Syntheses and Structures of Nine-Coordinate
NH₄[Hoᴵᴵᴵ(Edta)(H₂O)₃] · 1.5H₂O, (NH₄)₄[Hoᴵᴵᴵ(Dtpa)₂] · 9H₂O,
and (NH₄)₃[Hoᴵᴵᴵ(Ttha)] · 5H₂O Complexes

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INTRODUCTION

The rare-earth metals and their corresponding compounds have been attracting researchers’ great interest due to their diverse biological activities and many potential applications [1–3]. For instance, certain Nd(III) complexes have good antiinflammation activity; some Gd(III) complexes were often used as contrast agent in magnetic resonance imaging (MRI) diagnosis for its most high-spin (seven) single electrons [4]; the Tb(III) and Eu(III) complexes have been used to diagnose some diseases qua the ionic probes for their characteristic fluorescence [5]. Some Er(III) complexes were used in synovectomy of the rheumatoid knee and curing skin disease [6]. To be similar to the same reason, because many Ho(III) complexes can usually be applied in the diagnoses and therapies of some disease, it is very important to determine and investigate their molecular and crystal structures.

In general, the rare-earth metal ions can form eight-, nine-, and ten-coordinate complexes with various amphopolycarboxylic acid ligands, since they have different ionic radii and electronic configurations. In the past several years of research work, it has also been found that these rare-earth metal complexes have some intrinsic laws in coordination number and coordinate structure [7–12]. Taking rare-earth metal complexes with ethylenediamine–N,N,N',N'-tetaacetic acid (Edta), diethylenetriamine–N,N,N',N'',N''',N'''-pentaacetic acid (Dtpa), and triethylenetetramine–N,N,N',N'',N''',N'''-hexaacetic acid (Ttha) ligands, for example, the La³⁺ and Ce³⁺ ions having particularly large ionic radius and few f-orbital electrons can form ten-coordinate complex [13]. Contrarily, the Tm³⁺, Yb³⁺, and Lu³⁺ ions having much smaller ionic radii and many f-orbital electrons can form eight-coordinate complexes [14]. Then, the rest of them, such as Eu³⁺, Gd³⁺, Tb³⁺, Dy³⁺, Er³⁺, and Ho³⁺ ions, can form only nine-coordinate complexes [15–19]. As a part of our ongoing research in this field, what we eagerly want to know is the differ-

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ences between these nine-coordinate Ho(III) complexes with Edta, Dtpa, and Ttha ligands and the effects caused by these differences. Therefore, three title complexes were synthesized to compare their molecular and crystal structures. To the best our knowledge, the molecular and crystal structures of the Ho(III) complex are reported for the first time.

EXPERIMENTAL

Synthesis of NH₄[Ho(III)(Edta)(H₂O)]·1.5H₂O (I). H₄Edta (1.47 g, 5.0 mmol) was added to 100 ml of water, and H₂O₃ powder (0.94 g, 2.5 mmol) was slowly added to above solution. The solution became transparent when the mixture had been stirred and refluxed for 15 h, and then the pH was adjusted to 6.5 with NH₃ aqueous solution. Finally the solution was concentrated to 25 ml. A white crystal appeared after three weeks at room temperature. The C, H, and N were determined by element analysis and Ho was analyzed using oxalic acid, respectively.

For C₁₇H₂₅HoN₅O₁₂.5
analytical (%): Ho, 29.97; C, 21.75; H, 4.56; N, 7.61.
Found (%): Ho, 29.98; C, 21.71; H, 4.57; N, 7.63.

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

Synthesis of (NH₄)₃[Ho(III)(Dtpa)]·9H₂O (II). H₄Dtpa (1.82 g, 5.0 mmol) was added to 100 ml of water, and H₂O₃ powder (0.94 g, 2.5 mmol) was slowly added to above solution. The solution became transparent when the mixture had been stirred and refluxed for 15 h, and then the pH was adjusted to 6.5 with NH₃ aqueous solution. Finally the solution was concentrated to 25 ml. A white crystal appeared after seven weeks at room temperature. The C, H, and N were determined by element analysis and the Ho was analyzed using oxalic acid, respectively.

