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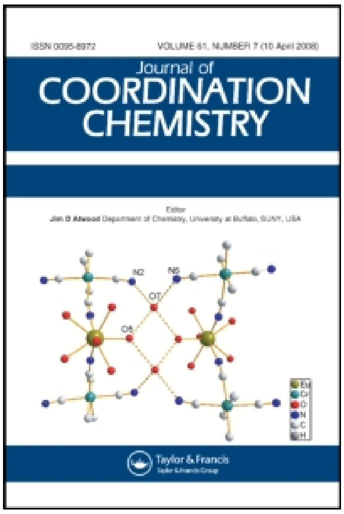

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
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First published on: 13 July 2010

To cite this Article Wang, Jun , Hu, Ping , Liu, Bin , Jin, Xudong , Kong, Yumei , Gao, Jingqun , Wang, Dan , Wang, Baoxin , Xu, Rui and Zhang, Xiangdong(2010) 'Investigation on coordination number and geometrical conformation of rare earth complexes with catenulate aminopolycarboxylic acid ligands', Journal of Coordination Chemistry, 63: 13, 2193 — 2222, First published on: 13 July 2010 (iFirst)

To link to this Article: DOI: 10.1080/00958972.2010.500378

URL: http://dx.doi.org/10.1080/00958972.2010.500378

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Journal of Coordination Chemistry
Vol. 63, No. 13, 10 July 2010, 2193–2222

Investigation on coordination number and geometrical conformation of rare earth complexes with catenulate aminopolycarboxylic acid ligands

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(*Received 18 February 2010; in final form 22 April 2010*)

This article gives an overview on the molecular and crystal structures of rare earth metal (REM) complexes with a series of aminopolycarboxylic acid (APCA) ligands, nitrilotriacetic acid (NTA), ethylenediamine-*N,N,N′,N′*-tetraacetic acid (EDTA), diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid (DTPA), and triethylenetetramine-*N,N,N′,N″,N‴,N‴*-hexaacetic acid (TTHA). Among the REM complexes with the same APCA ligand, the coordination law of coordination numbers and geometrical conformation are discussed. The research results indicate that the coordination numbers and geometrical conformation of REM complexes with various APCA ligands mainly depend on the ionic radii and electronic configurations of central REM ions, the shape of APCA ligands, as well as the category of counter ion.

Keywords: Rare earth metal (REM) complexes; Aminopolycarboxylic acid (APCA); Coordination number; Geometrical conformation; Coordination law

Abbreviations: REM – rare earth metal; APCA – aminopolycarboxylic acid; NTA – nitrilotriacetic acid; EDTA – ethylenediamine-*N,N,N′,N′*-tetraacetic acid; DTPA – diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid; TTHA – triethylenetetramine-*N,N,N′,N″,N‴,N‴*-hexaacetic acid; SAP – square antiprism; MCSAP – monocapped square antiprism; BCSAP – bicapped square antiprism; TCTP – tricapped trigonal prism; BCTAP – bicapped trigonal antiprism

1. Introduction

The investigation of the physical and chemical properties of the rare earth metals (REMs) and their compounds have been attracting attention for many years because they play an increasingly important role in the applications of function materials, preparations of special catalysts, research and development of new medicines, and other aspects. [1–9]. For instance, some Gd^{III} complexes are used as contrast agents for magnetic resonance imaging (MRI) diagnoses since there are seven high-spin single

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2010 Taylor & Francis
DOI: 10.1080/00958972.2010.500378

electrons in the f-orbits of Gd^{III}, the most in all the REM ions [10–17]. Eu^{III} and Tb^{III} complexes have been used as ionic probes to study the functions and structures of biological molecules because of their characteristic fluorescence [18–21]. In addition, by means of appropriate half-life and moderate energy, many radioactive REM ions such as ^{86}Y^{III}, ^{149}Pm^{III}, ^{153}Sm^{III}, ^{166}Ho^{III}, and ^{172}Lu^{III} can emit radiation, whose complexes are adopted to diagnose and treat various tumors [22–26]. Although many REM ions, whether they are provided with radioactivity or not, are regarded as therapy drugs, diagnostic reagents, and good effects of treatment and diagnosis, there are still many limitations and insufficiencies [27, 28]. Especially, after completing the treatment or diagnosis, the treatment drugs or diagnosis reagents still stay in the patient's body chronically, which is not expected. In general, patients and doctors expect that when the treatment drugs or diagnosis reagents enter the human body, they are steady and soluble, and then are quickly excreted [29]. Synchronously, it is expected that these treatment drugs and diagnosis reagents possess selectivity and affinity to the corresponding purpose [30]. However, all improvements should be based on the knowledge of the structures of REM complexes. In addition, because all REM ions can yield stable complexes and construct various perfect coordinate structures with aminopolycarboxylic acid (APCA) ligands, their structural information, spectral characteristics, and chemical properties have engaged chemists' attention for many years. Generally, the coordination number and geometrical conformation of transition metal complexes depend on the ionic radius, electronic configuration, and oxidation state of central metal ions as well as the shape of APCA ligands [31–43]. Nevertheless, even though the splitting energy of f-orbit is fairly low in ligand field, it is a very important factor influencing the coordination number and geometrical conformation of REM complexes.

It is considered that REM complexes are similar in their structures due to the tiny difference among the radii of the REMs and little effect by ligand field. However, several years of effort of synthesis and determination of REM complexes with APCA ligands convinces us that the coordination number and geometrical conformation of these complexes are rich and diverse, and to a certain extent, rely on the shape of the ligand.

Differing from transition metal ions, the coordination number of REM complexes with APCA ligands is usually eight, nine, or ten in aqueous medium and solid state owing to the relatively big ionic radii. The APCA occupies the majority of coordination sites and the rest are generally occupied by water, small anions, or small neutral molecules. In general, nine-coordinate complexes are chosen as an example to explain how to ascertain their geometrical conformation in the crystal state. The commonest and most perfect geometrical conformations are tricapped trigonal prism (TCTP) and monocapped square antiprism (MCSAP), as shown in figure 1. Without steric effects of chelate rings, Guggenberger and Muetterties considered TCTP the most favorable polyhedron modality for a nine-coordinate (ML$_9$) complex [44]. When the square-basal plane (1, 4, 3, 7) of a MCSAP is bent above along the (4, 7) diagonal, the MCSAP will become TCTP. There are three vital distinguishing features between these two geometrical conformations. The first is the dihedral angle between the trigonal surface Δ(4, 5, 6) and the trigonal surface Δ(7, 8, 9), which is 180° for TCTP and 163.5° for MCSAP in perfect polyhedra. The second is the dihedral angle between the trigonal surface Δ(1, 4, 7) and the trigonal surface Δ(3, 4, 7), which should be 26.4° for TCTP and 0° for MCSAP, respectively. The third is the mean deviation in basal plane

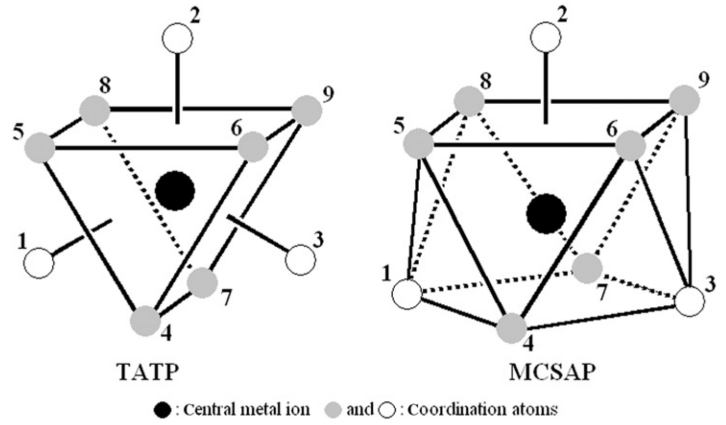
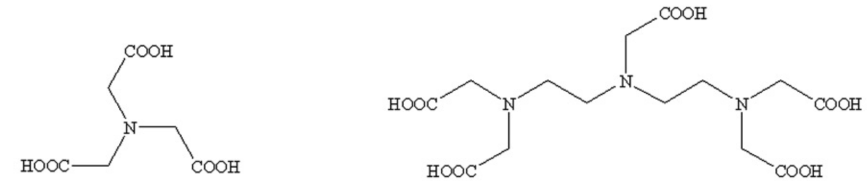


Figure 1. Basic coordination configurations of the nine-coordinate rare earth metal complexes with APCA ligands.

Δ(1, 4, 3), which should be small for MCSAP. For nine-coordinate REM complexes, their structures are usually described as distorted TCTP or distorted MCSAP. Because there is a close relationship between these two geometrical conformations, it is possible to describe a particular structure as any of two conformations. For eight- and ten-coordinate complexes, there is a close relationship between their geometrical conformation and MCSAP. When the second ligand above the square basal plane (5, 6, 9, 8) in MCSAP is taken away, the nine-coordinate MCSAP will become an eight-coordinate square antiprism (SAP) conformation. Contrarily, when another coordinate atom as the tenth ligand is added above the square basal plane (1, 4, 3, 7) in MCSAP, the nine-coordinate MCSAP will become a ten-coordinate bicapped square antiprism (BCSAP). Otherwise, if two opposite coordination bonds in eight-coordinate SAP become considerably longer than others, the eight-coordinate bicapped trigonal antiprism (BCTAP) will occur. Up to now, each REM complex with an APCA ligand (as shown in scheme 1) adopts one of these five geometrical conformations: TCTP, MCSAP, SAP, BCSAP, and BCTAP, according to the ionic radius, electronic configuration, and oxidation state of REM ions as well as the shape of ligands.

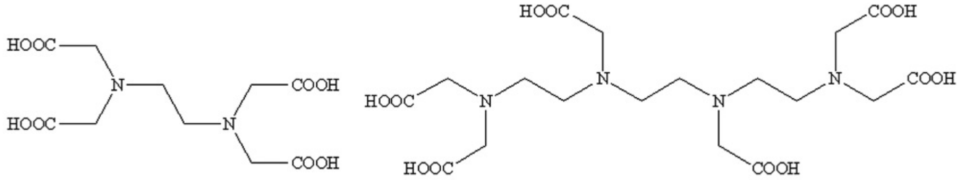
2. Nitrilotriacetic acid series

Nitrilotriacetic acid (NTA) is a tetradentateAPCA. In general, the coordination number of REM complexes with APCA ligands is eight, nine, or ten, and therefore the trivalent REM ions should coordinate one or two NTA ligands. Three carboxyl groups existing in one NTA ligand, however, make it easy to yield a series of neutral, insoluble, and non-crystalline REM complexes. Consequently, this handicapped studies on coordination number and geometrical conformation of REM complexes with NTA. Recently, a series of soluble REM complexes with two NTA ligands was reported, adopting various methods such as long heating, accurately adjusting pH values, and altering



nta = nitrilotriacetic acid

dtpa = diethylenetriaminepentaacetic acid



edta = ethylenediaminetetraacetic acid

ttha = triethylenetetraminehexaacetic acid

Scheme 1. Schematic representation of aminopolycarboxylic acids used in this review.

Table 1. Molecular and crystal structures of rare earth metal complexes with NTA.

Complex	Coordination number	Crystal system	Space group	Coordinate conformation	Reference
$K_3[Nd^{III}(NTA)_2(H_2O)]\cdot 6H_2O$	9	Monoclinic	$C2/c$	MCSAP	[49]
$K_3[Gd^{III}(NTA)_2(H_2O)]\cdot 6H_2O$	9	Monoclinic	$C2/c$	MCSAP	[50, 51]
$K_3[Tb^{III}(NTA)_2(H_2O)]\cdot 5.5H_2O$	9	Orthorhombic	$Pccn$	MCSAP	[46]
$K_3[Dy^{III}(NTA)_2(H_2O)]\cdot 5H_2O$	9	Monoclinic	$C2/c$	TCTP	[52]
$K_3[Ho^{III}(NTA)_2(H_2O)]\cdot 5H_2O$	9	Monoclinic	$C2/c$	MCSAP	[53]
$K_3[Er^{III}(NTA)_2(H_2O)]\cdot 5H_2O$	9	Monoclinic	$C2/c$	MCSAP	[49]
$K_3[Yb^{III}(NTA)_2(H_2O)]\cdot 5H_2O$	9	Monoclinic	$C2/c$	MCSAP	[45, 46]
$K_3[Y^{III}(NTA)_2(H_2O)]\cdot 6H_2O$	9	Monoclinic	$C2/c$	MCSAP	[54]
$K_3[Yb^{III}(NTA)_2]\cdot 5H_2O$	8	Monoclinic	$P2_1/c$	SAP	[45, 47, 48]
$KNa_2[Tb^{III}(NTA)_2(H_2O)]\cdot 5H_2O$	9	Orthorhombic	$Pnaa$	MCSAP	[55]
$Na_3[Eu^{III}(NTA)_2(H_2O)]\cdot 5H_2O$	9	Orthorhombic	$Pnaa$	MCSAP	[55]
$Na_3[Dy^{III}(NTA)_2(H_2O)]\cdot 5.5H_2O$	9	Orthorhombic	$Pccn$	TCTP	[56]
$Na_3[Yb^{III}(NTA)_2]\cdot 6H_2O$	8	Monoclinic	$P2_1/c$	SAP	[45]
$(NH_4)_3[Tb^{III}(NTA)_2(H_2O)]\cdot 4H_2O$	9	Monoclinic	$C2/c$	MCSAP	[57]
$(NH_4)_3[Dy^{III}(NTA)_2]$	8	Monoclinic	$C2/c$	BCTAP	[52]
$(NH_4)_3[Ho^{III}(NTA)_2]$	8	Rhombohedral	$R3c$	BCTAP	[58]
$(NH_4)_3[Er^{III}(NTA)_2]$	8	Rhombohedral	$R3c$	BCTAP	[57]
$[Pr^{III}(NTA)(H_2O)_2]\cdot H_2O$	9	Orthorhombic	$Pbca$	MCSAP	[51]
$[Tm^{III}(NTA)(H_2O)_2]\cdot 2H_2O$	8	Orthorhombic	$P2_12_12_1$	SAP	[51, 59]
$(HPy)_2[Gd^{III}(HNTa)(NTA)(H_2O)]\cdot 5H_2O$	9	Monoclinic	$P2_1/n$	MCSAP	[58]

the order of adding reagents. Fortunately, many single crystals were also determined successfully. They are all listed in table 1.

