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New phenylhydrazinium complexes of lanthanide (III) with ethylenediaminetetraacetate: Spectral, thermal and XRD studies

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ABSTRACT

Synthesis, structural characterization and thermal degradation studies on novel precursors, phenyl hydrazinium lanthanum (III) ethylenediaminetetraacetate hydrates, $PhNHNH_3[Ln(EDTA)(H_2O)_2](H_2O)_3$ where Ln= La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy to potential binuclear μ-hydroxo clusters are reported. The conductivity measurements reveal that the phenyl hydrazinium part, $PhNHNH_3^+$ is ionic and outside the coordination spheres. The infrared spectra shows the presence of both coordinated and lattice water molecules and characteristic bands for ethylenediaminetetraacetate moiety along with the N-N stretching for non coordinated phenyl hydrazinium ion. The simultaneous TG-DTA experiments in air reveal the presence of two coordinated and three lattice water molecules. All the complexes undergo multi-step degradation to yield respective oxides and Ln_2O_3 as the final residue. The metal analyses, infrared spectra and X-ray powder technique have been used to confirm the end product. The X-ray diffraction patterns of the complexes are in accordance with the isomorphism among the series. Due to the presence of several unpaired electrons and large size of lanthanide (III) ions, these complexes are expected to possess antioxidantal properties. Among the lanthanide complexes praseodymium complex shows maximum activity and the gadolinium complex shows poor activity. However, the free radical quenching powers of other complexes depend on the number of unpaired electrons in the respective rare earth metal ion.

Key words: Ln (III) complexes; phenyl hydrazinium cation; hexadendate ligand; Coordinated water and eight coordination

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INTRODUCTION

Lanthanide ions and complexes occupy a special position in developing synthetic nucleases capable of catalyzing the hydrolytic cleavage of RNA and DNA. Trivalent lanthanide ions are expected to be more effective in this capacity than transition metal complexes due to their strong Lewis acidity and kinetic lability of their complexes [1, 2]. Ligand controlled hydrolysis of the lanthanide ions is a new avenue in lanthanide coordination chemistry which is a effective approach to assemble structurally well defined polynuclear lanthanide – hydroxo complexes of definite size. Polynuclear lanthanide complexes exhibit a variety of unusual symmetries and structural patterns. Polyamino polycarboxylic acids and α-amino carboxylic acids are the novel and effective supporting ligands for controlling the hydrolysis of Ln (III) ions. These auxiliary ligands occupy a part of the metal coordination sphere, thereby reducing the number of sites available for water coordination and thus prevent the extent of hydrolysis. The pH of the reaction medium exert a strong influence on lanthanide complexation which takes place either through carboxylate group or simultaneous coordination by carboxylate and amino moieties.

The lanthanide – amino acid complexes generated under neutral or basic conditions exist as polynuclear lanthanide – hydroxo clusters, while at low pH mono, di or non cluster polynuclear forms dominate. The pH of the lanthanide – EDTA mixture when raised, the aqua ligand of initially formed nine or eight coordinated complexes would be deprotonated giving rise to a μ-hydroxo bimolecular complexes which further leads to the formation of the μ_2-hydroxo bridged diamond-shaped intermediates which on subsequent condensation offered a tetranuclear lanthanide clusters. The binuclear core, doubly bridged by the μ-OH group encapsulated by two hexadented EDTA ligand, one on each metal atom has been reported [3-6]. Obviously the water of coordination plays a vital role in the formation of polynuclear complexes. Hence the number of coordinated water is crucial in deciding the extent of polymerization. With polyamino polycarboxylic acids it was observed that the maximum number of water molecules inside the sphere is three as reported in the case of simple L^{III}HEDTA hydrates [7-9] and $M[Ln^{III}(EDTA)(H_2O)_3].H_2O$ complexes where M= K^+, Na^+, NH_4^+ and $N_2H_5^+$ [10-15]. The serious limitations with these compounds in exploiting them as precursors to μ-hydroxo bridged complexes is that while increasing the pH of the medium, deportanation of all the water molecules takes place leading to uncontrolled polymerization. Hence, synthesis of bi, and tri- nuclear species could not be realized. Hence, search for di hydrated and mono hydrated complexes considered worth for controlled deportanation and hence controlled polymerization. Only a few Ln (III) polyamino polycarboxylates with two coordinated water molecules have been prepared and structurally characterized and reported to yield binuclear hydroxo complexes [6, 7].

