New Nine Coordinated Hydrated Heavier Lanthanide Ethylenediaminetetraacetates Containing Hydrazinium Cation: Molecular Structure of N₂H₅[Tb(EDTA)(H₂O)₃]·5H₂O and N₂H₅[Gd(EDTA)(H₂O)₃]·5H₂O

L. Vikram, C. Sonia and B.N. Sivasankar*

Department of Chemistry, Government Arts College, Udhagamandalam, The Nilgiris-643 002, India

*Corresponding author: E-mail: sivabickol@yahoo.com

Two complexes of lanthanide with the composition $N_2H_5[Tb(III)(EDTA)(H_2O)_3]\cdot5H_2O$ (**I**) and $N_2H_5[Gd(III)(EDTA)(H_2O)_3]\cdot5H_2O$ (**II**) (EDTA = ethylenediaminetetraacetic acid) were prepared and characterized by X-ray single crystal diffraction technique. For **I** and **II** the Tb(III) and Gd (III) ions are nine coordinated by an EDTA ligand and three coordination water molecules, yielding a monocapped square-antiprisamatic (MCSAP) conformation. Complexes **I** and **II** are crystallizes in the orthorhombic system with Fd22 space group. The crystal data are as follows: $a = 19.5030(9)$, $b = 35.3459(17)$, $c = 12.2825(5)$, $\alpha = \beta = \gamma = 90$, $V = 8467(7)$ Å^3, $Z = 16$, $\rho = 1.704$ Mg/m^3, $\mu = 3.405$ mm^{-1}, $F_{(000)} = 4208$, $R_1 = 0.0390$ and $wR_2 = 0.1101$ for 22995 observed reflections with $I \geq 2\sigma(I)$. The crystal data of the complex **II** are as follows: $\alpha = 19.5336(7)$ Å, $b = 35.3788(14)$ Å, $c = 12.2792(5)$ Å, $\alpha = \beta = \gamma = 90º$, $V = 8485.9(6)$, $Z = 16$, $\rho = 1.745$ Mg/m^3, $\mu = 3.196$ mm^{-1}, $F_{(000)} = 4320$, $R_1 = 0.0226$ and $wR_2 = 0.0666$ for 8558 observed reflections with $I = 2\sigma(I)$. According to thermal analyses, the collapsing temperatures of crystal structure are 260 ºC for **I** and 240 ºC for **II**, which indicate that the crystal structure of **I** is more stable.

Key Words: Tb³⁺, Gd³⁺, Lanthanide complexes, EDTA complexes, Structures, X-Ray, Nine-coordination.

INTRODUCTION

Over the past decade, there has been a resurgence of interest in coordination chemistry of rare-earth 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 Tb(III) complexes with aminopolycarboxylic acid ligands have unusual spectroscopic characterstic including millisecond excited state lifetime, sharply spiked emission spectra (few nm) and large stroke shifts (> 150 nm), so that they have been used as probes in fluoroimmunoassay[3-5] and 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 Tb(III) complexes. In order to explain these phenomena exactly, it is necessary to determine their molecular and crystal structure first, which is the right intention of this work. In a given oxidation state, the crystal and molecular structure of rare-earth 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 the unobvious difference among the radius of neighboring rare-earth metal ions, while the differences among

the crystal and molecular structures of their complexes with aminopolycarboxylic acid ligands are derived from these unobvious differences. For the Tb(III) complexes with aminopolycarboxylic acid ligands, the coordination numbers are usually nine and their coordination polyhedra adopt monocapped square-antiprisamatic conformation, such as $K_3[Tb(III)(Nta)_2(H_2O)]\cdot5.5H_2O^7$, $KNa_2[Tb(III)(Nta)_2(H_2O)]\cdot5H_2O^8$ and $K_4[Tb_2(III)(Httha)_2]\cdot14H_2O^9$.

The principal applications of lanthanides are as MRI paramagnetic contract agents, while interest in the radioisotopes of lanthanides for radionuclide therapy is becoming more evident. The ability of lanthanide complexes to catalyze DNA hydrolysis(artificial nucleases) has been reviewed[10]. Further development of MRI contrast agents centers mainly on gadolinium chelated by polydentate aminocarboxylate and related ligands. Gadolinium also has potential for use in neutron capture therapy with the advantage that its uptake can be monitored by MRI[11]. There are two principal goal for future development. One is to control biological behaviour by incorporating Gd into bioconjugates such as lipids with acid labile bonds hydroxymethyl dota derivatives[12], enhanced stability dtpa derivatives[13] and polymers[14-16]. The other is to improve the efficiency with which the complexes induce spin relaxation in protons of water molecules, by designing chelators to control exchange

rates of coordinated[17,18-20] or hydrogen bonded[21] water molecules and by controlling the mobility and rotation of complexes[22-26]. The spin relaxation properties are dependent on the physiological environment; so that MRI scans provide biochemical/ physiological information as well as structural. Thus, complexes in which relaxivity depends on local pH[27] have been designed. Relaxivity of Dy(III)[28] and Eu(II) and (III)[29,30] complexes is controlled by similar factors. Sequestration of Dy in red blood cell enhances relaxivity effects, suggesting potential application in vascular MRI[31]. Further lanthanide complexes containing hydrazine or hydrazinium ions are scarce because lanthanide ion precipitates as lanthanide hydroxide in basic medium and hence the pH of the medium decides the complex formation.

