Phenylbutazone의 란탄(III) 착물에 대한 합성, 스펙트럼 및 열적 연구

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Synthesis, Spectral and Thermal Studies of Lanthanide(III) Complexes of Phenylbutazone

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요 약. 1,2-diphenyl-4-butyl-3,5-pyrazolidinedione(phenylbutazone, PB)의 란탄(III) 착물을 합성하여 원소분석, 몰전기전도도 측정, IR, UV-Vis. 및 NMR 스펙트럼으로 특성을 조사하였다. 스펙트럼 데이터로부터 PB가 pyrazolidinedione 고리의 두 카르보닐 산소를 통해 이배위 및 일이온화 리간드로 배위됨을 규명하였다. 몰전기전도도 데이터로부터 이들 착물이 비전해질임을 규명하였다. 이들 착물의 열적 행동을 공기 중에서 TG 및 DTG로 연구한 결과, 탈수화, 열적 안전성 및 열분해에 관한 정보를 얻을 수 있었다. 최종 생성물은 해당 금속의 산화물로 밝혀졌다. 탈수화 및 분해 단계에 대한 열역학 및 반응속도 파라메터를 구하였다. 분해 단계에 대한 음의 엔트로피 값은 반응물보다 활성화 착물이 더 질서있는 구조를 갖는다는 것을 의미하며, 이때 반응은 정상보다 느렸다. 이러한 연구를 바탕으로 착물의 분자식이 [Ln(PB)₃]·5H₂O(Ln=La 및 Ce) 그리고 [Ln(PB)₃ (H₂O)₂]·2H₂O(Ln=Pr, Nd 및 Sm)임을 규명하였다.

주제어: Phenylbutazone, IR, ^{1}H NMR, ^{13}C NMR, 열분석, 란탄(III) 착물

ABSTRACT. Lanthanide(III) complexes of 1,2-diphenyl-4-butyl-3,5-pyrazolidinedione(phenylbutazone, PB) have been synthesized and characterized by elemental analyses, molar conductance measurements, IR, UV-Vis. and NMR spectra. The spectral data reveal that the PB acts as a bidentate and mono-ionic ligand coordinating through both the carbonyl oxygens of the pyrazolidinedione ring. The molar conductance data suggest that the complexes are non-electrolytes. The thermal behaviour of the complexes was studied by TG and DTG in air atmosphere and the results provide information about dehydration, thermal stability and thermal decomposition. The final products are found to be the corresponding metal oxides. The thermodynamic parameters and kinetic parameters were evaluated for the dehydration and decomposition stages. The negative entropy values of the decomposition stages indicate that the activated complexes have a more ordered structure than the reactants and that the reactions are slower than normal. Based on these studies, the complexes have been formulated as [Ln(PB)₃]·5H₂O(Ln=La and Ce) and [Ln(PB)₃ (H₂O)₂]·2H₂O(Ln=Pr, Nd and Sm).

Keywords: Phenylbutazone, IR, ^{1}H NMR, ^{13}C NMR, Thermal analysis, Lanthanide(III) complexes

INTRODUCTION

Coordination chemistry of lanthanides is a promising research area motivated by the wide range of applications for these compounds in catalysis, asymmetric synthesis and advanced materials.[1,2] Highly luminescent lanthanide complexes are attracting attention in a wide variety of photonic application such as light emitting diodes and bio-inspired luminescent probes.[3,4] In addition these complexes

have been found to exhibit anticancer and fungicidal properties.[5] The lanthanide ions belong to the hard acid class in the Pearson designation.[6] Lanthanide(III) ions because of their large size and high positive charge form stable complexes with high coordination number. The lanthanide ions prefer hard donor atoms such as neutral or negatively charged oxygen atoms and hence they have a strong tendency to bind water molecules.[7] Metal complexes of some biologically important ligands are some times
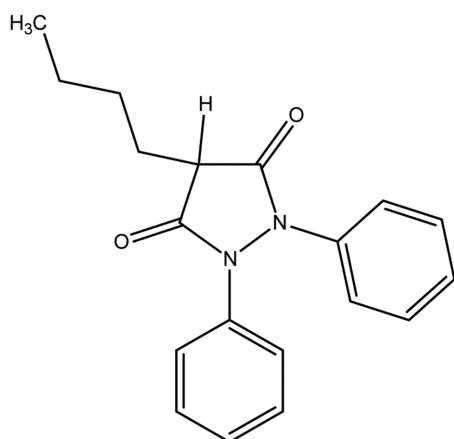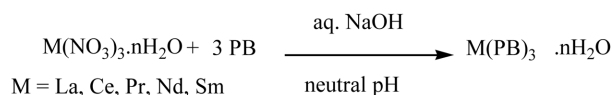
Fig. 1. Structure of PB.