However, no singe method was found satisfactory in synthesizing a series of structurally similar complexes with desired composition, with two coordinated water molecules, which also lacks uniformity. Hence attempts have been made in this row by changing the counter ion instead of ligands. In the present investigation, when phenyl hydrazine was used as a base or charge neutralizing species, we were able to synthesize a series of new phenyl hydrazinium diaquoethylenediaminetetraacetatolanthanate(III) trihydrates. Furthermore, so for no such phenyl hydrazinium complexes of metal/lanthanide carboxylates have been investigated except a cobalt pyridine dicarboxylate complex repotted recently [16]. Hence in this paper we wish to report the synthesis, characterization, spectral, thermal, X-ray diffraction and antioxidant studies on $PhNHNH_3[Ln(EDTA)(H_2O)_2](H_2O)_3$ where Ln= La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy which could be used as precursors to the bi and tri nuclear lanthanide complexes.

EXPERIMENTAL SECTION

The chemicals used were of AnalaR or equivalent grade. The solvents were distilled before use and distilled water was used for the preparation and analyses. Phenyl hydrazine (99-100%), H_4EDTA (99.5%) and rare earth oxides were used as received from S.D. fine chemicals. The Ln (III) nitrates, ligands and complexes were prepared and analyses were carried out using fresh doubly distilled water and the solvents were distilled before use. The metal contents were determined by complexometric titrations after decomposing the complex with concentrated nitric acid to eliminate the organic part [17]. The C,H and N analyses were carried out using a Perkin – Elmer model 1240 CHN analyzer. The molar conductivity at room temperature was determined in conductivity water using a Century digital conductivity meter model CC 601 and a dip type cell with a smooth platinum electrode. The magnetic susceptibility measurements were made by Gouy's method at room temperature using powdered samples of complexes. $Hg[Co(NSC)_4]$ 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 molecule. 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 500-4000 cm^{-1} were recorded on a Perkin – Elmer 597/1650 spectrophotometer using KBr pellets. The thermal analyses (TG-DTA) for the complexes were recorded on a STA 1500 thermal analyzer using about 5mg of the samples with the heating rate of 10 ^oC per min and the platinum cups as sample holders. The X-ray powder diffraction patterns were recorded on a Philips PW 1050/70 diffractometer using Cu-Kα radiation (λ=1.540598 Å) and scintillation counter as detector.

Antioxidant testing

The effect of complexes on DPPH radical was estimated according to the procedure described in literature [18]. The concentration of the antioxidant required to decrease by 50% of the initial substrate concentration (IC_{50}) is a parameter widely used to measure the antioxidant power (Molyneux 2004). The lower the $IC_{50,}$ the higher is the antioxidant power. Free radical activity was measured by a decrease in absorbance at 516 nm of a methanolic solution of coloured DPPH (diphenylpicrylhydrazide) brought about by the sample. A stock solution of DPPH was prepared such that 125 ml of it in 5 ml methanol gave an initial absorbance of 0.88. This stock solution was used to measure the antiradical activity. Decrease in the absorbance in the presence of the sample solution at different concentrations was noted after 15 minutes. IC_{50} was calculated from percentage inhibition. Efficient concentration is the concentration of that causes 50% loss of DPPH activity. BHA (butylated hydroxyanizole) was used as positive control. Percentage inhibition was calculated using the formula

% inhibition = 100-A

Where A= sample absorbance x 100 /initial absorbance by DPPH.

Preparation of $(C_6H_5NHNH_3)_2H_2$edta:

The ligand, di(phenyl hydrazinium) dihydrogen ethylenediaminetetraacetate, $(C_6H_5NHNH_3)_2H_2$edta was prepared by the acid-base neutralization reaction of ethylenediaminetetraacetic acid and phenyl hydrazine hydrate in 1:2 ratio. Aqueous solution (5ml) phenyl hydrazine (2 ml, 0.02M) was added to an aqueous solution (30ml) suspension of H_4edta (2.92 g, 0.01M). The acid was slowly dissolved to obtain the clear solution. The clear solution was filtered through Whatmann filter paper and finally concentrated to about 25ml using a water bath. The clear solution thus obtained was kept for crystallization. The colourless crystals obtained after 2-3 days was filtered, washed with 1:1 water-alcohol mixture and dried in air. The crystals were further purified by recrystallization using distilled water.

Preparation of $C_6H_5NHNH_3[Ln(edta)(H_2O)_2](H_2O)_3$:

The lanthanide nitrate hydrates were prepared by dissolving 0.01mol of respective lanthanum oxides in 6N nitric acid and evaporating the clear solution thus obtained to dryness. The residue, the respective hydrated lanthanide nitrates were dissolved in 30ml of distilled water. To the above solution, an aqueous solution (30ml) of ligand (5.08g, 0.02mol) was added with constant stirring. The mixture when stood at atmospheric pressure and room temperature became turbid. This turbid solution was filtered through Whatmann filter paper, the colour less powder thrown out was identified as free acid, H_4edta. The clear solution thus obtained was evaporated to 30ml. This concentrated solution thus obtained was kept at room temperature to yield the crystals of the respective lanthanum(III) complexes. The crystals finally obtained were filtered, washed quickly several times with ice-cold distilled water through suction pump and dried in air.

