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SPECTRAL STUDIES AND CHARACTERISATION OF Ln (III) COMPLEXES WITH 2, 4–PYRIMIDINE DIAMINE–5 [(4–CHLOROPHENYL)] 6–ETHYL

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ABSTRACT

Complexes of La^{+3}, Pr^{+3}, Nd^{+3}, Sm^{+3}, Gd^{+3}, Tb^{+3} and Dy^{+3} with 2,4–pyrimidine diamine–5[(4-chlorophenyl)]-6-ethyl) have been prepared and structures of the complexes have been established on the basis of elemental analysis, magnetic moment, infrared, nuclear magnetic resonance, thermal analysis and electronic spectra. The ligand is bonded through nitrogen with metal ion and slight participation with *4f* electron in bonding.

Key words : Spectral studies, Ln (III) complexes, 2,4 - Pyrimidine diamine-5-[(4 -chlorophenyl)] -6-ethyl

INTRODUCTION

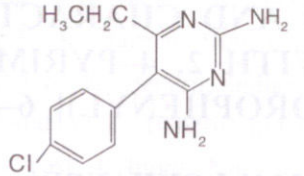
The chemical bonds in lanthanide (III) complexes are considered for the most part to be ionic, partly because of their well-shifted *4f* orbital, and partly because of their inert gas electronic configuration. Recently, however, partial covalency in the metal-ligand bonds has been noticed both theoretically and experimentally. There is a growing interest in the study of lanthanide metal complexes with 2, 4-pyrimidine diamine –5 [(4- chlorophenyl)]-6-ethyl

Common name : Pyrimethamine.
IUPAC name : 2, 4-pyrimidine diamine –5 [(4- chlorophenyl)]-6-ethyl
Molecular formula : $C_{12}H_{13}Cl\ N_4$.
Molecular weight : 248.71
Color : colorless (amorphous powder)
Solubility: Methanol and slightly in ethanol.
Melting point : 240°C.

Elemental analysis :

	C %	H %	Cl %	N %
Calcd.	57.95	5.27	14.25	22.53
Found	57.78	5.14	14.09	22.38

Structure of ligand



The purity of this ligand was checked on thin layer chromatography (99.4% pure). The literature survey shows that much is known about pharmacological activity of 2,4-pyrimidine diamine–5 [(4- chlorophenyl)]-6-ethyl, which is used to control the prophylaxis and in treatment of malaria. The antimalarial effects of pyrimethamine have been reviewed[1-4]. In a series of investigations, the 2,4-diaminopyrimidines were shown to act by inhibiting dihydrofolate reductase of plasmodia at concentrations far lower than required to produce comparable inhibition[5].

The present work deals with the 2,4-pyrimidine diamine –5 [(4- chlorophenyl)] 6- ethyl complexes with La^{+3}, Pr^{+3} , Nd^{+3} ,Sm^{+3} , Gd^{+3}, Tb^{+3} and Dy^{+3} metal ions. Literatures shows that most of the complexes are biologically active and act as an antimalarial drug having less side effects[6].