We report herein the preparation and X-ray single crystal studies on some new hydrazinium heavier lanthanide complexes containing EDTA as a chelating ligand. To the best of our knowledge, this is the first report on the hydrazinium complexes with of heavier lanthanides with aminopolycarboxylic acid.

EXPERIMENTAL

Chemicals such as hydrazine hydrate (99-100 %), H₄EDTA (99.5 %), terbium and gadolinium oxides used were of Analar or equivalent grade received from SD fine chemicals. Solvents were distilled before use. For the preparation and analysis, doubled distilled water was used.

The metal content in the complexes were determined by complexometric titration after converting the complex to the metal nitrate by decomposing a known weight of the complex with concentrated nitric acid. The hydrazine contents were determined by volumetric analyses using a standard KIO₃ solution (0.025 mol) under Andrew's conditions[32]. A Perkin-Elmer CHN analyzer (model 1240) was used for C, H and N analyses. The Infrared spectra of solid samples in the range 4000-400 cm⁻¹ were recorded on a Perkin-Elmer 597/1650 spectrophotometer using KBr pellets.

X-Ray intensity data were collected on a Kappa Apex II CCD diffractometer system with graphite mono-chromated Mo-Kα radiation (λ = 0.71073 Å). The structure was solved by direct method using SIR-92 Program and completed using Fourier Techniques and refined applying full matrix least square techniques. Refinement was carried out using SHELXL-97 program[33,34].

Preparation of (N₂H₅)₂H₂EDTA): The ligand, dihydrazinium dihydrogen ethylenediaminetetraacetate was prepared by adding aqueous solution of hydrazine hydrate (10 mL, 0.2 mol) to an aqueous suspension of H₄EDTA (29.24 g, 0.1 mol) in 100 mL distilled water with stirring. The resulting solution was filtered through a Whatman filter paper and the clear solution after concentration on a water bath was stored at room temperature. The colourless crystals formed after 2-3 days were filtered, washed and dried in air.
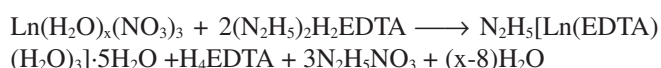
Preparation of N₂H₅[Ln(EDTA)(H₂O)₃]·5H₂O: The lanthanide nitrate hydrates were prepared by dissolving 0.01 mol of the respective metal oxide in 6 N nitric acid and evaporating the clear solution thus obtained to dryness. The residue containing the respective hydrated lanthanide nitrate was dissolved in 30 mL of distilled water.

To the aqueous solution of respective lanthanide nitrate hydrate, an aqueous solution (30 mL) of ligand (7.12 g, 0.02 mol) was added with constant stirring. The resulting solution was kept at atmospheric pressure and room temperature for 0.5 h. The acid, ethylenediaminetetraacetic acid precipitated, was filtered through Whatmann filter paper and the clear solution was concentrated to 30 mL. The concentrated solution was allowed for several days for crystallization. Colourless crystal obtained Tb and Gd were filtered, washed quickely several times with ice-cold distilled water and dried in air.
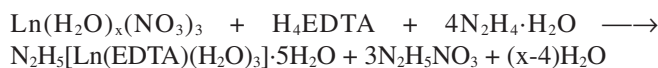
The complexes were also prepared by adding an aqueous mixture (50 mL) containing H₄EDTA (2.92 g, 0.01 mol) and hydrazine hydrate (2 mL, 0.04 mol) to an aqueous solution of Ln(H₂O)ₓ(NO₃)₃ (0.01 mol) prepared as described above. The solutions thus obtained were filtered to remove any insoluble acid and other impurities and allowed to stand at room temperature. After 8-9 weeks, the crystalline complexes formed at the bottom of the beaker were processed as above.

RESULTS AND DISCUSSION

Hydrazinium lanthanide ethylenediaminetetraacetate hydrates, N₂H₅[Ln(EDTA)(H₂O)₃]·5H₂O where Ln = Tb and Gd were prepared by the aqueous reaction between respective lanthanide nitrate hydrates and dihydrazinium dihydrogen ethylenediaminetetraacetate. The chemical reaction involved during the complexation are as follows:

Ln(H₂O)ₓ(NO₃)₃ + 2(N₂H₅)₂H₂EDTA ⟶ N₂H₅[Ln(EDTA)(H₂O)₃]·5H₂O +H₄EDTA + 3N₂H₅NO₃ + (x-8)H₂O

where Ln = Tb and Gd.