RESULTS AND DISCUSSION

The di(phenyl hydrazinium) dihydrogen ethylenediaminetetraacetate, $(C_6H_5NHNH_3)_2H_2$edta was prepared by the neutralization reaction between aqueous solution of H_4edta and phenyl hydrazine in 1:2 ratio. The chemical reaction may be represented as follows.

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$H_4edta + 2C_6H_5(NHNH_2) \rightarrow (C_6H_5NHNH_3)_2H_2edta$

The salt obtained was highly crystalline, stable in air, soluble in water and insoluble in ethanol. The composition of the salt was determined by microanalysis and hydrazine analysis. Our attempts to prepare mono phenyl hydrazinium salt were not successful, because the addition of base to H_4EDTA in1:1 ratio resulted in dissolution of a part of the acid, which on filtration and evaporation yielded only the diphenyl hydrazinium. Our attempt to prepare corresponding tri and tetra salts were also unsuccessful and resulted in a viscous liquid after evaporation. The formation of these two salts is not quite expected because of the high pKa values of two protons (6.61 and 10.26) and hence weak bases like ammonia, hydrazine or phenyl hydrazine cannot replace them. The high PKa values for two protons are attributed to the zwitter ion formation.

Phenyl hydrazinium lanthanide ethylenediaminetetraacetate hydrates, $PhNHNH_3[Ln(EDTA)(H_2O)_2](H_2O)_3$ were prepared by the reaction of di(phenyl hydrazinium) salt and respective lanthanide nitrate hydrates in 2:1 ratio. Since the complexes are 1:1 complexes with respect to the metal and EDTA, the excess EDTA was precipitated from the solution, which was removed by filtration. The complexes are highly crystalline, stable in air, soluble in water and insoluble in alcohol, ether and chloroform. The composition of the complexes was determined by elemental and metal analyses. The results of chemical analyses are summarized in Table 1. The preparation of these complexes by mixing ligand and lanthanide nitrate in 1:1 failed to yield the above complexes. However, an aqueous solution of H_4EDTA and phenyl hydrazine hydrate in 1:4 ratios when added to respective lanthanide nitrate yielded crystalline complexes. This observation reveals the fact that inclusion of phenyl hydrazinium ion is possible only if it is present in excess. The chemical reaction is represented as follows.

$Ln(NO_3)_3 . xH_2O + 2 [C_6H_5 N_2H_4]_2 H_2 EDTA + yH_2O \rightarrow C_6H_5 N_2H_4 [Ln (EDTA) (H_2O)_3] (H_2O)_5 + H_4EDTA + 3C_6H_5 NHNH_3.NO_3 + (x+y -8) H_2O$

Where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy

$Ln (NO_3)_3 . xH_2O + H_4EDTA + 4C_6H_5 N_2H_3 + yH_2O \rightarrow C_6H_5 N_2H_4 [Ln (EDTA) (H_2O)_3] (H_2O)_5 + 3C_6H_5 N_2H_4.NO_3 + (x+y -8) H_2O$

Where Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy

Molar conductance
The molar conductivity of the complexes in aqueous solutions at infinite dilution gives useful information about the total number of ions formed by the complexes in solutions and the charge type on each ion.

The molar conductance value (Table 1) of the complexes (0.01 mol) in aqueous solution were found to be in the range 80-130 $ohm^{-1}cm^2mol^{-1}$ indicating these complexes are of 1:1 type electrolytes. This is, infact, a strong evidence for the presence of phenyl hydrazinium ion outside the coordination sphere as charge neutralizing species.

Magnetic properties
In the case of lanthanides, except La^{3+} and Lu^{3+} ions, which have no unpaired electrons which are diamagnetic all other Ln^{3+} ions, are paramagnetic in nature (Table 1). The effective magnetic moments are similar to those observed in the case of hydrazinium complexes [13, 14]**.**

Electronic spectra
The electronic spectra of Pr, Nd and Sm complexes recorded in water were compared with that of respective aqueo complexes. These data shows the shift in band positions towards greater wave numbers when compared to the aquated ions. Furthermore, the electronic spectral patterns obtained for the present set of complexes are similar to those of known ammonium and the hydrazinium analogues. The electronic spectra of Pr, Nd and Sm complexes are shown in Figs. 1, 2 and 3 respectively.

