

Review

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# Synthesis and Spectral Characterization of Mixed Legend Complexes of Lanthanide Ions with Morph line-N-Thiohydrozone and 1, 10-Phenanthroline

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#### **ABSTRACT:**

The complexes of aryl hydrazones have been reported to act as inhibitors for enzymes <sup>[1].</sup> A number of transition metal complexes with various hydrazones have been synthesized <sup>[2,3]</sup>, the metal complexes of Nibium(V) with furoic acid hydrazones have been synthesized in dry chloroform under nitrogen atmosphere and characterised by elemental analysis, molar conductance, electronic, infrared, NMR spectral studied and thermal studies. It is proposed that complexes exhibit coordination number seven. Hydrazides and hydrazones have in testing ligation properties due to the presence of several potential coordination sites, and transition metal complexes of these legends have been studied extensively <sup>[4-6]</sup>. Hydrazones also exhibit pharmacological activity <sup>[7-10]</sup>. And analytical applications <sup>[11]</sup> Due to their biological activity especially a potent inhibitors for many enzymes, the coordination chemistry of aroyl hydrazine and related compounds has been the subject of extensive investigation <sup>[12, 13]</sup>. Edward <sup>[14]</sup> and co-workers have shown that the replacement of the aromatic group by the ferrocenyl moiety inn penicillin's and cephalosporins improves their antibiotic activity. Therefore a series of hydrazones containing the ferricenyl moiety and their complexes with anhydrous lanthanide chloride have been investigated <sup>[15-19]</sup>.

Key Words: Morph line, Thiohydrozone, Hydrazones, cephalosporin's, furoic,

### 1. INTRODUCTION:

The complexes of aryl hydrazones have been reported to act as inhibitors for enzymes <sup>[1].</sup> A number of transition metal complexes with various hydrazones have been synthesized <sup>[2,3]</sup>, the metal complexes of Nibium(V) with furoic acid hydrazones have been synthesized in dry chloroform under nitrogen atmosphere and characterised by elemental analysis, molar conductance, electronic, infrared, NMR spectral studied and thermal studies. It is proposed that complexes exhibit coordination number seven. Hydrazides and hydrazones have in testing ligation properties due to the presence of several potential coordination sites, and transition metal complexes of these legends have been studied extensively <sup>[4-6]</sup>. Hydrazone also exhibit pharmacological activity <sup>[7-10]</sup>. And analytical applications <sup>[11]</sup>. Due to their biological activity especially a potent inhibitors for many enzymes, the coordination chemistry of aroyl hydrazine and related compounds has been the subject of extensive investigation <sup>[12, 13]</sup>. Edward <sup>[14]</sup> and co-workers have shown that the replacement of the aromatic group by the ferrocenyl moiety inn penicillin's and cephalosporians improves their antibiotic activity. Therefore a series of hydrazones containing the ferricenyl moiety and their complexes with anhydrous lanthanide chloride have been investigated <sup>[15-19]</sup>.

The mixed ligand complexes of hydrazones containing the morph line-N-thiohydrazide with hydrated lanthanide chloride and other ligands have not, however been reported as yet. In the present studies,

acetone Morpholine-N-thiohydrazone (HL) and mixed ligand lanthanide complexes containing 1, 10-phenanthroline (phen) have been studied.

#### 2. EXPERIMENTAL:

Morph line-N-thohydrazide was prepared according to the literature method <sup>[20-22]</sup>. Hex hydrated lanthanide chloride was prepared from the respective oxides and hydrochloric acid. The other chemicals were analytical reagent grade.

#### 2.1 Preparation of acetone-Morph line-N-thiohyrazone:

A mixture of Morph line-N-thihydrazine and acetone with a molar ratio of 1:1 was reached in anhydrous ethanol under reflux for five hour. After filtering the filtrate was concentrated to dryness, recrycallised from benzene, and the organic crystals were collected on a Buchner funnel, washed with cold benzene and dried in vacuo. Yield 70% (mp 156<sup>o</sup>C) Found C- 47.76; H-7.46; N- 20.89 Calculated for ( $C_{18}H_{15}N_3OS$ ), C- (47.62), H - (7.34), N- (20.74).

