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Preparation, Characterization, Thermal Degradation and X-Ray Structural Studies on Anhydrous and Hydrated Hydrazinium Lanthanide(III) Ethylenediaminetetraacetate

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Anhydrous hydrazinium lanthanide(III) ethylenediaminetetraacetates, $[N_2H_5Ln(EDTA)]$, where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy have been prepared by the reaction of the respective lanthanide(III) nitrate hydrate and dihydrazinium dihydrogen ethylenediaminetetraacetate in alcoholic medium. These complexes were characterized by CHN, hydrazine and metal analyses, spectral, thermal and X-ray diffraction studies. The infrared spectral studies reveal the multidentate coordination of $EDTA^{4-}$ and monodentate coordination behaviour of $N_2H_5^+$ cation. Thermal degradation studies in argon and oxygen atmospheres clearly show the formation of different end products. Attempt to recrystallize the anhydrous complexes in water yielded respective hydrated hydrazinium lanthanide(III) ethylenediaminetetraacetates as crystalline complexes. During this process the coordination sphere expanded from seven to nine by water coordination. However, in slightly acidic solution (pH = 4), simple lanthanide(III) ethylenediaminetetraacetate hydrates were formed. The formation and structures of the hydrated hydrazinium lanthanide(III) ethylenediaminetetraacetates were confirmed by comparing X-ray powder diffraction patterns with the previously reported complexes. The X-ray crystal structure of new hydrated samarium(III) ethylenediaminetetraacetate complex has been determined as a representative model for the confirmation of the composition and hydration.

Keywords: Anhydrous lanthanide(III), Ethylenediaminetetraacetate, X-ray crystal structure.

INTRODUCTION

Lanthanide(III) ions in aqueous medium always exist as hydrated species and show higher coordination numbers from 8 to 10. Substitution of water molecules from the primary coordination sphere is difficult with monodentate and bidentate ligands due to the strong binding between water and Ln(III) ions. However, multidentate negative ligands with strong chelating abilities are capable of replacing water molecules from the coordination sphere, though not completely, to yield hydrated complexes. One of such multidentate chelating ligand is ethylenediaminetetraacetate which is known to form hydrated complexes in aqueous medium [1-5]. Formation of hydrazinium complexes has been extensively studied [6-10] and the reactions were carried out under specific conditions, though the presence of hydrazine in aqueous medium usually resulted in the formation of lanthanide(III) hydroxides which makes much more difficult to isolate the desired complexes.

Formation of anhydrous complexes with lower coordination numbers such as 6 and 7 are rare due to the water of hydration in aqueous medium and also due to the larger size of lanthanide(III) ions than the transition metal ions. In aqueous medium, presence of large number of water molecules, though nitrogen in $N_2H_5^+$ ion is better donor, was not able to compete with water molecules for coordination and hence it was found to present outside the coordination sphere as ionic species.

Hydrazinium cation, $N_2H_5^+$ due to the presence of a lone pair of electron over one of the nitrogen atoms is capable of coordination with metal ions though in many instances it was present outside the sphere without coordination. However, its presence inside the coordination sphere is expected to modify both the structure around the metal ion and also the thermal behaviour of the whole system due to the endothermic nature of N-N bond. Attempts to prepare anhydrous complexes by careful thermal dehydration of hydrated analogs were not successful due to the continuous decomposition of the later. Furthermore, inclusion of hydrazinium cation in the primary sphere is not probable during degradation which in fact prefers the exclusion of hydrazine moiety during pyrolysis. Hence, it is proposed to synthesize anhydrous Ln-EDTA complexes containing hydrazinium cation in which the absence of water molecules provide space for hydrazinium ion to coordinate with central metal ion. Synthesis of such complexes with lower coordination number enables the inclusion of desired ligands and it is possible to alter the coordination number, the structure and also the thermal and biological properties of these

complexes for varied application in diverse fields. Besides this, the water soluble complexes on recrystallization undergo hydration with modification in the coordination sphere and yielded crystalline hydrazinium Ln(III)EDTA hydrates. The formation of $N_2H_5[Ln(EDTA)(H_2O)_3]\cdot 5H_2O$ where Ln = La, Pr, Nd, Sm, Gd, Tb or Dy and $N_2H_5[Ln(EDTA)(H_2O)_3]\cdot 4H_2O$ where Ln = Ce or Eu were confirmed by chemical analyses, spectral and X-ray powder diffraction studies. In acidic medium at pH = 4, these complexes dissolve and form simple lanthanide(III) ethylenediaminetetraacetate hydrates. These complexes were confirmed by analytical and spectral studies. The structure of samarium complex has been determined by X-ray single crystal study.

EXPERIMENTAL

The chemicals used were of AR grade. The solvents were distilled before use and distilled water was used for recrystallization and analyses. Hydrazine hydrate (99-100 %) was used as received. The hydrazine content in the salt and complexes was determined by volumetric analysis under Andrew's conditions using a 0.025 mol KIO_3 [11].

The metal contents were determined by complexometric titrations after decomposing a known weight of complexes with concentrated nitric acids so as to convert them to respective lanthanide nitrate hydrates [11].