EXPERIMENTAL

The lanthanide chlorides used were from Indian Rare Earth Limited kerla (India). The 2,4-pyrimidine diamine–5 [(4- chlorophenyl)] 6- ethyl was made available from Lupin laboratories, Aurangabad and IPCA laboratories, Mumbai. The solvents were purified using standard procedure. The metals contents were determined by destroying the organic matter by successive treatment with aqua regia and sulfuric acid. The metal contamination were determined by volumetric titration.[3] The infrared spectra were recorded using KBr pellets on Perkin-Elmer Paragon–500 FTIR spectrophotometer at UDCT-Mumbai. Electronic spectra were recorded on Cintra-500 UV-VIS spectrophotometer and NMR at TIFR–Mumbai. The magnetic susceptibility measurements were carried out on Faraday electro balance using $Hg[Co(CNS)_4]$ as standard at Dr. Babasaheb Ambedkar Marathwada University, Aurangabad. The thermal analysis data were recorded in the range 25-1000°C at 10°C/min using Mettler Toledo star^e system at C-MET-Pune. Molar conductivity measurements were carried out on Equi-tonic digital conductivity bridge. The 0.25 molar solutions of 2, 4-pyrimidine diamine–5 [(4-chlorophenyl)]-6-ethyl and La^{+3}, Pr^{+3}, Nd^{+3}, Sm^{+3}, Gd^{+3}, Tb^{+3} and Dy^{+3} solutions were prepared in methanol. The metal chloride and ligand solution were mixed in 1 : 3 molar ratios. The pH of the solution was adjusted at 5.8-6.2. This solution was refluxed for ~3 hours, using water condenser. After 1.5 hours, slight precipitation is there, which increases with time. After complete relaxation, the colored solid product was obtained. This solid product was filtered, washed with methanol and then, with alcohol and dried at 60°C in oven.

RESULTS AND DISCUSSION

The analytical and physical data are given in Table-1. These complexes are insoluble in organic solvents like benzene, acetone, ether, chloroform and acetonitrile, but soluble in dimethyl sulfoxide and dimethyl formamide. The chlorides were estimated by Mohr's method[7] and the metal content were estimated by ethylene diamine tetraacetate using xylenol orange as an indicator. The conductivity measurements of 10^{-3} molar solution of complexes in dimethyl formamide were carried out. The molar conductivity of the complexes is electrolytic in nature[8]. The complexes decompose in the range 251-298°C. The melting point and decomposition point are reported in open capillary and are uncorrected. The metal ligand ratios of the complexes is 1 : 3.

S.No.	Complexes	Color	Molecular weight
1	$[La\,(C_{12}H_{13}\,Cl\,N_4)_3.2H_2O]\,Cl_3$	Colorless	1027.40
2	$[Pr\,(C_{12}H_{13}Cl\,N_4)_3.2H_2O]\,Cl_3$	Light green	1029.40
3	$[Nd\,(C_{12}H_{13}Cl\,N_4)_3.2H_2O]\,Cl_3$	Purple	1031.73
4	$[Sm\,(C_{12}H_{13}Cl\,N_4)_3.2H_2O]Cl_3$	Tannic	1038.84
5	$[Gd\,(C_{12}H_{13}\,Cl\,N_4)_3.\,2H_2O]\,Cl_3$	Cream	1045.73
6	$[Tb\,(C_{12}H_{13}\,Cl\,N_4)_3.\,2H_2O]\,Cl_3$	Light plum	1047.41
7	$[Dy\,(C_{12}H_{13}\,Cl\,N_4)_3.\,2H_2O]\,Cl_3$	Colorless	1051.03

TABLE 1. Analytical and physical data of lanthanide (III) complexes with 2, 4 - pyrimidine diamine –5 [(4- chlorophenyl)]-6 - ethyl.