#### 2.2 Preparation of complexes:

Acetone-Morphine-n-thiohydrazone (1.4 m mol) and 1, 10-phenanthrline (1.4 m mol) were dissolved in 30 cc of anhydrous ethanol under heating hexa hydrated lanthanide chlorides (0.7 m mol) in ethanol (8 cc) were added drop wise to the above solution. The mixture was maintained under refluxed for 8 hr. After filtration the filtrate was concentrated to 10 cc and ether was added with stirring. The precipitate which formed was collected, washed four times with 1:4 ethanol/ether and twice with ether and dried in vacuo. Yield 58%

#### 2.3 Spectral Measurement

IR - spectra were recorded with a Perkin-Elmer spectrophotometer using KBr disc in the region 4000-4400 cm<sup>-1</sup>, NMR – spectra were obtained on an AC -80 spectrophotometer using deutero sulpha oxide as solvent and TMS – as an internal standard UV – spectra were measured with Hitachi –U-3400, UV – visible spectrophotometer in the region 215 – 500 nm using a solution in methanol. Electrolytic conductance measurements were made with Elico- conduct meter and methanol as solvent at room temperature. Thermal characterisation studies were carried out with a Pye – DTA thermal analyser in an argon atmosphere

#### 3.1 Results and discussions

The lanthanide complexes are amorphous reddish-orange solids. They are soluble in methanol, ethanol dimethyl sulfoxide and dimethyl form amide, sparingly soluble in dimethyl ether. Their elemental analysis show that the formula of these complexes is  $[Ln(HL)(Phen)_2]Cl_3.4/5H_2O$ .

#### **3.2. Magnetic studies:**

The room temperature magnetic moments for all the complexes except that of La(III) complex which is diamagnetic, show little deviation from the van vleck values <sup>[23]</sup>. This indicates slight participation of 4felectrons in bond formation. The higher  $\mu$ -effective values observed in the case of Sm(III) complex may be explained in terms of low J-J- separation. The energy difference between the ground state (6H<sub>5/6</sub>) and next J- level (6H<sub>7/2</sub>) is the order of KT which leads to thermal population of the higher energy levels thus showing susceptibility due to a first order Zeeman Effect <sup>[24]</sup>.

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### TABLE (1): DECOMPOSITION TEMPERATURE AND ELEMENTAL ANALYSIS OF THE COMPLEXES