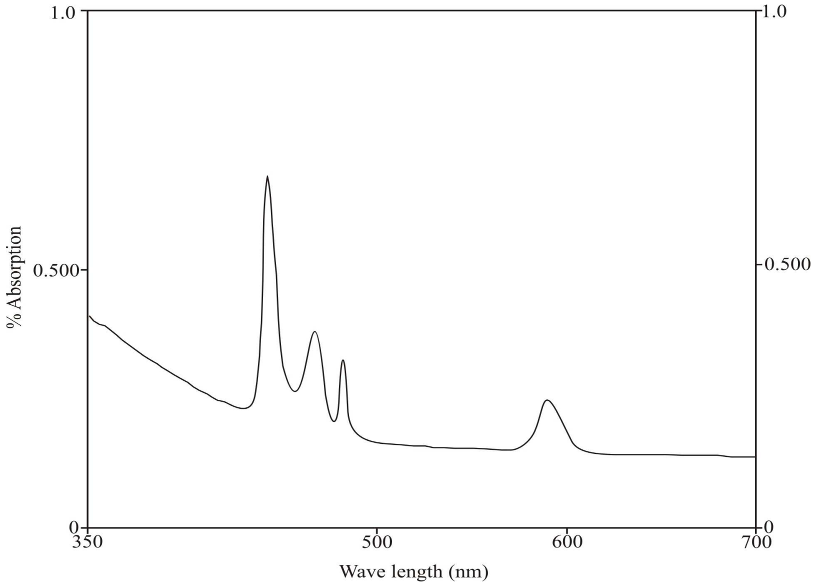

Fig.1 Electronic Spectrum of $C_6H_5NHNH_3 [Pr(edta)(H_2O)_2](H_2O)_3$

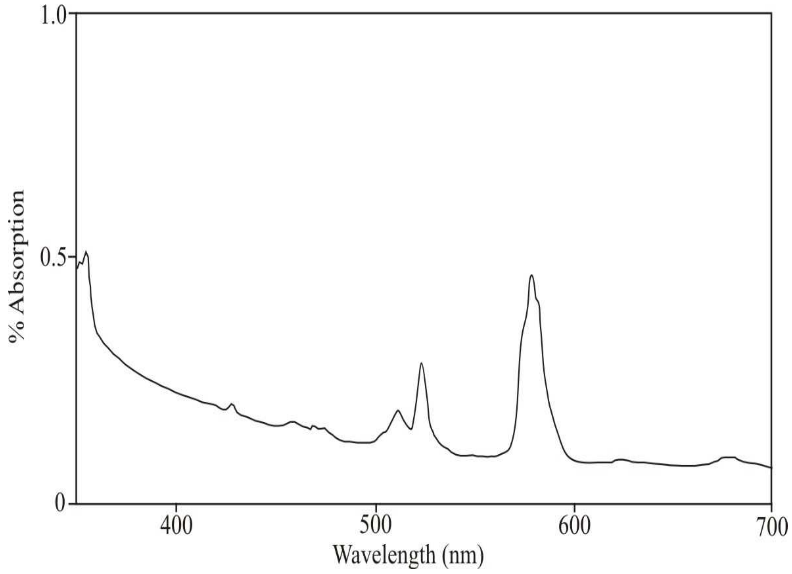

Fig.2 Electronic Spectrum of $C_6H_5NHNH_3[Nd(edta)(H_2O)_2](H_2O)_3$

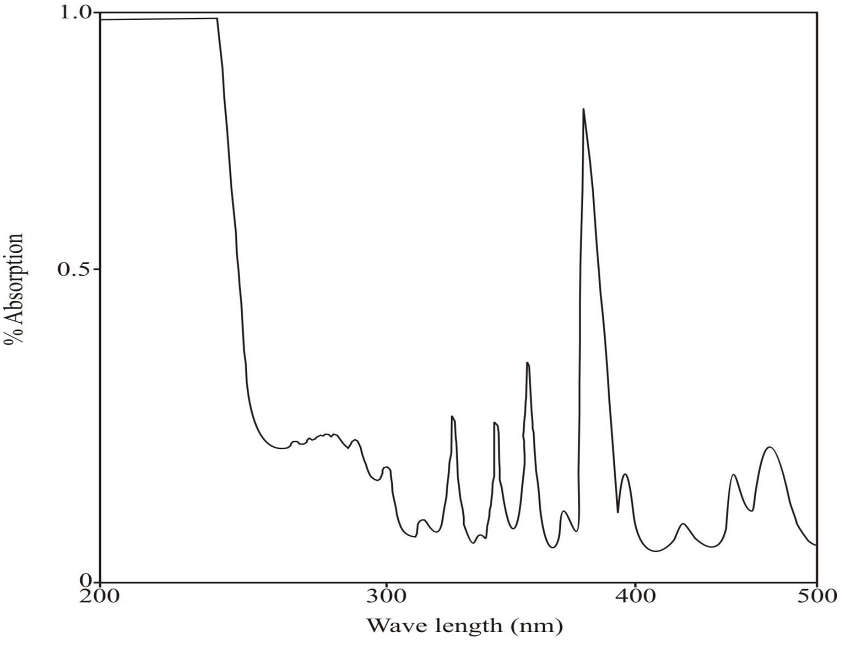

Fig.3 Electronic Spectrum of $C_6H_5NHNH_3[Sm(edta)(H_2O)_2](H_2O)_3$

Infrared Spectra

The infra red spectrum of $(N_2H_5)_2$ (H_2edta) exhibits bands around 1600cm^{-1} which are assigned to CO and COO respectively. The sharp band observed for N-N stretching at 960cm^{-1} indicates the presence of $C_6H_5NHNH_3^+$ ion.
The N-N stretching frequency of these complexes is observed in the range 960-970 cm^{-1} which corresponds to non-coordination of $C_6H_5NHNH_3^+$ ions present in these complexes [19]. This is well in coincidence with the conductance values observed for these complexes.

