

Synthesis and Characterization of some Hippurato Rare Earth Metal Complexes

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요 약. 희토류 원소들은 마뇨산(HL)과, $ML_3 \cdot nH_2O$ (M=La(III), n=4; M=Ce(III), n=7; M=Sm(III), n=8; HL=hippuric acid) 라는 일반식으로 표현될 수 있는 화합물들을 생성한다. 생성된 고체 화합물들의 특성이 원소분석, IR, 1H NMR, 전자 스펙트라, 그리고 열중량 분석을 통해 조사되었다. 리간드와 금속 이온들간의 배위 형태도 결정되었다.

주제어: 합성, infrared 스펙트라, TG, 1H NMR, 마뇨산(hippuric acid)

ABSTRACT. Rare earth elements form complexes with hippuric acid with the general formula, $ML_3 \cdot nH_2O$ (M=La, Ce and Sm(III) where n=4, 7 and 8 respectively, HL=hippuric acid). The solid complexes formed were characterized through their elemental analysis, IR, 1HNMR and electronic spectral as well as thermogravimetric analysis. The mode of coordination between the ligand and the metal ions were determined.

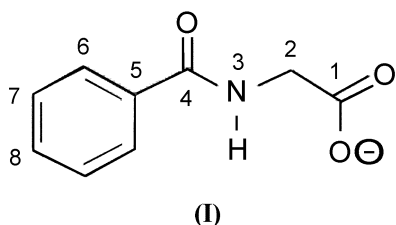
Keywords: Synthesis, Infrared Spectra, TG, 1HNMR , Hippuric Acid

INTRODUCTION

The study of the reaction between metals and hippuric acid, 4-amino hippuric acid, nucleoside or related base type is a topic of increasing interest due to their presence in biological system. It is produced in the renal metabolism of P-amino benzoic and it is also involved in sulfate transport in human neutrophils.¹⁻³ From the chemical studies for the hippuric acid derivatives such as 4-amino hippuric acid indicate that the presence of an NH_2 group on the phenyl ring could, in principle, be a potential

donor group in metal coordination.⁴⁻⁸ In these studies the ligand is reported to act as an N, O bridging ligand besides its normal monodentate behavior through the carboxylate oxygen.

Hippurates of Mn(II), Cd(II), Ag(I), Zn(II) and Hg(II) were isolated from solutions as crystal solids.⁹⁻¹² The infrared spectra for all studied hippurate complexes and X-ray crystal structure of the Cd(II) hippurate complex⁸ indicate that metal-hippurate coordination involves only the carboxylate group via the two oxygen atoms as a chelating ligand.



The aim of this work is to synthesize and examine systematically, in the solid state, the new hippurate complexes formed on the reaction of lanthanum(III) nitrate and cerium(III), Samarium(III) chlorides with hippuric acid shown in (I) in alkaline media. The products complexes were characterized by their elemental analysis, IR, ^1H NMR and electronic spectra as well as thermo gravimetric analysis to elucidate the coordination properties of hippuric acid with these metal ions.

EXPERIMENTAL

All of the reagent employed in this investigation was of analytical grade. The white solid complex $[\text{La}(\text{hip})_3] \cdot 4\text{H}_2\text{O}$ was prepared by adding lanthanum(III) nitrate hexahydrate (0.866 g, 2 mmole) in 10 ml bidistilled water dropwisly to a stirred mixture of hippuric acid (1.074 g, 6 mmol) in 5 ml ethanol and sodium hydroxide (0.240 g, 6 mmol) in 50 ml bidistilled water. The reaction mixture was heated to about 60°C for about 3 h., the resulting precipitate was filtered, washed several times with hot water, and dried over phosphorous pentoxide. The hippurate complexes $[\text{Ce}(\text{hip})_3] \cdot 7\text{H}_2\text{O}$ and $[\text{Sm}(\text{hip})_3] \cdot 8\text{H}_2\text{O}$ were prepared in a similar way to that described above by the reaction of, $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and $\text{SmCl}_3 \cdot 6\text{H}_2\text{O}$ with hippuric acid in a molar ratio of 1:3, respectively.

Elemental C, H, N analysis were carried out on a

Perkin Elmer CHN 2400. Lanthanum, cerium and samarium contents were determined gravimetrically by transforming the product into the corresponding oxides. The obtained analytical data are summarized in *Table 1*. Infrared spectra ($4000\text{-}400\text{ cm}^{-1}$) were recorded as KBr pellets on a Gensis II FT IR spectrometer and the electronic spectra were registered on a Shimadzu UV -spectrophotometer model 1601 PC in the region of $700\text{-}200\text{ nm}$. ^1H NMR spectra were recorded on a Varian Gemini 200 MHz, at room temperature.

