



SYNTHESIS AND CHARACTERIZATION OF INNER TRANSITION METAL COMPLEXES OF *N''*-[(*Z*)-(4- FLUOROPHENYL)METHYLIDENE]-*N'''*-[(1*E*, 2*E*)-2- (HYDROXYIMINO)-1,2- DIPHENYLETHYLIDENE] THIOCARBONOHYDRAZIDE

Dr. Sharad Sankhe^{1*}, Mr. Shashank Parab²

Abstract

Inner transition metal complexes of the *N''*-[(*Z*)-(4-fluorophenyl)methylidene]-*N'''*-[(1*E*,2*E*)-2-(hydroxyimino)-1,2-diphenylethylidene]thiocarbonohydrazide (HBMTpFB) ligand with Sm(III), Gd(III), La(III), Nd(III), Dy(III), Pr(III), Tb(III), Lu(III), Ce(III) and Ho(III) have been prepared. Their structures are elucidated by elemental analysis, molar conductance and magnetic susceptibility measurements, FT(IR), and electronic spectra. The physicochemical and analytical data reveal that the Ln(III) complexes are composed as [M(BMTpFB)₂]. The 1:1 electrolytic behaviour of prepared Ln(III) complexes is suggested by molar conductivity data in nitrobenzene solvent (10⁻³ M) and seven coordinated geometry suggested by magnetic moment data of Ln(III) complexes. The FT(IR) spectra of lanthanide (III) complexes show that they are formed by a five-membered ring structure where the central atom is bonded to six nitrogen atoms.

Keywords: FT(IR), electronic spectra, and Molar conductance and magnetic susceptibility measurements.

¹*Professor, Department of Chemistry, Patkar-Varde College, Goregaon West, Mumbai-62, India.

²PhD scholar, Department of Chemistry, Patkar-Varde College, Goregaon West, Mumbai-62, India.

*Corresponding Author: Dr. Sharad Sankhe

*Professor, Department of Chemistry, Patkar-Varde College, Goregaon West, Mumbai-62, India.

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Introduction:

The inner transition metal complexes of benzilmonoximes formed coordination complexes have been investigated regarding their stability constants and antimicrobial activities¹⁻³. Benzilmonoxime and its derivatives are employed largely in the spectrophotometric evaluation and extraction of various transition and inner transition metal ions, and some of them are better-participating agents, useful in volumetric analysis⁴⁻⁵. The work on stability constant and biological activities of inner transition metal complexes formed by these oximes derivatives is very common⁶. The benzilmonoxime and its derivatives chelating ability have recently investigated as chelating agents⁷⁻⁸. The halo-benzaldehyde is an important derivative of benzilmonoximethiocarbohydrazide which have been reported to be one of the best analytical reagents⁹⁻¹⁰. No work has been reported on preparing and characterising the inner transition metal complexes of *p*-fluorobenzaldehyde derivative of α -benzilmonoximethiocarbohydrazide (HBMT_{*p*}FB) ligand. The preparation of *p*-fluorobenzaldehyde derivatives of benzilmonoximethiocarbohydrazide and its trivalent inner transition metal complexes have been reported first time. Hence the present research work describes the synthesis and characterization of Sm(III), Gd(III), La(III), Nd(III), Dy(III), Pr(III), Tb(III), Lu(III), Ce(III) and Ho(III) complexes of HBMT_{*p*}FB ligand by various physico-chemical and spectral techniques.

Experimental:

All solvents and reagents used were of AR grade. C, H, N and O elemental analysis data recorded on Thermo flinging FLASH -1112 series analyser. PMR spectral data were recorded on JEOL (Japan) ECZR series 600 MHz. Electronic absorption spectra were recorded on the JASCO V650 Uv-visible spectrophotometer and FT(IR) spectra on Perkin-Elmer spectrum-100 FT-IR spectrometer. The prepared Ln(III) metal complexes' magnetic susceptibility measurement was recorded on Gouy balance at 301K using calibrate Hg[Co(NCS)₄], and molar conduction was done using an ELICO-CM-180 conductivity meter.

The HBMT_{*p*}FB ligand was prepared by condensation between benzilmonoxime thiocarbohydrazide (0.10mole) and *p*-fluorobenzaldehyde (0.125mole) in ethanol. The final reaction mixture

was refluxed for 5h, cool and allowed to stand overnight at room temperature. Filter the yellow solid and wash with hot distilled water.