In the case of hydrazinium transition metal ethylenediaminetetraacatate hydrates also the non-coordination of $N_2H_5^+$ ions to the transition metals has been reported. The ionic nature of phenyl hydrazinium cation is quite expected because for the electronic reasons it would be anticipated that the nitrogen lone pair adjacent to the phenyl ring in the $C_6H_5NHNH_3^+$ cation must be not readily available for donation to the Ln (III) cation. Further, the steric effect also plays a vital role so that the rare earth metal ions could not accommodate the phenyl hydrazinium cation inside the sphere.

The asymmetric and symmetric stretching frequencies of carboxylate groups in the complexes are observed in the range 1600-1620cm^{-1} and 1340-1380cm^{-1}. The separation is in the range 180-220cm^{-1} is indicative of the fact that the OCO groups from the all the four carboxylate groups present in the edta^{4-} are coordinated to the lanthanide ions in the monodentate fashion [20].

The infrared spectra of the complexes were closely observed and it is seen that a broad band is present in the regions 3000-3500cm^{-1}. In the most of the hydrazinium metal carboxylates, the band in the above region are expected to be sharp and these bands are due to the presence of N-H and O-H stretching vibrations. Further, the presence of both coordinated and non-coordinated water molecule may also be responsible for the broad band. The chemical analysis data indicate the presence of five water molecules. Hence, two water molecules should be present inside and three outside the coordination sphere.

From the literature survey it is evident that the proposed molecular formula $C_5H_5NHNH_3[Ln(edta)(H_2O)_2](H_2O)_3$ complexes are quite probable because similar potassium diaqua(cydta) ytterbium(III) pentahydrate have been thoroughly studied [12] and the crystal structure of the lanthanum complexes has been investigated. Infrared spectrum of Ce complex is given in Fig. 4 as a representative model.

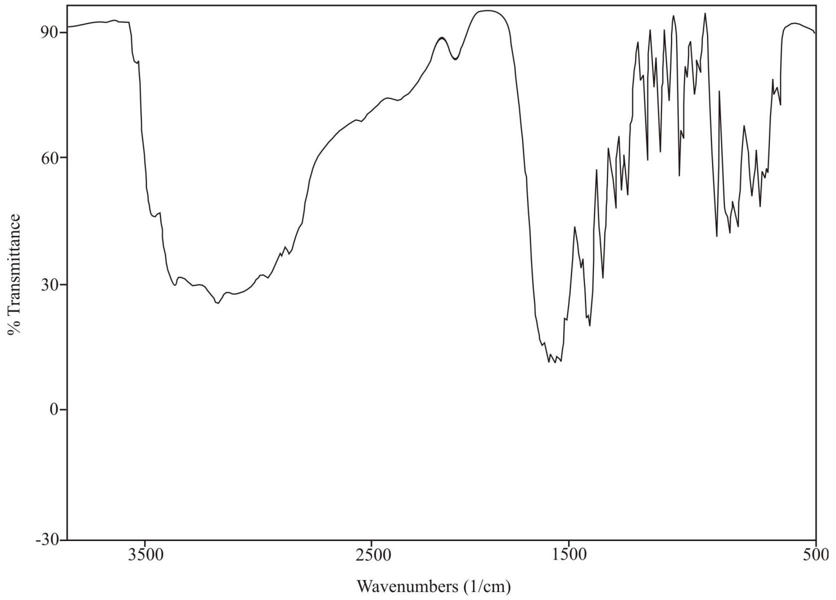

Fig. 4 Infrared Spectrum of $C_6H_5NHNH_3$ [Ce(edta)$(H_2O)_2$]$(H_2O)_3$

Thermal analysis

Since all the lanthanide ions form similar type of complexes their thermal degradation patterns are also expected to be similar. Hence, the TG-DTA of only two lighter lanthanide and two heavier lanthanide complexes were recorded as representative examples.