more effective than the free ligands.[8-10] It is well documented that pyrazolidinedione derivatives possess a wide variety of biological and pharmaceutical activities and are also used as colour agents, photographic light sensitive and thermal printing materials.[11-13] Phenylbutazone belongs to the family of non-steroidal anti-inflammatory drugs (NSAID).[14]

In the present paper, we describe the synthesis, spectroscopic and thermal decomposition studies of a series of Ln(III) (Ln=La^{3+}, Ce^{3+}, Pr^{3+}, Nd^{3+}, Sm^{3+}) complexes with phenylbutazone.

EXPERIMENTAL

Materials and measurements

Phenylbutazone was purchased from Sigma Company (USA). All other chemicals used were of AR grade. Elemental analysis of the complexes was carried out on a VarioEL 111 CHNS analyzer. Molar conductivity of the complexes in DMF was measured using Systronics Conductivity meter 304. The FT-IR spectrum was recorded on a DR/Jasco FT-IR-6300 spectrometer (4000-400 cm^{-1}) in KBr pellets. The solid state UV-Vis. spectra of complexes were recorded on a Varian Cary 5000 spectrometer in the range 200-800 nm. ^{1}H and ^{13}C NMR spectrum of PB and

$$M(NO_3)_3 \cdot nH_2O + 3\ PB \xrightarrow[\text{neutral pH}]{\text{aq. NaOH}} M(PB)_3 \cdot nH_2O$$

M = La, Ce, Pr, Nd, Sm

Scheme 1.

its lanthanum complex were recorded in MeOD and DMSO-d_6 on a Joel GSX 400 FT-NMR spectrometer. Thermo gravimetric analysis (TG/DTG) was carried out in air at a heating rate of 10 °C/min using Perkin Elmer (Pyris Diamond) analyzer.

Preparation of metal complexes

Sodium salt of phenylbutazone (0.3 g, 1 mmol) was prepared in 0.1 M NaOH solution (pH~7). A slight excess of the ligand was used to exclude excess alkali. The resulting suspension was filtered. To the clear solution an aqueous solution of Ln (NO$_3$)$_3$·nH$_2$O [Ln=La, Ce, Pr, Nd or Sm] (0.3 mmol) was added drop wise with stirring. The solid complexes formed were filtered, separated, washed several times with water and dried in air.

RESULTS AND DISCUSSION

Elemental analysis

The proposed compositions of five lanthanide(III) complexes of phenylbutazone were confirmed on the basis of the elemental analysis and the data are summarized in *Table* 1. The experimental data are in good agreement with the theoretical values. The melting points, yields and colour of the complexes are also shown in *Table* 1. The molar conductance data suggest that the complexes are non-electrolytic in nature.

FT-IR Analysis

The main IR spectral bands of PB and its complexes and their tentative assignments are summarised in *Table* 2. The IR spectrum of the ligand shows two C=O stretching frequencies, one at 1760 cm^{-1} and the other at 1722 cm^{-1}.[15,16] The shifting of these two carbonyl peaks in metal complexes to lower wavenumbers indicates the involvement of both

Table 1. Analytical data of lanthanide (III) complexes

Complex	Yield %	Colour	M.P. °C	Found (calc.%)		
				C	H	N
[La (PB)$_3$]·5H$_2$O	75	White	196	9.15 (59.27)	5.61 (6.06)	7.32 (7.28)
[Ce (PB)$_3$]·5H$_2$O	73	Yellow	196	59.61 (59.20)	5.36 (6.05)	7.33 (7.27)
[Pr (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	72	White	198	60.07 (60.10)	5.13 (6.15)	7.31 (7.38)
[Nd (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	74	White	196	60.03 (59.90)	5.22 (6.13)	7.35 (7.35)
[Sm (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	74	Yellow	198	59.41 (59.60)	5.52 (6.09)	7.34 (7.32)

