

Magnetic, Physico-chemical and Spectral Studies on benzilmonoximehydrazide-m-hydroxybenzaldehyde and complexes of Trivalent Lanthanides

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Abstract:

The studies of three new lanthanide (III) nitrate complexes of benzilmonoximehydrazide-m-hydroxybenzaldehyde ligand are discussed. Title ligand was obtained by the condensation of benzilmonoximehydrazide with m-hydroxybenzaldehyde. Lanthanide(III) nitrates, viz. gadolinium(III) nitrate, samarium(III) nitrate and praseodymium(III) nitrate were chosen to synthesize new complexes. The complexes were characterized on the basis of physico-chemical studies viz. elemental analysis, spectral, viz. IR and electronic spectral and magnetic studies. The electronic spectra of the complexes of Pr^{3+} , Sm^{3+} and Gd^{3+} have been analyzed and discussed. The spectral parameters show covalent nature of bonding between the metal and the synthesized ligand.

Keywords —Lanthanides, electronic spectra, m-hydroxybenzaldehyde and gadolinium.

I. INTRODUCTION

Lanthanides or lanthanons form a longest series of the periodic table. It is 4f-inner transition series. Lanthanide(III) ions, because of their size and charge are the best ions to form stable complexes with high coordination number¹⁻⁵. Coordination compounds of lanthanide in which lanthanide ions exhibit coordination number 6-10 are reported⁶⁻⁷. Schiff base metal complexes have played a major role in the development of coordination chemistry⁸⁻¹¹. In this work, we wish to report lanthanide(III) nitrate complexes with benzilmonoximehydrazide-m-hydroxybenzaldehyde, IUPAC name of 3-[3-(hydroxyimino)butan-2-ylidene]hydrazinylidene}methyl]phenol) (hereafter abbreviated as HBMHmHB) derived from the condensation of equimolar of benzilmonoximehydrazide and m-hydroxybenzaldehyde.

II. EXPERIMENTAL

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Lanthanide (III) nitrates viz. praseodymium (III) nitrate, samarium (III) nitrate and gadolinium(III) nitrate were obtained from S. d. Fine Chemicals and used as such. All the physico-chemical methods were similar to that employed earlier⁵⁻⁷. 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.

A: Synthesis of HBMHmHB ligand:

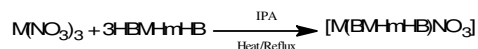
To a mixture of benzilmonoximehydrazide (0.5 mol) and m-hydroxybenzaldehyde (0.52 mol) dissolved in ethanol (50 mL), hydrochloric acid (2 mL) was added while stirring for 10 min. The reaction mixture was then stirred for 15h at 55-60°C. The solid product separates out on dilution with water (150-200mL). It was filtered, washed with cold water and crystallized from 60% ethyl alcohol.

B: Synthesis of complexes:

Complexes were prepared by treating corresponding lanthanide(III) nitrate (1 mmol) in isopropanol with ligand solution (1:4 mmol) in the same solvent. In some cases complexes were isolated immediately in cold while in other cases in hot solution. In some cases resulting solution were refluxed on the water bath for 1-3 h (70-75°C). The resulting complexes were collected after filtration washed with isopropanol and finally with ether and dried in vacuum over CaCl₂⁸.

III. RESULTS AND DISCUSSIONS:

Interaction of lanthanide(III) nitrates viz. praseodymium(III) nitrate, samarium(III) nitrate and gadolinium nitrate(III) with benzilmonoximehydrazide-m-hydroxybenzaldehyde ligand results in the formation of complexes with general composition Ln(BMHmHB)₃(NO₃)₃ [Where Ln = Pr, Sm and Gd]. The general equation for the preparation of the complexes is shown below:



[M = Pr, Sm and Gd]

The elemental analysis of these complexes is given in **Table-1**. New complexes are fairly stable and can be stored for a long period. All are sufficiently soluble in common organic solvents and are non-hygroscopic in nature. These complexes show electrical conductivity in nitrobenzene medium which shows their 1:1 electrolytic nature⁹. The molecular weight data of the complexes also supports this fact. Magnetic moment data show that all complexes are

paramagnetic due to presence of 4f-electrons which are effectively shielded by 5s²p² electrons¹⁰. This shows that 4f-electrons do not participate in the bond formation¹¹⁻¹². Magnetic moment data of the complexes are assembled in **Table-1**.