The results indicate that the coordination number and geometrical conformation of these complexes lie on the ionic radius and electronic configuration of the central REM ions. Otherwise, different counter ions also affect the coordination number and geometrical conformation. For the same counter ion, the complexes possess their own coordinate law and structural characteristics. In the arrangement of REM ions, the Yb^{III} ion is considered as the division of the coordination number and geometrical conformation between eight- and nine-coordination for potassium salts of the REM

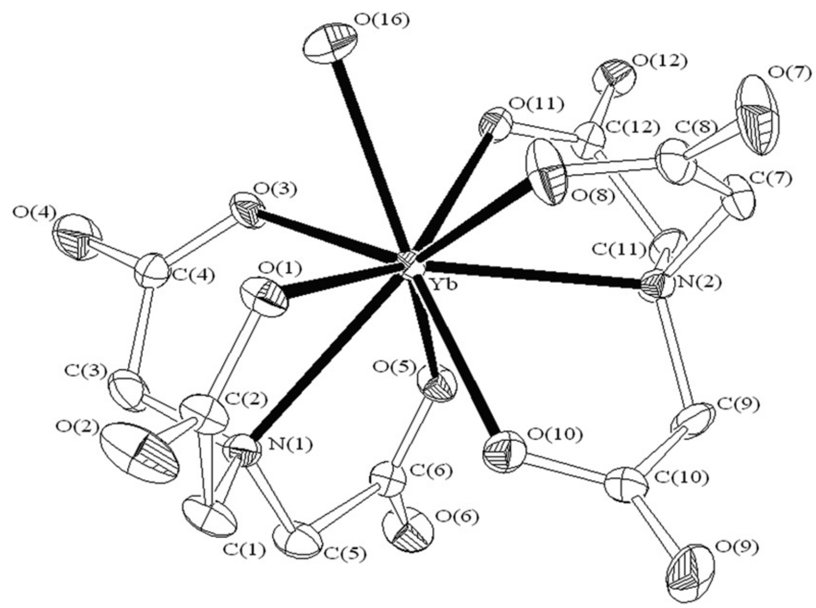


Figure 2. Molecular structure of $[Yb^{III}(NTA)_2(H_2O)]^{3-}$ coordination anion in $K_3[Yb^{III}(NTA)_2(H_2O)] \cdot 5H_2O$.

complexes with NTA ligands, while the Dy^{III} ion is the division for the ammonium salts of the REM complexes.

2.1. *Potassium salts*

For potassium salts of REM complexes with NTA ligand, the ratio of REM ions to NTA ligands is 1 : 2. From table 1, it can be seen that Yb^{III} can be either nine-coordinate, such as $K_3[Yb^{III}(NTA)_2(H_2O)] \cdot 5H_2O$ [45, 46] (figure 2) or eight-coordinate, such as $K_3[Yb^{III}(NTA)_2] \cdot 5H_2O$ [45, 47, 48] (figure 3). So, the Yb^{III} ion is regarded as the division between the nine-coordinate and eight-coordinate structures. The REM ions ahead of the Yb^{III} ion, except for La^{III} and Ce^{III} ions with big ionic radii, are nine-coordinate, such as $K_3[Nd^{III}(NTA)_2(H_2O)] \cdot 12H_2O$ [49], $K_3[Gd^{III}(NTA)_2(H_2O)] \cdot 6H_2O$ [50, 51], $K_3[Tb^{III}(NTA)_2(H_2O)] \cdot 5.5H_2O$ [46], $K_3[Dy^{III}(NTA)_2(H_2O)] \cdot 5H_2O$ [52], $K_3[Ho^{III}(NTA)_2(H_2O)] \cdot 5H_2O$ [53], $K_3[Er^{III}(NTA)_2(H_2O)] \cdot 10H_2O$ [49], and $K_3[Y^{III}(NTA)_2(H_2O)] \cdot 6H_2O$ [54]. It is because they have relatively big ionic radii, ranging from 1.123 to 1.030 Å, and the number of f-orbital electrons is appropriate, ranging from 3 to 11. Nevertheless, Lu^{III}, whose ionic radius is the smallest of all the REM ions, is only eight-coordinate. The La^{III} and Ce^{III} ions may be nine-coordinate or ten-coordinate, and the two possibilities exist synchronously.

For the nine-coordinate structure, two NTA ligands occupy eight coordination sites with two amine nitrogens and six carboxyl oxygens; one oxygen from water molecule occupies the capped site yielding a pseudo MCSAP conformation. Because of repulsion from the top plane, the bond distance between the central REM ion and the capped coordinate atom is long. For the eight-coordinate structure, two NTA ligands occupy

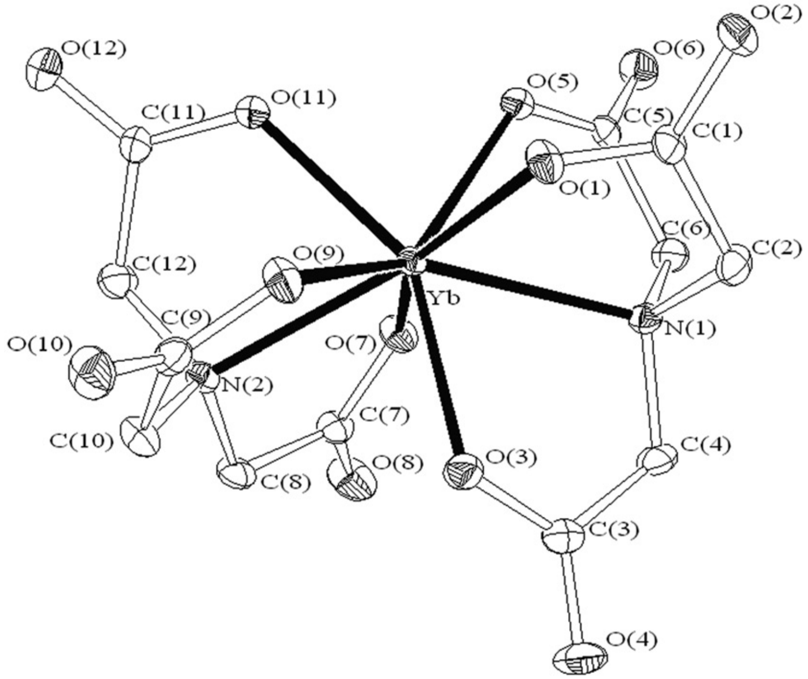


Figure 3. Molecular structure of $[Yb^{III}(NTA)_2]^{3-}$ coordination anion in $K_3[Yb^{III}(NTA)_2] \cdot 5H_2O$.

the whole coordination yielding an almost standard SAP conformation. With negligible repulsion force, the bond distances of the central REM ion and all coordinate oxygens are similar.

2.2. *Sodium salts*

For sodium salts of REM complexes with NTA, the change rules of coordination number and geometrical conformation are similar to those of potassium salts. These complexes are all nine-coordinate except for $Na_3[Yb^{III}(NTA)_2] \cdot 5H_2O$ [45] (figure 4), which is similar to $K_3[Yb^{III}(NTA)_2] \cdot 5H_2O$ [45, 48] and adopts an eight-coordinate structure with SAP conformation, crystallizing in monoclinic system with $P2_1/n$ space group. In these nine-coordinate complexes, the $Na_3[Eu^{III}(NTA)_2(H_2O)] \cdot 5H_2O$ [55] and $KNa_2[Tb^{III}(NTA)_2(H_2O)] \cdot 5H_2O$ [55] crystallize in the orthorhombic system with *Pnaa* space group and possess MCSAP conformation, while $Na_3[Dy^{III}(NTA)_2(H_2O)] \cdot 5.5H_2O$ [56] (figure 5) crystallizes in orthorhombic system with *Pccn* space group and adopts a TCTP conformation.

2.3. *Ammonium salts*

For the ammonium salts of REM complexes with NTA ligand, there are some differences in the coordinate law and geometrical conformation compared with the corresponding potassium and sodium salts. Here, the Dy^{III} ion should still be

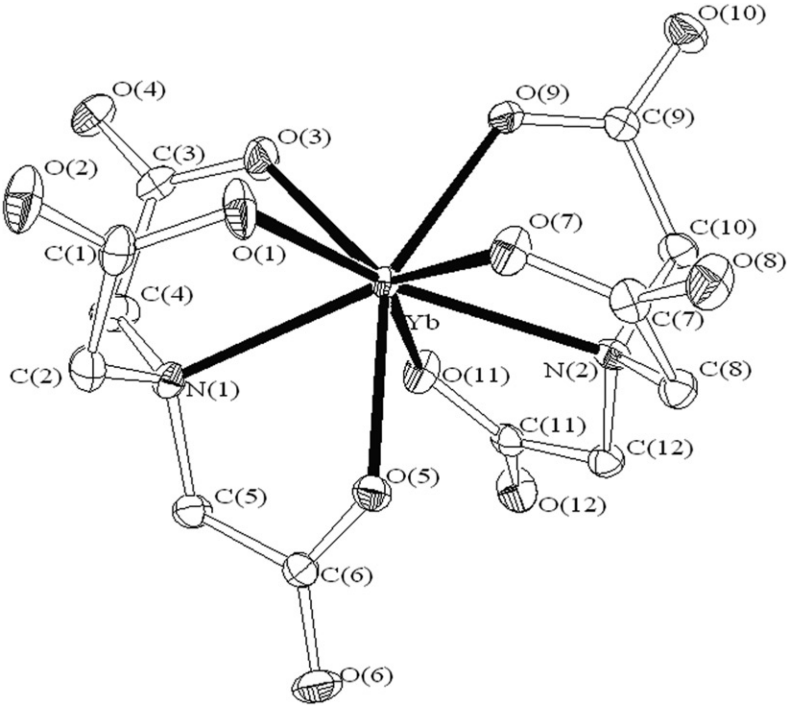


Figure 4. Molecular structure of $[Yb^{III}(NTA)_2]^{3-}$ coordination anion in $Na_3[Yb^{III}(NTA)_2] \cdot 5H_2O$.

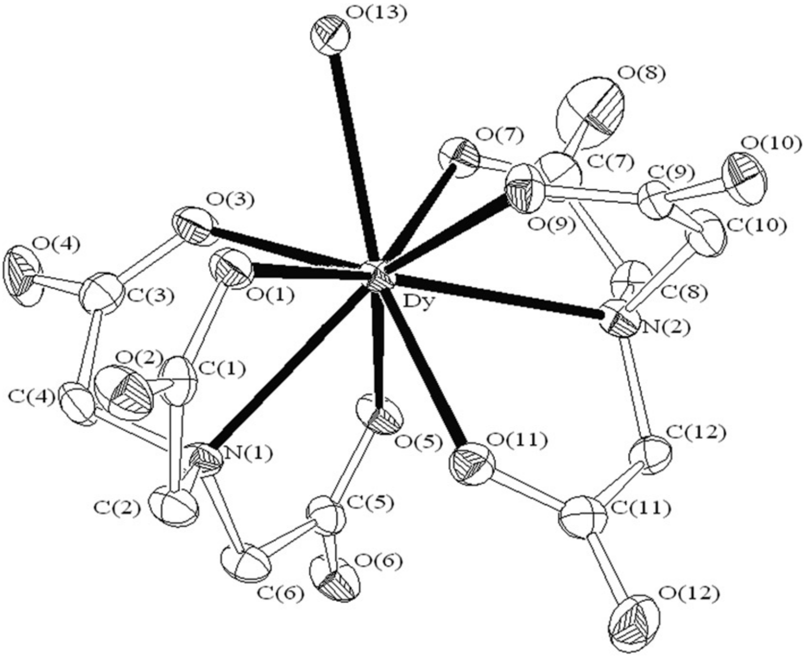


Figure 5. Molecular structure of $[Dy^{III}(NTA)_2(H_2O)]^{3-}$ coordination anion in $Na_3[Dy^{III}(NTA)_2(H_2O)] \cdot 5.5H_2O$.

