

“Synthesis and characterization of lanthanide (III) complexes of 4-[3-(hydroxyimino)butan-2- ylidene]hydrazinylidene}methyl]phenol”

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Abstract

Lanthanide (III) complexes of the type $[Ln(DMHpHB)_2NO_3]$ where $Ln = La^{3+}, Nd^{3+}, Sm^{3+}, Gd^{3+}, Tb^{3+}$ and Dy^{3+} , 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 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 ML_3 complex.

Keywords:Lanthanide (III) complexes, magnetic moments, electronic, FT(IR) and PMR spectra

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I. 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 are reported to give laser action in solution; the Nd(III) ion also provides laser action when present in aprotic solvents. 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 temperature¹. Several lanthanides (III) ions are useful as shift reagents in MRI and Gd(III) have been shown to be an effective contrast agent for *in vivo* nuclear magnetic resonance imaging²⁻⁵. 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 diacetylmonoximehydrazide-p-hydroxybenzaldehyde, abbreviated as HDMHpHB (IUPAC name: 4-[3-(hydroxyimino)butan-2-ylidene]hydrazinylidene }methyl]phenol)

II. Materials And Methods:

Hydrated metal nitrates (S.d. fine chem., 99.99% pure) were used as such. Physical measurements were carried out as reported earlier^{6,7}. 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. HNO_3 and H_2SO_4 and finally metal contents were estimated complexometrically by EDTA using xylenol orange at pH-6.

2.1: Synthesis of HDMHpHB:

The ligand HDMHpHB was prepared by condensing p-hydroxybenzaldehyde with diacetylmonoximehydrazide in presence of conc. HCl in ethanol solution. The reaction mixture was refluxed for 7h. After refluxed, reaction mixture was cool and filters the precipitated, washed with ethanol, dried at 100°C. [Found: C: 60.19, H: 5.90, N: 19.16, O: 14.55, Calc for $C_{11}H_{13}N_3O_2$: C: 60.26, H:5.98, N:19.17, O:14.60%]

2.2: Synthesis of complexes:

The coordination complexes of the types [Ln(DMHpHB)₂NO₃] were synthesized by refluxing ethanolic solution of ligand HDMHpHB and the corresponding metal salts in stoichiometric amounts at 70-80°C for 5-10h. The solid complexes were filtered off and washed with aliquots of ethanol followed by diethylether, recrystallised from chloroform and finally dried in ho air oven.

III. Results and Discussions:

The ligand HDMHpHB is strong chelating ligand and has two potential donor sites for coordination. This ligand from well defined complexes with lanthanide (III) ions is presented in **Table-1**. These complexes are soluble in common organic solvents and the molar conductance of the complexes shows them to be 1:1 electrolyte⁹. A higher molar conductivity of the complexes in nitrobenzene further suggests coordination of the anion to the metal ions.

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

Compound	Colour	% Yield	MP/DP in °C	% Element Content, Expected (Observed)					Molar Cond	Magntic Moments
				C	H	N	O	M		
HDMHpHB	Brown	72.11	199	60.26 (60.19)	5.98 (5.90)	19.17 (19.16)	14.60 (14.55)	-	-	-
[La(DMHpHB) ₃]NO ₃	Yellow	69.91	279	47.39 (47.36)	4.31 (4.30)	15.08 (15.03)	11.49 (11.43)	16.62 (16.55)	20.49	Dia
[Nd(DMHpHB) ₃]NO ₃	Yellow Brown	69.83	273	47.09 (47.05)	4.28 (4.25)	14.98 (14.99)	11.41 (11.40)	17.15 (17.13)	26.13	3.52
[Sm(DMHpHB) ₃]NO ₃	Light Brown	67.28	269	46.67 (46.61)	4.25 (4.19)	14.87 (14.86)	11.33 (11.29)	17.75 (17.71)	24.21	1.47
[Gd(DMHpHB) ₃]NO ₃	Yellow Brown	69.22	277	48.81 (48.77)	4.44 (4.42)	15.53 (15.51)	11.83 (11.79)	19.38 (19.36)	23.51	7.93
[Tb(DMHpHB) ₃]NO ₃	Brown	71.98	269	46.28 (46.26)	4.21 (4.21)	14.72 (14.71)	11.22 (11.15)	18.57 (18.51)	25.21	9.51
[Dy(DMHpHB) ₃]NO ₃	Brown	69.86	293	48.50 (48.47)	4.41 (4.35)	15.43 (15.39)	11.75 (11.73)	19.90 (19.80)	23.67	10.54

