



# “Studies On Inner Transition Metal Complexes With (*N'*)-[(1*E*)-2-Imino-1, 2- Diphenylethylidene]Thiocarbohydrazide”

Patil Jayashree Shailesh <sup>1\*</sup>

<sup>1</sup>Department of Chemistry, J.S.M. College, Alibag, Raigad

## Abstract:

The title ligand and its inner transition metal complexes La(III), Nd(III), and Pr(III) have been prepared. The ligand is made by combining  $\alpha$ -Benzilmonoxime and thiocarbohydrazide in the presence of Conc. HCl, and the inner transition metal complexes are made by  $\text{LnL}_3$  (Ln = La, Nd, Pr, and L = Ligand). Electronic, FT-IR, PMR, and physicochemical techniques were used to determine the structures of the prepared compounds. For natural Ln(III) complexes, the spectral data suggests nine coordinated geometries.

**Keywords:**  $\alpha$ -Benzilmonoxime, Thiocarbohydrazide, La(III), Nd(III), and Pr(III)

## 1. Introduction:

For over 150 years, Schiff bases have been used in coordination chemistry<sup>1-2</sup>. Because they form stable complexes with the majority of transition metals, these ligands have played an important role in the development of coordination chemistry. Researchers are interested in Schiff base ligands with additional donor atoms appended to the ring because of their ability to bind and transport metal ions, the possibility of preparing and studying their mixed-valence forms, and as metalloprotein models<sup>3</sup>. Because of their sensitivity, selectivity, and synthetic flexibility, transition metal complexes with Schiff base ligands are being studied<sup>4</sup>. They are used in medicine as catalysts, such as antibiotics and anti-inflammatory agents, and in industry as corrosion inhibitors<sup>5</sup>. In view of this, we synthesized the Schiff base  $\alpha$ -Benzilmonoximethiocarbohydrazide (HBMTCH) ligand and its Ln(III) metal complexes. The ligand's IUPAC name is *N'*-[(1*E*)-2-imino-1, 2-diphenylethylidene]thiocarbohydrazide<sup>6-7</sup> also reported the benzilmonoximethiocarbohydrazide ligand and its Ln(III) metal complexes. This paper describes the synthesis and characterization of the title ligand and its inner transition metal complexes La(III), Nd(III), and Pr(III). The spectral properties of the HBMTCH ligands and its

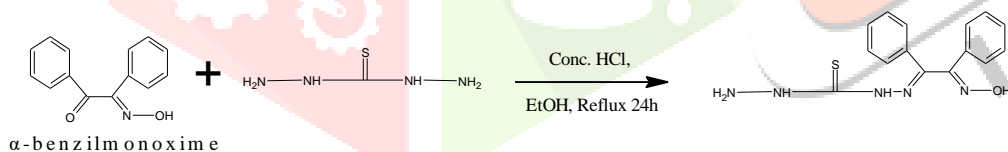
Ln(III) metal complexes have been measured, and the results have been discussed in order to gain insight into the stereochemistry of the compound in the solid state.

## 2. Experimental Section:

Sigma-Aldrich made all reagents available, which were used without purification. The metal contents were determined gravimetrically<sup>8-15</sup>. Uncorrected melting point measured with an I-Therm AI-7782 instrument. Molecular weight is determined by Rast's method<sup>16</sup>. The conductivity measurements were carried out on a Toshcon CL54 conductivity bridge in nitrobenzene. Electronic spectra were recorded with the JASCO V60 spectrophotometer. Perkin-Elmer Spectrum100 was used to measure FT(IR) spectra in KBr disc. On a Bruker AV300 NMR instrument with TMS as an internal standard, PMR spectra in *d*<sub>6</sub>-DMSO were recorded. The Gouys method was used to determine the room-temperature magnetic susceptibilities of all metal complexes reported in this work, with Hg, [Co(SCN)<sub>4</sub>], and [Ni(en)<sub>3</sub>S<sub>2</sub>O<sub>3</sub>] as celebrants<sup>17</sup>.

