Syntheses and Structural Determination of the Nine-coordinate Rare Earth Metal Complexes: \([\text{Tb}^{III}(\text{Eg}3a)(\text{H}_2\text{O})_2] \cdot 4.5\text{H}_2\text{O}\) and \(\text{K}[\text{Tb}^{III}(\text{Edta})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}\)

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Received March 19, 2007

**Abstract**—Two title complexes, \([\text{Tb}^{III}(\text{Eg}3a)(\text{H}_2\text{O})_2] \cdot 4.5\text{H}_2\text{O}\) (I) (\(\text{H}_2\text{Eg}3a = 3\)-carboxymethyl–6, 9-dioxa–3,12-diazatetradecanedioic acid) and \(\text{K}[\text{Tb}^{III}(\text{Edta})(\text{H}_2\text{O})_3] \cdot 5\text{H}_2\text{O}\) (II) (\(\text{H}_2\text{Edta} = \text{ethylendiamine-N,N,N’,N’-tetraacetic acid}\)), were prepared and characterized by FT–IR, elemental analyses, TGA–DTA–DTG, and single-crystal X-ray diffraction technique. For I, the \(\text{Tb}^{3+}\) ion is nine-coordinated by an \(\text{Eg}3a\) ligand and two coordination water molecules, yielding a monocationic square-antiprismatic (MCSAP) conformation. Complex I crystallizes in the monoclinic system with \(P2_1/c\) space group. The crystal data are as follows: \(a = 9.237(3), b = 10.018(3), c = 23.580(7)\) Å, \(\beta = 99.021(5)°, V = 2155.2(11)\) Å\(^3\), \(Z = 4, \rho = 1.822\) Mg m\(^{-3}\), \(\mu = 3.353\) mm\(^{-1}\), \(F(000) = 1180, R_p = 0.0445\) and \(wR_2 = 0.1034\) for 4262 observed reflections with \(I \geq 2\sigma(I)\). For II, the \(\text{Tb}^{3+}\) ion is nine-coordinated by an Edta ligand and three coordinate water molecules also yielding a MCSAP conformation. Complex II crystallizes in the orthorhombic system with \(Fdd2\) space group. The crystal data are as follows: \(a = 19.373(5), b = 35.429(10), c = 12.1134(7)\) Å, \(V = 8315(4)\) Å\(^3\), \(Z = 16, \rho = 2.014\) Mg m\(^{-3}\), \(\mu = 2.014\) mm\(^{-1}\), \(F(000) = 5024, R_p = 0.0224\) and \(wR_2 = 0.0557\) for 3189 observed reflections with \(I \geq 2\sigma(I)\). The potassium cations bridge the coordination spheres yielding many infinite long 1-D zigzag-type chains. The molecular structure of I is more stable than that of II. According to thermal analyses, the collapsing temperatures of crystal structure are 314°C for I and 348°C for II, which indicates that the crystal structure of II is more stable.

**DOI**: 10.1134/S1070328408050072

**INTRODUCTION**

Over the past decade there has been a resurgence of interest in coordination chemistry of rare-earth (RE) metal complexes. The excitement in this work can be related to an enhanced appreciation of their special biological activities and potential value of application [1, 2]. Some \(\text{Tb}(III)\) complexes with aminopolycarboxylic acid ligands have unusual spectroscopic characteristics including millisecond excited-state lifetime, sharply spiked emission spectra (few nm), and large Stokes shifts (>150 nm), so that they have been used as probes in fluoroimmunoassay [3–5] and show considerable promise in luminescence imaging and as sensors for certain bioactive ions [6]. Therefore, it is significant to carry out the advanced research of luminescence properties and spectra of these \(\text{Tb}(III)\) complexes. In order to explain these phenomena exactly, it is necessary to determine their molecular and crystal structures first, which is the right intention of our work. In a given oxidation state, the crystal and molecular structures of RE metal complexes with aminopolycarboxylic acid ligands generally depend on the radius of central metal ions and the nature of counter cation(s). It is well known that, due to lanthanide contraction, there is only one unobvious difference among the coordination numbers are usually nine, and their coordination polyhedra adopt monocapped square-antiprismatic conformation, such as \(\text{K}_3[\text{Tb}^{III}(\text{Nta})_2(\text{H}_2\text{O})] \cdot 5.5\text{H}_2\text{O}\) [7], \(\text{KNa}_3[\text{Tb}^{III}(\text{Nta})_2(\text{H}_2\text{O})] \cdot 5\text{H}_2\text{O}\) [8] and \(\text{K}_4[\text{Tu}^{III}(\text{HTtha})_2] \cdot 14\text{H}_2\text{O}\) [9].

