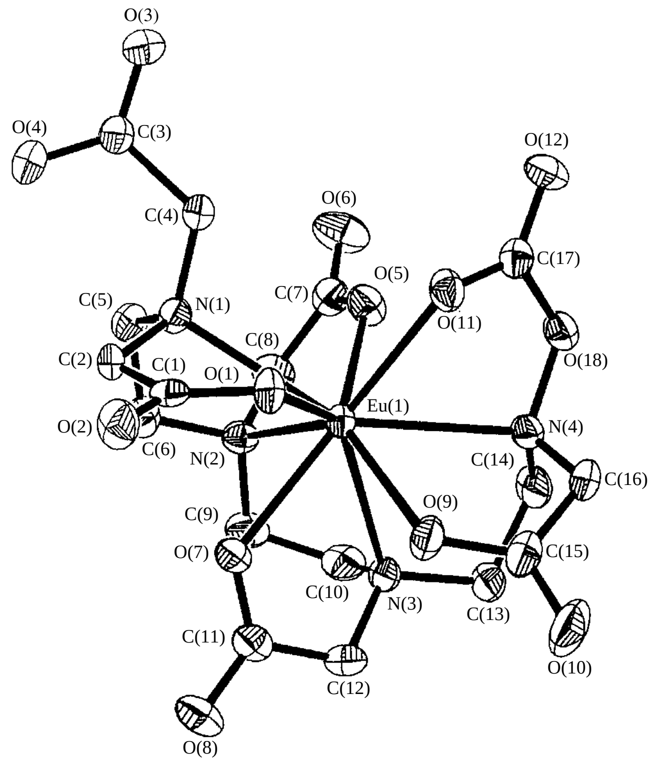

Fig. 3. Molecular structure of $[Eu^{III}(Ttha)]^{3-}$.

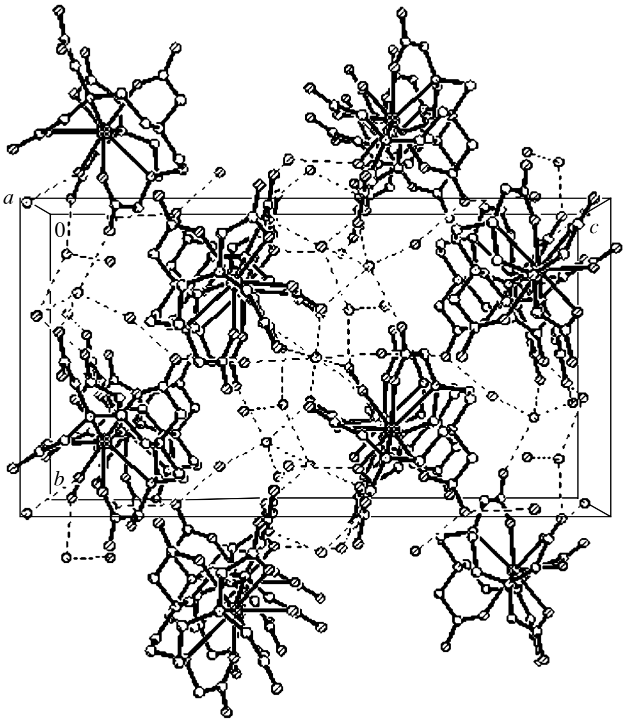

Fig. 4. Packing of $(NH_4)_3[Eu^{III}(Ttha)] \cdot 5H_2O$ molecules in unit cell.

