Thermoanalytical and spectroscopic studies on hydrazinium lighter lanthanide complexes of 2-pyrazinecarboxylic acid

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Abstract The new hydrazinium lanthanide metal complexes of 2-pyrazinecarboxylic acid (HpyzCOO) of the formulae $(N_2H_5)_2[Ln(pyzCOO)_5] \cdot 2H_2O$ (**1**), where Ln = La or Ce and $(N_2H_5)_3[Ln(pyzCOO)_4(H_2O)] \cdot 2NO_3$ (**2**), where Ln = Pr, Nd, Sm or Dy have been synthesized and characterized by physico-chemical methods. The IR absorption bands of N–N stretching at 960 cm^{-1} unambiguously prove the existence of $N_2H_5^+$ ions. The bonding parameters β, $b^{1/2}$, % δ and η, have been calculated from the electronic spectroscopic (hypersensitive) bands of Pr(III) and Nd(III) complexes. All the complexes undergo endothermic followed by exothermic decomposition to leave the respective metal oxides as the end products. However, the DTA of the complexes **2** demonstrate rather sharp peak than the complexes **1**, owing to overwhelming exothermicity, which may be due to the loss of both hydrazine and nitrate moieties in the same step. The X-ray powder diffraction studies reveal the existence of isomorphism among the member complexes.

Keywords Chemical synthesis · Lanthanides · Oxides · Thermal properties · Thermogravimetric analysis (TGA)

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Introduction

The nitrogen containing heteroaromatic carboxylic acids are being intensely studied because of their varied ligational modes towards metal ions and manifestation of novel structural features of the metal complexes [1–3]. Among these acids, pyrazinecarboxylic acids are known to form many structurally important complexes [4, 5]. Further, among the pyrazinecarboxylic acids, the 2-pyrazinecarboxylic acid (HpyzCOO) is the simplest one and it acts as bidentate ligand through the nitrogen atom and the unidentate carboxylate group [5, 6]. The HpyzCOO forms coordination compounds with divalent 3d metal ions [6] and uranyl ion [7], in which the central ion is chelated by two HpyzCOO ligands via their (N, O) moieties consisting of a hetero-ring nitrogen atom and an oxygen atom belonging to the nearest monodentate carboxylic group. Similar monomeric molecules have been found in the crystals of calcium and strontium [8] pyrazinecarboxylate. Although the interaction of 2-pyrazinecarboxylate with various divalent metals [5–9] has been carried out and the structures of these complexes have been studied, no work has been done with trivalent metals in general, trivalent lanthanides in particular, except our recent work on the lanthanum 2-pyrazinecarboxylate hydrate [10].

Our interest in the chemistry of hydrazine lanthanide complexes with O, N donor ligands come from their interesting thermal behaviour. Hydrazine is, in fact, a substrate [11, 12] as well as a product of functioning nitrogenase and has been isolated by quenching the enzyme [13, 14]. Furthermore, the coordination chemistry of hydrazine and substituted hydrazines present some aspects of interest, including the influence that the ancillary ligands and central metal may have in determining the different coordination modes, of hydrazine ligand and understanding of the properties that coordination to a metal fragment may

include on an NH_2NH_2 or $RNHNH_2$ molecule towards deprotonation reactions.

The coordination chemistry of lanthanides, the hard acids, was limited initially to strong chelating ligands with oxygen as donor atoms. The notion that neutral nitrogen bases precipitate the hydrous oxide or hydroxide of lanthanides [15] hindered the progress of the coordination chemistry of the lanthanides. Nevertheless, with the development of new synthetic techniques, some complexes of lanthanides (La–Nd, Sm, Dy, Er and Lu) with hydrazine and anions like halides, carbonate, nitrate, sulphate and perchlorate have been reported [16]. However, complexes with carboxylate anions have not been studied except for acetate [17], oxalate [18] and phthalate [19]. The structures of these complexes have been inferred by chemical analysis and IR spectra. The complexes of the type $N_2H_5Ln(SO_4)_2$ H_2O (Ln is La–Tb, except Pm) have been characterized by spectral, magnetic, thermal and X-ray structural studies [20, 21]. In these complexes, $N_2H_5^+$ ion is coordinated. There have been two cases where $N_2H_5^+$ does not participate in the coordination sphere of $UO_2(II)$ [22] but counterbalances the $[(UO_2)(C_2O_4)_5(H_2O)_2]^{6-}$ anion.