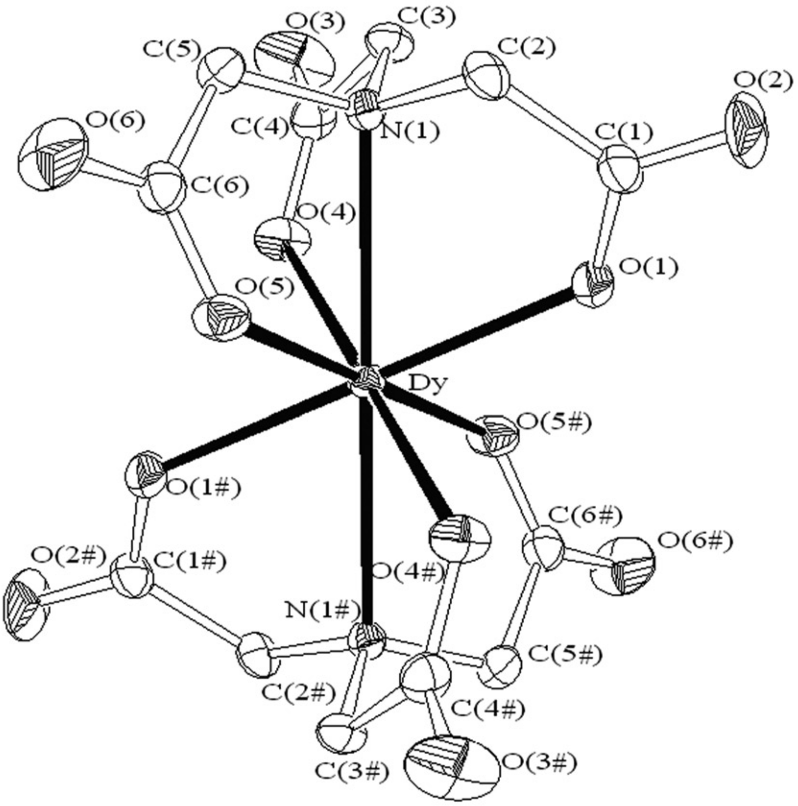


Figure 6. Molecular structure of $[Dy^{III}(NTA)_2]^{3-}$ coordination anion in $(NH_4)_3[Dy^{III}(NTA)_2]$.

considered as the division between the eight-coordinate and nine-coordinate structures. As shown in figure 6, the $(NH_4)_3[Dy^{III}(NTA)_2]$ [52] adopts an eight-coordinate structure, but crystallizes in monoclinic system with $C2/c$ space group. The REM ions ahead of Dy^{III} are nine-coordinate, such as $(NH_4)_3[Tb^{III}(NTA)_2(H_2O)] \cdot 6H_2O$ [57] (figure 7), which crystallizes in monoclinic system with $C2/c$ space group and adopts a MCSAP conformation. However, those ions behind Dy^{III} ion are eight-coordinate, such as $(NH_4)_3[Er^{III}(NTA)_2]$ [57] and $(NH_4)_3[Ho^{III}(NTA)_2]$ [58], which crystallize in rhombohedral system with $R3c$ space group and adopt a BCTAP conformation. Particularly, the $(NH_4)_3[Dy^{III}(NTA)_2]$ [52] almost possesses a standard BCTAP conformation, and the whole molecule has a highly centrosymmetric structure.

2.4. *Neutral complexes*

In both Pr^{III} and Tm^{III} complexes with NTA ligand, there is no counter ion, no matter what method is adopted. Perhaps it is because the Pr^{III} and Tm^{III} ions have particular ionic radii (1.000 and 1.020 Å) and electronic configurations ($4f^2$ and $4f^{12}$), respectively, which cause both to be coordinated by only one NTA ligand yielding electroneutral complexes. These two complexes are isomorphic but not isostructural.

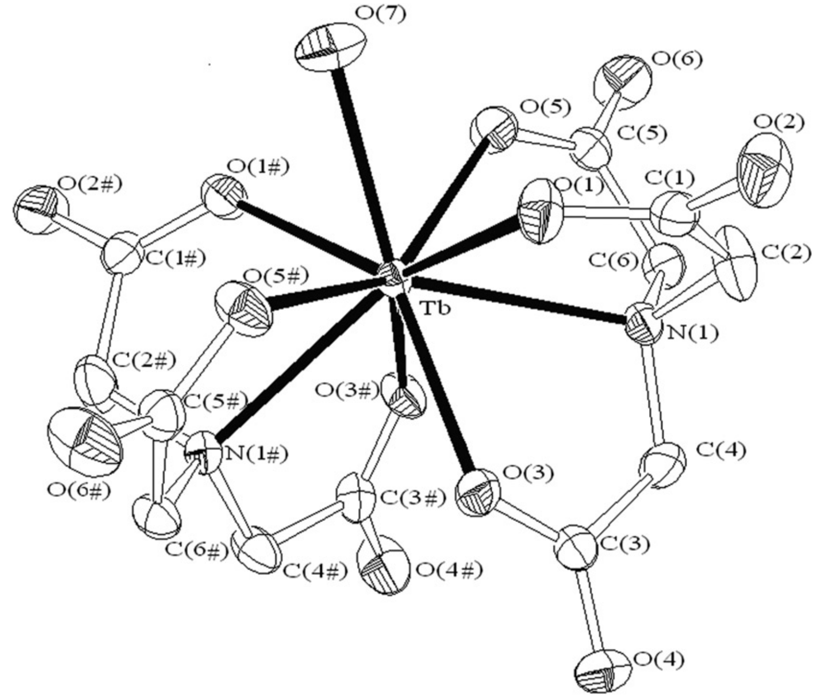


Figure 7. Molecular structure of $[Tb^{III}(NTA)_2(H_2O)]^{3-}$ coordination anion in $(NH_4)_3[Tb^{III}(NTA)_2(H_2O)] \cdot 6H_2O$.

The $[Pr^{III}(NTA)(H_2O)_2] \cdot H_2O$ [51] possesses a nine-coordinate structure, crystallizing in the orthorhombic system with *Pbca* space group and adopts a MCSAP conformation, as shown in figure 8, whereas $[Tm^{III}(NTA)(H_2O)_2] \cdot 2H_2O$ [51, 59] is eight-coordinate, crystallizing in the orthorhombic system with a $P2_12_12_1$ space group and adopting a SAP conformation, as shown in figure 9. It seems to be happenchance but actually is attributed to the integrative effects of their particular ionic radii and electronic configurations.

For $[Pr^{III}(NTA)(H_2O)_2] \cdot H_2O$, NTA provides four coordination sites, an amine nitrogen and three carboxyl oxygens, and two adjacent NTA ligands provide three coordination oxygens together. Other oxygens are from two waters. For $[Tm^{III}(NTA)(H_2O)_2] \cdot 2H_2O$ [51, 59], the central metal only coordinates two oxygens from two adjacent NTA ligands, and others are the same as in $[Pr^{III}(NTA)(H_2O)_2] \cdot H_2O$ [51].

2.5. *Protonated complexes*

Gd^{III} yields many nine-coordinate complexes with various APCA ligands, indicating that Gd^{III} complexes tend to adopt nine-coordinate structures. In order to further affirm this tendency, pyridine was utilized as the counter ion to validate whether the coordination number and/or geometrical conformation of the Gd^{III} complex underwent change, instead of potassium, sodium, and ammonium counter ions. As a result, $(HPy)_2[Gd^{III}(HNTA)(NTA)(H_2O)] \cdot 5H_2O$ [58], as shown in figure 10, was obtained

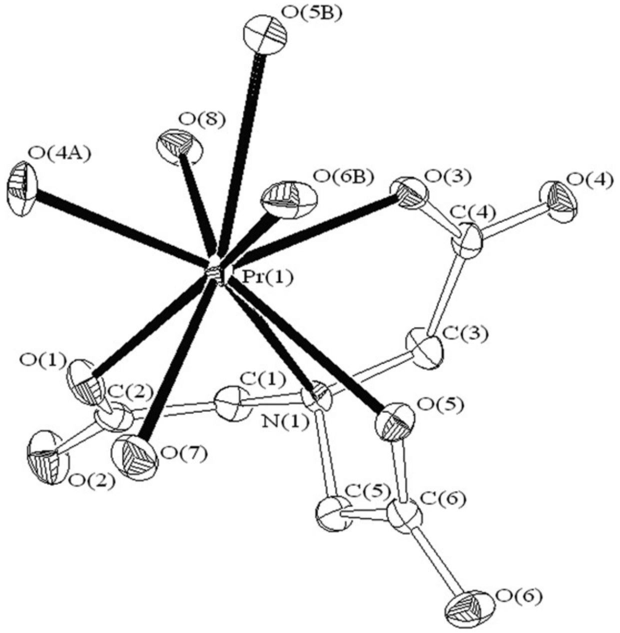


Figure 8. Molecular structure of $[Pr^{III}(NTA)(H_2O)_2]$ in $[Pr^{III}(NTA)(H_2O)_2] \cdot H_2O$.

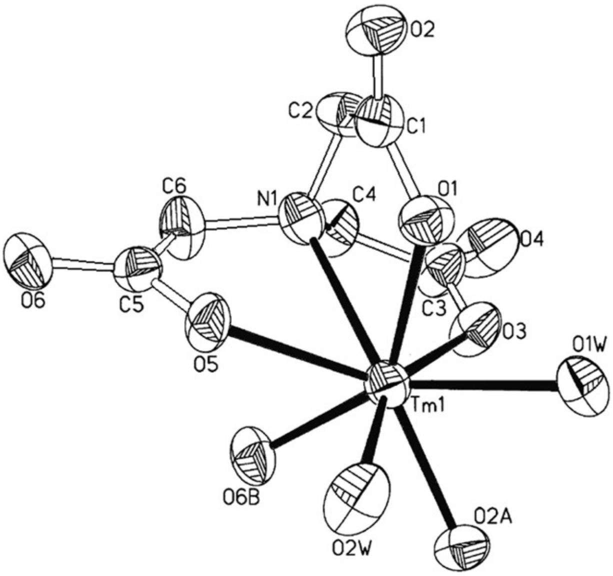


Figure 9. Molecular structure of $[Tm^{III}(NTA)(H_2O)_2]$ in $[Tm^{III}(NTA)(H_2O)_2] \cdot 2H_2O$.

and was the first protonated complex with NTA ligand. Although one carboxyl group of NTA ligand is protonated in an acidic solution (pH = 4.20), the Gd^{III} complex still keeps the nine-coordinate structure. The big ionic radius and seven high-spin f-orbital electrons of Gd^{III} result in the tendency to nine-coordinate structures.

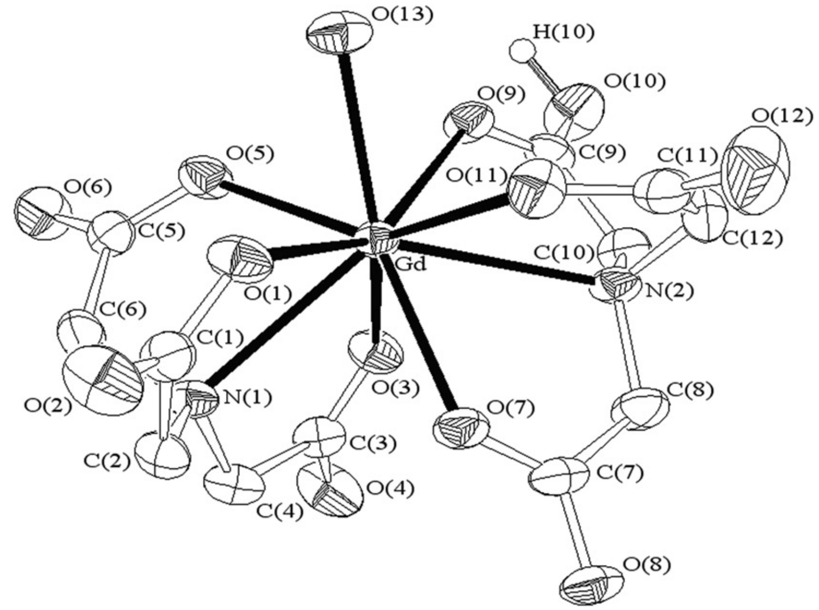


Figure 10. Molecular structure of $[Gd^{III}(HNTA)(NTA)(H_2O)]^{2-}$ coordination anion in $(HPy)_2[Gd^{III}(HNTA)(NTA)(H_2O)] \cdot 5H_2O$.

The five-membered ring composed of Gd^{III}, N(2), C(12), C(11), and O(11) almost becomes vertical simultaneously with two other five-membered rings, Gd(1)N(2)C(8)C(7)O(7) and Gd(1)N(2)C(10)C(9)O(9). Because the Gd(1)–O(9) (2.478(3) Å) and Gd(1)–O(7) (2.418(3) Å) bond distances are both longer than the bond distance of Gd(1)–O(13), in which O(9) comes from the protonated carboxyl group, the O(7) comes from the hydrogen-bonded carboxyl group and O(13) is the capped atom, respectively, so that the geometrical conformation of the complex anion is seriously distorted.