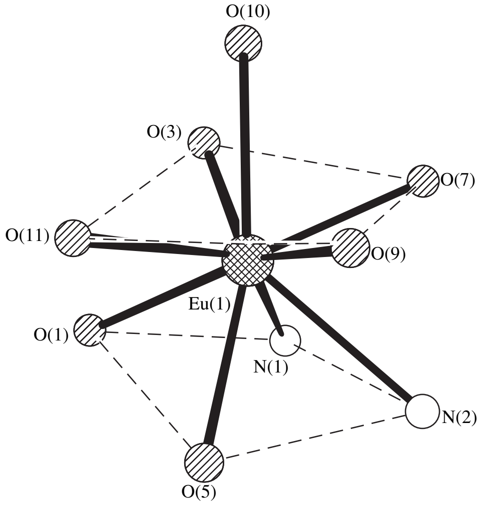

Fig. 5. Coordination polyhedrons around Eu(III) in $[Eu^{III}(Edta)(H_2O)_3]^{-}$.

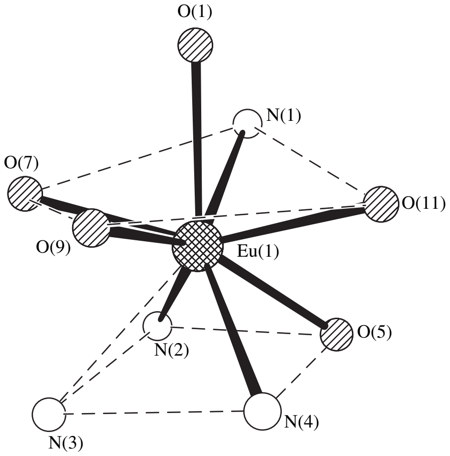

Fig. 6. Coordination polyhedrons around Eu(III) in $[Eu^{III}(Ttha)]^{3-}$.

atom O(10) from a coordinated H_2O molecule is above the plane formed by O(3), O(7), O(9) and O(11) atoms and the average value of the angles O(3)Eu(1)O(10), O(7)Eu(1)O(10), O(9)Eu(1)O(10) and O(11)Eu(1)O(10) is 71.73° close to 70° that most complexes with nine-coordinate pseudo-monocapped square antiprismatic structure adopt, in which the biggest and smallest angles are 74.13° and 69.13°, respectively. Because of the repulsion of these four coordinated O atoms, the Eu^{III}–O(10) distance (0.2539(8) nm) is the longest among all the Eu^{III}–O distances, while the Eu^{III}–O(9) and Eu^{III}–O(11) distances (O(9) and O(11) atoms also come from coordinated water molecules) are only 0.2458(8) and 0.2474(8) nm, respectively. The results in this paper and the ones reported previously indicate that the Eu^{3+} ion having the ionic radius of 0.1087 nm

Table 2. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic thermal parameters U_{eq} ($\times 10^3$) in the crystal structure **I**

Atom	*x*	*y*	*z*	U_{eq}, nm^2	Atom	*x*	y	*z*	U_{eq}, nm^2
Eu(1)	1683(1)	9044(1)	10082(1)	34(1)	C(1)	1502(8)	9661(4)	12061(12)	58(4)
N(1)	1957(5)	9784(2)	10200(10)	42(2)	C(2)	1591(10)	9934(5)	11096(14)	66(5)
N(2)	1038(5)	9441(3)	8518(8)	40(3)	C(3)	3010(9)	9521(5)	10964(12)	68(4)
O(1)	1536(5)	9315(3)	11858(7)	53(2)	C(4)	2671(8)	9826(4)	10383(11)	58(4)
O(2)	1412(8)	9800(3)	12981(8)	92(5)	C(5)	1752(8)	9973(5)	9154(14)	57(5)
O(3)	2797(5)	9181(3)	10829(8)	57(3)	C(6)	1063(8)	9846(4)	8798(12)	53(4)
O(4)	3534(7)	9576(4)	11603(11)	102(4)	C(7)	43(7)	9252(3)	9638(10)	42(3)
O(5)	468(4)	9182(2)	10364(7)	43(2)	C(8)	315(7)	9318(4)	8518(10)	46(3)
O(6)	–598(5)	9255(3)	9761(7)	64(3)	C(9)	1371(5)	9362(3)	7455(11)	40(3)
O(7)	2361(5)	9156(2)	8510(7)	41(2)	C(10)	2129(6)	9252(3)	7591(12)	38(3)
O(8)	2467(5)	9246(3)	6732(8)	59(3)	N(3)	557(7)	352(3)	3604(10)	66(4)
O(9)	1163(5)	8591(2)	8827(7)	42(2)	O(12)	1354(13)	8853(6)	3569(16)	78(7)
O(10)	2475(5)	8479(2)	9908(7)	50(2)	O(13)	8470(20)	9041(6)	8310(30)	137(15)
O(11)	1230(5)	8538(3)	11252(7)	50(3)					