Thermogravimetric (TG) was carried out under N_2 -atmosphere using detectors model Shimadzu TGA-50 H.

RESULTS AND DISCUSSION

Hippuric acid reacts with La (III) nitrate and Ce (III), Sm (III) chlorides in alkaline aqueous media at about 60°C to form the obtained solid hippurate complexes formulated as $[\text{La}(\text{hip})_3] \cdot 4\text{H}_2\text{O}$, $[\text{Ce}(\text{hip})_3] \cdot 7\text{H}_2\text{O}$ and $[\text{Sm}(\text{hip})_3] \cdot 8\text{H}_2\text{O}$, respectively. The infrared spectra of hippuric acid and its complexes are given in *Fig. 1*, and their band assignments are given in *Table 2*. In the infrared spectra of the La(III), Ce(III) and Sm(III) complexes some bands disappear at 1758 and 1750 cm^{-1} , arising from the free carboxylic acid ($-\text{COOH}$) group as shown in the spectrum of hippuric acid. This indicates that the hydrogen ion in the hippuric acid molecule is substituted by the metal ions. However, the IR spectra of the prepared hippurates show strong absorption bands in the region of $1578\text{-}1537\text{ cm}^{-1}$ due to the asymmetrical vibration of the carboxylate anion, $\nu_{\text{as}}(\text{COO}^-)$. The corresponding symmetric vibration $\nu_{\text{s}}(\text{COO}^-)$ is observed in the region $1426\text{-}1405\text{ cm}^{-1}$. The shift of the absorption band of $\nu_{\text{as}}(\text{COO}^-)$ to lower frequencies, suggests that carboxylate anion

Table 1. Analytical data

Compounds	C%		H%		N%		M ³⁺ %	
	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$[\text{La}(\text{hip})_3] \cdot 4\text{H}_2\text{O}$	43.37	43.48	4.26	4.29	5.60	5.63	18.59	18.65
$[\text{Ce}(\text{hip})_3] \cdot 7\text{H}_2\text{O}$	51.42	51.59	4.79	4.74	5.19	5.24	17.49	17.51
$[\text{Sm}(\text{hip})_3] \cdot 8\text{H}_2\text{O}$	39.08	39.13	4.79	4.83	5.03	5.07	18.08	18.11

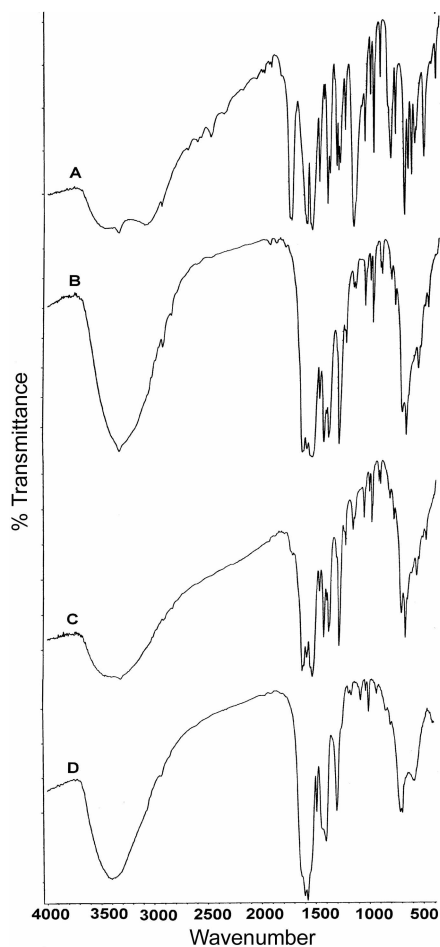


Fig. 1. Infrared spectra of: (A): Hippuric acid, (B): $[La(hip)_3] \cdot 4H_2O$, (C): $[Ce(hip)_3] \cdot 7H_2O$, (D): $[Sm(hip)_3] \cdot 8H_2O$.

