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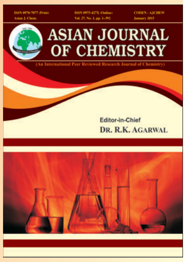

Synthesis, Characterization, Spectral and Antimicrobial Studies of Some Trivalent Ln(III) Metal Complexes with Ligands Containing 'N' and 'O' Donor Atoms

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Ten new coloured solid complexes of type [ML_2X_2], Where M=La(III), Pr(III), Nd(III), Sm(III) & Dy(III), 'L' = Ligand *i.e.*, N-(3-methyl-thiocarbamyl-5-oxo-2-pyrazolin-4-ylene-N'-(4'-antipyrine)hydrazine (HATP) and N-(3-methyl-1-thiocarbamyl-5-oxo-2-pyrazolin-4-ylene)-N'-(4'-benzothiazole)hydrazine (HBTP) and 'X'=H_2O have been synthesized and characterized by their elemental analysis, molar conductance values, magnetic susceptibilities, UV, IR and NMR spectral studies. Elemental analysis confirms 1:2 stoichiometry of the synthesized complexes. Spectral studies confirms that the ligand 'HATP' and 'HBTP' acts as tetradentate and tridentate, respectively and coordinates to central metal ion by 'N' and 'O' donor atoms. Complexes are ten and eight coordinated. Further the ligands and synthesized complexes have been screened for their antibacterial activity against some Gram-positive and Gram-negative bacteria.

Keywords: Synthesis, Ln(III), Metal complexes.

INTRODUCTION

Hydrazones of pyrazolone derivatives are of much interest due to their high chelating ability and applications in analytical chemistry[1,2]. Such ligands and their derivatives are an active moiety in the class of non-steroidal, antiinflammatory agents used in the treatment of arthritis and other musculoskeletal and joint disorders. The pyrazolone derivatives shows remarkable antibacterial, antioxidant and analgesic activity[3]. Also, azo hydrazone tautomerism of aryl azo derivatives of β-dicarbonyls, naphthols and 2-pyrazolin-5-ones has provided controversy and interest both in the past[4,5]. These have varied ligational behaviour towards different metal ions and have created specific structural features in their metal complexes[6]. A large number of ligands containing 'N' and 'O' donor atoms coordinate with rare earth metals forming stable complexes have been reported[7-16]. Synthesis and characterization of nickel(II) and copper(II) complexes with 3-(*p*-chlorobenzyl)-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one[17] and synthesis, characterization and DNA-binding of cobalt(II) complex with 3-benzyl-4-(*p*-hydroxy-*m*-methoxybenzylidenamino)-1*H*-1,2,4-triazole-5-one[18] have been reported. Synthesis, characterization and biocidal activities of mixed ligand complexes of dioxomolybdenum(VI) derived from sulpha drugs and 4-benzoyl-3-methyl-1-phenyl-2-pyrazoline-5-one[19] and structural and spectroscopic aspects of 2,3-butanedionemonoxime monohydrazone have also been reported[20].

But the literature survey revealed that the complexation of ligands under our study with trivalent lanthanides have not been studied so far. In view of this, we report here the synthesis, characterization and antibacterial screening of a few complexes of N-(3-methyl-thiocarbamyl-5-oxo-2-pyrazolin-4-ylene-N'-(4'-antipyrine)hydrazine (HATP) and N-(3-Methyl-1-thiocarbamyl-5-oxo-2-pyrazolin-4-ylene)-N'-(4'-benzothiazole)-hydrazine (HBTP) with some trivalent lanthanide metal ions.

EXPERIMENTAL

Thiosemicarbazide and 2-aminobenzothiazole were purchased from Loba. 4-Aminoantipyrine were purchased from Fluka. All other chemicals, solvents were purchased from CDH and metal salts (99.97 % purity) used were of AR grade and were purchased from Indian Rare Earth Udyog Mandal, Kerala, India.

Synthesis of N-(3-methyl-thiocarbamyl-5-oxo-2-pyrazolin-4-ylene-N'-(4'-antipyrine)hydrazine (HATP): 3-Methyl-1-thiocarbamyl-2-pyrazolin-5-one (MTP) has been prepared by as in literature[21]. 4-Aminoantipyrine (20 g, 0.1 mol) was diazotized and the diazonium salt solution was added slowly with stirring to an ice-cold alkaline solution of (0.1 mol 15.70 g) MTP. This mixture was kept in an ice-bath for 1 h with occasional stirring.Bright red crystals of HATP separated. It was filtered under suction, washed with ether and then recrystallized from ethanol. The purity of the compound was checked by TLC using silica gel plate and its elemental analysis. Its m.pt. was found to be 210 °C.

