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## Structural Elucidation Of Lanthanide(III) Nitrates Complexes With Azomethins



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### ABSTRACT

Synthesis and characterization of some lanthanide(III) complexes of azomethines have been reported. The ligands are bibasic tetradentate azomethines having  $O^{\wedge}N^{\wedge}N^{\wedge}O$  donor system. The resulting complexes have been characterized by elemental analysis, molecular weight determinations and conductivity measurements. Based on the these studies and the spectral studies including IR and X-ray powder diffraction spectra the probable structures of the complexes have been proposed. ©

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### KEYWORDS

Lanthanides complexes;  
Azomethines;  
IR spectra;  
X-Ray powder diffraction spectra.

### INTRODUCTION

Schiff base metal complexes have played a major role in the development of coordination chemistry. Metal complexes with ligands having N and O donor ligands aroused considerable interest in view of their industrial and biological importance<sup>[1]</sup>. Many of these compounds possess a wide spectrum of medicinal properties, including activity against tuberculosis, leprosy and bacterial and viral infections<sup>[2]</sup>. The chemistry of azomethines has become more and more apparent and occupied the place of consider-

able attention because of their well established industrial and biological importance<sup>[3]</sup>.  $O^{\wedge}N$  donor compounds have received great impetus in recent years due to perhaps their remarkable, potential in inhibiting ribonucleotide reductase, an obligatory enzyme in DNA synthesis<sup>[4]</sup>. They are also useful as potential drugs, fungicidal and antibacterial agents<sup>[5]</sup>. The chelating properties of the Schiff bases derived from 2-hydroxy aldehydes and ketones display manifold applications in medicine, industry and agriculture<sup>[6]</sup>.

Over the past few years, trivalent lanthanide com-

plexes have been confirmed useful in many applications, such as luminescent probes, lasers and organic light emitting diodes<sup>[7]</sup>. Complexes of rare earth metal ions have been extensively studied<sup>[8,9]</sup> and an interesting property, which the complexes exhibit is the hypersensitivity of some of the transition on replacement of water molecules in the coordination sphere by some other ligands. Some of the rare earth complexes are useful laser materials<sup>[10]</sup>. Lanthanide chelates used as fluorescence labels in diagnosis and biotechnology. Certain lanthanide complexes are known to emit strong luminescence<sup>[11]</sup>. Lanthanides fulfill all the optimum conditions for high coordination i.e. high charge and small size<sup>[12]</sup>. Therefore, there is a wide scope to study the lanthanide complexes with azomethines. During these investigations such com-

plexes with two bifunctional tetratentate azomethines have been synthesized and characterized.

## EXPERIMENTAL

The chemicals and solvents used were of analytical grade and pure quality. Hydrated nitrates of lanthanides were used as such. All the chemicals and solvents were dried and purified by the standard methods.

### Preparation of the azomethines[SBH<sub>2</sub>]

N,N'-1,2-propylenebis(2-hydroxyacetophenoneimine) and N,N'-1,3-propylenebis (2-hydroxyacetophenone imine) were prepared by the condensation of 2-hydroxyacetophenone with 1,2-