S.	Complex Formula	Decomposition	Molar	% Chem	nical Co	mposition	Found
No.		Temp. (°C)	Conductance	(Calculate	ed)	-	
				C	Н	N	М
1	$La(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	273	82.80	25.73	3.45	7.44	14.84
				(25.85)	(3.55)	(7.54)	(14.96)
2	$Ce(C_{8}H_{15}N_{3}OS)(C_{12}H_{8}N_{2})Cl_{2}.5H_{2}O$	268	86.63	25.71	3.45	7.45	14.96
				(25.70)	(3.55)	(7.53)	(15.07)
3	$Pr(C_{*}H_{15}N_{2}OS)(C_{12}H_{*}N_{2})Cl_{2}.5H_{2}O$	266	90.14	25.70	3.45	7.41	15.01
C			,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,,	(25.80)	(3.55)	(7.52)	(15.14)
4	$Nd(C_{*}H_{15}N_{2}OS)(C_{12}H_{*}N_{2})Cl_{2}.5H_{2}O$	270	88.76	25.60	3.45	7.39	15.35
				(25.70)	(3.53)	(7.50)	(15.45)
5	$Sm(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_{3.5}H_2O$	260	86.65	25.44	3.45	7.35	15.90
5		200	00.00	(25.30)	(3.51)	(7.45)	(16.00)
6	$E_{11}(C_{\circ}H_{15}N_{2}OS)(C_{12}H_{\circ}N_{2})C_{12}SH_{2}O$	268	85 44	25.38	3 40	7 32	16.02
0		200	00.11	(25.49)	(3.51)	(7.43)	(16.14)
7	Gd(C <sub>2</sub> H <sub>15</sub> N <sub>2</sub> OS)(C <sub>12</sub> H <sub>2</sub> N <sub>2</sub> )Cl <sub>2</sub> 4H <sub>2</sub> O	256	84.12	25.74	3 28	7 46	16.81
,		250	02	(25.84)	(3 34)	(754)	(16.93)
8	$Tb(C_{2}H_{15}N_{2}OS)(C_{12}H_{2}N_{2})Cl_{2}5H_{2}O$	253	85.10	25.25	3 40	7 30	16 64
0		255	05.10	(25, 70)	(355)	(7, 38)	(16.76)
9	$D_{V}(C_{0}H_{1}N_{2}OS)(C_{1}H_{0}N_{2})C_{1}AH_{2}O$	248	90.33	25.55	(3.55)	7 36	17 30
		2-10	70.35	(25, 70)	(3, 32)	(7.49)	(17.30)
10	Ho(CoHypNaOS)(CyaHoNa)Cla 5HaO	255	94.16	25.03	3 33	7 20	17 15
10		233	74.10	(25.05)	(3.46)	(7, 33)	(15.28)
11	$Fr(C_{9}H_{15}N_{2}OS)(C_{12}H_{9}N_{2})Cl_{2}5H_{2}O$	253	97 33	24.95	3 35	7 22	17 38
11		233	71.55	(25.08)	(3.45)	(7, 32)	(17.30)
12	$Tm(C_0H_1 rN_2OS)(C_1 rH_0N_2)Cl_2 5H_2O$	252	101 33	23.00)	(3.43)	7 16	17 50
14		252	101.55	(25.04)	(3.44)	(7.30)	(17.63)
13	$Y_{b}(C_{0}H_{1}N_{2}OS)(C_{1}H_{0}N_{2})C_{1}S_{b}S_{0}$	250	105 60	24.83	3 33	7 16	17.80
15		250	105.00	(24.93)	(343)	(7.27)	(17.98
14	$L_{11}(C_{\circ}H_{15}N_{2}OS)(C_{12}H_{\circ}N_{2})C_{12}5H_{2}O$	251	105 60	24.95	3 30	7.16	18.00
1.		251	105.00	(25.04)	(3.42)	(7.26)	(18, 14)
				(23:01)	(3.12)	(7.20)	(10.11)
15	$Y(C_0H_1,N_2OS)(C_1,H_2N_2)C_1,5H_2O$	258	102.11	27.22	3.66	7.85	10.00
15		230	102.11	(27.32)	(3.76)	(7.97)	(10.00)
				(27.52)	(3.70)	(1.57)	(10.12)
16	$(C \parallel N OS)(C \parallel N)$			62.76	5.00	10.05	14.06
10	$(C_8\pi_{15}N_3O_5)(C_{12}\pi_8N_2)$	-	-	(62.00)	5.90	10.23	14.90
				(02.99)	(0.03)	(10.57)	(13.07)

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**3.3. Infrared spectral studies:** The IR spectra of the ligands and complexes are measured with the help of Perkin-Elmer in the region 4000-400 cm<sup>-1</sup>. The important IR frequencies of the ligands and their complexes together with their relative assignments are given in table 2. The IR spectrum of the ligand in KBr shows a band at 3200 cm<sup>-1</sup> assigned to v(N-H) which remains practically unchanged in the spectra of all the adducts. However v(C=N) and thioamide(IV) bands occurring in the ligand at nd 1640 and 840 cm<sup>-1</sup>, respectively, shows a negative shift of 10-30 and 15-30 cm<sup>-1</sup>, respectively in the spectra of adducts indicating coordinating through azomethine nitrogen and thoine sulphur. These bonding sites are further supported by positive shifts of 10-35 cm<sup>-1</sup> in thioamide-I and II bands and of 10-20 cm<sup>-1</sup> in v(N-N) which appears in free ligand at 1430, 1275 and 970 cm<sup>-1</sup>, respectively. The IR spectra of the complexes are similarly compared with the IR spectra of ligand v(C=S) thioamide I and v(C=N) were shifted to lower frequencies where as the v(N-N) and  $\delta$ (N-H) (amide II) were shifted to higher frequencies by 2-8 cm<sup>-1</sup> and 20-25 cm<sup>-1</sup>, respectively. These changes show that the ligand coordinated with lanthanide ions in the form, with sulphur atom of the thione group and the nitrogen atom of the azomethine group <sup>[25-26]</sup>. Compared with spectra of 1:10-phenanthroline ligand  $\delta$ (C-H) was shifted to higher frequencies by ca 6 cm<sup>-1</sup>. These changes show that phenanthroline participates in coordination <sup>[27-30]</sup>.

