

**PHYSICO-CHEMICAL, SYNTHESIS AND CHARACTERIZATION STUDIES OF
METAL COMPLEXES OF SCHIFF BASE DERIVED FROM P-
HYDROXYBENZALDEHYDE AND BENZILMONOXIMEHYDRAZONE**

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ABSTRACT

Lanthanide (III) complexes of the type [Ln(BMHpHB)₂NO₃] where Ln = La³⁺, Nd³⁺, Sm³⁺, Gd³⁺, Tb³⁺ and Dy³⁺, have been synthesized and characterized by various physico-chemical techniques, magnetic moments, electronic, FT(IR) and PMR spectral investigations. The studies revealed that the ligand behaves as a monobasic acid in spite of two probable dissociable protons being present in it viz. the oximino proton and the phenolic proton. The nature of this monobasic character is studied. The metal complexes show that the most stable species in the ML₃ complex.

Keywords: Lanthanide (III) complexes, magnetic moments, Schiff base

Introduction

Spectroscopic measurements have been used in coordination chemistry to determine the symmetry, dissociation constants, number of bond, metal-metal distances, number of distinct metal environments and bonding nature of the ligand. Certain Eu(III) complexes had been reported to give laser action in solution; the Nd(III) ion also provides laser action when present in aprotic solvents. Arora et. al.(2002) had discussed the compounds of Tb(III), Dy(III), Er(III) and Ho(III) have the highest known magnetic moments, in the range 9-11 B.M. at room temperature. Several lanthanide (III) ions are useful as shift reagents in MRI and Gd(III) have been used as an effective contrast agent for *in vivo* nuclear magnetic resonance imaging Sharma et. al. (1998), Kishor and Kiran (2007), Chakraborti et. al. (2002), Agrawal and Himanshu (2001). Trivalent lanthanides behave as hard acids and these are expected to form stronger complexes with ligands containing 'O' and 'N' donor atoms. In view of the many interesting properties of lanthanides, we report here the synthesis and characterization of complexes with bidentate ligand benzilmonoximehydrazone-p-hydroxybenzaldehyde, abbreviated as HBMHpHB (IUPAC name: 4-[2-(hydroxyimino)-1,2-diphenylethylidene]hydrazinylidene} methyl]phenol

Materials and methods

Hydrated metal nitrates (S. d. fine chem., 99.99% pure) were used as procured. Physical measurements were carried out as reported earlier Indrasenn and Raj (2000), Addison and Logan (1964). The electronic absorption spectra of the complexes were recorded on JASCO V-650 Spectrophotometer. ¹H NMR spectra of the ligand and its metal complexes were obtained on Bruker AV300 NMR spectrometer using TMS as internal standard. The FT-IR spectrum was recorded in the range 400–4000 cm⁻¹ by KBr pellet using a 'Perkin-Elmer Spectrum 100' model FT(IR) spectrophotometer. Complexes were decomposed by repeated treatment with conc. HNO₃ and H₂SO₄ and finally metal contents were estimated complexometrically by EDTA using xylenol orange at pH-6.

Synthesis of HBMHpHB

0.100M solution of α-benzilmonoximehydrazide (20ml ethanol) was added to 0.115M alcoholic solution of p-hydroxybenzaldehyde, and then few drops of concentrated hydrochloric acid added to the reaction mixture. The contents were refluxed for 12 hours. The refluxed solution was cooled and filtered, after completion of reaction process as monitored on TLC. Ligand formed out as precipitate was yellow solid, its purity being checked by TLC.

Synthesis of complexes

The coordination complexes of the types $[\text{Ln}(\text{BMHpHB})_2\text{NO}_3]$ were synthesized by refluxing ethanolic solution of ligand HBMHpHB and the corresponding metal salts in stoichiometric amounts at 70-80°C for 5-10h. The solid complexes were filtered off and washed with small aliquots of ethanol followed

by diethylether, recrystallised from chloroform and finally dried in hot air.

Results and Discussions

The ligand HBMHpHB is strong chelating ligand and has two potential donor sites for coordination. This ligand form well defined complexes with lanthanide (III) ions is presented in **Table-1**.

Table-1: Physical and Analytical data of HBMHpHB ligand and its Ln(III) complexes

