



Synthesis and Characterization of Tb(III), Yb(III), Lu(III), Eu(III) and Ce(III) complexes with diacetylmonoximethiocarbohydrazide-*p*-bromobenzaldehyde

Vinay H. Singh and Gajanan C. Upadhye

Konkan Gyanpeeth Karjat College of ASC, Ladivali, Karjat, Raigad, Maharashtra-410201

Abstract

Condensation of *p*-bromobenzaldehyde with diacetylmonoximethiocarbohydrazide potentially yielded tridentate diacetylmonoximethiocarbohydrazide-*p*-bromobenzaldehyde (HBMHpBB) which was utilized in the synthesis of Tb(III), Yb(III), Lu(III), Eu(III) and Ce(III) complexes of the type $[M(\text{DMTpBB})_3\text{NO}_3]$ in presence of nitrate counter ion. Structure of these Ln(III) complexes were elucidated by physico-chemical studies, magnetic susceptibility, molar conductance studies, electronic and FT(IR) spectra. Spectral data revealed that the ligand HDMPpBB coordinated to Ln(III) metal ion through oximino and azomethine nitrogen atoms and sulphur atom of thiocarbo group.

Keywords: diacetylmonoximethiocarbohydrazide, *p*-bromobenzaldehyde, thiocarbohydrazide

Introduction:

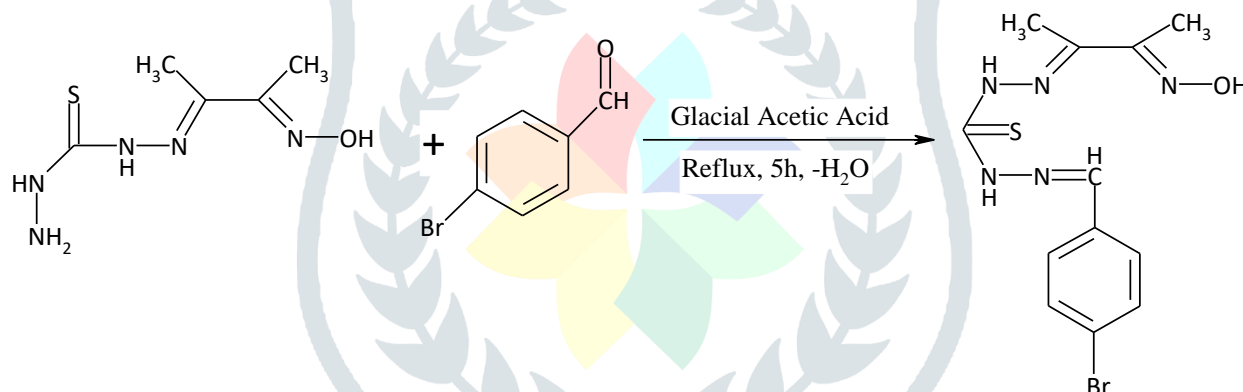
In the coordination chemistry of inner transition elements, Schiff bases have distinctly their importance as chelating ligands¹⁻². Among the variety and phenomenal number of Schiff base complexes from diacetylmonoxime find extensive applications in various fields³. The imino-oximes based Schiff bases had been remarkably found to exhibit good bacterial activity and are well documented in literatures⁴. Condensation of diacetylmonoxime with thiocarbohydrazide produced a tridentate ligand, which are forming a series of transition and inner transition metal complexes under well defined conditions⁵. In present communication we report, the synthesis and characterization of a Tb(III), Yb(III), Lu(III), Eu(III) and Ce(III) complexes, with HDMPpBB ligand with nitrate counter anion. IUPAC name of the prepared ligand is *N*'-[*(E)*-(2-bromophenyl)methylidene]-*N*''-[*(2E,3E)*-3-(hydroxyimino)butan-2-ylidene]thiocarbohydrazide.