Two new bands observed at ca 540-550 cm<sup>-1</sup> and 415-440 cm<sup>-1</sup> attributed to v(Ln-N) and v(Ln-S), respectively <sup>[31, 32]</sup>. The IR spectra of the ligand acetone morpholine-N-thiohydrazone show medium, sharp peaks of v(N-H) at 3240 cm<sup>-1</sup>, where as the spectra of complexes exhibit a strong broad peak of

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v(S-H) at 3200 cm<sup>-1</sup>. The bands assigned to thioamide I-IV vibrations are absent and v(C-N) of azomethine is shifted to lower wave number. These complexes show new bands assigned  $^{[33-35]}$  to v(S-C=N) and v(C-S) vibrations. The bands assigned to v(C=C) and v(C-N) of morpholine ring remaining around the same position suggests that they do not take part in complexation. The spectra of the complexes exhibit a broad band within the range 3500-3170 cm<sup>-1</sup> which is arrtibuted to v(O-H) of water molecules associated with the complex formation. Water is usually present in the solid complexes as water of hydration or coordination water <sup>[36, 37]</sup>. A bending of v(O-H) was observed in the range 972-813 cm<sup>-1</sup>. The other bending vibration of  $\delta$ (O-H) are usually fund near 1600 cm<sup>-1</sup> which overlaps with other bands. In addition other charcterstic frequencies of morpholine moiety appear at 1300, 960, 780 and 485 cm<sup>-1</sup> and the bands at 1375 are attributed to  $\delta$ (CH<sub>3</sub>) in morpholine-N-Thiohydrazone-acetone (HL) ligand and in all the complexes<sup>(38)</sup>.





# TABLE 2 – IMPORTANT IR – ABSORPTION BANDS (in cm<sup>-1</sup>) OF THE LIGANDS AND THEIR COMPLEXES

S.	Complex Formula	v(C=S)	δ(N-H)	v(C=N	v(N-N)	v(Ln-	v(Ln-N)	δ(C-H)	δ(C-H)	v (C-H)
No.	-			)		<b>S</b> )				
1	$La(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	810vs	1540vs	1580vs	1005m	415w	545m	845vs	730vs	1425vs
2	$Ce(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	820vs	1538vs	1580vs	1003m	417w	540m	840vs	730vs	1420vs
3	$Pr(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	800vs	1540vs	1585vs	1002m	410w	540m	845vs	725vs	1420vs
4	$Nd(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	810vs	1535vs	1580vs	1003m	415w	540m	845vs	730vs	1425vs
5	$Sm(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	820vs	1539vs	1585vs	1003m	410w	544m	840vs	725vs	1430vs
6	$Eu(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	800vs	1540vs	1586vs	1002m	420w	550m	848vs	730vs	1424vs
7	$Gd(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.4H_2O$	800vs	1540vs	1587vs	1003m	419w	549m	845vs	730vs	1420vs
8	$Tb(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	800vs	1540vs	1580vs	1002m	420w	545m	840vs	725vs	1425vs
9	$Dy(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.4H_2O$	800vs	1542vs	1580vs	1003m	420w	550m	850vs	730vs	1423vs
10	$Ho(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	800vs	1545vs	1600vs	1002m	418w	540m	840vs	725vs	1420vs
11	$Er(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	800vs	1540vs	1600vs	1004m	420w	550m	840vs	720vs	1420vs
12	$Tm(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	800vs	1540vs	1580vs	1003m	420w	540m	848vs	725vs	1420vs
13	$Yb(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	810vs	1544vs	1595vs	1002m	418w	520m	840vs	720vs	1420vs
14	$Lu(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	815vs	1540vs	1600vs	1004m	415w	530m	825vs	720vs	1415vs
15	$Y(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	815vs	1542vs	1600vs	1003m	410w	520m	820vs	720vs	1410vs
16	$(C_8H_{15}N_3OS)(C_{12}H_8N_2)$	840vs	1519vs	1620vs	1000m	-	-	850vs	735vs	1420vs