Ln(H₂O)ₓ(NO₃)₃ + H₄EDTA + 4N₂H₄·H₂O ⟶ N₂H₅[Ln(EDTA)(H₂O)₃]·5H₂O + 3N₂H₅NO₃ + (x-4)H₂O

The complexes prepared are crystalline solids, which are stable at room temperature in air and light. They are soluble in water and insoluble in organic solvents such as alcohol, ether, acetone and chloroform. The complete study of chemical analyses, CHN analyses, molar conductance, magnetic moments and electronic spectra of the Tb and Gd complexes has been made thoroughly in the previous paper[35]. Hence, in this paper we report only the molecular and crystal structure of Gd and Tb complexes. The infra red spectra of these two complexes are similar and almost super imposable. The spectra shows a broad band in the region 3500-3000 cm⁻¹ which is assigned to the O-H stretching of water and N-H stretching of NH₂-NH₃⁺ ions. Two sharp, strong and distinct bands are observed in these two complexes in the region 1590-1580 and 1425-1415 cm⁻¹ these bands are attributed to the νₐₛy and νₛym stretching of monodentate carboxylate ions. The Δν = *ca.* 175 cm⁻¹ indicate the bonding is primarily ionic. A strong band at 965 cm⁻¹ observed in these complexes supports the ionic nature of hydrazinium cation. The thermal profile of these complexes reflects the presence of two types of water molecule inside and outside of the sphere. The anhydrous complex after dehydration undergoes continous degradation in multistage to give corresponding lanthanide oxide as the end residue. Due to the continous decomposition, it was not possible to isolate the intermediate.

Crystal structure of $N_2H_5[Tb(EDTA)(H_2O)_3]\cdot5H_2O$:
The X-ray study together with density measurement shows that hydrazinium salts of terbium ethylenediaminetetraacetate hydrate crystallize in the space group F2dd and the crystal system is orthorhombic, the observed crystal density is 1.70 mg/m³, which is close to that of the calculated from X-ray analysis (1.704 mg/m³).

TABLE-1
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $N_2H_5[Tb(EDTA)(H_2O)_3]\cdot5H_2O$ AND $N_2H_5[Gd(EDTA)(H_2O)_3]\cdot5H_2O$

Complex	Tb	Gd
Empirical formula	$C_{10}H_{33}N_4O_{15}Tb$	$C_{10}H_{33}N_4O_{16}Gd$
Formula weight	543.14	557.47
Temperature	293(2) K	293(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Orthorhombic	Orthorhombic
Unit cell dimensions	a = 19.5030(9) Å α = 90º	a = 19.5336(7) Å α = 90º
	b = 35.3459(17) Å β = 90º	b = 35.3788(14) Å β = 90º
	c = 12.2825(5) Å γ = 90º	c = 12.2792(5) Å γ = 90º
Volume	8467.0(7) Å³	8485.9(6) Å3
Z	16	16
Density (calculated)	1.704 mg/m³	1.745 mg/m³
Absorption coefficient	3.405 mm⁻¹	3.196 mm⁻¹
$F_{(000)}$	4208	4320
Theta range for data collection	2.04-31.23º	2.30-35.31º
Index ranges	-27 ⇐ h ⇐ 21, -51⇐ k ⇐ 43, -15 ⇐ l ⇐ 17	-31 ⇐ h ⇐ 23, -19 ⇐ k ⇐ 57, -19 ⇐ l ⇐ 16
Reflections collected	22995	16957
Independent reflections	5928 [$R_{(int)}$ = 0.0572]	8558 [$R_{(int)}$ = 0.0140]
Completeness to theta = 25.00°	99.9 %	99.8 %
Refinement method	Full-matrix least-squares on F²	Full-matrix least-squares on F²
Data / restraints / parameters	5928/1/245	8558/3/263
Goodness-of-fit on F2	1.092	1.042
Final R indices [I>2σ(I)]	R1 = 0.0390, wR2 = 0.1101	R1 = 0.0226, wR2 = 0.0666
R indices (all data)	R1 = 0.0437, wR2 = 0.1142	R1 = 0.0256, wR2 = 0.0723
Absolute structure parameter	-0.001(18)	0.052(10)
Largest diff. peak and hole	2.418 and -0.955 e Å⁻³	0.844 and -1.103 e Å⁻³

TABLE-2
ATOMIC COORDINATES ($\times 10^4$) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS
($\mathring{A}^2 \times 10^3$) FOR $N_2H_5[Tb(EDTA)(H_2O)_3]\cdot5H_2O$ AND $N_2H_5[Gd(EDTA)(H_2O)_3]\cdot5H_2O$ (U(eq) IS DEFINED AS ONE THIRD OF
THE TRACE OF THE ORTHOGONALIZED UIJ TENSOR