Experimental:

Analytical grade solvents and chemicals were purchased from Merck and Loba chemie. The Ln(III) metal contents of prepared complexes were estimated volumetrically and gravimetrically. FT(IR) spectra were recorded on Perkin-Elmer spectrum-100 FT-IR spectrometer. PMR spectra of HDMPBB ligand and its Ln(III) complex were recorded on JEOL (Japan) ECZR 600 MHz NMR spectrometer. Electronic absorption spectra were recorded using JASCO V650 UV-visible spectrophotometer at 301K. The molar conductance of Ln(III) complexes were conducted using nitrobenzene as solvent on a ELICO CM-180 conductivity meter. Magnetic moments were quantified with Gouy balance at 301K.

Synthesis of the HDMPBB:

Coordinating ligand i.e. diacetylmonoximethiocarbohydrazide (HDMPBB) was prepared by literature method⁶. A hot ethanolic solution of diacetylmonoximethiocarbohydrazide (0.01mol) was mixed with *p*-bromobenzaldehyde (0.0125mol) dissolved in 30 ml of hot ethanol. The reaction mixture was permitted to reflux for 5h and after completion of reaction as monitored on TLC, the reacting mixture was brought at room temperature. The ligand in solid form were collected after filtration, subsequently washed with hot distilled water and dried under vacuum.

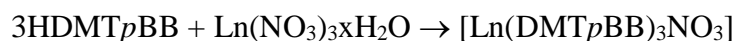


A general method of synthesis of Ln(III) metal complexes:

An aqueous solution of corresponding Ln(III) nitrate salt (0.01M) was added to ethanolic solution of HDMPBB ligand (0.03M). Further, the reaction mixture was refluxed for 7-10h after adjusting pH to 7. On cooling, coloured solid Ln(III) complex was separated from the solution. Solid complex was collected as residue by filtration followed by washing with hot distilled water and dried under vacuum.

Results and Discussion:

The Ln(III) complex formation can be represented by the following equation;



The analytical and physical data of HDMPBB ligand and its Ln(III) complexes are illustrated in **Table-1**. All lanthanide (III) complexes are colored solid, air stable, non hygroscopic and possess good keeping qualities. They are soluble in common organic solvents. The Ln(III) complex formation was ascertained primarily on the basis of their magnetic susceptibility and conductance measurement, elemental analytical data. The values of molar conductivity for prepared Ln(III) complexes support in favour of 1:1 electrolytic nature⁷⁻⁸. Analytical data indicates

that Ln(III) complexes occurred in 1:3 molar ratio (metal: ligand). The structures of Ln(III) complex of the HDMPBB ligand were elucidated by PMR, FT(IR) and electronic absorption spectral studies.

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

Compound	Color	Yield %	M.P. point °C	Elemental Analysis							Magnetic Moments (B.M.)	Electrical Conductance 10^{-3} M(in DMF) mhos
				% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% O Found (Calcd)	% S Found (Calcd)	% Br Found (Calcd)		
HDMHPBB	Yellow	79.38	209	-	40.46 (39.92)	3.96 (3.98)	19.66 (19.02)	4.49 (4.65)	4.49 (4.65)	9.00 (8.70)	-	-
[Tb(DMHPBB) ₃]N O ₃	Brown	75.61	241	11.91 (11.81)	32.39 (32.02)	2.92 (2.90)	16.79 (16.49)	7.20 (7.16)	7.20 (7.11)	17.97 (17.90)	9.53	23.77
[Yb(DMHPDB) ₃]N O ₃	Brown	74.86	239	12.84 (12.30)	32.05 (31.44)	2.89 (2.86)	16.62 (16.53)	7.12 (7.11)	7.12 (7.09)	17.84 (17.80)	4.51	29.06
[Lu(DMHPBB) ₃]N O ₃	Orange	79.05	241	11.26 (11.17)	32.00 (32.01)	2.89 (2.79)	16.59 (16.51)	7.11 (7.08)	7.11 (7.09)	17.80 (17.66)	-	24.85
[Eu(DMHPBB) ₃]N O ₃	Yellow	82.24	238	11.45 (11.09)	32.56 (32.19)	2.94 (2.93)	16.88 (16.37)	7.24 (7.20)	7.24 (7.21)	18.06 (17.88)	3.55	23.01
[Ce(DMHPBB) ₃]N O ₃	Brown	79.79	244	10.65 (10.14)	32.85 (32.33)	2.97 (2.92)	17.03 (16.79)	7.30 (7.20)	7.30 (7.25)	18.20 (17.99)	2.42	20.49

