



# METAL-BASED BENZILMONOXIMETHIOCARBOHYDRAZIE- P-CHLOROBENZALDEHYDE: THEIR PREPARATION, CHARACTERISATION, COORDINATION BEHAVIOUR AND BIOLOGICAL ACTIVITY

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## Abstract

Some thiocarbohydrazide-derived benzilmonoximethiocarbohydrazie-*p*-chlorobenzaldehyde (HBMT<sub>*p*</sub>CB) and its inner transition metal (Sm(III), Pr(III), Eu(III), Lu(III) and Ce(III)) complexes have been prepared and characterised. These analytical (elemental analysis, physical conductivity and magnetic susceptibility measurement) and spectral (PMR, FT(IR), electronic absorption spectra) properties were used to infer the prepared complex structures and their bonding in nature. All prepared trivalent metal complexes have seven-coordinate geometry. Antifungal and antibacterial activities against two gram-positive species, *B. subtilis* (MCC 2010) and *S. aureus* (MCC 2408) and two gram-negative species, *P. aeruginosa* (MCC 2080) and *E. coli* (MCC 2412).

**Keywords:** Lanthanide complexes, benzilmonoxime, thiocarbohydrazie, *p*-chlorobenzaldehyde

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## Introduction:

Thiocarbohydrazide denotes an important class of drugs, and their appearance significance is only when thiocarbohydrazide is reported<sup>1-3</sup> to be the first method of antimicrobial drug application. Many thiocarbohydrazide derivatives were synthesised, characterised, and tested for antitumor, antibacterial, hypoglycemic, anti-carbonic anhydrase, antithyroid, diuretic, and protein inhibitory activities<sup>4-8</sup>. Gained research in the last decade and increased interest in new methodology seeking and targeting that could effectively treat bacteria and ailments-related viruses. So far, metal-based therapeutics have proven to be the most effective approaches for their treatment<sup>9</sup>. The ability of metal ions to bind with peptides and proteins is a critical component of this. Simple and *N*-substituted thiocarbohydrazide has drawn much attention to this promising metal-based therapy, inspired by the successful introduction of thiocarbohydrate metal complexes to prevent bacterial infections<sup>10</sup>. These are made by trivalent metal complexes that use the slow release of the metal ion from the source, which is completely binding nature-dependent<sup>11-12</sup>.

Because of the versatile chemistry of thiocarbohydrazide and benzilmonoxime, it is possible to combine their chemistry while preparing their intriguing biological and structural properties. More thiocarbohydrazide-derived

benzilmonoximethiocarbohydrazide-*p*-chlorobenzaldehyde complexes and their inner transition metal [Sm(III), Pr(III), Eu(III), Lu(III), and Ce(III)] complexes will be discussed in the following sections, as well as their binding behaviour and *in vitro* antifungal and antibacterial activities.

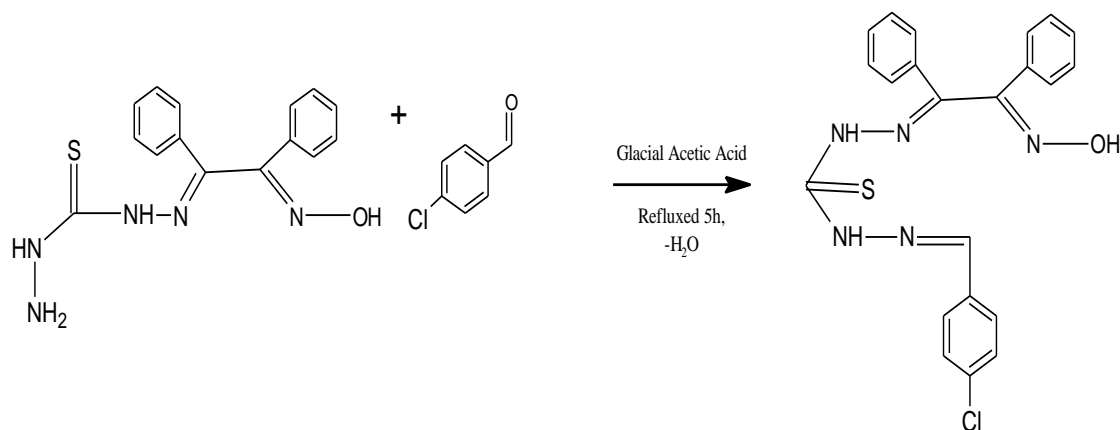
## Experimental:

