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THERMOANALYTICAL AND SPECTRAL PROPERTIES OF NEW RARE-EARTH METAL 2-PYRAZINECARBOXYLATE HYDRATES

T. Premkumar and S. Govindarajan[*]

Department of Chemistry, Bharathiar University, Coimbatore 641 046, India

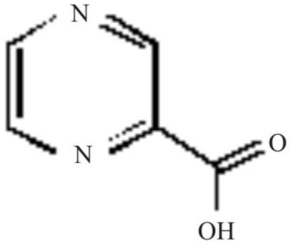
New 4f-trivalent lanthanide 2-pyrazinecarboxylate hydrates of composition Ln(pyzCOO)$_3$·3.5H$_2$O, where *Ln*=La, Ce, Pr, Nd, Sm and Dy have been isolated from aqueous solution containing the respective metal nitrates and 2-pyrazinecarboxylic acid (HpyzCOO), in 1:3 molar ratios. The complexes have been characterized by analytical, electronic and IR spectroscopic, thermal analysis and X-ray diffraction studies. The OCO$^-$ group of 2-pyrazinecarboxylate bridges in both mono- and bidentate fashion ($\nu_{as(COO)}$=1612 and 1578 cm^{-1}; $\nu_{s(COO)}$=1423 and 1388 cm^{-1}) as evidenced by IR data. The IR spectra further indicate that coordination takes place through the carboxyl group and the nearest hetero-ring nitrogen atom. The bonding parameters β, $b^{1/2}$, %δ and η have been calculated from the electronic spectral (hypersensitive) bands of Pr(III) and Nd(III) complexes. Both IR and thermal data reveal the presence of a coordinated water and two and a half lattice water molecules in the complexes. It is further substantiated by single crystal X-ray study for the corresponding lanthanum compound. Based on the results obtained, nine coordination is proposed for the lanthanide ions. Simultaneous TG-DTA of the complexes show that they are thermally stable up to 150ºC and undergo endothermic (~155 and 250ºC) followed by exothermic (~480ºC) decompositions to give the respective metal oxides as the final product. The compounds are found to be isostructural as evidenced from X-ray powder patterns.

Keywords: *IR spectra, 2-pyrazinecarboxylic acid, rare-earth complexes, thermal decomposition*

Introduction

There has been a significant amount of interest in the chemistry of rare earth complexes with the carboxylic acids, due to their wide use as precursors for fine particle metal oxides [1]. In recent years 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 [2–4]. We have become particularly interested in the chemistry of 2-pyrazinecarboxylic acid, HpyzCOO, since it has a number of attractive features. It is sterically compact, planar and has multi-donor coordination sites.

2-pyrazinecarboxylic acid (Scheme 1) is a simple model suitable for testing the ability of the N, COO$^-$ donor set to bind with transition metal systems [5, 6]. The 2-pyrazinecarboxylic acid has three potential oxygen- and nitrogen-based coordination sites, but in most of the metal complexes, it acts as bidentate ligands via their (N, O) bonding moieties consisting of a heteroring nitrogen atom and an oxygen atom belonging to the nearest unidentate carboxylate group [7, 8]. Although the interaction of 2-pyrazinecarboxylate with various divalent metals, viz., 3d transition metals [5, 6, 9], UO$_2^{2+}$ [10], Ca^{2+}and Mg^{2+} [11] has been carried out and the structure of these complexes studied, no work has been done with trivalent metals in general, and trivalent lanthanides in particular except our recent work on the lanthanum 2-pyrazinecarboxylate hydrate [12]. Therefore, further, we have carried out the thermal and spectral studies aimed at establishing the structure and thermal reactivity relationship in the compounds.



Scheme 1 2-Pyrazinecarboxylic acid (HpyzCOO)

Experimental

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

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[*] Author for correspondence: drsgovind@yahoo.co.in

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Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Preparation of the compounds

The respective metal oxide (e.g., 1.63 g of La_2O_3, 0.01 mol) was dissolved in 5 mL of 4 N nitric acid and evaporated to dryness. To this residue 50 mL of distilled water was added, and the solution was heated over a water bath for about 10 min. The 2-pyrazinecarboxylic acid (3.72 g, 0.03 mol) dissolved in 50 mL of hot water was slowly added to the metal ion solution and the resulting solution was kept for crystallization at room temperature. The crystalline compounds deposited after 1 h were filtered off after standing overnight, which were washed with ice-cold water and ethanol, and dried in air.

Physico-chemical studies

The metals after destroying the organic part by treatment with concentrated HNO_3 and evaporating the excess HNO_3, were determined volumetrically by EDTA titration. Simultaneous TG-DTA measurements were carried out on an ULVAC (SINKU-RIKO) TGD 9000 instruments. The experiments were carried out in air using platinum cups as sample holders with 5–10 mg of the samples at a heating rate of 10°C min^{-1}. Other physico-chemical techniques are the same as described earlier [13].