in the complexes under study behaves as a chelating ligand¹³ (Table 2). The coordination of the metal ions via oxygens of the carboxylate is confirmed by observing M-O band stretching vibrations, $\nu(M-O)$ at 538 and 494 cm^{-1} for La (III), at 588, 530 and 499 cm^{-1} for Ce (III) and at 588 and 446 cm^{-1} for Sm (III) complex. These bands are not observed in the spectrum of hippuric acid. A new broad band is also observed in the complexes spectra in the region 3400-3470 cm^{-1} due to the vibration $\nu(OH)$ of lattice water in the hydrated complexes. The infrared spectra of M(III) hippurates display a group of bands due to N-H vibrations at 3365-3070 cm^{-1} and 1650-1598 cm^{-1} . This last band exhibits both bend-

ing motion, $\delta(N-H)$ and ring vibrational character. The assignment of those bands agrees quite well with those for related complexes containing typical hippurate ligands.^{8,13-16} The complexes were also investigated by 1H NMR in DMSO- d_6 as a solvent Fig. 2, where the data obtained are in agreement with the proposed coordination through the carboxylic group (disappearance of the H(1) signal) in a symmetrical geometry and the peaks characteristic for water molecules were observed around δ 3.52 ppm. The 1H NMR data for free hippuric acid: δ 12.5 (H, H(1), COOH), 8.84, 8.80 [H, H(3)], 7.91 [2H, H(6)], 7.53 [3H, H(7,8)], 3.97, 3.94 [2H, H(2)], for $[La(hip)_3] \cdot 4H_2O$: δ 8.34 [1H, H(3)], 7.88 [2H, H(6)], 7.45 [3H, H(7,8)], 3.85 [2H, H(2)], 3.25, 3.17 [H, (H₂O)], for $[Ce(hip)_3] \cdot 7H_2O$: δ 9.24 [1H, H(3)], 7.96 [2H, H(6)], 7.51 [3H, H(7,8)], 4.93 [2H, H(2)], 3.76 [H, (H₂O)] and for $[Sm(hip)_3] \cdot 8H_2O$: δ 8.8 (1H, H(3)), 7.88 (2H, H(6)), 7.50 (3H, H(7,8)), 3.94 [2H, H(2)], 3.31 [H, (H₂O)]. The aromatic signals H(6), H(7) and H(8) nearly do not shift significantly, thus showing that the magnetic environment of the aromatic ring has not changed significantly with coordination.

To make sure about the proposed structure for our hippurate complexes the electronic spectra were carried out in dimethyl sulfoxide, which absorbed around 260 nm, Fig. 3. The absorption spectra of M(III) hippurate are compared with the absorption maxima of hippuric acid, there are evident that the increasing in the absorbance (hyperchromic effect) classified in all of the three mentioned hippuric acid complexes attributed to the complexation behaviour of hippuric acid towards metal ions.

Thermogravimetric (TG) was carried out under a N_2 atmosphere, Fig. 4. Decomposition mechanisms have been shown in Table 3. Decomposition of the complexes starts at different temperatures and exhibits two degradation stages. The hydrated complexes of Ce(III) and Sm(III) lose upon heating some water molecules in one step within the temperature range of 50-150 $^{\circ}C$ with an accompanying a weight loss of 9.12% and 6.22%, corresponding with the loss of four and three water molecules in agreement with the theoretical values of 9.00% and 6.52%, respec-

Table 2. Infrared frequencies^a (cm⁻¹) and tentative assignments^b for hippuric acid and of its La(III), Ce(III) and Sm(III) complexes

Hippuric	[La(hip) ₃]·4H ₂ O	[Ce(hip) ₃]·7H ₂ O	[Sm(hip) ₃]·8H ₂ O	Assignments
	3400 mbr	3470 w 3417w	3423 mbr	ν (OH); H ₂ O
3344 w	3328 mbr	3328 w	3365 w	ν (NH)
3100 vw	3260 w	3066 vw	3070 vw	
3074 vw	3076 vw			
2940 w	2935 w	2930 vw	2950 vw	ν (CH)
2699 w	2862 vw	2846 vw	2860 vw	
2605 w				
2480 m				
1758 sh				ν (C = O) ₂ (COOH)
1750 vs				
1630 sh	1650 ms	1646 s	1610 sh	δ (NH)
1615 vs	1636 ms	1640 sh	1598 vs	δ (H ₂ O)
1562 vs	1610 m	1610 s		
	1572 m 1552 m	1537 s	1553 s	ν _{as} (COO ⁻)
1494 s	1489 s	1489 s	1495 vs	C-H deformation - CH ₂
1447 m	1452 vs	1458 vs	1442 sh	
1420 s	1426 w	1426 m	1406 m	ν _s (COO ⁻)
1400 ms	1405 s	1410 vs		
1342 s	1311 vs	1306 vs	1306 vs	δ (CH ₂)
1427 s				
1300 s				
1259 s	1253 m	1253 s	1255 sh	ν (C-C)
1180 vs	1185 m 1175 m	1180 s	1180 w 1165 w	δ (CH), in-plane bend
1080 s	1080 s	1075 s	1086 m	δ _r (CH ₂)
1033 s	1033 ms	1033 s	1023 m	
1007 vs	1077 vs	1012 s		
949 s	976 vw	939 m	997 ms	ν (C - C)
855 vs	939 w	923 s	942 w	
803 vs	923 m 839 m 798 m	839 m 803 m	840 w 808 w	
729 vs	729 m	729 ms	714 ms	δ (COO ⁻)
698 s	689 vs	693 s	693 ms	ν (M - O) + Ring def.
667 s	635 sh	635 sh	588 m	
625 s	583 ms	588 m	446 vw	
551 s	494 m	562 vw		
473 w		530 vw		
431 m		499 m		