TABLE 1: Analysis of the azomethines and their complexes

Compound	Analysis (%)			
	Ln found (calcd.)	C found (calcd.)	H found (calcd.)	N found (calcd.)
N,N'-1,2-Propylenebis(2-hydroxyacetophenoneimine) OC <sub>6</sub> H <sub>4</sub> CCH <sub>3</sub> NHCH <sub>2</sub> CH(CH <sub>3</sub> )NHCCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> )	-	72.78 (72.55)	7.25 (7.14)	8.90 (9.01)
N,N'-1,3-Propylene bis(2-hydroxyacetophenoneimine) OC <sub>6</sub> H <sub>4</sub> CCH <sub>3</sub> NHCH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> NHCCH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> O(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> )	-	72.98 (72.55)	7.22 (7.14)	9.00 (9.01)
[La(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	14.87 (14.69)	48.59 (48.27)	4.58 (4.69)	10.45 (10.37)
[Pr(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	14.69 (14.87)	47.93 (48.16)	4.75 (4.68)	10.19 (10.35)
[Nd(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	15.36 (15.17)	48.31 (47.99)	4.60 (4.66)	10.47 (10.31)
[Sm(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	15.45 (15.71)	48.0-3 (47.68)	4.71 (4.63)	10.09 (10.24)
[Gd(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	16.09 (16.31)	47.94 (47.35)	4.67 (4.60)	10.31 (10.17)
[Tb(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	16.73 (16.46)	47.03 (47.28)	4.66 (4.59)	10.33 (10.16)
[Dy(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ](NO <sub>3</sub> ) <sub>3</sub>	16.39 (16.77)	47.32 (47.10)	4.45 (4.57)	10.25 (10.12)
[La(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]*(NO <sub>3</sub> ) <sub>3</sub>	14.91 (14.69)	48.74 (48.27)	4.57 (4.68)	10.22 (10.37)
[Pr(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]*(NO <sub>3</sub> ) <sub>3</sub>	14.64 (14.87)	48.38 (48.16)	4.75 (4.68)	10.54 (10.35)
[Nd(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]*(NO <sub>3</sub> ) <sub>3</sub>	15.06 (15.17)	50.37 (47.99)	4.60 (4.66)	10.10 (10.31)
[Sm(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]*(NO <sub>3</sub> ) <sub>3</sub>	15.82 (15.71)	48.09 (47.68)	4.54 (4.63)	10.39 (10.24)
[Gd(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]*(NO <sub>3</sub> ) <sub>3</sub>	16.39 (16.31)	47.79 (47.35)	4.71 (4.60)	10.29 (10.17)
[Tb(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]*(NO <sub>3</sub> ) <sub>3</sub>	16.27 (16.46)	47.01 (47.28)	4.67 (4.59)	10.03 (10.16)
[Dy(C <sub>19</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub> ) <sub>2</sub> ]*(NO <sub>3</sub> ) <sub>3</sub>	16.90(16.77)	47.49 (47.10)	4.49 (4.57)	10.27 (10.12)

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propylenediamine and 1,3-propylenediamine in 2:1 molar ratio in the medium of absolute alcohol. The contents were refluxed on a water bath for few hours and on cooling, fine crystals separated out. These were filtered and further purified by recrystallization from the same solvent. The particulates of their analyses are given in TABLE 1.

### Synthesis of the complexes

Reactions of lanthanon nitrate hexahydrates  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  with  $\text{N,N}'$ -(1,2 or 1,3)propylenebis (2-hydroxyacetophenoneimine) Lanthanon nitrate hexahydrates,  $\text{Ln}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  [Where  $\text{Ln}=\text{La}(\text{III}), \text{Pr}(\text{III}), \text{Nd}(\text{III}), \text{Gd}(\text{III}), \text{Tb}(\text{III}), \text{Dy}(\text{III})$  and  $\text{Sm}(\text{III})$ ] were dissolved in anhydrous acetone and the solution of bibasic tetradentate ligands,  $\text{N,N}'$ -(1,2 or 1,3)propylenebis(2-hydroxyacetophenoneimine) ( $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$  or  $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2^*$ ) in a slightly excess amount than the stoichiometric ratio of 1:2 in the same solvent was added to it followed by con-

tinuous stirring. A yellow insoluble product separated out immediately in the case,  $\text{N,N}'$ -1,3-propylenebis(2-hydroxyacetophenoneimine) ( $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2^*$ ) while it appeared on standing at the room temperature in case of  $\text{N,N}'$ -1,2-propylenebis (2-hydroxyacetophenoneimine) ( $\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2$ ). It was filtered, washed several times with the same solvent so as to remove the excess of the ligand if any and then air dried. Finally, the resulting complexes were dried at  $50\text{-}70^\circ\text{C}/0.05\text{mm}$  for 3-4 hours. The details of the analyses of the resulting compounds are given in TABLE 1.