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#### 3.4. Thermal studies:

The thermal characterization studies were carried out with a PYE-DTA THERMAL ANALYSER in argon atmosphere. The thermal analysis data of the legends and their complexes are given in table....It can be seen that the water in the complexes exists in two different forms, crystal and coordinated. The number of coordinated water molecules decreases with a change of lanthanide from light to heavy i.e. the coordination number of central ions decreases, progressively due to heavy i.e. the coordination. Throughout the process the temperature of decomposition we can see that the thermal stability of the complexes is increased much more than that of the legends after forming complexes is decreased with a change of lanthanide from light to heavy. Table 3 shows thermal analysis data of the legends and their complexes.

### **3.5.** <sup>1</sup>H NMR spectral studies:

The NMR- spectra data of the legends and the complexes are shown in table (4). The protons on the morph line ring, methyl, the nitrogen atom and all the protons on 1:10 phenanthroline are shifted down field. These changes are caused by the deshielding effect which occurs after forming the complexes <sup>(39)</sup>. This is also shows that the acetone morph line -N - Thiohydrazone (HL) legend coordinate with lanthanide ions in the throne form and that the molar<sup>(40)</sup> ratio HL/Phen in the complexes is 1:2.

#### 3.6. UV Spectral studies

The UV spectra of the legends and their complexes in methanol are measured with the help of Hitachi-U-3400, UV visible spectrophotometer in the region 215-500 nm and the observed values are shown in table. The UV spectra of complexes are similar, but they are somewhat different from those of ligands <sup>[41]</sup>. The k ( $\pi - \pi^*$ ) band transition of HL legend is observed at 220 nm, but in complexes bath chromic shift of ca 8 nm occurs resulting from the chelating of the legend with lanthanide ions, and the band appear at 270 nm and overlaps with the B-band of phenanthroline in the complexes. The broad band near 460 nm in the ligand and the complexes is artibuted to change charge transfer. The band at 230 nm shows that phenanthroline participates in coordination <sup>[42]</sup>.