The coordination chemistry of carboxylates with trivalent lanthanide metals in the presence of hydrazine has received rather scant attention, contrary to various divalent metals for which their complexes are known. Our research group has long been involved in the study of hydrazine carboxylate system [19, 22–24] and we have recently reported thermal behaviour of several hydrazine metal carboxylates, which act as precursors for various metal oxides [25–29]. In this study we wanted to investigate thermal behaviour of the lanthanide compounds of hydrazine with hyterocyclic nitrogen containing carboxylate ligands and to study their coordination behavior. To the best of our knowledge, no work has been done on the thermal property of hydrazinium lanthanide metal complexes of HpyzCOO. Hence, in this paper we report for the first time the preparation, spectroscopic and thermal studies on hydrazinium trivalent lanthanide metal complexes of HpyzCOO.

Experimental section

Materials

All the manipulations were performed under aerobic conditions using 2-pyrazinecarboxylic acid (Aldrich Co), metal oxide (99%) of La-Sm except Pm and Dy (Indian Rare Earth Ltd.), hydrazine hydrate of 99–100% purity (Glaxo Indio Ltd.) as received. All chemicals and solvents used were pure analytical grade and the solvents were distilled before use.

Preparation of ligand solution

Pyrazine carboxylic acid (620 mg, 5 mmol) was added to a solution of 10% hydrazine hydrate (2 mL, 4 mmol) in 25 mL of water with constant stirring. The mixture was heated at 80 °C for 30 min. The pH of the resulting clear solution was raised from 4 to 7 by careful addition of 10% hydrazine hydrate. This resulting clear solution (pH = 7) was heated over a water bath for about 10 min and allowed to stand for 1 h at room temperature.

Preparation of the complexes

Millimole samples of respective metal oxides were dissolved in 5 mL of 4 N nitric acid and evaporated to dryness and the residue dissolved in 25 mL of distilled water. The metal nitrate solution (25 mL, pH = 2.5) obtained was added to the prepared ligand solution with constant stirring. The pH of the resulting solution was adjusted to 5 by adding a few drops of 10% $N_2H_4 \cdot H_2O$ and concentrated over a steam bath to one half of its volume and was allowed to crystallize at 5 °C. The crystalline solids formed after a week was filtered off, washed with ice-cold water and ethanol and dried in air, which corresponds to lanthanide 2-pyrazinecarboylate hydrate compounds [10, 30]. Then, the filtrate was allowed to evaporate slowly at 5 °C. The needle crystals of the complexes of type **1** and **2** suitable for X-ray analysis were formed after 45 days, which were isolated, washed with ice-cold absolute alcohol and dried in vacuo over $CaCl_2$ in a desiccator (yield 50–53%).

Pysico-chemical studies

The hydrazine content of the complexes was determined volumetrically using a standard KIO_3 solution (0.025 M) under Andrews' condition [31]. The metals after destroying the organic part and hydrazine by treatment with concentrated HNO_3 and evaporating the excess HNO_3, were determined volumetrically by EDTA titration [31]. Elemental analyses were performed on Perkin Elmer-240 B CHN analyzer. The solid-state absorption spectra of the samples were recorded on a JASCO V-530 UV–Visible spectrophotometer in the range 300–800 nm by dispersing the solid samples in nujol mull. IR spectra were recorded as KBr pellets with a Shimadzu FTIR 8000 model spectrophotometer in the range 4000–400 cm^{-1}. Simultaneous TG-DTA measurements were carried out on a STA 1500 thermal analyzer. The experiments were carried out in air using platinum cups as sample holders with 5–10 mg of the samples at the heating rate of 10 °C min^{-1}. X-ray powder diffraction patterns of the compounds were recorded on a Seimens D-5005 X-ray diffractometer using Cu-K_α radiation with nickel filter.