Metal	x	y	z	U(eq)	Metal	x	y	z	U(eq)
Tb(1)	6686(1)	4050(1)	1246(1)	26(1)	C(1)	3030(2)	494(1)	-57(3)	42(1)
O(1)	7357(2)	4145(1)	-327(4)	35(1)	C(2)	2705(2)	174(1)	601(4)	47(1)
O(3)	6168(2)	3603(2)	-5(4)	40(1)	C(3)	1542(2)	329(1)	-1137(3)	40(1)
O(4)	7449(2)	3483(1)	1084(4)	40(1)	C(4)	1601(2)	60(1)	-187(4)	45(1)
O(5)	6227(2)	3562(2)	2428(4)	41(1)	C(5)	1752(2)	23(1)	1775(4)	38(1)
N(6)	6972(2)	4780(1)	1331(5)	37(1)	C(6)	1058(2)	156(1)	2140(3)	36(1)
O(8)	5494(2)	4181(1)	1547(4)	37(1)	C(7)	54(1)	745(1)	1266(3)	32(1)
C(1)	6611(5)	4939(2)	2259(7)	48(2)	C(8)	319(1)	683(1)	2418(3)	33(1)
C(2)	6057(3)	4841(2)	-64(6)	41(1)	C(9)	1371(1)	638(1)	3461(3)	34(1)
O(2)	574(2)	730(2)	984(4)	47(1)	C(10)	2117(1)	762(1)	3371(3)	29(1)
C(7)	7128(2)	4237(1)	-1276(6)	32(1)	N(1)	1964(1)	219(1)	759(3)	34(1)
C(9)	6753(4)	4976(2)	291(7)	42(2)	N(2)	1041(1)	563(1)	2401(2)	28(1)
O(10)	7456(2)	4228(2)	-2108(4)	50(1)	O(1)	1225(1)	1445(1)	-349(2)	36(1)
O(11)	7785(2)	4176(2)	2006(4)	47(1)	O(2)	1158(1)	1398(1)	2093(2)	37(1)
O(12)	6539(2)	4325(1)	3017(4)	43(1)	O(3)	2455(1)	1518(1)	998(2)	37(1)
C(13)	6364(3)	4354(2)	-1357(5)	39(1)	O(4)	2791(1)	822(1)	85(2)	42(1)
O(9)	3549(4)	197(2)	9176(5)	68(2)	O(5)	1547(1)	676(1)	-923(2)	41(1)
N(10)	6045(2)	4438(1)	-313(4)	31(1)	O(6)	491(1)	816(1)	540(2)	32(1)
C(3)	5052(3)	4256(2)	830(5)	36(1)	O(7)	2350(1)	850(1)	2435(2)	31(1)
C(5)	5316(3)	4318(2)	-319(5)	36(1)	O(8)	3512(2)	418(1)	-684(4)	73(1)
C(14)	7707(4)	4823(2)	1476(6)	52(2)	O(9)	1467(2)	193(1)	-2068(3)	68(1)
O(17)	619(4)	373(2)	4737(6)	70(2)	O(10)	-580(1)	732(1)	1112(2)	49(1)
C(15)	8027(3)	4506(2)	2148(6)	44(1)	O(11)	2444(1)	771(1)	4229(2)	48(1)
C(10)	6546(4)	4670(2)	3224(6)	45(2)	O(12)	611(2)	-379(1)	-2636(4)	71(1)
O(14)	1454(6)	955(2)	9442(10)	99(3)	O(13)	-1454(4)	949(1)	2708(6)	106(2)
O(15)	8525(4)	4576(2)	2750(7)	80(2)	O(14)	1344(7)	1129(3)	-2690(6)	134(4)
O(16)	3725(6)	1086(4)	9766(8)	113(3)	O(14')	1437(10)	807(5)	-3622(10)	134(4)
–	–	–	–	–	Gd(1)	1685(1)	952(1)	846(1)	23(1)
–	–	–	–	–	O(15)	5016(8)	581(7)	471(15)	158(5)
–	–	–	–	–	O(15')	4816(8)	224(6)	37(15)	158(5)

The crystal data for the Tb complex are given in Table-1. The final fractional atomic coordinates and equivalent isotropic thermal parameters for all non hydrogen atoms are given in Table-2. The important bond lengths and bond angles are given Tables 3 and 4, respectively. The atom numbering scheme with the ORTEP model and close packing diagram are shown in Figs. 1 and 2, respectively. The crystal contain discrete $N_2H_5^+$ ions, $[Tb(EDTA)(H_2O)_3]^{3-}$ ions and water molecule. The $N_2H_5^+$ ion is not coordinated to Tb^{3+} ion. The plane of terbium and two nitrogen atoms serves as quasi-mirror for the coordination group. Water in the quasi mirror two nitrogen and four oxygen positions of EDTA are at seven of the eight verticals of a dodecahedron of $Mo(CN)_8^{4-}$ type with in which Tb^{3+} is off centre that is out of plane from the four oxygen atoms. The chelation pattern in $Tb(EDTA)(H_2O)_3$ is basically same as that described for $La(EDTA)(H_2O)_3^-$ and $La(HEDTA)(H_2O)_4$ but loss of H^+ from ten coordinated molecule is accompanied by a significant tightening of all chelating linkages and rejection of water molecule. Thus, the displacement of Tb^{3+} from the mean plane of a trapezoidal array of four complexed oxygen atoms of EDTA is observed.