Table 3. Coordinates of atoms ($\times 10^4$) and their equivalent isotropic thermal parameters U_{eq} ($\times 10^3$) in the crystal structure **II**

Atom	*x*	*y*	*z*	U_{eq}, nm^2	Atom	*x*	*y*	*z*	U_{eq}, nm^2
Eu(1)	2443(1)	2311(1)	8670(1)	21(1)	C(6)	–354(4)	2312(4)	7856(2)	31(1)
O(1)	1588(3)	2214(3)	9616(1)	27(1)	C(7)	1992(5)	4071(4)	7632(2)	31(1)
O(2)	–61(3)	1535(3)	10096(2)	33(1)	C(8)	1288(5)	3205(4)	7311(2)	31(1)
O(3)	–715(4)	5795(3)	9289(2)	50(1)	C(9)	1239(5)	1320(4)	7342(2)	36(1)
O(4)	–1987(3)	4438(3)	9184(2)	45(1)	C(10)	2665(5)	1101(4)	7309(2)	35(1)
O(5)	2543(3)	3834(3)	8103(2)	33(1)	C(11)	1672(5)	–122(4)	8449(2)	28(1)
O(6)	1994(4)	4957(3)	7416(2)	51(1)	C(12)	2904(5)	–125(4)	8100(2)	34(1)
O(7)	1287(3)	736(3)	8646(2)	29(1)	C(13)	4702(5)	997(4)	7823(2)	35(1)
O(8)	1125(4)	–972(3)	8522(2)	46(1)	C(14)	5159(5)	2121(4)	7887(2)	37(1)
O(9)	3753(3)	1078(3)	9168(2)	30(1)	C(15)	4980(5)	1043(4)	9178(2)	33(1)
O(10)	5613(3)	321(3)	9390(2)	52(1)	C(16)	5673(5)	1965(4)	8917(2)	33(1)
O(11)	3599(3)	3633(3)	9244(2)	29(1)	C(17)	4443(5)	4182(4)	8995(2)	27(1)
O(12)	4682(4)	5114(3)	9106(2)	41(1)	C(18)	5191(5)	3667(4)	8515(2)	32(1)
N(1)	101(4)	3155(3)	8809(2)	23(1)	N(5)	1369(5)	7076(4)	9081(2)	43(1)
N(2)	1004(4)	2287(3)	7675(2)	26(1)	N(6)	4120(5)	8419(4)	9407(2)	68(2)
N(3)	3273(4)	913(3)	7882(2)	26(1)	N(7)	2080(4)	5005(4)	4992(2)	33(1)
N(4)	4912(4)	2533(3)	8474(2)	26(1)	O(13)	3389(4)	6366(3)	9896(2)	50(1)
C(1)	389(5)	2035(3)	9681(2)	23(1)	O(14)	6780(4)	6469(3)	9524(2)	59(1)
C(2)	–519(4)	2423(4)	9214(2)	26(1)	O(15)	1553(4)	4849(4)	6222(2)	59(1)
C(3)	–918(5)	4860(4)	9188(2)	29(1)	O(16)	3026(4)	6302(3)	8246(2)	59(1)
C(4)	270(5)	4193(4)	9072(2)	28(1)	O(17)	6391(6)	8251(4)	8733(3)	114(2)
C(5)	–634(5)	3218(4)	8253(2)	30(1)					