For C₂₉H₄₀HoN₁₀O₂₉
analytical (%): Ho, 20.66; C, 27.13; H, 5.81; N, 12.31.
Found (%): Ho, 20.66; C, 27.13; H, 5.81; N, 12.31.

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

Synthesis of (NH₄)₃[Ho(III)(Ttha)]·5H₂O (III). H₄Ttha (2.47 g, 5.0 mmol) was added to 100 ml of water, and H₂O₃ powder (0.94 g, 2.5 mmol) was added to above solution slowly. The solution became transparent when the mixture had been stirred and refluxed for 7 h, and then the pH was adjusted to 6.5 with NH₃ aqueous solution. Finally the solution was concentrated to 25 ml. A white crystal appeared after eleven weeks at room temperature. The C, H, and N were determined by element analysis and the Ho was analyzed using oxalic acid, respectively.

For C₁₈H₄₆HoN₇O₁₇
analytical (%): Ho, 20.68; C, 27.11; H, 5.81; N, 12.30.
Found (%): Ho, 20.66; C, 27.13; H, 5.81; N, 12.31.

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

X-ray Structure Determination. Data were collected with a Bruker SMART CCD type X-ray diffractometer system using graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved by directed methods. The total non-hydrogen atoms were refined with anisotropic thermal parameters by full-matrix. All calculations were carried out using the SHELXTL-97 program on PDP11/44 and Pentium MMX/166 computers. The crystallographic characteristics and X-ray experiment details are presented in Table 1, the coordinates and thermal parameters of atoms are listed in Table 2, the bond lengths and angles of the structures of complexes I–III are given in Table 3. Molecular structures of these complexes are shown in Fig. 1, the coordination polyhedrons of the complexes are presented in Fig. 2, and molecular packing of the complexes in unit cell is shown in Fig. 3.

IR determination. H₄Edta, H₄Dtpa, and H₄Ttha and complexes I, II, and III were milled and pressed into slice with KBr, respectively. Their IR spectra were determined with a Shimadzu-IR 408 spectrograph.

RESULTS AND DISCUSSION

From IR spectrum complex of I, it can be seen that ν(C–N) band is at 1083 cm⁻¹ and red-shifts 45 cm⁻¹ comparing with that of H₄Edta (1128 cm⁻¹). It indicates that the amine nitrogen atoms from Edta ligand are coordinated by central Ho³⁺ ion. The all ν(CH) bands in H₄Edta at 1690 cm⁻¹ disappeared in the complex and it shows that there is no free carboxylic group in complex I. The ν(CH) band at 1610 cm⁻¹ of H₄Edta shifts to 1575 cm⁻¹ and ν(CO) at 1390 cm⁻¹ of H₄Edta shifts to 1405 cm⁻¹ in complex. This fact confirms that the oxygen atoms of all –COO⁻ groups are coordinated by central Ho³⁺ ion too. There is a wide ν(OH) band of H₂O near 3430 cm⁻¹ showing the existence of a water molecule in complex I.

From IR spectrum of complex II, it can be seen that ν(C–N) band is at 1108 cm⁻¹ and red-shifts 28 cm⁻¹ comparing with that of H₄Dtpa (1128 cm⁻¹), which indicates that the amine nitrogens atoms from Dtpa ligand are coordinated by central Ho³⁺ ion. The all ν(CO) bands in H₄Dtpa at 1728 cm⁻¹ disappeared in the complex. The all ν(ν(CO)) at 1728 cm⁻¹ of H₄Dtpa at 1728 cm⁻¹ in complex. It shows that there is no free carboxylic group in complex II. The ν(ν(CO)) at 1642 cm⁻¹ of H₄Dtpa shifts to 1582 cm⁻¹ and ν(ν(CO)) at 1413 cm⁻¹ of H₄Dtpa shifts to 1395 cm⁻¹ (bridge carboxylic groups) and 1612 cm⁻¹ (non-bridge carboxylic