Table 2. IR spectral data of phenylbutazone and its complexes

Compound	ν(O-H) H₂O	arylν(C-H)	saturated ν(C-H)	tertiary ν(C-H)	ν_as(C=O)	ν_s(C=O)	ν(C-N)	ν(N-N)	ν(M-O)
PB	-	3067(m)	2957(m)	2859(w)	1760(vs)	1722(vs)	1153(m)	1134(w)	-
[La (PB)₃]·5H₂O	3605(b)	3065(w)	2954(m)	-	1598(s)	1536(vs)	1126(m)	1098(m)	550(m)
[Ce (PB)₃]·5H₂O	3604(b)	3064(w)	2955(m)	-	1598(s)	1537(vs)	1126(m)	1099(m)	548(m)
[Pr (PB)₃(H₂O)₂]·2H₂O	3602(b)	3064(w)	2955(m)	-	1598(s)	1537(vs)	1126(m)	1099(m)	548(m)
[Nd (PB)₃(H₂O)₂]·2H₂O	3605(b)	3064(w)	2955(m)	-	1598(s)	1537(vs)	1126(m)	1099(m)	548(m)
[Sm (PB)₃(H₂O)₂]·2H₂O	3605(b)	3068(w)	2955(m)	-	1598(s)	1537(vs)	1126(m)	1099(m)	552(m)

the carbonyl groups in coordination.[17,18] The band at 2859 cm⁻¹ in the free ligand is assigned to the stretching of the tautomeric CH group.[19,20] This band is absent in all the complexes which confirms that the complexation takes place after deprotonation. The above observations indicate that PB acts as a monoionic bidentate ligand and coordinates through both the carbonyl groups. The new bands in the range 506-551 cm⁻¹ in the spectra of the complexes are assigned to ν(M-O).[21-23] The broad band in the range 3000-3600 cm⁻¹ and bands at 657 cm⁻¹ and 1099 cm⁻¹ are assigned to the different vibrational modes of lattice and coordinated water molecules in complexes.[24,25] This was further confirmed by thermal studies.

¹H NMR Spectra

The NMR spectral data are shown in *Table* 2 and the NMR spectra of PB and La(III) complex are shown in *Fig.* 2 and *Fig.* 3, respectively. A triplet at 2.19 ppm is assigned to tertiary CH proton. This triplet signal is absent in the La(III) complex, which confirms that this proton is abstracted by the base and the participation of two carbonyl groups in coordination All other signals are well reproduced in the spectra of the complex.
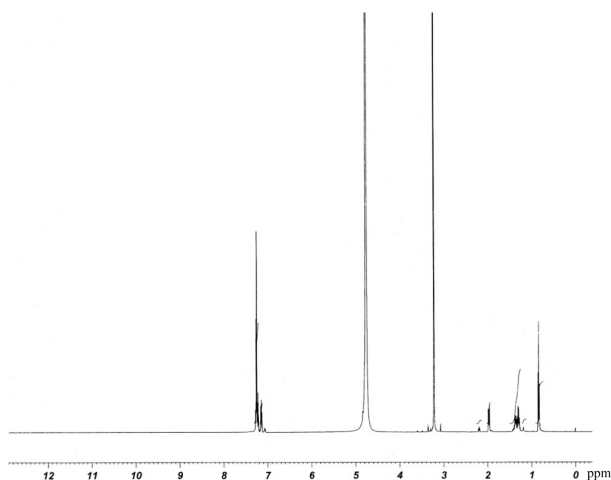
Fig. 2. ¹H NMR spectrum of PB.
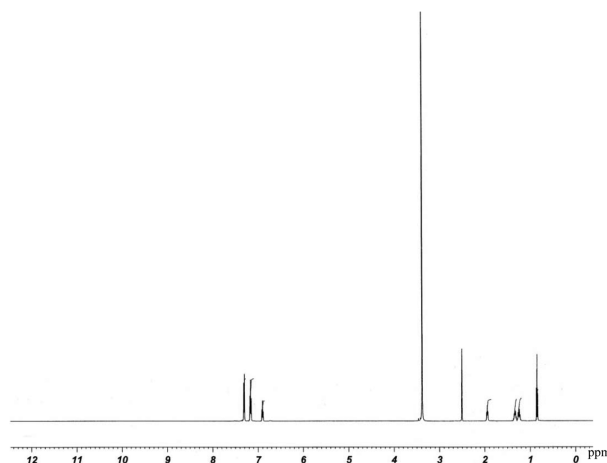
Fig. 3. ¹H NMR spectrum of La(III) complex.