Table 4. Bond lengths and angles in the crystal structure **I**

Bond	*d*, nm	Bond	*d*, nm	Bond	*d*, nm
Eu(1)–O(1)	0.2427(9)	Eu(1)–O(3)	0.241(1)	Eu(1)–O(5)	0.2446(8)
Eu(1)–O(7)	0.2394(9)	Eu(1)–O(9)	0.2458(8)	Eu(1)–O(10)	0.2539(8)
Eu(1)–O(11)	0.2474(8)	Eu(1)–N(1)	0.2679(9)	Eu(1)–N(2)	0.271(1)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Eu(1)O(3)	71.1(3)	O(1)Eu(1)O(5)	71.1(3)	O(1)Eu(1)O(7)	138.0(3)
O(1)Eu(1)O(9)	142.0(3)	O(1)Eu(1)O(10)	117.5(3)	O(1)Eu(1)O(11)	73.1(3)
O(1)Eu(1)N(1)	65.6(3)	O(1)Eu(1)N(2)	113.2(3)	O(3)Eu(1)O(5)	141.0(3)
O(3)Eu(1)O(7)	77.5(3)	O(3)Eu(1)O(9)	138.4(3)	O(3)Eu(1)O(10)	69.1(3)
O(3)Eu(1)O(11)	103.9(3)	O(3)Eu(1)N(1)	66.5(3)	O(3)Eu(1)N(2)	126.2(3)
O(5)Eu(1)O(7)	128.3(3)	O(5)Eu(1)O(9)	79.8(3)	O(5)Eu(1)O(10)	139.5(3)
O(5)Eu(1)O(11)	73.4(3)	O(5)Eu(1)N(1)	89.4(3)	O(5)Eu(1)N(2)	63.2(3)
O(7)Eu(1)O(9)	79.5(3)	O(7)Eu(1)O(10)	74.1(3)	O(7)Eu(1)O(11)	143.0(3)
O(7)Eu(1)N(1)	76.8(3)	O(7)Eu(1)N(2)	65.4(3)	O(9)Eu(1)O(10)	71.4(3)
O(9)Eu(1)O(11)	75.7(3)	O(9)Eu(1)N(1)	139.2(3)	O(9)Eu(1)N(2)	72.1(3)
O(10)Eu(1)O(11)	72.2(3)	O(10)Eu(1)N(1)	130.9(3)	O(10)Eu(1)N(2)	129.1(3)
O(11)Eu(1)N(1)	138.5(3)	O(11)Eu(1)N(2)	129.3(3)	N(1)Eu(1)N(2)	67.9(3)

Table 5. Bond lengths and angles in the crystal structure **II**

Bond	*d*, nm	Bond	*d*, nm	Bond	*d*, nm
Eu(1)–O(1)	0.2369(3)	Eu(1)–O(5)	0.2342(3)	Eu(1)–O(7)	0.2338(3)
Eu(1)–O(9)	0.2363(3)	Eu(1)–O(11)	0.2445(3)	Eu(1)–N(1)	0.2683(4)
Eu(1)–N(2)	0.2718(4)	Eu(1)–N(3)	0.2694(4)	Eu(1)–N(4)	0.2626(4)
Angle	ω, deg	Angle	ω, deg	Angle	ω, deg
O(1)Eu(1)O(5)	125.2(2)	O(1)Eu(1)O(7)	77.2(1)	O(1)Eu(1)O(9)	75.0(1)
O(1)Eu(1)O(11)	74.2(1)	O(1)Eu(1)N(1)	63.8(1)	O(1)Eu(1)N(2)	124.5(1)
O(1)Eu(1)N(3)	135.5(1)	O(1)Eu(1)N(4)	123.0(1)	O(5)Eu(1)O(7)	136.4(1)
O(5)Eu(1)O(9)	142.3(1)	O(5)Eu(1)O(11)	72.8(1)	O(5)Eu(1)N(1)	77.4(1)
O(5)Eu(1)N(2)	64.4(1)	O(5)Eu(1)N(3)	98.9(1)	O(5)Eu(1)N(4)	76.3(1)
O(7)Eu(1)O(9)	74.5(1)	O(7)Eu(1)O(11)	148.5(1)	O(7)Eu(1)N(1)	83.1(1)
O(7)Eu(1)N(2)	72.2(1)	O(7)Eu(1)N(3)	65.6(1)	O(7)Eu(1)N(4)	126.2(1)
O(9)Eu(1)O(11)	85.5(1)	O(9)Eu(1)N(1)	136.5(1)	O(9)Eu(1)N(2)	135.0(1)
O(9)Eu(1)N(3)	72.5(1)	O(9)Eu(1)N(4)	66.3(1)	O(11)Eu(1)N(1)	95.6(1)
O(11)Eu(1)N(2)	136.3(1)	O(11)Eu(1)N(3)	131.3(1)	O(11)Eu(1)N(4)	63.0(1)
N(1)Eu(1)N(2)	67.5(1)	N(1)Eu(1)N(3)	130.2(1)	N(1)Eu(1)N(4)	150.1(1)
N(2)Eu(1)N(3)	66.5(1)	N(2)Eu(1)N(4)	112.4(1)	N(3)Eu(1)N(4)	68.4(1)