TABLE-3
BOND LENGTHS [Å] OF $N_2H_5[Tb(EDTA)(H_2O)_3]\cdot 5H_2O$
AND $N_2H_5[Gd(EDTA)(H_2O)_3]\cdot 5H_2O$

Tb(1)-O(1)	2.358(4)	N(1)-Gd(1)	2.654(2)
Tb(1)-O(11)	2.381(5)	N(2)-Gd(1)	2.671(2)
Tb(1)-O(8)	2.399(4)	O(1)-Gd(1)	2.449(2)
Tb(1)-O(12)	2.400(5)	O(2)-Gd(1)	2.428(2)
Tb(1)-O(5)	2.426(5)	O(3)-Gd(1)	2.511(2)
Tb(1)-O(3)	2.424(5)	O(4)-Gd(1)	2.399(2)
Tb(1)-O(4)	2.505(4)	O(5)-Gd(1)	2.396(2)
Tb(1)-N(6)	2.642(5)	O(6)-Gd(1)	2.4110(19)
Tb(1)-N(10)	2.666(5)	O(7)-Gd(1)	2.372(2)

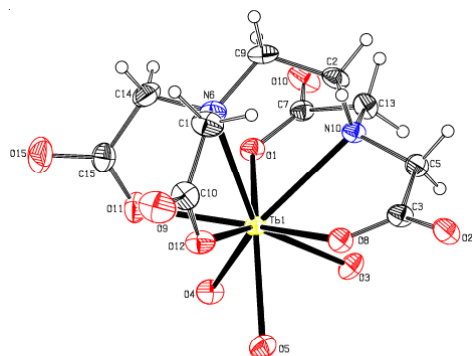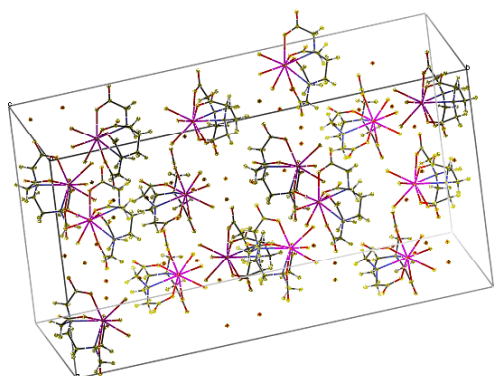Fig. 1. ORTEP diagram of $N_2H_5[Tb(EDTA)(H_2O)_3]\cdot 5H_2O$