Compound	Colour	% Yield	MP/DP in °C	% Element Content, Expected (Observed)					Molar Cond	Magnetic Moments
				C	H	N	O	M		
HBMHpHB	Yellow	76.98	205	73.45 (73.33)	4.99 (4.90)	12.24 (12.21)	9.32 (9.29)	-	-	-
$[\text{La}(\text{BMHpHB})_3]\text{NO}_3$	Yellow	69.39	288	61.62 (61.58)	3.91 (3.86)	11.41 (11.35)	11.70 (11.65)	11.32 (11.30)	19.5	-
$[\text{Nd}(\text{BMHpHB})_3]\text{NO}_3$	Red	65.22	289	61.35 (61.30)	3.90 (3.83)	11.36 (11.31)	11.70 (11.69)	11.70 (11.68)	20.3	3.59
$[\text{Sm}(\text{BMHpHB})_3]\text{NO}_3$	Light Brown	67.28	269	61.05 (61.00)	3.88 (3.79)	11.31 (11.29)	11.60 (11.49)	12.14 (12.11)	24.21	1.47
$[\text{Gd}(\text{BMHpHB})_3]\text{NO}_3$	Yellow Brown	69.22	277	60.71 (60.67)	3.87 (3.82)	11.24 (11.22)	11.60 (11.59)	12.62 (12.60)	23.51	7.93
$[\text{Tb}(\text{BMHpHB})_3]\text{NO}_3$	Brown	63.91	283	60.67 (60.64)	3.85 (3.80)	11.24 (11.22)	11.60 (10.56)	12.76 (12.71)	23.6	9.62
$[\text{Dy}(\text{BMHpHB})_3]\text{NO}_3$	Brown	73.33	287	60.48 (60.49)	3.84 (3.80)	11.20 (11.19)	11.50 (11.44)	13.00 (12.94)	22.9	10.58

These complexes were soluble in common organic solvents and the molar conductance of the complexes showed them to be 1:1 electrolyte Akhtar and Akhil (2012). A higher molar conductivity of the complexes in nitrobenzene further suggests the coordination of the anion to the metal ions.

Electronic absorption spectra:

UV region properties of the complexes were performed in chloroform of spectroscopic

grade. An intense band at 235nm was assigned due to the $\pi \rightarrow \pi^*$ transition. It is found that external crystal field plays a role in making 4f forbidden to allowed transitions when degeneracy of 4f orbitals is disrupted, Frederick (1982), Alexandra et.al. (2018). As per nephelauxetic effect, The spectra (**Table-2**) shows a shift of the band towards lower energy, compared with those of the aqua ions, Kavita and Agrawala (1996).

Table-2: UV-Visible spectral data of HDMHpHB ligand and its Ln(III) metal complexes

Compound	λ_{nm}	ϵ (dm ³ /mol/cm)	Transition
HBMHpHB	320	11875	Phenolic $\pi \rightarrow \pi^*$
	235	8163	Azomethine $\pi \rightarrow \pi^*$
	220	8500	Oximino $\pi \rightarrow \pi^*$
$[\text{Nd}(\text{BMHpHB})_3]$	811	612	$^4F_{9/2} \leftarrow ^4H_{5/2}$
	756	816	$^4P_{13/2} \leftarrow ^4H_{5/2}$
	625	500	$^4P_{9/2} \leftarrow ^4H_{5/2}$
	560	1250	$^4P_{7/2} \leftarrow ^4H_{5/2}$
$[\text{Tb}(\text{BMHpHB})_3]$	600	1265	$^7F_4 \leftarrow ^5D_4$
	530	4239	$^7F_5 \leftarrow ^5D_4$
	408	9887	$^7F_6 \leftarrow ^5D_4$
$[\text{La}(\text{BMHpHB})_3]$	419	7615	MLCT
	346	7544	MLCT
	269	14968	MLCT
$[\text{Sm}(\text{BMHpHB})_3]$	685	1100	$^4F_{9/2} \leftarrow ^4H_{5/2}$

	555	2560	$^4P_{13/2} \leftarrow ^4H_{5/2}$	$b^{1/2} = 0.00933$
	476	1877	$^6P_{7/2} \leftarrow ^4H_{5/2}$	$\delta\% = 3.874$
	408	29557	$^4P_{9/2} \leftarrow ^4H_{5/2}$	$\eta = 1.0775$
[Gd(BMHpHB) ₃]	358 309	5623 19269	$^8S_{1/2} \rightarrow ^6P_{1/2}$ MLCT	$\beta_{ave} = 0.9953$, $b^{1/2} = 0.00118$, $\delta\% = 1.01309$
[Dy(BMHpHB) ₃]	427	6691		$^4H_{15/2} \rightarrow ^4F_{9/2}$
	348	7178		$^4H_{15/2} \rightarrow ^4I_{15/2}$
	303	11730		MLCT

The bonding parameter ($b^{1/2}$) and the covalency parameter (β) are less than unity, while Sinha's parameter (δ) is positive, indicating a moderate covalent character for the bond between the metals and ligand, Tondon et.al. (1971).

FT(IR) spectra

FT(IR) spectra of synthesized compounds was studied in order to clarify the mode of bonding

and the effect of the metal ion on the ligand, the FT(IR) spectra of the benzilmonoximehydrazone-p-hydroxybenzaldehyde, and the metal complexes were studied and assigned based on careful comparison of their spectral characteristic absorption bands. The FT (IR) data is presented in **Table-3**.