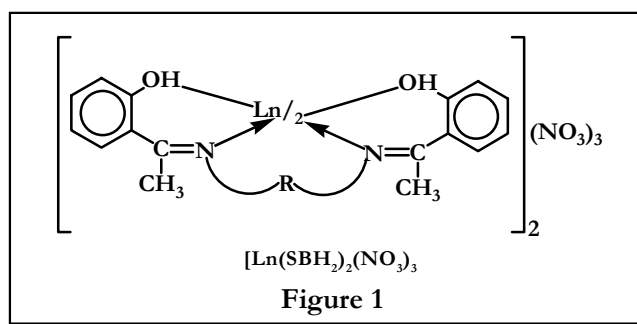


TABLE 2: Physical properties of the complexes

Compound	Characteristics	M.P. ( $^\circ\text{C}$ )	Molecular weight Found (Cald.)	Molar conductance $\text{Ohm}^{-1}\text{cm}^2\text{Mole}^{-1}$	$X_s^{**}\times 10^{-6}$ (c.g.s. unit)	$\mu_{\text{eff}}$ exp. (B.M.)
$[\text{La}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Light yellow solid	300d	973.45 (945.73)	234	-0.43	Dia
$[\text{Pr}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Lemon yellow solid	182d	911.04 (947.75)	251	5.57	3.60
$[\text{Nd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Light yellow solid	170-71	937.58 (951.10)	236	5.90	3.71
$[\text{Sm}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Lemon yellow solid	180-81	915.25 (957-18)	240	1.08	1.59
$[\text{Gd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Light yellow solid	184	1008.91 (964.09)	232	2.61	7.85
$[\text{Tb}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Light yellow solid	180	989.94 (965.75)	246	39.03	9.62
$[\text{Dy}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Light yellow solid	179	945.94 (969.33)	242	43.83	10.21
$[\text{La}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2]^*(\text{NO}_3)_3$	Yellow solid	168	907.58 (945.73)	234	-0.39	Dia.
$[\text{Pr}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2]^*(\text{NO}_3)_3$	Yellow solid	225-26	925.40 (947.75)	251	5.63	3.62
$[\text{Nd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2]^*(\text{NO}_3)_3$	Yellow solid	175-76	995.76 (951.10)	247	5.53	3.61
$[\text{Sm}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2]^*(\text{NO}_3)_3$	Yellow solid	260-61	991.54 (957-18)	258	1.11	1.62
$[\text{Gd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2]^*(\text{NO}_3)_3$	Yellow solid	265-66	931.02 (964.09)	261	26.23	7.88
$[\text{Tb}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2]^*(\text{NO}_3)_3$	Yellow solid	255-56	984.89 (965.76)	255	39.94	9.73
$[\text{Dy}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2]^*(\text{NO}_3)_3$	Yellow solid	260	992.25 (969.33)	244	43.29	10.15

TABLE 3: X-ray powder diffraction pattern data of  $[\text{Sm}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$ 