### 2.1. Preparation of $\alpha$ -benzilmonoximethiocarbahydrazide Ligand:

The reported method was used to synthesise  $\alpha$ -Benzilmonoxime<sup>24</sup> and Thiocarbahydrazide<sup>25</sup>. A hot aqueous solution of thiocarbohydrazide (0.11 mol) was mixed with an ethanolic solution of benzilmonoxime (0.10 mol) to make HBMTCH. The mixture was refluxed for 24 hours on a water bath in the presence of conc. HCl, yielding a colourless solid. This has been filtered, washed in hot water, and dried at 100°C. [The yield of a product was 73.80% of the theoretical. The melting point is 168°C]. ; UV-vis (MeOH)  $\lambda_{\max}$ : 239nm, 290, (0.1N NaOH)  $\lambda_{\max}$ : 222nm, 271nm; <sup>1</sup>H NMR (*d*<sub>6</sub> DMSO, 300MHz)  $\delta$ 12.53(s, 1H),  $\delta$ 8.00(d, 2H),  $\delta$ 8.67(s, 1H),  $\delta$ 7.44-7.95(m, 10H); FT(IR)(KBr); 3288, 3300, 2345, 1600, 1693, 1589, 1000, 1072 cm<sup>-1</sup>; Anal Calcd for C<sub>15</sub>H<sub>15</sub>N<sub>5</sub>O<sub>2</sub>S: C: 57.51, H 4.89, N 22.36, O 5.11, S: 10.22; found C :57.11, H 4.42, N 22.48, O 5.29, S: 10.00.



**Scheme-I:** One step preparation of  $\alpha$ -benzilmonoximethiocarbahydrazide

## 2.2. Synthesis of metal complexes:

All Ln(III) metal complexes were prepared in a nitrogen atmosphere and using the following methods:

### 2.2.1. Tris( $\alpha$ -benzilmonoximethiocarbahydrazide) Lanthanum (III), [La(BMTCH)<sub>3</sub>]:

The HBMTCH (3 mmol) was dissolved in ethanol (20 mL) by heating at 80 °C; drop by drop, with continuous stirring, alcoholic lanthanum nitrate (1 mmol) was added to this hot solution. The reaction mixture was then refluxed for 5 hours. After cooling, the solid product was filtered, thoroughly washed with hot ethanol, and recrystallized from chloroform to yield 83.77%. ; m.p. 208°C; UV-vis (MeOH)  $\lambda_{\max}$ : 550nm; <sup>1</sup>H NMR (*d*<sub>6</sub> DMSO, 300MHz)  $\delta$ 7.45-7.90 (m, 30H),  $\delta$ 7.80 (d, 6H),  $\delta$ 8.66(s, 2H); FT(IR)(KBr)  $\nu$ : 3220, 2350, 1667, 1728,

1582, 1022, 1091, 580, 523 $\text{cm}^{-1}$ ; Anal Calcd for  $\text{C}_{45}\text{H}_{42}\text{N}_{15}\text{O}_3\text{S}_3\text{La}$ : C 54.88, H 4.28, N 21.38, O:4.87, S:9.56, La:4.86; found C 53.00, H 4.21, N 21.07, O:4.81, S:9.13, La:4.71.

### 2.2.2. Tris( $\alpha$ -benzilmonoximethiocarbahydrazide)Neodymium(III), $[\text{Nd}(\text{BMTCH})_3]$ :

Neodymium nitrate (1 mmol) was added to an alcoholic solution (20 mL) of the ligand (3 mmol) and refluxed for 5 hrs. Afterward, the dark yellow solution obtained was evaporated to half of its original volume and allowed to crystallize, dark yellow complex that separated was filtered, washed with hot ethanol, and recrystallized from chloroform to yield 86.21%; m.p.206 $^\circ\text{C}$ ; UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ : 761, 585, 503, 361nm;  $^1\text{H}$  NMR ( $d_6$  DMSO, 300MHz)  $\delta$ 7.40-7.85 (m, 30H),  $\delta$ 7.82 (d, 6H),  $\delta$ 8.60(s, 3H); FT(IR)(KBr)  $\nu$ : 3222, 2358, 1666, 1730, 1588, 1026, 1085, 570, 511 $\text{cm}^{-1}$ ; Anal Calcd for  $\text{C}_{45}\text{H}_{42}\text{N}_{15}\text{O}_3\text{S}_3\text{Nd}$ : C 54.45, H 4.24, N 21.19, O:4.84, S:9.69, Nd:5.54; found C 53.00, H 4.21, N 21.07, O:4.81, S:9.13, Nd:5.71.