The lanthanide (III) metal complexes were prepared by mixing an aqueous Ln(III) nitrate salts with an ethanol solution of HBMT_{*p*}FB ligand in a 1:2 ratio. The reaction mixture pH was adjusted to 7.0 by 0.1N sodium hydroxide solution, and the final reaction mixtures were refluxed for 6-9h. The coloured solid complexes were collected by filtration, washed with hot water, dried and analysed.

Antimicrobial test:

The ligand and metal complexes were tested for antibacterial activity using a standard method against various Gram-positive (*S. aureus*, *B. subtilis*) and Gram-negative (*E. coli*, *P. aeruginosa*) and fungal (*Candida albicans*) strains. The filter paper disc agar diffusion method was utilised to identify the antibacterial activity. After incubating the disc of blotting paper at 37°C for 24 hours with a plate of sensitivity testing agar uniformly loaded with the test organism, the disc was examined for signs of growth. Diffusion of the ligand and complexes occurred away from the disc associated with the organisms' sensitivity. Resistance causes a narrower zone of inhibition or growth up to the disc's edge in strains sensitive to the ligand/complexes. After incubation, the typical inhibition gradient was determined.

Results and Discussion:

All the prepared trivalent lanthanide complexes are coloured solid non-hygroscopic, air-stable and soluble in common organic solvents. The Ln (III) complexes are analytical and physicochemical data suggest 1:2 metal-ligand stoichiometry (**Tablet-1**) for Sm(III), Gd(III), La(III), Nd(III), Dy(III), Pr(III), Tb(III), Lu(III), Ce(III) and Ho(III) complexes. These prepared Ln (III) complexes' molar conductivity values found in the range 26.38-27.27 Ω^{-1} mol²cm⁻¹ in 10⁻³ M nitrobenzene medium indicates their 1:1 electrolytic in nature¹¹⁻¹³.

All the prepared trivalent lanthanide complexes' magnetic moment data are illustrated in **Table-1**. The Sm(III), Gd(III), La(III), Nd(III), Dy(III), Pr(III), Tb(III), Lu(III), Ce(III) and Ho(III) complexes magnetic moment values suggests that they are paramagnetic and La(III) and Lu(III) complexes are diamagnetic in nature¹⁴⁻¹⁷.

Table-1: Analytical and physical data of the ligand and its lanthanide (III) metal complexes

Compound	Colour	Yield %	M.P. / Dec point°C	Elemental Analysis							Magnetic Moments (B.M.)	Electrical Conductance 10^{-3} M(in NB) mhos
				% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% O Found (Calcd)	% S Found (Calcd)	% F Found (Calcd)		
HBMTpFB	Yellow	81.61	209	-	62.99 (62.92)	4.33 (4.28)	16.70 (16.62)	3.81 (3.75)	7.64 (7.55)	4.53 (4.50)	-	-
[Tb(BMTpFB) ₂]	Brown	80.69	239	10.42 (10.29)	51.91 (51.00)	3.34 (3.21)	14.68 (14.50)	6.29 (6.20)	6.29 (6.20)	6.29 (6.20)	9.52	0.150
[La(BMTpFB) ₂]	Yellow	86.47	244	10.21 (10.33)	56.86 (56.86)	3.61 (3.66)	15.07 (15.08)	3.43 (3.45)	6.83 (6.89)	4.08 (4.09)	Dia	0.740
[Dy(BMTpFB) ₂]	White	80.23	238	10.81 (11.47)	55.70 (55.91)	3.59 (3.60)	14.57 (14.83)	3.38 (3.39)	6.58 (6.78)	4.00 (4.02)	10.46	0.489
[Gd(BMTpFB) ₂]	White	81.25	243	10.45 (10.65)	55.89 (56.12)	3.51 (3.61)	14.82 (14.88)	3.41 (3.40)	6.71 (6.80)	3.98 (4.00)	7.79	0.996
[Nd(BMTpFB) ₂]	White	79.77	241	10.24 (10.32)	56.41 (56.64)	3.58 (3.65)	14.88 (15.02)	3.35 (3.43)	6.85 (6.87)	4.00 (4.08)	3.60	0.679
[Sm(BMTpFB) ₂]	Yellow	80.14	239	10.72 (10.79)	55.91 (56.40)	3.54 (3.63)	14.68 (14.95)	3.29 (3.42)	6.79 (6.84)	4.05 (4.06)	3.54	0.249
[Lu(BMTpFB) ₂]	Green	81.26	244	14.70 (14.03)	51.86 (52.23)	3.26 (3.36)	13.68 (13.85)	3.09 (3.17)	6.29 (6.33)	3.65 (3.76)	Dia	0.336
[Pr(BMTpFB) ₂]	White	78.88	238	10.11 (10.20)	56.70 (56.78)	3.59 (3.66)	14.97 (15.05)	3.38 (3.44)	6.78 (6.88)	4.00 (4.09)	3.60	1.172
[Ce(BMTpFB) ₂]	Yellow	81.45	243	10.00 (10.05)	52.79 (52.81)	3.41 (3.66)	14.92 (15.06)	3.41 (3.44)	6.71 (6.83)	4.08 (4.09)	3.45	0.778
[Ho(BMTpFB) ₂]	L. Brown	77.89	245	14.03 (14.13)	55.29 (52.31)	3.45 (3.59)	14.33 (14.79)	3.32 (3.38)	6.72 (6.78)	4.00 (4.01)	1042	11.515