Even so, the oxygen from the protonated carboxyl still coordinates to Gd^{III}, keeping a nine-coordinate structure. The coordination capability of the protonated carboxyl in many kinds of APCA ligands should have decreased. So, there is usually a non-coordinated and free protonated carboxyl group in $[Fe^{III}(HEDTA)(H_2O)]$ [60], $[Ge^{IV}(HEDTA)(OH)]$ [61] and $[Ru^{III}(HEDTA)Cl] \cdot 2H_2O$ [62]. Of course, for those metal ions with big ionic radii and appropriate electronic configurations, they also tend to yield high-coordinate complexes or keep the original coordination number. That is, the oxygen from the protonated carboxyl group still coordinates, such as $[Fe^{II}(H_2O)_4][Fe^{II}(HEDTA)(H_2O)]_2 \cdot 4H_2O$ [31], $[Fe^{II}(H_2EDTA)(H_2O)] \cdot 2H_2O$ [21], $[Ti^{III}(HEDTA)(H_2O)] \cdot H_2O$ [32], $[V^{III}(HEDTA)(H_2O)] \cdot H_2O$ [32], $[Mn^{II}(H_2O)_4][Mn^{II}(HEDTA)(H_2O)]_2 \cdot 4H_2O$ [63], Ψ-seven-coordinate $[Sb^{III}(HEDTA)] \cdot H_2O$ [64] and ten-coordinate $[La^{III}(HEDTA)(H_2O)_4]$ [65], as well as eight-coordinate $[Yb^{III}(HEGTA)] \cdot 2H_2O$ (H_4EGTA = ethyleneglycol-bis(2-aminoethylether)-*N,N,N′,N′*-tetraacetic acid) [66]. In fact, the $(HPy)_2[Gd^{III}(HNTA)(NTA)(H_2O)] \cdot 5H_2O$ [58] is the first protonated complex with NTA ligand, although the coordination capability of NTA as a tetradentate ligand is not so strong as hexadentateEDTA, octadentate DTPA, and decadentate TTHA. That is to say, the Gd^{III} complexes have strong tendency to keep a nine-coordinate structure, even if their ligands change to some extent.

3. Ethylenediamine-*N,N,N′,N′*-tetraacetic acid series

Ethylenediamine-*N,N,N′,N′*-tetraacetic acid (EDTA), one of the commonest hexadentate ligands, occupies six coordination sites with four carboxyl oxygens and two amine nitrogens, leaving the remaining coordination sites to water, small anions or other small neutral molecules in REM complexes. Compared with other APCA ligands, the EDTA series was thoroughly studied by many researchers. Usually, REM complexes with the same coordination number possess similar geometrical conformation; eight-coordinate complexes adopt a SAP conformation, almost all nine-coordinate complexes adopt a MCSAP conformation, and ten-coordinate complexes have BCSAP conformation.

Transition metal complexes with APCA have various coordination numbers and crystal structures from the differences in ionic radius and electronic configuration of the metal ions. Whether the coordination number changes from six to seven, seven to eight, or eight to nine, the ionic radius of the metal ion always swells by an increment of about 0.20 Å. As to REMs, however, the difference in ionic radius from biggest to smallest is only 0.171 Å, which results in the change from eight-coordination to ten-coordination. Table 2 shows that the coordinate law of REM complexes with EDTA ligand are quite obvious: La^{III} and Ce^{III} with big ionic radii are ten-coordinate; most REM ions such as Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, and Ho^{III} are nine-coordinate; the rest, such as Er^{III}, Tm^{III}, Yb^{III}, and Lu^{III} ions, with small ionic radii are only eight-coordinate. The influence of ionic radius and f-orbit electronic configuration should not be neglected when coordination number and crystal structure of REM complexes with APCA ligands are prognosticated.

3.1. *Eight-coordinate complexes*

Increasing the ionic radius of the counter ion could make REM ions, if their ionic radius is appropriate, become eight-coordinate instead of nine-coordinate. $Cs[Dy^{III}(EDTA)(H_2O)_2]\cdot 3H_2O$ [67] (figure 11) and $Cs[Ho^{III}(EDTA)(H_2O)_2]\cdot 3H_2O$ [67] are typical examples, which crystallize in monoclinic system with $P2_1/c$ space group, and whose geometrical conformation belong to eight-coordinate SAP conformations.

However, the REM ions with reasonably big ionic radii remain nine-coordinate, no matter how big the radius of counter ion, such as $Cs[Nd^{III}(EDTA)(H_2O)_3]\cdot 3.5H_2O$ [67], $Cs[Sm^{III}(EDTA)(H_2O)_3]\cdot 4H_2O$ [67] and $Cs[Gd^{III}(EDTA)(H_2O)_3]\cdot 4H_2O$ [67]. For the cesium salts of EDTA series, REM ions ahead of Tb^{III}, including Tb^{III} ion, are nine-coordinate while those behind Tb^{III} ion are commonly eight-coordinate. Hence, the Tb^{III} ion is considered as the division between nine-coordinate and the eight-coordinate structures.

3.2. *Nine-coordinate complexes*

The potassium, sodium, and ammonium salts of REM complexes with EDTA ligand are mostly nine-coordinate (table 2). They all crystallize in orthorhombic system with

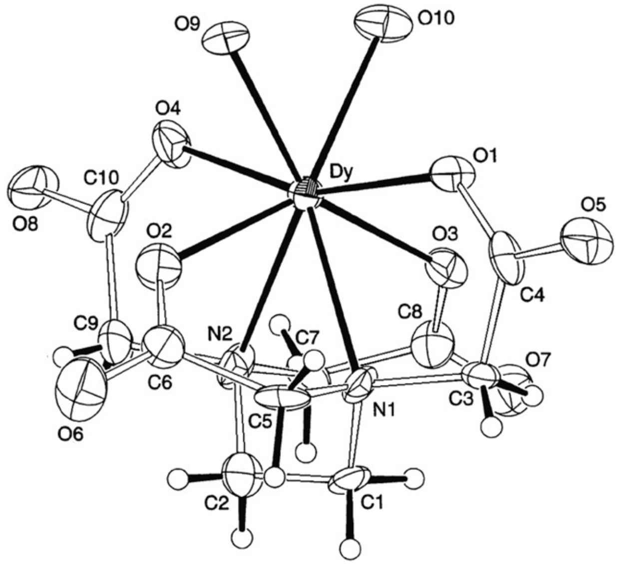


Figure 11. Molecular structure of $[Dy^{III}(EDTA)(H_2O)_2]^-$ coordination anion in $Cs[Dy^{III}(EDTA)(H_2O)_2] \cdot 3H_2O$.

Table 2. Molecular and crystal structures of rare earth metal complexes with EDTA.

Complex	Coordination number	Crystal system	Space group	Coordinate conformation	Reference
$[La^{III}(HEDTA)(H_2O)_4] \cdot 3H_2O$	10	Monoclinic	$P2_1/a$	BCSAP	[65]
$K[Sm^{III}(EDTA)(H_2O)_3] \cdot 2H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[68]
$K[Eu^{III}(EDTA)(H_2O)_3] \cdot 3.5H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[69, 70, 103]
$K[Gd^{III}(EDTA)(H_2O)_3] \cdot 5H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[71]
$K[Tb^{III}(EDTA)(H_2O)_3] \cdot 5H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[72]
$K[Ho^{III}(EDTA)(H_2O)_3] \cdot 2H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[67]
$Na[Sm^{III}(EDTA)(H_2O)_3] \cdot 5H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[48]
$Na[Eu^{III}(EDTA)(H_2O)_3] \cdot 4H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[48, 73]
$Na[Gd^{III}(EDTA)(H_2O)_3] \cdot 5H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[74]
$Na[Dy^{III}(EDTA)(H_2O)_3] \cdot 3.25H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[56, 67]
$Na[Er^{III}(EDTA)(H_2O)_3] \cdot 5H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[67]
$Na[Y^{III}(EDTA)(H_2O)_3] \cdot 5H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[75]
$NH_4[Eu^{III}(EDTA)(H_2O)_3] \cdot H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[76]
$NH_4[Y^{III}(EDTA)(H_2O)_3] \cdot 3H_2O$	9	Orthorhombic	$Fdd2$	MCSAP	[77]
$Cs[Nd^{III}(EDTA)(H_2O)_3] \cdot 3.5H_2O$	9	Monoclinic	$C2/c$	MCSAP	[67]
$Cs[Sm^{III}(EDTA)(H_2O)_3] \cdot 4H_2O$	9	Monoclinic	$C2/c$	MCSAP	[67]
$Cs[Gd^{III}(EDTA)(H_2O)_3] \cdot 4H_2O$	9	Monoclinic	$C2/c$	MCSAP	[67]
$Cs[Dy^{III}(EDTA)(H_2O)_2] \cdot 3H_2O$	8	Monoclinic	$P2_1/c$	SAP	[67]
$Cs[Ho^{III}(EDTA)(H_2O)_2] \cdot 3H_2O$	8	Monoclinic	$P2_1/c$	SAP	[67]

*Fdd*2 space group [68–77]. The common characters in their geometrical conformation are as follows: first, they all are nine-coordinate MCSAP conformation; second, the EDTA is six-coordinate to the central REM ion; and third, there are generally three waters coordinated to the central REM, one occupying the capped site and the other two in composing the above plane of nine-coordinate MCSAP conformation.

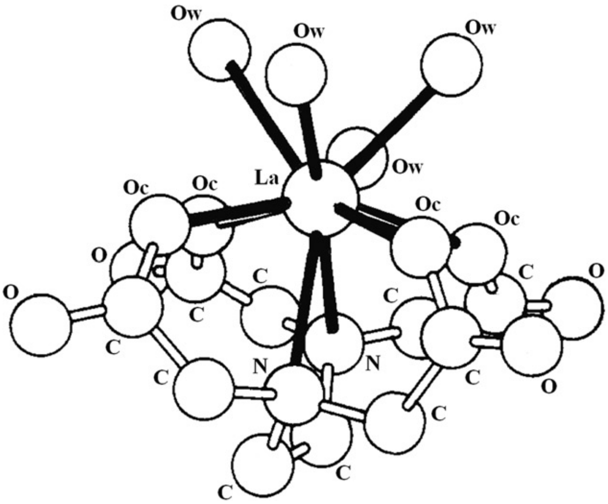


Figure 12. Molecular structure of $[La^{III}(HEDTA)(H_2O)_4]$ coordination molecule in $[La^{III}(HEDTA)(H_2O)_4] \cdot 3H_2O$.

3.3. *Ten-coordinate complexes*

Among REM ions, La^{III} possesses the biggest ionic radius and is ten-coordinate by EDTA with four waters. For example, the ten-coordinate $[La^{III}(HEDTA)(H_2O)_4] \cdot 3H_2O$ [65] (figure 12) crystallizes in monoclinic system with $P2_1/a$ space group and belongs to ten-coordinate BCSAP conformation. The Ce^{III} ion, with a slightly smaller ionic radius than that of La^{III} ion, should also yield the ten-coordinate complex, but its crystal structure and molecular structure have not been reported yet, perhaps because Ce^{III} is easily oxidized in aqueous solution during preparation.

4. Diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid series

As an octadentate ligand, diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid (DTPA) can coordinate to all REM ions, yielding fairly stable complexes [78–84]. Among these complexes, the central REM ions are all nine-coordinate. The DTPA takes eight coordination sites, leaving the last one to a water, a small anion, or a small neutral molecule. It is evident from table 3 that there is a rule to partition mononuclear or binuclear structures: the Dy^{III} ion is regarded as the division between mononuclear and binuclear molecular structures for potassium salts, while all the ammonium salts are binuclear molecular structures. So, it can be seen that the ionic radius and electronic configuration of the central metal ions, the shape of the ligand and the different counter ions play an important role in the coordination number and crystal structure of these complexes.

4.1. *Potassium salts*

In this series, complexes with REM ions ahead of Dy^{III} (including Dy^{III}), are mononuclear nine-coordinate, such as $K_2[Dy^{III}(DTPA)(H_2O)] \cdot 6H_2O$ [85] (figure 13)

Table 3. Molecular and crystal structures of rare earth metal complexes with DTPA.