d(Å) (obsd.)	$Q_{(\text{obsd})}=1/d^2$	$Q_{(\text{calcd})}$	hkl	Relative intensity I/I MaxX100	d(Å)(obsd)	$Q_{(\text{obsd})}=1/d^2$	$Q_{(\text{calcd})}$	hkl	Relative intensity I/IMaxX100
16.9798	0.0035	0.0035	100	4.90 vw	4.4578	0.0503	0.0500	220	24.1w
13.6917	0.0053	0.0053	010	7.6 vw	4.3286	0.0534	0.0532	331	35.50s
9.7096	0.0106	0.0103	001	100.0vs	4.2069	0.0565	0.0565	122	38.05
9.5012	0.0111	0.0119	210	100.0vs	4.0187	0.0619	0.0619	421	24.6m
8.8377	0.0128	0.0128	101	21.0w	3.9054	0.0656	0.0656	222	34.6s
8.2227	0.0148	0.0148	101	40.2sh	3.8306	0.0681	0.0692	240	19.9w
8.1099	0.0152	0.0156	011	44.7s	3.7047	0.0728	0.0729	312	29.2m
7.5894	0.0146	0.0176	120	28.1m	3.6085	0.0748	0.0753	122	46.4vs
7.1608	0.0195	0.0204	220	54.5vs	3.5728	0.0783	0.0787	302	28.6w
6.5292	0.0235	0.0238	111	20.1m	3.5379	0.0799	0.0797	412	29.0m
6.3429	0.0248	0.0257	310	27.2m	3.4306	0.0850	0.0848	040	25.5m
5.8050	0.0297	0.0305	320	14.7w	3.4048	0.0863	0.0870	521	23.9w
5.6041	0.0318	0.0315	300	23.7m	3.2876	0.0925	0.0925	432	23.7w
5.5004	0.0331	0.0330	311	26.3m	3.1839	0.0986	0.0986	213	33.9m
5.2727	0.0360	0.0360	211	25.7m	3.1618	0.1000	0.1007	203	32.3sh
5.1960	0.0370	0.0378	321	30.8m	3.1292	0.1021	0.1022	113	27.7sh
5.0348	0.0395	0.0395	230	42.0s	3.0253	0.1092	0.1093	412	25.7m
4.9238	0.0412	0.0412	002	40.9s	2.9520	0.1148	0.1148	442	23.21w
4.7536	0.0442	0.0443	112	43.5s	2.9378	0.1158	0.1158	351	25.00w
4.5599	0.0481	0.0483	112	54.5vs	2.8509	0.1230	0.1229	522	19.0vw
2.7692	0.1304	0.1308	442	23.4m	1.9960	0.2509	0.2516	541	20.5w
2.7362	0.1336	0.1332	442	26.8m	1.9633	0.2595	0.2594	215	20.1w
2.6922	0.1380	0.1382	303	26.8m	1.9356	0.2668	0.2661	352	20.8vw
2.5474	0.1542	0.1544	233	21.9w	1.8790	0.2832	0.2831	544	19.4w
2.5061	0.1593	0.1597	431	23.8m	1.7810	0.3152	0.3153	154	18.5w
2.3629	0.1791	0.1794	332	18.7vw	1.7446	0.3284	0.3285	434	17.4vw
2.2767	0.1929	0.1928	523	23.0w	1.7323	0.334	0.3335	405	20.1w
2.2548	0.1966	0.1964	143	24.8w	1.7278	0.3350	0.3355	534	18.3vw
2.2307	0.2009	0.2009	424	22.8w	1.7202	0.381	0.3375	344	18.7vw
2.1994	0.2068	0.2068	124	20.5w	1.7113	0.3415	0.3423	045	16.1vw
2.1641	0.2135	0.2132	224	22.3m	1.6584	0.3638	0.3637	552	17.4vw
2.1420	0.2180	0.2190	153	21.6m	1.5938	0.3938	0.3938	515	16.5vw
2.1063	0.2255	0.2252	513	19.2vw	1.5499	0.4163	0.4170	155	16.9vw
0.2417	0.2419	532	19.9w	-	-	-	-	-	-

### Physical measurements

Molecular weights were determined by the rast camphor method. The metal contents were estimated complexometrically with EDTA using erichrome black T as an indicator. Infrared spectra were recorded on a nicolet magna FTIR-550 spectrophotometer on KBr pellets. Molar conductance measurements were made in anhydrous DMF on a systronic model 305

conductivity bridge. The magnetic moments and magnetic susceptibility were measured by the Gouy's method at room temperature ( $37 \pm 1^\circ\text{C}$ ). Nitrogen was estimated by the Kjeldahl's method.

