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Magnetic and Spectral Characterization of Benzilm on oxime hydrazidesali cyalidene Complexes of Lanthanoid (III) Ions

Patil S, Singh V
Dept of Physics
Konkan Gyanpeeth Karjat College,
Karjat, Dist: Raigad, Maharashtra-India,
vinayudc@gmail.com.

Kamble P
Dept of Chemistry
Patkar-Varde College,
Goregaon,
Maharashtra.

Badekar R
R and D Dept
RIVA Industries,
Ambernath MIDC,
Ambernath West, Maharashtra, India.

Abstract- The 1:3 complexes of lanthanide (III) ions of as Nd (III), Sm (III), Tb (III) and La (III) with benzilm on oxime hydrazi desali cyalidene have been prepared and characterized by elemental analysis, IR, PMR, electronic spectra, molar conductance and magnetic moments. The results show that the benzilm on oxime hydrazidesali cyalidene ligand acts as a bidentate monobasic donor, coordinating through the azo methine nitrogen and deprotonated oximino proton.

Keywords: Lanthanoid (III), Benzilmonoximehydrazidesalicyalidene, Neodymium (III) and Terbium (III).

I. INTRODUCTION

Lanthanides forms a longest series of the periodic table, 4f inner transition series. Lanthanoid (III) ions, forms stable complexes with higher coordination number because their charge and size[1-5]. Coordination number[6-10] of lanthanoid ions of coordination compounds of lanthanoid are reported[6-7]. Metal complexes of Schiff base have played a major role in the development of coordination chemistry[8-11].

Due to their special electronic configuration, lanthanoid complexes have inspired many efforts on the design and synthesis as potential anticancer and antibacterial agents[12-15]. In this work, we wish to reports lanthanoid complexes such as Nd (III), Sm (III), Tb (III) and La (III) complexes with benzilm on oxime hydrazi desali cyalidene [HBMHSA].

II. MATERIALS AND METHODS

Lanthanoid (III) nitrates, viz, Samarium (III) nitrate, Terbium (III) nitrate, Lanthanum (III) nitrate, Neodymium (III) nitrate, were obtained from Merck and used as such. Solvents were obtained from various sources such as, S.D. Fine Chemicals, Loba Chemie and B.D.H. and were used as such or after distillation if felt necessary. ^{1}H-NMR spectrum in d_6 DMSO was recorded on Brucker 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. The UV–Vis spectrum in methanol was recorded with a JASCO V-650 Spectrophotometer.

1. Preparation of HBMHSA ligand:

α-benzilm on oxime hydroxide prepared by reported method[15]. 0.100M solution of α-benzil m on oxime hydrazide (20ml ethanol) was added to 0.110M alcoholic solution of salicyal dehyde, than few drops of concentrated hydrochloric acid added to the reaction mixture, refluxed for 5 hours at 50-60^{o}C, cool and collected precipitated after filtration. After complication reaction process precipitate of ligand are formed out yellow solid and purity checked by TLC.

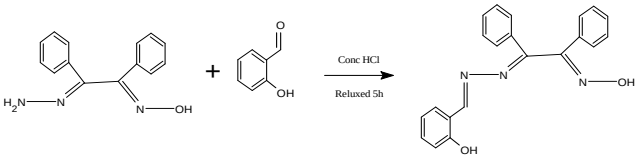

Fig 1. Reaction scheme of preparation of ligand HBMHSA.

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2. Preparation of Ln (III) Metal Complexes:

Complexes were prepared by treating corresponding lanthanoid (III) nitrate (1 mmol) in ethanol with ligand solution (3 mmol) in the same solvent. The resulting solutions were refluxed on the water bath for about 9h (50-60°C). The resulting complexes were washed with 50% hot ethanol and separated by filtration.

III. RESULTS AND DISCUSSIONS

The Schiff base ligand benzilmonoxime hydrazidesalicylidene (HBMHSA) is yellow crystalline solid, air sensitive in nature and soluble in common organic solvents. The physical and analytical data of ligand and its Ln (III) metal complexes represented in Table-1.

Table 1.Physical and Analytical data of HBMHSA ligand and its Ln(III) complexes.