(a): s=strong, w=weak, m=medium, sh=shoulder, v=very, br=broad.

(b): ν, stretching; δ and δ_r correspond to bending and rocking motions, respectively.

tively, while the complex [La(hip)₃]·4H₂O is dehydrated completely in one step at a maximum temperature of 89 °C. The relatively low value of temperature of this step may indicate that these water molecules

undergoes less H-bonding with hippurate anion. The trihydrated Ce(III) hippurate and penta hydrated Sm(III) complex are simultaneously dehydrated and decomposed to the corresponding oxide at the

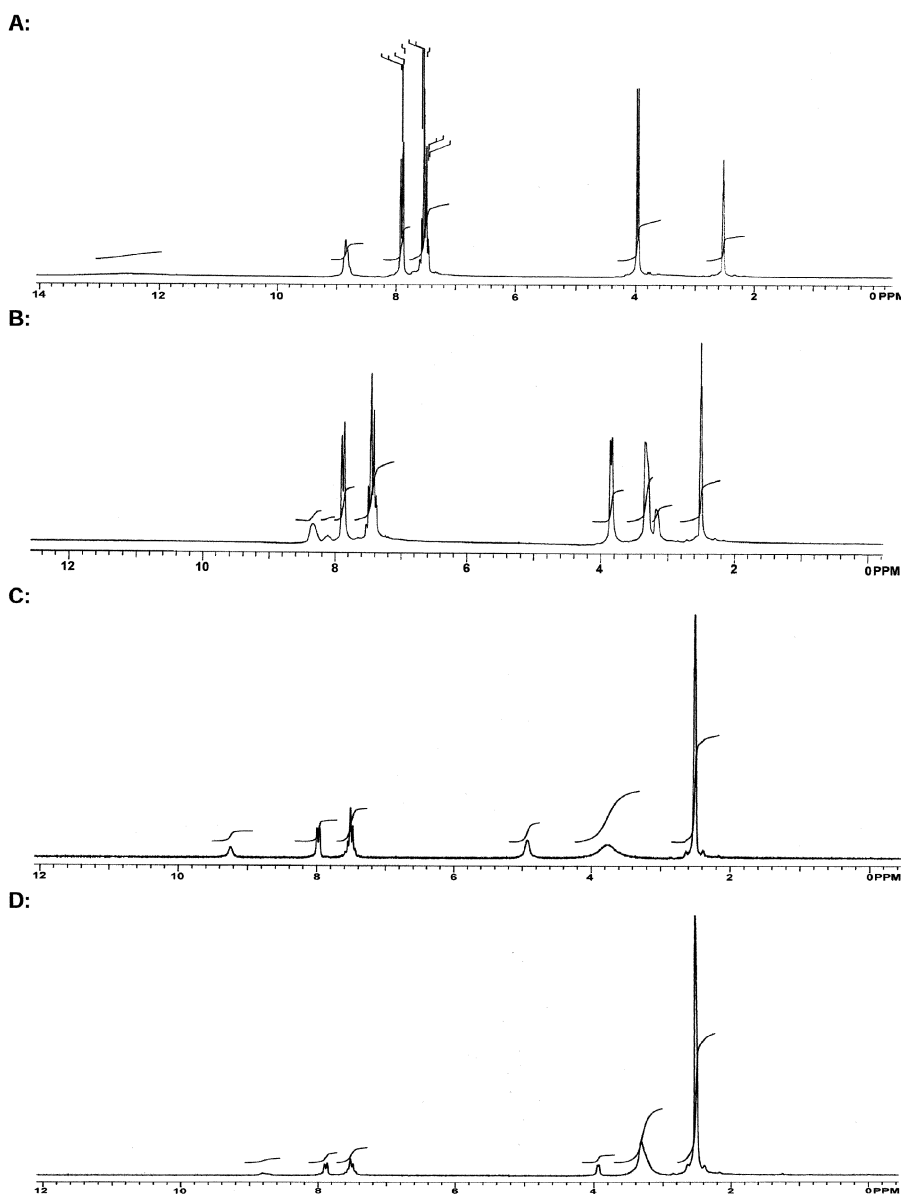
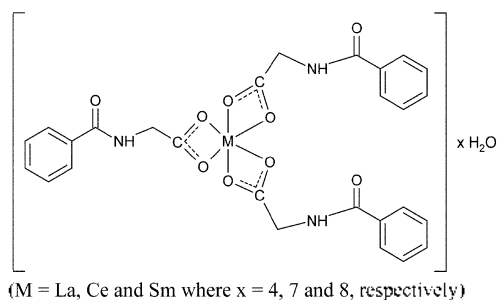