Fig. 2. Close packing diagram of $N_2H_5[Tb(EDTA)(H_2O)_3]\cdot 5H_2O$

TABLE-4
BOND ANGLES [°] OF $N_2H_5[Tb(EDTA)(H_2O)_3]\cdot 5H_2O$
AND $N_2H_5[Gd(EDTA)(H_2O)_3]\cdot 5H_2O$

O(1)-Tb(1)-O(11)	78.15(18)	O(7)-Gd(1)-O(5)	138.12(8)
O(1)-Tb(1)-O(8)	129.58(15)	O(7)-Gd(1)-O(4)	78.31(9)
O(11)-Tb(1)-O(8)	140.92(17)	O(5)-Gd(1)-O(4)	70.73(9)
O(1)-Tb(1)-O(12)	138.71(17)	O(7)-Gd(1)-O(6)	128.82(7)
O(11)-Tb(1)-O(12)	71.08(18)	O(5)-Gd(1)-O(6)	70.65(8)
O(8)-Tb(1)-O(12)	70.54(16)	O(4)-Gd(1)-O(6)	140.55(9)
O(1)-Tb(1)-O(5)	142.81(17)	O(7)-Gd(1)-O(2)	79.19(8)
O(11)-Tb(1)-O(5)	103.35(19)	O(5)-Gd(1)-O(2)	142.11(8)
O(8)-Tb(1)-O(5)	71.74(16)	O(4)-Gd(1)-O(2)	138.80(8)
O(12)-Tb(1)-O(5)	72.62(17)	O(6)-Gd(1)-O(2)	79.55(8)
O(1)-Tb(1)-O(3)	78.75(16)	O(7)-Gd(1)-O(1)	143.35(8)
O(11)-Tb(1)-O(3)	138.22(17)	O(5)-Gd(1)-O(1)	72.92(9)
O(8)-Tb(1)-O(3)	79.60(16)	O(4)-Gd(1)-O(1)	103.53(10)
O(12)-Tb(1)-O(3)	142.07(16)	O(6)-Gd(1)-O(1)	72.26(7)
O(5)-Tb(1)-O(3)	76.23(15)	O(2)-Gd(1)-O(1)	76.12(8)
O(1)-Tb(1)-O(4)	73.68(16)	O(7)-Gd(1)-O(3)	74.46(8)
O(11)-Tb(1)-O(4)	69.28(17)	O(5)-Gd(1)-O(3)	117.40(9)
O(8)-Tb(1)-O(4)	137.89(15)	O(4)-Gd(1)-O(3)	69.06(9)
O(12)-Tb(1)-O(4)	117.83(17)	O(6)-Gd(1)-O(3)	138.71(8)
O(5)-Tb(1)-O(4)	72.40(16)	O(2)-Gd(1)-O(3)	71.88(9)
O(3)-Tb(1)-O(4)	71.04(18)	O(1)-Gd(1)-O(3)	72.37(8)
O(1)-Tb(1)-N(6)	77.07(17)	O(7)-Gd(1)-N(1)	76.76(9)
O(11)-Tb(1)-N(6)	67.12(18)	O(5)-Gd(1)-N(1)	65.66(9)
O(8)-Tb(1)-N(6)	90.63(16)	O(4)-Gd(1)-N(1)	67.12(9)
O(12)-Tb(1)-N(6)	66.03(18)	O(6)-Gd(1)-N(1)	89.78(8)
O(5)-Tb(1)-N(6)	138.47(18)	O(2)-Gd(1)-N(1)	138.40(10)
O(3)-Tb(1)-N(6)	138.58(19)	O(1)-Gd(1)-N(1)	138.36(9)
O(4)-Tb(1)-N(6)	131.25(15)	O(3)-Gd(1)-N(1)	131.24(7)
O(1)-Tb(1)-N(10)	66.35(15)	O(7)-Gd(1)-N(2)	65.85(7)
O(11)-Tb(1)-N(10)	127.39(18)	O(5)-Gd(1)-N(2)	112.61(8)
O(8)-Tb(1)-N(10)	63.74(14)	O(4)-Gd(1)-N(2)	127.12(9)
O(12)-Tb(1)-N(10)	112.74(17)	O(6)-Gd(1)-N(2)	63.37(7)
O(5)-Tb(1)-N(10)	128.51(15)	O(2)-Gd(1)-N(2)	71.61(9)
O(3)-Tb(1)-N(10)	71.68(17)	O(1)-Gd(1)-N(2)	128.56(8)
O(4)-Tb(1)-N(10)	129.31(16)	O(3)-Gd(1)-N(2)	129.82(8)
N(6)-Tb(1)-N(10)	67.97(17)	N(1)-Gd(1)-N(2)	67.71(8)

The average Tb-N distance is 2.654 Å. The length of Tb-O bond is in the range 2.358-2.400 Å is significantly less than that of similar nine coordinated sodium salt of lanthanum complex (2.537-2.555 Å) which indicate the strong interaction between Tb and oxygen atoms due to the lanthanide contraction.

Further, the Tb-O (water) bond length is also shorter (2.426-2.505 Å) than the lanthanum complexes, which indicates that the three water molecules are strongly held to the Tb^{3+} ion.

Crystal structure of $N_2H_5[Gd(EDTA)(H_2O)_3]\cdot 5H_2O$: This complex exhibit the coordination sphere of $[Gd(EDTA)(H_2O)_3]^-$, in which the Gd^{3+} ion is nine coordinated by an EDTA ligand and three water molecules taking the similar coordinate structure as $[Tb(EDTA)(H_2O)_3]^{3-}$. Gadolinium complex crystallizes in the orthorhombic system with Fd22 space group. As a hexadentate ligand, the EDTA is unable to supply enough coordination atoms either, so that there are three coordination positions taken up by the oxygen atoms from water molecules. Therefore, two nitrogen atoms and four carboxyl oxygen atoms come from the EDTA ligand yielding a slightly distorted monocapped square antiprismatic polyhedron in which the top tetragon is composed of O(2), O(7), N(1) and O(6) and the bottom tetragon plane is composed of O(5), O(1), O(3) and O(4). They form a square anti-prismatic. The capped position above the

top tetragon plane is occupied by N(2). Because of the mutual repulsion between the top tetragon plane and the capped nitrogen atom, the bond distance of Gd-N(2) (2.671 Å) is the longest one of all the coordination bonds. Moreover, the distance between two planes becomes shorter than that of standard square anti prismatic. Hence, the coordination poly-hedra cannot keep standard monocapped square anti prismatic but the slightly pseudo one. In this complex all the coordination atoms could be only divided into three groups.

Group	Coordination atom	Category	Average bond distance (Å)
I	O(4), O(5), O(6) and O(7)	Carboxyl oxygen atom (O$_c$)	2.4627
II	O(1), O(2), O(3)	Oxygen atom from water (O$_w$)	945
III	N(1) and N(2)	Nitrogen atom	2.6625

Comparing the average bond distances of corresponding groups of two complexes, it is found that the value of Gd complex is slightly larger than those of Tb complex. This further suggests that the Tb complex is slightly stable than the Gd complex which is also in accordance with thermal data. The crystal contain discrete $N_2H_5^+$ ions, $[Gd(EDTA)(H_2O)_3]^{3-}$ ions and water molecule. The $N_2H_5^+$ ion is not coordinated to Tb^{3+} ion. The cell contain $N_2H_5Tb(EDTA)\cdot 8H_2O$ to give a calculated density of 1.745 mg/m^3.