A: Electronic Absorption spectra:

Electronic spectral studies of lanthanide(III) metal complexes are significant and are important tool for the measurement of covalency in complexes. The line like spectra of lanthanide(III) metal compound appearing in the UV-visible and near IR regions arise from electronic transitions within the 4f-levels which are normal forbidden¹³⁻¹⁴ but may become allowed after removal of degeneracy of 4f-orbitals by external crystal field¹⁵⁻¹⁶. The absorption bands of samarium(III) in visible and near IR region may appear due to transitions from ground levels ⁴H_{5/2} to the excited J levels. The shift of hypersensitive bands has been utilized to calculate the nephelauxetic effect (β), Sinha's covalency parameter (δ%) (metal-ligand covalency percentage) and the covalency factor (b^{1/2}) along with covalency angular overlap parameter (η) these parameters have been calculated using the following expressions¹⁷.

$$b^{1/2} = \frac{1}{2} [(1-\beta)^{1/2}]$$

$$\delta\% = [(1-\beta)/\beta] \times 100 \beta^{1/2}$$

$$\eta = (1-\beta^{1/2})/\beta^{1/2}$$

The electronic spectral studies of lanthanide(III) metal complexes yield positive value for (1-β) and (δ%) which suggest that the bonding between metal and ligand is covalent in the complexes. The values of parameter of bonding (β^{1/2}) and angular overlap parameter (η) are also found to be positive indicating covalent bonding complexes. The electronic spectral data are presented in **Table-2**.

B: FT(IR) Spectra:

The I.R. Spectra were recorded in the 4000-400 cm⁻¹ range using KBr pallets. IR spectra of the Schiff base ligand was analyzed by comparison of the spectra of substituted benzene and the corresponding assignments were listed with comparing the IR spectra of previously reported data¹². The ligand shows broad band at 3260cm⁻¹ due to oximino group is absent in its all prepared metal complexes, indicated prepared ligand

coordinate to metal ion through oximino group. The ligand shows broad band at 3112cm^{-1} due to phenolic hydroxyl group on free ligand which show shift in frequency in complex indicating coordination through metal atom. In case of complexes a notable peaks 1575 and 1460cm^{-1} of ligand shows positive shift and appears in the range of $[1608-1609$ and $1504-1509\text{cm}^{-1}]$. These notable peaks is attributed to azomethinev($\text{C}=\text{NN}$) and oximinov($\text{C}=\text{NO}$) respectively¹⁸⁻¹⁹ stretching and its shift indicates that in complexes coordination of ligand in complexes is through azomethinic and oximino nitrogen atoms²⁰⁻²¹. The IR spectra of complexes give a $|v_4 - v_1|$ separation in the range $119-133\text{cm}^{-1}$ suggesting monodentate bonding for the nitrate group. Some new medium to weak bands were also observed in the range $(491-522\text{cm}^{-1})$ in

case of complexes of HDMHmHB ligand has no absorption. These new medium to weak bands are assigned as; $v(\text{Ln}-\text{N})$ or/and $v(\text{Ln}\rightarrow\text{N})$ modes observed for various Ln(III) complexes. The partial IR data for HBMHmHB ligand and their corresponding complexes are given in **Table-3**.

The preferred coordination number for lanthanide(III) metal ions is either 6, 8 or 10. These Coordination numbers depend upon the nature of the anions present. Conductance and molecular weight data show that one nitrate ion is present inside the coordination sphere in the complexes. FT(IR) spectral data also reveal that nitrate ion is monodentately covalently bonded to lanthanide metal ions in all the complexes studied. Hence coordination number 7 is suggested for metal ion in these lanthanide(III) nitrate complexes²²⁻²³. The possible structure of the complexes is given **Figure-1**.

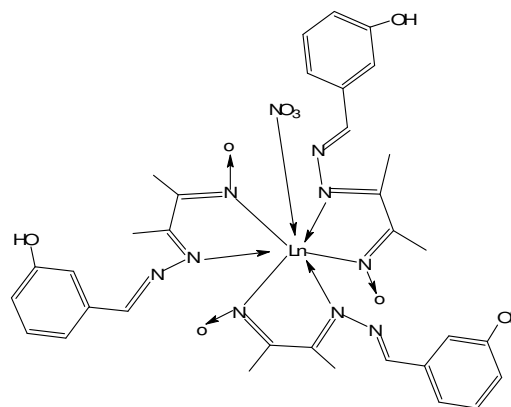


Figure-1: Structure of metal complexes of HBMHmHB ligand

Table-1: Physical and Analytical data of

Compound	Colour	% Yield	MP/DP in °C	% Element Content, Expected (Observed)					Molar Cond	Magnetic Moments
				C	H	N	O	M		
HBMHmHB	Yellow	74.82	209	73.45 (73.41)	4.99 (4.96)	12.24 (12.19)	9.32 (9.28)	-	-	-
[Pr(BMHmHB) ₃]NO ₃	Brown	62.36	278	61.52 (61.50)	3.92 (3.86)	11.39 (11.36)	11.72 (11.66)	11.47 (11.43)	25.30	3.49
[Sm(BMHmHB) ₃]NO ₃	Light Brown	62.59	272	61.05 (61.02)	3.88 (3.81)	11.31 (11.27)	11.60 (11.51)	12.14 (12.12)	21.25	1.45
[Gd(DMHmHB) ₃]NO ₃	Yellow Brown	68.77	273	60.71 (60.70)	3.87 (3.86)	11.24 (11.20)	11.60 (11.51)	12.62 (12.57)	27.87	7.99