¹³C NMR spectra

The ¹³C NMR spectrum provides direct information about the carbon skeleton of PB and its lanthanum(III) complex. The two carbonyl groups show the same chemical shift values, confirming that the carbonyl groups were equivalent in the molecule.[26]

Signals at 173.6 and 171.4 δ ppm are attributed to two carbonyl carbons in the ligand and the complex respectively. Aromatic carbons appear at135.3, 128.8, 127.3 and 123.8 δ ppm for PB and 142.9, 128.3, 122.4 and 120.9 δ ppm for the lanthanum(III) complex. The methyl carbons of the butyl group appear at12.8 δ ppm for the ligand and

Table 3. ¹H NMR spectral data (δ, ppm) of PB and its La (III) complexes

Proton	PB (ligand)	La(III) complex
Aromatic protons	7.06(t, 2H)	6.90(t, J=7.5Hz, 2H)
Aromatic protons	7.14(m, 4H)	7.17(t, J=7.8Hz, 4H)
Aromatic protons	7.24(m, 4H)	7.31(d, J=8.0Hz, 4H)
-CH	2.19(t, 1H)	-
-CH₃	0.83(t, 3H)	0.85(t, J=7.5Hz, 3H)
-CH₂	1.30(m, 2H)	1.24(m, J=7.5Hz, 2H)
-CH₂	1.36(t, 2H)	1.34(t, J=7.5Hz, 2H)
-CH₂	1.97(t, 2H)	1.94(t, J=7.5Hz, 2H)

14.6 δ ppm for the complex. The three methylene carbon atoms of the butyl group appear at 22.1, 27 and 27.7 δ ppm for PB and at 22.1, 22.7 and 32.1 δ ppm for the complex. The -CH carbon signals are merged with the solvent signals in both the spectra.

Thermal analysis

The TG-DTG curves of lanthanide(III) complexes of phenylbutazone at a heating rate of 10 $^{\circ}$C/min are given in *Figs.* 4-8. It provides information about the thermal stability and thermal decomposition of the complexes. The thermo analytical data for the synthesized lanthanide(III) complexes are shown in *Table* 4.

The La(III) and Ce(III) complexes undergo decomposition in two stages. The initial weight loss of 7.8% (calc. 7.8%) in the temperature range 89.5-150.4 $^{\circ}$C[28] corresponds to the loss of five water molecules. This temperature range suggests the presence of lattice water molecules. A further weight loss of 78.2% (calc. 78.1%) in the temperature range 344.4-455.0 $^{\circ}$C is due to the thermal decomposition
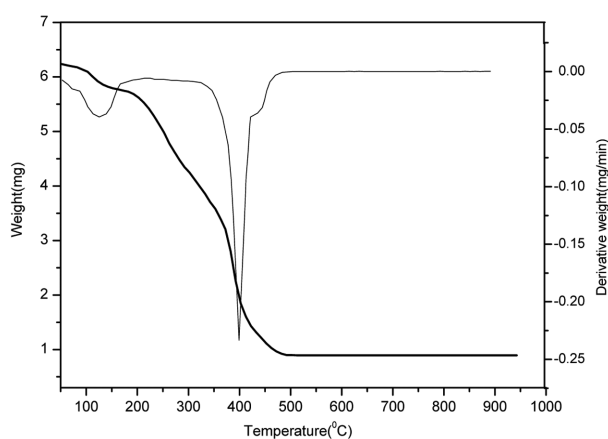