Results and discussion

Compounds of composition $Ln(pyzCOO)_3 \cdot 3.5H_2O$, where *Ln*=La, Ce, Pr, Nd, Sm and Dy have been prepared for which the results of the analyses are given in Table 1. The general equation for the formation of metal 2-pyrazinecarboxylate hydrates may be written as follows.

$$Ln(NO_3)_3 \cdot xH_2O + 3pyzCOOH \xrightarrow{pH\sim3} [Ln(pyzCOO)_3 \cdot H_2O] \cdot 2.5H_2O + 3HNO_3 + (x-3.5) \cdot H_2O$$

where *Ln*=La, Ce, Pr, Nd, Sm or Dy.

The above composition was proved by X-ray crystal structure analysis for $[La(pyzCOO)_3(H_2O)] \cdot 2.5H_2O$ [12]. The empirical formula of the compound is $C_{15}H_{16}N_6O_{9.5}La$ and crystallizes in the orthorhombic space group Pbcn with a=16.154(3), b=12.357(2), c=20.525(4) Å, V=4097.0 Å^3, Z=8, and R=0.0291. The metal complexes are insoluble in water and other common organic solvents such as alcohol, acetone and chloroform. All of them are hydrated and stable in air.

The compounds have very similar infrared spectra and the IR spectrum of the lanthanum compound is given in Fig. 1 as a representative example. All of them show strong bands in 3545–3320 cm^{-1} range assignable to ν_{OH} stretching vibrations of lattice and/or coordinated water molecules [14]. The number and nature of the water content are further substantiated by the results of elemental and thermal analyses. The N–H stretching vibrations of the complexes appear in the 3255–3010 cm^{-1} region. In contrast to the free acid (ν_{CO}: 1721 cm^{-1}), these complexes show C–O absorption bands between 1635 and 1610 cm^{-1} region indicating the presence of coordinated $-COO^-$ group. The bands due to ring vibrations [15] of the pyrazine moiety move to higher frequency and the band due to the carboxyl group moves to a lower frequency, in the compounds, suggesting that the nitrogen atoms in the aromatic ring and the oxygen of the carboxyl groups are coordinated to the metal atom [16]. According to [17] the sharp band between 441 and 451 cm^{-1} region corresponds most probably to a M–N stretching mode. Also, these complexes exhibit peaks at 1612 and 1578 cm^{-1} assignable to $\nu_{as(COO)}$ and, 1423 and 1388 cm^{-1} to $\nu_{s(COO)}$, which are consistent with the bridging carboxylate groups [14]. Further, the insolubility of the compounds in both polar and non-polar solvents implies that the compounds have polymeric structure [16].

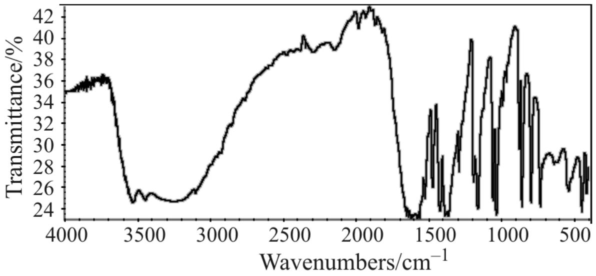

Fig. 1 IR spectrum of $[La(pyzCOO)_3(H_2O)] \cdot 2.5H_2O$

The absorption spectra of Pr and Nd have been recorded in solid-state and the spectral data along with the various calculated bonding parameters are given in Table 1. 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 [18], making it especially suitable for probing the coordination environment around the Nd^{3+} ion. The spectral profiles of the above transition (solid-state) in the present Nd^{3+} complex resemble those of the nine-coordinated complexes [19, 20]. All the bands show a weak perturbation due to complexation and an increase in intensity compared to the aquo ion [21], presumably due to nephelauxetic effect [22]. Further, from the electronic spectra of the complexes under present discussion, various spectral parameters, viz., nephelauxetic ratio (β), bonding parameter ($b^{1/2}$), Sinha's covalency parameter (%δ) and covalency angular overlap parameter (η), were calculated [20, 23] (Table 1) using the equations,

$$\beta = (1/n)\sum(\nu^i_{complex}/\nu^i_{aquo})$$

where β is the average value of the ratio $\nu^i_{complex}/\nu^i_{aquo}$ and n the number of transitions considered.

