INTRODUCTION

The rational design and synthesis of rare earth (RE) metal complexes have attracted a great deal of attention due to their potential application in medicinal and biochemical applications [1–7]. For instance, some Nd(III) complexes have good anti-inflammation activity, and Gd(III) complexes were often used as contrast agents in magnetic resonance imaging [8–10]. The Sm(III) complexes as radioactive drugs expand treatment options for osteosarcoma, offering patients with bone cancer a treatment that specifically targets and kills tumor cells in the bone [11–14]. Some Dy\(^{3+}\) and Ho\(^{3+}\) ions, owing to desirable radioactive characteristics, their corresponding complexes become excellent candidates for radiation synovectomy and radioimmunotherapy [15–17]. The Er(III) complexes play an important role in the production and development of laser fields [18].

The last period of intense research activity on highly sensitive fluorescence of rare-earths metal complexes and the fluorescence properties of the Eu(III) complexes have been reported. These complexes are very popular as fluorescent probes [19–23]. Further, due to the interesting fluorescence properties of the Eu(III) complexes, such as narrow line fluorescence with a long lifetime, they are strong candidates for diverse applications, such as sensors, functional materials, liquid-crystalline functional materials, optical fiber lasers and amplifiers, fluorescent label design for specific biomolecule interactions, and magnetic molecular materials and emitters in light-emitting diodes [24–26]. Benefits for all these applications are unusual spectroscopic characteristics of these complexes. Furthermore, the root cause of spectroscopic characteristics is molecular structure.

In this article, the choice of aminopolycarboxylic acid as the ligand was deliberated. Since the Eu\(^{3+}\) ion as a heavy metal is not only poisonous but also is weakly fluorescent, it is difficult to apply its in reality. If choosing a suitable ligand, the complexes have better characteristics. Aminopolycarboxylic acid can form extraordinarily stable and water-soluble complexes with RE metals [27, 28]. So, diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid (H\(_5\)Dtpa), octadentate ligand, is chosen to form complexes with Eu\(^{3+}\) ion. Two novel complexes, namely,
Na₂[Eu³⁺(Dtpa)(H₂O)]₂ ⋅ 11.5H₂O (I) and (NH₄)₂[Eu³⁺(Dtpa)₂] ⋅ 10H₂O (II), were successfully synthesized and detected. The results showed that they form stable and water-soluble nine-coordinate complexes and their fluorescence can significantly increase. Due to different counterions, complexes I and II have different coordinate structures, the coordinate field consists of various coordinated atoms determining the molecular spectral characteristic; therefore, the positions of emission peaks are different. Hence, counterion species have some effect on the crystal and molecular structures and fluorescence properties.

EXPERIMENTAL

Synthesis of I. H₃Dtpa (A.R., Beijing SLHHT Science & Trade Co., Ltd., China) (1.9668 g, 5.0 mmol) was added to 100 mL of warm water and Eu₂O₃ powder (99.999%, Yuelong Rare Earth Co., Ltd., China) (0.8797 g, 2.5 mmol) 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 value was adjusted to 6.5 by dropping a dilute NaHCO₃ aqueous solution. Finally, the solution was concentrated to 25 mL. A white crystal appeared after three weeks at room temperature.

Synthesis of II. H₃Dtpa (A.R., Beijing SLHHT Science & Trade Co., Ltd., China) (1.9668 g, 5.0 mmol) was added to 100 mL of warm water and Eu₂O₃ powder (99.999%, Yuelong Rare Earth Co., Ltd., China) (0.8797 g, 2.5 mmol) was added to the above solution slowly. After the mixture had been stirred and refluxed for 18 h, the solution became transparent. Then the pH value was adjusted to 6.5 by dropping a dilute NH₄HCO₃ aqueous solution. Finally, the solution was concentrated to 25 mL. A white crystal appeared after two weeks at room temperature.

The samples of H₃Dtpa, I, and II were skived and pressed to the slices with KBr, respectively, and their IR spectra were determined on a Shimadzu-IR 408 spectrophotometer (Cary 50, Varian Company, USA) and a fluorescence spectrophotometer (Cary 300, Varian Company, USA). TG–DTA curves of I and II were determined on a Mettler-Toledo 851° thermogravimetric analyzer in the presence of air (20 mL min⁻¹) from room temperature to 800°C at a heating rate of 25°C min⁻¹.

Determination of molecular and crystal structures. X-ray intensity data were collected on a Bruker SMART CCD type X-ray diffractometer system with graphite–monochromatized MoKα radiation (λ = 0.71073 Å). The structure was solved by direct methods (on F²). 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. Figure 1 illustrates the perspective views of two complexes. Figure 2 shows their coordination polyhedrons. Figure 3 provides coordinate structures of the Na ion in complex I. Figure 4 displays their molecular packing in a unit cell. Figure 5 gives the extended 2D planar structure of complex II. The crystal data and structure refinement for two complexes are listed in Table 1. The selected bond distances and bond angles of two complexes are listed in Table 2. Supplementary material has been deposited with the Cambridge Crystallographic Data Centre (nos. 808458 (I) and 808460 (II); deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSION

In the FT-IR spectrum I, the ν(C–N) band appears at 932 cm⁻¹, which displays a red shift (28 cm⁻¹) compared with that (960 cm⁻¹) of H₃Dtpa. It indicates that the amine nitrogen atoms of the Dtpa ligand are coordinated to the central Eu³⁺ ion. The νₐ(COO) band of H₃Dtpa at 1733 cm⁻¹ disappears in the FT-IR spectrum of I. Also, it can be found that the νₐ(COO) band of I appears at 1601 cm⁻¹, revealing a red shift (33 cm⁻¹) compared with that (1634 cm⁻¹) of H₃Dtpa. The ν(CO) band of I appears at 1405 cm⁻¹, showing a blue shift (54 cm⁻¹) compared with that (1351 cm⁻¹) of H₃Dtpa. These changes confirm that the oxygen atoms of carboxyl groups are also coordinated to the central Eu³⁺ ion. In addition, there is a broad ν(OH) band near 3416 cm⁻¹, which reveals the presence of H₂O in I.

The ν(C–N) band of II appears at 930 cm⁻¹, which displays a red shift (30 cm⁻¹) compared with that (960 cm⁻¹) of H₃Dtpa. It indicates that the amine nitrogen atoms of the H₂Dtpa ligand are coordinated to the central Eu³⁺ ion. The νₐ(COO) band of H₂Dtpa at 1733 cm⁻¹ disappears in the FT-IR spectrum of II, while the νₐ(COO) band of II appears at 1597 cm⁻¹, revealing a red shift (37 cm⁻¹) compared with that (1634 cm⁻¹) of H₂Dtpa. The ν(CO) band of II appears at 1403 cm⁻¹, showing a blue shift (52 cm⁻¹) compared with that (1351 cm⁻¹) of H₂Dtpa. These changes confirm that the oxygen atoms of carboxyl groups are also coordinated to the Eu³⁺ ion. In addition, there is a broad ν(OH) band near 3432 cm⁻¹, which reveals the presence of H₂O in II.

UV-Vis absorption spectra of I and II in water solution at room temperature present a narrow absorption peak at 395 nm, because, they have the same metal ion and ligand. However, II displays a stronger absorbance than that of I. Maybe, it is because II takes a binuclear molecular structure, which causes the distortion of the ligand field.

The emission spectra of I and II were also investigated in an aqueous solution at room temperature, when measured at 700 V with the maximum excitation wavelength at 395 nm. Complex I exhibits a strong fluorescence intensity but presents a broad emission peak.