Synthesis of N-(3-methyl-1-thiocarbamyl-5-oxo-2-pyrazolin-4-ylene)-N'-(4'-benzothiazole)hydrazine (HBTP): 0.1 mol, 20 g of 2-aminobenzothizaole was diazotized and diazonium salt solution was added slowly with stirring to an ice-cold alkaline solution of MTP (15.70 g, 0.1 mol). The mixture was kept in ice for 40 min, fine yellowish brown crystals of HBTP separated out. It was filtered under suction washed with ether and then recrystallized from ethanol. The purity was checked by TLC and its elemental analysis. Its melting point was 195 °C.

Synthesis of complexes: Complexes were prepared by refluxing aqueous ethanolic solution of corresponding metal salts (0.1 mol) and ligands (0.12 mol) in ethanol for 1 h on a water thermostat. On cooling the coloured solid complexes separated. These were filtered and washed with ethanol to remove excess ligand if any and then with benzene. It was now dried over P_4O_{10}.

Metal contents were estimated by usual procedure after digesting the complexes with conc. H_2SO_4. Chloride in the complex was estimated by Volhards method[22]. Nitrogen content was determined using elemental analyzer Heraeus Carlo Erba-1108 at CDRI Lucknow. Magnetic moments of the complexes were determined in Gouy Balance Calibrated using $[HgCo(NCS)_4]$ at room temperature in Inorganic Research Laboratory. P.G. Deptt. Of Chemistry, L.N.M.U. Darbhanga. Molar conductance of the complexes was measured by digital conductance meter systronics model 304. Analytical data, decomposition temperature, conductance, colour and μ_{eff} values are listed in Table-1.

IR spectra of the ligand and complexes were recorded on a Perkin-Elmer IR spectrometer using KBr Pellet method by the courtesy of CDRI and Deptt. of Chemistry, IIT Delhi. ^{1}H NMR spectra were recorded on Perkin Elmer 90 MHz NMR spectrometer from CDRI Lucknow.

Biological evaluation: The bacterial activity of HATP and HBTP and their Ln(III) metal complexes were tested against Gram-positive bacteria *Staphylococcus aureus* and Gram-negative bacteria *Pseudomonas aeruginosa*, *E. coli* and *Klebsiella pneumonia* by disc-diffusion method using Agar Nutrient as medium and ofloxacin as control[23].

DMSO was used as solvent for making test solutions of all the compounds studied. The paper disc (6 mm) containing the compound (100 μg/disc) was placed on the surface of the nutrient agar plate previously spread with 0.1 mL of sterilized culture of micro-organism. These were incubated at 37 °C for 2 days. The diameter of inhibition zone around the paper disc was measured (Table-2).

RESULTS AND DISCUSSION

The complexes are non-hygroscopic, almost coloured stable solids and are soluble in DMSO and DMF. They decompose above 300 °C. The molar conductance values show their non-electrolytic nature. IR spectra of the ligands shows a band at 1660 cm^{-1} assignable to ν(C=O) of thiocarbamyl pyrazolone[24]. The band at 1640 cm^{-1} in the spectra of HATP is due to ν(C=O) at antipyrine[25]. The bands at 1620 and at 1585 cm^{-1} can be due to C=N mode of HATP and HBTP, respectively[26]. A weak band at 3100 cm^{-1} can be assigned to stretching frequency of intramolecularly hydrogen bonded NH in HATP and the band at 3175 cm^{-1} in the spectrum of HBTP is due to NH of hydrazone part[27]. The ν(NH_2) and ν(C=N) appeared at 3360 cm^{-1} and 1160 cm^{-1}, respectively[28]. The –N=C=S ring stretching frequency in HBTP is observed at 2020 cm^{-1}.