Complex	Coordination number	Crystal system	Space group	Coordinate conformation	Reference
$K_2[Dy^{III}(DTPA)(H_2O)]\cdot 6H_2O$	9	Triclinic	$P1$	MCSAP	[85]
$K_4[Ho_2^{III}(DTPA)_2]\cdot 4H_2O$	9/9	Triclinic	$P1$	MCSAP	[85]
$K_2[Y^{III}(DTPA)(H_2O)]\cdot 7H_2O$	9	Triclinic	$P1$	MCSAP	[86]
$Na_4[Gd^{III}(DTPA)(H_2O)]_2\cdot 14H_2O$	9	Monoclinic	$P2_1/n$	MCSAP	[74, 87]
$Na_4[Dy^{III}(DTPA)(H_2O)]_2\cdot 16H_2O$	9	Monoclinic	$P2_1/n$	MCSAP	[56]
$(NH_4)_4[Gd_2^{III}(DTPA)_2]\cdot 6H_2O$	9/9	Triclinic	$P1$	MCSAP	[88]
$(NH_4)_4[Tb_2^{III}(DTPA)_2]\cdot 9H_2O$	9/9	Triclinic	$P1$	MCSAP	[89]
$(NH_4)_2[Dy_2^{III}(DTPA)_2]\cdot 4H_2O$	9/9	Triclinic	$P1$	MCSAP	[90]
$(NH_4)_2[Ho_2^{III}(DTPA)_2]\cdot 4H_2O$	9/9	Triclinic	$P1$	MCSAP	[90]
$(NH_4)_2[Er_2^{III}(DTPA)_2]\cdot 4H_2O$	9/9	Triclinic	$P1$	MCSAP	[90]
$(NH_4)_2[Yb_2^{III}(DTPA)_2]\cdot 4H_2O$	9/9	Triclinic	$P1$	MCSAP	[90]
$Cs_4[Dy_2^{III}(DTPA)_2]\cdot 13H_2O$	9/9	Monoclinic	$C2/c$	MCSAP	[91]

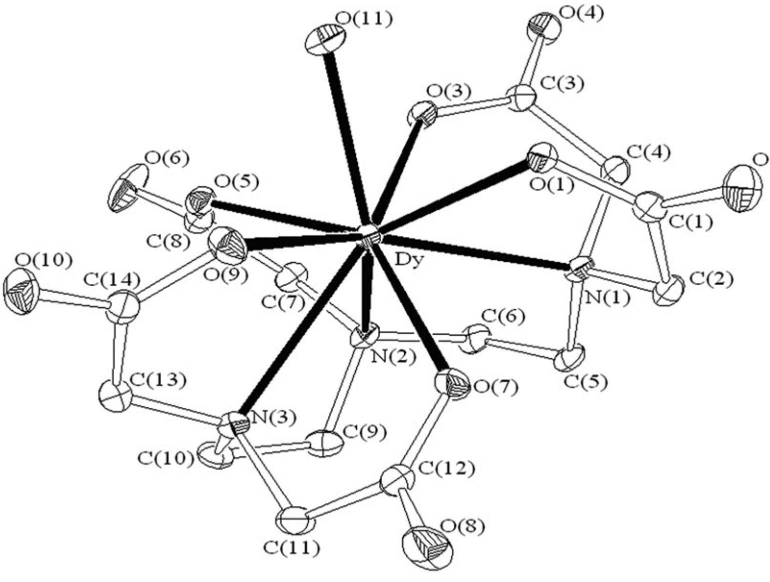


Figure 13. Molecular structure of $[Dy^{III}(DTPA)(H_2O)]^{2-}$ coordination anion in $K_2[Dy^{III}(DTPA)(H_2O)]\cdot 6H_2O$.

and $K_2[Y^{III}(DTPA)(H_2O)]\cdot 7H_2O$ [86]; for the metal ions behind Dy^{III} have a binuclear nine-coordinate structure. In the binuclear complexes, two REM ions are coordinated by two DTPA ligands synchronously such as $K_4[Ho_2^{III}(DTPA)_2]\cdot 4H_2O$ [85] (figure 14). Hence, the Dy^{III} is regarded as the division between mononuclear nine-coordinate molecular structure and binuclear nine-coordinate molecular structure for this series.

Regardless of mononuclear or binuclear REM complexes, their geometrical conformations adopt a pseudo nine-coordinate MCSAP conformation, crystallizing in the triclinic system with $P1$ space group. In the mononuclear ones, the top plane is composed of four carboxyl oxygens, and the bottom plane is composed of three amine nitrogens and one carboxyl oxygen. The capped site is occupied by an oxygen from

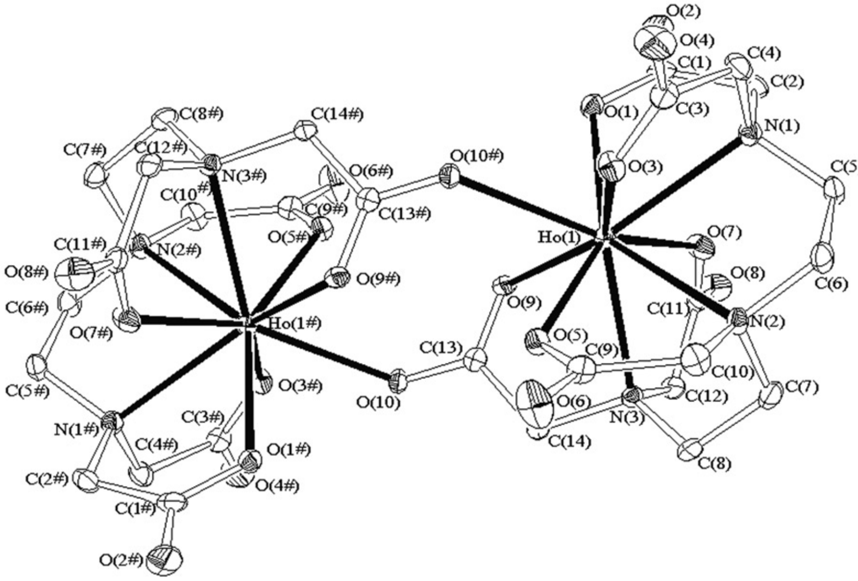


Figure 14. Molecular structure of $[Ho_2^{III}(DTPA)_2]^{4-}$ coordination anion in $K_4[Ho_2^{III}(DTPA)_2] \cdot 4H_2O$.

coordinated water. For binuclear structures, two adjacent REM ions are bridged by two carboxylates giving the binuclear structure. Differing from mononuclear REM complexes, all coordination around the central REM ion comes from DTPA. Each DTPA coordinates through five carboxyl oxygens and three amine nitrogens, to one REM and also gives another carboxyl oxygen to the other REM. In the nine-coordinate MCSAP conformation of the binuclear complexes, the components of the top and bottom planes are the same as those of mononuclear complexes. The oxygen occupying the capped site, however, is no longer from water, but from the other DTPA ligand.

4.2. *Sodium salts*

There are only two sodium salts of REM complexes with DTPA, $Na_4[Gd^{III}(DTPA)(H_2O)]_2 \cdot 14H_2O$ [74, 87] (figure 15) and $Na_4[Dy^{III}(DTPA)(H_2O)]_2 \cdot 16H_2O$ [56], precluding a rule at present. These two complexes crystallize in monoclinic system with $P2_1/n$ space group and adopt a pseudo nine-coordinate MCSAP conformation, possessing a different binuclear nine-coordinate structure than the potassium salts. The central REM ion is nine-coordinate by a DTPA and water, then hydrogen bonds couple two complex anions into a binuclear molecular structure. Hence, hydrogen bonds play an important role in the binuclear molecular structure. The conformations of sodium salts in each half part are similar to those of potassium salts.

4.3. *Ammonium salts*

The REM complexes in this series, table 3, such as $(NH_4)_2[Gd_2^{III}(DTPA)_2] \cdot 6H_2O$ [87], $(NH_4)_4[Tb_2^{III}(DTPA)_2] \cdot 9H_2O$ [88, 89], $(NH_4)_4[Dy_2^{III}(DTPA)_2] \cdot 4H_2O$ [90] (figure 16), $(NH_4)_4[Ho_2^{III}(DTPA)_2] \cdot 4H_2O$ [90], $(NH_4)_4[Er_2^{III}(DTPA)_2] \cdot 4H_2O$ [90], and

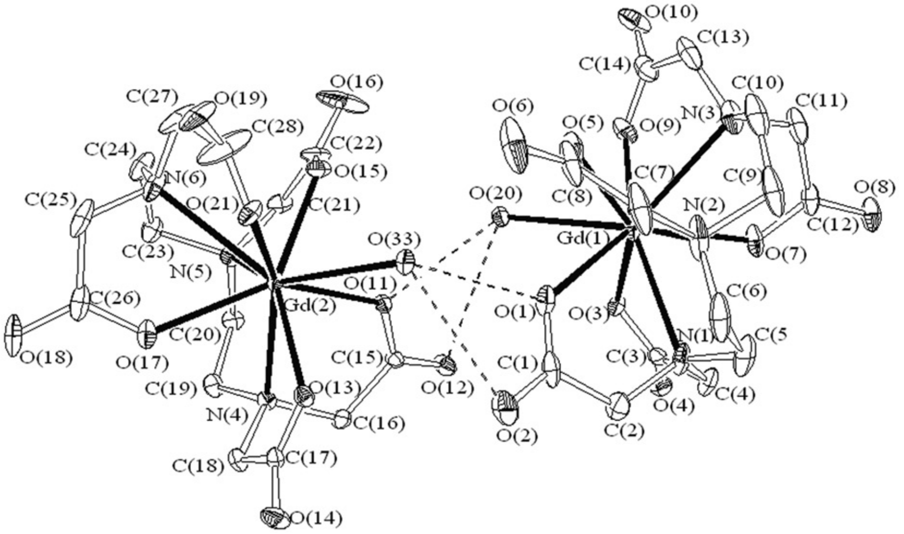


Figure 15. Molecular structure of $[Gd^{III}(DTPA)(H_2O)]_2^{4-}$ coordination anion in $Na_4[Gd^{III}(DTPA)(H_2O)]_2 \cdot 14H_2O$.

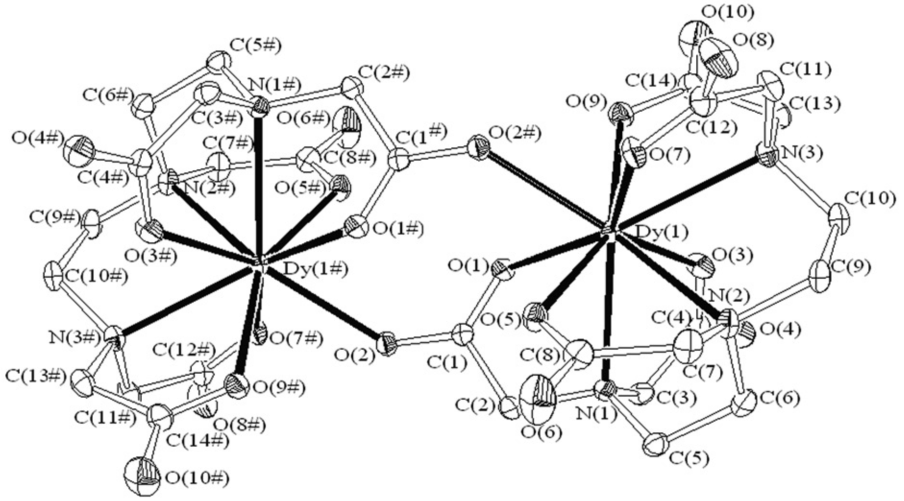


Figure 16. Molecular structure of $[Dy_2^{III}(DTPA)_2]^{4-}$ coordination anion in $(NH_4)_4[Dy_2^{III}(DTPA)_2] \cdot 4H_2O$.

$(NH_4)_4[Yb_2^{III}(DTPA)_2] \cdot 4H_2O$ [90, 91], possess a binuclear nine-coordinate molecular structure. It is not affected by the electronic configuration and ionic radius of the central REM, and there is no exact explanation to this phenomenon. The geometrical conformation of these REM complexes adopts a pseudo nine-coordinate MCSAP conformation and crystallize in triclinic system with $P1$ space group. Their binuclear molecular structures are similar to corresponding potassium salts. One of the coordinated oxygens is hydrogen-bonded to a crystal water and an ammonium cation, making the coordination bond distance between the central REM and the coordinated oxygen the longest REM–O bond.

5. Triethylenetetramine-*N,N,N′,N″,N‴,N‴*-hexaacetic acid series

Triethylenetetramine-*N,N,N′,N″,N‴,N‴*-hexaacetic acid (TTHA), as a decadentate ligand, has enough capability to occupy all the coordination sites of REM ions [92–95]. The results given in table 4 indicate that the coordinate laws of REM complexes with TTHA are quite obvious. Along with the variety of the ionic radius and the f-orbit electrons, the coordination number of the REM complexes changes from ten to eight. The La^{III}, Ce^{III}, Pr^{III}, and Nd^{III} ions with big ionic radii are always ten-coordinate by a TTHA ligand, Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, and Er^{III}, each of which possesses moderate ionic radius, giving nine-coordinate complexes, in which one carboxylate either fails to coordinate or acts as a bridge to coordinate to another REM ion and Tm^{III} and Lu^{III}, with extraordinarily small ionic radii and many f-orbit electrons, are eight coordinate. Because they cannot provide TTHA enough coordination sites, TTHA is a bridge to coordinate with two REM ions. The ten-coordinate complexes are provided with the same geometrical conformation, which is similar to the eight-coordinate complexes. It is a little more complicated, however, for nine-coordinate complexes. Dy^{III} is regarded as the division between mononuclear and binuclear molecular structures for potassium salts of nine-coordinate complexes. As for ammonium salts of nine-coordinate complexes, they are all binuclear. The coordination number and geometrical conformation of these complexes are closely related to ionic

Table 4. Molecular and crystal structures of rare earth metal complexes with TTHA.