The FT(IR) spectrum of HDMPBB ligand exhibited a band at 3317 cm^{-1} which is characteristic of (-OH) vibration of oximino moiety. After complexation, this band disappeared and suggested that this group participated in complexation⁹. The sharp peak due to azomethine, oximino and thiocarbo groups are observed at 1617 , 1571 and 1089 cm^{-1} respectively in FT(IR) spectrum of HDMPBB ligand¹⁰⁻¹². These peaks are shifted to lower side by about $31-45\text{ cm}^{-1}$ in all the Ln(III) complexes, indicating that these groups are involved in coordination *via* nitrogen atoms of azomethine and oximino groups and sulphur atom of thiocarbo group. In complexes' spectrum, three well defined peaks are obtained at 1020 , 1343 and 1381 cm^{-1} . Here $\nu_5-\nu_1$ is about 148 cm^{-1} which proposed that the nitrate group is coordinated in a monodentate manner. The novel bands exhibited in all Ln(III) complexes in the region $496-500$ and $515-524\text{ cm}^{-1}$ which can be correlated to $\nu(\text{M-N})$ and $\nu(\text{M}\rightarrow\text{N})$ vibrations respectively.

Table-2: FT(IR) spectral bands of the ligand (HDMPBB) and its metal complexes (cm⁻¹)

Assignments	HDMPBB	Tb(III)	Yb(III)	Lu(III)	Eu(III)	Ce(III)
vOH Oximino	3417	-	-	-	-	-
N-H	3273	3316	3348	3226	3304	3185
vC=C Ar.	3173	3119	3121	3118	3118	3140
vC=NN	1617	1603	1596	1598	1603	1602
vC=NO	1571	1505	1529	1540	1540	1535
vC=S	1089	1033	1037	1033	1032	1035
vN→O	-	1008	1007	1009	1007	1008
vPh-Br	820	827	848	855	851	851
vM-N	-	533	546	536	539	536
vM←N	-	523	522	528	526	521
vM←S	-	505	504	508	505	509

PMR spectra:

The HDMPBB ligand's PMR spectrum exhibited sharp acidic peak at δ 11.75ppm due to v(OH) group. The absence of this peak in PMR of [Lu(DMPBB)₃NO₃] complex suggested that this group involved in coordination via deprotonation. The multiplet signal at δ 7.20-7.40ppm in PMR spectrum of HDMPBB ligand and its [Lu(DMPBB)₃NO₃] complex can be due to characteristic aromatic protons. A sharp singlet observed at δ 9.10 ppm in both compounds can be assigned to methine (-CH=) group.

Electronic spectra:

The electronic spectrum of Tb(III) complex exhibited four bands at 618, 588 545 and 491 cm⁻¹ which is assigned to transitions like ⁵D₄→⁷F₃, ⁵D₄→⁷F₄, ⁵D₄→⁷F₅ and ⁵D₄→⁷F₆ respectively. Observed five bands for paramagnetic orange colored [Yb(DMPBB)₃NO₃] complex at 725, 705, 600, 449 and 359 cm⁻¹ can be result of ⁴A_g→²T_{1g}, ⁴A_g→²E_{1g}, ⁴A_g→⁴T_{2g}, ⁴A_g→⁴T_{1g}(F) and ⁴A_g→⁴T_{1g}(P) transition respectively¹³.