PMR Spectra:

The PMR spectrum of ligand in *d*₆ DMSO solution exhibits an acidic peak at δ 10.551ppm due to the -OH proton of the oximino group¹⁸. The PMR spectrum of [La(BMTpFB)₂] and [Lu(BMTpFB)₂] complexes reveals the absence of the proton signal due to the N-OH group indicating that the proton signal due to oximino N-OH group is replaced on

complexation with the Ln(III) metal ion¹⁹⁻²⁰. The ¹H NMR spectrum of HBMTpFB ligand and La(III) and Lu(III), in DMSO-*d*₆ solvent show a singlet signal at \square 9.86 ppm equivalent to two protons assigned to -NH- group and singlet signal at \square 8.04 ppm equivalent to the first proton assigned to =CH- group. The multiple signals at \square 7.27-7.70ppm are due to aromatic hydrogen of carbon of ligand and metal complexes²¹⁻²².

Table-2: PMR spectral data of HBMTIFB ligand and its metal complexes

Compound	NOH	-NH-	=CH-	Aromatic Proton
HBMTpFB	10.596	12.436	8.290	6.789-7.965
[La(BMTpFB) ₂]	-	12.397	8.289	7.270-7.926
[Lu(BMTpFB) ₂]	-	12.430	8.291	6.789-7.965

FT(IR) spectra:

The HBMTpFB ligand and its Ln(III) metal complexes FT(IR) spectra have been recorded in the 4000 – 400 cm^{-1} region. The FT(IR) spectrum of the HBMTpFB ligand exhibits a broad band at 3287 cm^{-1} due to oximino (N-OH) group. After complexation, this band disappeared, indicating that the HBMTpFB ligand coordinated to central trivalent lanthanide metal ion through oximino group *via* deprotonation of this group²³⁻²⁴.

In the FT(IR) spectrum of the HBMTpFB ligand, strong and sharp bands were observed at 1475 and

1627 cm^{-1} , which have been assigned to $\nu(>\text{C}=\text{NOH})$ and $\nu(>\text{C}=\text{NN}-)$ vibrations²⁵⁻²⁷. These vibrations are shifted to lower sites in the Ln(III) metal complexes FT(IR) spectra confirming that both groups are participating in coordination with Ln(III) metal ions through nitrogen atoms²⁸. The non-ligand bands observed in FT(IR) spectra of inner transition metal complexes in the region 469-475 and 499-508 cm^{-1} attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}\rightarrow\text{N})$ vibrations respectively²⁹⁻³⁰.

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

Assignments	HBMTpFB	Nd(III)	Tb(III)	La(III)	Dy(III)	Sm(III)	Ho(III)	Tb(III)	Pr(III)	Ce(III)	Gd(III)
$\nu\text{OH Oximino}$	3101	-	-	-	-	-	-	-	-	-	-
N-H	3240	3337	3331	3335	3337	3336	3330	3339	3345	3340	3337
$\nu\text{C}=\text{C Ar.}$	2957	3085	3087	3083	3080	3083	3086	3087	3081	3086	3091
$\nu\text{C}=\text{NN}$	1597	1473	1601	1599	1595	1590	1593	1596	1599	1600	1599
$\nu\text{C}=\text{NO}$	1535	1460	1463	1467	1468	1460	1459	1458	1459	1460	1460
$\nu\text{N}-\text{N}$	1025	1045	1001	1009	1006	1007	1001	1006	1009	1010	1014
$\nu\text{N}\rightarrow\text{O}$	-	999	957	965	922	956	978	977	969	974	966
$\nu\text{M}-\text{N}$	-	554	508	499	507	500	503	505	508	504	499
$\nu\text{M}\rightarrow\text{N}$	-	513	467	469	475	472	470	473	475	474	473