The ethylenediamine-N,N,N’,N’-tetraacetic acid (\(\text{H}_2\text{Edta}\)) is a powerful hexadentate chelate agent of RE metal ions offering considerable versatility in industrial and household uses. However, oral exposures to \(\text{H}_2\text{Edta}\) produced adverse reproductive and developmental effects in vivo [10]. The 3,12-bis(carboxymethyl)-6,9-dioxa-3,12-diazatetradecanedioic acid (\(\text{H}_4\text{Egta}\)) also

1 The text was submitted by the authors in English.
has a much higher affinity for the RE metal ions with relatively big ionic radius, which is attributed to the complexation of additional ether oxygen atoms [11]. Otherwise, being different from the H₄Edta, the H₄Egta is unstable and decomposable in the nature environment. Hence, the H₄Egta can be chosen as a potential substitute of H₄Edta. Another substitute of H₄Edta is the 3-carboxymethyl-6,9-dioxo-1,12-diazatetradecanedioic acid (H₄Eg3a) which is an analog of H₄Egta. It is expected that the H₄Eg3a is similar to the Edta ligand forming stable and neutral complexes with RE metal ions.

The structures of mentioned above ligands are shown below:

\[
\text{HOOC} - \overset{\text{N}}{\text{C}} - \overset{\text{O}}{\text{H}} \quad \text{HOOC} - \overset{\text{N}}{\text{C}} - \overset{\text{O}}{\text{H}}
\]

(H₄Eg3a)

\[
\text{HOOC} - \overset{\text{N}}{\text{C}} - \overset{\text{O}}{\text{H}} \quad \text{HOOC} - \overset{\text{N}}{\text{C}} - \overset{\text{O}}{\text{H}}
\]

(H₄Egta)

\[
\text{HOOC} - \overset{\text{N}}{\text{C}} - \overset{\text{N}}{\text{C}} - \overset{\text{O}}{\text{H}} \quad \text{HOOC} - \overset{\text{N}}{\text{C}} - \overset{\text{N}}{\text{C}} - \overset{\text{O}}{\text{H}}
\]

(H₄Edta)

As a result, the title complex, [Tb⁺⁺⁺(Eg3a)(H₂O)₂] · 4.5H₂O (I), was synthesized and its molecular and crystal structures was also determined. In addition, the other title complex, K[Tb⁺⁺⁺(Edta)(H₂O)₃] · 5H₂O (II), was also synthesized synchronously in order to compare their molecular and crystal structures. To the best our knowledge, the molecular and crystal structures of the RE metal complexes with the Eg3a ligand are reported first.

**EXPERIMENTAL**

**Synthesis of I.** H₄Eg3a (3.2232 g, 10.0 mmol; A.R., Mashi Chem, China) and Tb₂O₇ powder (1.8692 g, 2.5 mmol; A.R., Yuelong, China) were added to 100 ml of hot water slowly. The solution became transparent when the mixture had been stirred and refluxed for 20 h, and then the pH value was adjusted to 6.0 by dilute aqua ammonia. Finally, the solution was concentrated to 25 ml, and a light yellow crystal of the Tb(III) complex was obtained after two weeks at room temperature. The elemental analyses for C, H, and N were carried out on a Perkin-Elmer 240 instrument.

For [Tb⁺⁺⁺(Eg3a)(H₂O)₂] · 4.5H₂O (I)

anal. caled (%): C, 24.21; H, 5.42; N, 4.71.

Found (%): C, 24.22; H, 5.44; N, 4.74.

**Synthesis of II.** H₄Edta (2.9225 g, 10.0 mmol; A.R., Mashi Chem, China) and Tb₂O₇ powder (1.8692 g, 2.5 mmol; A.R., Yuelong, China) were added to 100 ml of hot water slowly. The solution became transparent when the mixture had been stirred and refluxed for 22 h, and then the pH value was adjusted to 5.9 by dilute aqua KHCO₃. Finally, the solution was concentrated to 25 ml, and a light yellow crystal of the Tb(III) complex was obtained after two weeks at room temperature.

For K[Tb⁺⁺⁺(Edta)(H₂O)₃] · 5H₂O (II)

anal. caled (%): C, 19.07; H, 4.45; N, 4.47.

Found (%): C, 19.05; H, 4.48; N, 4.44.

The FT-IR spectra of two complexes, I and II, and the corresponding ligands, H₄Eg3a and H₄Edta, were determined on a Perkin Elmer Spectrum One FT-IR spectrometer. All the results are given in Fig. 1. Thermal analyses of these complexes were carried out by a