Table-3: IR spectral bands of the ligand (HBMHpHB) and its metal complexes (cm^{-1})

Compound	-OH (Oxo)	-OH (Phe)	Ar C-H	Ar C=C	>C=NN-	>C=NO-	$\nu_1(\text{N O}_3)$	$\nu_2(\text{N O}_3)$	$\nu_3(\text{N O}_3)$	$\nu_4(\text{N O}_3)$	Phe ring	M-N
HBMHpHB	3295	3187	3070	2976	1526	1430	-	-	-	-	741	-
La(BMHpHB) ₃	-	3135	3070	2977	1505	1409	1396	1033	1221	1278	743	494, 515
Nd(BMHpHB) ₃	-	3136	3070	2978	1506	1407	1397	1033	1250	1267	742	493, 513
Sm(BMHpHB) ₃	-	3182	3072	2979	1512	1401	1391	1034	1256	1278	741	492, 515
Dy(BMHpHB) ₃	-	3178	3076	2980	1507	1409	1392	1038	1257	1266	743	489, 519
Tb(BMHpHB) ₃	-	3181	3073	2980	1500	1403	1390	1039	1254	1267	743	497, 517
Gd(BMHpHB) ₃	-	3186	3072	2981	1506	1404	1389	1032	1334	1287	744	496, 519

The absence of broad band in the range of $3200\text{--}3300\text{cm}^{-1}$ in all complexes, which was earlier reported at 3295cm^{-1} for benzilmonoximehydrazone-p-hydroxybenzaldehyde ligand, indicated deprotonation of oximino group during coordination Agrawal et. al. (1993). A sharp band at 1526cm^{-1} in free benzilmonoximehydrazone-p-hydroxybenzaldehyde ligand is due to azomethine $\nu\text{C}=\text{NN}-$ vibration. The shifting of this band to lower frequency ($1500\text{--}1512\text{cm}^{-1}$) in the metal complexes suggests the coordination of metal ion through nitrogen atom of azomethine group, as metal atom would reduce the electron density in the azomethine link and thus lower the $\text{HC}=\text{N}$ absorption frequency, Burns (1968). The

involvement of another nitrogen atom of oximino group in bonding with metal ions was evident from observed band at 1430cm^{-1} in benzilmonoximehydrazone-p-hydroxybenzaldehyde ligand, but was shifted to lower frequency $1401\text{--}1409\text{cm}^{-1}$ in the metal complexes, Swaminathan and Irwing (1964), Zucchi and Le Goff (2012). The IR spectra of complexes give a $|\nu_4-\nu_1|$ separation in the range $103\text{--}130\text{cm}^{-1}$ suggesting monodentate bonding for the nitrate group. In addition, the new bands at about $513\text{--}519\text{cm}^{-1}$ and $489\text{--}494\text{cm}^{-1}$ are assigned to M-N and M \rightarrow O vibrations, respectively which support the involvement of N and O atoms in complexation with metal ions under investigation Binnemans et. al. (2002).

PMR spectra

PMR Spectra of Schiff base and their complexes were recorded in d_6 DMSO solution and TMS used as internal standard. On comparison of the spectrum with that of the ligand, it was noted that the oximino proton of

the ligand (12.23 δ) is missing in the pmr spectra of its metal complexes, confirming the proposed replacement of the oximino proton by the metal ion during complex formation as shown in **Table 4**.

Table-4: PMR spectrum of HBMHpHB and its metal complexes in d_6 DMSO

Compounds	-OH	Phenolic -OH	-CH=	Phenyl rings
HBMHpHB	12.23	11.65	8.21	6.90-7.80
La(BMHpHB) ₃	-	11.65	8.20	7.30-7.8

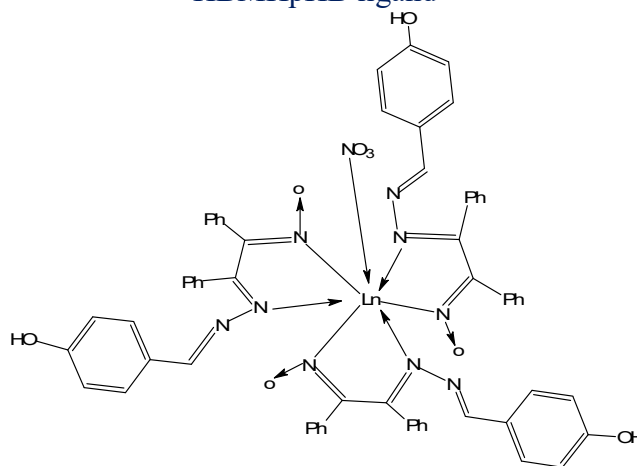
The aromatic proton in schiff base appeared at 6.90 ppm to 7.80 ppm and in their metal complex in the range of 7.30 ppm to 7.80 ppm, Bunzliand Piguet(2002).

Conclusion

The preferred coordination number of Ln(III) metal ion is 7. This coordination number depends upon the nature of the ligand. Conductance and molecular weight data show present of nitrate anion inside the coordination sphere in the complexes. FT(IR) spectral data reveal that ligand is coordinated to metal ions nitrogen atoms of oximino and azomethine linkages in all the complexes studied. Hence, coordination number 7 is suggested for metal ion in these lanthanoid complexes. The

possible structure of the complexes is given **Figure-1**.

Figure-1: Structure of metal complexes of HBMHpHB ligand



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