3.1: Electronic absorption spectra:

The electronic spectra of all complexes were recorded in chloroform. In the UV region an intense band appears at 235nm de to the $\pi \rightarrow \pi^*$ transition. The 4f transitions are normally forbidden, but are followed when degeneracy in the 4f orbitals is lifted due to external crystal field¹⁰⁻¹¹. The electronic spectra (**Table-2**) shows a shift of the band towards lower energy, compared with those of the aqua ions¹² owing to nephelauxetic effect. 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 ligand¹³.

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

Compound	λ_{nm}	ϵ (dm ³ /mol/cm)	Transition	
HDMHpHB	374	1499	$\pi^* \leftarrow \pi$	
	268	4670	$\pi^* \leftarrow \pi$	
	235	56688	$\pi^* \leftarrow \pi$	
[Nd(DMHpHB) ₃]	811	612	${}^4F_{9/2} \leftarrow {}^4H_{5/2}$	$\beta_{ave} = 0.9867$
	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	${}^4P_{7/2} \leftarrow {}^4H_{5/2}$	$\eta = 1.0267$
[Tb(DMHpHB) ₃]	600	1265	${}^7F_4 \leftarrow {}^5D_4$	
	530	4239	${}^7F_5 \leftarrow {}^5D_4$	
	408	9887	${}^7F_6 \leftarrow {}^5D_4$	
[La(DMHpHB) ₃]	419	7615	MLCT	
	346	7544	MLCT	
	269	14968	MLCT	
[Sm(DMHpHB) ₃]	685	1100	${}^4F_{9/2} \leftarrow {}^4H_{5/2}$	$\beta_{ave} = 0.9627$
	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	${}^4P_{9/2} \leftarrow {}^4H_{5/2}$	$\eta = 1.077$
[Gd(DMHpHB) ₃]	358	5623	${}^8S_{1/2} \rightarrow {}^6P_{1/2}$	$\beta_{ave} = 0.9953, b^{1/2} = 0.00118, \delta\% = 0.4970, \eta = 1.0092$
	309	19269	MLCT	
[Dy(DMHpHB) ₃]	427	6691	${}^4H_{15/2} \rightarrow {}^4F_{9/2}$	

	348	7178	$^4H_{15/2} \rightarrow ^4I_{15/2}$
	303	11730	MLCT

3.2: FT(IR) spectra:

The FT(IR) spectrum of the title ligand shows an intense broad band at 3292cm^{-1} , which is due to oximino $\nu(\text{OH})$, is absent in its inner transition metal complexes, indicated that hydroxyl group deprotonated during complex formation and oximino group participating in complexation. The absorption band bands in the region $3126\text{-}3202\text{cm}^{-1}$ of the free ligand and its metal complexes are assigned to phenolic $-\text{OH}$. In the spectrum of the ligand, a band occurring at 1599cm^{-1} has been assigned to the azomethine ($>\text{C}=\text{NN}$) group¹³. This band in the complexes appears at higher frequencies (**Table-3**), indicating coordination through the azomethine nitrogen. The oximino band occurs in HDMHpHB at 1599cm^{-1} and is shifted to higher frequencies, indicated that involvement of oximino group in coordination. The IR spectra of complexes give a $|\nu_4-\nu_1|$ separation in the range $72\text{-}128\text{cm}^{-1}$ suggesting monodentate bonding for the nitrate group. A weak band appearing in the range $519\text{-}576\text{cm}^{-1}$ in these complexes has been assigned to the metal-nitrogen stretching¹⁴⁻¹⁶.