### 2.2.3. Tris( $\alpha$ -benzilmonoximethiocarbahydrazide)Praseodymium(III) $[\text{Pr}(\text{BMTCH})_3]$ :

A solution containing ligand (3 mmol) in 20 mL ethanol and holmium nitrate (1 mmol) was refluxed for 3 hours on an oil bath. On cooling, the solid green product was collected by filtration and recrystallized from chloroform to yield 78.96%; m.p.205 $^\circ\text{C}$ ; UV-vis ( $\text{CHCl}_3$ )  $\lambda_{\text{max}}$ : 290nm;  $^1\text{H}$  NMR ( $d_6$  DMSO, 300MHz)  $\delta$ 7.40-7.80 (m, 30H),  $\delta$ 7.82 (d, 6H),  $\delta$ 8.60(s, 3H); FT(IR)(KBr)  $\nu$ : 3233, 2346, 1660, 1728, 1580, 1020, 1091, 592, 529 $\text{cm}^{-1}$ ; Anal Calcd for  $\text{C}_{45}\text{H}_{42}\text{N}_{15}\text{O}_3\text{S}_3\text{Pr}$ : C 54.32, H 4.32, N 21.11, O:4.83, S:9.65, Pr:5.90; found C 53.87, H 4.19, N 20.98, O:4.69, S:9.13, Pr:5.78.

## 3. Results and Discussions:

All lanthanoid complexes are non-hygroscopic, stable at room temperature in an open environment, sparingly soluble in methanol, and only moderately soluble in other solvents such as  $\text{CHCl}_3$ , DMF, DMSO, ACN, nitrobenzene, etc. The chemical results for the ligand and its metal complexes agree with the suggested molecular formulas for these compounds. According to the statistics on the molar conductivity of metal chelates (Table 1), none of the metal complexes are electrolytes. Because the metal compounds are insoluble in diluted alkali solutions, it is likely that the ligand was changed during formation.

**Table-1:** Physical and analytical data of the HBMTCH ligand and its metal complexes

Compound	D.P.(°C)	% Yield	% of expected (found)						Conductance 10 <sup>-3</sup> M Nitrobenzene mhos	Magnetic moments (BM)
			C	H	N	O	S	M		
HBMTCH	168	73.80	57.51 (57.11)	4.89 (4.42)	22.36 (22.48)	5.11 (5.29)	10.22 (10.00)	-	-	-
[La(BMTCH) <sub>3</sub> ]	208	83.77	54.88 (53.00)	4.28 (4.21)	21.38 (21.07)	4.87 (4.81)	9.56 (9.13)	4.86 (4.71)	0.95	Dia
[Nd(BMTCH) <sub>3</sub> ]	206	86.21	54.45 (53.00)	4.24 (4.21)	21.19 (21.07)	4.84 (4.81)	9.69 (9.13)	5.54 (5.71)	0.83	3.84
[Pr(BMTCH) <sub>3</sub> ]	205	78.96	54.32 (53.87)	4.32 (4.19)	21.11 (20.98)	4.83 (4.69)	9.65 (9.13)	5.902 (5.78)	0.91	3.63

### 3.1. Electronic Spectra and magnetic moments:

Two strong bands are visible in the electronic spectrum of HBMTCH in methanol in the UV region at wavelengths of 239 nm and 290 nm, respectively (Table 2). These bands may be the result of  $\pi \rightarrow \pi^*$  transitions that may occur between the molecules' oximino and azomethine habitats. The band at 239 nm in the methanolic solution spectrum has been damaged, and there has also been a bathochromic shift to 222 nm, according to the UV spectrum of HBMTCH in diluted alkali (0.1N NaOH) solution. This suggests that the band at 271 nm in the spectrum of the diluted alkali solution could be attributed to the azomethine linkage and that this band may have its genesis in the oximino linkage in the molecules as such. When comparing this band to a methanolic solution, a bathochromic change occurs<sup>8</sup>.