### RESULTS AND DISCUSSION

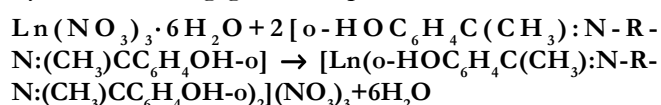
The reactions of lanthanon nitrates with bibasic

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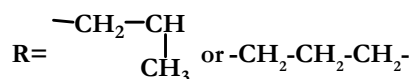
TABLE 4: X-ray powder diffraction pattern data of  $[\text{Sm}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_{2=2})_2](\text{NO}_3)_{3/2}$ 

d(Å) (obsd.)	Q <sub>(obsd)</sub> =1/d <sup>2</sup>	Q <sub>(calcd)</sub>	hkl	Relative intensity I/I Max×100	d(Å) (obsd)	Q <sub>(obsd)</sub> =1/d <sup>2</sup>	Q <sub>(calcd)</sub>	hkl	Relative intensity I/IMax×100
15.2245	0.0043	0.0043	100	16.1w	3.6376	0.0755	0.0754	140	51.85
12.8930	0.0060	0.0059	010	11.6vw	3.6157	0.0765	0.0763	131	46.4sh
11.1816	0.0080	0.0079	001	18.7m	3.5587	0.0790	0.0789	143	34.8m
8.8642	0.0127	0.0125	021	100.0vs	3.0763	0.1057	0.1057	435	33.9m
8.7938	0.0129	0.0133	332	98.2sh	2.9378	0.1158	0.1155	113	27.7w
8.2227	0.0148	0.0145	132	73.2vs	2.7734	0.1300	0.1297	135	33.0m
7.9286	0.0159	0.0159	110	82.2vs	2.4859	0.1617	0.1617	251	32.2w
7.6881	0.0169	0.0169	112	58.0s	2.3932	0.1746	0.1740	024	29.5w
7.3566	0.018	0.0185	012	50.9s	2.2711	0.1939	0.1936	404	33.9m
6.5533	0.0233	0.0233	011	48.2s	2.0970	0.2274	0.2277	533	30.4w
6.2537	0.0256	0.0255	133	25.9w	1.9918	0.2520	0.2509	015	32.2m
5.7119	0.0307	0.0310	142	28.6w	1.9473	0.2637	0.2647	405	32.2m
5.6041	0.0318	0.0316	002	36.6m	1.8754	0.2845	0.2844	006	29.5w
5.0490	0.0392	0.0391	244	48.2s	1.8486	0.2925	0.2935	034	26.8w
4.8177	0.0431	0.0431	121	35.7m	1.8040	0.3073	0.3073	152	27.7w
4.6306	0.0466	0.0469	212	33.0m	1.6865	0.3514	0.3516	406	25.9w
4.5253	0.0488	0.0485	013	52.7s	1.6461	0.3692	0.3697	461	25.8w
4.2771	0.0547	0.0549	112	57.2s	1.6182	0.3819	0.3825	463	26.8w
4.1873	0.0571	0.0572	222	42.0sh	1.5764	0.4025	0.4017	533	27.7w
4.0368	0.0614	0.0617	212	46.4m	1.5087	0.4391	0.4391	154	26.8w
3.8635	0.0670	0.0672	400	35.7m	1.4858	0.4529	0.4530	551	-
3.7047	0.0729	0.0723	24s	37.5w	-	-	-	-	-

tetradentate azomethines(SBH<sub>2</sub>) have been carried out in 1:2 molar ratio in anhydrous acetone followed by continuous stirring. The reaction can be shown by the following general equation:



[Where, Ln=La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III);



The resulting complexes after being repeatedly washed with dry acetone were found to be fairly stable at the room temperature. The purity of these compounds was further checked by thin layer chromatography on silica gel-G. The physical properties of the complexes are given in TABLE 2.

### Molar conductance

The molar conductance values of all the lanthanide

chelates ranging from 235-258ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> indicating that these chelates behave as 1:3 electrolytes in DMF. The cation species in these complexes may, therefore, be formulated as [Ln(SBH<sub>2</sub>)<sub>2</sub>]<sup>+3</sup> (where Ln=La(III), Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III); SBH<sub>2</sub>=N,N'-(1,2or1.3) propylenebis(2-hydroxyacetophenoneimine) showing that all the three nitrate anions remain outside the coordination sphere and do not take part in coordination to the metal atom. Thus, the lanthanide chelates may be structurally represented as shown in figure 1.