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

Assignments	HDMHpHB	Nd(III)	Tb(III)	La(III)	Sm(III)	Gd(III)	Dy(III)
Oximino -OH	3392	-	-	-	-	-	-
Phenolic -OH	3191	3139	3126	3202	3155	3181	3193
$\nu\text{C}=\text{C}$ Ar.	2918	3057	3055	3084	3085	3029	3026
$\nu\text{C}=\text{NN}$	1599	1625	1614	1614	1606	1607	1609
$\nu\text{C}=\text{NO}$	1492	1538	1507	1506	1504	1492	1493
$\nu_1(\text{NO}_3)$	-	1455	1457	1451	1445	1452	1459
$\nu_2(\text{NO}_3)$	-	1033	1029	1331	1033	1029	1028
$\nu_3(\text{NO}_3)$	-	1340	1340	1334	1324	1323	1324
$\nu_4(\text{NO}_3)$	-	1366	1359	1345	1369	1363	1349
$ \nu_4(\text{NO}_3) - \nu_1(\text{NO}_3) $	-	83	93	109	100	100	128
$\nu\text{N}-\text{N}$	975	1009	1010	1009	1010	1009	1008
$\nu\text{N}\rightarrow\text{O}$	---	1212	1123	1223	1226	1219	1223
$\nu\text{M}-\text{N}$	---	563	569	571	576	564	575
$\nu\text{M}\rightarrow\text{N}$	---	525	521	522	519	521	525

3.3: PMR spectra:

The PMR spectra recorded in $\text{DMSO-}d_6$ medium provide conclusive evidence in favor of the bonding. Spectral data of HDMHpHB reveals two singlet peaks at 11.59 and 11.21δ . The intensity of the peaks suggests that these are due to single deshielded protons and assigned as oximino and phenolic protons respectively¹⁷. The peak observed in free ligand HDMHpHB at 11.59δ is absent in prepared $[\text{La}(\text{DMHpHB})_3]$ metal complex, suggested that oximino group deprotonated in complex formation¹⁸⁻¹⁹. Multiplet observed at in the region $6.44\text{-}7.19\delta$ (4H), 1, 3-disubstituted benzene ring and free methyl protons 2.39δ (6H). Another singlet peak reveals at 9.08δ (1H) assigned as methane ($-\text{CH}=\text{}$) group of HDMHpHB. All these group unchangeable in La(III) metal complex, indicated that their non-involvement in complex formation and also suggest monobasic character of HDMHpHB ligand²⁰.

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

Compound	Oximino -OH	Phenolic -OH	-CH=	Phenyl Ring	-CH ₃
HDMHpHB	11.59	11.21	9.08	6.44-7.19	2.39
$[\text{La}(\text{DMHpHB})_3]$	-	10.74	9.01	7.08-7.41	2.41

IV. 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 this lanthanoid complexes. The possible structure of the complexes is given **Figure-1**.

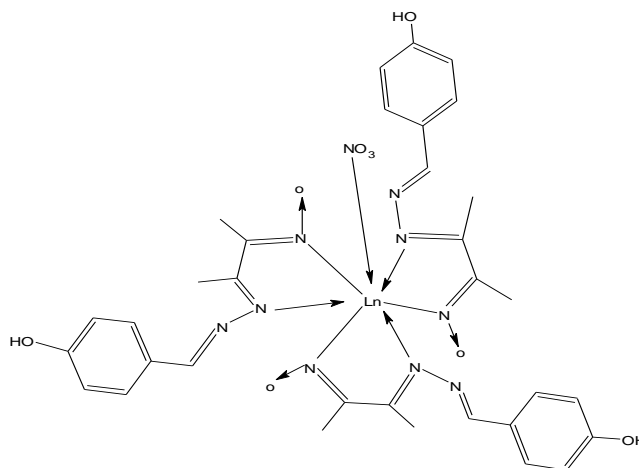


Figure-1: Structure of metal complexes of HDMHpHB ligand

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