The C, H and N analyses were done on a Perkin-Elmer (model 1240) CHN analyzer. Melting points were determined on a Metter FP5 instrument and are uncorrected. The molar conductivity at room temperature was determined in water using a Centuary Digital Conductivity meter (model cc 601) and a dip type cell with a smooth platinum electrode. Magnetic susceptibility measurements were made by Gouy's method at room temperature using powdered samples of the complexes. $Hg[Co(CNS)_4]$ was used as the calibrant and the diamagnetic corrections were applied by summing up the Pascal's constants for the diamagnetic contributions of various atoms of the molecules. The electronic absorption spectra of the complexes in water were recorded on a Shimadzu 160A/240A UV-visible spectrophotometer. The infrared spectra of the solid samples in the region 4000-500 cm^{-1} were recorded on a Perkin-Elmer 597/1650 spectrophotometer using KBr pellets. Simultaneous TG-DTA experiments in argon for the complexes of La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy and in oxygen atmosphere for La, Gd, Nd, Dy complexes were carried out using a STA 1500 thermal analyzer. About 10 mg of the sample was used for each experiment. The heating rate employed was 10 °C/min and platinum cups were used as sample holders. The X-ray powder diffraction patterns of the complexes were obtained with a Philips PW 1050/70 diffractometer using Cu-K_α radiation.

The X-ray intensity data were collected on a Kappa-Apex II CCD diffractometer system with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods using SIR92 program and completed using Fourier techniques and refined applying full-matrix least square techniques. Refinement was carried out using SHELXL-97 program [12,13].

Synthesis of $[N_2H_5Ln(EDTA)]$ (where: Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy): The lanthanide nitrate hydrate was prepared by decomposing 0.01 mol of respective metal oxide in 6 N nitric acid and evaporating the resultant solution to dryness. The residue containing the respective hydrated lanthanide nitrate thus obtained was dissolved in required quantity of alcohol and used for the preparation of the complex.

The dihydrazinium dihydrogen ethylenediaminetetraacetate was prepared by mixing ethylenediaminetetraacetate acid (2.92 g, 0.01 mol) in 20 mL of alcohol and hydrazine hydrate (2 mL, 0.04 mol) in 10 mL alcohol. Then, the ligand solution was added slowly to the flask containing the metal solution. The content was refluxed for about 8 h. The solid derivative obtained was filtered, through a Whatmann 41 filter paper using a vacuum pump and washed repeatedly with ethanol and dried. The amount of Ln(III) oxides used are given in Table-1.

Preparation of $N_2H_5[Ln(EDTA)(H_2O)_3]\cdot nH_2O$: The complexes were prepared by dissolving the anhydrous complexes $[N_2H_5Ln(EDTA)]$ obtained by the previous method in 20 mL of distilled water and evaporating the resultant solution to 10 mL. The complexes were crystallized after cooling and allowing to stand at room temperature for about 24 h. The composition of the complexes were found to be $N_2H_5[Ln(EDTA)(H_2O)_3]\cdot nH_2O$ where n = 4, for Ln = La, Pr, Nd, Sm, Gd, Tb or Dy and n = 4, for Ln = Ce or Eu.

Preparation of $[Ln(HEDTA)(H_2O)_3]\cdot 4H_2O$: These complexes were prepared by dissolving the anhydrous complexes $[N_2H_5Ln(EDTA)]$ in 20 mL of distilled water containing 1 mL of 4N HCl and evaporating the resultant solution to 10 mL. The complexes were crystallized after cooling and allowing to stand at room temperature for about 24 h. The composition of the complexes were found to be $[Ln(EDTA)(H_2O)_3]\cdot 4H_2O$ where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy.

TABLE-1
ANALYTICAL DATA

Complex	Yield	Colour	Elemental analysis (%): Found (calcd.)		Molar conductance (mho cm^2 mol^{-1})
			Hydrazine	Ln	
$[N_2H_5La(EDTA)]$	80 % (1.629 g)	Colourless	6.70 (6.97)	29.70 (30.19)	128
$[N_2H_5Ce(EDTA)]$	70 % (2.752 g)	Colourless	6.85 (6.95)	29.80 (30.37)	133
$[N_2H_5Pr(EDTA)]$	85 % (1.702 g)	Pale green	6.80 (6.93)	30.10 (30.49)	120
$[N_2H_5Nd(EDTA)]$	80 % (1.682 g)	Pale pink	6.75 (6.88)	31.30 (30.99)	123
$[N_2H_5Sm(EDTA)]$	85 % (1.744 g)	Pale yellow	6.70 (6.80)	31.20 (31.88)	130
$[N_2H_5Eu(EDTA)]$	70 % (1.760 g)	Colourless	6.70 (6.77)	31.60 (32.11)	115
$[N_2H_5Gd(EDTA)]$	75 % (1.813 g)	Colourless	6.65 (6.70)	32.20 (32.86)	112
$[N_2H_5Tb(EDTA)]$	75 % (1.869 g)	Colourless	6.60 (6.67)	32.60 (33.10)	117
$[N_2H_5Dy(EDTA)]$	80 % (1.865 g)	Pale yellow	6.50 (6.63)	33.10 (33.59)	120