S. No.	Complexes	% Yield	D.P/M.P°C	C %	H %	N%	Cl %	M %	Ω(ohm^{-1} cm^2 mol^{-1})	B.M.μeff
1	$[La\,(C_{12}H_{13}\,Cl\,N_4)_3$ $.2H_2O]Cl_3$	68.6	251-254	42.03^a 41.57^b	4.18 4.02	16.34 16.02	20.72 19.42	13.51 12.77	149.8	Dimag.
2	$[Pr\,(C_{12}H_{13}\,Cl\,N_4)_3$ $.2H_2O]\,Cl_3$	64.2	262-265	41.95 39.38	4.17 3.98	16.310 15.98	20.68 19.46	13.67 12.89	154.6	3.52
3	$[Nd\,(C_{12}H_{13}\,Cl\,N_4)_3$ $.2H_2O]\,Cl_3$	65.5	295-298	41.82 39.28	4.16 4.96	16.26 15.96	20.62 19.38	13.95 13.36	148.1	3.56
4	$[Sm\,(C_{12}H_{13}\,Cl\,N_4)_3$ $.2H_2O]\,Cl_3$	61.0	277-280	41.58 39.02	4.13 3.98	16.17 15.92	20.50 19.24	14.56 13.78	149.6	2.14
5	$[Gd\,(C_{12}H_{13}\,Cl\,N_4)_3$ $.2H_2O]\,Cl_3$	63.1	272-275	41.30 39.56	4.10 3.94	16.06 15.84	20.36 19.14	15.02 14.86	153.8	7.91
6	$[Tb\,(C_{12}H_{13}\,Cl\,N_4)_3$ $.2H_2O]\,Cl_3$	67.3	279-282	41.23 40.18	4.09 3.88	16.02 15.75	20.33 19.12	15.15 14.88	150.4	9.71
7	$[Dy\,(C_{12}H_{13}\,Cl\,N_4)_3$ $.2H_2O]\,Cl_3$	58.4	264-267	41.09 38.90	4.06 3.86	15.98 15.64	20.26 19.03	15.44 14.89	155.7	10.53

2,4-pyrimidine diamine–5 [(4-chlorophenyl)]-6-ethyl exhibits bands of the high intensity at about 3318 cm^{-1} and 3210 cm^{-1} due to two NH_2 groups. They may be assigned to asymmetric ν (NH) of terminal–NH_2 group and the symmetric ν (NH) of two–NH_2 groups[9]. It has been suggested that the vibrations of the terminal–NH_2 group is responsible for the two bands at higher frequency region, as they are slightly shifted to the higher frequency region. Therefore, the–NH group is responsible for the lower frequency bands between 3295-3250 cm^{-1} and 3160–3130 cm^{-1} in the lanthanide metal complexes. The intensity of the bands is considerably lowered. Moreover, the number of bands in this region decreases, and they become broad. These observations attributed to fact amine groups participate in the formation of the complexes with lanthanide metal ions. The bands at 1450 and 1590 cm^{-1} are assigned to ν (C=C) and ν (C=N) and the skeleton frequencies[10], respectively. A medium broad bands appears around 3586-3570 and 3548-3530 cm^{-1} region may be assigned to ν (O-H) of two coordinated water molecules. Thus, the coordination is through two amine nitrogen and there is no indication of the coordination of nitrogen of pyrimidine. This has been further substantiated by the observation of the two band in Far-ir region at 465-450 cm^{-1} and 515-505 cm^{-1} due[11] to ν (M-O) and ν (M-N), respectively.

The proton nuclear resonance spectra of 2, 4-pyrimidine diamine–5 [(4-chlorophenyl)]-6-ethyl exhibits signals at δ 2.4-2-1, δ 3.9-3.8 and δ 8.2-7.2 ppm, which are assigned to CH_3, NH_2 and aromatic protons. In the spectrum of $[Sm (C_{12}H_{13}Cl\ N_4)_3 2H_2O]\ Cl_3$ the signal due to –NH_2 proton (δ 3.74) shows downfield shift suggesting that the amine nitrogen is bonded with metal ion. The bonding through the amine nitrogen is also evident from the downfield shift of aromatic protons (δ 7.8-7.3). This shift suggests coordination of the amine nitrogen with metal ion. The signal due to proton of water and CH_3 group overlaps and appears as the broad signal accounting for 9 protons on the integration.

