

Interaction of Trivalent Lanthanide (III) Cations with Bidentate Schiff Base (1E,2E) Diphenylethane-1,2- Hydrazone Oxime

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Abstract: The novel lanthanide (III) complexes $[Ln(BMOH)_3] (NO_3)$ ($Ln=Pr, Nd$ and La), where $(BMOH)^- = (1E,2E)$ -1,2- diphenylethane - 1,2 - diene hydrazone oxime, have been obtained by direct condensation reaction of the Schiff base HBMOH ligand and corresponding hydrated lanthanide (III) nitrates in ethanol. All prepared complexes were characterized by traditional physico-chemical and spectral techniques. In the molecular structure of synthesized complexes, central inner transition metal ions are surrounded by all donor atoms of the HBMOH ligand (two nitrogen donor atoms) and nitrogen atom belonging to monodentate chelating nitrito ligand.

Keywords: Lanthanide (III) Complexes, Spectral Techniques, Transition Metal

I. INTRODUCTION

With advances in complex chemistry, applications of complexes of Schiff bases is widely distributed and helped in establishing the important physico-chemical and bio-chemical process involving metal interaction of metals with ligands.¹ The condensation of Schiff bases can be promoted convincing and greener approach by lanthanide cations. It has been cited that progressive advancements in the applications of inner transition metal complexes with macrocyclic rings emerging from medicine and biology has boosted research on these area² medicine and used as water protonrelaxing agents for NMR imaging.³⁻⁴ A surge in number of research publication in recent years on lanthanide complexes with bidentated Schiff base derived from condensation of hydrazine hydrate and carbon oximes⁵⁻⁶. The synthesized complexes were found to be enough at ambience.

In past, some transition metal complexes⁷⁻¹⁰ with (1E,2E)- 1, 2 diphenylethane - 1,2-diene hydrazone oxime had been reviewed. Here we are attempting to synthesize and characterize the coordination compounds of HBMOH ligand with inner transition metal (III) cations and to assess their magnetic and electric characteristics.

II. EXPERIMENTAL

2.1 Materials and Instrumentation

All manipulation was carried out under aerobic conditions. Organic molecules, solvents and lanthanide metal salts were purchased commercially from s.d. fine chem. and used without further purification. Elemental analysis (Thermo Finnigan, Flash EA 1112 series), FT (IR)(Perkin-Elmer spectra 100 spectrophotometer using KBr pellets), UV- Visible spectra (JASCO V650 spectrophotometer using chloroform as solvent) and molar conductivity (Systronic Conductivity Bridge type 305) were performed for both quantitative and qualitative estimation.

2.2 Preparation of the HBMOH ligand:

The ligand HBMOH was prepared from condensation of benzilmonoxime and hydrazine hydrate by reported method¹⁰.

2.3 Preparation of Lanthanide (III) Complexes

To a stirred solution of benzilmonoximehydrazide (3mmol) in ethanol and the corresponding hydrated lanthanide nitrates (1mmol) in 20mL of ethanol were added. The resulting reaction mixtures were subjected to reflux for 3-6 hrs and then left undisturbed for evaporation at room temperature, resulting in appearance of micro crystals after two days. These micro crystals were washed with small aliquots of cold ethanol, dried under vacuum over calcium carbonate. The yield was within the range 60-70%.

III. RESULTS AND DISCUSSION

Schiff base i.e., HBMOH ligand was synthesized by condensation between hydrazinehydrate and benzilmonoxime. The HBMOH and hydrated lanthanide (III) nitrates with water of crystallization in the molar ratio (1:3) are mixed. The curiosity about denticity and chelating atoms of HBMOH ligand were solved by recording and interpreting the spectral scans such as PMR, FTIR and UV-Visible spectra.

The all-prepared lanthanide (III) nitrate complexes are stable in open atmosphere; non hygroscopic and have high melting points $>300^{\circ}\text{C}$ and they are soluble in common organic solvents. The percentage values of elemental contents i.e., C, H, N, Ln (III) are in accordance with the tentative formula of complexes. The physical and analytical data of lanthanide (III) metal complexes are represented in Table-1.

The molar conductance of the lanthanide (III) complexes of HBMOH ligand are in the range of $22-27\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ showing that 1:1 electrolyte¹¹. These lower values of conductance can be attributed to the coordination of nitrate ion in these complexes. Unfortunately, attempts to prepare single crystals for x-ray diffraction studies were unsuccessful.