TABLE-1
ANALYTICAL DATA OF LIGAND AND METAL COMPLEXES

S. No.	Compound / Colour	m.w. obs. (calcd.)	Elemental analysis (%): Obs. (calcd.) C	H	N	S	Ln	Decomp. temp. (°)	Λ_m (ohm^{-1} cm^2 mol^{-1})	μ_{eff} (BM)
1	HATP Bright Red	371.02 (371.00)	51.77 (51.75)	4.62 (4.58)	26.45 (26.41)	8.64 (8.62)	–	–	–	–
2	$[La(HATP)_2(H_2O)_2]$ Light Blue	915.13 (915.00)	42.00 (41.96)	3.97 (3.93)	21.48 (21.42)	7.01 (6.99)	15.24 (15.19)	342	10.5	Dia
3	$[Pr(HATP)_2(H_2O)_2]$ Blue	917.45 (917.00)	41.89 (41.87)	3.94 (3.92)	21.43 (21.37)	7.02 (6.97)	15.42 (15.37)	338	14.3	3.67
4	$[Nd(HATP)_2(H_2O)_2]$ Light Blue	920.38 (920.00)	41.77 (41.73)	3.97 (3.91)	21.35 (21.30)	6.99 (6.95)	15.72 (15.65)	355	12.2	3.60
5	$[Sm(HATP)_2(H_2O)_2]$ Blue	926.47 (926.00)	41.52 (41.46)	3.95 (3.88)	21.19 (21.16)	7.00 (6.91)	16.25 (16.19)	346	14.5	1.66
6	$[Dy(HATP)_2(H_2O)_2]$ Bluish White	938.27 (938.00)	40.95 (40.93)	3.87 (3.83)	20.94 (20.89)	6.84 (6.82)	17.35 (17.27)	370	16.2	11.31
7	HBTP Yellowish Brown	333.12 (333.00)	47.00 (46.84)	3.94 (3.90)	25.27 (25.22)	19.26 (19.21)	–	–	–	–
8	$[La(HBTP)_2(H_2O)_2]$ Light Yellowish Brown	839.64 (839.00)	37.20 (37.18)	3.39 (3.33)	20.08 (20.02)	15.28 (15.25)	16.64 (16.56)	332	10.2	Dia.
9	$[Pr(HBTP)_2(H_2O)_2]$ Yellowish Brown	841.07 (841.00)	37.11 (37.09)	3.37 (3.32)	20.00 (19.97)	15.24 (15.21)	16.84 (16.76)	339	13.7	3.59
10	$[Nd(HBTP)_2(H_2O)_2]$ Deep Yellowish Brown	844.45 (844.00)	37.02 (36.96)	3.35 (3.31)	19.98 (19.90)	15.19 (15.16)	17.09 (17.06)	348	12.3	3.48
11	$[Sm(HBTP)_2(H_2O)_2]$ Yellowish Brown	850.23 (850.00)	36.78 (36.70)	3.32 (3.29)	19.83 (19.76)	15.09 (15.05)	17.67 (17.64)	337	15.1	1.59
12	$[Dy(HBTP)_2(H_2O)_2]$ Pale Yellow	862.74 (862.00)	36.25 (36.19)	3.27 (3.24)	19.52 (19.48)	14.92 (14.84)	18.83 (18.79)	328	16.7	10.99

TABLE-2
ANTIBACTERIAL ACTIVITIES OF THE LIGANDS AND COMPLEXES (ZONE FORMATION IN mm)

Compound	*Pseudomonas aeruginosa*	*S. aureus*	*E. coli*	*Klebs.*
Control (Ofloxacin)	20	22	16	18
HATP	18	10	10	–
[La(HATP)$_2$(H$_2$O)$_2$]	30	32	23	20
[Pr(HATP)$_2$(H$_2$O)$_2$]	31	35	24	30
[Nd(HATP)$_2$(H$_2$O)$_2$]	28	34	32	29
[Sm(HATP)$_2$(H$_2$O)$_2$]	38	33	34	37
[Dy(HATP)$_2$(H$_2$O)$_2$]	22	25	31	35
HBTP	–	18	–	16
[La (HBTP)$_2$(H$_2$O)$_2$]	32	34	28	32
[Pr(HBTP)$_2$(H$_2$O)$_2$]	30	33	37	28
[Nd(HBTP)$_2$(H$_2$O)$_2$]	35	28	36	34
[Sm(HBTP)$_2$(H$_2$O)$_2$]	37	33	–	25
[Dy(HBTP)$_2$(H$_2$O)$_2$]	26	28	32	29

The ^{1}H NMR spectra of ligands are recorded in DMSO. δ^s and peaks are observed at 7.3-7.7 δ and 7-7.9 δ. These are assigned to aromatic C-H of the ligands HATP showed low field signal for the hydrazone proton at 13.3 δ[29]. This low field shift is due to intramolecular hydrogen bonding. The hydrazone proton of HBTP appears at 8.7 δ. The signals at 2.1 δ-(6H), 2.5 δ(3H) and 3.0 δ(2H) may be due to two identical C-CH$_3$, N-CH$_3$ and NH$_2$ protons, respectively.