Compound	Colour	% Yield	MP/DP in °C	% Element Content, Expected (Observed)					Molar Cond	Magnetic Moment
				C	H	N	O	M		
SA	Yellow	79.83	218	73.45	4.99	12.24	9.32	-	-	-
$La(SA)_3NO_3$	Yellow	65.74	289	61.62 (61.60)	3.91 (3.89)	11.41 (11.39)	11.70 (11.72)	11.32 (11.31)	21.23	-
$Tb(SA)_3NO_3$	Red	69.64	291	61.35 (61.31)	3.90 (3.87)	11.36 (11.35)	11.70 (11.66)	11.70 (11.66)	27.66	3.61
$La(SA)_3NO_3$	Light Brown	68.12	297	61.05 (61.04)	3.88 (3.81)	11.31 (11.27)	11.60 (11.54)	12.14 (12.13)	25.74	1.44
$Sm(SA)_3NO_3$	Brown	72.14	278	60.67 (60.65)	3.85 (3.82)	11.24 (11.23)	11.60 (10.59)	12.76 (12.72)	22.14	9.69

Interaction of lanthanoid (III) nitrates with HBMHSA ligand results in the formation of complexes with general composition $[LnL_3]$ (where Ln = Nd (III), Sm (III), Tb (III), La (III) and L = HBMHSA). The general equation for the preparation of the complexes is shown below;

$$Ln(NO_3)_3 + 3HBMHSA \rightarrow Ln(BMHSA)_3 + 3HNO_3$$

(Where, Ln = Nd, Sm, Tb, La)

All synthesized complexes are stable and can be stored for a long time. They are non-hygroscopic in nature and sufficiently soluble in common organic solvents. The molar conductivity values of these complexes were in the range of 19.5-25.1$\Omega^{-1}cm^2mol^{-1}$, indicating the 1:1 electrolyte nature of these complexes[17].

Magnetic moments data shows Lanthanum (III) complex is essentially diamagnetic in nature[18], while all other complexes are paramagnetic due to presence of unpaired electrons 4*f* which are effectively shielded by $5s^25p^2$ electrons. This shows that 4*f* electrons do not participate in the bond formation[19].

1. Spectroscopic Studies:

1.1 Electronic Absorption Spectra:

The UV absorption spectra of the free ligand HBMHSA and its Ln (III) metal complexes were measured in DMF and displayed an absorption maxima at 298 and 233nm with high extinction coefficient for the azomethine and oximino linkages of the free ligand HBMHSA assigned as π*← π transition (Table-2).

The visible spectral bands of Ln (III) complex were hypersensitive to stereochemistry. This may be probably attributed to the fact that the f-f transitions are very weak. The electronic spectra of the aqueous solutions of the nitrates of Tb(III), Nd(III) and Sm(III) are compared with the corresponding complexes. The data are summarized in Table-2.

The data indicate that the energy of *f–f* transitions in the complexes is slightly reduced compared to the corresponding aqua ions either because of the slight covalent interaction of the 4*f* orbital's with vacant ligand orbital's, leading to some delocalization with consequent reduction in inter-electronic repulsion (correlation energy) 20 or by increased nuclear

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shielding of the orbital's due to a slight covalent ligand–metal electron drift. The bonding parameter ($b^{1/2}$), the covalence parameter (*d*) and nephelauxetic ratio (β) have been calculated using the literature procedures[21-22].

The value of (1b) being less than unity[23] for the complexes, the small and positive values of the bonding parameter $b^{1/2}$ and Sinha's parameter δ% suggest the possibility of a partial covalent nature of the metal–ligand bond[21,24]. Based on electronic spectral studies, a coordination number of six around the metal ion is suggested[25-26].

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

Compound	λnm	ε (dm^3/mol /cm)	Transition	
HBMHSA	298	7132	$\pi^* \leftarrow \pi$	
	233	4595	$\pi^* \leftarrow \pi$	
[Nd $(BMHSA)_3$]	811	53	$^4F_{9/2} \leftarrow {}^4H_{5/2}$	β_{ave} = 0.9867
	752	187	$^4P_{13/2} \leftarrow {}^4H_{5/2}$	$b^{1/2}$ = 0.0665
	585	875	$^4P_{9/2} \leftarrow {}^4H_{5/2}$	δ% = 1.348
	519	3564	$^4P_{7/2} \leftarrow {}^4H_{5/2}$	η = 1.0270
[Tb $(BMHSA)_3$]	595	1145	$^7F_4 \leftarrow {}^5D_4$	
	547	2754	$^7F_5 \leftarrow {}^5D_4$	
	479	7325	$^7F_6 \leftarrow {}^5D_4$	
[La $(DMHSA)_3$]	395	108	MLCT	
	245	16478	MLCT	
[Sm $(DMHSA)_3$]	739	111	$^4F_{9/2} \leftarrow {}^4H_{5/2}$	β_{ave} = 0.9553
	465	4345	$^4P_{13/2} \leftarrow {}^4H_{5/2}$	$b^{1/2}$ = 0.0024
	436	5547	$^6P_{7/2} \leftarrow {}^4H_{5/2}$	δ% = 0.9553
	405	6978	$^4P_{9/2} \leftarrow {}^4H_{5/2}$	η = 1.0936