All the complexes show multi step degradation. The first stage is dehydration of three lattice water molecules in the temperature range 40-90 ^{o}C showing the non-coordination of water molecules. The two coordinated water molecule are lost in the temperature range 100-160 ^{o}C. The DTA shows two endotherms for these stages. Then the anhydrous complex decomposes to give ammonium salt. DTA shows an endotherm corresponding to this stage. The ammonium salt further undergoes decomposition in the temperature ranges 365-450 ^{o}C and 460-500 ^{o}C to give respective lanthanide (III) oxalate as an intermediates, and oxide as the end product. The last two stages are exothermic. The intermediates were assigned on the basis of TG weight loss. The formation of end products has been confirmed on the basis of metal analyses, IR spectra, TG weight loss X-ray powder diffraction and combustion studies. The simultaneous TG-DTA of the Pr and Nd complexes are shown in Figs.5 and 6 respectively. The general scheme of thermal degradation is given below.

PhNHNH$_3$[Ln(EDTA)(H$_2$O)$_2$](H$_2$O) → PhNHNH$_3$[Ln(EDTA)(H$_2$O)$_2$] ---------- (1)
PhNHNH$_3$[Ln(EDTA)(H$_2$O)$_2$] → PhNHNH$_3$[Ln(EDTA)] --------- (2)
PhNHNH$_3$[Ln(EDTA)] → NH$_4$[Ln(EDTA)] ---------- (3)
NH$_4$[Ln(EDTA)] → ½ Ln$_2$(C$_2$O$_4$)$_3$ ---------- (4)
Ln$_2$(C$_2$O$_4$)$_3$ → Ln$_2$O$_3$ ---------- (5)

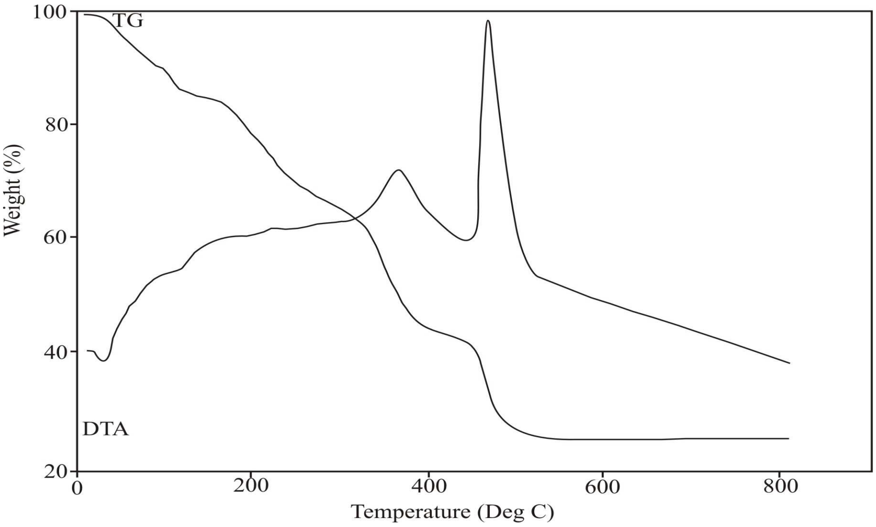

Fig. 5 Simultaneous TG-DTA of $C_6H_5NHNH_3$ [Pr(edta)(H$_2$O)$_2$](H$_2$O)$_3$

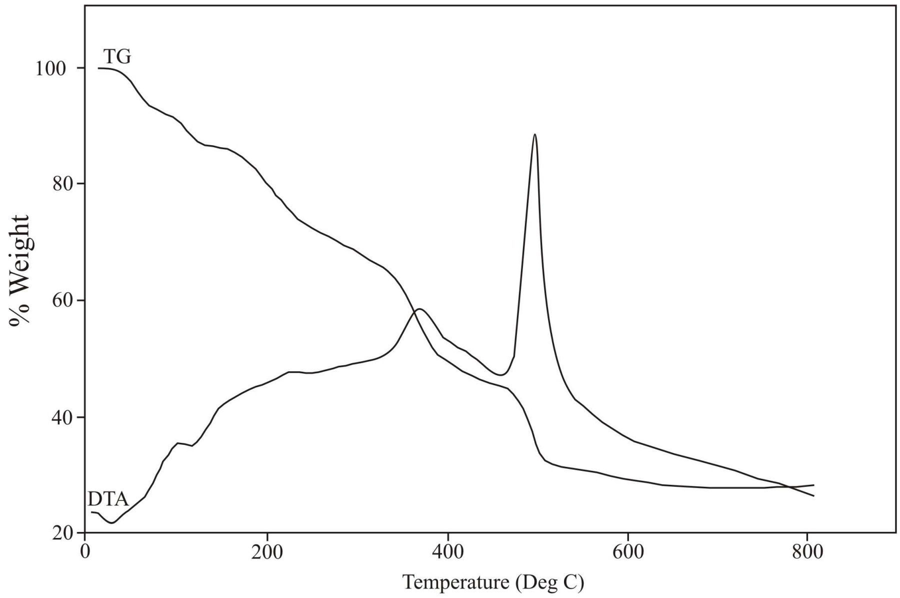

Fig. 6 Simultaneous TG-DTA of $C_6H_5NHNH_3$ [Nd(edta)(H$_2$O)$_2$](H$_2$O)$_3$

X-ray powder diffraction

The X-ray powder diffraction patterns of the complexes were recorded to confirm the isomorphism. The patterns are almost identical and the peaks are very sharp indicating the structural similarity among these complexes. The X-ray powder patterns of Ce and Pr complexes are shown in Figs.7 and 8 respectively for comparison.