Fig. 2. ¹H NMR Spectra of: (A): Hippuric acid, (B): [La(hip)₃]·4H₂O, (C): [Ce(hip)₃]·7H₂O (D): [Sm(hip)₃]·8H₂O.

temperature range 150-800°C with intermediate formation of very unstable products¹³ which were not identified. The dehydrated La(III) complex is stable within the temperature range of 110-250 °C and then decompose to oxide, La₂O₃ within the temperature range of 250-800 °C. The proposed structural formula on the basis of the results discussed in our paper located as follows:



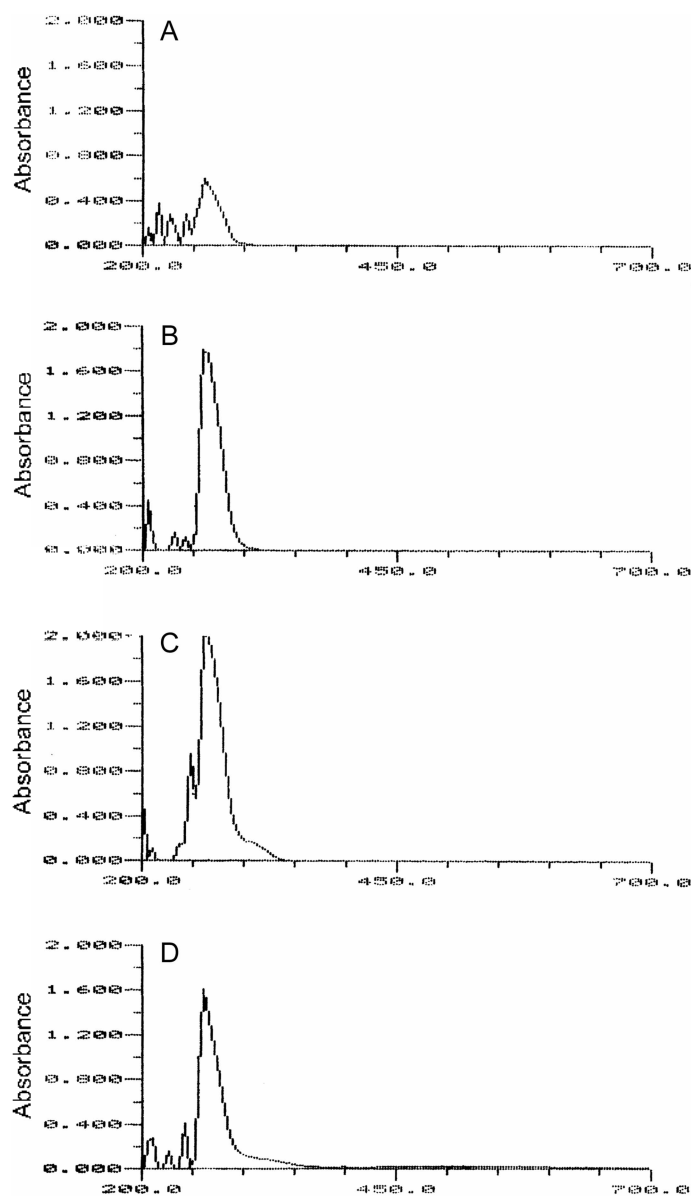
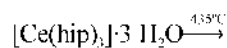
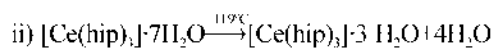
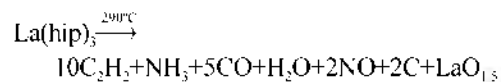
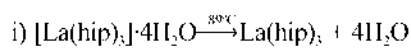