Table 1: Analytical and physical data of the HBMOH ligand and its Ln (II) metal complexes.

Compound	Color	Yield %	M.P. / Dec. Point $^{\circ}\text{C}$	Elemental Analysis					Magnetic Moments (B.M.)	Electrical Conductance (10^{-3}M) $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$
				% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% O Found (Calcd)		
HBMOH	Colorless	72.03	172	-	70.29 (70.27)	5.44 (5.32)	17.57 (17.58)	6.69 (6.75)	-	-
[Pr(BMOH) ₃]NO ₃	Brown	77.26	254	15.50 (15.02)	54.97 (53.83)	3.93 (3.45)	15.27 (15.18)	10.50 (10.48)	3.45	22.00
[Nd(BMOH) ₃]NO ₃	Light Green	78.22	239	15.70 (15.68)	54.89 (54.83)	3.92 (3.45)	15.25 (15.18)	10.50 (10.40)	3.60	27.00
[La(BMOH) ₃]NO ₃	Green	79.19	243	15.20 (14.78)	55.09 (54.29)	3.93 (3.41)	15.30 (15.28)	10.50 (10.39)	Diamagnetic	25.15

3.1 Characterization of the Complexes

A. FT(IR) Spectra

The FT(IR) of the synthesized lanthanide (III) complexes are compared with the free HBMOH ligand in order to determine the coordination site involved in chelation (Table-2). The presence of the broad band at 3387cm^{-1} assigned to stretching vibration frequency of oximino-OH group in the FT(IR) spectrum of the HBMOH ligand is absent in the spectra of all prepared lanthanide (III) metal complexes ascertaining coordination of HBMOH ligand to central lanthanide (III) metal ions through oximino nitrogen via deprotonated¹²oximino group. The FT(IR) spectrum of HBMOH ligand showed strong stretching band at 1647cm^{-1} and stretching vibration of azomethine group at 1493cm^{-1} . The shift of the characteristic band of the oximino and azomethine groups to lower frequencies (Table-2) conveying an idea of involvement through the oximino and azomethine groups in the interaction with central lanthanide (III) metal ion¹³⁻¹⁴. The stretching vibration of LnN and Ln-N is characterised by the appearance of new bands with varying

intensities in the spectra of isolated solid lanthanide (III) complexes in the range 502-475 cm^{-1} . These absorption peaks are absent in the FT (IR) spectrum of the HBMOH ligand¹⁵.

The metal ion might coordinate to a nitrate ligand in three different ways: uncoordinated, monodentate, or bidentate ion. The IR spectra of lanthanide (III) complexes of HBMOH ligand, the measured $|v_4 - v_1|$ separation in the range 118-133 cm^{-1} suggested monodentate bonding for the nitrate group¹⁶.

Table 2: FT(IR) spectral data for HBMOH and its Ln (III) metal complexes

Compound	$\nu(\text{O}-\text{H})$	$\nu(\text{N}-\text{H})$	Ar. C-H	C=N N	C=O O	N-O O	N-N	NO ₃				M-N
								ν_1	ν_2	ν_3	ν_4	
HBMOH	328	3387	3058	1647	1493	926	1072	-	-	-	-	-
[Pr(BMOH) ₃]NO ₃	7	3400	3069	1628	1438	1000	1093	1453	1033	832	1335	492, 478
[Nd(BMOH) ₃]NO ₃	-	3387	3025	1626	1450	1001	1099	1470	1033	832	1337	502, 500
[La(BMOH) ₃]NO ₃	-	3391	3012	1628	1498	1000	110	1414	1033	833	1340	501, 472

B. PMR Spectra

Table -3 is detailing about the PMR of complexes synthesized. The resonance at δ 12.42 ppm in the spectrum of free HBMOH ligand due to oximino -OH group, this group is absent in [La(BMOH)₃]NO₃ complex PMR spectrum, suggesting deprotonation of oximino (-OH) group while coordinating the HBMOH ligand to the lanthanide (III) metal ion¹⁷.