The electronic spectra of Pr^{+3} and Nd^{+3}complexes were recorded in dimethyl sulfoxide and compared with those of aqueous metal chloride solution[12] The feature of hypersensitive transitions $^4I_{9/2}\rightarrow{}^4G_{5/2}{:}G_{7/2}$ in the neodymium complexes in dimethyl sulfoxide and that of aqua ion is indicated. The hypersensitive band observed at 17606 cm^{-1} in $[Nd(C_{12}H_{13}ClN_4)_3.2H_2O]Cl_3$ is observed at lower energy compared to aqua ion. The slight red shift clearly indicates interaction of metal with ligand[13] and these shifts are attributed to the effect of crystal field upon the inter electronic repulsion among the *4f* electrons i.e. to lowering of inter electronic repulsion parameter (ß) in the complex. The other parameters like bonding ($b^{1/2}$) and Sinha's parameter (δ) have also been calculated using literature procedures[14, 15] These values indicate partial developing covalent bond between the metal ion and the ligand[16]. The spectral feature of the hypersensitive transitions ($^4I_{9/2}\rightarrow{}^4G_{5/2} : G_{7/2}$) consist with coordination number eight around the metal ion[17-18]. The assigned parameters calculated are given in Table-2.

Table-2. Electronic spectra and assignments

Complex : (i) $[Pr\ (C_{12}H_{13}\ Cl\ N_4)_3.\ 2H_2O]\ Cl_3$.
: (ii) $[Nd\ (C_{12}H_{13}\ Cl\ N_4\ )_3.\ 2H_2O]\ Cl_3$.
Solvent : DMSO
Concentration : (i) 1.80×10^{-3} mole lit^{-1}.
: (ii) 1.90×10^{-3} mole lit^{-1}.
Wave length : 380-900 nm.

S.No.	Band cm^{-1}	Assignment	Spectral Parameter
1	16892	$^3H_4 \rightarrow {}^1D_2$	β = 0.9926
	20667	$\rightarrow {}^3P_0$	δ = 0.7455
	21186	$\rightarrow {}^3P_1$	$b^{1/2}$ = 0.0608
	22321	$\rightarrow {}^3P_2$	
2	11494	$^4I_{9/2} \rightarrow {}^4F_{3/2}$	
	12315	$\rightarrow {}^4F_{5/2}$	β = 0.9902
	13055	$\rightarrow {}^4F_{7/2}$	
	14620	$\rightarrow {}^4F_{9/2}$	δ = 0.9896
	17606	$\rightarrow {}^4G_{5/2}$	
	18657	$\rightarrow {}^4G_{7/2}$	$b^{1/2}$ = 0.07
	20833	$\rightarrow {}^2G_{9/2}$	
	22123	$\rightarrow {}^4G_{11/2}$	
	24752	$\rightarrow {}^2P_{1/2}$	

The $[La(C_{12}H_{13}Cl\ N_4)_3.2H_2O]\ Cl_3$ is diamagnetic, while other complexes are paramagnetic at room temperature. The magnetic susceptibility of all complexes except those of Sm^{+3} show a little deviation from Van Vleck[19] values indicating slight participation of the *4f* electrons in the bonding . The relatively high values obtained in case of Sm^{+3} complex is due to *J-J* separation, which leads to thermal population of higher energy levels and show susceptibility due to a first order Zeemann effect[20].