Results and discussion

Synthesis

Compounds of composition $(N_2H_5)_2[Ln(pyzCOO)_5] \cdot 2H_2O$ (**1**), where $Ln = La$ or Ce and $(N_2H_5)_3[Ln(pyzCOO)_4 (H_2O)] \cdot 2NO_3$ (**2**), where $Ln = Pr$, Nd, Sm or Dy have been prepared for which the results of the analyses are given in Table 1. The compounds of the type **1** and **2** are soluble in water probably due to their ionic and monomeric nature of the complexes and are insoluble in most of the common organic solvents such as alcohol, chloroform, acetone etc. All of these complexes are hydrated and stable in air. Combining appropriate mole ratio of HpyzCOO and metal nitrate solutions alone (without hydrazine) yielded only crystalline solid products, not single crystals. It is also noteworthy that the reverse addition of metal and ligand solution leads to immediate formation of insoluble metal carboxylate hydrates. It was observed that the filtrate on evaporation at room temperature also resulted in the same compounds, **1** and **2** in 30 days, but with crystals of inferior quality.

Attempt to synthesize similar type of hydrazinium complexes of lanthanides using the related 2-pyridinecarboxylic acid (picolinic acid), instead of 2-pyrazinecarboxylic acid, was unsuccessful. The reason for this could be, picolinic acid is rather a weak acid ($pK_a = 4.66$) than the 2-pyrazine-carboxylic acid ($pK_a = 2.92$) [32]. Further, the additional N atom present in the aromatic ring of the HpyzCOO makes it more acidic facilitating not only the complex formation but also hydrogen bonding leading to the stability of the crystal.

IR spectra

The infrared spectroscopic results of the complexes are presented in Table 2. The respective sets of complexes

Table 1 Analytical data of the complexes

Compound	D.pt. (°C)	Yield (%)	Colour	Found (calculated) (%)				
				Hydrazine	Metal	C	N	H
$(N_2H_5)_2[La(pyzCOO)_5] \cdot 2H_2O$	68	53	White	7.24 (7.47)	15.83 (16.22)	34.87 (35.03)	22.09 (22.89)	3.28 (3.39)
$(N_2H_5)_2[Ce(pyzCOO)_5] \cdot 2H_2O$	60	51	Yellow	7.31 (7.46)	15.93 (16.34)	34.53 (34.97)	22.17 (22.85)	3.32 (3.38)
$(N_2H_5)_3[Pr(pyzCOO)_4(H_2O)] \cdot 2NO_3$	136	50	Green	10.54 (10.98)	15.34 (16.12)	26.97 (27.45)	25.08 (25.62)	3.19 (3.32)
$(N_2H_5)_3[Nd(pyzCOO)_4(H_2O)] \cdot 2NO_3$	140	51	Purple	10.57 (10.94)	16.07 (16.43)	26.92 (27.34)	25.01 (25.52)	3.28 (3.31)
$(N_2H_5)_3[Sm(pyzCOO)_4(H_2O)] \cdot 2NO_3$	146	52	Dull white	10.68 (10.86)	16.59 (17.01)	26.87 (27.16)	25.21 (25.35)	3.20 (3.28)
$(N_2H_5)_3[Dy(pyzCOO)_4(H_2O)] \cdot 2NO_3$	143	52	Dull white	10.67 (10.72)	17.89 (18.14)	26.57 (26.79)	24.50 (25.00)	3.19 (3.24)

Table 2 Infrared and electronic spectral data

Compound	IR Spectra (cm^{-1})						Electronic spectral data		
	ν_{O-H} (H$_2$O)	ν_{N-H}	ν_{asyCOO}	ν_{syCOO}	Ring vibration	ν_{N-N}	Band max (cm^{-1})	Assignment	Parameters
La	3380 b	3082	1629	1392 b	1459	962 m	–	–	–
Pr	3340 b	3069	1629	1394 s	1459	961 m	16,610	$^3H_4 \rightarrow {}^1D_2$	$\beta = 0.9958$
							20,576	$^3P_0$	$b^{1/2} = 0.0457$
							21,276	$^3P_1$	$\% \delta = 0.4218$
							22,421*	$^3P_2$	$\eta = 0.0021$
Nd	3355 b	3084	1631	1392 s	1458	960 m	12,490	$^4I_{9/2} \rightarrow {}^4F_{5/2}, {}^2H_{9/2}$	$\beta = 0.9911$
							13,485	$^4F_{7/2}$	$b^{1/2} = 0.0044$
							14,690	$^4F_{9/2}$	$\% \delta = 0.8908$
							17,170*	$^4G_{7/2}, {}^2G_{7/2}$	$\eta = 0.0044$
							19,040	$^4G_{7/2}$	
							19531	$^4G_{9/2}$	
Sm	3478	3321	1626	1385 s	1458	961 m	–	–	–
		3120							
Dy	3422	3093	1627	1394 s	1458	961 m	–	–	–
		2924							
Ce	3347	3163	1636	1396 s	1458	960 m	–	–	–
		3110							