### Magnetic susceptibilities and magnetic moments

The values of magnetic susceptibilities and magnetic moments reveal that the lanthanum complexes of N,N'-(1,2or1.3) propylenebis(2-hydroxyacetophenoneimine) are diamagnetic, whereas the corresponding azomethine derivatives of Pr(III), Nd(III), Sm(III), Gd(III), Tb(III) and Dy(III) are paramagnetic in nature.

TABLE 5: X-ray powder diffraction pattern data of  $[\text{Gd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_{2=2})_2](\text{NO}_3)_2$ 

d(Å) (obsd.)	$Q_{(\text{obsd})}=1/d^2$	$Q_{(\text{calcd})}$	hkl	Relative intensity I/I Max×100	d(Å) (obsd.)	$Q_{(\text{obsd})}=1/d^2$	$Q_{(\text{calcd})}$	hkl	Relative intensity I/IMax×100
15.6284	0.0041	0.0042	100	10.5vw	4.3287	0.0534	0.0533	221	37.9m
13.2803	0.0057	0.0058	010	9.50vw	4.2168	0.0562	0.0564	130	41.6m
11.1114	0.0081	0.0079	001	13.7vw	4.0368	0.0614	0.0610	320	26.8w
9.8720	0.0103	0.0100	110	100.0vs	3.9569	0.0639	0.0640	301	34.2m
9.6043	0.0108	0.0103	011	100.0vs	3.9224	0.0650	0.0651	403	41.0m
8.9267	0.0126	0.0125	201	28.0w	3.8306	0.0681	0.0679	423	25.3w
8.3388	0.0144	0.0149	211	51.0sh	3.7123	0.0726	0.0728	202	32.1w
8.1848	0.0149	0.0152	111	70.0vs	3.6085	0.0768	0.0756	333	43.2s
7.6549	0.0171	0.0171	011	35.8m	3.4371	0.0847	0.0848	122	32.1w
7.1898	0.0193	0.0182	101	68.4vs	3.3606	0.0855	0.0854	212	23.7w
6.5533	0.0233	0.0232	020	24.7w	3.2995	0.0918	0.0917	241	32.1m
6.3656	0.0247	0.023	021	33.2m	3.1895	0.0984	0.0984	114	38.4m
5.8817	0.0289	0.0289	221	21.6w	3.1292	0.1021	0.1022	124	30.0w
5.6041	0.0318	0.0318	312	27.4w	3.0608	0.1068	0.1066	341	25.3w
5.5004	0.0331	0.0332	122	33.7m	0.0354	0.1086	0.1156	411	30.5w
5.2884	0.0358	0.0360	121	33.7sh	2.9425	0.1155	0.1156	322	26.3w
5.211	0.0368	0.0369	201	41.0m	2.8289	0.1249	0.1246	141	23.2vw
5.0634	0.0390	0.0393	211	47.9s	2.776	0.1295	0.1295	421	28.9w
5.0634	0.0390	0.0393	211	47.9s	2.776	0.1295	0.1295	421	28.9w
4.9511	0.0408	0.0412	022	49.5s	2.7403	0.1331	0.1330	325	28.9w
4.77901	0.0438	0.0438	321	49.4s	2.6961	0.1375	0.1372	123	27.4w
4.5715	0.0478	0.0480	102	56.3s	2.6650	0.1408	0.1405	213	24.7w
4.4689	0.0501	0.0500	402	30.0w	2.5758	0.1508	0.1570	124	23.2vw
2.5509	0.1537	0.1539	03	24.7w	2.0170	0.2458	0.2459	435	23.4vw
2.5095	0.1590	0.1590	152	23.7vw	1.9877	0.2530	0.2530	153	24.7w
2.3810	0.1764	0.1764	133	23.2vs	1.9572	0.2612	0.2611	453	25.8w
2.3659	0.1786	0.1786	332	22.4vw	1.8717	0.2855	0.2850	234	22.6w
2.3218	0.1855	0.1854	333	22.4vw	1.8433	0.2944	0.2943	433	20.0vw
2.2413	0.1992	0.1989	251	26.8w	1.8312	0.2983	0.2981	215	18.9vw
2.1943	0.2078	0.2074	323	22.9vw	1.7892	0.3125	0.3112	523	22.6w
2.1641	0.2135	0.2133	255	24.7w	1.7308	0.3337	0.3325	225	24.2w
2.1518	0.2160	0.2158	343	25.3w	1.6543	0.3656	0.3648	534	21.6w
2.0517	0.2374	0.2374	304	24.2w	1.6169	0.3824	0.3833	255	21.6w