Fig. 4. TG and DTG curves of $[La(PB)_3] \cdot 5H_2O$.
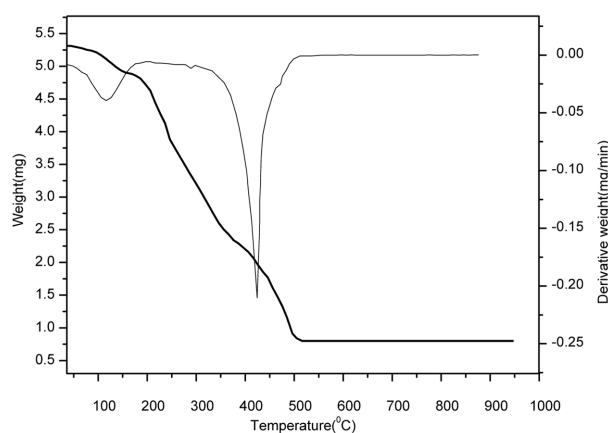
Fig. 5. TG and DTG curves of $[Ce(PB)_3] \cdot 5H_2O$.
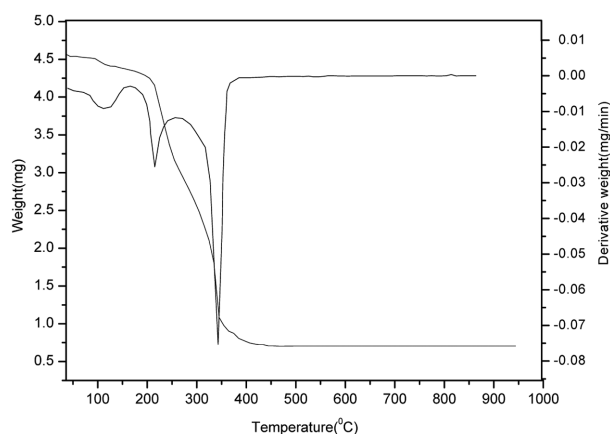
Fig. 6. TG and DTG curves of $[Pr(PB)_3(H_2O)_2] \cdot 2H_2O$.
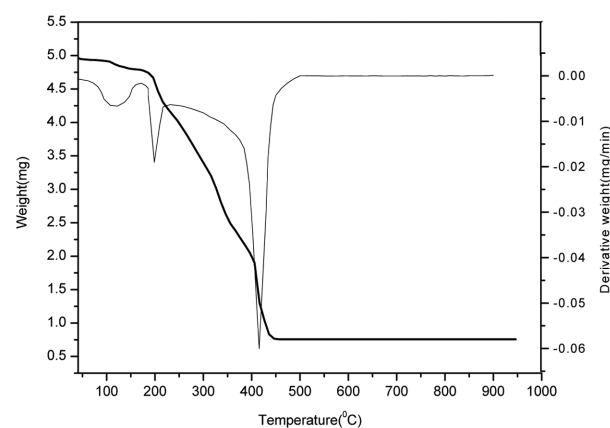
Fig. 7. TG and DTG curves of $[Nd(PB)_3(H_2O)_2] \cdot 2H_2O$.
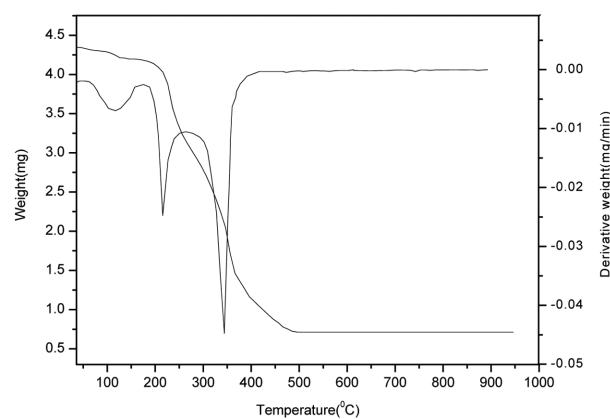
Fig. 8. TG and DTG curves of $[Sm(PB)_3(H_2O)_2] \cdot 2H_2O$.

of the anhydrous compound corresponding to the loss of three PB molecules. The final mass loss agrees with the conversion of the complexes to their oxides. Based on the above observations, the thermal decomposition of lanthanum (III) and cerium(III) complexes can be expressed as follows.