RESULTS AND DISCUSSION

Hydrazinium lanthanide ethylenediaminetetraacetate, $[N_2H_5Ln(EDTA)]$ where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy were prepared by the reaction between respective lanthanide nitrate hydrates and dihydrazinium dihydrogen ethylenediaminetetraacetate in alcohol. The general chemical reaction is represented as follows:

$$Ln(H_2O)\cdot(NO_3)_3 + H_4EDTA + 4N_2H_4\cdot H_2O \longrightarrow N_2H_5Ln(EDTA) + 3N_2H_5NO_3 + (x + 4)H_2O$$

where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb or Dy.

The complexes prepared are solid derivatives, which are stable at room temperature. They are soluble in water and insoluble in organic solvents such as alcohol, ether, acetone and chloroform. The chemical analyses and CHN analyses for the compound are in good agreement with the assigned chemical composition (Table-1). The method ensures that excess hydrazine is required to isolate the complex though only one hydrazinium ion is found in the complexes. It is also proposed to prepare the corresponding hydrated complexes from anhydrous complexes in aqueous medium for the conformation of the composition of the anhydrous complexes. Previous studies revealed that it is not possible to prepare the anhydrous complexes by thermal degradation because of the continues decomposition and the presence of three water molecules inside the coordination sphere which make difficult to dehydrate them without disturbing the structure. Hydrazinium ion $N_2H_5^+$ being present outside the coordination sphere readily eliminated during thermal degradation, hence its inclusion into the coordination sphere is rather difficult.

In alcoholic medium, hydrazinium cation easily enters and occupies the coordination sphere by competing with minimum number of water molecules. This resulted in the formation of seven coordinated anhydrous complexes.

Attempt to recrystallize these complexes in water or 1:1 water-alcohol mixture was not successful and the clear solution yields only hydrated complex in crystalline state. The composition of the compounds thus separated was found to be $N_2H_5[Ln(EDTA)(H_2O)_3]\cdot nH_2O$. Hence, during the above process water molecules enter into the primary sphere of coordination leaving hydrazinium cation outside the primary sphere as ionic species for charge neutralization. The chemical transformation in aqueous medium is represented as follows:

$$[N_2H_5Ln(EDTA)] + nH_2O \rightarrow N_2H_5[Ln(EDTA)(H_2O)_3]\cdot(n-3)H_2O$$

where Ln = La, Pr, Nd, Sm, Gd, Tb or Dy, n = 8 and Ln = Ce or Eu, n = 7.

However, when the anhydrous complexes are dissolved in slightly acidic solution (pH = 4) by adding few drops of dilute HCl, after evaporation and crystallization it was found that the complexes formed are lanthanide(III) hydrogen ethylenediaminetetraacetate hydrates. These complexes were isolated and the compositions were confirmed by chemical analyses and spectral studies. The X-ray single crystal structure of samarium complex has been determined for further confirmation.

All hydrated hydrazinium complexes were separated and their compositions were determined by hydrazinium and metal analyses. The infrared spectra of complexes along with their X-ray powder diffraction patterns are well in agreement with the previously reported hydrated complexes. The number of water molecules in the hydrated sphere was confirmed by thermal studies.

In aqueous medium both the anhydrous hydrazinium complexes and their respective hydrated derivatives obtained by the above method show almost same molar conductance values which are also an evidence for the reorganization of the structure of hydrazinium lanthanide(III) ethylenediaminetetraacetates in water. The molar conductance values of the anhydrous complex are given in Table-1.

Electronic spectra: The electronic spectra of Pr, Nd, Sm and Er complexes recorded in water were comparable with the respective aqueous complexes and already reported hydrated hydrazinium Ln(III) ethylenediaminetetraacetates [14]. All the complexes show sharp and weak bands due to *f-f* transitions.

Infrared spectra: Careful analyses of infrared spectra of the anhydrous complexes reveal that hydrazinium cation is coordinated to metal ion through nitrogen atom possessing a lone pair. A sharp band is observed at 990 cm^{-1} for all the complexes are in well accordance with the literature report [15] for the N-N stretching of coordinated $N_2H_5^+$ ion. Though in EDTA complexes many sharp signals are found in the finger print region, in the present set of complexes no bands are observed in 1000-950 cm^{-1} region except a band at 990 cm^{-1} which avoids any ambiguity. The ν_{asym} and ν_{sym} stretching frequency are seen at 1650 and 1380 cm^{-1}, respectively indicating the unidentate coordination behaviour of carboxylate ions of $EDTA^{4-}$ ion [16].

The infrared spectra of hydrated complexes are almost similar to that already reported [14]. The IR spectra of anhydrous samarium and hydrated samarium complexes are shown in Figs. 1 and 2. The infrared spectrum of simple lanthanide(III) hydrogen ethylenediaminetetraacetate hydrates are also similar to the compounds reported earlier. However, the samarium complex is not reported in literature, its crystal structure has been determined for comparison and confirmation.