The diamagnetic [Lu(DMPBB)₃NO₃] complex exhibited¹⁴ a metal to ligand band at 430 and 273 cm⁻¹. The Eu(III) complex exhibited five peaks at 706, 649, 611, 592 and 577cm⁻¹ which is assigned to transition ⁵D₀→⁷F₄, ⁵D₀→⁷F₃, ⁵D₀→⁷F₂, ⁵D₀→⁷F₁ and ⁵D₀→⁷F₀ respectively¹⁵.

The paramagnetic [Ce(DMPBB)₃NO₃] complex peaks exhibited at 589 and 545cm⁻¹ due to ²D→²F_{7/2} and ²D→²F_{5/2} transitions respectively¹⁶. For solutions of these complexes in solvent such as chloroform, some nephelauxetic effect or red shift is observed. This nephelauxetic effect is usually accepted as stronger evidence of covalency than the presence of aqua compounds. In all prepared lanthanide (III) complexes, there is a significant increase in the intensity of the observed band, and this nephelauxetic effect (b) is calculated using hypersensitive bands. Using the below expression, the Sinha parameters (%), covalence factor (b^{1/2}), and covalency angular overlap parameter (η) were calculated²⁰ from the values.

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

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

$$\delta\% = [(1-\beta)/\beta] \times 100$$

In these coordination compounds, the $\delta\%$ and $(1-\beta)$ values are positive showing that, in contrast to the link between the aqua ion and the metal ion, the bond between the ligand and the metal ion is covalent. The angular overlap (η) and bonding parameter ($b^{1/2}$) values are both positive indicating that there is covalent bonding¹⁷⁻²⁰.

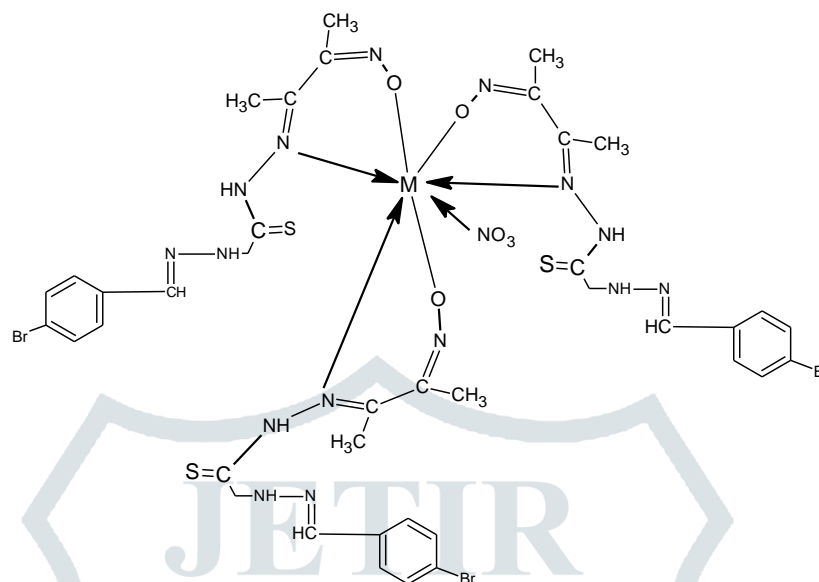
Table-2: Electronic absorption spectral data of HDMT*p*BB ligand and its Ln(III) metal complexes