The electronic absorption of spectrum of [Nd(BMTCH)<sub>3</sub>], complex exhibit five absorption bands at 512, 582, 679, 741 and 801 nm which is assigned to be transitions  $^4I_{9/2} \rightarrow ^4G_{9/2}$ ,  $^4I_{9/2} \rightarrow ^5G_{5/2}$ ,  $^4I_{9/2} \rightarrow ^4F_{9/2}$ ,  $^4I_{9/2} \rightarrow ^2S_{3/2}$ ,  $^4F_{7/2}$  and  $^4I_{9/2} \rightarrow ^4F_{5/2}$  respectively for seven coordinated geometry, confirmed by its magnetic moment found to be 3.84 BM. The electronic absorption spectrum of Pr(III) complex observed bands at 590, 480, 468 and 444 nm assigned to transitions  $^3H_4 \rightarrow ^1D_2$ ,  $^3H_4 \rightarrow ^3P_1$ ,  $^3H_4 \rightarrow ^1F_6$ , and  $^3H_4 \rightarrow ^3P_2$ , respectively confirmed by it magnetic moment found to be 3.63B.M.

**Table-2:** Electronic spectral data of the HBMOTCH ligand and its metal complexes

Compound	Solvent	Bands in nm	Transitions
HBMOTCH	Methanol	239	Oximino $\pi \rightarrow \pi^*$
		290	Azomethine $\pi \rightarrow \pi^*$
	0.1M NaOH	222	Oximino $\pi \rightarrow \pi^*$
		271	Azomethine $\pi \rightarrow \pi^*$
[Nd(BMTCH) <sub>3</sub> ]	Chloroform	550	$^4I_{9/2} \rightarrow ^4G_{9/2}$ ,
		512	$^4I_{9/2} \rightarrow ^5G_{5/2}$
		582	$^4I_{9/2} \rightarrow ^4F_{9/2}$
		679	$^4I_{9/2} \rightarrow ^2S_{3/2}, ^4F_{7/2}$
		741	$^4I_{9/2} \rightarrow ^4F_{5/2}$
[Pr(BMTCH) <sub>3</sub> ]	Chloroform	590	$^3H_4 \rightarrow ^1D_2$
		480	$^3H_4 \rightarrow ^3P_1$
		468	$^3H_4 \rightarrow ^1F_6$
		444	$^3H_4 \rightarrow ^3P_2$
[La(BMTCH) <sub>3</sub> ]	Chloroform	550	M $\rightarrow$ LCT

### 3.2. <sup>1</sup>H NMR Spectra:

The spectrum of <sup>1</sup>H NMR in d<sub>6</sub> DMSO solvent was recorded and reported in **Table-3**. In ligand showed sharp peak at  $\delta$ 12.53 (s, 1H) due to oximino –OH group, but in the metal complexes case which has been disappeared, indicating the involvement of oximino (>C=N-OH) group in the coordination via deprotonation<sup>14</sup>. The peak appeared at  $\delta$ 8.00 (d, 2H) due to azomethine (>C=N-NH<sub>2</sub>) group in the ligand and this is unshifted to metal complexes indicating non-involvement of this for complexation and also the ten aromatic protons due to two phenyl rings have resonated in region  $\delta$ 7.44-7.95 (m, 10H) as a multiplet is unchanged in all metal complexes. Suggests this group also non-involve in coordination<sup>15</sup>. The <sup>1</sup>H NMR spectral data indicated that, only oximino proton is deprotonated and rest's of the groups are unchangeable or unshifted during formation of complex.