HBMHmHB ligand and its Ln(III) complexes

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

Compound	λ_{nm}	ϵ ($\text{dm}^3/\text{mol}/\text{cm}$)	Transition	
HBMHmHB	325	11875	$\pi^* \leftarrow \pi$	
	230	8163	$\pi^* \leftarrow \pi$	
[Pr(BMHSA) ₃]	606	875	$^1D_2 \leftarrow ^3H_4$	$\beta_{\text{ave}} = 0.992$ $b^{1/2} = 0.063$
	485	4560	$^3P_0 \leftarrow ^3H_4$	$\delta\% = 0.806$
	470	4958	$^3P_1 \leftarrow ^3H_4$	$\eta = 1.0161$
	445	5659	$^3P_2 \leftarrow ^3H_4$	
[Sm(BMHmHB) ₃]	750	789	$^4F_{9/2} \leftarrow$ $^4H_{5/2}$	$\beta_{\text{ave}} = 0.9949$ $b^{1/2} = 0.0053$
	521	2156	$^4P_{13/2} \leftarrow$	

			$^4H_{5/2}$	$\delta\% = 0.515, \eta = 1.0101$
	433	3547	$^6P_{7/2} \leftarrow$ $^4H_{5/2}$	
	390	5478	$^4P_{9/2} \leftarrow$ $^4H_{5/2}$	
[Gd(BMHmHB) ₃]	357 269	9875 21456	$^8S_{1/2} \rightarrow ^6P_{1/2}$ MLCT	$\beta_{ave} = 0.9458, b^{1/2} = 0.0271, \delta\% = 5.42, \eta = 1.0161$

Table-3: IR spectral bands of the ligand (HBMHmHB) and its metal complexes (cm⁻¹):

Compound	-OH (Oxo)	-OH (Phe)	Ar C-H	Ar C=C	>C=NN-	>C=NO-	Phe ring	$\nu_1(\text{NO}_3)$	$\nu_2(\text{NO}_3)$	$\nu_3(\text{NO}_3)$	$\nu_4(\text{NO}_3)$	M-N
HBMHmHB	3260	3112	3070	2960	1575	1460	729	-	-	-	-	-
Pr(BMHmHB) ₃	-	3119	3068	2961	1609	1503	725	1451	1031	1334	1318	499, 521
Sm(BMHmHB) ₃	-	3121	3062	2962	1608	1504	729	1444	1039	1340	1311	491, 522
Gd(BMHmHB) ₃	-	3111	3073	2969	1609	1509	728	1428	1033	1323	1309	493, 518

REFERENCES

- Huneey J E, Keiter E A and Keiter R L; *Inorganic Chemistry Principles of Structure and Reactivity*, Pearson Education, Singapore, **2002**.
- Kleber E V; *Rare Earth Research*, Macmillan, New York, **1961**.
- Moeller T; *The Chemistry of Lanthanides*; Reinhold, New York, **1963**.
- Cotton F A and Wilkinson G; *Advanced inorganic Chemistry*, 3rd Edⁿ, Interscience New York.; **1972**.
- Koppikar D K, Sivapulliah P V, Ramakrishna L and Soundararajan S; *Structure and Bonding*; **1978**, 34, 135.
- Bradley J G, Gothra J S and Hart F A; *J Chem Soc Dalton*; **1973**, 1021.
- Harrison E; *Acta Chem Scand.*; **1975**, 27, 2827.
- Kishor Arora and Kiran Burman; *J Saudi Chem Soc.*; **2007**, 11(3), 445.
- Chakravarthi I, Ray H C, Goel N and Hashmi N M; *Asian J Chem.*; **2002**, 14, 143.
- Agarwal R K and Himanshu Agarwal; *Synth React Inorg Met Org Chem.*; **2001**, 31, 263.
- Indersenan P and Raj N K Kala; *J Indian Chem Soc.*; **2000**, 77, 259.
- Agarwal R K, Arora K, Priyanka and Chakravarthi I; *Polish J Chem.*; **1993**, 67, 1913.
- Dutt N K and Rahut S; *J InorgNucl Chem.*; **1970**; 32, 2105.
- Butter E; *Chem Abstr.*; **1972**, 77, 830-840.
- Kh A Cherches, Ezerskaya T P and Yalazere M; *Chem Abstr.*; **1971**, 74, 105621.
- Lapitskaya A V and Pirkers S B; *ZhNeorgKhim.*; **1971**, 16, 369.
- Tondon S P and Mehta P C; *J Chem Phys.*; **1970**, 52, 4314.
- Radhakrishnan P S and Indersenan P; *J Indian Chem Soc.*; **1990**, 67, 243.
- Shankar G, Prem Kumar R R and Ramalingham S K; *Polyhedron*, **1986**, 5, 991.
- Burns G R; *Inorg Chem.*; **1968**, 7, 277.
- Swaminathan K and Irving N H; *J InorgNucl Chem.*; **1964**, 26 1291.
- Agarwal R K, Kishor Arora and Sarin R K; *Synth React Inorg Met Org Chem.*; **1994**, 24(5) 735.
- Agarwal R K and Gupta S K; *J Indian Chem Soc.*; **1986**, 63, 994.