NMR and IR spectra of ligands reveals that coupling of 4-diazoantipyrine and 2-diazobenzothiazole with 3-methyl-1-thiocarbamyl-2-pyrazolin-5-one at its 4th position has resulted in the production of a hydrazone *via* rearrangement[30,31].

In the IR spectra of HATP metal complexes we find a shift in the ν(N-H) mode of NH$_2$ to 3300 from 3360 cm^{-1}, it reveals the coordination of N-atom of NH$_2$. Also, stretching frequencies of C=O and C=N bonds are lowered by 40-60 cm^{-1}. So, in addition of coordination *via* NH$_2$, both carbonyl oxygen atoms and azomethine nitrogen atoms are coordinated to the metal ions. Thus HATP acts as tetradentate of N$_2$O$_2$ type ligands. Similar negative shift in the frequencies of ν(C=O), ν(C=N) and ν(N-H) of NH$_2$ is found in the spectra of HBTP metal(III) complexes revealing the coordination through carbonyl oxygen, azomethine nitrogen and amino nitrogen atoms, so that HBTP acts as ONN donor ligand. The bands around 3500-3300 cm^{-1} and 830-800 cm^{-1}, found in both *i.e.*, HATP and HBTP metal(III) complexes indicate the presence of coordinated water molecule. Presence of coordinated water molecule is further confirmed by TG analysis[32]. The presence of additional non-ligands band in the spectra of the all metal complexes around 560-520 cm^{-1} and 450-400 cm^{-1} are assignable to M-N and M-O stretching frequencies[33].

Electronic spectral data for the solution of Ln(III)-pyrazolone complexes investigated in CH$_3$CN are reported in Table-3.

TABLE-3
ELECTRONIC SPECTRAL DATA ALONG WITH BAND ASSIGNMENTS (kk)