Electronic Spectra:

The prepared Ln(III) complexes' electronic spectral data are given in **Table-4**. In the [Ce(BMTpFB)₂] complex electronic spectrum in chloroform solution, three absorption bands are exhibited at 687, 275, and 245 nm, which are attributed to ²F_{5/2}→²D_{5/2}, ²F_{5/2}→²D_{3/2} and metal to ligand charge transitions respectively³¹⁻³². These are consistent with most of the six coordinated geometry. The Gd(III) complex electronic spectrum observed bands 693, 654, 617, 599 and 565, which attributed to transitions ⁵D₀→⁷F₄, ⁵D₀→⁷F₃, ⁵D₀→⁷F₂, ⁵D₀→⁷F₁ and ⁵D₀→⁷F₀, respectively, for six coordinated octahedral geometry confirmed by this complex magnetic moment found to be 7.81 B.M³³⁻³⁵.

The electronic spectra of the La(III) and Lu(III) complexes charge transfer bands at 503-510 and 320-330nm. The [Nd(BMTpFB)₂] complex electronic absorption spectrum exhibited seven bands at 798, 689, 583 and 525nm attributed to ⁴I_{9/2}→²F_{5/2}, ²H_{9/2}, ⁴I_{9/2}→²S_{3/2}, ⁴F_{7/2}, ⁴I_{9/2}→⁴G_{5/2}, ⁴F_{7/2}, ⁴I_{9/2}→²G_{9/2}, and ⁴I_{15/2}→⁴G_{11/2} transitions respectively³⁶⁻³⁷. The observed magnetic moment of this complex was 3.65 BM. and absorptions suggest a seven-coordinated geometry for this

complex³⁸. The high green-coloured [Ho(BMTpFB)₂] complex exhibited three bands at 588, 497 and 421nm due to ⁴I₈→⁵F₄, ⁴I₈→⁵G₆ and ⁴I₈→⁵G₄ transitions respectively³⁹⁻⁴⁰. For six octahedral environments around Ho(III) in its complexes, which is confirmed by the observed magnetic value at 10.30 B.M. On the other hand, the bands observed for Sm (III) complex corresponded to the 4f-4f transition⁴¹⁻⁴³ from the ground state ⁶H_{5/2} to the excited states of ⁴F_{3/2}, ⁴F_{9/2}, ⁶F_{11/2}, and ⁴G_{5/2}.

Transitions from the ground levels of ³H₄, ⁴I_{9/2}, ⁶H_{5/2}, ⁸S_{7/2}, and ⁶H_{15/2} to the excited J-levels of the 4f-configuration cause the absorption bands of praseodymium(III), neodymium(III), samarium(III), gadolinium(III), and dysprosium(III) to appear in the visible and near-infrared region. In the chloroform solutions of these complexes, some redshift or nephelauxetic effect is observed. The presence of aquo compounds is usually accepted as evidence of a higher degree of covalency than this redshift. The intensity of the bond has been significantly increased in all complexes. The nephelauxetic effect in these chelate complexes has been calculated using the redshift of the hypersensitive bands⁴⁴⁻⁵⁰.

Table-3: Electronic absorption spectral data of HBMTpFB ligand and its Ln(III) metal complexes