### Materials and Measurement:

All the required starting materials were of chemical purity. The solvent used in the spectral and physical measurements was used as AR grade. Lanthanide (III) salts were used as nitrates. FT(IR), PMR, electronic spectra, C, H, N, S, and O analyses, and magnetic and conductance measurements were carried out using the respective instruments. *In vitro* antifungal and antibacterial activities were studied at Rahul Dharkar College of Pharmacy and Research Institute, Karjat, Raigad, India.

### Synthesis of HBMTpCB ligand

To a hot solution of benzilmonoximethiocarbohydrazide (10 mmol) in ethanol (50 ml) was added hot *p*-chlorobenzaldehyde (15 mmol) in ethanol (50 ml). The final reaction mixture was refluxed for nine hours. The final reaction mixture was allowed to be cooled to room temperature, collected by filtration, washed with hot distilled water, and dried under a vacuum over anhydrous calcium chloride.

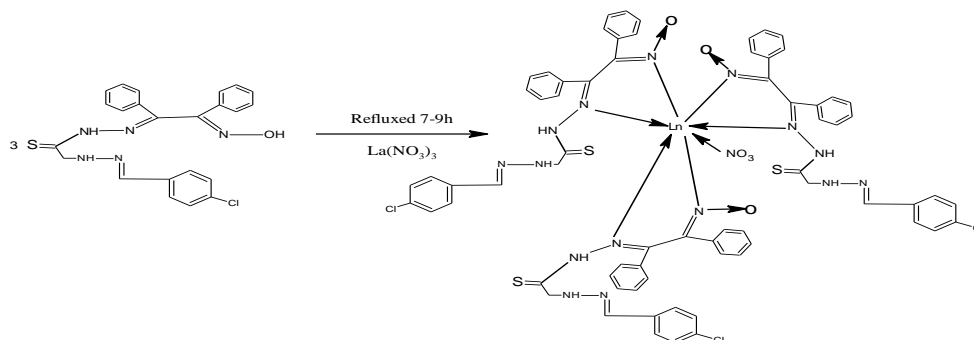


**Scheme-I:** Preparation of benzilmonoximethiocarbohydrazide-*p*-chlorobenzaldehyde ligand

### Preparation of metal complexes:

An aqueous solution of Ln(III)NO<sub>3</sub> (where Ln = Sm(III), Pr(III), Eu(III), Lu(III), and Ce(III) (15 mmol) was added to a hot stirred ethanol (25 ml) solution of HBMTpCB ligand (5 mmol). The

reaction mixture was refluxed for 5–10 hours, filtered, and reduced to half volume by evaporating the solvent in a vacuum. The concentrated solution was filtered and washed with hot distilled water.



**Scheme-II:** Preparation of metal complexes of benzilmonoximethiocarbohydrazi-*p*-chlorobenzaldehyde ligand

### Biological activity:

The ligand and its complexes were tested for their bactericidal efficacy against two gram-positive species, *B. subtilis* (MCC 2010) and *S. aureus* (MCC 2408) and two gram-negative species, *P. aeruginosa* (MCC 2080) and *E. coli* (MCC 2412) bacteria using the agar-plate method. To get a final concentration of 5 mM, all the chemicals were freshly synthesized by dissolving them in ethanol. The bacterial cultures were grown on nutrient agar.

### In vitro cytotoxicity

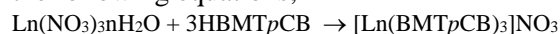
Using the Meyer et al. technique<sup>13</sup>, the synthesized Schiff bases and their Sm(III), Pr(III), Eu(III), Lu(III) and Ce(III) complexes were tested for their cytotoxicity (brine shrimp bioassay). A shallow, 22 x 32 cm, rectangular plastic dish was used to hatch brine shrimp (*Artemia salina leach*) eggs. The fake saltwater was made by combining double-distilled water with a commercial salt solution. The plastic dish was divided unevenly with the use of a perforated tool. The major compartment was darkened and filled with about 50 mg of eggs, while the minor compartment was exposed to natural light.