### Infrared spectra

Both the azomethines,  $\text{N,N}'-(1,2\text{ or }1.3^*)$  propylenebis (2-hydroxyacetophenoneimine) do not show any absorption band of free OH group in the region,  $3500\text{-}3200\text{cm}^{-1}$  on account of strong hydrogen bonding. A broad band appears in the range  $3050\text{-}2850\text{cm}^{-1}$  in the ligands and this may be attributed to the O---H-N or O-H---N type of hydrogen bonding

and overlapping with vCH vibrations. However, in the IR spectra of these azomethine derivatives of lanthanides, a medium broad band is observed in the region.  $3450\text{-}3200\text{cm}^{-1}$  and this may be due to the presence of vOH indicating the breaking of hydrogen bonding in the ligands on complexation through both the oxygen and nitrogen atoms of the phenolic and azomethine groups respectively to the lanthanon atoms. A very strong band at  $\sim 1610\text{cm}^{-1}$

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TABLE 6: X-ray powder diffraction pattern data of  $[\text{Gd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_2$ 

d(Å) (obsd.)	$Q_{(\text{obsd})}=1/d^2$	$Q_{(\text{calcd})}$	hkl	Relative intensity I/I Max×100	d(Å) (obsd)	$Q_{(\text{obsd})}=1/d^2$	$Q_{(\text{calcd})}$	hkl	Relative intensity I/IMax×100
147±75	0.0046	0.0046	100	27.1m	3.1618	0.1000	0.0995	223	43.7w
10.9736	0.003	0.0082	010	21.5w	3.0660	0.1064	0.1064	420	46.5w
10.0972	0.0098	0.0099	001	24.7m	2.9425	0.1155	0.1152	330	39.6vw
8.7504	0.0131	0.0128	110	93.7vs	2.7692	0.1304	0.1306	431	42.4vw
8.1099	0.0152	0.0158	201	74.30s	2.6961	0.1375	0.1372	141	43.0w
7.8237	0.0163	0.0159	111	100.0vs	2.5615	0.1525	0.1530	333	42.7w
7.5571	0.0175	0.0175	011	94.4vs	2.3451	0.1819	0.1813	133	42.0w
7.3384	0.0186	0.0186	011	56.2sh	2.3189	0.1860	0.1856	524	43.0w
6.9370	0.0208	0.0208	101	38.2vw	2.2767	0.1929	0.1933	313	4.4w
6.5053	0.0236	0.0235	211	66.7s	2.2657	0.1947	0.1946	243	45.5m
6.2100	0.0259	0.0266	210	40.3w	2.2202	0.2029	0.2034	341	42.4w
5.6041	0.0318	0.0317	102	50.0w	2.1994	0.2068	0.2070	415	43.0w
5.5174	0.0329	0.0328	020	53.5m	2.1276	0.2209	0.2208	105	42.7w
5.2417	0.0364	0.0374	120	50.0m	1.9513	0.2628	0.2627	452	42.4w
5.0348	0.0395	0.0396	002	55.6n	1.9240	0.2702	0.2708	544	45.1m
4.7919	0.0436	0.0435	302	54.9m	1.8381	0.2959	0.2959	551	41.0w
4.6068	0.0471	0.0467	012	48.6w	1.8024	0.3079	0.3077	513	39.6w
4.5026	0.0493	0.0495	211	61.1s	1.7810	0.3152	0.3154	345	39.9w
4.2267	0.0560	0.0567	102	79.2vs	1.7354	0.3322	0.3320	404	37.2vw
3.9482	0.0642	0.0642	321	49.3m	1.7217	0.3373	0.3373	345	39.6w
3.8225	0.0684	0.0680	222	52.1m	1.6794	0.3548	0.3552	334	38.2w
3.7509	0.0711	0.0703	412	50.0w	1.6488	0.3678	0.3677	045	36.8vw
3.6013	0.0771	0.0765	213	56.2m	1.6169	0.3824	0.3827	305	36.1vw
3.5728	0.0783	0.0784	130	54.0sh	1.6091	0.3864	0.3864	355	36.1vw
3.5310	0.0802	0.0804	131	47.2w	1.6014	0.3901	0.3897	045	36.1vw
3.2639	0.0939	0.0938	422	48.6w	-	-	-	-	-