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TABLE 3: THERMAL ANALYSIS DATA OF THE LIGANDS AND

THEIR COMPLEXES

S. No.	Complex Formula	Ln <sup>3+</sup>	Decomposition temp (°C)	Leaving group	Weight loss found (calculated)
1	La(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>3</sub> .5H <sub>2</sub> O	La	50 165 240 290-700 Upto 700	$\begin{array}{c} 2H_2O\\ H_2O\\ 2\ H_2O\\ Residue\\ +3Cl \end{array} \hspace{0.1cm} (La$	3.86 (4.02) 3.95 (4.01) 1.95 (2.01) 27.12 (27.40)
2	Ce(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>3</sub> .5H <sub>2</sub> O	Ce	52 200 270-660 Upto 600	$2H_2O$ $2H_2O$ $H_2O$ Residue (Ce $+3Cl)$	3.85 (4.01) 3.87 (4.01) 1.96 (2.01) 26.94 (27.51)
3	$Pr(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2O$	Pr	50 160 240 300-580	$\begin{array}{c} 2H_2O\\ 2H_2O\\ H_2O\\ Residue\\ +3Cl \end{array} (Pr$	3.96 (4.01) 3.96 (4.01) 1.94 (2.01) 26.75 (27.57)
4	Nd(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>3</sub> .5H <sub>2</sub> O	Nd	60 140 250 280-550	$\begin{array}{c} 2H_2O\\ 2H_2O\\ H_2O\\ Residue\\ +3Cl) \end{array} (Nd$	3.84 (3.99) 3.84 (3.99) 1.94 (1.99) 27.72 (27.83)
5	Gd(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>3</sub> .4H <sub>2</sub> O	Gd	50 210 280-640	$2H_2O$ $2H_2O$ Residue (Gd +3Cl)	3.93 (4.01) 3.93 (4.01) 28.76 (29.44)
6	Dy(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>3</sub> .4H <sub>2</sub> O	Dy	55 180 260-600	$2H_2O$ $2H_2O$ Residue (Dy +3Cl)	3.80 (3.99) 3.80 (3.99) 26.92 (29.85)
7	Yb(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>3</sub> .5H <sub>2</sub> O	Yb	50 170 240 260-550	$2H_2O$ $2H_2O$ $H_2O$ Residue (Yb +3Cl)	4.06 (4.26) 4.06 (4.26) 1.97 (2.13) 32.88 (33.06)
8	Lu(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )Cl <sub>3</sub> .5H <sub>2</sub> O	Lu	45 205 260-575 Upto 575	$2H_2O$ $H_2O$ $2H_2O$ Residue (Yb +3Cl)	6.75 (7.73) 1.80 (1.93) 29.78 (30.22)
9	HL(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)	-	160-375 375-490	Substituent morpholine ring	56.98 (57.21) 41.60 (42.78)
10	Phenanthroline (C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )	-	115 168-325	H <sub>2</sub> O completly decomposed	8.95 (9.18)

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#### TABLE 4: NMR – SPECTRAL DATA OF THE LIGANDS AND THEIR COMPLEXES

<b>S. No.</b>	Complex Formula	Morpholine moiety C <sub>4</sub> H <sub>8</sub>							
		4H(2 ,3)	4H(4, 5)	(N– H) <sup>a</sup>	CH <sub>3</sub> <sup>b</sup>	a	b	С	D
1.	(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)	4.32 (2H, m)	4.87 (2H,t)	9.65 (1H,S)	2.0 (6H, d)	6.58 (2H, m)	6.70 (2H,S)	7.19 (2H,m )	8.14 (2H,m)
2.	La(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )	4.35	4.91	9.75	2 50	7.81	8.03	8.54	9.17
	C1.5H <sub>2</sub> O	(2H, m)	(2H,t)	(1H,S)	2.30	(4H, m)	(4H,S)	(4H,m )	(4H,m)
3.	Lu(C <sub>8</sub> H <sub>15</sub> N <sub>3</sub> OS)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )	4.35	4.95	9.77	2.50	7.86	8.01	8.55	9.13
	Cl.5H <sub>2</sub> O	(2H, m)	(2H,t)	(1H,S)	2.30	(4H, m)	(4H,S)	(4H,m )	(4H,m)

# S – singlet; d – doublet; t – triplet; m – multiplet



- (a) The signal of this proton disappears after adding  $D_2O$ .
- (b) The signal of these protons is overlapped with that of the protons in deuteron dimethyl sulphoxide.

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## TABLE 5: Important Uv Spectral Data Of The Ligands And Their complexes