Complex	Coordination number	Crystal system	Space group	Coordinate conformation	Reference
$K_3[La^{III}(TTHA)]\cdot 5H_2O$	10	Triclinic	$P1$	BCSAP	[109]
$K_2[La^{III}(HTTHA)(H_2O)]\cdot 8H_2O$	10	Monoclinic	$P2_1/c$	BCSAP	[110]
$K_6[Pr^{III}(TTHA)]_2\cdot 10H_2O$	10	Triclinic	$P1$	BCSAP	[98]
$(CH_2NH_3)_3[Nd^{III}(TTHA)]\cdot CH_2NH_2\cdot 4H_2O$	10	Triclinic	$P1$	BCSAP	[107]
$K_4[Sm_2^{III}(HTTHA)_2]\cdot 14H_2O$	9/9	Monoclinic	$P2_1/n$	MCSAP	[98]
$K_4[Eu_2^{III}(HTTHA)_2]\cdot 13.5H_2O$	9/9	Monoclinic	$P2_1/n$	MCSAP	[69, 70, 99]
$K_4[Gd_2^{III}(HTTHA)_2]\cdot 14H_2O$	9/9	Monoclinic	$P2_1/n$	TCTP	[100]
$K_4[Tb_2^{III}(HTTHA)_2]\cdot 14H_2O$	9/9	Monoclinic	$P2_1/n$	MCSAP	[72, 99]
$K_3[Dy^{III}(TTHA)]\cdot 5H_2O$	9	Monoclinic	$P2_1/c$	MCSAP	[99–101]
$K_3[Ho^{III}(TTHA)]\cdot 5H_2O$	9	Monoclinic	$P2_1/c$	TCTP	[99, 102]
$K_3[Er^{III}(HTTHA)]\cdot 5H_2O$	9	Monoclinic	$P2_1/c$	TCTP	[103]
$K_3[Yb^{III}(TTHA)]\cdot 5H_2O$	9	Monoclinic	$P2_1/c$	TCTP	[104]
$K_4[Y_2^{III}(HTTHA)_2]\cdot 14H_2O$	9/9	Monoclinic	$P2_1/n$	TCTP	[101]
$Na_4[Eu_2^{III}(HTTHA)_2]\cdot 10H_2O$	9/9	Monoclinic	$P2_1$	MCSAP	[73]
$(NH_4)_3[Eu^{III}(TTHA)]\cdot 5H_2O$	9	Monoclinic	$P2_1/c$	MCSAP	[76]
$(NH_4)_2[Gd^{III}(HTTHA)]\cdot 6H_2O$	9	Monoclinic	$P2_1/c$	TCTP	[105]
$(NH_4)_3[Dy^{III}(TTHA)]\cdot 5H_2O$	9	Monoclinic	$P2_1/c$	TCTP	[106]
$(NH_4)_2[Er^{III}(HTTHA)]\cdot 6H_2O$	9	Monoclinic	$P2_1/c$	TCTP	[107]
$(NH_4)_2[Y^{III}(HTTHA)]\cdot 5H_2O$	9	Monoclinic	$P2_1/c$	TCTP	[108]
$[Tm_2^{III}(TTHA)(H_2O)_6][Tm_2^{III}(TTHA)(H_2O)_4]\cdot 21H_2O$	8/8	Triclinic	$P1$	SAP	[96]
$[Lu_2^{III}(TTHA)(H_2O)_6][Lu_2^{III}(TTHA)(H_2O)_4]\cdot 21H_2O$	8/8	Triclinic	$P1$	SAP	[97]

radius and electronic configuration of the central REM, the shape of the ligand and the different counter ions.

5.1. *Eight-coordinate complexes*

For eight-coordinate complexes of the TTHA series, the ionic radius of the central REM ions should be quite small. There are only a few reports about these complexes. $[Tm^{III}_2(TTHA)(H_2O)_6][Tm^{III}_2(TTHA)(H_2O)_4] \cdot 21H_2O$ [96] and $[Lu^{III}_2(TTHA)(H_2O)_6][Lu^{III}_2(TTHA)(H_2O)_4] \cdot 21H_2O$ [97] (figure 17) are typical eight-coordinate REM complexes, both crystallizing in the triclinic system with $P1$ space group in a pseudo eight-coordinate SAP conformation. Taking $[Lu^{III}_2(TTHA)(H_2O)_6][Lu^{III}_2(TTHA)(H_2O)_4] \cdot 21H_2O$ as an example, it adopts a 1-D and infinite chain structure, which is composed of two alternately arranged building blocks, $[Lu^{III}_2(TTHA)(H_2O)_6]$ and $[Lu^{III}_2(TTHA)(H_2O)_4]$. The building blocks connect through a carboxyl group as a side bridge.

5.2. *Nine-coordinate complexes*

Most REM ions are nine-coordinate by TTHA ligands. For their potassium salts, either binuclear complexes or mononuclear complexes can be formed; sodium salt complexes are connected by two carboxyl groups, not by hydrogen bonds like binuclear structures

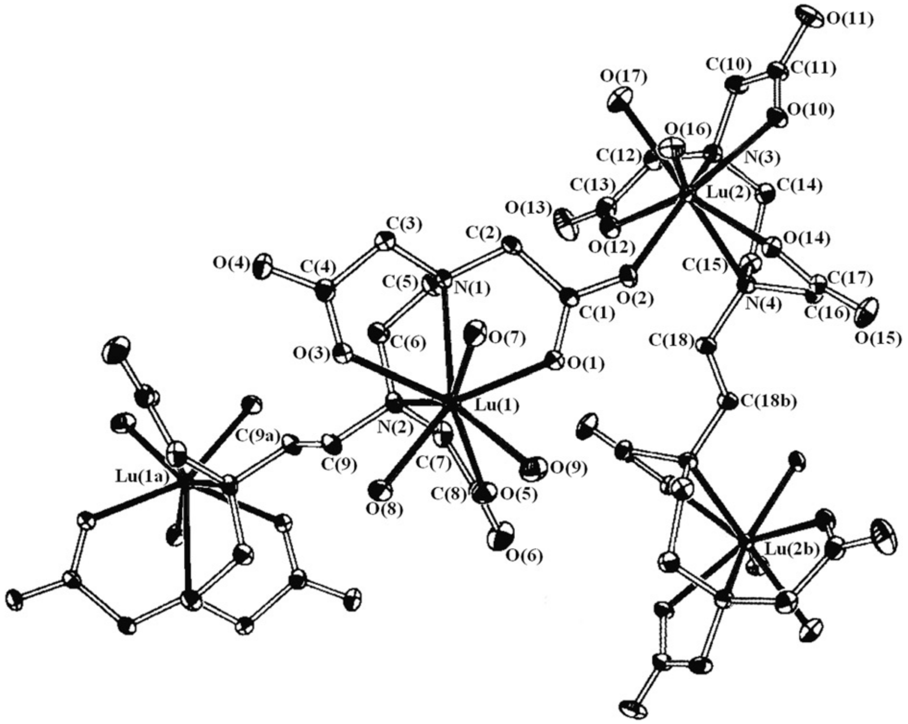


Figure 17. Molecular structure of $[Lu^{III}_2(TTHA)(H_2O)_6]$ coordination molecule in $[Lu^{III}_2(TTHA)(H_2O)_6][Lu^{III}_2(TTHA)(H_2O)_4] \cdot 21H_2O$.

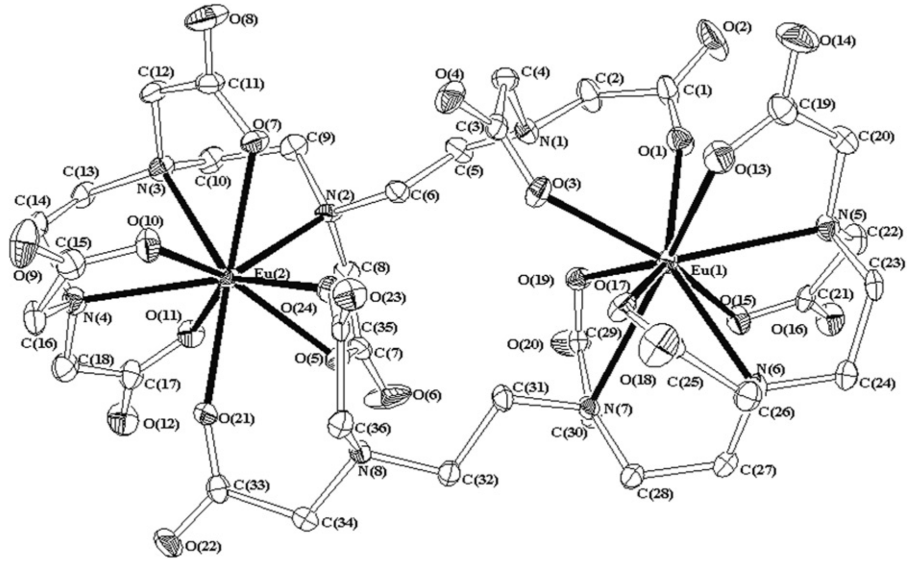


Figure 18. Molecular structure of $[Eu_2^{III}(HTTHA)_2]^{4-}$ coordination anion in $K_4[Eu_2^{III}(HTTHA)_2]\cdot 13.5H_2O$.

of the sodium salts of the DTPA series. All the reported ammonium salts adopt mononuclear structures, contrary to those of the DTPA series.

5.2.1. Potassium salts. The potassium salts with REM ions ahead of Dy^{III} ion (excluding La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, and Pm^{III} ions) are binuclear complexes, such as $K_4[Sm_2^{III}(HTTHA)_2]\cdot 14H_2O$ [98], $K_4[Eu_2^{III}(HTTHA)_2]\cdot 13.5H_2O$ [69, 70, 99] (figure 18), $K_4[Gd_2^{III}(HTTHA)_2]\cdot 14H_2O$ [100], $K_4[Tb_2^{III}(HTTHA)_2]\cdot 14H_2O$ [72, 100] (figure 19), and $K_4[Y_2^{III}(HTTHA)_2]\cdot 14H_2O$ [101] (figure 20). They crystallize in the monoclinic system with $P2_1/n$ space group. For those behind Dy^{III} (except for Tm^{III} and Lu^{III}, but including Dy^{III}) their potassium salts are mononuclear, such as $K_3[Dy^{III}(TTHA)]\cdot 5H_2O$ [99] (figure 21), $K_3[Ho^{III}(TTHA)]\cdot 5H_2O$ [99, 102] (figure 22), $K_3[Er^{III}(TTHA)]\cdot 5H_2O$ [99, 103], and $K_3[Yb^{III}(TTHA)]\cdot 5H_2O$ [104], crystallizing in the monoclinic system with $P2_1/c$ space group. Hence, among the nine-coordinate REM complexes, Tb^{III} could be considered as the division between the binuclear and mononuclear structure, as well as between the $P2_1/n$ and $P2_1/c$ space groups.

Even among these five binuclear nine-coordinate complexes, $K_4[Sm_2^{III}(TTHA)_2]\cdot 14H_2O$ [98], $K_4[Eu_2^{III}(HTTHA)_2]\cdot 13.5H_2O$ [69, 70, 99], $K_4[Gd_2^{III}(HTTHA)_2]\cdot 14H_2O$ [100], $K_4[Tb_2^{III}(HTTHA)_2]\cdot 14H_2O$ [72, 100], and $K_4[Y_2^{III}(HTTHA)_2]\cdot 14H_2O$ [101], there are differences in their coordinating polyhedra. The coordination anions of $K_4[Sm_2^{III}(TTHA)_2]\cdot 14H_2O$, $K_4[Eu_2^{III}(HTTHA)_2]\cdot 13.5H_2O$, and $K_4[Tb_2^{III}(HTTHA)_2]\cdot 14H_2O$ are composed of two identical sub-anions whose coordination polyhedra are nine-coordinate MCSAP. Three oxygens and one nitrogen constitute the top plane and the bottom plane is composed of two oxygens and two nitrogens. The only capping site is occupied by an oxygen. Similarly, the complex anion of $K_4[Gd_2^{III}(HTTHA)_2]\cdot 14H_2O$ is constituted by two sub-anions, but as shown in figure 13, both possess nine-coordinate TCTP conformation, as is $K_4[Y_2^{III}(HTTHA)_2]\cdot 14H_2O$. The top plane is

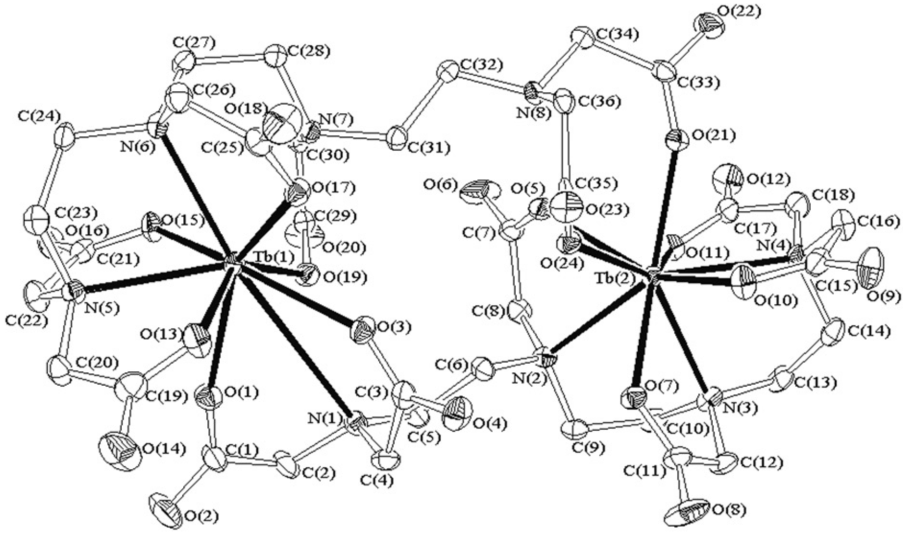


Figure 19. Molecular structure of $[Tb_2^{III}(HTTHA)_2]^{4-}$ coordination anion in $K_4[Tb_2^{III}(HTTHA)_2] \cdot 14H_2O$.