Thermal analysis: The thermal profiles of anhydrous hydrazinium complexes clearly indicate that the initial weight loss at temperature range 50-230 °C corresponds to elimination of hydrazinium molecule. The complex undergoes continuous degradation in two or three steps to give corresponding lanthanide carbonate (Tables 2 and 3).

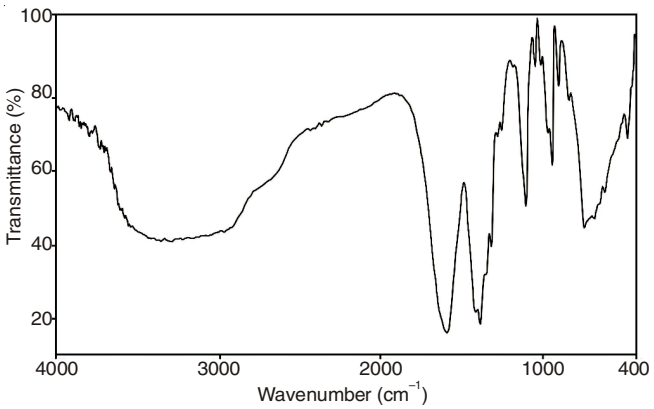

Fig. 1. IR Spectrum of $[N_2H_5Sm(EDTA)]$ complex

TABLE-2
THERMAL DATA OF $[N_2H_5Ln(EDTA)]$ IN ARGON ATMOSPHERE

Complex	Stage	TG-temperature range (°C)	Weight loss (%)		Product
			Found	Calcd.	
$[N_2H_5La(EDTA)]$	I	50-230	6.00	6.97	A
	II	230-450	42.00	41.12	B
	III	450-600	52.00	50.25	C
$[N_2H_5Ce(EDTA)]$	I	60-210	8.00	6.95	A
	II	210-470	51.00	50.12	C
$[N_2H_5Pr(EDTA)]$	I	50-160	7.00	6.93	A
	II	160-420	43.00	40.95	B
	III	420-600	48.00	50.04	C
$[N_2H_5Nd(EDTA)]$	I	50-170	8.00	6.88	A
	II	170-410	42.00	40.65	B
	III	410-550	48.00	49.68	C
$[N_2H_5Sm(EDTA)]$	I	70-200	6.00	6.80	A
	II	200-580	40.00	40.13	B
$[N_2H_5Eu(EDTA)]$	I	70-160	6.00	6.77	A
	II	160-400	40.00	40.00	B
	III	400-600	49.00	48.87	C
$[N_2H_5Gd(EDTA)]$	I	50-130	8.00	6.70	A
	II	130-410	40.00	39.55	B
	III	410-600	50.50	48.33	C
$[N_2H_5Tb(EDTA)]$	I	80-200	5.50	6.67	A
	II	200-500	50.00	48.16	C
$[N_2H_5Dy(EDTA)]$	I	70-170	6.00	6.63	A
	II	170-600	46.00	47.80	C

TABLE-3
THERMAL DATA OF $[N_2H_5Ln(EDTA)]$ IN OXYGEN ATMOSPHERE

Complex	Stage	TG-temperature range (°C)	Weight loss (%)		Product
			Found	Calcd.	
$[N_2H_5La(EDTA)]$	I	100-200	6.00	6.95	A
	II	200-320	41.00	41.12	B
	III	320-800	60.00	61.93	D
$[N_2H_5Gd(EDTA)]$	I	220-300	10.00	6.70	A
	II	300-800	61.2	62.12	D
$[N_2H_5Nd(EDTA)]$	I	100-130	10.00	6.88	A
	II	130-400	37.00	40.66	B
	III	400-800	62.00	63.86	D
$[N_2H_5Dy(EDTA)]$	I	300-340	12.00	6.62	A
	II	340-370	30.00	34.8	B
	III	370-800	62.00	61.45	D

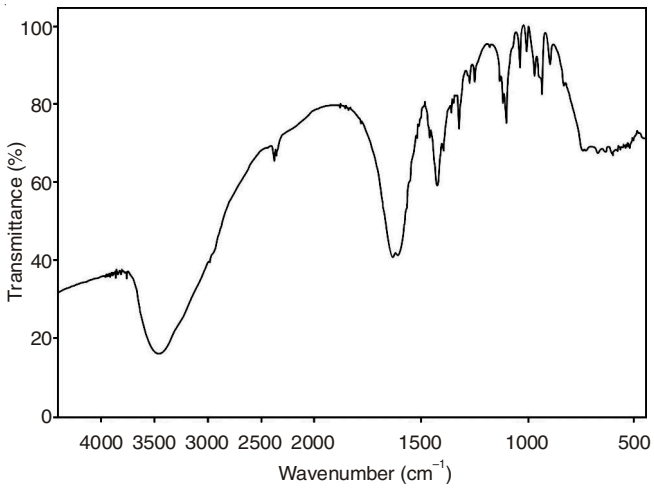

Fig. 2. IR Spectrum of $N_2H_5[Sm(EDTA)(H_2O)_3]\cdot 5H_2O$ complex

Anhydrous complexes are expected to decompose at lower temperatures than the corresponding hydrated complexes. Further, the absence of water molecule (coordinated and non-coordinated) simplified the decomposition pattern. These anhydrous complexes are expected to yield corresponding hydrated complexes when dissolved in water.