S. No.	Complex Formula	Ln <sup>3+</sup>	Absoption bands (log $\epsilon$ ) nm, $\lambda_{max}$				
1	HL(C8H15N3OS)	-	220 (4.5)	-	268 (4.04	460	
2	$Phen(C_{12}H_8N_2)$	-	-	229.6 (4.70)	268.7 (4.57)	-	
3	HL + Phen	-	-	228	268.5	460	
4	$\begin{array}{c} Dy(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.4H_2\\ O\end{array}$	Dy	228.3(5.01)	229.4(4.99)	270.1 (4.83)	460	
5	$\begin{array}{c} Ho(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2\\ O\end{array}$	Но	228.0(5.03)	229.4(5.01)	269.7 (4.83)	460	
6	$\frac{\text{Er}(\text{C}_8\text{H}_{15}\text{N}_3\text{OS})(\text{C}_{12}\text{H}_8\text{N}_2)\text{C}l_3.5\text{H}_2}{\text{O}}$	Er	228.5(5.02)	229.4(5.02)	269.0 (4.84)	460	
7	$\frac{\text{Tm}(\text{C}_8\text{H}_{15}\text{N}_3\text{OS})(\text{C}_{12}\text{H}_8\text{N}_2)\text{Cl}_3.5\text{H}}{_2\text{O}}$	Tm	227.5(4.97)	230.4(4.94)	270 (4.80)	460	
8	$\begin{array}{c} Yb(C_{8}H_{15}N_{3}OS)(C_{12}H_{8}N_{2})Cl_{3}.5H_{2}\\ O\end{array}$	Yb	228.9(5.12)	229.9(5.11)	269.3 (4.93)	460	
9	$\begin{array}{c} Lu(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2\\ O\end{array}$	Lu	228.2(5.05)	229.4(5.01)	269.7 (4.82)	460	
10	$\begin{array}{c} Y(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_{3.5}H_2\\ O\end{array}$	Y	227.6(4.97)	229.3(4.96)	269.3 (4.79)	460	
11	$(C_8H_{15}N_3OS) + (C_{12}H_8N_2)$						
12	$\begin{array}{c} La(C_{8}H_{15}N_{3}OS)(C_{12}H_{8}N_{2})Cl_{3}.5H_{2}\\ O\end{array}$	La	228.4 (5.08)	229.6 (4.72)	270.0 (4.88)	460	
13	$\begin{array}{c} Ce(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2\\ O\end{array}$	Ce	228.0 (5.11)	229.0 (5.07)	275.6 (4.92)	460	
14	$\begin{array}{c} Pr(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2\\ O\end{array}$	Pr	228.8 (5.09)	229.1 (5.06)	274.6 (6.90)	460	
15	$ \begin{matrix} Nd(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2 \\ O \end{matrix} $	Nd	227.4 (5.06)	229.3 (5.06)	274.3 (4.91)	460	
16	$\begin{array}{c} Sm(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2\\ O\end{array}$	Sm	228.4 (5.08)	228.8 (5.02)	274.5 (4.83)	460	
17	$ \begin{array}{c} Eu(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2\\ O \end{array} $	Eu	227.4 (5.00)	229.1 (5.00)	273.8 (4.83)	460	
18	$ \begin{array}{c} Gd(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.4H_2\\ O \end{array} $	Gd	227.9 (5.02)	229.5 (5.03)	274 (4.82)	460	
19	$\begin{array}{c} Tb(C_8H_{15}N_3OS)(C_{12}H_8N_2)Cl_3.5H_2\\ O\end{array}$	Tb	227.6 (5.04)	229.3 (5.03)	274 (4.84)	460	

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- (a) Concentrations (HL)  $(C_8H_{15}N_3OS) = 9.80 \times 10^{-5} \text{ M}$ ; Phen = 3.96 x 10<sup>-5</sup> M, HL + Phen + HL = 2.44 x 10<sup>-5</sup> M; Phen = 3.96 x 10<sup>-5</sup> M, Complex = approx. = 2.00 x 10<sup>-5</sup> M.



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#### Molar conductance

The conductance measurement were made at  $10^{-3}$  M solution of the complexes in Dimethyl formamide using Elico conductivity bridge, type Cm – 82,provided with a cell having constant 0.51. The molar conductance values of ligand (acetone morpholine – N – thiohydrazone), phenanthroline and the complexes are 17.32, 15.0 and 82.80, 105.6 ohm-1 cm2 mol-1 respectively. These values indicate that in dimethyl formamide solution ligand and phenanthroline are non electrolytes but the complexes are (1 : 1) electrolyte <sup>(43-47)</sup>.

#### **CONCLUSIONS:**

Acetone morpholine-N-Thiohydrazone and 1,10-phanthroline are bidantate ligands. One molecule of HL and two molecules of Phe, tw chloride ions and one to three molecules of water coordinated with one lanthanide ion. The water molecules in these complexes are variable and hence with the help of the all the studies the following structures have been suggested.



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