ORIGINAL RESEARCH PAPER

Chemistry

PHYSICO-CHEMICAL, MAGNETIC, SPECTRAL AND BIOLOGICAL STUDIES ON N''-[(1E)- 2-IMINO-1, 2-DIPHENYLETHYLIDENE]THIOCARBONOHYDRAZIDE AND ITS COMPLEXES OF TRIVALENT LANTHANIDES

KEY WORDS: Lanthanides, electronic spectra, thiocarbohydrazide and benzilmonoximehydrazide

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ABSTRACT

A new Schiff base N''-[(1E)- 2-imino-1, 2- diphenylethylidene]thiocarbonohydrazide has been synthesized by the condensation of thiocarbohydrazide, sodium acetate and benzilmonoxime (2:2:1 molar ratio). Its complexes with trivalent lanthanides (Pr^{3+}, Gd^{3+}, and Dy^{3+}) have been synthesized. The ligand has three coordination sites, azomethine and oximino nitrogens and sulfur atom of thiocarbohydrazide take part in coordination. The complexes have been assigned the general formula $[Ln(BMTCH)_2NO_3]$ based on elemental analysis, molar conductance, magnetic moment, PMR, electronic absorption, and FT(IR) spectral studies. The electronic spectra of the complexes of Pr^{3+}, Gd^{3+}, and Dy^{3+} have been analyzed and discussed. The spectral parameters show the covalent nature of bonding between the metal and the synthesized ligand. The HBMTCH ligand and its inner transition metal complexes have been screened for their antimicrobial activities. The complexes and ligand exhibit more antibacterial activity against three-gram positive bacteria (*B. subtilis, S. aureus, S. Typhi*) and three gram-negative bacteria (*E. coli, K. pneumoniae, P. aeruginosa*) as compared to standard streptomycin. While Pr^{3+}, Gd^{3+}, and Dy^{3+} complexes exhibit good antifungal activity with more than 90% reduction in growth against *penicillium sp., Canilida Albicans, Aspergillus Flaves, Aspergillus Niger*, and *Colletotrichum Gloeosporiodes penz* respectively.

1. INTRODUCTION:

Several Schiff base complexes of transition and inner transition metals have been reported in the literature [1-4]. The recent reports include complexes of diacetyl monoxime hydrazides alicylidene[5], diacetyl monoximehydrazide [6], benzilmonoxime [7], benzilmonoximehydrazide [8-9], and isonitrosopropio-phenonehydrazidesalicyalidene [10]. In this paper we report lanthanide (Pr^{3+}, Gd^{3+}, and Dy^{3+}) complexes of Schiff base benzil monoxime thio carbohydrazide, IUPAC name of N''-[(1E)- 2-imino-1, 2- dipheny lethylidene] thio carbon ohydrazide (hereafter abbreviated as HBMTCH) derived from the condensation of equimolar of benzil monoxime, sodium acetate and *thiocarbohydrazide*.

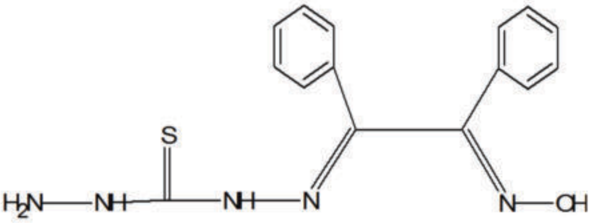

Figure-1: N''-[(1E)- 2-imino-1, 2 diphenylethylidene] thiocarbonohydrazide

1. Experimental:

The hydrated lanthanides salts (–"S.D. Fine Chemicals, Loba Chemie and B.D.H., 99.99% pure) were used as such. All the physico-chemical methods were similar to that employer earlier [5-7]. The electronic absorption spectra of the complexes were recorded on JASCO V-650Spectrophotometer. 1H NMR spectra of the ligand and its metal complexes were obtained on Brucker AV300 NMR spectrometer using TMS as internal standard. The FT-IR spectrum was recorded in the range 4004000 cm-1 by KBr pellet using a Perkin- Elmer spectrum 100 model FT-IR spectrophotometer. Complexes were decomposed by repeated treatment with conc. HNO3 and H2SO4 and finally metal contents were estimated complexometrically by EDTA using xylenol orange at pH-6.2.1: Synthesis of HBMTCH ligand: HBMTCH was prepared by mixing hot aqueous solution of 20.000 g ofthiocarbohydrazide (0.188 mol) with ethanolic solution of 10.000 g of α-benzilmonoxime (0.044 mol) in presence of sodium acetate (20.000 g), the mixture was refluxed for 7h on a water bath and kept overnight, a colorless solid was obtained. This was filtered and washed by hot water and dried at 100 oC. 2.2: Synthesis of complexes:

The coordination complexes of the type $[Ln(BMTCH)_2NO_3]$ were synthesized by refluxing ethanolic solution of the ligand HBMTCH and the corresponding metal salts in stoichiometric amounts at 70-80 °C for 3-15 h. The solid complexes were filtered off and washed with aliquots of ethanol and recrystallised from chloroform and finally dried in hot air oven.

1.3. Antibacterial Screening:

Antibacterial activity was carried out by agar cup method against *P. aeruginosa(G^+), S. aureus(G^+), K. pneumoniqe(G^+), B. subtilis(G^+), S. typhi(G^+)*, and *E. coli(G^-)*. 50, 100, 200, 500ppm concentrations were used for determination of the activity and zone of inhibition was measured in mm.

1.4. Antifungal Activity:

Antifungal activities of synthesized HBMTCH ligand and its inner transition metal ion complexes towards five plant pathogenic and mould fungi were studied, viz. *Colletotrichum Gloeosporiodes penz, Canilida Albicans, Aspergillus Niger, Aspergillus Flaves* and *penicillium sp.* Antifungal activity was assessed in a modified condition [11] by the poisoned food technique [12]. Standard fungicides used as Fluconazole (200g/disc). For test fungi basal medium used as proton dextrose sugar (PDA) and sterilized glass petri dishes were used. Sterilized melted PDA medium at 45°C was poured at the rate of 15mL into each petri dish (90mm). After solidification of the medium small portions of the mycelium of each fungus were spread carefully over the center of each PDA plate with the help of sterilized needles. Thus, each fungus was transferred to a number of PDA plates, which were then incubated at 25°C (2) and ready for use after five days of incubation. Prepared disc of sample were placed gently on solidified agar plates, freshly seeded with the test organisms with sterile forceps. A control disc was also placed on the test plates compare the effect of solvent respectively. The plates were then kept in a refrigerator at 4°C for 24hrs, so that the materials had sufficient time to diffuse over a considerable area of the plates. After this the plates were incubated at 37°C for 72hrs. DMF was used as solvent to prepare desired solutions 110mg/mL) of the compounds initially and also to maintain proper control.

1. RESULTS AND DISCUSSIONS:

The ligand HBMTCH interacts with the trivalent lanthanide ions and yields complexes which based on elemental analyses and molar conductance (**Table 1**) have been given the general formula $[Ln(BMTCH)_2NO_3]$ i.e. $(LnC_{45}H_{42}N_{16}O_6S_3)$.

$$Ln(NO_3)_3.6H_2O + 3HBMTCH \xrightarrow[\text{(Ethanol)}]{\text{Stirring + Heating}} [Ln(BMTCH)_3.NO_3]$$

The complexes were well-defined solids with high decomposition points and they are soluble in common organic solvents. The stoichiometric data (**Table 1**) show the presence of three nitrates ions per lanthanide metal; this is quite understandable since the ligand is neutral and lanthanide is originally trivalent.

The molar conductance of the complexes at 10^{-3} M dilution in nitrobenzene is in the range 20.63-26.13^{-1}cm^{2}mol^{-1}, expected for 1:1 electrolytes [13]. It is, therefore, concluded that one out of the three nitrates is present inside the coordination sphere.