Table **4.** Thermal decomposition of lanthanide(III) complexes of phenylbutazone in air

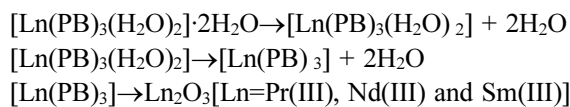| Complexes	Metal Oxide (%)		Ligand (Lost) (%)			H$_2$O (%)			Metal Residue
	Calcd	TG	Temp. range	calcd	TG	Temp. range	calcd	TG	
[La (PB)$_3$]·5H$_2$O	14.1	14.1	344-441	79.2	78.6	88-148	7.8	7.3	La$_2$O$_3$
[Ce (PB)$_3$]·5H$_2$O	14.9	14.1	396-510	79.1	78.6	74-159	7.8	7.6	CeO$_2$
[Pr (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	15.0	14.0	263-362	80.3	79.2	94-260	6.3	6.7	Pr$_6$O$_{11}$
[Nd (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	14.7	15.1	299-464	80.1	79.1	91-298	6.3	6.0	Nd$_2$O$_3$
[Sm (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	15.2	15.3	389-431	79.7	78.7	84-216	6.3	6.0	Sm$_2$O$_3$

$$[Ln(PB)_3]\cdot 5H_2O \rightarrow [Ln(PB)_3] + 5H_2O$$
$$[Ln (PB)_3] \rightarrow Ln_2O_3 \ [Ln= La(III) \ and \ Ce(III)]$$
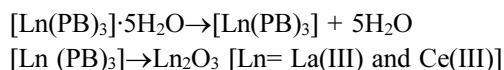
The thermal decomposition of Pr(III), Nd(III) and Sm (III) complexes take place in three stages. The weight loss of 3.2% in the TG curves between 84-150 °C reveals the loss of two lattice water molecules (calc. 3.1%)[27]. The second dehydration step is in the range 160-250 °C with a mass loss of 3.1% corresponding to the loss of two coordinated water molecules (calc. 3.1%).[28] The thermal decomposition of the anhydrous compound takes place in the range 260-480 °C with a mass loss of 79.0% (calc. 80.0%) corresponding to the loss of three PB molecules.[27] Finally the most stable metal oxides are formed. The three stages can be represented as follows.

$$[Ln(PB)_3(H_2O)_2]\cdot 2H_2O \rightarrow [Ln(PB)_3(H_2O)_2] + 2H_2O$$
$$[Ln(PB)_3(H_2O)_2] \rightarrow [Ln(PB)_3] + 2H_2O$$
$$[Ln(PB)_3] \rightarrow Ln_2O_3 [Ln=Pr(III), Nd(III) \ and \ Sm(III)]$$

Kinetic studies

The kinetic parameters of the lanthanide(III) complexes were calculated for each clear cut stage using Mac Callum-Tanner (I),[29] Madusudhanan Ninan (II) and Coats Redfern's (III)[30] equations. The activation energy is in the range 52.0-88.5 kJ·mol^{-1} for the first dehydration stage, 94.7-108.4 kJ·mol^{-1} for the second dehydration stage and 79.0-146.2 kJ·mol^{-1} for the decomposition stage, respectively. The negative entropy for the dehydration and decomposition stages indicates that the activated complexes are more ordered than the reactants and the reactions are slower than normal.[19] The correlation coefficient values are in well agreement.[31] The information from the kinetic studies are summarised in *Tables* 5, 6 and 7.

Electronic spectra

The solid state electronic spectral data of Pr (III) and Sm (III) complexes are given in *Table* 8. The UV-Vis. spectrum of Pr(III) complex is shown in *Fig.* 9. The electronic spectra shows two ligand based transitions at 280 and 305 nm, respectively, corresponds to π→π* and n→π* transitions.[13] The absorption bands of Pr(III) and Sm(III) complexes in the visible region appear due to the transition from the ground levels $^3H_4$ and $^4H_{5/2}$, respectively.