Nauplius was removed with a pipette from the lit side after two days. 20 mg of each chemical was

dissolved in 2 ml of DMF to prepare a sample of the test substance. One vial was preserved as a reference and contained just 2 ml of DMF. From this stock solution, 100, 50, and 10 µg/ml were transferred to nine vials (three for each dilution were used for each test sample, and LD<sub>50</sub> is the mean of three values). Overnight, the solvent was allowed to evaporate. When the shrimp larvae were ready after two days, 1 ml of seawater and 10 shrimp (30 shrimp/dilution) were put into each vial. The volume was then adjusted with seawater to 5 ml of each vial. The number of survivors was counted after 24 hours. The LD<sub>50</sub> values were calculated using data analysis provided by a Finney computer program.

### Results and discussion:

The prepared lanthanide (III) complexes of the HBMT<sub>p</sub>CB ligand were synthesised according to the following equations;



Where Ln = Sm(III), Pr(III), Eu(III), Lu(III) and Ce(III)

The prepared HBMT<sub>p</sub>CB ligand and its lanthanide (III) metal complexes are insoluble in water but in common organic solvents.

**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 <sup>-3</sup> M (nitrobenzene) mhos
				% M Found (Calcd)	% C Found (Calcd)	% H Found (Calcd)	% N Found (Calcd)	% O Found (Calcd)	% Cl Found (Calcd)		
HBMH <sub>p</sub> CB	Yellow	81.61	209	-	60.61 (59.92)	4.16 (4.98)	16.07 (16.02)	3.67 (3.65)	8.13 (8.00)	-	-
[Sm(BMH <sub>p</sub> CB) <sub>3</sub> ] NO <sub>3</sub>	Brown	75.61	241	9.91 (9.81)	52.20 (52.02)	3.36 (3.30)	14.76 (14.49)	6.33 (6.16)	6.33 (6.66)	1.54	23.77
[Pr(BMH <sub>p</sub> CB) <sub>3</sub> ] NO <sub>3</sub>	Brown	74.86	239	9.35 (9.30)	52.56 (52.44)	3.38 (3.26)	14.87 (14.53)	6.37 (6.31)	7.07 (6.99)	3.51	29.06
[Eu(BMH <sub>p</sub> CB) <sub>3</sub> ] NO <sub>3</sub>	Orange	79.05	241	10.01 (9.77)	52.15 (52.01)	3.36 (3.29)	14.75 (14.51)	6.32 (6.28)	7.01 (6.91)	3.52	24.85
[Lu(BMH <sub>p</sub> CB) <sub>3</sub> ] NO <sub>3</sub>	Yellow	82.24	238	11.34 (11.09)	51.37 (51.19)	3.31 (3.23)	14.53 (14.37)	6.23 (6.20)	6.91 (6.86)	-	23.01
[Ce(BMH <sub>p</sub> CB) <sub>3</sub> ] NO <sub>3</sub>	Brown	79.79	244	9.30 (9.14)	52.56 (52.33)	3.38 (3.32)	14.86 (14.79)	6.37 (6.20)	7.07 (7.01)	2.42	20.49

**Conductance and magnetic measurements:**

The prepared lanthanide (III) complex's molar conductance values in nitrobenzene are observed in the range 20.49-29.06  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , fall within the range of 20.00-30.00  $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$ , showing their 1:1 electrolytic nature<sup>14</sup>. The magnetic moments for the [Sm(BMTpCB)<sub>3</sub>]NO<sub>3</sub> complex are 1.54 BM, indicating that the Tb(III) ion has eight unpaired electrons, implying octahedral geometry. The measured value of 3.52 BM for the [Eu(BMTpCB)<sub>3</sub>]NO<sub>3</sub> complex suggests it has seven coordinated geometries. The [Lu(BMTpCB)<sub>3</sub>]NO<sub>3</sub> complex was discovered to be diamagnetic<sup>15</sup>. Furthermore, the magnetic moments of [Ce(BMTpCB)<sub>3</sub>]NO<sub>3</sub> at room temperature were 2.42 BM.