and high-spin f^6 electronic configuration should form nine-coordinated complexes with aminopolycarboxylic acids if all chelate rings are five-membered cycles in the structure.

In one unit cell, there are sixteen complex molecules. The hydrogen bonds contact among crystal water and crystal water, crystal water and O atom of Edta ligand as well as crystal water and coordinated water. A net structure is formed among complex molecules in a unit cell through the hydrogen bonds and static electricities.

It can be seen in Fig. 3 that the central Eu^{3+} ion of the **II** structure is coordinated with four N atoms and five O atoms from one Ttha ligand. The $Eu^{III}N_4O_5$ part in nine-coordinated $[Eu^{III}(Ttha)]^{3-}$ complex anion forms a pseudo-monocapped square antiprismatic structure in which the set of O(7), O(9), O(11), and N(1) atoms and the set of N(2), N(3), N(4), and O(5) atoms form two approximate squares (Fig. 6), respectively. The ninth coordinated atom O(1) is above the plane formed by O(7), O(9), O(11), and N(1) atoms. In general, the Eu^{III}–O(1) distance (0.2369(3) nm) should originally be the longest among all the Eu^{III}–O distances for the repulsion of other four coordinate atoms in plane, but O(11) atom not only coordinates with center Eu^{3+} ion but also forms hydrogen bond with one crystal water molecule which results in the longest Eu^{III}–O(11) distance (0.2445(3) nm) among all the Eu^{III}–O distances in the structure **II**. Through comparing the coordination bonds in complexes **I** and **II**, it can be found that the coordination bonds of $[Eu^{III}(Ttha)]^{3-}$ complex anion are all shorter than those of $[Eu^{III}(Edta)(H_2O)_3]^-$ complex anion, which indicates that the coordination capacity of Ttha ligand is stronger than that of Edta ligand.

The results mentioned above show again that the Eu(III) can form a nine-coordinated complex with Ttha ligand like $(NH_4)_3[Dy^{III}(Ttha)] \cdot 5H_2O$ [13], $(NH_4)_2[Gd^{III}(HTtha)] \cdot 9H_2O$ [14] and $(NH_4)_3[Y^{III}(Ttha)] \cdot 5H_2O$ [15] complexes since it has the ionic radius of 0.1087 nm being similar to ones of Dy(III) (0.1052 nm), Gd(III) (0.1078 nm) and Y(III) (0.1040 nm) and high-spin f^6 electronic configuration. These structures prove that the theoretical inferences about the coordination number or structure were accurate [16, 17]. In addition, it can also be seen that this nine-coordinated complex **II** contains a non-coordinated free carboxyl group ($-CH_2COOH$). The $-CH_2COOH$ group can be modified by chemical method using some biological molecules and make the complex form targeting ionic fluorescence probe having directional function to some abnormal tissues.