Compound	λ_{nm}	ϵ (dm ³ /mol/cm)	Transition	
HDMH <i>p</i> BB	353	7740	$\pi \rightarrow \pi^*$	
	274	10730	$\pi \rightarrow \pi^*$	
	225	12756	$\pi \rightarrow \pi^*$	
[Tb(DMT <i>p</i> BB) ₃]NO ₃	618,	985	$^5D_4 \rightarrow ^7F_3$,	$\beta_{ave} = 0.9799$, $\eta = 6.3375$, $b^{1/2} = 0.6999$, $\delta\% = 0.0296$
	588	3064	$^5D_4 \rightarrow ^7F_4$,	
	545	7789	$^5D_4 \rightarrow ^7F_5$	
	491	12645	$^5D_4 \rightarrow ^7F_6$	
[Lu(DMT <i>p</i> BB) ₃]NO ₃	430	8369	MLCT	
	273	10567	MLCT	
[Ce(DMT <i>p</i> BB) ₃]NO ₃	520	6578	$^5F_5 \rightarrow ^2D_{3/2}$	$\beta_{ave} = 0.9959$, $\eta = 0.00205$, $b^{1/2} = 0.0442$, $\delta\% = 0.410$
	410	9354	$^5F_5 \rightarrow ^2D_{5/2}$	
Eu(DMT <i>p</i> BB) ₃]NO ₃	706	1450	$^5D_0 \rightarrow ^7F_4$	$\beta_{ave} = 0.9942$, $\eta = 0.00292$, $b^{1/2} = 0.0531$, $\delta\% = 0.5860$
	649	3680	$^5D_0 \rightarrow ^7F_3$	
	611	8854	$^5D_0 \rightarrow ^7F_2$	
	592	11345	$^5D_0 \rightarrow ^7F_1$	
[Yb(DMT <i>p</i> BB) ₃]NO ₃	725	9580	$^4A_g \rightarrow ^2T_{1g}$	$\beta_{ave} = 0.9918$, $\eta = 0.00412$, $b^{1/2} = 0.0635$, $\delta\% = 0.8249$
	705	9750	$^4A_g \rightarrow ^2E_{1g}$	
	600	10980	$^4A_g \rightarrow ^4T_{2g}$	
	449	11345	$^4A_g \rightarrow ^4T_{1g}(F)$	
	359	12547	$^4A_g \rightarrow ^4T_{1g}(P)$	

Conclusion:

The geometry, physico-chemical and spectral data advising that HDMT*p*BB ligand and the lanthanide (III) ions were complexed with nitrogen, oxygen and sulphur atoms of the higher carbohydrazide group. The metal:ligand

ratio in trinuclear lanthanide (III) complexes of HDMTpBB ligand is 1:3. All prepared complexes of HBMTpBB ligand have been assumed to follow seven coordinate geometry and the results are in good agreement with the proposed structure for the efficient lanthanide (III) complexes.



Where: Ln = Tb(III), Yb(III), Eu(III), Lu(III) and Ce(III)

References:

1. Khalil E, Mahmoud W and Mohamed G; Synthesis, Spectral, Thermal and Biological Studies of Some Transition and Inner Transition Schiff base Metal Complexes; *Egyptian Journal of Chemistry*; **2021**, 1:64(7), 3555-71.
2. Khalil EA and Mohamed GG; Preparation, spectroscopic characterization and antitumor-antimicrobial studies of some Schiff base transition and inner transition mixed ligand complexes; *Journal of Molecular Structure*; **2022**, 5:1249, 131612.
3. Maity D, Drew MG, Godsell JF, Roy S and Mukhopadhyay G; Synthesis and characterization of Cu (II) complexes of tetradentate and tridentate symmetrical Schiff base ligands involving o-phenelenediamine, salicylaldehyde and diacetylmonoxime; *Transition Metal Chemistry*; **2010**, 35(2), 197-204.
4. Sawant DC and Deshmukh RG; Square Planar Cobalt (II) complexes of chloro-substituted hydroxy-imino ligands containing sulphur; *Asian Journal of Research in Chemistry*; **2018**, 30;11(2), 298-306.
5. Dash DC, Mohapatra RK, Ghosh S and Naik P; Synthesis and characterization of some homo binuclear UO^{2+} , Th^{4+} , ZrO^{2+} and VO^{2+} complexes with Schiff base monohydrazone derivatives; *J. Indian Chem. Soc.*; **2009**, 86, 874-7.
6. Dash DC, Mahapatra A, Mahapatra RK, Ghosh S and Naik P; *Ind J of Chem.*; **2008**, 47A, 1009-1013.
7. Makode JT, Yaul AR, Bhadange SG and Aswar AS; Physicochemical characterization, thermal, and electrical conductivity studies of some transition metal complexes of bis-chelating Schiff base; *Russian Journal of Inorganic Chemistry*; **2009**, 54(9), 1372-7.