Table **5.** Kinetic parameters for the first dehydration stage of the complexes

Complexes	Method	n	E/KJ mol^{-1}	ΔS/J K^{-1} mol^{-1}	logA/s^{-1}	r
[La (PB)$_3$]·5H$_2$O	I	1.0	84.87	-84.66	8.84	0.993195
	II	1.1	88.50	-74.79	9.37	0.992222
	III	1.1	88.32	-75.47	9.32	0.992180
[Ce (PB)$_3$]·5H$_2$O	I	3.0	75.56	-111.08	7.46	0.984731
	II	3.0	75.98	-107.50	7.64	0.981623
	III	3.0	75.78	-108.62	7.59	0.981471
[Pr (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	I	3.0	67.08	-159.72	4.92	0.997720
	II	2.9	68.72	-155.92	5.12	0.997205
	III	3.0	68.59	-156.93	5.06	0.997218
[Nd (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	I	3.0	52.00	-197.79	2.93	0.998132
	II	3.0	53.85	-194.54	3.10	0.997675
	III	3.0	53.64	-195.87	3.30	0.997663
[Sm (PB)$_3$(H$_2$O)$_2$]·2H$_2$O	I	3.0	68.44	-156.95	5.06	0.994956
	II	2.9	69.94	-153.44	5.24	0.993847
	III	3.0	69.82	-154.42	5.19	0.993817

Table 6. Kinetic parameters for the second dehydration stage of the complexes

Complexes	Method	n	$E/KJ\ mol^{-1}$	$\Delta S/J\ K^{-1}\ mol^{-1}$	$logA/s^{-1}$	r
$[Pr(PB)_3(H_2O)_2]\cdot 2H_2O$	I	3.0	94.90	-120.22	6.98	0.987071
	II	3.0	94.93	-119.19	7.03	0.984665
	III	3.0	94.70	-120.28	6.98	0.984553
$[Nd(PB)_3(H_2O)_2]\cdot 2H_2O$	I	3.0	104.66	-104.08	7.82	0.988040
	II	3.0	104.58	-103.13	7.87	0.986024
	III	3.0	104.36	-104.16	7.82	0.985919
$[Sm(PB)_3(H_2O)_2]\cdot 2H_2O$	I	2.3	106.82	-100.64	8.00	0.992949
	II	2.9	108.37	-96.00	8.24	0.991143
	III	3.0	108.42	-96.39	8.22	0.991101

Table 7. Kinetic parameters for the decomposition stage of the complexes

Complexes	Method	n	$E/KJ\ mol^{-1}$	$\Delta S/J\ K^{-1}\ mol^{-1}$	$logA/s^{-1}$	r
$[La(PB)_3]\cdot 5H_2O$	I	3.0	125.67	-101.63	7.95	0.995959
	II	3.0	123.70	-104.15	7.82	0.995261
	III	3.0	123.40	-105.19	7.76	0.995229
$[Ce(PB)_3]\cdot 5H_2O$	I	1.1	123.12	-123.07	6.83	0.992707
	II	1.2	123.93	-121.18	6.93	0.991350
	III	1.2	123.59	-122.33	6.87	0.991293
$[Pr(PB)_3(H_2O)_2]\cdot 2H_2O$	I	2.4	78.99	-161.37	4.83	0.990807
	II	2.5	79.62	-159.56	4.92	0.988624
	III	2.5	79.33	-160.86	4.86	0.988502
$[Nd(PB)_3(H_2O)_2]\cdot 2H_2O$	I	0.9	134.64	-73.43	9.42	0.987393
	II	0.9	132.59	-76.07	9.29	0.985632
	III	0.9	132.33	-77.06	9.23	0.985571
$[Sm(PB)_3(H_2O)_2]\cdot 2H_2O$	I	2.8	146.24	-75.66	9.31	0.997250
	II	2.9	145.98	-75.36	9.32	0.996838
	III	2.9	145.68	-76.36	9.27	0.996798

Table 8. Electronic spectral data of Pr (III) and Sm(III) complexes of PB

Complex	λ_{max}	Assignments
$[Pr(PB)_3(H_2O)_2]2H_2O$	440	$^3H_4 \cdots\blacktriangleright\ ^3P_2$
	476	$\cdots\blacktriangleright\ ^3P_0$
	580	$\cdots\blacktriangleright\ ^1D_2$
$[Sm(PB)_3(H_2O)_2]2H_2O$	404	$^4H_{5/2}\cdots\blacktriangleright\ ^4P_{9/2}$
	472	$\cdots\blacktriangleright\ ^4P_{13/2}$

Fig. 9. UV-Vis spectrum of Pr (III) complex.