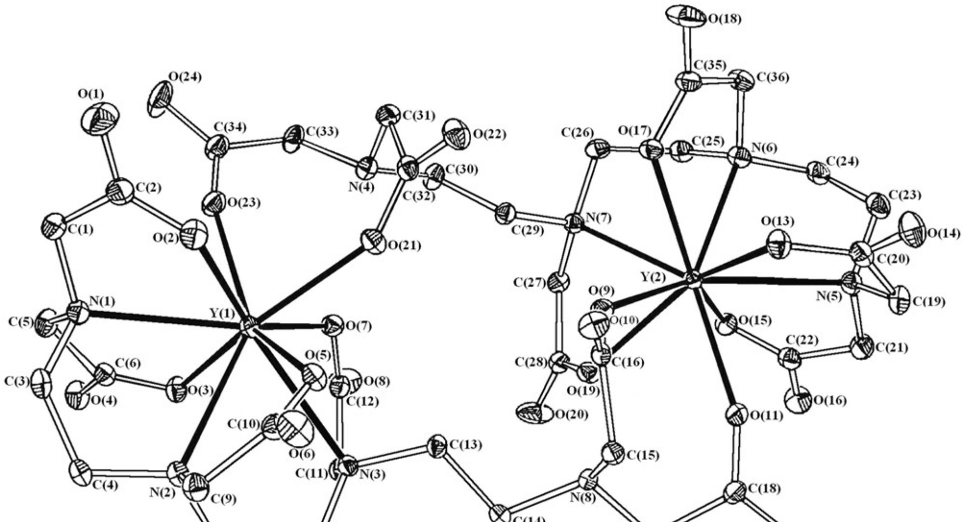


Figure 20. Molecular structure of $[Y_2^{III}(HTTHA)_2]^{4-}$ coordination anion in $K_4[Y_2^{III}(HTTHA)_2] \cdot 14H_2O$.

composed of one oxygen and two nitrogens and the bottom plane is composed of three oxygens. Three capping sites are occupied by two oxygens and one nitrogen. The central REM ion and three capping atoms are coplanar. These binuclear complexes form in such a low pH solution that TTHA does not dissociate completely and retains a $–NH^+–$ group. Since there is static repulsion between $–NH^+–$ and the central REM, a nitrogen is unable to coordinate to REM. Other nine coordinate complexes of TTHA do not coordinate to the same metal ion, with four oxygens and three nitrogens coordinating

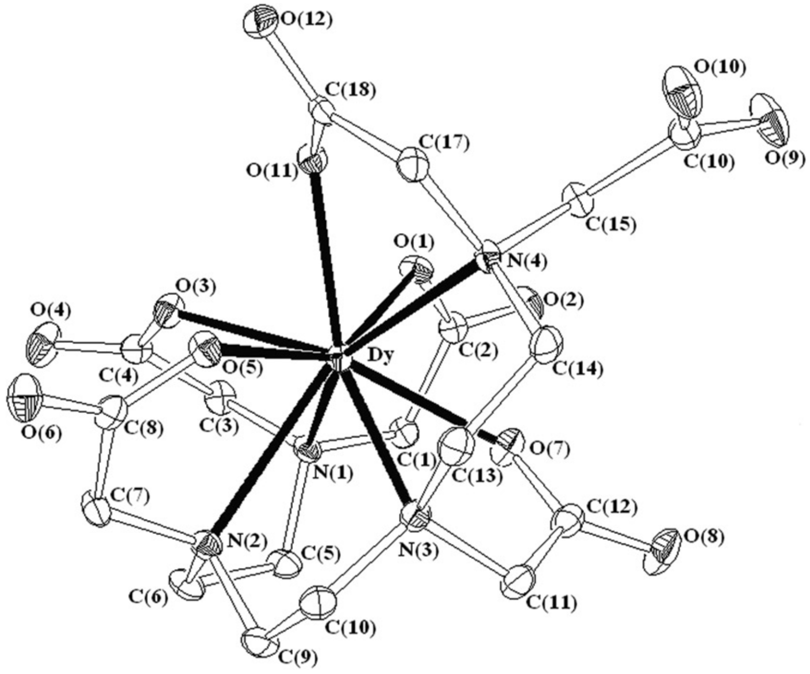


Figure 21. Molecular structure of $[Dy^{III}(TTHA)]^{3-}$ coordination anion in $K_3[Dy^{III}(TTHA)] \cdot 5H_2O$.

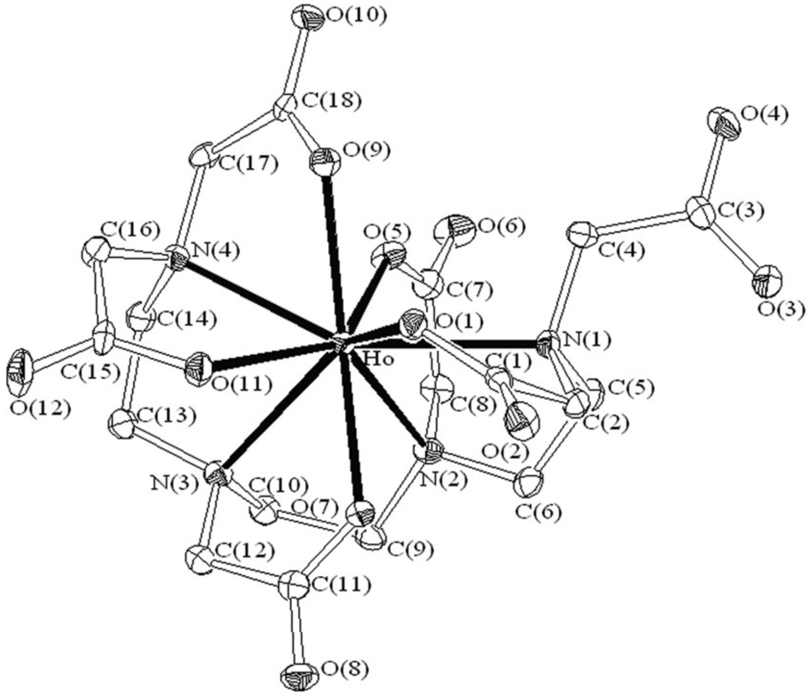


Figure 22. Molecular structure of $[Ho^{III}(TTHA)]^{3-}$ coordination anion in $K_3[Ho^{III}(TTHA)] \cdot 5H_2O$.

to one REM, and other two oxygens coordinating to another REM. Thus, two sub-anions are combined.

For mononuclear complexes, coordination polyhedron of $K_3[Dy^{III}(TTHA)] \cdot 5H_2O$ only possesses a nine-coordinate MCSAP conformation. Its top plane is composed of three oxygens and one nitrogen and the bottom plane is composed of one oxygen and three nitrogens. The capping site is occupied by an oxygen. The coordination polyhedra of $K_3[Ho^{III}(TTHA)] \cdot 5H_2O$, $K_3[Er^{III}(TTHA)] \cdot 5H_2O$, and $K_3[Yb^{III}(TTHA)] \cdot 5H_2O$ possess a nine-coordinate TCTP conformation with the top and bottom planes composed of two oxygens and one nitrogen. Three capping sites are occupied by one oxygen and two nitrogens; the central REM and three capping atoms are coplanar.

5.2.2. Sodium salts. There are only three sodium salts of REM complexes with TTHA; so, it is difficult to illuminate the coordinate law of the sodium salts systematically, but the coordinate law is similar to those of potassium salts.

These sodium salts are all binuclear and the geometrical conformation of both parts adopt a nine-coordinate MCSAP conformation, similar to those of binuclear potassium salts with nine-coordinate MCSAP conformation. These three sodium salts exhibit some differences in their crystal structure: the $Na_4[Eu_2^{III}(HTTHA)_2] \cdot 10H_2O$ (figure 23) crystallizes in monoclinic system with $P2_1$ space group; the $Na_6[Gd_2^{III}(HTTHA)_2] \cdot 7.5H_2O$ crystallizes in orthorhombic system with *Pccn* space group; and $Na_4[Tb_2^{III}(HTTHA)_2] \cdot 14H_2O$ crystallizes in monoclinic system with $P2_1/c$ space group. Because of the pH of aqueous solution an amine nitrogen of TTHA is protonated yielding $-NH^+-$, only three amine nitrogens coordinate to central REM. Each TTHA ligand is a bridge to make two sub-anions combine.

5.2.3. Ammonium salts. Ammonium salts of REM complexes with TTHA, such as $(NH_4)_3[Eu^{III}(TTHA)] \cdot 5H_2O$ [76], $(NH_4)_2[Gd^{III}(HTTHA)] \cdot 6H_2O$ [105], $(NH_4)_3[Dy^{III}(TTHA)] \cdot 5H_2O$ [106] (figure 24), $(NH_4)_2[Er^{III}(HTTHA)] \cdot 6H_2O$ [107], and $(NH_4)_3[Y^{III}(TTHA)] \cdot 5H_2O$ [108] (figure 25), are mononuclear, crystallizing in monoclinic system with $P2_1/c$ space group. Complexes of REM ahead of Dy^{III} (excluding Y^{III}, but including Dy^{III}) adopt a nine-coordinate MCSAP conformation while Y^{III} and those ions behind Dy^{III} yield nine-coordinate complexes with TCTP conformation. Hence, Dy^{III} is considered as the division between nine-coordinate MCSAP and nine-coordinate TCTP conformations. Because of the differences in ionic radius and electronic configuration of REM, the nine-coordinate ammonium salts adopt different geometrical conformation.

For the nine-coordinate MCSAP conformation, the top plane is composed of three carboxyl oxygens and one amine nitrogen. The bottom plane is composed of one carboxyl oxygen and three amine nitrogens. The capping site is occupied by a carboxyl oxygen. For nine-coordinate TCTP conformation, the top and bottom planes are composed of two carboxyl oxygens and one amine nitrogen. Out of the profiles, three capping sites are occupied by one carboxyl oxygen and two amine nitrogens with central REM coplanar with them. There is a free carboxyl group ($-CH_2COO-$) which does not take part in coordination.

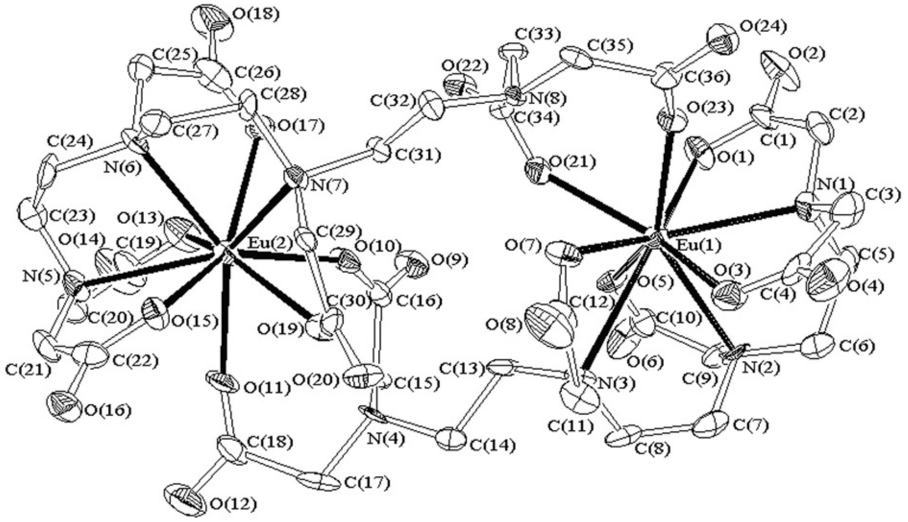


Figure 23. Molecular structure of $[Eu_2^{III}(TTHA)_2]^{4-}$ coordination anion in $Na_4[Eu_2^{III}(HTTHA)_2] \cdot 10H_2O$.