have identical infrared spectra. The IR spectra of all the complexes show strong bands in the range of 3545–3320 cm^{-1} assignable to $v_{(OH)}$ stretching vibrations of lattice and/or coordinated water molecules [33]. The difference in this region between complexes of the types **1** and **2** is consistent with the different water content and this is further substantiated by the results of elemental and thermal analyses. In contrast to the free acid ($v_{(CO)}$: 1721 cm^{-1}), the complexes show C–O absorption bands between 1635 and 1610 cm^{-1} indicating the presence of coordinated –COO^- group. The bands due to the ring vibrations [33] of the pyrazine molecule are found to move to higher frequency and the band due to the carboxyl group which moves to a lower frequency, in the compounds, suggests that the nitrogen atoms in the aromatic ring and the oxygen of the carboxyl groups are coordinated to the metal atom [34, 35]. The N–N stretching vibration of complexes **1** and **2** is seen at 960 cm^{-1} and is consistent with the existence of $N_2H_5^+$ ions [16].The IR spectra of parent acid, La and Nd complexes are shown in Fig. 1a–c, respectively, as examples.

Electronic spectra

The electronic spectra of the lanthanides, constituting mainly Laporte-forbidden 4f-transitions, are not much influenced by the ligand environment, as in the case of d-block metal complexes. The spectral data along with the various calculated bonding parameters are given in Table 2. The absorption band associated with nearly degenerate $^4I_{9/2} \rightarrow {}^2G_{7/2}$, $^4G_{5/2}$ transitions of Nd^{3+} is known to exhibit strong hypersensitive behaviour [36], making it especially suitable for probing the coordination environment around the Nd^{3+} ion. The spectral profile of the above transition in the present Nd^{3+} complex resemble those of the nine-coordinated complexes [37]. All the bands show a weak perturbation due to complexation and an increase in intensity compared to the aquo ion [38], presumably due to nephelauxetic effect [39, 40]. Various spectral parameters, viz., nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha's covalency parameter ($\% \delta$) and covalency angular overlap parameter (η), were calculated [41, 42] from the electronic spectra of the complexes. Depending upon the ligands, the values of δ may either be positive (covalent bonding) or negative (ionic bonding). All these parameters suggest a weak covalent interaction between the lanthanide and the ligand. The electronic spectra of the Pr and Nd complexes of **2**, are shown in Fig. 2a and b, respectively, as representative examples.
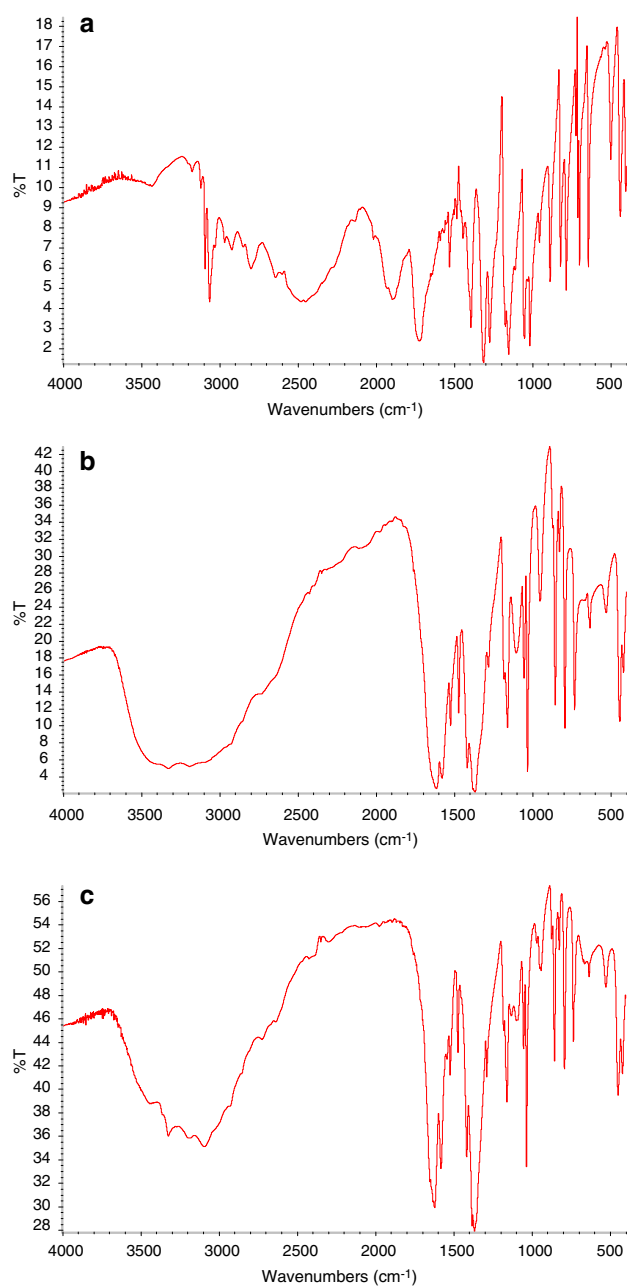