**Electronic absorption spectra:**

The [Sm(BMTpCB)<sub>3</sub>]NO<sub>3</sub> complex exhibited well-resolved low-energy bands as 560, 480, 465, 418, 364 and 355 nm, which are assigned<sup>16</sup> to <sup>6</sup>H<sub>5/2</sub>→<sup>4</sup>G<sub>5/2</sub>, <sup>6</sup>H<sub>5/2</sub>→<sup>4</sup>G<sub>7/2</sub>, <sup>6</sup>H<sub>5/2</sub>→<sup>4</sup>I<sub>18/2</sub>, <sup>6</sup>H<sub>5/2</sub>→<sup>6</sup>P<sub>5/2</sub>, <sup>6</sup>H<sub>5/2</sub>→<sup>6</sup>G<sub>3/2</sub> and <sup>6</sup>H<sub>5/2</sub>→<sup>9</sup>H<sub>9/2</sub> transitions respectively. The [Eu(BMTpCB)<sub>3</sub>]NO<sub>3</sub> complex electronic absorption spectrum shows the *f-f* bands at 702, 650, 616, 595 and 580 nm. These are assigned to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>4</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>3</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub> and <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>0</sub> transitions, respectively, with their well-defined octahedral configuration. The diamagnetic [Lu(BMTpCB)<sub>3</sub>]NO<sub>3</sub> complex electronic spectrum exhibits only a high-intensity band at 515, 420, and 370 nm are assigned<sup>17</sup> to a charge transfer metal to the ligand.

[Ce(BMTpCB)<sub>3</sub>]NO<sub>3</sub> shows *f-f* transitions at 520 and 410 nm corresponding to <sup>5</sup>F<sub>5</sub>→<sup>2</sup>D<sub>3/2</sub> and <sup>2</sup>F<sub>5</sub>→<sup>2</sup>D<sub>5/2</sub> transitions, respectively<sup>18</sup>. The brown-coloured [Pr(BMTpCB)<sub>3</sub>]NO<sub>3</sub> complex electronic absorption spectrum shows the *f-f* bands at 584 and 482 nm. These are assigned<sup>19</sup> to the <sup>3</sup>H<sub>4</sub>→<sup>1</sup>D<sub>2</sub> and <sup>3</sup>H<sub>4</sub>→<sup>3</sup>P<sub>0</sub> transitions, respectively, with their well-defined octahedral configuration.

In chloroform solutions of these complexes, some nephelauxetic effect or redshift 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 ( $\beta$ ) is calculated using hypersensitive bands. Using the expression below, the Sinha parameters ( $\beta$ ), covalence factor ( $b^{1/2}$ ), and covalency angular overlap parameter ( $\eta$ ) were calculated<sup>20</sup> 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, indicating that the bonding between the ligand and metal ion is covalently compared to the bonding between the aqua and metal ion. The angular overlap ( $\eta$ ) and bonding parameter ( $b^{1/2}$ ) values are positive, indicating that covalent bonding exists.