TABLE 7: Unit cell parameters of bis-[N,N'-1,2 or 1,3-propylenebis(2-hydroxyacetophenoneiminato)] samarium(III) or gadolinium(III) nitrate complexes

Compound	Symmetry	a (Å)	b (Å)	c (Å)	$\alpha$	$\beta$	$\gamma$	v Å <sup>3</sup>	d(gm/cm <sup>3</sup> )	z
$[\text{Sm}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Triclinic	18.75	15.19	9.89	87°47'	95°12'	115°15'	2538	1.78	3
$[\text{Sm}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Triclinic	26.35	30.95	21.173	148°54'	46°	144°14'	5373	1.53	5
$[\text{Gd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Triclinic	18.41	13.75	13.87	107°12'	123°1'	80°44'	2808	1.80	3
$[\text{Gd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$	Triclinic	16.64	11.05	11.35	91°58'	117°5'	89°5'	1849	1.82	2

may be attributed to the  $\nu\text{C}=\text{N}$  of the ligands. The bands at  $\sim 1385\text{cm}^{-1}$  of strong intensity and  $\sim 815\text{cm}^{-1}$  of medium intensity are observed in the azomethine derivatives of lanthanons due to the ionic nitrate with  $D_3$  symmetry. This indicates that all the three nitrate anions remain outside the coordination sphere and do not participate in the coordination.

Further, two new bands at  $660\pm 10\text{cm}^{-1}$  and

$390\pm 10\text{cm}^{-1}$  in the IR spectra of the lanthanon complexes are observed. The former may be assigned to the ring deformation coupled with Ln-O stretching and C-CH<sub>3</sub> stretching modes while the latter may be due to Ln-N coordinate linkage.

## X-ray diffraction

The X-ray diffraction studies have been carried

out with the help of finely powdered samples to have an idea about the type of molecular symmetry and the lattice constants. The X-ray powder diffractograms for a few representative complexes like, bis-[N,N'-1,2or1,3-propylenebis(2-hydroxyacetophenone iminato)]samarium(III)nitrate  $[\text{Sm}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$ , bis-[N,N'-1,2or1,3-propylenebis(2-hydroxyacetophenoneiminato)] gadolinium(III) nitrate  $[\text{Gd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2](\text{NO}_3)_3$ , bis-[N,N'-1,2or1,3-propylenebis(2-hydroxyacetophenoneiminato)] samarium(III) nitrate  $[\text{Sm}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2^*](\text{NO}_3)_3$  and bis-[N,N'-1,2or1,3-propylenebis(2-hydroxyacetophenoneiminato)] gadolinium(III) nitrate  $[\text{Gd}(\text{C}_{19}\text{H}_{22}\text{N}_2\text{O}_2)_2^*](\text{NO}_3)_3$  have been recorded and their interplanar spacings values 'd' as well as the relative intensities of the peaks have been measured and summarized in TABLES 3 to 6 along with the reciprocal lattice values  $Q_{\text{obsd.}} (=1/d^2\text{obsd.})$  for each 'd' values. These results show that the newly isolated complexes crystallize in triclinic type of lattice symmetry and their unit cell parameters are mentioned in TABLE 7.

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