Fig. 1 IR spectra of **a** HpyzCOO, **b** $(N_2H_5)_2[La(pyzCOO)_5] \cdot 2H_2O$ and **c** $(N_2H_5)_3[Nd(pyzCOO)_4(H_2O)] \cdot 2NO_3$

Thermal decomposition of hydrazinium compounds (**1** and **2**)

The thermal decomposition characteristics of the complexes are summarized in Table 3. The simultaneous TG and TDA results of the La and Ce complexes are similar as are those of Pr, Nd, Sm and Dy. Both the set of compounds undergo three-step decomposition to give the respective metal oxide as the final products. The first stage weight loss

Fig. 2 Electronic spectra of **a** $(N_2H_5)_3[Nd(pyzCOO)_4 (H_2O)] \cdot 2NO_3$ and **b** $(N_2H_5)_3[Pr(pyzCOO)_4 (H_2O)] \cdot 2NO_3$
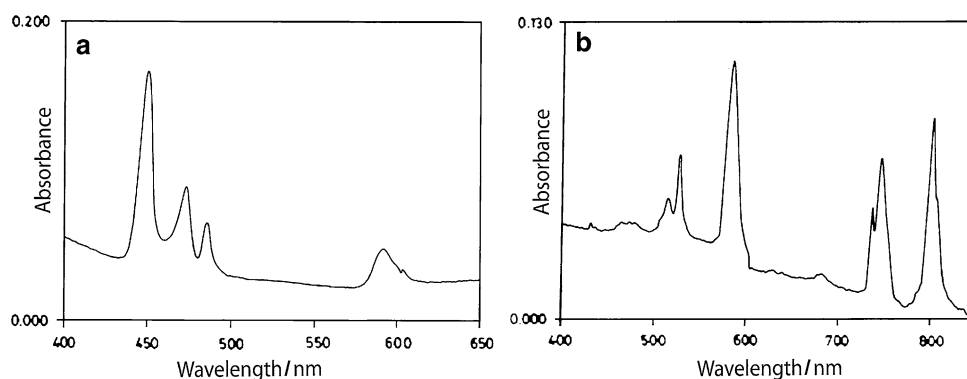
Table 3 Thermal data[a]