Complex	Band assignments	Bands of Ln^{3+}-aqua ions (kk)	Bands of complex (kk)	Calculated bonding parameter				
				(1-β)	β	B$^{1/2}$	δ (%)	η
[Pr(HATP)$_2$(H$_2$O)$_2$]	$3H_4 \rightarrow {}^3P_2$	22.5	21.9	0.0267	0.9733	0.0817	2.7432	0.0136
	$\rightarrow {}^3P_1$	21.7	21.1	0.0277	0.9723	0.0832	2.8489	0.0141
	$\rightarrow {}^3P_0$	20.4	19.8	0.0295	0.9705	0.0858	3.0396	0.0151
	$\rightarrow {}^1D_2$	16.6	16.1	0.0302	0.9698	0.0868	3.1140	0.0155
[Nd(HATP)$_2$(H$_2$O)$_2$]	${}^4I_{9/2} \rightarrow {}^4G_{9/2}$	19.27	18.99	0.0146	0.9854	0.0604	1.4816	0.0074
	$\rightarrow {}^4G_{5/2},{}^2G_{7/2}$	17.32	16.98	0.0197	0.9803	0.0701	2.0095	0.0099
	$\rightarrow {}^4F_{9/2}$	14.38	14.01	0.0258	0.9742	0.0803	2.6983	0.0131
	$\rightarrow {}^2S_{3/2},{}^4F_{7/2}$	13.76	13.21	0.0400	0.9600	0.1000	4.1666	0.0207
	$\rightarrow {}^4F_{5/2},{}^4H_{9/2}$	12.81	12.12	0.0539	0.9461	0.1160	5.6970	0.0281
[Sm(HATP)$_2$(H$_2$O)$_2$]	${}^6H_{5/2} \rightarrow {}^7F_{5/2}$	33.85	33.37	0.0142	0.9858	0.0595	1.4404	0.0072
	$\rightarrow {}^4H_{7/2}$	28.764	28.42	0.0120	0.9880	0.0547	1.2145	0.0061
	$\rightarrow {}^4I_{7/2}$	26.56	26.17	0.0147	0.9853	0.0606	1.4919	0.0074
	$\rightarrow {}^4I_{15/2}$	22.43	22.00	0.0192	0.9808	0.0692	1.9575	0.0097
[Dy(HATP)$_2$(H$_2$O)$_2$]	${}^6H_{15/2} \rightarrow {}^6F_{5/2}$	12.18	11.98	0.0165	0.9835	0.0642	1.6776	0.0083
	$\rightarrow {}^4I_{15/2}$	22.62	22.16	0.0204	0.9796	0.0714	2.0824	0.0104
	$\rightarrow {}^4G_{11/2}$	23.69	23.05	0.0271	0.9729	0.0823	2.7854	0.0138
[Pr(HBTP)$_2$(H$_2$O)$_2$]	$3H_4 \rightarrow {}^3P_2$	22.3	21.5	0.0359	0.9641	0.0947	3.7236	0.0185
	$\rightarrow {}^3P_1$	21.9	21.0	0.0411	0.9589	0.1013	4.2861	0.0212
	$\rightarrow {}^3P_0$	20.2	19.7	0.0248	0.9752	0.0787	2.5430	0.0126
	$\rightarrow {}^1D_2$	16.8	15.9	0.0536	0.9464	0.1157	5.6635	0.0279
[Nd(HBTP)$_2$(H$_2$O)$_2$]	${}^4I_{9/2} \rightarrow {}^4G_{9/2}$	19.48	19.12	0.0185	0.9815	0.0680	1.8848	0.0093
	$\rightarrow {}^4G_{5/2},{}^2G_{7/2}$	17.24	17.05	0.0111	0.9889	0.0526	1.1224	0.0056
	$\rightarrow {}^4F_{9/2}$	14.26	13.97	0.0204	0.9796	0.0714	2.0824	0.0104
	$\rightarrow {}^2S_{3/2},{}^4F_{7/2}$	13.50	13.00	0.0371	0.9629	0.0963	3.8529	0.0191
	$\rightarrow {}^4F_{5/2},{}^4H_{9/2}$	12.78	12.11	0.0525	0.9475	0.1145	5.5408	0.0274
[Sm(HBTP)$_2$(H$_2$O)$_2$]	${}^6H_{5/2} \rightarrow {}^7F_{5/2}$	33.67	33.12	0.0164	0.9836	0.0640	1.6673	0.0083
	$\rightarrow {}^4H_{7/2}$	28.54	28.11	0.0151	0.9849	0.0614	1.5331	0.0076
	$\rightarrow {}^4I_{7/2}$	26.42	26.09	0.0125	0.9875	0.0559	1.2675	0.0063
	$\rightarrow {}^4I_{15/2}$	22.01	21.87	0.0064	0.9936	0.0400	0.6441	0.0033
[Dy(HBTP)$_2$(H$_2$O)$_2$]	${}^6H_{15/2} \rightarrow {}^6F_{5/2}$	11.90	11.13	0.0648	0.9352	0.1272	6.9289	0.0341
	$\rightarrow {}^4I_{15/2}$	22.75	22.29	0.0203	0.9797	0.0712	2.0720	0.0104
	$\rightarrow {}^4G_{11/2}$	23.28	22.99	0.0125	0.9875	0.0559	1.2658	0.0063

For comparison, the spectral data for the corresponding aqueous salt solution are also given in Table-3. Lanthanum(III) has no significant absorption in the UV-visible region. The absorption bands of Pr^{3+}, Nd^{3+}, Sm^{3+} and Dy^{3+} in the visible and near infrared region appear due to transitions from ground levels $^3H_4$, $^4I_{9/2}$, $^6H_{5/2}$ and $^6H_{15/2}$, respectively to the excited *J*-levels of $4f^n$-configuration[34] of Ln(III) central metal ions. Some red shift or, nephlauxetic effect is observed. This red shift proves a higher degree of covalency in the complexes than that existing in their aquo salts[35]. The various spectral parameters like nephlauxetic ratio (*i.e.*, β), covalence factor (*i.e.*, $b^{1/2}$), metal-ligand covalency % *i.e.*, Sinhas parameter (δ %) and covalency angular overlap parameter (η) have been calculated. Calculation reveals that the value of δ % and ($1-\beta$) in all the synthesized Ln(III) complexes comes out to be positive throughout which indicates strong coordinate covalent bonding in all the complexes.

Unlike the *d*-electrons of the transition metal ions, the *f*-electrons of the lanthanide ions are almost unaffected by the chemical environment and the energy levels are the same as in the free ion due to very effective shielding by the overlying $5s^2$ and $5p^6$ shells. The magnetic moment values of the complexes showed that only La(III) complex is diamagnetic while the rest are paramagnetic, showing close agreement with the calculated values except for the Sm(III), indicating an insignificant participation of the 4*f*-electrons in the bonding. The relatively high value obtained in the case of samarium(III) complex may be due to small *J*-*J* separation, which leads to the thermal population of the higher energy levels and show susceptibilities due to first order Zeemann effect[36].