Synthesis of such complexes with low coordination number enables the inclusion of the desired ligands and hence it is possible to alter the coordination number, structure and also the thermal and biological properties of these complexes for desired applications.

The earlier investigation extensively reported the thermal behaviour of the hydrated complexes in different atmosphere. Though lanthanide(III) oxalates and carbonate have been proposed as intermediate due to the continues degradation to final Ln(III) oxides made the isolation of the intermediate difficult and could be assigned only on the basis of TG/DTA studies. Hence, it is believed that the oxidation in inert atmosphere could lead to different pattern of degradation and helps in confirming the formation of such compounds by isolation and analyses.

The general scheme of thermal degradation of anhydrous hydrazinium lanthanide(III) ethylenediaminetetraacetates in argon atmosphere is given below:

Stage-I: $[N_2H_5La(EDTA)] \longrightarrow [Ln(HEDTA)]$ (A)

Stage-II: $[Ln(HEDTA)] \longrightarrow 0.5[Ln_2(C_2O_4)_3]$ (B)

Stage-III: $0.5[Ln_2(C_2O_4)_3] \longrightarrow 0.5[Ln_2(CO_3)_3]$] (C)

It is obvious from the above scheme that in inert atmosphere these complexes decompose in three stages to give respective lanthanide carbonate as the end residue. However, in oxygen atmosphere though the intermediate is respective lanthanide oxalates the end product is the respective lanthanide oxide. In some cases the intermediate A undergoes one step decomposition to respective lanthanide carbonate C. In the case of samarium complex the final product formed up to 580 °C is found to be samarium oxalate and carbonate is not formed at this temperature.

The general scheme of thermal degradation of anhydrous hydrazinium lanthanide(III) ethylenediaminetetraacetates in oxygen atmosphere is given below:

Stage-I: $[N_2H_5La(EDTA)] \longrightarrow [Ln(HEDTA)]$ (A)

Stage-II: $[Ln(HEDTA)] \longrightarrow 0.5[Ln_2(C_2O_4)_3]$ (B)

Stage-III: $0.5[Ln_2(C_2O_4)_3] \longrightarrow 0.5Ln_2O_3$ (D)

X-ray crystal structure of $[Sm(HEDTA)(H_2O)_3]\cdot 4H_2O$: The X-ray study together with density measurement shows that hydrazinium salts of samarium ethylenediaminetetraacetate hydrate crystallize in the space group Fdd2 and the crystal system is orthorhombic. The observed crystal density is 1.728 mg/m^3, which is close to that of that calculated from X-ray analyses. The crystal data is given in Table-4. The final fractional atomic coordinates and equivalent isotropic thermal parameters for all non-hydrogen atoms are given in Table-5. The important bond lengths and bond angles are summarized in Table-6. The atom numbering scheme with ORTEP model and close packing diagram are shown in Figs. 3 and 4, respectively. The Sm(III) complex is nine coordinated with hexadentate

TABLE-4
CRYSTAL DATA AND STRUCTURE REFINEMENT FOR $[Sm(HEDTA)(H_2O)_3]\cdot 4H_2O$

Identification code	SHELXL
Empirical formula	$C_{10}H_{19}N_2O_{15}Sm$
Formula weight	557.62
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Orthorhombic, Fdd2
Unit cell dimensions	a = 19.6140(2) Å; α = 90°
	b = 35.5636(7) Å; β = 90°
	c = 12.2894(2) Å; γ = 90°
Volume	8572.4(2) A^3
Z, Calculated density	16, 1.728 mg/m^3
Absorption coefficient	2.810 mm^{-1}
F(000)	4400
Crystal size	0.35 mm × 0.30 mm × 0.20 mm
Theta range for data collection	2.29 to 25.00°
Limiting indices	-23 <= h <= 22; -42 <= k <= 41
	-13 <= l <= 14
Reflections collected/unique	16708/3701 [R(int) = 0.0203]
Completeness to θ = 25.00	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.6236 and 0.4239
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3701/11/282
Goodness-of-fit on F^2	1.141
Final R indices [I > 2σ(I)]	R1 = 0.0214, wR2 = 0.0641
R indices (all data)	R1 = 0.0217, wR2 = 0.0643
Absolute structure parameter	-0.001(14)
Extinction coefficient	0.00043(3)
Largest diff. peak and hole	1.187 and -0.479 e A^{-3}