Compound	DTA Peak temperature (°C)	Thermogravimetry (TG)			Intermediates/end products
		TG temperature range (°C)	Mass loss (%)		
			Obsd.	Cacld.	
$(N_2H_5)_2[La(pyzCOO)_5] \cdot 2H_2O$	68 (+)	50–75	6.50	4.20	$(N_2H_5)_2[La(pyzCOO)_5]$
	253 (−)b	75–325	40.00	40.66	$[La(pyzCOO)_3]$
	411 (−)				
	468 (−)	325–745	80.00	80.98	La_2O_3
$(N_2H_5)_2[Ce(pyzCOO)_5] \cdot 2H_2O$	60 (+)	45–70	6.00	4.19	$(N_2H_5)_2[Ce(pyzCOO)_5]$
	253 (−)	70–340	39.00	40.59	$[Ce(pyzCOO)_3]$
	403 (−)s	340–410	75.00	79.93	CeO_2
$(N_2H_5)_3[Pr(pyzCOO)_4(H_2O)] \cdot 2NO_3$	136 (+)b	105–145	2.00	2.06	$(N_2H_5)_3[Pr(pyzCOO)_4] \cdot 2NO_3$
	263 (−)s	145–270	43.00	41.64	$[Pr(pyzCOO)_3]$
	419 (−)sh				
	439 (−)				
	448 (−) t				
	459 (−)	270–595	80.00	80.53	Pr_6O_{11}
$(N_2H_5)_3[Nd(pyzCOO)_4(H_2O)] \cdot 2NO_3$	137 (+)	75–155	2.00	2.05	$(N_2H_5)_3[Nd(pyzCOO)_4] \cdot 2NO_3$
	240 (−)s	155–250	41.00	41.49	$[Nd(pyzCOO)_3]$
	430 (−)				
	450 (−)	250–590	78.00	80.83	Nd_2O_3
$(N_2H_5)_3[Sm(pyzCOO)_4(H_2O)] \cdot 2NO_3$	128 (+)	75–155	2.00	2.04	$(N_2H_5)_3[Sm(pyzCOO)_4] \cdot 2NO_3$
	146 (+)d				
	256 (−)s	155–260	40.00	41.19	$[Sm(pyzCOO)_3]$
	417 (−)				
	456 (−)s	260–640	79.00	80.27	Sm_2O_3
$(N_2H_5)_3[Dy(pyzCOO)_4(H_2O)] \cdot 2NO_3$	147 (+)	100–175	2.00	2.01	$(N_2H_5)_3[Dy(pyzCOO)_4] \cdot 2NO_3$
	253 (−)	175–300	39.00	40.60	$[Dy(pyzCOO)_3]$
	449 (−)				
	509 (−)	300–610	77.00	79.18	Dy_2O_3

[a] *b* Broad, *s* sharp, *sh* shoulder, *d* doublet, *t* triplet

of the complexes **1** occurs in the range 50–75 °C, whereas complexes **2** show in the range 105–150 °C, and is attributed to the loss of water molecules. This loss observed as an endotherm at around 65 and 140 °C, respectively, confirms the presence of lattice water in the former and coordinated water in the latter complexes. In the second step, the anhydrous hydrazinium compounds undergo an exothermic decomposition between 250 and 265 °C to give
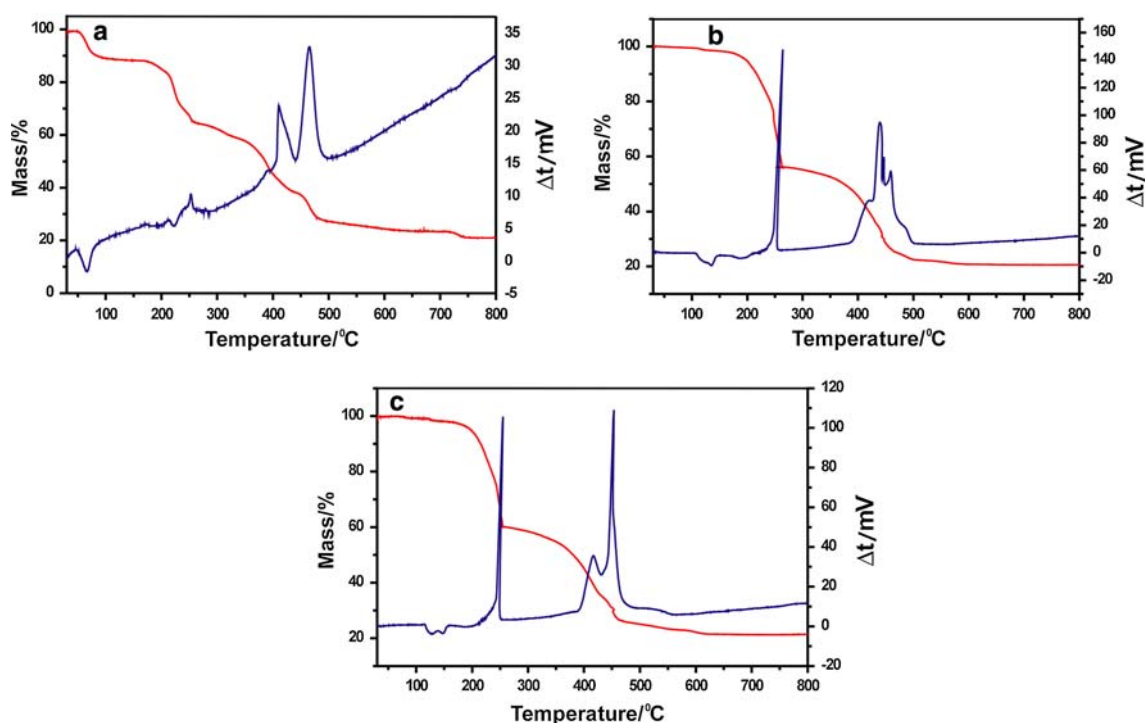
Fig. 3 Simultaneous TG-DTA of a $(N_2H_5)_2[La(pyzCOO)_5] \cdot 2H_2O$, b $(N_2H_5)_3[Pr(pyzCOO)_4(H_2O)] \cdot 2NO_3$, and c $(N_2H_5)_3[Sm(pyzCOO)_4(H_2O)] \cdot 2NO_3$