The crystal data for the Gd complex are given in Table-1. The final fractional atomic coordinates and equivalent isotropic thermal parameters for all non hydrogen atoms are given in Table-2. The important bond lengths and bond angles together with their estimated standard deviations derived from the least squares inverse matrix are given Tables 3 and 4, respectively. The atom numbering scheme with the ORTEP model, electron density map and close packing diagram are shown in Figs. 3-5, respectively.
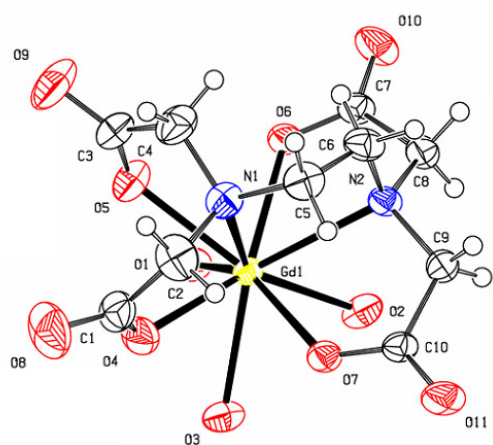

Fig. 3. ORTEP diagram of $N_2H_5[Gd(EDTA)(H_2O)_3]\cdot 5H_2O$
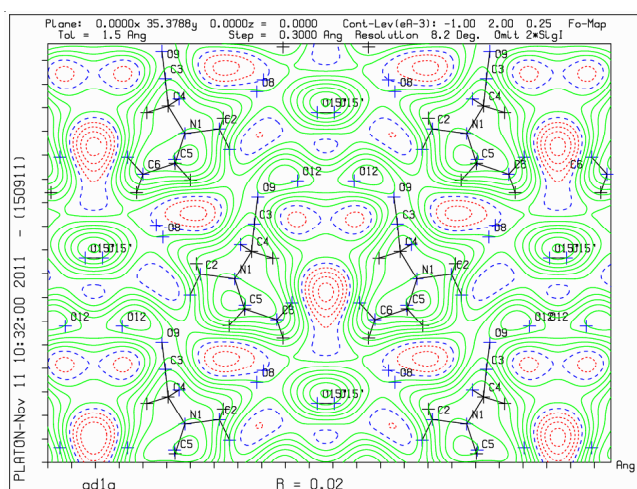
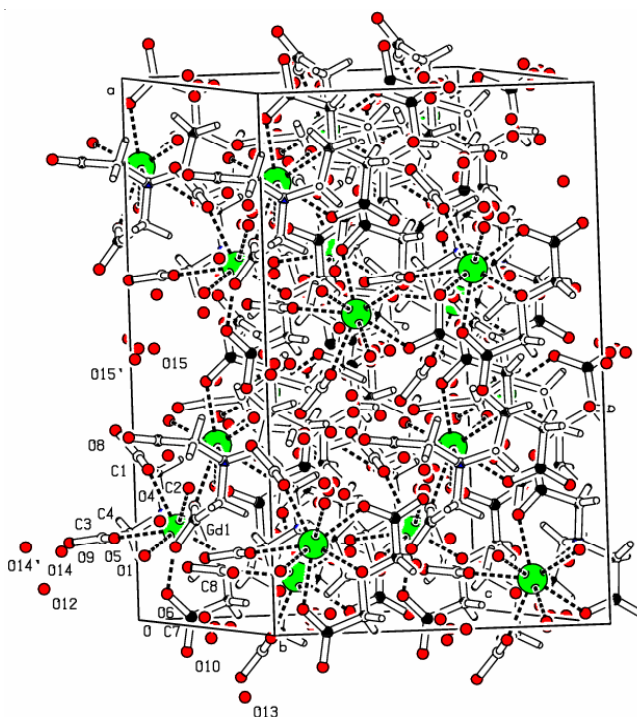Fig. 4. Electron density map of $N_2H_5[Gd(EDTA)(H_2O)_3]\cdot 5H_2O$