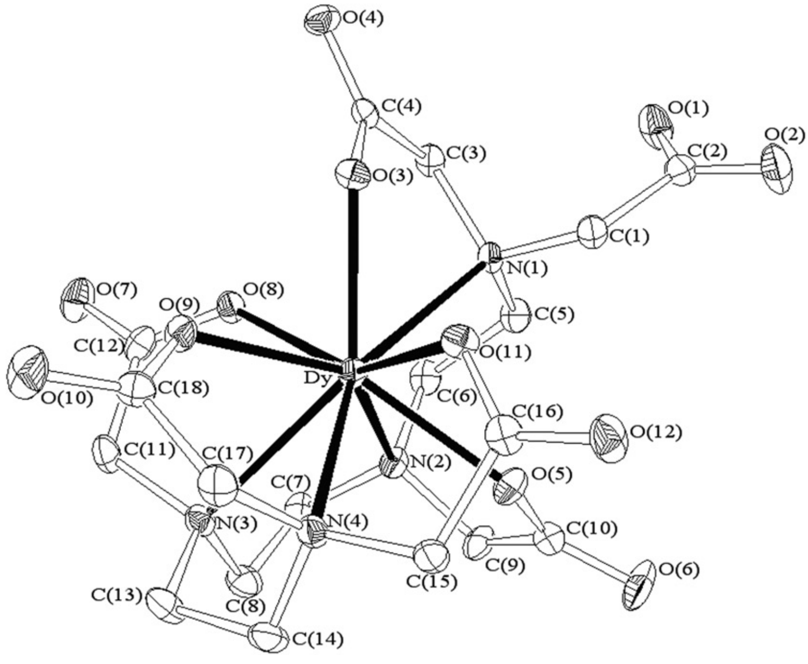


Figure 24. Molecular structure of $[Dy^{III}(TTHA)]^{3-}$ coordination anion in $(NH_4)_3[Dy^{III}(TTHA)] \cdot 5H_2O$.

5.3. *Ten-coordinate complexes*

It is expected that REM ions with big ionic radii, such as La^{III}, Ce^{III}, Pr^{III}, and Nd^{III} ions, would be ten-coordinate by TTHA, like $K_3[La^{III}(TTHA)] \cdot 5H_2O$ [109], $K_2[La^{III}(HTTHA)(H_2O)] \cdot 8H_2O$ [110], $K_6[Pr^{III}(TTHA)]_2 \cdot 10H_2O$ [98], and

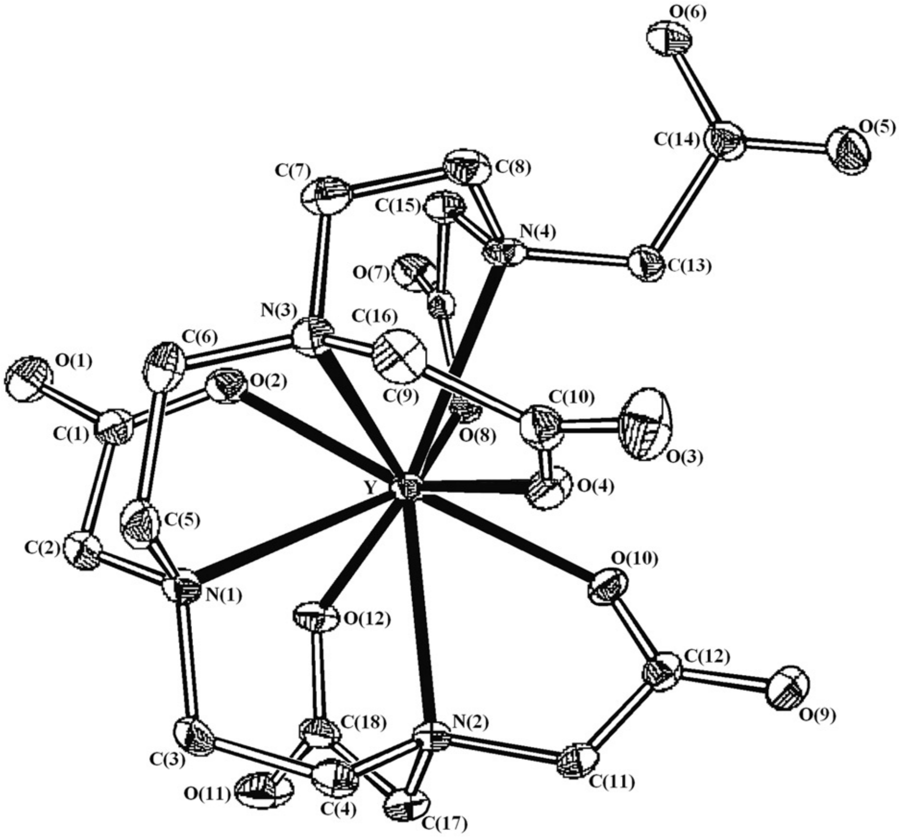


Figure 25. Molecular structure of $[Y^{III}(TTHA)]^{3-}$ coordination anion in $(NH_4)_3[Y^{III}(TTHA)] \cdot 5H_2O$.

$(CH_3NH_3)_3[Nd^{III}(TTHA)] \cdot CH_3NH_2 \cdot 4H_2O$ [107] (figure 26). All adopt a ten-coordinate BCSAP conformation. In these complexes, $K_3[La^{III}(TTHA)] \cdot 5H_2O$, $K_6[Pr^{III}(TTHA)]_2 \cdot 10H_2O$, and $(CH_3NH_3)_3[Nd^{III}(TTHA)] \cdot CH_3NH_2 \cdot 4H_2O$ crystallize in triclinic system with $P1$ space group, while $K_2[La^{III}(HTTHA)(H_2O)] \cdot 8H_2O$ crystallizes in monoclinic system with $P2_1/c$ space group. There is no report about the Ce^{III} complex with TTHA.

Taking $(CH_3NH_3)_3[Nd^{III}(TTHA)] \cdot CH_3NH_2 \cdot 4H_2O$ as an example, it is composed of four parts, three methylamine cations, one coordination anion, one methylamine molecule, and four crystalline waters. The Nd^{III} is ten-coordinate with four amine nitrogens and six carboxyl oxygens yielding a BCSAP conformation. The top and bottom planes are three carboxyl oxygens and one amine nitrogen. Two capping sites are occupied by two amine nitrogens. Two capped nitrogens and Nd^{III} are nearly linear.

For simple eight-coordinate SAP conformation, repulsion between the top and bottom planes makes the distance between two planes elongated. As shown in figure 27, θ ranges from 56° to 57°, the value of which is slightly less than the theoretical value (58.52°) in standard eight-coordinate SAP conformation. However, in $(CH_3NH_3)_3[Nd^{III}(TTHA)] \cdot CH_3NH_2 \cdot 4H_2O$, two planes also suffer repulsion from the capping coordination atoms and approach each other, making θ much larger than

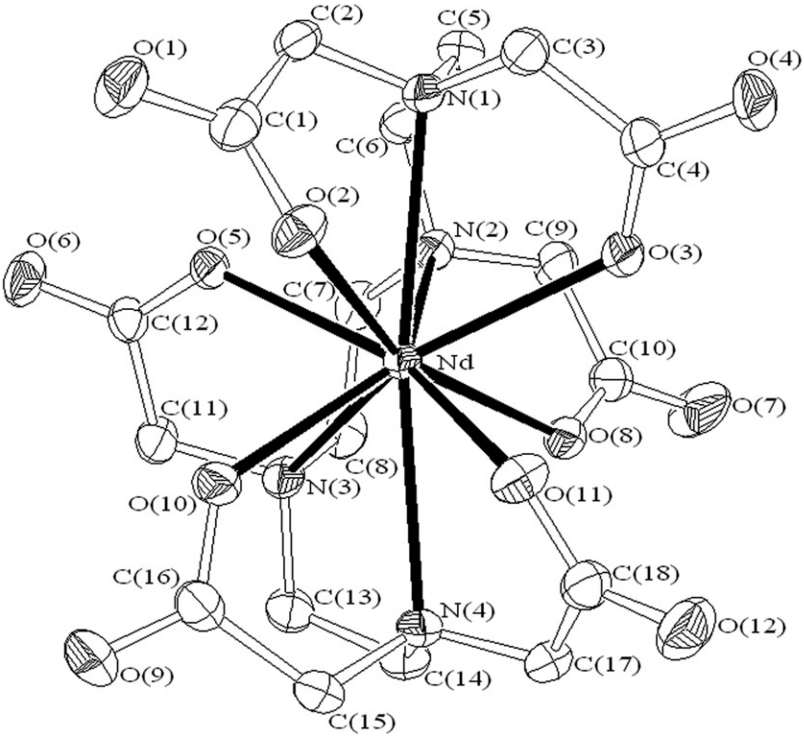


Figure 26. Molecular structure of $[Nd^{III}(TTHA)]^{3-}$ coordination anion in $(CH_3NH_3)_3[Nd^{III}(TTHA)] \cdot CH_3NH_2 \cdot 4H_2O$.

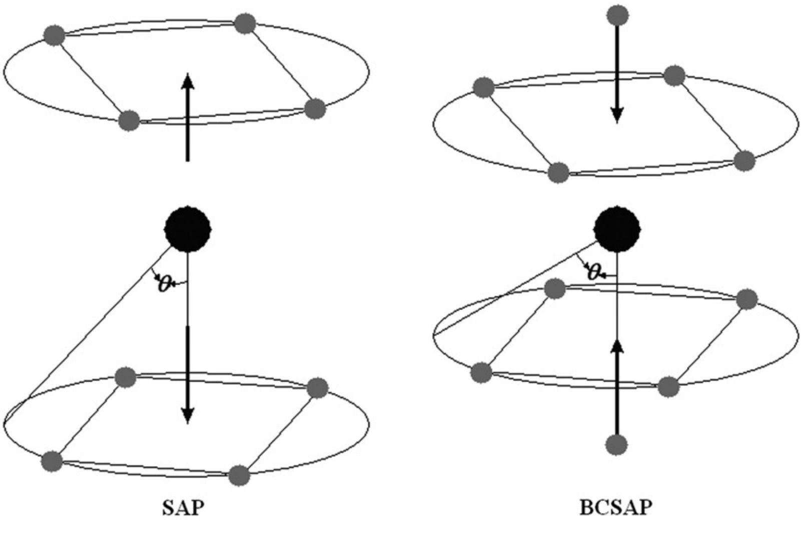


Figure 27. Molecular structure of $[Nd^{III}(TTHA)]^{3-}$ coordination anion in $(CH_3NH_3)_3[Nd^{III}(TTHA)] \cdot CH_3NH_2 \cdot 4H_2O$.

the theoretical value. The average angles are 63.74(8)° for the top plane and 63.24(8)° for the bottom plane, respectively, in which the biggest one reaches 71.40(8)°.

6. Conclusion

Rare earth metal complexes with various APCA ligands possess obvious regularities in coordination number, geometrical conformation, and crystaland molecular structures. These regularities primarily relate to the ionic radius and electronic configuration of central REM, the shape of APCA, and the nature of counter ions. For some APCA ligands, such as nitrilotriacetic acid, ethylenediamine-*N,N,N′,N′*-tetraacetic acid, diethylenetriamine-*N,N,N′,N″,N″*-pentaacetic acid, and triethylenetetramine-*N,N,N′,N″,N‴,N‴*-hexaacetic acid, with the number of carboxyls increasing gradually, the molecular structure of REM complexes all present a certain regularity. First, the ratio of REM to APCA changes from 1 : 2 to 1 : 1. Second, the number of coordinated waters varies depending on APCA. Third, the molecular structure transforms from mononuclear to binuclear structure. Thus, in summary, REM complexes with APCA ligands keep the coordination number eight, nine, or ten and tend to form multiple structures. From La^{III} with the biggest ionic radius (1.172 Å) to Lu^{III} with the smallest ionic radius (1.001 Å), the difference of ionic radius is only 0.171 Å. However, for coordination number of the REM complexes with APCA ligands, the ionic radius and electronic configuration of REM, ligand structure, and counter cation play important roles. For REM complexes with APCA, the coordination number and geometrical conformation are rich and various. Eight-coordinate REM complexes adopt the SAP and BCTAP conformations, mononuclear or binuclear nine-coordinate complexes adopt MCSAP and TCTP conformations, and ten-coordinate complexes have either mononuclear or binuclear BCSAP conformations. Therefore, influence of ionic radius and f-orbit electronic configuration should not be neglected when the coordination number and geometrical conformation of REM complexes with APCA are predicted, though the differences among ionic radius and crystal field stabilization energy are very small. In REM ions, Dy^{III} is generally considered as the division of molecular structure and coordination number. Along with increasing atomic number of REM, there are increasing electrons in the 4f-orbital, so that repulsion from these 4f-orbit electrons also increases. REM ions with big ionic radii and few 4f electrons are inclined to ten-coordinate complexes with APCA ligands, while those with small ionic radii and many 4f electrons yield eight-coordinate complexes. The middle ones, of course, can form either mononuclear or binuclear nine-coordinate complexes.

Acknowledgments

The authors appreciate Professors K. Miyoushi and T. Mizida heartily, who work in the Department of Chemistry, Hiroshima University, for their assistance and instruction. The authors also greatly acknowledge the National Natural Science Foundation of China, Liaoning Province Natural Science Foundation of Education Department and

Liaoning Province Natural Science Foundation of Science and Technology Department for financial support.

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