Table 3: PMR spectral data for HBMOH and its La (III) complex

Compounds	-OH	-NH ₂	N-H	Phenyl ring
HBMOH	12.42	8.00	8.67	7.44-7.95
[La(BMOH) ₃].NO ₃ -	-	7.90	8.65	7.45-7.90

C. Electronic Absorption Spectra

The electronic absorption spectra of free HBMOH ligand exhibit bands at 210 and 235nm due to transition of azomethine and oximinogroups of HBMOH ligand. The f-f transitions of inner transition metal ions are obscured in the visible range except for Nd (III) and Pr(III) and Table -4 is encompassing major transitions occurred in the complexes.

The Sinhas parameter ($\% \delta$) considered as a covalency measurement, is given by the formula $\% \delta = [(1 - \beta_{\text{ave}}) / \beta_{\text{ave}}] \times 100$, where β_{ave} is the average value of the ratio of $v_{\text{complex}} / v_{\text{aquo}}$. The bonding parameter ($b^{1/2}$), a factor to see the involvement of 4f orbitals in ligand metal bonding which also is related to the nephelauxetic ration, is given by the expression¹⁸⁻¹⁹, $b^{1/2} = [(1 - \beta_{\text{ave}}) / 2]$.

The values of the parameters β , $b^{1/2}$ and δ (Table - 4) indicate metal-ligand weak covalent bond. The lower values of $b^{1/2}$ decrease the covalence for Pr(III) complex due to lanthanide contraction.

Table 4: UV-Visible spectral data of HBMOH ligand and its Ln (III) metal complexes

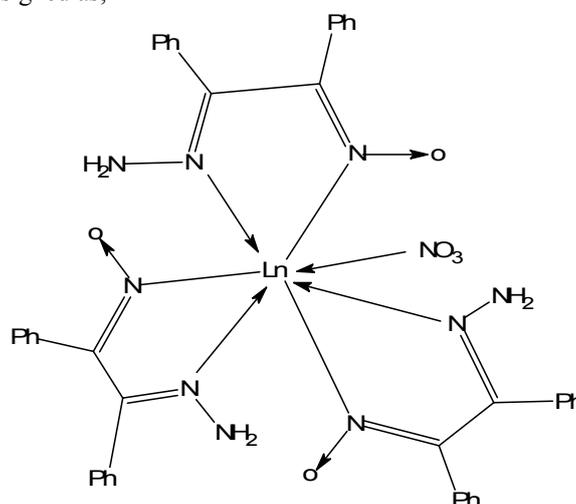
Compound	λ_{nm}	ϵ (dm ³ /mol/cm)	Transition	
HBMOH	374	1499	$\pi^* \leftarrow \pi$	
	268	4670	$\pi^* \leftarrow \pi$	
	235	56688	$\pi^* \leftarrow \pi$	
[Nd(DMHpHB) ₃]	811	612	${}^4F_{9/2} \leftarrow {}^4H_{5/2}$	$\beta_{\text{ave}} = 0.9867$
	756	816	${}^4P_{13/2} \leftarrow {}^4H_{5/2}$	$b^{1/2} = 0.0304$
	625	500	${}^4P_{9/2} \leftarrow {}^4H_{5/2}$	$\delta\% = 1.353$
	560	1250	${}^4P_{7/2} \leftarrow {}^4H_{5/2}$	$\eta = 1.0267$
[Pr(BMOH) ₃]NO ₃	591	1265	${}^1D_2 \leftarrow {}^3H_4$	
	482	4239	${}^3P_1 \leftarrow {}^3H_4$	



	469	9887	$^1F_6 \leftarrow ^3H_4$	$\delta\% = 0.1002$
	445	10325	$^3P_2 \leftarrow ^3H_4$	$\eta = 1.0154$
[La(BMOH) ₃]NO ₃	419	7615	MLCT	
	346	7544	MLCT	
	269	14968	MLCT	

IV. CONCLUSION

We describe the synthesis, physico-chemical studies, FT(IR), PMR, and electronic absorption spectra of solid lanthanide (III) complexes using HBMOH ligands that may form stable solid complexes in this study. In the lanthanide (III) nitrate complexes, the Schiff base HBMOH ligand behave as mono-negative ([BMOH]⁻) bidentate and oximino group in position six and one nitrate ion. Based on inferences of spectral techniques, the structure of prepared complexes may be tentatively assigned as;



Where Ln = Pr, Nd, La

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