the isomeric lanthanide 2-pyrazinecarboxylate intermediate. The DTA of the complexes **2** show rather sharp peak than the complexes **1**, due to overwhelming exothermicity, which may be due to the loss of both hydrazine and nitrate moieties in the same step. Final step weight loss corresponds to the decomposition of the intermediates to metal oxides. This loss is observed as a sharp exothermic peak for Ce compound (may be due to the oxidative decomposition to form CeO_2 as the final product) and two successive exotherms for La, Nd, Sm and Dy, and exothermic multiplets for Pr compound. The metal oxide formation is significantly low. The simultaneous TG and DTA curves of the La, Pr and Sm complexes are given in Fig. 3 (a, b and c), respectively, as examples. Our effort, to isolate the intermediates was unsuccessful due to their continuous decomposition as evident from the TG. Hence, we have tried to assign the possible intermediates as observed from the TG mass losses, which are in agreement with the calculated mass losses.

The aforesaid results suggest that the $N_2H_5^+$ ions and water molecules are not involved in coordination and hence lanthanide ions in **1** are coordinated only by 2-pyrazinecarboylate anions. Thus, the lanthanum and cerium complexes may have rare ten coordination by five N, O bonding moieties. The metal ions in complex **2** are nine coordinated by four 2-pyrazinecarboxylate anions and one water oxygen. The $N_2H_5^+$ and NO_3^- ions are

not bonded to the central metal ion. However, in order to confirm this assignment unambiguously it was considered to determine the crystal structure of these compounds. Therefore, the final proof of the coordination environment of the metal was confirmed by a single crystal X-ray study of the compounds.

Crystal structures of $(N_2H_5)_2[La(pyzCOO)_5] \cdot 2H_2O$ (**1a**) and $(N_2H_5)_3[Nd(pyzCOO)_4(H_2O)] \cdot 2NO_3$ (**2a**)

The structure of $(N_2H_5)_2[La(pyzCOO)_5] \cdot 2H_2O$ (**1a**) and $(N_2H_5)_3[Nd(pyzCOO)_4(H_2O)] \cdot 2NO_3$ (**2a**) have been determined from single crystal X-ray analysis [43]. The crystallographic data for the compound **1a** are monoclinic, space group P2₁/n with $a = 16.4018$ (4), $b = 22.8727$ (6), $c = 14.9608$ (9) Å, $\beta = 102.660$ (2)°, $Z = 8$ and $R = 0.0592$. The compound **2a** crystallizes in the monoclinic space group C2/c, with $a = 10.7176(7)$, $b = 21.7630(13)$, $c = 14.9608(9)$ Å, $\beta = 104.468(4)°$ and $Z = 4$. The structure analysis shows that the **1a** crystals consist of $N_2H_5^+$ cations, water molecules and the $[La(pyzCOO)_5]^{2-}$ anions. The asymmetric unit of complex **1a** contains two crystallographically independent lanthanum complexes. Interestingly, each lanthanum atom has ten coordination formed by five 2-pyrazinecarboxylate (bidentate chelate) ligands, via its N, O bonding moieties. The other pyrazine N atom present in the ring is not involved in coordination. The