TABLE-5
ATOMIC COORDINATES (× 10^4) AND EQUIVALENT ISOTROPIC DISPLACEMENT PARAMETERS (A^2 × 10^3) FOR $[Sm(HEDTA)(H_2O)_3]\cdot 4H_2O$ U(eq) IS DEFINED AS ONE THIRD OF THE TRACE OF THE ORTHOGONALIZED Uij TENSOR

	x	y	z	U(eq)
C(1)	8951(3)	157(1)	2722(4)	36(1)
C(2)	8259(3)	23(2)	3082(5)	35(1)
C(3)	8400(3)	59(2)	5052(5)	42(1)
C(4)	8472(3)	323(1)	6017(4)	37(1)
C(5)	7302(3)	176(1)	4267(4)	44(1)
C(6)	6991(3)	486(2)	4921(4)	40(1)
C(7)	9695(2)	682(2)	2447(4)	33(1)
C(8)	9958(2)	741(1)	3608(4)	31(1)
C(9)	8648(2)	640(1)	1395(4)	31(1)
C(10)	7903(2)	767(1)	1469(4)	26(1)
N(1)	8970(2)	563(1)	2465(3)	26(1)
N(2)	8043(2)	216(1)	4107(4)	32(1)
O(1)	7579(2)	778(1)	616(3)	45(1)
O(2)	7665(2)	852(1)	2408(3)	30(1)
O(3)	10588(2)	727(1)	3753(3)	46(1)
O(4)	9527(2)	810(1)	4332(3)	32(1)
O(5)	8545(3)	184(1)	6934(3)	62(1)
O(6)	8471(2)	667(1)	5804(3)	38(1)
O(7)	7215(2)	814(1)	4775(3)	41(1)
O(8)	6507(3)	409(1)	5555(4)	69(1)
O(9)	7544(2)	1521(1)	3880(3)	36(1)
O(10)	8798(2)	1445(1)	5234(3)	36(1)
O(11)	8858(2)	1403(1)	2767(3)	36(1)
Sm(1)	8323(1)	953(1)	4029(1)	22(1)
O(12)	9378(3)	-385(1)	7533(4)	60(1)
O(13)	6464(4)	950(2)	7161(7)	101(2)
O(15)	5153(6)	348(5)	4689(10)	244(8)
O(14)	8769(4)	1123(2)	7474(9)	72(4)
O(14')	8680(8)	761(4)	8521(9)	88(5)