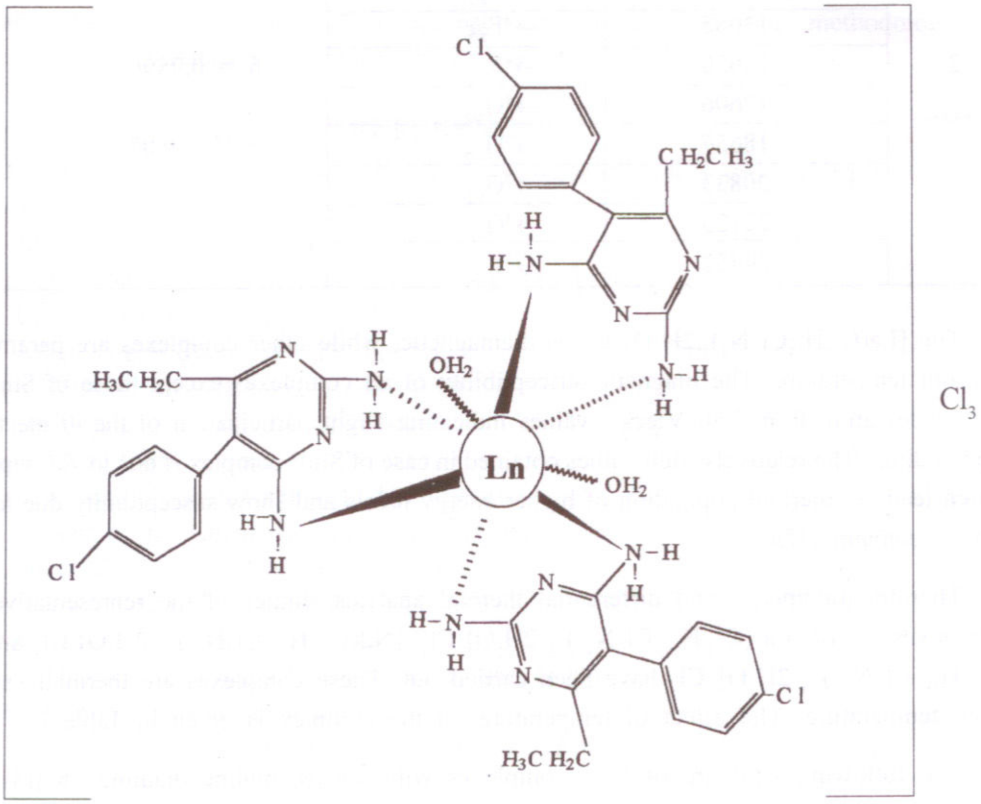
Thermo gravimetric and differential thermal analysis studies of the representative metal complexes [21-22] of $[La\ (C_{12}\ H_{13}\ Cl\ N_4\ )_3\ 2H_2O]\ Cl_3$, $[Nd(C_{12}\ H_{13}\ Cl\ N_4\ )_3\ 2H_2O]\ Cl_3$ and $[\ Sm\ (C_{12}\ H_{13}\ Cl\ N_4\ )_3\ 2H_2O]\ Cl_3$ have been carried out. These complexes are thermally stable at room temperature. The effect of temperature on the complex is given in Table-3

The following structure of Ln^{+3} complexes with 2,4-pyrimidine diamine –5 [(4- chloro phenyl)]-6- ethyl has been proposed.

Table - 3 Thermal analysis [TGA/DTA] and their assignments.

S.No.	Complex	Peak range °C	Theoretical (%)	Experimental (%)	Possible leaving group
1	[La $(C_{12}H_{13}ClN_4)_3$ $2H_2O]Cl_3$	100-180	17.17[a]	16.89	$2.H_2O$, C_6H_4, CH_2CH_3, Cl
		210-280	31.28[a]	30.18	$C_4H_5N_4$, Cl
		290-450	49.24[b]	48.69	$C_4H_5N_4$, C_6H_4
		460-830	68.32[a]	69.19	La_2O_3
		110-270	14.27[a]	10.46	$2H_2O$, C_6H_5, Cl
2	[Nd $(C_{12}H_{13}ClN_4)_3$ $2H_2O]Cl_3$	290-410	30.93[b]	30.46	$C_4H_5N_4$, C_6H_4, CH_2CH_3, Cl,
		430-830	67.46[a]	68.61	Nd_2O_3
		110-210	09.67[a]	10.09	$2H_2O$, CH_2CH_3, Cl
3	[Sm $(C_{12}H_{13}ClN_4)_3$ $2H_2O]Cl_3$	220-380	36.47[b]	35.74	$2CH_2CH_3$, Cl, C_6H_4, $C_4H_5N_4$
		400-830	66.47[a]	67.13	Sm_2O_3

a = Endothermic reaction and b = Exothermic reaction



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