Table 1 Analytical and electronic spectral data of the compounds

Compound	D.pt/°C	Yield/%	Colour	Found (calculated) /%				Electronic spectra data		
				Metal	C	N	H	Band max/cm^{-1}	Assignment	Parameters
La	155	88	White	23.02	30.98	13.97	2.77	–	–	–
				(23.94)	(31.51)	(14.71)	(2.82)			
Ce	165	85	Yellow	23.72	31.02	13.73	2.80	–	–	–
				(24.09)	(31.44)	(14.67)	(2.81)			
Pr	156	92	Light	23.56	29.98	13.81	2.78	16.620	$^3H_4 \rightarrow {}^1D_2$	β=0.9916
			green	(24.20)	(31.40)	(14.65)	(2.81)	20.532	$^3P_0$	$b^{1/2}$=0.0647
								21.050	$^3P_1$	%δ=0.8441
								22.317*	$^3P_2$	η=0.0042
Nd	155	93	Purple	24.17	31.07	13.98	2.72	12.431	$^4I_{9/2} \rightarrow {}^4F_{5/2}$, $^2H_{9/2}$	β=0.9903
				(24.63)	(31.22)	(14.57)	(2.79)	13.272	$^4F_{7/2}$	$b^{1/2}$=0.0696
								14.731	$^4F_{9/2}$	%δ=0.9795
								17.293*	$^4G_{7/2}$, $^2G_{7/2}$	η=0.0048
								19.071	$^4G_{7/2}$	
								19605	$^4G_{9/2}$	
Sm	157	83	White	24.17	30.21	13.53	2.69	–	–	–
				(24.63)	(30.89)	(14.42)	(2.76)			
Dy	156	89	Dull	26.01	29.21	13.27	2.65	–	–	–
			White	(26.91)	(30.26)	(14.12)	(2.71)			

D.pt.: decomposition point; *: hypersensitive band

Table 2 Thermal data

Compound	DTApeak temperature/°C	Thermogravimetry (TG)			Intermediates/end products
		TG temperature range/°C	Mass loss/%		
			Obsd.	Calc.	
$La(pyzCOO)_3{\cdot}3.5H_2O$	157 (+)*b*	150–165	7.5	7.88	$La(pyzCOO)_3{\cdot}H_2O$
	252 (+)	165–280	11	11.03	$La(pyzCOO)_3$
	480 (–)	280–490	70	71.48	La_2O_3
$Ce(pyzCOO)_3{\cdot}3.5H_2O$	156 (+)	150–170	7.5	7.86	$Ce(pyzCOO)_3{\cdot}H_2O$
	250 (+)	170–265	10.5	11.59	$Ce(pyzCOO)_3$
	434 (–)*s*	265–480	70.0	69.93	CeO_2
$Pr(pyzCOO)_3{\cdot}3.5H_2O$	158 (+)*b*	150–170	7.5	7.85	$Pr(pyzCOO)_3{\cdot}H_2O$
	253 (+)	170–270	11	10.99	$Pr(pyzCOO)_3$
	422(–)*sh*				
	450 (–)	270–480	69	70.30	Pr_6O_{11}
$Nd(pyzCOO)_3{\cdot}3.5H_2O$	154 (+)*b*	150–165	8	7.81	$Nd(pyzCOO)_3{\cdot}H_2O$
	254 (+)	165–285	11	10.93	$Nd(pyzCOO)_3$
	389(–)*sh*				
	421(–)*sh*				
	449 (–)	285–490	68	70.82	Nd_2O_3
$Sm(pyzCOO)_3{\cdot}3.5H_2O$	156 (+)	150–165	8	7.72	$Sm(pyzCOO)_3{\cdot}H_2O$
	250 (+)	165–265	10	10.81	$Sm(pyzCOO)_3$
	449 (–)	265–485	69	70.08	Sm_2O_3
$Dy(pyzCOO)_3{\cdot}3.5H_2O$	158 (+)	150–170	7	7.57	$Dy(pyzCOO)_3{\cdot}H_2O$
	252 (+)	170–270	11	10.59	$Dy(pyzCOO)_3$
	454 (–)	270–490	68	68.64	Dy_2O_3

b: broad; *s*: sharp; *sh*: shoulder

$$b^{1/2}=[1/2(1-\beta)]^{1/2}$$

$$\%\delta=[(1-\beta)/\beta]\cdot 100$$

$$\eta=(1-\beta^{1/2})/\beta^{1/2}$$

Depending upon the ligands, the values of δ may either be positive (covalent bonding) or negative (ionic bonding). All these parameters (Table 1) indicate a weak covalent interaction between lanthanide metal and ligand.