In one unit cell, there are four complex molecules shown in Fig. 4. The hydrogen bonds contact among crystal water and crystal water, crystal water and O atom of Ttha ligand as well as crystal water and ammonium cation. A net structure is formed in a unit cell through the hydrogen bonds and static electricities.

Thus, the Eu(III) complexes with Edta and Ttha ligands are prepared and their compositions and structures are determined as $(NH_4)[Eu^{III}(Edta)(H_2O)_3] \cdot H_2O$ and $(NH_4)_3[Eu^{III}(Ttha)] \cdot 5H_2O$, respectively, by single-crystal X-ray diffraction analyses and elemental analyses. In the nine-coordinated $[Eu^{III}(Edta)(H_2O)_3]^-$ complex anion, the $Eu^{III}N_2O_7$ part forms a mono-capped square antiprism. In the nine-coordinate $[Eu^{III}(Ttha)]^{3-}$ complex anion, the $Eu^{III}N_4O_5$ part forms a mono-capped square antiprism. In addition, the $[Eu^{III}(Ttha)]^{3-}$ complex anion supplies a non-coordinated free carboxylic group.

ACKNOWLEDGMENTS

The authors thank Prof. K. Miyoshi and T. Mizuta (Faculty of Science, Hiroshima University, Japan) for teaching and Dr. H.G. Wang (Central Laboratory, Nankai University) for the X-ray structure determination.

REFERENCES

1. Zhou, J., Wang, L.F., Wang, J.Y., *et al.*, *J. Inorg. Biochem.*, 2001, vol. 8, no. 1, p. 41.
2. Akaboshia, M., Suminoa, T., Tanakaa, Y., *et al.*, *J. Radio. Nucl. Chem.*, 1997, vol. 217, no. 2, p. 179.
3. Banaszka, J.E., Rittmann, B.E., and Reed, D.T., *Nucl. Chem.*, 1999, vol. 41, p. 385.
4. Lauffer, R.B., *Chem. Rev.*, 1988, vol. 87, p. 901.
5. Richardson, F.R., *Chem. Rev.*, 1982, vol. 82, p. 541.
6. Kang, J.G., Hong, J.P., Yoon, S.K., *et al.*, *J. Alloys Compd.*, 2002, vol. 339, p. 248.
7. Miyoshi, K., Wang, J., and Mizuta, T., *Bull. Chem. Soc. Jpn.*, 1993, vol. 66, p. 2547.
8. Mizuta, T., Wang, J., and Miyoshi, K., *Inorg. Chim. Acta*, 1993, vol. 230, p. 249.
9. Sakagami, N., Homma, J., Konno, T., *et al.*, *Inorg. Chim. Acta*, 1999, vol. 288, p. 1376.
10. Hoard, J.L., Lee, B., and Lind, M.D., *J. Am. Chem. Soc.*, 1965, vol. 87, p. 1612.
11. Wang, J., Zhang, X.D., and Zhang, W.Q., *Chin. Rare Metal*, 2001, vol. 20, p. 267.
12. Wang, J., Zhao, J., and Zhang, X.D., *Chin. Rare Metal*, 2002, vol. 21, p. 106.
13. Wang, J., Zhang, X.D., and Jia, W.G., *Chin. Rare Earth*, 2002, vol. 8, p. 765.
14. Wang, R.Y., Zhang, H.J., and Jin, T.Z. *Chem. J. Chin. Univ.*, 1999, vol. 20, p. 176.
15. Wang, J., Zhang, X.D., and Ma, R., *Acta Chim. Sinica*, 1998, vol. 61, p. 536.
16. Mizuta, T., Wang, J., and Miyoshi, K., *Bull. Chem. Soc. Jpn.*, 1993, vol. 66, p. 3662.
17. Wang, J., Zhang, X.D., and Ma, R., *Chin. Inorg. Chem.*, 2001, vol. 17, no. 1, p. 119.