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

Compound	$\lambda_{\text{nm}}$	$\epsilon$ (dm <sup>3</sup> /mol/cm)	Transition	
HBMHpCB	353	7740	$\pi \rightarrow \pi^*$	
	274	10730	$\pi \rightarrow \pi^*$	
	225	12756	$\pi \rightarrow \pi^*$	
[Sm(BMHPpCB) <sub>3</sub> ]NO <sub>3</sub>	560	985	<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> G <sub>5/2</sub>	$\beta_{\text{ave}} = 0.9799$ , $\eta = 6.3375$ , $b^{1/2} = 0.6999$ , $\delta\% = 0.0296$
	480	3064	<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> G <sub>7/2</sub>	
	465	7789	<sup>6</sup> H <sub>5/2</sub> → <sup>4</sup> I <sub>18/2</sub>	
	418	12645	<sup>6</sup> H <sub>5/2</sub> → <sup>6</sup> P <sub>5/2</sub>	
	364	13645	<sup>6</sup> H <sub>5/2</sub> → <sup>6</sup> G <sub>3/2</sub>	
	355	11268	<sup>6</sup> H <sub>5/2</sub> → <sup>9</sup> H <sub>9/2</sub>	
[Lu(BMHPpCB) <sub>3</sub> ]NO <sub>3</sub>	515	8369	MLCT	
	420	10567	MLCT	
	370	12457	MLCT	
[Ce(BMHPpCB) <sub>3</sub> ]NO <sub>3</sub>	520	6578	<sup>5</sup> F <sub>5</sub> → <sup>2</sup> D <sub>3/2</sub>	$\beta_{\text{ave}} = 0.9959$ , $\eta = 0.00205$ , $b^{1/2} = 0.0442$ , $\delta\% = 0.410$
	410	9354	<sup>5</sup> F <sub>5</sub> → <sup>2</sup> D <sub>5/2</sub>	
Eu(BMHPpCB) <sub>3</sub> ]NO <sub>3</sub>	702	1450	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>4</sub>	$\beta_{\text{ave}} = 0.9942$ , $\eta = 0.00292$ , $b^{1/2} = 0.0531$ , $\delta\% = 0.5860$
	650	3680	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>3</sub>	
	595	9580	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>2</sub>	
	580	9750	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>1</sub>	
	616	10980	<sup>5</sup> D <sub>0</sub> → <sup>7</sup> F <sub>0</sub>	
Pr(BMHPpCB) <sub>3</sub> ]NO <sub>3</sub>	584	8854	<sup>3</sup> H <sub>4</sub> → <sup>1</sup> D <sub>2</sub>	$\beta_{\text{ave}} = 0.9918$ , $\eta = 0.00412$ , $b^{1/2} = 0.0635$ , $\delta\% = 0.8249$
	482	11345	<sup>3</sup> H <sub>4</sub> → <sup>3</sup> P <sub>0</sub>	

### FT(IR) spectra:

The important FT(IR) spectra bands of the HBMTpCB ligand and its trivalent lanthanide (III) metal complexes are given in **Table-3**. The broad band observed  $3641\text{cm}^{-1}$  due to the oximino (-OH) group of the HBMTpCB ligand is absent in spectra of lanthanide (III) metal complexes, indicating HBMTpCB ligand coordinated<sup>21</sup> to metal ion *via* deprotonation of oximino group. In the FT(IR) spectrum of the HBMTpCB ligand, sharp bands observed at  $1613$  and  $1580\text{cm}^{-1}$  are assigned to the

(>C=NN-) and (>C=NOH) groups, respectively. These bands are shifted to the lower frequencies in the spectra of lanthanide (III) metal complexes and were suggested by HBMTpCB ligand coordinated to central lanthanide (III) metal ions through oximino and azomethine nitrogens. This is further supported<sup>22-23</sup> by the new band's appearance at  $465-479$  and  $525-539\text{cm}^{-1}$  due to the  $\nu(\text{M-S})$  and  $\nu(\text{M-N})$  bands, respectively, in all lanthanide (III) metal complexes<sup>24-25</sup>.

**Table-2:** IR spectral bands of the ligand (HBMHpCB) and its metal complexes ( $\text{cm}^{-1}$ ):

Assignments	HBMHpCB	Sm(III)	Pr(III)	Lu(III)	Eu(III)	Ce(III)
vOH Oximino	3641	-	-	-	-	-
N-H	3297	3303	3282	3297	3302	3300
vC=C Ar.	3046	2919	2921	2918	2918	3140
vC=NN	1613	1638	1634	1645	1599	1633
vC=NO	1588	1502	1586	1588	1492	1578
vN-N	974	1057	1021	1056	1022	1014
vN→O	-	914	968	957	928	923
vPh-Cl	820	816	817	735	825	834
vM-N	-	544	548	559	538	562
vM→N	-	515	511	514	505	512

### PMR spectra:

PMR spectra of the free HBMTpCB ligand and its diamagnetic  $[\text{Lu}(\text{BMTpCB})_3]\text{NO}_3$  complex were recorded in  $d_6$  DMSO. The sharp singlet observed at  $\delta 11.65\text{ppm}$  due to oximino protons of the free HBMTpCB ligand, this band has disappeared in its  $[\text{Lu}(\text{BMTpCB})_3]\text{NO}_3$  complex, indicated that the oximino group involved coordination through metal ions *via* deprotonation of this group. The other singlet at  $\delta 9.68\text{ppm}$  is due to the azomethine proton of HBthe MTpCB ligand and Lu(III) complex. The aromatic proton multiplet is observed between  $7.68-8.10\text{ppm}$  for both the HBMTpCB ligand and  $[\text{Lu}(\text{BMTpCB})_3]\text{NO}_3$  complex.