CONCLUSION

Five lanthanide(III) complexes with phenylbutazone were synthesized and characterized by elemental analyses, IR, UV-Vis., ^1H NMR, ^{13}C NMR and thermal studies. The analytical data indicate that the complexes can be represented as $[Ln(PB)_3]\cdot 5H_2O$ for Ln=La(III) and Ce(III) and $[Ln(PB)_3(H_2O)_2]\cdot 2H_2O$ for Ln=Pr(III), Nd(III) and Sm(III). The IR and NMR spectral data indicate that PB coordinates as a monoionic bidentate ligand through both
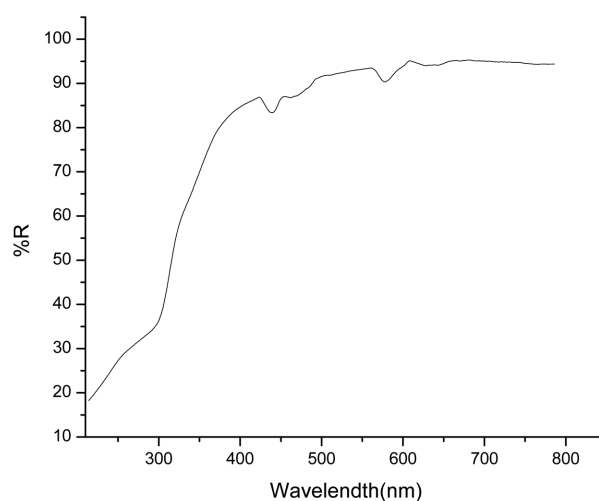
the carbonyl groups after deprotonation. On the basis of the results obtained, the following most probable schematic structures for lanthanide (III) complexes with PB
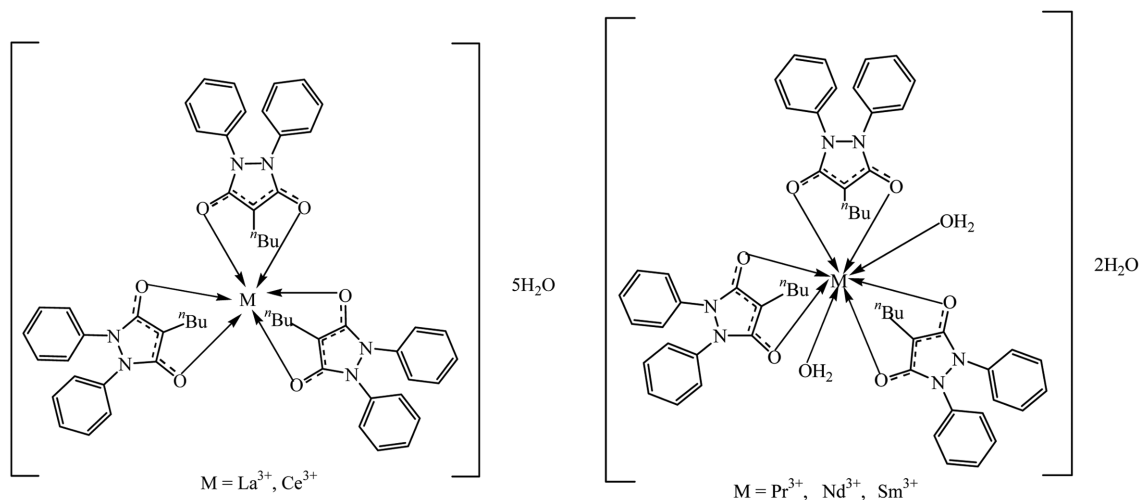
Fig. 10. Tentative structure of Lanthanide(III) complexes.

are proposed.

The thermal decomposition of these complexes provides information about the thermal stability and all complexes give a stable metal oxide residue around 500 ºC. The negative value of the entropy of activation indicates that the activated complexes have a more ordered structure than the reactants and the reactions are slower than normal.

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