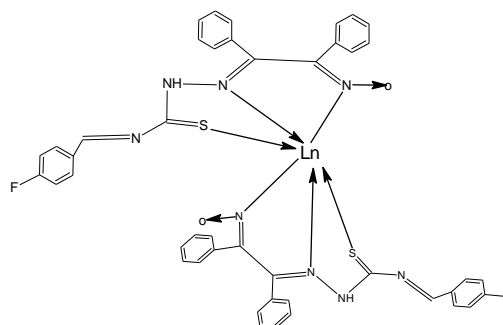
Compound	λnm	ε dm ³ /mol/cm	Transition	
HBMTpFB	375	7367	π→π*	
	272	9478	π→π*	
	227	11392	π→π*	
[Ce(BMTpFB) ₂]	687	103	² F _{5/2} → ² D _{5/2}	β _{ave} = 0.9968 b ^{1/2} = 0.0402 δ% = 0.3258, η = 0.0016
	275	127	² F _{5/2} → ² D _{3/2}	
	245	5698	MLCT	
[Tb(BMTpFB) ₂]	625	1170	⁵ D ₄ → ⁴ F ₃	β _{ave} = 0.9952, η = 0.0024, b ^{1/2} = 0.0480, δ% = 0.0475
	592	3257	⁵ D ₄ → ⁷ F ₄	
	546	7568	⁵ D ₄ → ⁷ F ₅	
	492	9291	⁵ D ₄ → ⁷ F ₆	
[La BMTpFB) ₂]	392	110	MLCT	
	243	13541	MLCT	
[Dy(BMTpFB) ₂]	740	589	⁴ H _{15/2} → ⁴ I _{15/2}	β _{ave} = 0.9908, η = 0.0046, b ^{1/2} = 0.0674, δ% = 0.9263
	450	4952	⁴ H _{15/2} → ⁴ I _{15/2}	
[Gd(BMTpFB) ₂]	693	1659	⁵ D ₀ → ⁷ F ₄	β _{ave} = 0.9942, η = 0.0029, b ^{1/2} = 0.0532, δ% = 0.5859
	654	1035	⁵ D ₀ → ⁷ F ₃	
	617	1978	⁵ D ₀ → ⁷ F ₂	
	599	1647	⁵ D ₀ → ⁷ F ₁	
	565	2345	⁵ D ₀ → ⁷ F ₀	
[Ho(BMTpFB) ₂]	588	675	⁴ I ₈ → ⁵ F ₄	β _{ave} = 0.9933, η = 0.0034, b ^{1/2} = 0.0539, δ% = 0.6738
	497	4589	⁴ I ₈ → ⁵ G ₆	
	421	9786	⁴ I ₈ → ⁵ G ₄	
[La(BMTpFB) ₂]	377	119	MLCT	
	239	13600	MLCT	
[Nd(BMTpFB) ₂]	801	176	⁴ I _{9/2} → ² H _{9/2}	β _{ave} = 0.9979, η = 0.00106, b ^{1/2} = 0.0294, δ% = 0.2113
	741	456	⁴ I _{9/2} → ² F _{7/2} , ⁴ F _{5/2}	
	581	1089	⁴ I _{9/2} → ² G _{5/2} , ² G _{7/2}	
	520	1345	⁴ I _{9/2} → ² K _{13/2} , ⁴ G ₇ , ⁴ G _{9/2}	
	431	3069	⁴ I _{9/2} → ⁴ P _{1/2}	

Antimicrobial activity:

Antimicrobial activity of Schiff base ligand and their metal complexes at 10, 20, and 30 $\mu\text{g/ml}$ against Gram-positive *S. aureus*, *B. subtilis*) and Gram-negative (*E. coli*, *P. aeruginosa*) bacterial and fungal species - *Candida albicans*. Except for *Candida albicans*, against which the Schiff base ligand showed moderate activity at 10 and 20 $\frac{\mu\text{g}}{\text{ml}}$ concentrations. Although *E. coli* and *P. aeruginosa* showed little activity, *S. aureus*, *B. subtilis*, and *C. albicans* showed very good activity upon complexation to generate Nd(III) complexes. At concentrations of 10, 20, and 30 $\mu\text{g/ml}$, the Sm(III) complex was also effective against all the species except *E. coli*, which was resistant to the La(III) complex. Ho(III) complexes are effective against *S. aureus*, *B. subtilis*, *E. coli*, *P. aeruginosa*, and *C. albicans*. Compared to Ho(II) and Sm(II) complexes, Nd(III) was shown to be the most active in the investigation. The metal complexes' activities increased with increasing concentration in the following order: Nd>Ho>Sm. The antibacterial activity is enhanced by complexation because the complexes display higher potency-related activities than the free ligand. Overtone's concept and Tweedy's chelation theory, which propose that the lipid membrane surrounding the cell favours the passage of only lipophilic substances, explain the enhanced activity of the metal complexes compared to their parent ligands.

Conclusion

The condensation of p-fluorobenzaldehyde with benzilmonoximethiocarbohydrazide and its Ln (III) complexes is reported in this study as the manufacture of a Schiff base HBMTpFB ligand. The nitrogen of the azomethine ligand in the Schiff base is connected with the metal ion. Infrared spectrum evidence confirms this. Octahedral geometries are supported by observations of electronic spectral bands for Ln(III). The complexes are non-electrolytes, as shown by their low molar conductivity in nitrobenzene. Except for petroleum ether and ethyl acetate, all the complexes are air-stable and soluble in at least some of the tested solvents. The in vitro antimicrobial assay demonstrates that the complexes are more active than the free ligand.



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