Fig. 3. Electronic spectra of: (A): Hippuric acid, (B): $[\text{La}(\text{hip})_3] \cdot 4\text{H}_2\text{O}$, (C): $[\text{Ce}(\text{hip})_3] \cdot 7\text{H}_2\text{O}$ (D): $[\text{Sm}(\text{hip})_3] \cdot 8\text{H}_2\text{O}$.

The infrared spectra of the final products *Fig. 5*, show the absence of all bands associated with the hippurate anion and water molecules and instead the characteristic spectra for oxides are appeared. According to the above discussion, the mechanisms proposed for the thermal decomposition of hippurato complexes are summarized as follow:



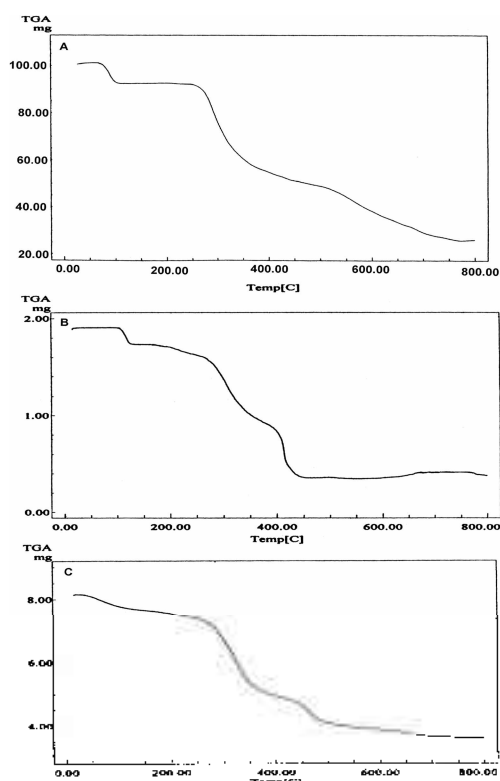


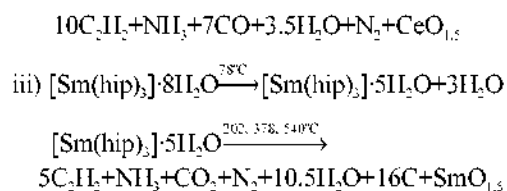
Fig. 4. TG diagrams of: (A): $[La(hip)_3] \cdot 4H_2O$, (B): $[Ce(hip)_3] \cdot 7H_2O$, (C): $[Sm(hip)_3] \cdot 8H_2O$.



Fig. 5. The final decomposition products of: (A): $[La(hip)_3] \cdot 4H_2O$, (B): $[Ce(hip)_3] \cdot 7H_2O$ (C): $[Sm(hip)_3] \cdot 8H_2O$.

Table 3. Thermal data of the decomposition reactions of La(III), Ce(III) and Sm(III) hippurates

Compounds	Decomposition	$T_{max}/^{\circ}C$	Lost species	%weight losses	
				Found	Calc.
$[La(hip)_3] \cdot 4H_2O$	First stage	89 °C	$4H_2O$	9.11%	9.66%
	Second stage	290 °C	$10C_2H_2 + NH_3 + 5CO + H_2O + 2NO$	65.74%	65.23%
	Total loss			74.85%	74.89%
	Residue			25.16%	25.10%
$[Ce(hip)_3] \cdot 7H_2O$	First stage	119 °C	$4H_2O$	9.12%	9.00%
	Second stage	435 °C	$10C_2H_2 + NH_3 + 7CO + 3.5H_2O + N_2$	71.22%	70.50%
	Total loss			80.34%	79.50%
	Residue			19.66%	20.50%
$[Sm(hip)_3] \cdot 8H_2O$	First stage	78 °C	$3H_2O$	6.22%	6.52%
	Second stage	202 °C	$5C_2H_2 + NH_3 + CO_2 + N_2 + 10.5H_2O$	49.77%	49.27%
	Total loss			55.99%	55.79%
	Residue			44.01%	44.20%



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