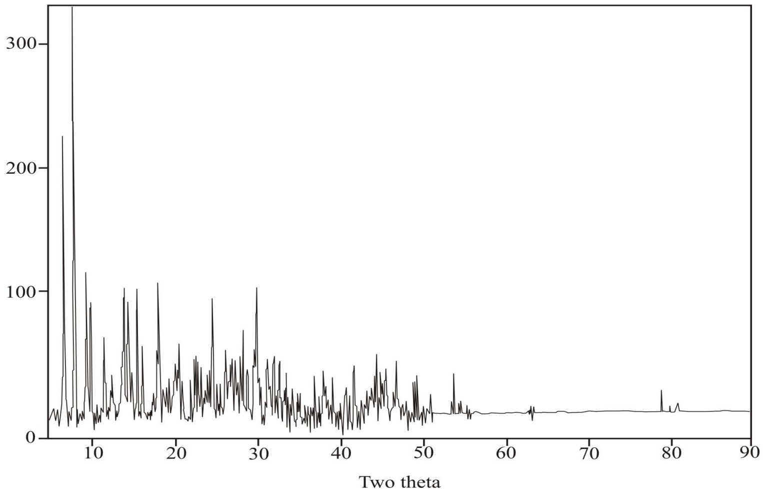

Fig. 7 X-ray powder diffraction pattern of $C_6H_5NHNH_3$ [Ce(edta)(H_2O)$_2$](H_2O)$_3$

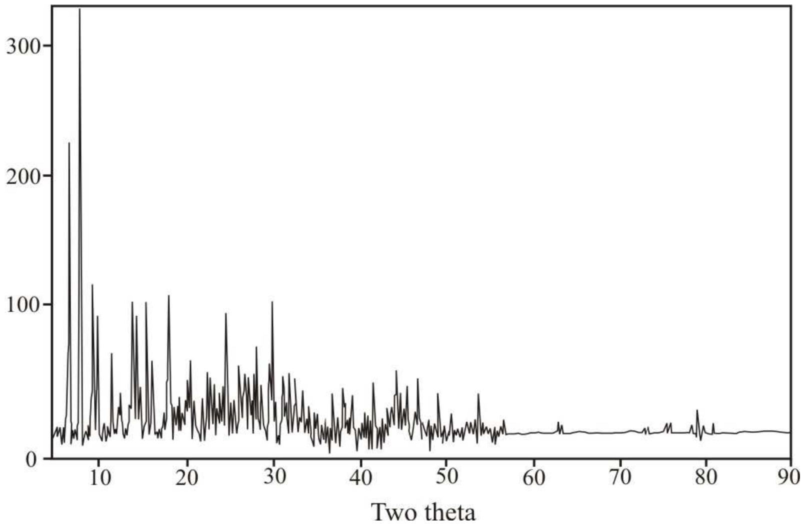

Fig. 8 X-ray powder diffraction pattern of $C_6H_5NHNH_3$ [Ln(edta)(H_2O)$_2$](H_2O)$_3$

Coordination Geometry

Due to their large size, lanthanide ions generally have coordination number higher than that of transitions metal ions. Coordination numbers greater than 6 for transition metal ions are formed with difficulty because of the strong ligand repulsion in the coordination sphere.

Based on the analytical, spectral, thermal and X-ray powder diffraction data, the eight coordination around the Ln (III) ions is proposed. The phenyl hydrazinium cation and three water molecules are expected to be outside the coordination sphere. The lanthanide ions are expected to posses eight coordinated geometry with hexadendate ethylenediaminetetraacetate ion and two coordinated water molecules.