Thermal studies of the metal-complexes were carried under static air condition. The thermogram of HBTP metal(II) complexes indicate two clear cut stages, first corresponding to the dehydration of the coordinated water molecule and second to the decomposition process[37].

A comparison of the diameters of inhibition zone of compounds investigated shows that all the Ln(III) complexes exhibit higher antibacterial activity against *Pseudomonas* and *Klebsiella* than even the control ofloxacin at the same concentration and identical conditions. The complexes are more antibacterial than the respective ligands against all the bacteria studied.

Conclusion

On the basis of above discussion coordination number ten for Ln(III)-HATP and eight for Ln(III)-HBTP complexes has been suggested. The proposed structure of complexes may be as shown in Fig. 1.

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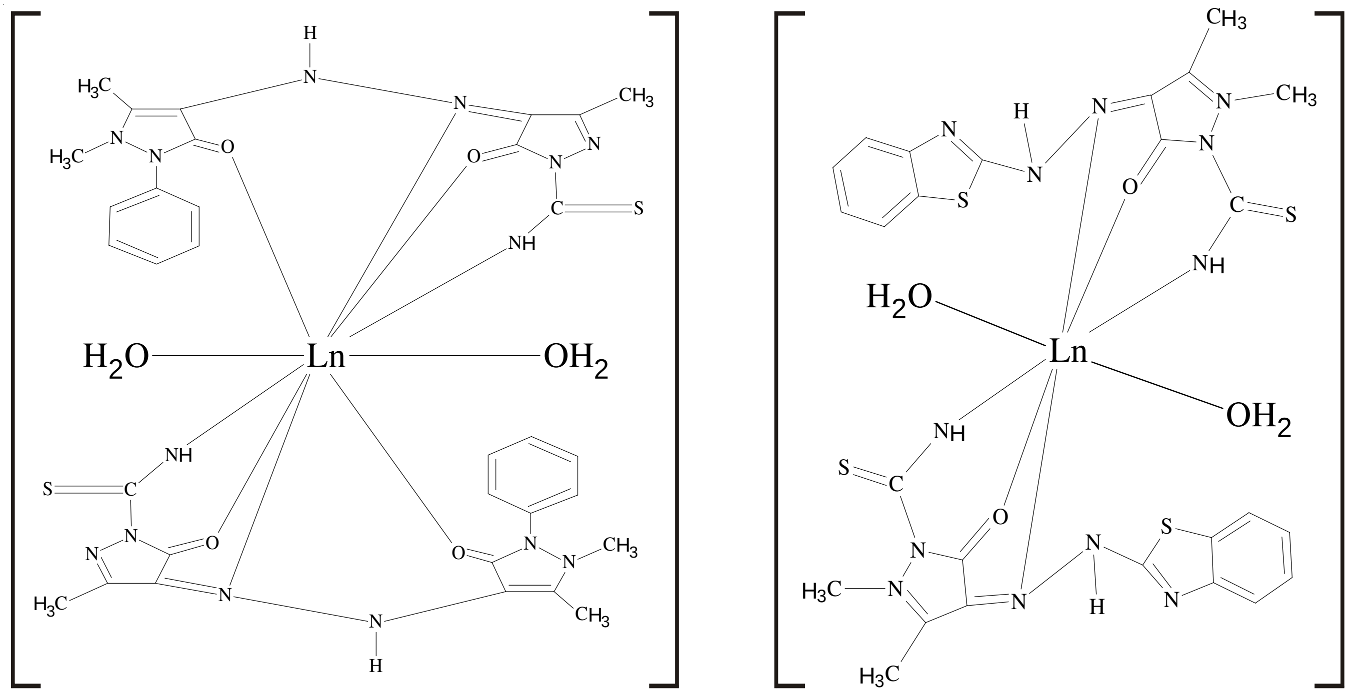

(I) $[Ln(HATP)_2(H_2O)_2]$
Where, Ln=Nd(III), Sm(III) & Dy(III)

(II) $[Ln(HBTP)_2(H_2O)_2]$
Where, Ln=Nd(III), Sm(III) & Dy(III)

Fig. 1.

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