Fig. 5. Close packing diagram of $N_2H_5[Gd(EDTA)(H_2O)_3]\cdot 5H_2O$

REFERENCES

1. J. Zhou, L.F. Wang and J.Y. Wang, *J. Inorg. Biochem.*, **83**, 41 (2001).
2. M. Shibasaki and N. Yoshikawa, *Chem. Rev.*, **102**, 2187 (2002).
3. M. Xiao and P.R. Selvin, *J. Am. Chem. Soc.*, **123**, 7067 (2001).
4. C. Lin, J.H. Yang and X. Wu, *Anal. Chim. Acta*, **403**, 219 (2000).
5. G. Mathis, *Clin. Chem.*, **41**, 1391 (1995).
6. D. Parker, *Coord. Chem. Rev.*, **205**, 109 (2000).
7. J. Wang, X.D. Zhang and Y. Wang, *Chin. J. Struct. Chem.*, **23**, 890 (2004).
8. J.G. Kang, J.P. Hong and S.K. Yoon, *J. Alloys Comp.*, **339**, 248 (2002).
9. J. Wang, Y. Wang and Z.H. Zhang, *J. Coord. Chem.*, **59**, 295 (2006).
10. S.J. Franklin, *Curr. Opin. Chem. Biol.*, **5**, 201 (2001).
11. H. Kobayashi, S. Kawamoto, T. Saga, N. Sato, T. Ishimori, J. Konishi, K. Ono, K. Togashi and M.W. Brechbiel, *Bioconjugate Chem.*, **12**, 587 (2001).
12. P.L. Anelli, A. Beltrami, M. Franzini, P. Paoli, P. Rossi, F. Uggeri and M. Virtuani, *Inorg. Chim. Acta*, **317**, 218 (2001).
13. P. Caravan, C. Comuzzi, W. Crooks, T.J. McMurry, G.R. Choppin and S.R. Woulfe, *Inorg. Chem.*, **40**, 2170 (2001).

14. M.G. Duarte, M.H. Gil, J.A. Peters, J.M. Colet, L. Vander Elst, R.N. Muller and C. Geraldes, *Bioconjugate Chem.*, **12**, 170 (2001).

15. H. Kobayashi, N. Sato, S. Kawamoto, T. Saga, A. Hiraga, T. Ishimori, J. Konishi, K. Togashi and M.W. Brechbiel, *Magn. Reson. Med.*, **46**, 457 (2001).

16. H. Kobayashi, N. Sato, S. Kawamoto, T. Saga, A. Hiraga, T. Ishimori, J. Konishi, K. Togashi and M.W. Brechbiel, *Magn. Reson. Med.*, **46**, 579 (2001).

17. I. Lukes, J. Kotek, P. Vojtisek and P. Hermann, *Coord. Chem. Rev.*, **216**, 287 (2001).

18. Y. Bretonniere, M. Mazzanti, J. Pecaut, F.A. Dunand and A.E. Merbach, *Chem. Commun.*, 621 (2001).

19. D.M. Corsi, L. Vander Elst, R.N. Muller, H. van Bekkum and J.A. Peters, *Chem. Eur. J.*, **7**, 1383 (2001).

20. T.H. Cheng, Y.M. Wang, K.T. Lin and G.C. Liu, *J. Chem. Soc. Dalton Trans.*, 3357 (2001).

21. M. Mikawa, H. Kato, M. Okumura, M. Narazaki, Y. Kanazawa, N. Miwa and H. Shinohara, *Bioconjugate Chem.*, **12**, 510 (2001).

22. D.M.J. Doble, M. Botta, J. Wang, S. Amie, A. Barge and K.N. Raymond, *J. Am. Chem. Soc.*, **123**, 10758 (2001).

23. F.A. Dunand, E. Toth, R. Hollister and A.E. Merbach, *J. Biol. Inorg. Chem.*, **6**, 247 (2001).

24. L.V. Elst, F. Chapelle, S. Laurent and R.N. Muller, *J. Biol. Inorg. Chem.*, **6**, 196 (2001).

25. S. Rast, A. Borel, L. Helm, E. Belorizky, P.H. Fries and A.E. Merbach, *J. Am. Chem. Soc.*, **123**, 2637 (2001).

26. E. Zitha-Bovens, L. Vander Elst, R.N. Muller, H. van Bekkum and J.A. Peters, *Eur. J. Inorg. Chem.*, 3101 (2001).

27. M.P. Lowe, D. Parker, O. Reany, S. Aime, M. Botta, G. Castellano, E. Gianolio and R. Pagliarin, *J. Am. Chem. Soc.*, **123**, 7601 (2001).

28. P. Caravan, M.T. Greenfield and J.W.M. Bulte, *Magn. Reson. Med.*, **46**, 917 (2001).

29. E. Toth, L. Burai and A.E. Merbach, *Coord. Chem. Rev.*, **363**, 216 (2001).

30. S.R. Zhang, P. Winter, K.C. Wu and A.D. Sherry, *J. Am. Chem. Soc.*, **123**, 1517 (2001).

31. K.M. Johnson, J.Z. Tao, R.P. Kennan and J.C. Gore, *Magn. Reson. Med.*, **45**, 920 (2001).

32. I.A. Vogel, A Text Book of Quantitative Inorganic Analysis; Longmans Green, London (2005).

33. G.M. Sheldrik, SHELX-97 Programs for Crystal Structure Determination; University of Cambridge, UK (1977).

34. A. Braibanti, F. Dallavalle, M.A. Pellinghelli and E. Laporati, *Inorg. Chem.*, **7**, 1430 (1968).

35. L. Vikram and B.N. Sivasankar, *Indian J. Chem.*, **47A**, 25 (2008).