### Biological Activity Studies

The MICs of HBMTpCB ligand and  $[\text{Ln}(\text{BMTpCB})_3]\text{NO}_3$  complexes against gram-positive *B. subtilis* (MCC 2010) and *S. aureus* (MCC 2408) and gram-negative *P. aeruginosa* (MCC 2080) and *E. coli* (MCC 2412) bacteria are determined through a broth dilution assay to determine the products' antimicrobial activity.  $[\text{Sm}(\text{BMTpCB})_3]\text{NO}_3$  complex showed high activity and  $[\text{Ce}(\text{BMTpCB})_3]\text{NO}_3$  complex showed good activity against gram-positive organisms from the antibacterial results of the series provided, whereas compounds  $[\text{Eu}(\text{BMTpCB})_3]\text{NO}_3$  and  $[\text{Pr}(\text{BMTpCB})_3]\text{NO}_3$  complexes showed good

activity against gram-negative organisms. The remaining compounds exhibited moderate to good activity. Antibacterial activities such as ciprofloxacin, and norfloxacin are the norm. Each prepared compound was tested for efficacy against *C. albicans*, *A. clavatus*, and *A. niger*, three common types of fungi. The most effective compounds against both types of fungi are  $[\text{Eu}(\text{BMTpCB})_3]\text{NO}_3$  and  $[\text{Pr}(\text{BMTpCB})_3]\text{NO}_3$  complexes. In contrast, the remaining compounds only displayed mild action. The most common antifungal standard is *fluconazole*.

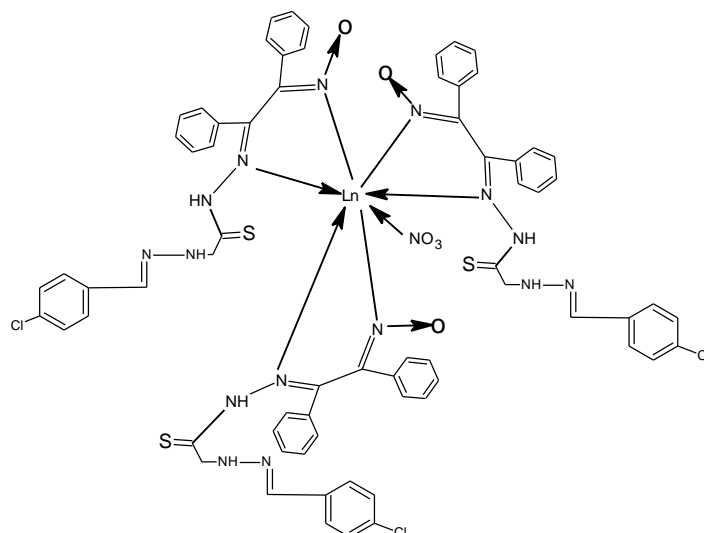
### In vitro cytotoxicity:

Only Sm(III) and Ce(III) compounds showed modest cytotoxic action against *A. salina* in the case of cytotoxic activity, whereas the other compounds gave values of  $\text{LD}_{50}$  and can therefore be regarded as non-cytotoxic.

### Conclusion:

Geometry, physicochemical and spectral data of the HBMTpCB ligand and the lanthanide (III) ions were complex with nitrogen atoms of am, oxygen, and sulphur atoms of the higher carbohydrazide group. The trinuclear lanthanide (III) complexes of the HBMTpCB ligand have a 1:3 metal: ligand ratio. All prepared complexes of this HBMTpCB ligand have seven coordinate geometry, and the results agree with the proposed structure for the efficient lanthanide (III) complexes.





Where: Ln = Sm(III), Pr(III), Eu(III), Lu(III) and Ce(III)

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