Table 1: Physical and Analytical data of HBMTCH ligand and its Ln(III) complexes

Compound	**Colour**	**% Yield**	**MP/DP in °C**	**% Element Content, Expected (Observed)**						**Molar Cond**	**Magntic Moments**
				C	**H**	**N**	**O**	**S**	**M**		
HBMTCH		73.80	168	57.51 (57.11)	4.89 (4.42)	22.36 (22.48)	5.11 (5.29)	10.22 (10.00)	-	-	-
$[Pr(BMTCH)_3]NO_3$	Red	65.22	289	50.14 (49.30)	4.24 (4.23)	19.81 (19.31)	8.45 (8.39)	8.45 (8.40)	12.38 (11.68)	20.3	3.59
$[Gd(BMTCH)_3]NO_3$	Brown	63.91	283	49.39 (48.64)	4.18 (4.10)	19.15 (19.12)	8.36 (8.26)	8.36 (8.31)	12.20 (11.71)	23.6	9.62
$[Dy(BMTCH)_3]NO_3$	Brown	73.33	287	49.20 (49.09)	4.16 (4.10)	19.44 (19.19)	8.33 (8.24)	8.33 (8.30)	14.10 (13.94)	22.9	10.58

3.1: Electronic absorption spectra

The electronic absorption spectra of all prepared inner transition metal ion complexes were recorded in chloroform and presented in **Table 2**. The spectrum of the complexes shows a red shift of the bands as compared to those of respective aqua-ions which is known as nephelauxetic effect [14]. The nephelauxetic (□), bonding ($b^{1/2}$) and covalency () parameters have been calculated by the same method as reported elsewhere [15]. The parameter □ is less than one, and $b^{1/2}$ and are positive for these complexes showing covalent nature of bonding between the metal and the ligand. It is evident from the **Table 2** that the present complexes can be arranged in the following decreasing order of covalency: La>Nd>Sm>Gd>Tb>Dy.

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

Compound	nm	(dm^3/mol/cm)	Transition	
HBMTCH	222	12252	Oximino *p*→*p** transition	
	271	11181	Azomethine *p*→*p** transition	
$[Pr(BMTCH)_3]NO_3$	606	875	$^1D_2 \leftarrow {}^3H_4$	$_{ave}$ = 0.992
	485	4560	$^3P_0 \leftarrow {}^3H_4$	$b^{1/2}$ = 0.063
	470	4958	$^3P_1 \leftarrow {}^3H_4$	δ% = 0.806
	445	5659	$^3P_2 \leftarrow {}^3H_4$	= 1.0161
$[Gd(BMTCH)_3]NO_3$	360	5465	MLCT	
	312	13456	$^8S_{1/2}\ {}^6P_{1/2}$	
$[Dy(BMTCH)_3]NO_3$	429	6530	$^4H_{15/2}\ {}^4F_{9/2}$	
	348	7458	$^4H_{15/2}\ {}^4I_{15/2}$	
	302	12670	MLCT	

3.2: FT(IR) Spectra:

The FT(IR)Spectra provide valuable information regarding the nature of a functional group attached to metal atom. The important I.R frequencies exhibited by the Schiff base ligand and their corresponding ligand complex are tabulated in **Table 3** .The ligand shows broad band at 3288cm^{-1} due to oximino group is absent in its all prepared metal complexes, indicated prepared ligand coordinate to metal ion through oximino group. The Bands are observed at 1600 and 1580cm^{-1} in prepared ligand, due to azomethine and oximino group respectively, is shifted to higher frequencies in its metal complexes, indicating the participation of azomethine and oximino group in complex formation. The IR spectra of complexes give a $|\nu_{4-\nu 1}|$ separation in the range 74-148cm^{-1} suggesting monodentate bonding for the nitrate group. Moreover, the appearance of additional weak bands in the region 490-570cm^{-1} attributed to υ(M-N), further confirmed complexation[15]. This showed that the Schiff base ligand coordinated to the metal via 'N' atoms.

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

Compound	**-OH (Oxo)**	**Ar C-H**	**Ar C=C**	**>C=NN-**	**>C=NO-**	**$_1$(NO$_3$)**	**$_2$(NO$_3$)**	**$_3$(NO$_3$)**	**$_4$(NO$_3$)**	**Phe ring**	**M—N**
HBMTCH	3288	3070	2960	1600	1580	-	-	-	-	729	-
$[Pr(BMTCH)_3]NO_3$	-	3070	2960	1626	1599	1451	1033	1334	1377	729	495, 533
$[Gd(BMTCH)_3]NO_3$	-	3076	2960	1627	1603	1452	1032	1340	1345	730	489, 519
$[Dy(BMTCH)_3]NO_3$	-	3073	2960	1630	1610	1477	1034	1323	1329	733	499, 517

3.3: The PMR spectra:

PMR Spectra of Schiff base and their complexes were recorded in d_6 DMSO solution and TMS used as internal standard. On comparison of the spectrum with that of the ligand, it noted that the oximno proton of the ligand (10.53) is missing in the pmr spectra of its metal complexes, confirming the proposed replacement of the oximino proton by the metal ion during complex formation [16]. The aromatic proton in Schiff base appears at 7.45-7.95 ppm and in their La(III) metal complex in the range of 7.46-7.98 ppm[17].