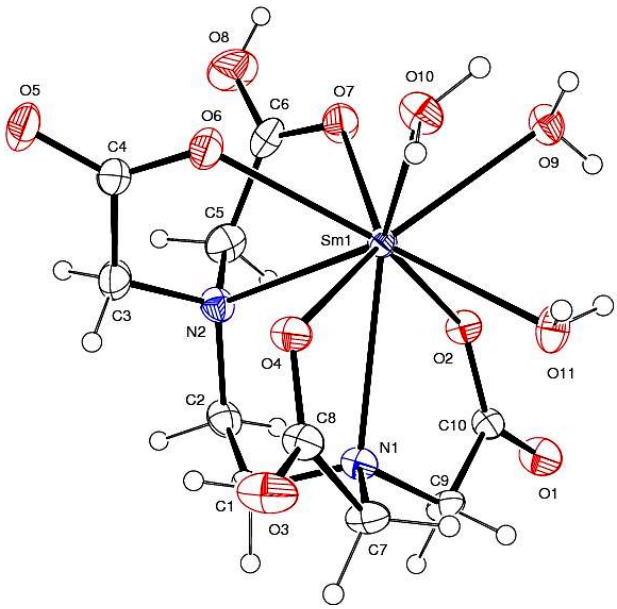

Fig. 3. ORTEP model for $[Sm(HEDTA)(H_2O)_3]\cdot 4H_2O$

TABLE-6
BOND LENGTHS (Å) AND ANGLES (°)
FOR $[Sm(HEDTA)(H_2O)_3]\cdot 4H_2O$

C(1)-N(1)	1.477(6)	C(8)-O(4)	1.253(6)
C(1)-C(2)	1.506(8)	C(9)-N(1)	1.485(6)
C(1)-H(1A)	0.9700	C(9)-C(10)	1.531(6)
C(1)-H(1B)	0.9700	C(9)-H(9A)	0.9700
C(2)-N(2)	1.496(7)	C(9)-H(9B)	0.9700
C(2)-H(2A)	0.9700	C(10)-O(1)	1.227(6)
C(2)-H(2B)	0.9700	C(10)-O(2)	1.281(6)
C(3)-N(2)	1.467(7)	N(1)-Sm(1)	2.689(4)
C(3)-C(4)	1.519(8)	N(2)-Sm(1)	2.679(3)
C(3)-H(3A)	0.9700	O(2)-Sm(1)	2.401(3)
C(3)-H(3B)	0.9700	O(4)-Sm(1)	2.442(3)
C(4)-O(5)	1.239(6)	O(6)-Sm(1)	2.423(3)
C(4)-O(6)	1.252(6)	O(7)-Sm(1)	2.410(3)
C(5)-N(2)	1.473(6)	O(8)-H(8)	0.8200
C(5)-C(6)	1.495(8)	O(9)-Sm(1)	2.543(3)
C(5)-H(5A)	0.9700	O(9)-H(9C)	0.827(19)
C(5)-H(5B)	0.9700	O(9)-H(9D)	0.813(19)
C(6)-O(8)	1.257(7)	O(10)-Sm(1)	2.477(3)
C(6)-O(7)	1.258(6)	O(10)-H(10B)	0.854(19)
C(7)-N(1)	1.484(5)	O(10)-H(10A)	0.832(19)
C(7)-C(8)	1.533(6)	O(11)-Sm(1)	2.465(3)
C(7)-H(7A)	0.9700	O(11)-H(11A)	0.835(19)
C(7)-H(7B)	0.9700	O(11)-H(11B)	0.833(19)
C(8)-O(3)	1.249(6)	–	–
N(1)-C(1)-C(2)	113.3(4)	C(5)-N(2)-C(2)	110.3(4)
N(1)-C(1)-H(1A)	108.9	C(3)-N(2)-Sm(1)	107.6(3)
C(2)-C(1)-H(1A)	108.9	C(5)-N(2)-Sm(1)	107.5(3)
N(1)-C(1)-H(1B)	108.9	C(2)-N(2)-Sm(1)	111.2(3)
C(2)-C(1)-H(1B)	108.9	C(10)-O(2)-Sm(1)	125.9(3)
H(1A)-C(1)-H(1B)	107.7	C(8)-O(4)-Sm(1)	125.9(3)
N(2)-C(2)-C(1)	110.9(4)	C(4)-O(6)-Sm(1)	126.7(3)
N(2)-C(2)-H(2A)	109.5	C(6)-O(7)-Sm(1)	124.0(3)
C(1)-C(2)-H(2A)	109.5	C(6)-O(8)-H(8)	109.5
N(2)-C(2)-H(2B)	109.5	Sm(1)-O(9)-H(9C)	109(4)
C(1)-C(2)-H(2B)	109.5	Sm(1)-O(9)-H(9D)	113(4)
H(2A)-C(2)-H(2B)	108.0	H(9C)-O(9)-H(9D)	117(3)
N(2)-C(3)-C(4)	115.3(5)	Sm(1)-O(10)-(10B)	108(4)
N(2)-C(3)-H(3A)	108.4	Sm(1)-O(10)-(10A)	124(4)
C(4)-C(3)-H(3A)	108.4	H(10B)-O(10)-(10A)	110(3)
N(2)-C(3)-H(3B)	108.4	Sm(1)-O(11)-(11A)	110(5)
C(4)-C(3)-H(3B)	108.4	Sm(1)-O(11)-(11B)	103.1(17)
H(3A)-C(3)-H(3B)	107.5	H(11A)-O(11)-(11B)	116(3)
O(5)-C(4)-O(6)	125.5(5)	O(2)-Sm(1)-O(7)	78.48(12)
O(5)-C(4)-C(3)	118.3(5)	O(2)-Sm(1)-O(6)	138.48(12)
O(6)-C(4)-C(3)	116.2(5)	O(7)-Sm(1)-O(6)	71.31(13)
N(2)-C(5)-C(6)	113.8(4)	O(2)-Sm(1)-O(4)	127.98(11)
N(2)-C(5)-H(5A)	108.8	O(7)-Sm(1)-O(4)	140.45(12)
C(6)-C(5)-H(5A)	108.8	O(6)-Sm(1)-O(4)	70.15(11)
N(2)-C(5)-H(5B)	108.8	O(2)-Sm(1)-O(11)	78.68(12)
C(6)-C(5)-H(5B)	108.8	O(7)-Sm(1)-O(11)	139.15(12)
H(5A)-C(5)-H(5B)	107.7	O(6)-Sm(1)-O(11)	141.99(12)
O(8)-C(6)-O(7)	123.6(5)	O(4)-Sm(1)-O(11)	79.59(12)
O(8)-C(6)-C(5)	118.7(5)	O(2)-Sm(1)-O(10)	143.51(12)
O(7)-C(6)-C(5)	117.6(4)	O(7)-Sm(1)-O(10)	104.85(13)
N(1)-C(7)-C(8)	110.4(4)	O(6)-Sm(1)-O(10)	73.34(12)
N(1)-C(7)-H(7A)	109.6	O(4)-Sm(1)-O(10)	72.07(11)
C(8)-C(7)-H(7A)	109.6	O(11)-Sm(1)-O(10)	75.88(11)
N(1)-C(7)-H(7B)	109.6	O(2)-Sm(1)-O(9)	74.65(12)
C(8)-C(7)-H(7B)	109.6	O(7)-Sm(1)-O(9)	69.39(12)
H(7A)-C(7)-H(7B)	108.1	O(6)-Sm(1)-O(9)	118.07(12)
O(3)-C(8)-O(4)	125.1(4)	O(4)-Sm(1)-O(9)	139.20(11)
O(3)-C(8)-C(7)	117.4(4)	O(11)-Sm(1)-O(9)	72.12(13)
O(4)-C(8)-C(7)	117.4(4)	O(10)-Sm(1)-O(9)	72.91(11)
N(1)-C(9)-C(10)	114.1(4)	O(2)-Sm(1)-N(2)	76.90(13)
N(1)-C(9)-H(9A)	108.7	O(7)-Sm(1)-N(2)	66.50(12)
C(10)-C(9)-H(9A)	108.7	O(6)-Sm(1)-N(2)	65.33(13)
N(1)-C(9)-H(9B)	108.7	O(4)-Sm(1)-N(2)	89.44(11)
C(10)-C(9)-H(9B)	108.7	O(11)-Sm(1)-N(2)	138.23(13)
H(9A)-C(9)-H(9B)	107.6	O(10)-Sm(1)-N(2)	138.43(13)
O(1)-C(10)-O(2)	125.0(4)	O(9)-Sm(1)-N(2)	131.10(11)
O(1)-C(10)-C(9)	116.9(4)	O(2)-Sm(1)-N(1)	65.38(11)
O(2)-C(10)-C(9)	118.1(4)	O(7)-Sm(1)-N(1)	126.30(12)
C(1)-N(1)-C(7)	107.9(4)	O(6)-Sm(1)-N(1)	111.78(12)
C(1)-N(1)-C(9)	111.1(4)	O(4)-Sm(1)-N(1)	63.02(10)
C(7)-N(1)-C(9)	109.9(4)	O(11)-Sm(1)-N(1)	71.61(12)
C(1)-N(1)-Sm(1)	109.8(3)	O(10)-Sm(1)-N(1)	127.98(11)
C(7)-N(1)-Sm(1)	108.4(2)	O(9)-Sm(1)-N(1)	129.97(12)
C(9)-N(1)-Sm(1)	109.7(3)	N(2)-Sm(1)-N(1)	67.53(12)
C(3)-N(2)-C(5)	109.2(4)	–	–
C(3)-N(2)-C(2)	110.9(3)	–	–