8. Kaya I, Bilici A and Saçak M; Study on synthesis, characterization, thermal stability and conductivity properties of a new conjugated oligoazomethine and some of its metal complexes; *Journal of Inorganic and Organometallic Polymers and Materials*; **2009**, 19(4), 443-53.
9. Laila A, Ahmed M, Rafet M and Shimag M; Sonochemical synthesis, DNA binding, antimicrobial evaluation and *in vitro* anticancer activity of three new nano-sized Cu(II), Co(II) and Ni(II) chelates based on tridentate NOO imine ligands as precursors for metal oxides; *J of Photochem and Photobiology*; **2016**, 162, 298-308.
10. Shankar K, Rohini M, Ravinder Reddy P and Ho M; Synthesis of tetraazo macrocyclic Pd(II) complexes: antibacterial and catalytic studies; *J of the Ind Chem Soc*; **2009**, 86.
11. Kinnojiia P and Sahdev; Synthesis, characterization and antibacterial activities of titanium complexes with Schiff bases derived from benzofuran; *Ori J of Chem*; **2011**, 27(1), 239-243.
12. Ibrahim O, Mohamed M and Refat M; Synthesis and characterization of medical and physical applications of metal complexes of Schiff bases in nano sized shape: Mg(II), Cd(II) and Ba(II) Schiff base complexes; *IJRSET*; **2013**, 2(11), 6355-6370.
13. Zapała L, Kosińska M, Woźnicka E, Byczyński Ł and Zapała W; Synthesis, spectral and thermal study of La (III), Nd (III), Sm (III), Eu (III), Gd (III) and Tb (III) complexes with mefenamic acid; *Journal of Thermal Analysis and Calorimetry*; **2016**, 124(1), 363-74.
14. Czajka B, Bocian B, Ferenc W; Investigation of 5-chloro-2-methoxybenzoates of La (III), Gd (III) and Lu (III) Complexes; *Journal of thermal analysis and calorimetry*; **2002**, 1, 67(3), 631-42.
15. Wang BD, Yang ZY and Li TR; Synthesis, characterization, and DNA-binding properties of the Ln (III) complexes with 6-hydroxy chromone-3-carbaldehyde-(2'-hydroxy) benzoyl hydrazone; *Bioorganic & medicinal chemistry*; **2006**, 1;14(17), 6012-21.
16. Shebl M, Khalil SM and Al-Gohani FS; Preparation, spectral characterization and antimicrobial activity of binary and ternary Fe (III), Co (II), Ni (II), Cu (II), Zn (II), Ce (III) and UO₂ (VI) complexes of a thiocarbohydrazone ligand; *Journal of Molecular Structure*; **2010**, 10, 980(1-3), 78-87.
17. Sengupta SK, Pandey OP, Rai A and Sinha A; Lanthanum (III) and praseodymium (III) complexes of acetylferrocenyl mercaptotriazoles; *Transition metal chemistry*; **2000**, 25(2), 150-3.
18. Holz RC and Thompson LC; Spectroscopically distinct geometrical isomers in a single crystal. Characterization of the eight-coordinate adducts of tris (dipivaloylmethanato) lanthanide (III) with 2, 9-dimethyl-1, 10-phenanthroline; *Inorganic Chemistry*; **1993**, 32(23), 5251-6.
19. Peacock RD and Weakley TJ; Heteropolytungstate complexes of the lanthanide elements. Part II. Electronic spectra: a metal–ligand charge-transfer transition of cerium (III); *Journal of the Chemical Society A: Inorganic, Physical, Theoretical*; **1971**, 1937-40.
20. Regulacio MD, Pablico MH, Vasquez JA, Myers PN, Gentry S, Prushan M, Tam-Chang SW and Stoll SL; Luminescence of Ln (III) dithiocarbamate complexes (Ln= La, Pr, Sm, Eu, Gd, Tb, Dy); *Inorganic chemistry*; **2008**, 3, 47(5), 1512-23.