1.2 The PMR spectra of ligand HBMHSA and its La (III) metal complex:

PMR spectra were recorded using d6 DMSO as solvent and TMS was used as an internal standard. Spectral data of HBMHSA reveals two singlet peaks at 12.25 and 12.00δ. The intensity of the peaks suggests that these are due to single deshielded protons and assigned as oximino and phenolic protons respectively. The peak observed in free ligand HBMHSA at 12.25δ is absent in all prepared La (III) metal complex, suggested that oximino group deprotonated in complex formation[27-28].

Multiplet observed at in the region 6.8-7.8δ, 1, 2-disubstitted benzene ring and singlet peak reveals at 8.30δ (1H) assigned as methane (-CH=) group of HBMHSA. These entire group unchangeable in La (III) metal complex, indicated that their non-involvement in complex formation and also suggest monobasic character of HBMHSA ligand[29].

Table 3. PMR spectrum of HBMHSA and its metal complexes in d6 DMSO.

Compound	-OH (oximi)	-OH Phenolic	-CH=	Phenyl Rings
HBMHSA	12.25	12.00	8.30	6.8-7.8
$La(BMHSA)_3.NO_3$	-	12.00	9.01	6.8-7.8

1.3 FT (IR) spectra ligand HBMHSA and its Ln (III) metal complexes:

The important FT (IR) stretching frequencies are given in Table-4. The spectrum of HBMHSA ligand has broad absorption band at 3500cm^{-1} which assigned as oximino-OH is disappeared in metal complexes, indicated successfully complex formation through deprotonation.

In case of complexes a notable peak at 1604cm^{-1} of HBMHSA shows positive shift and appears in the range of [1644-1658cm^{-1}], this is attributed to azomethine (>C=NN) 30-31 stretching and its shift indicates that coordination of ligand in complexes through azomethine nitrogen atom[32-33]. Oximino group (>C=NO-) observed at 1558cm^{-1} in HBMHSA ligand is shifted to higher frequencies (1558-1593cm^{-1}) indicates that oximino nitrogen involve in complex formation[33].

FT (IR) spectral data of ligand HBMHSA and its Ln (III) metal complexes indicated that ligand HBMHSA coordinated to Ln (III) ions through nitrogen atoms only [LnN_6]. Some new medium to weak bands were also observed in the range (507-691cm^{-1}) in case of complexes of HBMHSA ligand has no absorption.

These new medium to weak bands are assigned as; ν(Ln-N) or/and ν(Ln→N) modes observed for various Ln (III) complexes. The partial IR data for HBMHSA

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ligand and their corresponding complexes are given in Table-4.

Table 4. IR spectral bands of the ligand (HBMHSA) and its metal complexes (cm^{-1}).

Assignments	HDMHSA	Nd (III)	Tb (III)	La (III)	Sm (III)
νOH Oximino	3500	-	-	-	-
Phenolic - OH	3131	3389	3314	3380	3385
νC=C Ar.	3046	3055	3047	3053	3155
νC=NN	1604	1645	1658	1644	1646
νC=NO	1558	1593	1588	1589	1544
νN-N	974	1008	1064	1008	1014
νN→O	---	1212	1229	1210	1228
νM-N	---	547	593	569	606
νM→N	---	509	507	541	523

IV. STRUCTURE OF COMPLEXES

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 anions inside the coordination sphere in the complexes. 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[34-37]. The possible structure of the complexes is given Figure-2.

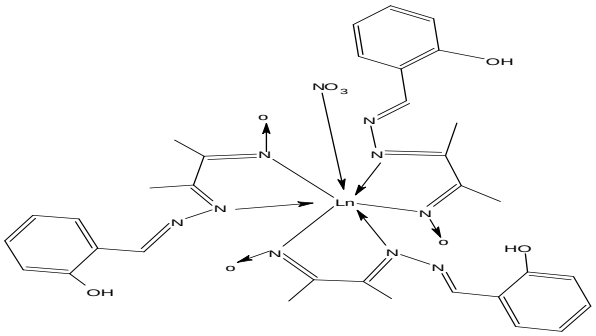

Fig 2. Structure of metal complexes of HBMHSA ligand.

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