Table 1 Analtical data of $C_6H_5NHNH_3[Ln(EDTA)(H_2O)_2](H_2O)_3$

Ln = La, Ce, Pr, Nd, Sm, Eu, Gd, Tb and Dy

Compound (Mol. Weight)	Colour (yield %)	C (%)		H (%)		N (%)		M (%)		Magnetic moment	Molar conductance (Ohm^{-1})
		Obs.	(Calc.)	Obs.	(calc.)	Obs.	(Calc.)	Obs.	(Calc)		
La (626.36)	Colourless (70)	30.72	(30.69)	4.93	(4.99)	8.96	(8.94)	21.93	(22.18)	-	103
Ce (627.57)	Colourless (85)	30.66	(30.62)	4.96	(4.98)	8.94	(8.93)	22.01	(22.33)	2.26	105
Pr (628.36)	Green (80)	30.53	(30.58)	4.99	(4.97)	8.90	(8.91)	22.51	(22.43)	3.49	111
Nd (631.69)	Pink (75)	30.47	(30.42)	4.92	(4.95)	8.83	(8.87)	22.87	(22.84)	3.60	125
Sm (637.80)	Pale yellow (75)	30.09	(30.13)	4.89	(4.90)	8.76	(8.78)	24.07	(23.58)	1.37	108
Eu (639.41)	Colourless (85)	30.02	(30.05)	4.92	(4.89)	8.70	(8.76)	24.91	(23.77)	1.33	106
Gd (644.70)	Colourless (80)	29.93	(29.81)	4.93	(4.85)	8.73	(8.69)	24.05	(24.40)	7.8	115
Tb (646.37)	Colourless (70)	29.65	(29.73)	4.90	(4.83)	8.71	(8.67)	24.15	(24.59)	11.5	115
Dy (649.95)	Pale yellow (85)	29.49	(29.57)	4.78	(4.81)	8.70	(8.62)	25.21	(25.00)	10.4	119

Table 2 Thermal data of $C_6H_5NHNH_3[Ln(EDTA)(H_2O)_2](H_2O)_3$

Compound	TG-Temp. Range (^{o}C)	DTA peak Temp. (^{o}C)	Weight loss (%) Found	Calcd.	Residue
Pr	40-80	60(+)	7.00	8.60	A
	80-140	112(+)	16.00	14.34	B
	160-220	205(+)b	26.50	28.84	C
	220-450	358(-)	58.00	56.56	D
	460-500	464(-)	73.50	72.91	E*
Nd	40-90	60(+)	7.00	8.56	A
	90-125	117(+)	13.00	14.26	B
	140-225	205(+)b	27.00	28.68	C
	225-450	367(-)	56.00	56.27	D
	460-540	496(-)	72.00	73.37	E
Eu	50-100	70(+)	8.00	8.45	A
	100-140	112(+)	15.00	14.09	B
	160-230	205(+)b	27.00	28.34	C
	230-440	357(-)	54.50	55.59	D
	460-530	482(-)	73.00	72.48	E
Gd	40-100	60(+)	7.50	8.38	A
	100-150	112(+)	14.00	13.97	B
	160-240	205(+)b	28.50	28.11	C
	240-450	357(-)	56.00	55.13	D
	460-500	474(-)	72.50	71.89	E

A: $PhNHNH_3[Ln(EDTA)(H_2O)_2]$, B: $PhNHNH_3[Ln(EDTA)]$, C:$NH_4[Ln(EDTA)]$

D: ½ $Ln_2(C_2O_4)_3$, E: Ln_2O_3, E: Pr_6O_{11}, (+): endothermic, (-): exothermic and b: broad*

Antioxidant properties

The results of antioxidant testing of the new pheny hydrazinium complexes are summarized in Table 3. The comparison of the results with the control, butylated hydroxyanizole shows that the present set of complexes are also very effective in neutralizing free radicals. The quantities of the compounds used to prepare the solutions of efficient concentrations are higher than the control is attributed to the higher molecular weight of the complexes. Among the series of complexes praseodymium complex shows higher activity.

Table 3 Antioxidant activity of $N_2H_5[Ln(edta)(H_2O)].5H_2O$

Ln	Mg/ml	Volume of solution used (ml)	% Inhibition	IC_{50}
La	20	0.5	8.96	39.9
		1.0	22.74	
		1.5	37.62	
		2.0	50.22	
Ce	25.9	0.5	7.04	61.1
		1.0	16.51	
		1.5	23.05	
		2.0	32.09	
		2.5	53.01	
Pr	8.6	0.5	9.79	17.9
		1.0	21.16	
		1.5	27.70	
		2.0	38.90	
		2.5	60.20	
Nd	14.5	0.5	12.28	26.7
		1.0	23.65	
		1.5	40.69	
		2.0	54.22	
Sm	16.8	0.5	13.39	33.3
		1.0	27.34	
		1.5	43.01	
		2.0	50.40	
Eu	20.6	0.5	15.83	34.8
		1.0	29.63	
		1.5	43.74	
		2.0	59.26	
Gd	20.0	0.5	10.20	25.0
		1.0	20.00	
		1.5	30.24	
		2.0	40.00	
Tb	18	0.5	7.24	43.4
		1.0	18.92	
		1.5	30.25	
		2.0	40.62	
		2.5	50.22	
Dy	24.2	0.5	16.34	35.3
		1.0	34.30	
		1.5	51.40	
		2.0	68.61	

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