Fig. 4 X-ray powder pattern of compounds **a 1** and **b 2**
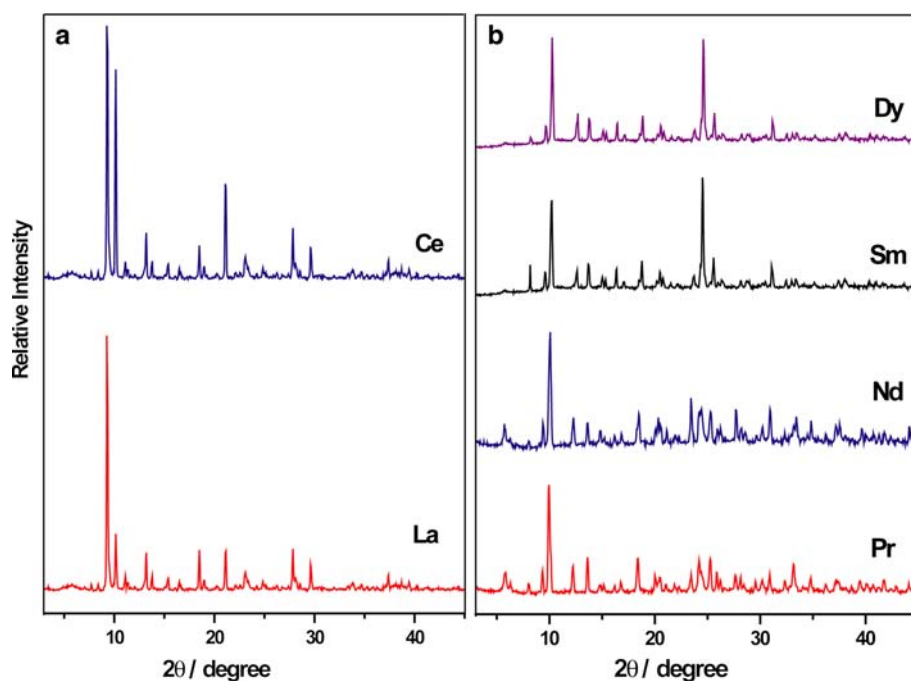
$N_2H_5^+$ ions and the water molecules are not coordinated to the metal. It is worthwhile to mention here that, the ten coordination of hydrazinium lanthanide complexes with carboxylate anions have been observed for the first time [43]. The structure is built up by lanthanum ions joined by 2-pyrazinecarboxylate groups forming two-dimensional sheets parallel to (001) plane. Whereas the **2a** is monomeric and the structure comprises of $N_2H_5^+$ cations, [Nd(pyz-COO)$_4$(H$_2$O)]$^-$ and NO$_3^-$ anions. The coordination number for neodymium is nine with four pyzCOO ligands, bidentate (N, O) to the metal and the lone water molecule completes the coordination sphere and the sheets like pattern in all are interlinked via multiple hydrogen bonds leading to three dimensional structure.

Powder X-ray pattern

In order to ascertain the isomorphic nature of the set of complexes, the powder diffraction patterns have been recorded and are depicted in Fig. 4. From the patterns, it is evident that the respective set of complexes are isostructural. The results from the IR and thermoanalytical studies are in accordance with these isostructural groupings.

Conclusions

In conclusion, the new di- and tri-hydrazinium lanthanide metal complexes of 2-pyrazinecarboxylic acid have been synthesized under identical experimental conditions. It is

pertinent to note that the cerium compound shows a low temperature, distinct single exothermic peak in contrast to other compounds, which show relatively high temperature exothermic multiplets in their final step of decomposition. The overwhelming exothermicity of the cerium compound may be due to its oxidative decomposition to give CeO$_2$ [26] as the end product as against Ln$_2$O$_3$ [19, 25] in other cases. Further, it is interesting to find out that the La and Ce compounds are ten coordinated and the latter tri-hydrazinimum compounds are nine coordinated in addition to having nitrate anions and this unusual behavior of lighter lanthanides, under identical experimental conditions, may be due to their difference in size, i.e., lanthanide contraction.

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