Table 4: PMR spectrum of HBMTCH and its metal complexes in d_6 DMSO

Compounds	**-OH**	**-CH=**	**Phenyl rings**
HBMTCH	10.53	8.20	7.45-7.95
$La(BMTCH)_3$	-	8.20	7.46-7.98

3.4. Antibacterial Activities:

The antibacterial activities of synthesized compounds have been assayed at the concentration of 500 g/disc against six human pathogenic bacteria [18-19]. Among them five were gram positive and one is gram negative. The inhibitory effects of compounds against these organisms are given in **Table-5**. The screening results indicate that synthesized compounds showed antibacterial activity to the bacteria used. All synthesized compounds showed low antibacterial activity to the gram negative bacteria as compare to gram positive bacteria (**Table-5**). From the above result, it can be concluded that the antibacterial activities of all synthesized compounds.

3.5. Minimum Inhibitory Activity:

The minimum inhibitory concentration of synthesized compounds were determined against *E. coli(G-), S. aureus(G+), S. typhi(G+), B. subtilis(G+), K. pneumoniqe(G+), P. aeruginosa(G+)* (**Table-5**) by the serial dilution method. The MIC levels were found 50g/ml against synthesized compounds.

Table 5: Antibacterial screening for HBMTCH and its inner transition metal complexes

Compound	*B. Substillis*	*P. Aeruginosa*	*S. Aureas*	*S. Typhi*	*E. Coli*	*K. Pneumoniae*
HBMTCH	15	12	17	11	09	12
$[Pr(BMTCH)_3]NO_3$	17	15	22	14	12	16
$[Gd(BMTCH)_3]NO_3$	19	14	19	12	10	16
$[Dy(BMTCH)_3]NO_3$	17	17	19	20	17	15

3.6. Antifungal screening:

The antifungal activities of all compounds have been assayed at concentration of 500ppm against five plant pathogens and mould fungi. The inhibitory effects of all compounds against these organisms are given in **Table 6**. The screening results indicate that all synthesized compounds show good antifungal activities against *Colletotrichum Gloeosporiodes penz, Canilida Albicans, Aspergillus Niger, Aspergillus Flaves* and *penicillium sp.*

Table 6: Antifungal screening (500ppm) for HBMTCH and its inner transition metal complexes

Compound	**^{a}C.G.**	**^{b}C.A.**	**^{c}A.N**	**^{d}A.F**	**^{e}P.S.**
HBMTCH	15	12	17	11	09
$[Pr(BMTCH)_3]NO_3$	17	15	22	14	12
$[Gd(BMTCH)_3]NO_3$	19	14	19	12	10
$[Dy(BMTCH)_3]NO_3$	17	17	19	20	17

Where: a = Colletotrichum Gloeosporiodes penz, b = Canilida Albicans, c = Aspergillus Niger, d = Aspergillus Flaves and e = Penicillium sp.

3. CONCLUSION:

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 anion inside the coordination sphere in the complexes. FT(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 [20-23]. Ligand and its metal complexes show good antibacterial and antifungal activities. The possible structure of the complexes is given **Figure 2**.

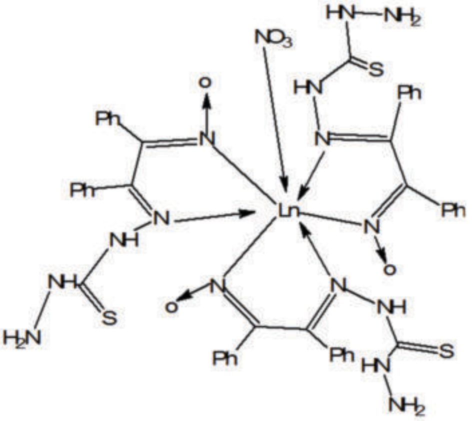

Figure-2: Structure of metal complexes of HBMTCH ligand

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