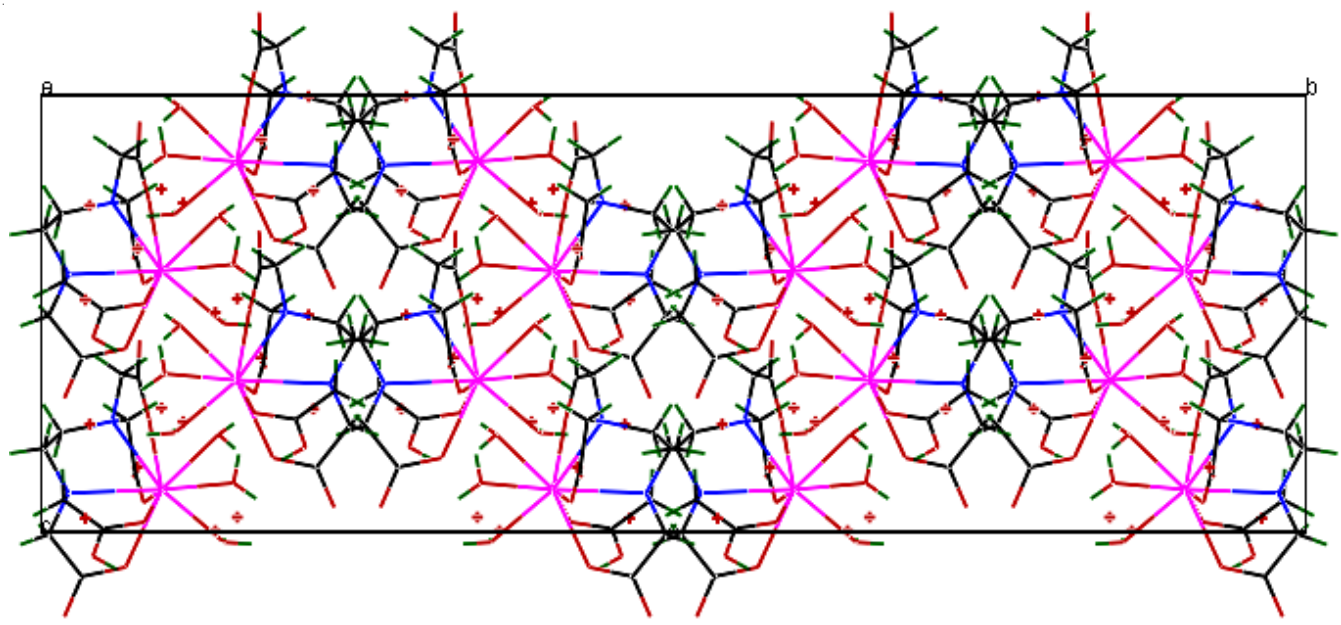

Fig. 4. Close packing diagram for $[Sm(HEDTA)(H_2O)_3]\cdot 4H_2O$

$HEDTA^{3-}$ and three water molecules. The two nitrogen atoms, three carboxylate oxygen atoms and one carbonyl oxygen of free carboxylic acid group of $HEDTA^{3-}$ are coordinated to Sm(III) ion in a hexadendate chelating fashion, while the three other sites are occupied by oxygen atoms of three water molecules resulting in a slightly disorted monocapped square antiprismatic polyhedron. The unit cell has sixteen complex molecules which are mainly associated through the intermolecular hydrogen bonding which plays a vital role in stabilizing the crystal structure.

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