**Table-3:** <sup>1</sup>HNMR data of the HBMOTCH ligand and its metal complexes

Compound	>C=N-OH( $\delta$ )	>C=N-NH <sub>2</sub> ( $\delta$ )	-NH-	-C <sub>6</sub> H <sub>5</sub> ( $\delta$ )
HBMOTCH	12.53 (s, 1H)	8.00 (d, 2H)	8.66(s,2H)	7.44-7.95 (m, 10H)
[La(BMTCH) <sub>3</sub> ]	-	7.80 (d, 6H)	8.66(s,6H)	7.45-7.90 (m, 30H)

### 3.3.FT(IR) Spectra:

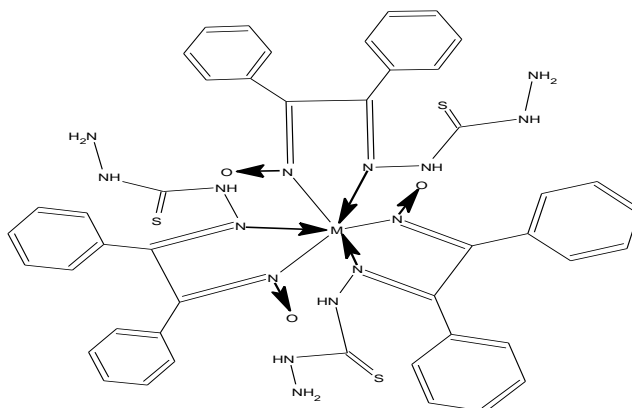
The Inorganic complexes derived from organic chelating groups tend to absorb in the IR region 400-660 $\text{cm}^{-1}$  which is of greatest practical values in the study of metal complexes<sup>16</sup>. Because N-OH is not present in metal complexes, the strong and broad band at 3288  $\text{cm}^{-1}$  for the free ligand indicates that the hydroxyl group of the oxime was deprotonated during the complexes' formation. The ligand shows the IR stretch in the region of 1600 $\text{cm}^{-1}$  for azomethine (>C=NN) group and 1493 $\text{cm}^{-1}$  for oximino (>C=NO) group, which agree with literature values<sup>17</sup>, they are shifted by higher frequencies in the complexes indicating that the nitrogen atom of both the group is coordinated to the metal<sup>18</sup>. A non-ligand band that appears in the complexes in the region 511-590 $\text{cm}^{-1}$  has been assigned to  $\nu(\text{M-N})$ <sup>20</sup>. Thus, it may be stated that the ligand acts towards the metal studies in a neutral, bidentate mode, mediating through the nitrogen "N" of azomethine and oximino moieties (M-N<sub>4</sub>) type.

**Table-4:** FT(IR) spectral data for HBMTCH and its metal complexes in  $\text{cm}^{-1}$

Compound	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{C-S-H})$	C=NN	C=NO	$\nu(\text{N-H})$	N - O	N-N	M-N
HBMTCH	3288	3300	2345	1600	1493	1693	1000	1072	-
[La(BMTCH) <sub>3</sub> ]	-	3220	2350	1667	1582	1698	1022	1091	580, 523
[Nd(BMTCH) <sub>3</sub> ]	-	3222	2358	1666	1588	1699	1026	1085	570, 511
[Pr(BMTCH) <sub>3</sub> ]	-	3233	2346	1660	1580	1696	1020	1091	592, 529

### 4. Conclusion:

The complexes of the title ligand La(III), Nd(III), and Pr(III) are non-electrolytes. Schiff bases perform as a neutral receptor for the bidentate, with the central metal ion coordinated via the azomethine and oximino nitrogen atoms. The observation of elemental analysis, magnetic susceptibility, electronic spectra, FT-IR, and <sup>1</sup>H NMR spectra revealed the following structures for these complexes: La(III), Nd(III), and Pr(III), which have a coordination number of six. based on magnetic and spectrum information, the structure of all metal complexes is tentatively assigned as follows:



Where; M = La(III), Nd(III) and Pr(III)

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