The thermal decomposition characteristics of the complexes are summarized in Table 2. The TG and DTA results of these complexes are similar and undergo three stages of mass loss upon heating. The observed mass loss (found: 7.5%; calcd: 7.88%) during the first step corresponds to the loss of two and a half water molecules. The corresponding DTA peak is observed as an endotherm around 157°C supporting the presence of two and a half hydrated water molecules in the lattice. This slight higher temperature of dehydration might be due to strong internal hydrogen bonding between these water molecules and other carboxylate oxygens, as observed in the [12]. The second step mass loss also takes place endothermally as shown by DTA, which is in accordance with the loss of a molecule of water around 252°C suggesting that this water molecule is strongly coordinated [24] to the metal, further supporting the infrared and structural data. In the final step, the isomeric anhydrous lanthanide pyrazine-carboxylate intermediates decompose exothermally in the range 265 to 490°C to give the corresponding metal oxide as the final residue. However, the close observation of the TG results show that lanthanide carbonates are formed as intermediates; but that decomposition is continuous so that this can not be quantified. All of these complexes decompose in a similar manner and the decomposition scheme of lanthanum compound is given below as an example.

$$[La(pyzCOO)_3(H_2O)]{\cdot}2.5H_2O \xrightarrow{157℃\text{, endo}}$$

$$[La(pyzCOO)_3{\cdot}H_2O)]+2.5H_2O$$

$$[La(pyzCOO)_3{\cdot}H_2O] \xrightarrow{252℃\text{, endo}}$$

$$La(pyzCOO)_3+H_2O$$

$$La(pyzCOO)_3 \xrightarrow{480℃\text{,}\mathit{endo}}$$

$$La_2O_3+N_2+CO_2+H_2O$$

Because of the close similarity of the rare-earth-metal complexes, the observed decomposition temperatures are in almost the same range. However, it is pertinent to note that the cerium compound shows distinct single exothermic peak (434°C) in contrast to other compounds which show a somewhat broad exotherm between 422 and 454°C, in their final step of decomposition. The overwhelming exothermicity of the cerium compound may be due to its oxidative decomposition to give CeO_2 as the end product as *vs.*

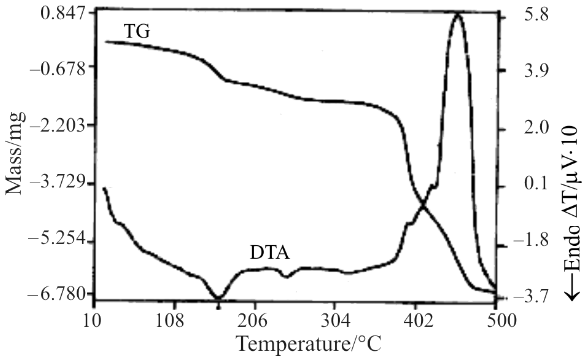

Fig. 2 Simultaneous TG-DTA of [Nd(pyzCOO)$_3$×H$_2$O)]·2.5H$_2$O

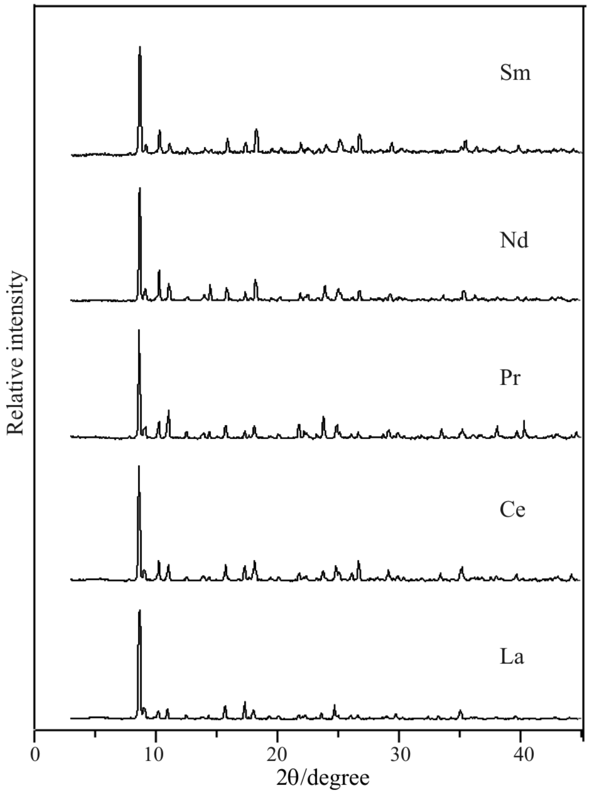

Fig. 3 X-ray powder diffraction pattern of [Ln(pyzCOO)$_3$(H$_2$O)]·2.5H$_2$O

Ln$_2$O$_3$ in other cases. This temperature range is significantly less than the metal oxide formation temperature of simple lanthanide phthalate complexes [25]. The simultaneous TG-DTA of the neodymium compound is shown in Fig.2 as a representative example.

In order to know the isomorphic nature among the complexes, the X-ray powder patterns have been compared. Figure 3 shows the X-ray powder diffraction pattern for the complexes. The pattern as well as 2θ and *d*-spacings of all the compounds suggest them to be isostructural. The results from IR and thermoanalytical studies are in accordance with these isomorphous structural groupings.

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